Preface

The organizing committee of the 1st ICABC 2019 would like to welcome all participants to the 1st congress on "1st International Congress on Analytical and Bioanalytical Chemistry" held in Antalya between 27-30 March 2019. The 1st ICABC 2019 is newly started and covers all areas of Analytical Bioanalytical Chemistry as well as applications of Chemical and Biochemical Analysis.

The scientific congress program consists of 19 sessions that include 18 invited and 82 oral presentations as well as 83 posters to be presented in the respective sessions. In addition, researchers of Academia (57 universities from 13 countries) and Research Institutes will present up-to-date development on analytical and bioanalytical chemistry as well as applications to a wide range of environmental, biological and food matrices. On 29 March, the participants’ can be joined to Perge Ancient city in Antalya, a living proof of the Hellenistic period.

We strongly believe that the discussions and the exchange of ideas among the participants during the 4 days of the meeting will make 1st ICABC a brilliant platform to initiate new research collaborations, particularly in favor of the young scientists participating in the conference.

We wish you all to enjoy this conference and have a pleasant stay in Antalya, hoping to meet you again during the next ICABCs.

With our best regards
The Chair (on behalf of Organizing Committee)
Prof. Dr. Mehmet YAMAN
Firat University, Science Faculty, Department of Chemistry, Elazig-Turkey
ICABC 2019

COMMITTEES

INVITED SPEAKERS
Antony Calokerinos (Athen U.-GR)
Arūnas Ramanavičius (Vilnius U.-Lithuania)
Bekir Salih (Hacettepe U.-TR)
Bezhan Chanvketadze (Tbilisi U.-GER)
Egon-Erwin Rosenberg (Wien Tech. U.-AT)
Engin Ulukaya (Istinye U.-TR)
Erdem Yesilada (Yeditepe U.-TR)
F. Nil Ertas (Ege U.-TR)
Hasan Turkez (Erzurum Tech. U.-TR)
Ilhami Gulcin (Ataturk U.-TR)
Ismail Hakki Boyaci (Hacettepe U.-TR)
Mustafa Soyak (Erciyes U.-TR)
Mustafa K. Sezginturk (Canakkale 18 Mart U.-TR)
Mutay Aslan-(Akdeniz U.-TR)
Osman Yavuz Ataman (METU—TR)
Resat Apak—(Istanbul U.-TR)
Ryszard Lobinski (Pau U.-FR)
Sezgin Bakirdere (Yildiz Tech. U.-TR)

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K. Arzum ERDEM-Ege U.-TR
Mustafa EROZ-Selcuk U.-TR
Serife TOKALIOGLU Erciyes U.-TR
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Bedia Ertem BERKER ITU-TR
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Bekir SALIH - Hacettepe U.-TR
Ilhame GULCIN - Ataturk U.-TR
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Resat APAK-Istanbul U.-TR
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Seref GUCER-Uludag U.-TR
Mehmet YAMAN- Firat U.-TR
Durishev UNAL- Istanbul U.-TR
Yusuf DILGIN, Canakkale 18 Mart U.-TR
Gokce KAYA- Firat U.-TR
Erdem YEŞİLADA- Yeditepe U.-TR
Utkan DEMIRCI- Stanford U.- USA
Suna TIMUR-Ege U.- Turkey
Zuhre SENTURK-Van Yuzuncu Yil U.-TR
Saadet GUMUSLU-Akdeniz U.-TR
Engin ULUKAYA-Istinye U.-TR
Sema ERDEMOGLU-Inonu U.-TR
Ibrahim ISILDAK-Yildiz Tech. U.-TR
Metin AK-Pamukkale U.-TR
Najma MEMON, Sindh U.-PK
Sema BAGDAT, Balikesir U.-TR
Mehmet Emin DURU- Mugla. U.-TR
Elif TUMAY OZER-Uludag U.-TR
Ersin KILINC, Dicle U.-TR
Emirhan NEMUTLU, Hacettepe U.-TR
Sadik OZDEMIR-Mersin U.-TR
Serap Saglik ASLAN, Istanbul U.-TR
Nagihan M KARAASLAN, Munzur U. TR
Umran SEVEN ERDEMIR-Uludag U. TR
Uygar TAMER, Gazi U. TR
Gulberk UCAR, Hacettepe U. TR
Elif Apohan, Inonu U. TR
Hikmet BUDAK-Montana St U.USA

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Prof. Dr. Yusuf DILGIN-Canakkale 18 Mart U
Prof. Dr. Durishev UNAL-Istanbul U.
Prof. Dr. Suna TIMUR-Ege U.
Prof. Dr. Gokce KAYA-Firat U.
Prof. Dr. Mehmet YAMAN-Firat U
ICABC 2019

Chair
Prof. Dr. Mehmet YAMAN-Firat University.

Organizing Committee-Secretariat

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Gokce Kaya (Firat U.),
Umran Seven Erdemir (Uludag U),
Mehmet Gumustas (Ankara U),
Gulsah Ozcan Sinir (Uludag U),
Nagihan Karaaslan (Munzur U),
Emine Akyuz Turumtay (Recep Tayyib Erdogan U),
Tulin Bicim (Firat U.),
Soykan Bicim (Firat U.),
Mert Akgun (Canakkale 18 Mart U),
Nur Tarimeri (Canakkale 18 Mart U),
Selen Ayaz (Canakkale 18 Mart U),
Maruf H. Demirel (Firat U.),
Murat Celiker(Firat U.),
Sevda Gultekin (Firat U.),
Nursu Aylin Kasa (Yildiz Technical U.),
Buse Tugba Zaman (Yildiz Technical U.),
Kenan Can Tok (Ankara U),
Batuhan Orman (Ege U.),
Filip Trakovski (Ege U.),
Inci Gullu (Ege U.),
Minel Ayazma (Ege U.),
Yasar Kaan Eren (Ege U.),
Meltem Tas (Mugla U.),
Bihter Sahin (Mugla U),
Busra Yilmaz Durak (YTU).

GENERAL INFORMATION

Introduction

The 1st International Congress on Analytical and Bioanalytical Chemistry will be held on 27-30 March 2019 in Antalya-Turkey is a four-days scientific meeting covering all areas of Analytical and bioanalytical Chemistry and applications of Chemical and biochemical Analysis. The international congresses have provided an excellent framework for the presentation of new concepts, instruments, methods, and applications in the area of modern chemical and biochemical analysis. Researchers and scientists from Universities, Research Institutions, State Organizations, and the Industry come together during the meeting to present and discuss the current state of the art in those areas. At the same time, it provides the grounds for the graduate and post graduate students to present their projects, discuss scientific collaborations with other groups, as well as to explore employment opportunities. An exhibition of analytical and bioanalytical instruments and accessories will be also organized in the conference place whereas social events are planned to be included in the program of the. 1st ICABC 2019.

I strongly believe that young researchers will have chance to improve their knowledge in deep of the analytical and bioanalytical chemistry by coming together with experienced scientists including invited speakers and scientific committee members.
ICABC 2019

Topics
To promote collaboration among analytical and bioanalytical (including biochemists, food engineering, molecular biology and genetics and similars) scientists from different countries, “1st ICABC 2019” will provide adequate opportunities.
The topics include all areas of analytical and bioanalytic chemistry in applications such as, but not limited to, environmental, biological and food matrices, environmental protection, biochemical studies, drug characterisation, method innovation and validation, instrumental development and applications, sensors and nanobiosensors, chromatography, spectrometry and electrochemistry.
The congress covers determination of inorganic and organic components in environmental, biological and food matrices as well as the following subjects: Food Safety: Omics analysis including GMO, all studies on interactions between metabolic disorders and foodstuffs.
The main aim and theme of the congress is to enlighten the innovations and current trends with analytical and bio analytical chemistry (including organic and food chemistry).

Location of Conference
1st ICABC 2019 will be held in Serik-Antalya in north-coast of the Mediterranean Sea. Serik-Antalya, a holiday district, is around 30 km away from the Antalya airport. Antalya is Turkey’s World famous tourism city.
Some historical Places to visit in Antalya, Turkey:
Perge, Olympos, Aspendos Antique Theater in Serik, Aspendos Bridge in Serik, Temple of Apollo, Side Ancient Theater and similar.
Among them, Perge was an important city for Christians of Perge who had worshipped the mother goddess Artemis. St. Paul and Barnabas visited the city and wealthy benefactors like Magna Plancia had a number of important memorials built here.

Papers presentation
Scientific program will include Invited Speakers, which will provide an up-to-date presentation of modern trends of Analytical and Bioanalytical Chemistry as well as of related subjects of chemical and biochemical analysis-interest. Oral Presentations will be presented in two halls. Contributed papers describing original research work will be also presented as posters in order to promote efficient discussion on new scientific ideas and results. The presenting authors should hang their posters before poster time, and remove them in the evening of the corresponding day. All posters are required to conform to portrait orientation. Posters should be clear and easy to read. Type size should be sufficiently large to allow people to read from 2-3 meters. All presentations should be in English. Poster and oral presentation will be accepted if at least one of the authors is registered and present at the conference for personal communication.

Best poster certificate
A competition for the best poster among the young scientists in each poster session will also take place. These certificates will be given to recognize excellence in research and presentation. The winners will be announced during the Gala Dinner and Dinner on 28-29 March, 2019.
Social events

Welcome reception-27 March, 2019: The Welcome Reception will be held on March 27, 2019 at the IC Santai hotel adjacent-sea. Event will close with local traditional dances and a folklore party.

Conference Gala dinner- 28 March, 2019: The Conference Gala Dinner will be held on March 28 at 20:00 in a restaurant of IC Santai Hotel. The menu will include a wide variety of traditional food, salads and drinks. Event will close with local traditional dances and a folklore party.

After welcome cocktail and Gala Dinner on nights of 27 and 28 March 2019, respectively, live modern and traditional music presentation will be done.
On 29 March 2019, an excursion to Perge Ancient city is planned in near the congress hotel by bus.
# CONGRESS PROGRAM

**1st International Congress on Analytical and Bioanalytical Chemistry**  
*(1st ICABC 2019)*  
27-30 March, 2019, Antalya-İC-Santai Hotel/Turkey

## 27 March, 2019

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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</table>
| 13.30  | **Registration**  
The registration desk will be open everyday during conference hours                              |
| 14.30  | Welcome Ceremony                                                                                  |
| 14.30  | Respect-Silence of Independence and Opening Speeches:  
Prof. Dr. Mehmet Yaman (Chair)                                                                  |
| 14.30  | Prof. Dr. Seref Gucer (on behalf of continuation committee)                                      |
| 14.30  | Commemorate(Alex Zacharia-Karel Vytras)                                                          |
| 14.30  | Honorable                                                                                        |
| 14.30  | **Inv. 1: Prof. Dr. Bekir Salih-Hacettepe U, TR:** State of the art in Mass Spectrometry-based Proteomics: Post-translational Modifications, Imaging and Ion Mobility |
| 15.45  | Tea/Coffee break                                                                                 |

## Session 1-Chairs: Resat Apak-Engin Ulukaya

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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</thead>
<tbody>
<tr>
<td>15.45-16.15</td>
<td><strong>Inv. 2: Prof. Dr. Ismail Hakki Boyaci-Hacettepe U:</strong> Food Safety and Quality:Molecular and Elemental Detection</td>
</tr>
<tr>
<td>16.15-16.45</td>
<td><strong>Inv. 3: Prof. Dr. M. Kemal Sezginturk-Canakkale 18 Mart U, TR:</strong> Disposable Electrode Materials and Their Applications to Biosensing Systems</td>
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## Session 2-Chairs: Erwin Rosenberg-Ilmutdin Abdulagatov

<table>
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<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>16.45-17.15</td>
<td><strong>Inv. 4: Prof. Dr. O. Yavuz Ataman-METU:</strong> Some ordeals/memories in environmental analysis.</td>
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## 28 March, 2019

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<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>08.30-09.00</td>
<td><strong>Inv. 6: Prof. Dr. E. Erwin Rosenberg Wienna Tech. U, AT:</strong> Increasing speed and increasing information contents-New approaches in Gas Chromatography</td>
</tr>
<tr>
<td>09.00-09.30</td>
<td>From Mariia Nesterkina-Odesa N.P. U on Alex Zacharia</td>
</tr>
<tr>
<td>09.30-10.00</td>
<td>Ersin Kilinc-Dicle U, Non-viral siRNA Delivery for Targeted Cancer Theranostic-OP24</td>
</tr>
<tr>
<td>10.00-10.30</td>
<td><strong>Inv. 7: Prof. Dr. Antony Calokerinos Athen U, GR:</strong> Luminescent Methods for the Quality Control of Natural Products</td>
</tr>
<tr>
<td>10.30-11.00</td>
<td><strong>Inv. 8: Prof. Dr. Arunas Ramanavicius-Vilnius U, LT:</strong> Sensors and Biosensors based on Conducting Polymers</td>
</tr>
<tr>
<td>11.00-11.15</td>
<td>Tea/Coffee break</td>
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## Session 3-Chairs: Nil Ertas-Ihhami Gulcin

<table>
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<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>11.15-11.30</td>
<td>Slawomira Skrzypek-Lodz, Application of ultra trace graphite electrode modified with graphene nanoplatelets in electroanalysis of metobromuron-OP35</td>
</tr>
<tr>
<td>11.30-12.00</td>
<td>SEM LAB, Suna Uçan-Aplikasyon Uzmanı, POLYARC, GC FID de çığır açan teknoloji, standart kullanmadan, tek enjeksiyon ile daha hızlı, daha kolay, daha ekonomik ve daha doğru miktarsal sonuçlar</td>
</tr>
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## Session 4-Chairs: Adil Denizli - Hasan Turkez

<table>
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<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>12.00-12.30</td>
<td><strong>Inv. 9: Prof. Dr. Ryszard Lobinski-Pau U, France:</strong> Hpyhenated techniques for the large scale speciation analysis of metals and metalloids in a biological milieu</td>
</tr>
<tr>
<td>12.30-13.00</td>
<td><strong>Inv. 10: Prof. Dr. Bezhan Chankvetadze-Trblishi State U, GE:</strong> Recent developments in separation of enantiomers using high-performance liquid chromatography</td>
</tr>
<tr>
<td>13.00-13.30</td>
<td>Lunch</td>
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<tr>
<td>Session 5: Chairs: Nikolaos L. Simantiris-Serife Tokaloglu</td>
<td>Hall A</td>
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<tr>
<td>Inv. 11: Prof. Dr. Mustafa Soyik-Encyclopedia U, TR: Microextraction and Solid Phase Microextraction Strategies for Traces Species and Nanoparticles in Envir.</td>
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<tr>
<td>M. Zahir Düz-Dicle U- Removal of Cadmium (II) in the aqueous solutions by biosorption of Bacillus licheniforms isolated from soil in the area of Tigris River-OP64</td>
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<tr>
<td>Furkan Özcan-Encyclopedia U- Deep eutectic solvent based microextraction of tartrazine at trace levels-OP40</td>
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<tr>
<td>Melek Avs-Bilkent U- Solid Phase Extraction of Cu2+, Ni2+ and Cd2+ using by N-N'-bis(5-methoxsalicylidene)-2-hydroxy-1,3 propanediamine modified silica gel-OP63</td>
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</tbody>
</table>

Tea/Coffee break

Session 7: Poster Session 1(1-42)


Session 8: Chairs: Erdem Yesilada-Ismail H. Boyaci | Hall B | Session 9: Chairs: Sibel Ozkan- Bekir Salih | Hall A |
<table>
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<tbody>
<tr>
<td>Inv. 13: Prof. Dr. Resat Apak-Istanbul U, Basic reasoning behind novel sensor and nanoprobe design for the on site/in field determination of energetic comp.</td>
<td></td>
<td>Inv 14: Prof. Dr. Ilham Gulcin-Ataturk U, TR: Phenolic Antioxidants: Potent Inhibitor/Drugs for Some Metabolic Enzymes</td>
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<tr>
<td>F. Bedir Erim- ITU- Rosmarinonic and Carnosic Acid Contents and Correlated Biological Activities of 15 Salvia Species from Anatolia-OP25</td>
<td></td>
<td>Mustafa Celehes- Hacettepe U- Is It Possible To Use Pooled Plasma Samples For Large-Scale Human Metabolic Studies? A Comparison Of The Metabolite Profiles Of Pooled Plasma Samples</td>
<td></td>
</tr>
<tr>
<td>Belgin Izgi-Uludag U- Examination of Screening Some Additives and Metabolites Used in Plastic Materials by LA-ICP-MS and GC-MS-OP69</td>
<td></td>
<td>Mehmet Atakay- Hacettepe U- Conformational Characterization of Protein-Polyelectrolyte Complexes Using Trapped Ion Mobility Spectrometry-Time-of-Flight Mass Spectrometry-OP52</td>
<td></td>
</tr>
<tr>
<td>M Fatat baran- Mardin U- Synthesis, Characterization and Applications Of Antimicrobial Activity Of Silver Nanoparticles From Juglans regia-OP48</td>
<td></td>
<td>Tuğba Yayuz-Ege U- Level of Some VOCs In Breath of Asthma Patients and Healthy Subjects-OP72</td>
<td></td>
</tr>
</tbody>
</table>

Tea/Coffee break

Session 10: Chairs: Eminhan Nemutlu

Mustafa Ersoz: COST

Gala Dinner-Music
<table>
<thead>
<tr>
<th>Time</th>
<th>Session 11</th>
<th>Session 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00</td>
<td>Inv 15: Prof. Dr. Adil Denizli- Hacettepe U- Plasmonic Nanosensors for Analytical Applications</td>
<td>Inv 16: Prof. Dr. Hasan Turkez- Erzurum Teknik U- Nanotechnology-Based Drug Delivery</td>
</tr>
<tr>
<td>10:00</td>
<td>Hasan Karadag-Adiyaman U- Determination of Changes in Glutathione Reductase Activity Exposed to Imidaclopid and Thiamethoxam-OP39</td>
<td>Burcak Demirbakan-18 Mart U- A sensitive novel electrochemical biosensor based on a silane agent modified disposable electrodes for cardiovascular disease biomarker-OP1</td>
</tr>
<tr>
<td>11:00</td>
<td>Akif Goktug Bozkur-Ardahan U- Detection of Alkaline Phosphatase Enzyme Activity with Different SERS Platforms-OP11</td>
<td>Elif Burcu Aydin-Namik K.- Electrochemical immunosensor for sensitive detection of p53 cancer biomarker based on benzaldehyde substituted poly(phosphazene) modified disposable ITO electrode-OP4</td>
</tr>
<tr>
<td>11:30</td>
<td>Sarah Albayati- Hacettepe U-A new and simple method for copper determination in aqueous samples: Effervescence-assisted dispersive LLME based on deep eutectic solvent-OP23</td>
<td>Hilal Inciay-Nevsahir U- A Nanostructured Composite System for the Electrochemical Quantification of Aspartame-OP8</td>
</tr>
<tr>
<td>12:00</td>
<td>Ibrahim Dolak-Dicle U- A New Molecularly Imprinted Polymer for Purification of Cytochrome C from Blood Serum-OP46</td>
<td>Burcu Ozcan-18 Mart U- A disposable and low-cost biosensor system for sensitive determination of leptin, a biomarker of obesity-OP2</td>
</tr>
<tr>
<td>12:30</td>
<td>Tea/Coffee break</td>
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<tr>
<td>13:00</td>
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<tr>
<td>13:30</td>
<td>Zuhre Senturk-Van 100. Yil U- The Performance Of Poly(Guanine) Modified Carbon Paste Electrode In Anionic Surfactant Media For Enhancing the Determination Of Codeine-OP19/</td>
<td>Inv 17: Prof. Dr. Nil Ertas- Eg-Ege U- The Use of Green Extraction Techniques for Pesticide Analysis in Food</td>
</tr>
<tr>
<td>14:00</td>
<td>Burcu Dogan Topal-Antakya U- Electrochemical Investigation of Calcium Channel Blockers-dsDNA Interaction on Glassy Carbon Electrode-OP38</td>
<td>Emine Akyuz-Turumtay- Rize U- Anthocyanidin profile of Stachys sylvatica extract and their antioxidant potentials-OP30</td>
</tr>
<tr>
<td>15:00</td>
<td>Sevinç Kurbangil-Antakya U- Electrochemical Determination of Catechol-Orto-Methyl transferase Inhibitor using NH2-Functionalized Multi Walled Carbon Nanotubes based nanosensor-OP5</td>
<td>Emine Akyuz-Turumtay- Rize U- Anthocyanidin profile of Stachys sylvatica extract and their antioxidant potentials-OP30</td>
</tr>
<tr>
<td>15:30</td>
<td>Goksu Ozcelik-Antakya U- A novel electrochemical nanosensor based on NH2-Functionalized MWCN Decorated with ZnO Nanoparticles and Graphene Quantum Dots for Pimozide Assay-OP6</td>
<td>Gulsaah Ozcan Sinir- Uludag U- Determination of Honey Adulteration Based on Volatile Profile using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) with Chemometrics-OP17</td>
</tr>
<tr>
<td>16:00</td>
<td>Ulu Guler-Hacettepe U- Developing On-Surface Enrichment Methods For Ubiquitination Detection-OP53</td>
<td>Havva Tumay-Bingol U- Comparison of Multivariate Calibration Methods to Determine Tahini Adulteration-OP16</td>
</tr>
<tr>
<td>17:00</td>
<td>Murat Celiker-Gaz. Dir of State Hydraulic Works, 9th Regional Directorate, Elazig- Investigation of Concentrations of Some Trace Element (Fe, Mn, Cu, Ni) in Spring Waters in Malatya (Turkey) Region-OP31</td>
<td>Kadir S Celik-Batman U- Determination of aflatoxins by HPLC in nuts and spices after post-column iodine derivatization-OP18</td>
</tr>
</tbody>
</table>

**29 March, 2019**

**Session 15: Poster Session 2 (43-84)**

**Chairs:** Yusuf Dilgin-Ibrahim Yilmaz- Aysegul Golu-Bedia Berker-Filiz Senkal-Mehmet Ozturk

**Excursion: Antalya City Center Tour**
Session 16: Chairs: Sezgin Bakirdere, Hadef Youcef

Najma Memon - Sindhi U, PK - TLC based chiral separation of amino acids onto β-cyclodextrin incorporated glutaraldehyde cross-linked polyvinyl alcohol electrospin fiber stationary phase - OP76

Umran Seven Erdemir-Uludag - Phenolic Contents and Bioaccessibility of Some Elements in Tea (Camellia sinensis L.) Samples Commonly Consumed in the Turkish Market - OP15

Nevin Oztekin - TTU - Determination of Ethylmalonic Acid in Urine by Capillary Electrophoresis with Capacitively Coupled Contactless Conductivity Detection - OP78

Maruf H Demirel-Firat - U - Synthesis and preparation of Biomonomerands for Cleaning of Polluted Wastewater by toxic metals - OP32

Tugce Unutkan - YTU - Vortex Assisted Deep Eutectic Solvent-Liquid Phase Microextraction-Slotted Quartz Tube-FAAS - OP68

Adem Demir - Rize U - Essential oils analysis of Paeonia daurica subsp. macrophylla by two different methods - OP9

Session 17: Chairs: Sławomira Skrzypek-O, Yavuz Ataman

Aysegul Golcu - ITU - Metal Based Drug Candidate Molecules in Chemistry - OP12

Lokman Liv - TUBITAK-UME - Voltammetric Determination of Molybdenum using Various Polymer Film Modified Pencil Graphite Electrodes - OP43

Emrah Uysal - TUBITAK-UME - Establishment of Primary Level Electrolytic Conductivity Measurement System and Uncertainty Estimation - OP42


Felin Senel - ITU - Spectroscopic and voltammetric studies of anticancer drug Fluorouracil bound to fish sperm double-stranded deoxyribonucleic acid (fssDNA) - OP13

Veselina Adimcilar - ITU - In Vitro Controlled Release of an Anticancer Drug Epirubicin from pH Sensitive Hydrogel Systems - OP14


Session 18: Chairs: Arturs Viksna, Belgin Izgi

Inv 18: Prof. Dr. Sezgin BAKIRDERE - YTU - Solid Phase Microextraction Strategies in the Determination of Organic/Inorganic Analytes

Molek Hasean - NEU & KKT - Centrifugelss Switchable Hydrophilic Solvent-Liquid Liquid Microextraction Of Non Steroidal Anti-Inflammatory Drugs In Biological Fluids Followed By Direct Injection Into HPLC - OP20

Ali Doner - Siirtak - Comparison of Corrosion Behaviors of Bare Ti and TiO2 - OP20

Melekh Guner - Magnetic Chitosan Nanocomposite for Effective Removal of Heavy Metals from Water - OP42

Onur Inam - Hacettepe - U- Electroanalytical Determination of Clinically Classified Ophthalmic Drugs - OP74

Session 19: Chairs: Najma Memon, Mustafa Erosl

Inv 19: Prof. Dr. Mutay Asian - Use of Tandem Mass Spectrometry in Fatty Acid and Sphingolipid Measurements


Mehmet Gümiysrás-ANKARA U - The Role and the Benefits of Core-Shell Silica Particles in HPLC - OP58

Burak Arabacs-Hacettepe - U-HPLC Method Development and Validation for the Simultaneous OP75 Analysis of Multi-vitamins in Pharmaceutical Dosage Forms: In Perspective of Industrial Requirements

Nilay Kahya - ITU - Novel Drug Delivery Candidates: Sodium Dodecyl Sulfate Modified Calcium Alginate Beads - OP28

Kenan Can Tok - Antalya U - Rapid Determination of Clozapine and Main Metabolite by High Performance Liquid Chromatography - OP59

Meltem Tay - Mugla U - Anti-inflammatory Activity of Atragapine Honey Collected from Anatolia - OP29

Biliter Sahin - Mugla U - Phenolic compounds of Anatolian Sunflower Honey with Chemicometric Approach - OP29

Closing
INVITED SPEAKERS (IS) .............................................................................................................. 25
S1 IS Luminescent Methods for the Quality Control of Natural Products ................................................... 25
Antony C. Calokerinos ..................................................................................................................... 25
Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece .............................................................................................................. 25
S2 IS The Use of Green Extraction Techniques for Pesticide Analysis in Food ................................................... 26
F. Nil Ertaş, Irem Aydınlı Kirlangıç, Imam Guney Afacan, Levent Pelit, Hasan Ertaş ........................................ 26
Ege University, Science Faculty, Chemistry Dep. Bornova İzmir, TURKEY ..................................................... 26
S3 IS Microextraction and Solid Phase Microextraction Strategies for Traces Species and Nanoparticles in Environment ................................................................................................................... 26
Mustafa Soylak ...................................................................................................................................... 26
Erciyes University, Faculty of Sciences, Chemistry Department, 38039, Kayseri, Turkey ........................................ 26
S4 IS Basic reasoning behind novel sensor and nanoprobe design for the on site/in field determination of energetic compounds ....................................................................................................................... 27
Resat APAK,1,2,*, Ayşem ARDA1, Ziya CAN1, Şener SAĞLAM1, Selen DURMAZEL1 ......................................................... 27
1Faculty of Engineering, Chemistry Department, Istanbul University-Cerrahpaşa, 34320 Istanbul, Turkey ................. 27
S5 IS State of the art in Mass Spectrometry-based Proteomics: Post-translational Modifications, Imaging and Ion Mobility .......................................................................................................................... 28
Bekir Salih ........................................................................................................................................... 28
Hacettepe University, Department of Chemistry, 06800-Ankara/TURKEY .......................................................... 28
S6 IS Recent developments in separation of enantiomers using high-performance liquid chromatography .......... 29
Bezhan Chankvetadze ................................................................................................................................... 29
Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi 0179, Georgia .................................................................................................................. 29
S7 IS Nanotechnology-Based Drug Delivery Approaches for the Treatment of Alzheimer Disease .................. 30
Hasan Turkez ........................................................................................................................................ 30
Department of Molecular Biology and Genetics, Faculty of Science, Erzrum Technical University, Erzrum, Turkey ....... 30
S8 IS Use of Tandem Mass Spectrometry in Fatty Acid and Sfingolipid Measurements ......................................... 32
Mutay Aslan ........................................................................................................................................... 32
Akdeniz University Faculty of Medicine, Department of Medical Biochemistry, Antalya, Turkey ....................... 32
S9 IS Solid Phase Microextraction Strategies in the Determination of Organic/Inorganic Analytes .................. 33
Sėzin Bakirdere …………………………………………………………………………………………………….. 33
Yıldız Technical University, Faculty of Art and Science, Department of Chemistry, 34349 Istanbul, Turkey ........... 33
S10 IS Hypenated techniques for the large scale speciation analysis of metals and metalloids in a biological milieu ........................................................................................................................................ 34
Ryszard Lobinski, Katarzyna Bierla, Laurent Ouerdane, Joanna Szpunar ……………………………………………… 34
Institute for Analytical and Physical Chemistry for the Environment and Materials, CNRS/UPPA UMR5254, Hélioparc. 2, av. Pr. Angot, 64053 Pau, FRANCE ……………………………………………………………………………….. 34
S11 IS Sensors and Biosensors based on Conducting Polymers ........................................................................ 35
Arunas Ramanavičius1,2,*, Mindaugas Gicevicius1, Povilas Genys1, Sarunas Zukauskas1, Linas Sinkievicius1, Vilius Auksionis1, Antanas Zinovicius1, Inga Vilkončienė1, Auša Vallūniūnė1,1, Lina Mikoliūnaitė1, Jurate Petronienė1, Elvydas Andriukonis1, Asta Kausaitė1, Aura Kisieliute1, Urtė Bubnienė1, Almira Ramanavičienė1 …………………………………………………………………………………………………………………………………………………………………………………………………………………………………….. 35
1Faculty of Chemistry and Geosciences, Naugarduko g. 24 03225 Vilnius, Lithuania ……………………………………… 35
2Center for Physical Sciences and Technology, Saulėtekio 3, 10257 Vilnius, Lithuania ……………………………………… 35
S12 IS Authentication of Qualification and Fraud in Natural Medicines by High Performance Thin Layer Chromatography .......................................................................................................................... 36
Erdem Yesilada ……………………………………………………………………………………………………... 36
Yeditepe University, Faculty of Pharmacy, Istanbul, Turkey ……………………………………………………………… 36
S13 IS Food Safety and Quality: Molecular and Elemental Detection ................................................................. 37
İsmail Hakkı Boyacı …………………………………………………………………………………………………… 37
Department of Food Engineering, Hacettepe University, Beytepe 06800, Ankara, Turkey ……………………………… 37
S14 IS Phenolic Antioxidants: Potent Inhibitor/Drugs for Some Metabolic Enzymes ........................................... 38
Ilhami Gülcin ……………………………………………………………………………………………………………... 38
Atatürk University, Faculty of Sciences, Department of Chemistry, 25240-Erzurum-Turkey …………………………….. 38
S15 IS Some ordeals/memories in environmental analysis ……………………………………………………………… 39
O. Yavuz Ataman ……………………………………………………………………………………………………… 39
Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey ……………………………………… 39
S16 IS Disposable Electrode Materials and Their Applications to Biosensing Systems ........................................... 40
Mustafa Kemal Sezginırk…………… ……………………………………………………………………………………….. 40
Çanakkale Onsekiz Mart University, Engineering Faculty, Bioengineering Department, Çanakkale …………………… 40
S17 IS A glance to anticancer drug development with regard to biological activity assays: Story of a metal (e.g. palladium) complex ………………………………………………………………………………… 43
ORAL PRESENTATIONS (OP)

OP1- A sensitive novel electrochemical biosensor based on a silane agent modified disposable electrodes for cardiovascular disease biomarker detection ......................................................... 45

Burak Demirbakan1, Mustafa Kemal Sezgintürk2

1-2 Çanakkale Onsekiz Mart University, Faculty of Engineering, Bioengineering Department Çanakkale/Turkey ........................................ 45

OP2- A disposable and low-cost biosensor system for sensitive determination of leptin, a biomarker of obesity ........................................ 48

Burcu Ozcan1, Mustafa Kemal Sezgintürk2

1-2Çanakkale Onsekiz Mart University, TÜRKÝ, PhD ......................................................... 48

OP3- Nanomaterial enhanced disposable neuro-biosensing platform: Selective detection of Alzheimer’s disease biomarker ......................................................... 51

Munteha Nur Sonuç Karaboga1, Mustafa Kemal Sezgintürk2

1 Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara, Turkey ......................................................... 51

OP4- Electrochemical immunoassay for sensitive detection of p53 cancer biomarker based on benzaldehyde substituted poly(phosphazene) modified disposable ITO electrode ......................................................... 54

Elif Burcu AYDIN1, Muhammet AYDIN1, Mustafa Kemal Sezgintürk2

1 Namık Kemal University, School of Technological and Scientific Research Center, Tekirdag – TURKEY ......................................................... 54

OP5- Electrochemical Determination of Catechol-Orto-Methyltransferase Inhibitor using NH2-Functionalized Multi Walled Carbon Nanotubes based nanosensor ......................................................... 62

Sevenc Kurbanoglu1, Saima Aftab1,2, Goksu Ozcelikay1, Afzal Shah3,2, Fazila Jan Iftikhar4, Sibel A. Ozkan1

1 Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara, Turkey ......................................................... 62

OP6- A novel electrochemical biosensor based on NH2-Functionalized Multi Walled Carbon Nanotubes

Decorated with ZnO Nanoparticles and Graphene Quantum Dots for Pimozide Assay ......................................................... 59

Goksu Özcelikay1, Saima Aftab1,2, Sevenc Kurbanoglu1, Afzal Shah3,2, Sibel A. Ozkan1

1 Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara, Turkey ......................................................... 59

OP7- Fabrication of A Novel Surfactant Based Electrochemical Nanosensor for Esmolol Determination ......................................................... 62

Leyla Karadurmus1,2,3, Nurgül Karadaş Bakıran4,5, Anum Zahid4,6, Afzal Shah7, Sibel A. Ozkan8

1,2 Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara, Turkey ......................................................... 62

OP8- A Nanostructured Composite System for the Electrochemical Quantification of Aspartame ......................................................... 64

Hilal İNCEBAY1

Neveshir Haci Bektas Veli University, Faculty of Arts and Sciences, Department of Molecular Biology and Genetics, Neveshir/Turkey ......................................................... 64

OP9- Evaluation of Antimicrobial Effect of Simvastatin on E. coli with Metabolomics Analysis ......................................................... 67

Engin Kocak1, Ceren Ozkul2, Ozan Kaplan1, Mustafa Celebi1, Emirhan Nemrutlu1, Sedef Kir1, Meral Sagirolu2

1 Hacettepe University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara-Turkey ......................................................... 67

OP10- Growth of ZnO Nano-flower on Nano-TiO2 Doped Biodegradable Hydrogel: An Investigation of Antibacterial Property ......................................................... 70

Fatma Ozge Gökmen1,2, Elif Yaman3, Sinan Temel2, Nurgül Özbay3

1,3 Bilecik Şeyh Edebali University, Central Research Laboratory, Bilecik, TURKEY ......................................................... 70

OP11- Detection of Alkaline Phosphatase Enzyme Activity with Different SERS Platforms ......................................................... 73

Aksen Gokturk Boykur1, Ismail Hakki Boyaci2, Ugur Tamer3

1 Department of Food Engineering, Faculty of Engineering, Ardahan University, 75002 Ardahan, Turkey ......................................................... 73

OP12- Metal Based Drug Candidate Molecules in Chemistry ......................................................... 76

Aysegul GOLCUL

Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, Maslak, 34469, Istanbul, Turkey ......................................................... 76

OP13- Spectroscopic and voltammetric studies of anticancer drug Fludarabine bound to fish sperm double-stranded deoxyribonucleic acid (fdsDNA) ......................................................... 78

Pelin SENEL, Aysegul GOLCUL

Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, Maslak, 34469, Istanbul, Turkey ......................................................... 78

OP14- In Vitro Controlled Release of an Anticancer Drug Epirubicin from pH Sensitive Hydrogel Systems ......................................................... 80

Veselina Admircal1, Vural Büttün2, Aysegul GOLCUL

1 Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, 34469, Maslak, ISTANBUL ......................................................... 80

OP15- Phenolic Contents and Bioaccessibility of Some Elements in Tea (Camellia sinensis L.) Samples Commonly Consumed in the Turkish Market ......................................................... 83

Umran Seven Erdemir1, Seref Gucer2

1 Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, 34469, Maslak, ISTANBUL ......................................................... 83
Bursa Uludag University, Faculty of Arts and Sciences, Department of Chemistry, Bursa-Turkey

OP16- Comparison of Multivariate Calibration Methods to Determine Tahini Adulteration

Havva Tunay Temiz1,2*, Uğur Tamer1, Ayseg Berkkan1, Ismail Hakki Boyaci1

1 Department of Food Engineering, Faculty of Engineering, Hacettepe University, Beytepe 06800, Ankara, Turkey
2 Department of Food Engineering, Faculty of Engineering, Bingöl University, 12000, Bingöl

OP17- Determination of Honey Adulteration Based on Volatile Profile using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) with Chemometrics

Gulsah OZCAN-SINIR1,2,*, Didem Peren AYKAS-CINKILIC1,3, Sheryl BARRINGER2

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2 Department of Food Engineering, Faculty of Engineering, Hacettepe University, Ankara, Turkey
3 Department of Food Engineering, Faculty of Engineering, Bingöl University, 12000, Bingöl

OP18- Determination of aflatoxin by HPLC in nuts and spices after post-column iodine derivatization

K. Serdar Celik1,2, M. Firat Baran2, Mehmet Duzgun1, Ibrahim Dolak1, M. Zahir Du2 and Ersin Kilinc1

1 Batman University, Science Faculty, Chemistry Department, Batman/TURKEY
2 Van Yuzuncu Yil University, Faculty of Science

OP19- The Performance Of Poly(Guanine) Modified Carbon Paste Electrode In Anionic Surfactant Media For Enhancing The Determination Of Codeine

Serkan Korkmaz1, Pinar Talay Pinar2, Zuhre Senturk1

1 Van Yuzuncu Yil University, Faculty of Science1 and Pharmacy2, Department of Analytical Chemistry, Van, Turkey

OP20- Comparison of Corrosion Behaviors of Bare Ti and TiO2

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OP21- Voltammetric Determination of Quercetin in Tea Samples

Ebru Kuyumcu Savan1

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OP22- Is It Possible To Use Pooled Plasma Samples For Large-Scale Human Metabolomic Studies? A Comparison Of The Metabolite Profiles Of Pooled Plasma Samples With Random Individual Samples Using Q-TOF LC/MS

Mustafa Celebier1,2, Ozan Kaplan1, Sule Ozel1, Yaprak Engin-Ustun1, Engin Kocak1

1 Hacettepe University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara-Turkey

OP23- A new and simple method for copper determination in aqueous samples: Effervescence-assisted dispersive liquid-liquid microextraction based on deep eutectic solvent

Sarah Albayati, Maha Yahya, Cigdem Arpa, F. Sema Bektas

Chemistry Department, Hacettepe University, Ankara, Turkey

OP24- Non-viral siRNA Delivery for Targeted Cancer Theranostic

A. Ismail Ozyak1, F. Cakmak1, O. Demirci1, U. Ozar1, V. Tolan1, Ersin Kilinc1

1 Department of Chemical and Chemical Processing Technologies, Vocational School of Technical Sciences, Dicle University, Diyarbakir, Turkey

OP25- Rosmarinic and Carnosic Acid Contents and Correlated Biological Activities of 15 Salvia Species from Anatolia

F. Bedir Erim1,2, Zeynep Kayacioglu1, Veselina Adicmlcar1, Nihal Aydogdu1, Tuncay Dirmenci2, Ahmet Kahraman3

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OP26- Preparation of N-(Tris(hydroxymethyl)ethyl) acrylamide hydrogel for removing boron from water

 Gulcin Torunoglu Turan, Bahire Filiz Senkal

Istanbul Technical University Chemistry Department, 34469, Maslak/Istanbul

OP27- Investigation of the Solubility of Polyphenolic Compounds in the Presence of Lactic Acid Butylether PEG (200)

Gulcemal Yildiz1, Bahire Filiz Senkal, Ebru Teknecli

Istanbul Technical University Chemistry Department, 34469, Maslak/Istanbul

OP28- Novel Drug Delivery Candidates: Sodium Dodecyl Sulfate Modified Calcium Alginate Beads

Nilay Kahya1, F. Bedir Erim1

Istanbul Technical University, Department of Chemistry, Maslak, 34469, Istanbul, Turkey

OP29- Essential oils analysis of Paeonia daurica subsp. macrophylla by two different methods

Adem Demiri1, Halbay Turumtay2, Cemal Sandalli1, Emine Akyuz Turumtay2

1 Department of Chemistry, Recep Tayyip Erdogan University, 53100 Rize, Turkey
2 Department of Pharmacy, Inonu University, Malatya, Turkey

OP30- Anthocyanin profile of Stachys sylvatica extract and their antioxidant potentials

Halbay Turumtay2, Adem Demiri1, Emine Akyuz Turumtay2

2 Department of Chemistry, Recep Tayyip Erdogan University, 53100 Rize, Turkey

OP31- Investigation of Concentrations of Some Trace Element (Fe, Mn, Cu, Ni) in Spring Waters in Malatya

(Turkey) Region

Murat Celiker

General Directorate of State Hydraulic Works, 9th Regional Directorate, Elazig, Turkey

OP32- Synthesis and Preparation of Bionanosorbents for Cleaning of Polluted Wastewater by toxic metals

Maruf Hursit Demirel, Mehmet Yaman

Firat University, Science Fac. Dep. of Chemistry, Elazig-Turkey

14
OP48- Synthesis, Characterization and Applications Of Antimicrobial Activity Of Silver Nanoparticles From Juglans regia ................................................................. 143
M. Firt Baran ........................................................................................................ 143
Mardin Artuklu University, Medical Laboratory Techniques, Vocational Higher School of Healthcare Studies, 47200 Mardin, Turkey ........................................................................................................ 143

OP49- A titania-glyco purification tip containing bioanalytical method for MS-based glycoproteomics and glycomics ........................................................................................................ 143
Haci Mehmet Kayilli1,2,*, Izzet Avci1, Bekir Salih1,2 ................................. 143
1Department of Chemistry, Hacettepe University; 06800-Ankara, Turkey ................................................................................................................................. 143

OP50- Synthesis and Antibacterial Properties of Nitrogen or Carbon Doped Titanium Oxide Nano Films ..................................................................................... 144
A.I. Abdulagatov1, Kr. N. Ashurbekova1, Ka. N. Ashurbekova1, R.R. Amashaev1, A.M. Maksumova1, A. Aliev2, M. Kh. Rabadano1, I. M. Abdulagatov1,2,*, 1Dagestan State University, Makhachkala, Batyraya 4 str., Dagestan, 367008 Russian Federation ........................................................................ 144

OP51- Study on the Interaction between St. John’s Wort and Sertraline with Plasma Proteins and Cell-Culture Medium .................................................................................. 145
Yasar Kaan EREN1,2, Inci GULLU1,2, F. Baris BARLAS2, Suna TIMUR1,2, Z. Pınar GUMUS2, 1Central Research Testing and Analysis Laboratory Research and Application Center (EGE-MATAL), Ege University, Bornova, İzmir, 35100, Turkey ........................................................................................................ 145

OP52- Conformational Characterization of Protein-Polyelectrolyte Complexes Using Trapped Ion Mobility Spectrometry–Time-of-Flight Mass Spectrometry ........................................................................................................ 146
Mehmet Atakay ......................................................................................................... 146
Department of Chemistry, Hacettepe University, Ankara, 06800, TURKEY ................................................................................................................................. 146

OP53- Developing On-Surface Enrichment Methods For Ubiquitination Detection ......................................................................................................................... 147
Ulku Guler ................................................................................................................. 147
Hacettepe University Department of Chemistry ................................................................................................................................. 147

OP54- HPLC Method Optimization for Determination of Recombinant Human Coagulation Factor VIII Concentrate ............................................................................. 148
Z. Pınar GUMUS2,*, Jude Caleb, Ihsan Çalış, Yılmaz UĞUR2,*, F. Baris BARLAS2, Suna TIMUR1,2, Z. Pınar GUMUS2, 1Central Research Testing and Analysis Laboratory Research and Application Center (EGE-MATAL), Ege University, Bornova, İzmir, 35100, Turkey ........................................................................................................ 148

OP55- An Experimental Design Approach For The Solid-Phase Extraction Of Organophosphorus Pesticides From Water Samples ........................................................................ 149
Elif Tumay Ozer*, Bilgen Osman, Buse Parlak ............................................. 149
Bursa Uludag University, Art and Science Faculty, Department of Chemistry, 16059, Bursa, Turkey ........................................................................................................ 149

OP56- Scaling-Up of Dispersive Liquid-Liquid Microextraction for the Isolation of Piperine from Black Pepper ................................................................. 150
Maisy Al-Nidawi1, Usama Alshana2,*, Jude Caleb1, Zia Ur Rahman1, Duygu Yiğit Haşoğlu1, İhsan Çalış2,*, 1Dep. of Analytical Chem., Faculty of Pharmacy, Near East University, 99138, Nicosia, TRNC, Mersin 10, Turkey ........................................................................................................ 150

OP57- A vortex assisted deep eutectic solvent based-liquid-liquid microextraction for the determination of caffeine in Turkish coffee samples by HPLC-UV ........................................... 151
Sezen Sivriyka ....................................................................................................... 151
Duzce University, Faculty of Technology, Polymer Engineering Department, Duzce-Turkey ........................................................................................................ 151

OP58- The Role and the Benefits of Core-Shell Silica Particles in HPLC ................................................................................................................................. 152
Mehmet GÜMÜSTAS .......................................................................................... 152
Ankara University, Institute of Forensic Sciences, Department of Forensic Toxicology, Ankara, Turkey ............................................................................................. 152

OP59- Rapid Determination of Clozapine and Main Metabolite by High Performance Liquid Chromatography ..................................................................................... 153
Kenan Can TOK1, Fezile OZDEMIR1, Mehmet GÜMÜSTAS2, H. Sinan SUZEN2,*, 1Ankara University, Institute of Forensic Sciences, Department of Forensic Toxicology, Ankara, Turkey ........................................................................................................ 153

OP60- Pharmacokinetic profiles of metamizole metabolites in horses ................................................................................................................................. 154
İsmet YILMAZ1, Zeynep MARAŞ2, Yılmaz UĞUR1, Mustafa Erkan Özgür3, Murat DURMAZ2, Halil İbrahim Ulusoy5, Selim ERDOGAN2,*, 1İnönü University, Faculty of Pharmacy, Department of Analytical Chemistry, 44280, Malatya, Turkey ........................................................................................................ 154

OP61- Intercomparison of Different Analytical Methods for the Quality Control of Calcium and Phosphorus Ratios in Hydroxyapatites ................................................................................ 155
Arturs Viksna1, Vladiens Grebnevs1, Karlis Agris Gross2, Liene Pluduma2, Oskars Purmalis3, Maris Klavins3,*, 1Department of Analytical Chemistry, University of Latvia, Jelgavas 1, LV-1004, Riga, Latvia ........................................................................................................ 155

OP62- Distribution of Elements in Milk Samples: The Single Step Fractionation Approach ........................................................................................................... 156
Feyzullah Tokay*, Sema Bağdat ................................................................. 156
Balıkesir University, Faculty of Science and Arts, Chemistry Departments, 10145 Çağış-Balıkesir, Turkey ........................................................................................................ 156

OP63- Solid Phase Extraction of Cu2+, Ni2+ and Cd2+ using by N-N’-bis(5-methoxysalicilylidene)-2-hydroxy-1,3 propanediamine modified silica gel ................................................................................ 156
Melek Avci1,2,*, Feyzullah Tokay2, Sema Bağdat2,*, 1Robert College, İstanbul, Turkey ........................................................................................................ 156
2Balıkesir University, Faculty of Science and Arts, Chemistry Departments, 10145 Çağış-Balıkesir, Turkey ........................................................................................................ 156

16
OP64 - Removal of Cadmium (II) in the aqueous solutions by biosorption of Bacillus licheniformis isolated from soil in the area of Tigris River. 

1M. Fırat Baran, 2Mohmet Düzgün, 3K. Serdar Celik, 4M. Zahir Duz,5Ersin Klın, 6A. Saydut ............................................. 157
1Mardin Artuklu University, Medical Laboratory Techniques, Vocational Higher School of Healthcare Studies, 47200 Mardin, Turkey ............................................. 157


Prior to Slotted Quartz Tube-Absorption Spectrometry ............................................. 158
Buse Tugba Zaman1, Emine Gulhan Bakirdere2* ............................................. 158
1Yildiz Technical University, Faculty of Art and Science, Department of Chemistry, 34349 Istanbul, Turkey ............. 158


Nursu Aylin Kasa1, Emine Gulhan Bakirdere2*, Sezgin Bakirdere3 ............................................. 159
1Chemistry Department, Faculty of Art and Science, Yildiz Technical University, 34210, Turkey ......................... 159


Sezin Erparat1, Suleyman Bodur1, Ersöz Özk2, Sezgin Bakirdere3* ............................................. 160
1Yildiz Technical University, Faculty of Art and Science, Department of Chemistry, 34210 Davutpasa, Esenler, Istanbul, Turkey ............................................. 160


Zeynep Tekin1, Tuğçe Unutkan1, Fatih Ahmet Erolu1, Emine Gulhan Bakirdere4, Sezgin Bakirdere1* ............................................. 161
1Yildiz Technical University, Department of Chemical Engineering, 34349 Istanbul, Turkey ..................... 161

OP69 - Examination of Screening Some Additives and Metabolites Used in Plastic Materials by LA-ICP-MS and GC-MS. 

Murat KAYAR1, Belgin İZGI2* ............................................. 162
1Bursa Uludağ University, Science and Art Faculty, Department of Chemistry BURSA ............................................. 162

OP70 - Toxic effect of terpenoid esters on the Aedes aegypti mosquitoes. 

Marina Nesterkina1, Ulrich Bernier2, Nurhayat Tabanca3, Iryna Kravchenko1 ............. 163
1Department of Organic and Pharmaceutical Technology, Odessa National Polytechnic University, 65044 Odessa, Ukraine ............................................. 163

OP71 - Metabolomics Studies in Urine Samples Prepared by Thin Film Extraction Method. 

İlkın Erbaş1, Fusun Okcu Pelit2, Fethullah Bayram3, Tuğberk Nail Dıdıças3, Kasım Ocakgöl3, Durmuş Özdemir3, Levent Pelit1 ............................................. 164
1Ege University, Faculty of Science, Department of Chemistry, Bornova Izmir/TURKEY ............................................. 164

OP72 - The Level Of Some Voc In Breath Of Asthma Patients And Healty Subjects. 

Tugba Yavuz1, Baysal E1, Dıdıças T. N1, Bayram F1, Ann A1, Göksel Ö2, Fusun Okcu Pelit, Göksel T3, F. Nil Ertas 1, Levent Pelit1* ............................................. 165
1Ege University, Faculty of Science, Department of Chemistry, Bornova Izmir/TURKEY ............................................. 165

OP73 - Flow Injection Amperometric Sensor for the Determination of Formaldehyde based on its electrocatalytic Oxidation at Cu Nanoparticles Modified Graphite Pencil Electrode. 

Didem Giray Dilgin ............................................. 166
Canakkale Onsekiz Mart University, Faculty of Education, Department of Mathematics and Science Eduction, Chemistry Education Programme, 17100, Çanakkale, Turkey ............................................. 166

OP74 - Electroanalytical Determination of Clinically Classified Ophthalmic Drugs. 

Onur İNAM1,2, Ersin DEMİR3, Bengi USLU4 ............................................. 167
1Hacettepe University, Faculty of Medicine, Department of Ophthalmology, Ankara, Turkey ............................................. 167

OP75 - HPLC Method Development and Validation for the Simultaneous Analysis of Multi-vitamins in Pharmaceutical Dosage Forms: In Perspective of Industrial Requirements. 

Fırat Yerlikaya1*, Burak Arabaci2, Kaan Yurtoğlu1, Ashlan Arslan1,3, Pelin Geňşer1, Eminhan Nemutlu4* ............. 168
1Elixir Pharmaceutical Research and Development Corporation, Hacettepe University Technology Development Zone, Ankara, Turkey ............................................. 168

OP76 - TLC based chiral separation of amino acids onto β-cyclodextrin incorporated glutaraldehyde cross-linked polyvinyl alcohol electrop spun fiber stationary phase. 

Sahriş Khatri1, Najma Memón1, Zeeshan Khatri2, Fawroq Ahmed2 ............................................. 169
1National Centre of Excellence in Analytical Chemistry, University of Sind, Jamshoro. 2Nanomaterial Research Group, Department of Textile Engineering, Mehran University of Engineering and Technology, Jamshoro, Pakistan. ............................................. 169

OP77 - Determination of Ethylnalonic Acid in Urine by Capillary Electrophoresis with Capacitively Coupled Contactless Conductivity Detection. 

Sirun Özçelik1, Nevin Oztekın3, Ertuğrul Krykm2 ............................................. 170
1Department of Chemistry, Technical University of Istanbul, Maslak, 34469 Istanbul, Turkey ............................................. 170
OP78- Magnetic Chitosan Nanocomposite for Effective Removal of Heavy Metals from Water
Melek GÜNER1, Betül ÇİÇEK ÖZKAN1, Hilal INCEBAY2, Niyazi ÖZDEMİR1
1Fırat University, Faculty of Technology, Department of Metallurgy and Materials Engineering, Elazığ/Turkey... 172
OP79- Does Aroma Ingredients Define the Origin of Citrus Honey? The Chemometric Approach of Aroma
Compounds of Citrus Honey collected from Antalya
Mehmet Öztürk1*, Selçuk Küçükaydın2, Meltem Taş1, Fatih Çayan3, Mehmet Emin Duru1
1Muğla Sitki Koçman University, Faculty of Science, Department of Chemistry, Menteşe-Muğla...... 173
OP80- Anti-inflammatory Activity of Astragalus Honey Collected from Anatolia
Meltem Taş1*, Selçuk Küçükaydın2, Mehmet Öztürk1, Mehmet Emin Duru1
1Muğla Sitki Koçman University, Faculty of Science, Department of Chemistry, Menteşe-Muğla...... 176
OP81- Phenolic compounds of Anatolian Sunflower Honey with Chemometric Approach
Bihter Şahin1*, Gülsen Tel-Çayan2, Mehmet Öztürk1, Mehmet Emin Duru1
1Muğla Sitki Koçman University, Faculty of Science, Department of Chemistry, Menteşe-Muğla...... 178
OP82- Centrifugeless Switchable-Hydrophilicity Solvent Liquid-Liquid Microextraction Of Non-Steroidal Anti-Inflammatory Drugs In Biological Fluids Followed By Direct Injection Into HPLC
Malek Hassan, Usama Alshana*
Department of Analytical Chemistry, Faculty of Pharmacy, Near East University, 99138, Nicosia, TRNC, Mersin 10, Turkey...... 181
Poster Presentations

PP1 - A label-free electrochemical biosensor for direct detection of IL 1β by using star-shaped poly(glycidyl methacrylate) modified ITO based electrode ......................................................... 182
Muhammet AYDIN1, Elif Burcu AYDIN1, Mustafa Kemal Sezgin12 ............................................ 182
1 Namik Kemal University, Scientific and Technological Research Center, Tekirdag – TURKEY .......... 182
PP2 - Amino acid functionalized perylene bisimide for the sequential determination of mercury and biotoxins ... 185
Sukriye Nihan KARUK ELMAS, Ibrahim Berk GUNAY, Abdurrahman KARAGOZ, Ibrahim YILMAZ ........ 185
Karmanoglu Mehmetbey University, Kamil Ozdag Science Faculty, Karaman, 70100, TURKEY .............. 185
PP3 - Disposable and cost-effective ITO based biosensor system to analyse Melanoma antigen1 .................. 185
Burcu Ozcan1, Mustafa Kemal Sezgin12 ......................................................................................... 185
1Çanakkale Onsekiz Mart University, TURKEY, PhD ................................................................. 185
PP4 - Development of an ITO based disposable and highly reproducible biosensor to quantify C1-INH in real human serum samples ........................................................................................................... 187
Nur TARIM, Mustafa Kemal Sezgin12 ................................................................. 187
1Department of Bioengineering, Faculty of Engineering, Çanakkale Onsekiz Mart University, Turkey .......... 187
PP5 - Selective Separation of Hemoglobin from Blood Serum by Lanthanide-Chelate Based Molecularly Imprinted Cryogel ................................................................. 188
Gurban Canpolat1, İbrahim Dolak1, Ruken Ona1, Beriin Ziyadanoğullan1, Arzu Ersöz1, Ridvan Say1 ........ 188
1Vocational School of Technical Sciences, Dicle University, Diyarbakir .............................................. 188
PP7 - A Novel colorimetric and fluorescence chemosensor based on coumarine derivate for the determination of copper(II) ion ........................................................................................................... 189
Sukriye Nihan KARUK ELMAS1, Ibrahim Berk GUNAY1, Furkan OZEN2, Kenan KORAN3, Ahmet Orhan GORGULU1, Ibrahim YILMAZ1 ........................................................................ 189
1Karmanoglu Mehmetbey University, Kamil Ozdag Science Faculty, Karaman, TURKEY ................. 189
PP8 - Primary Level High Precision Coulometry: Determination of HCl and KCl ................................. 189
Lokman Liv1, Emrah Uysal ........................................................................................................... 190
1TUBITAK UME, National Metrology Institute, Electroanalytical Chemistry Laboratory, PK 54, 41470 Gebze, Kocaeli 190
PP9 - ICP-MS Determination of Heavy Metals Concentrations in Eight Fish Species from Kayseri, Turkey and Chemometric Evaluation of the Results ......................................................... 191
Şerife Tokaloğlu1,2, Zafer Gönülalan2, Nurhan Ertaş Onmaz2, Erdal Yılmaz3, Emrah Şimşek3 ................. 191
1Erciyes University, Faculty of Science, Chemistry Department, 38039 Kayseri, Turkey ......................... 191
PP10 - A New Magnetic Solid Phase Bio-extractor (Anoxybacillus flavithermus SO-17) for Preconcentration of Cu(II) .................. 192
Sadıq Odzemir1,*, Zeynep Turkan1, Ersin Klinc1, M. Fırat Baran4, Mustafa Soylak5 ................................ 192
1Department of Chemical and Chemical Processing Technologies, Vocational School of Technical Sciences, Dicle University, 21280, Diyarbakir, Turkey ......................................................... 192
PP11 - Preconcentration of U(VI) by magnetized solid phase bio-extractor ..................................... 192
Sadıq Odzemir1,*, Ersin Klinc1, M. Serkan Yalcın2 ................................................................. 192
1Food Processing Programme, Technical Science Vocational School, Mersin University, TR-33343 Yenisehir, Mersin, Turkey ................................................................. 192
PP12 - Determination of Aluminium in Water Resources With New Synthesized N,N’-Bis (2,5-dihydroxybenzylidene)-4,4’-diamino Diphenyl Ether by Using Fluorimetric Method .......................... 193
S. Beniz Gündüz1, Havva Nur Köştekçi1, Mustafa Şahin1, Nuriye Koçak1 ................................................ 193
1Selçuk University Faculty of Science, Department of Chemistry, 42031, Campus-Konya/TÜRKİYE ........ 193
PP13 - Removal of Pb, Cu, Zn, Fe, Ni and Cd from drinking water and wastewater by Bacillus Subtilis using ICP-MS ........................................................................................................... 194
M. Fırat Baran1, M. Zahir Duz2, Mehmet Duzgun3, Serhat Uzan4, Husemettin Aygun5, Sadıq Odzemir6, Ersin Klinc1, Mustafa Soylak7 ................................................................. 194
1Mardin Artuklu University, Medical Laboratory Techniques, Vocational Higher School of Health care Studies, 47200 Mardin, Turkey ................................................................. 194
PP14 - Assessment with humic acid of trace elements by multivariate statistical methods of some agricultural soils in Diyarbakır area ......................................................... 196
Mehmet Düzgün1, M. Fırat Baran2, Ramazan Selçuk1, Ramazan Ceylan1, M. Zahir Duz2, A. Saydut4 .................. 196
2 Dicle University, Faculty of Science, Department of Chemistry, Diyarbakır, Turkey ......................... 196
PP15 - Evaluation by multivariate statistical methods of relationship humic acid and some elements in agricultural soil ........................................................................................................... 200
Mehmet Düzgün1, M. Fırat Baran2, Ramazan Selçuk1, Ramazan Ceylan1, M. Zahir Duz2, A. Saydut4 ........... 200
PP16- Reduction of Interferences of Ascorbic Acid, Uric Acid and Dopamine in Flow Injection Amperometric Glucose Biosensor at a Pt Nanoparticle Modified Pencil Graphite Electrode .................................................. 201
Serkan Karakaya*, Yusuf Dilgin.......................................................... 201
Canakkale Onsekiz Mart University, Faculty of Science and Arts, Department of Chemistry, Canakkale, Turkey..
PP17- Scaled-up Dispersive Liquid-liquid Microextraction for the Isolation of Three Major Capsaicinoids from Cultivars of Capsicum annuum L. ............................................................. 202
Jude Caleb*, Usama Alshana*, Azmi Hanoglu*, Ihsan Çalış* ................... 202
1Depart. of Analytical Chem., Faculty of Pharmacy, Near East University, 99138 Nicosia, TRNC, Mersin 10, Turkey

PP18- Effect of gold nanoparticles on the morphological changes in fish's tissues and internal organs ............ 203
Abdullaeva N.R., 1Mammarov S.N., 1,2 I. M. Abidulagatov .................................................. 203
1Dagestan State University, Makhachkala, Dagestan, Russian Federation ........................................ 203
PP19- Quercus alba Green and Amber Leaves Chemical Profile .................................................. 203
Nina Djapic .......................................................... 203

University of Novi Sad, Technical Faculty “Mihajlo Pupin”, Zrenjanin, Serbia ........................................ 203
PP20- Evaluation and Formation of Graphite Electrode by Composite Layer Based on Polypyrrole, Prussian Blue, Co, Ni Hexacyanoferrates and Glucose Oxidase .................................................................................. 204
Asta I. Rekertaite1, 2, Aušra Valiūnienė, Giedrė Medvickytė, Arunas Ramanavičius ............................. 204
1Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko St. 24, LT-03225 Vilnius, Lithuania .................................................. 204
PP21- A New Colorimetric Test for the Determination of Peanut Allergen Residues in Foods .................. 205
Izge Sanlitürk, Burhan Bora, Serap Evran* .................................................................................. 205
2Department of Biochemistry, Faculty of Science, Ege University, Izmir, 35040 Turkey .......................... 205

PP22- Quantitation design of ephedrines by GC/MS – Multivariate optimization, validation of methods and applications in urines .......................................................... 206
Youcef Hadsf 1,2, 3, Alain Nicolay 1, Henri Portugal 1, Jacques Kaloustian 3................................. 206
1Laboratoire de Chimie Analytique, Département de Pharmacie, Faculté de Médecine, Université Badji Mokhtar, BP 205, Annaba (23000), Algérie .................................................. 206
2Laboratoire de développement et de contrôle des préparations pharmaceutiques hospitalières .................. 206

PP23- Dispersive Liquid-Liquid Microextraction of Caffeine from Turkish Coffee Prior to Its Determination by HPLC .................................................................................. 207
Jude Caleb, Hüsun Tabur, Usama Alshana* .......................................................... 207
4Department of Analytical Chemistry, Faculty of Pharmacy, Near East University, 99138 Nicosia, TRNC, Mersin 10, Turkey

PP24- Investigation of the Combination of Fluoxetine and Clozapine on the U87 Cell Line ..................... 208
Incı GULLU1, 2, F. Baris BARLAS1, Z. Pınar GUMUS1, Suna TIMUR1, 2* .................................................. 208
1Central Research Testing and Analysis Laboratory Research and Application Center (EGE-MATAL), Ege University, Bornova, Izmir, 35100, Turkey .................................................. 208
2Department of Biochemistry, Faculty of Science, Ege University, Bornova, Izmir, 35100, Turkey .................. 208

PP25- Investigation of Drug-Drug Interactions of Venlafaxine and Sertraline in the Simulated Gastric Fluid ...... 209
Ozan MERT1, 2, Suna TIMUR1, 2, Z. Pınar GUMUS3* .......................................................... 209
1Central Research Testing and Analysis Laboratory Research and Application Center (EGE-MATAL), Ege University, Bornova, Izmir, 35100, Turkey .................................................. 209
2Department of Biochemistry, Faculty of Science, Ege University, Bornova, Izmir, 35100, Turkey .................. 209

PP26- Determination of α-Tocopherol, Vitamin A and β-Carotene by using Molecularly Imprinted Polymers ... 210
Batuhan ORMAN1, 2, Raif ILKTAÇ1, Z. Pınar GUMUS2* .......................................................... 210
1Central Research Testing and Analysis Laboratory Research and Application Center, Ege University, Bornova, Izmir, 35100, Turkey .................................................. 210
2Department of Biochemistry, Faculty of Science, Ege University, Bornova, Izmir, 35100, Turkey .................. 210

PP27- Determination of Plasma Protein Binding for Combination of Olanzapine and Sertraline Using HPLC ...... 211
Yasar Kaan EREN1, 2, Suna TIMUR1, 2, Z. Pınar GUMUS3* .......................................................... 211
1Central Research Testing and Analysis Laboratory Research and Application Center (EGE-MATAL), Ege University, Bornova, Izmir, 35100, Turkey .................................................. 211
2Department of Biochemistry, Faculty of Science, Ege University, Bornova, Izmir, 35100, Turkey .................. 211

PP28- An in-vitro Study of the Interaction between Fluoxetine and Olanzapine in Protein Binding by HPLC Coupled with Ultrafiltration .......................................................... 212
Minel AYAZMA1, 2, Figen ZİHNİOĞLU1, 2, Z. Pınar GUMUS3* .......................................................... 212
1Central Research Testing and Analysis Laboratory Research and Application Center (EGE-MATAL), Ege University, Bornova, Izmir, 35100, Turkey .................................................. 212
2Department of Biochemistry, Faculty of Science, Ege University, Bornova, Izmir, 35100, Turkey .................. 212

PP29- Competition of Quetiapine and Fluoxetine in Binding to Serum Albumin in Combination Therapy ...... 213
Umut Ozerk ONKOL1, 2, Figen ZİHNİOĞLU3, Z. Pınar GUMUS4* .......................................................... 213
PP45 - Determination of Anthocyanin Glucosides and Anthocyanidin Aglycones by HPLC-DAD and Validation Studies ................................................................. 226

Nagihan M. Karaaslan, Mehmet Yaman ........................................... 226

*1Munzur University, Faculty of Engineering, Department of Chemical Engineering, Tunceli, Turkey ................. 226

PP46 - Preconcentration and Determination of Cu (II) Ions in Environmental Samples by EDTA Modified Amorphous TiO2-SPE Column and FAAS ........................................... 227

Sema Erdemoglu, Esra Porgal Tuzer, Emrah Akgeyik ........................................ 227

*1Inonu University, Art and Science Faculty, Department of Chemistry, Malatya-TURKEY .................................................. 227

PP47 - Controlled Insulin Released Membrane Synthesis at Optimum Conditions and Detection of Membrane Efficiency by Mass Spectrometer .................................................. 228

Buse Kardelen VARLIOGLU, Ulku Guier, Gulay BAYRAMOGLU, M. Yakup ARICA, Bekir Salih ............................................... 228

Hacettepe University Department of Chemistry .................................. 228

PP48 - Proteomic Studies on HEPG-2 Liver Cancer Cell Line .................................................. 229

Firat Sakar, Mustafa Celebier*, Ayse Ercan ........................................ 229

1Hacettepe University, Institute of Science, Department of Nanotechnology and Nanomedicine, 06532 Beytepe-Ankara/Turkey........................................................................................................... 229

PP49 - Melatonin and Hyaluronic Acid Loaded Carboxymethylcellulose Hydrogel as a Possible Therapeutic Agent in Dental Medicine ........................................................................................................... 230

Aysenur Ertnuc* and Ibrahim Islidak .................................................. 230

1Department of Bioengineering, Faculty of Chemical-Metallurgical Engineering, Yildiz Technical University, Istanbul, Turkey ........................................................................................................... 230

PP50 - Investigation and Determination of Pencurion Fungicide by Square Wave Voltammetry .................................................. 231

Selvi ACER, Ersin DEMIR and Recai INAM ........................................... 231

1Department of Chemistry, Faculty of Science, Gazi University, Ankara, Turkey ........................................................................................................... 231

PP51 - Low-Transition Temperature Mixtures Based on Amino Acids: Synthesis and Extraction Efficiency of Phenolics from Olive Mill by-Products .................................................. 232

Nikos Lydakis-Simantiris*, Hamida Akli1,2, Spyros Grigorakis3, Sofia Loupasaki2, Mati Abderrahmane, Dimitris P. Makris* .................................................. 232

1Department of Environmental and Natural Resources Engineering, Technological Education Institute of Cretes, 232

PP52 - Elimination of hydrocarbon pollutants from water by adsorption using the coffee grounds activated by microwaves. .................................................. 232

Amira Khemmari; Abdelkader Namane; Jazia Arar; Amina Hellal; Dalila Hank .................................................. 232

Ecole Nationale Polytechnique, Departement de Genie de l’Environnement, Laboratoire de Sciences et Techniques de l’Environnement, 10 Avenue Hacen Badi BP 182, El Harrach, 16200 Alger, Algeria ........................................................................................................... 232

PP53 - Determination of Standard Glycosylated Proteins Using Borate Selective Electrode as a Deductor in FIA System ........................................................................................................... 233

Ibrahim Islidak, Duygu UNER BAHAR* .................................................. 233

1Yildiz Technical University, Department of Bioengineering, Istanbul, Turkey ........................................................................................................... 233

PP54 - Fatty acid composition of sweet white lupin (Lupinus albus L.) seeds from Algeria .................................................. 233

Zaouadi Nesrine1, Saglik Aslan Serap2, Hadji Ziane Amel1, Nesetoglu Neset1,2, Danis Ibrahim1,3, Ozer Unal Durisehvar2,3 .................................................. 233

1Department of Analytical Chemistry, Faculty of Pharmacy, Istanbul University, Turkey ........................................................................................................... 233

2Drug Research and Application Center, Istanbul University, Turkey ........................................................................................................... 233

PP55 - Evaluation Of Drug-DNA Interaction Using High Performance Liquid Chromatography (HPLC) .................................................. 234

Pelin SENEL1, Merve Keskek ARSLAN2, Durisehvar Ozer Unal2 and Aysegul GOLCU2 .................................................. 234

1Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, Maslak, 34469, Istanbul, Turkey ........................................................................................................... 234

PP56 - Synthesis of Advanced Titanium Oxide based Structures ........................................................................................................... 235

Simonas Ramanavičius*, Arūnas Jagminas .................................................. 235

1State institute Center for Physical Sciences and Technology, Savanorių ave. 231, Vilnius, Lithuania ........................................................................................................... 235

PP57 - Determination of the Change in Fatty Acid Composition During the Maceration of Hypericum perforatum L. ........................................................................................................... 236

Ibrahim Kivrak1,2, Seyda Kivrak2, Tolga Gökçekkı3 .................................................. 236

1Muğla Sıtkı Koçman University, Muğla Vocational School, Department of Chemistry and Chemical Treatment Technologies, 48000 Muğla-TURKEY ........................................................................................................... 236

PP58 - Development of immuno sensors: immobilization of antibodies on different surfaces .................................................. 239

Almira Ramanavičienė1,2, A. Kausaitė-Minkstimiene1,2, I. Morkvenaitė-Vilkonciene2, A. Popov1,2, B. Brasliunas1, Arunas Ramanavičius1,3 .................................................. 239

1Nano Technas – Center of Nanotechnology and Materials Science, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko st. 24, LT-03225, Vilnius, Lithuania ........................................................................................................... 239

PP59 - Cytarabine Determination from Urine by spectrophotometric and chromatographic methods for excretion studies ........................................................................................................... 240
PP75 - Polyaniline Coated Thin Film Extraction Blades for Residue Analysis in Water Samples
Ebru Çalışan Yıldırım, Fusun Okcu Pelit
Ege University, Faculty of Science, Department of Chemistry, 35100, İzmir, Turkey
258

PP76 - Assessment of Phenolic Compound Compositions of Olive Oil Samples Extracted by Different Techniques by Using LC/QTOF/MS with PCA
Z. Pinar GUMUS, Hasan Ertas
Central Research Testing and Analysis Laboratory Research and Application Center (EGE-MATAL), Ege University, Bornova, İzmir, 35100, Turkey
259

PP77 - The Investigation Of Heavy Metal And Mineral Content Of Growing Cowers (G. Tournefortics) In The Siverek Region
Hakan KIZILKAYA, Beşir DAG
Batman university, Art & Science Faculty department of chemistry, BATMAN
260

PP78 - Determination Of Lead By ICP-MS After Preconcentration With Magnetic Adsorbent Prepared From Lemon Peel and Fe3O4 Nanoparticles
Emre Çakmak, Tulay Oymak
261

PP79 - SYNTHESIS AND CHARACTERIZATION OF 4-AMINOANTIPIRINE DERIVATIVE OF HETEROCYCLIC NEW SCHIFF BASES AND AMIN COMPOUNDS
Hakan KIZILKAYA, Beşir DAG
262

PP80 - Environmental approach of utilizing co-polymeric hydrogel: An application of dye removal
Fatma Ozge Gokmen, Elf Yaman, Sinan Temel, Nurgül Ozbay
Bilecik Şeyh Edebali University, Central Research Laboratory, Bilecik, TURKEY
263

PP81 - Voltammetric Determination of Ascorbic Acid Using Modified Solid Contact Electrode
Nur Izli, Zafer Yazicigil, Tuğçe Göver
264

PP82 - Investigation of Electrochemical Behaviours of Some Schiff Base On The Surface of Solid Contact Electrode Using Voltammetry
Issa Malam Mahamadou, Tuğçe Göver, Ersin Guler, Ahmed Nuri Kurşunlu, Zafer Yazicigil
Selçuk University, Faculty of Science, Department of Chemistry, 42075, Konya, TURKEY
267

PP83 - Comparative Assessment Of Selected Elements In The Scalp Hair And Nails Of Chronic Obstructive Pulmonary Disease And Controls
Soykan Bicim, Tulin Bicim, Sevda Gultekin, Mehmet Yaman
1 Hekimhan State Hospital, Hekimhan, Malatya-Turkey
270
Luminescent methods are based on the excitation of molecules either by absorption of light (photoluminescence, fluorescence) or by a chemical reaction (chemiluminescence: CL) and are characterized by simplicity, sensitivity, low limits of detection, and relatively low cost of instrumentation. These advantages enabled the utilization of luminescence spectroscopy in numerous applications of analytical chemistry including food and edible oil analysis.

However, the majority of luminescent methods in oil analysis concerns oil extracts and not untreated oils due to the fact that the sample is not miscible with water. Nevertheless, any treatment of oil prior to analysis, such as extraction, changes the chemical composition of the tested sample which might lead to erroneous results. Hence, direct application of analytical methods to oil without any pretreatment except dilution would be preferable.

The CL reactions of luminol and lucigenin have been widely exploited for the determination of hydroperoxides in untreated oils using microemulsions and homogeneous solutions, naturally bringing certain problems associated with sample exposure to reagents, phase behavior, and possible interference from compounds present in oil. Additionally, two widely applied spectrophotometric methods, the Fe(III)-phenanthroline and the CUPRAC assays, have been adapted to untreated oils via selection of mixture of solvents (ethanol–butanol in 3:1 v/v ratio), and optimization of the reaction conditions (reagents concentration and reaction time).

This presentation describes the application of luminescent methods in the analysis of edible oils without any pretreatment such as extraction prior to analysis. Emphasis has been given to applications of chemiluminescence and fluorescence assays for determining quality parameters of edible oils, such as oxidative stability, antioxidant activity, and lipid hydroperoxides content, as well as classification or adulteration of vegetable oils. The results have been evaluated successfully and extended to the development of a variety of analytical methodologies for the evaluation of the total antioxidant activity of a wide range of natural products including oils, beverages, juices, wines and other related food products without modification of the relevant matrices.
Quantitative analysis of pesticides and their transformation products are of special interest for food safety and environmental concern. The most efficient approach to pesticide analysis involves the use of multiclass, multiresidue methods. Maximum residue levels have been established by regulatory bodies, which are typically in the range of 0.01 and 5 mg/kg, depending on the pesticide. Therefore, accurate and reliable analytical methods are required for their analysis. An important issue in the method development of quantitative analysis using a chromatographic system is the matrix effects. Nowadays, green extraction techniques are being searched for more rapid and effective analytical approaches.

Present study covers the development of green microextraction techniques and particularly, solid-phase microextraction (SPME) fibers for the determination of selected pesticides in food prior to the GC-MS analysis. Examples include the selected residue analysis in fruit juices by using lab-made SPME fibers modified with several nanomaterials. Carbon nanomaterials; graphene, functionalized multiwall carbon nanotubes (MWCNT) and fullerenes have been used for this purpose. Fiber surfaces have been characterized by SEM measurements and then, the fibers have been used in head space (HS) or direct immersion (DI) mode for volatile and non-volatile pesticides, respectively. After a predetermined extraction time, the fiber was introduced into the GC-MS system where the analysis was performed in SIM mode. Analytical characteristics of the methods have been evaluated.

Keywords: pesticide residue analysis, SPME, GC-MS, electropolymerization, carbon nanomaterials

The extraction of organic, inorganic species and nanoparticles from environmental samples has important place for the preconcentration and separation of them prior to their instrumental detection. Solid phase extraction and microextraction are two important techniques at these studies. For solid phase microextraction, the preparation and characterization of novel nanosized material including carbon nanotubes, modified carbon nanotubes, nanocomposites, titanium dioxide nanoparticles and magnetic nanoparticles (MNPs), nanoflowers etc. which has resistant for acid and bases; high surface area, high adsorption capacity, useable many times without any losses its adsorption properties are very popular recent studies in analytical chemistry.

The microextraction techniques are very simple, low the consumption of organic solvents (green), accurate and precise. The use of new generation solvents like deep eutectic solvents (DES) and switchable solvents (SHS) on the microextraction studies is very important for microextraction studies.

The preparation, characterization and usage of novel nanosized materials for solid phase extraction and solid phase microextraction of organic, inorganic and nanoparticle species from environmental samples have been discussed. The microextraction strategies for the separation and preconcentration of organic, inorganic and nanoparticle species have also been discussed.
Most explosive residues have extremely low vapour pressures, and are therefore detected from the liquid phase on solid substrate sensors (paper, resin, polymer membrane, nanoparticles, etc.). Such rapid colorimetric sensing applications may replace the more sophisticated, but high-cost LC/GC-MS/MS techniques in the field (especially in screening analysis of post-blast debris), and can be used for both qualitative and quantitative purposes. In this respect, our energetic compounds detection group has developed various colorimetric kits, spectroscopic and electrochemical sensors and nanoprobes utilizing the electron-transfer (ET) and charge-transfer (CT) ability of explosive compounds, exemplified as follows: Solid phase extraction of the Meisenheimer anion of trinitrotoluene (TNT) formed in alkaline solution onto a strongly basic anion exchange resin Dowex 1×8 (OH-form) enabled the stabilization of the orange-red color formed both in the solid resin and aqueous solution phases. The charge-transfer reagent, dicyclohexylamine, was entrapped in a polyvinylchloride polymer matrix plasticised with dioctylphthalate, and moulded into a transparent sensor membrane sliced into test strips capable of specifically sensing TNT (of max. absorption at 530 nm). Peroxide-based explosives were detected by the colorimetric Cu(II)-neocuproine procedure, based on the hydrolysis of peroxide explosives to $\text{H}_2\text{O}_2$, with subsequent oxidation of the product with the chromogenic oxidant, itself being reduced to the yellow-orange Cu(I)-neocuproine chelate. A field detection kit of explosive residues was devised by detecting unknown explosives in the field (retained on a chromatographic paper) as determined by their color change after successively spraying three reagents which were specific for nitro-aromatics, nitramines/nitrate esters, and inorganic nitrates. A sensitive colorimetric method for the simultaneous determination of RDX and HMX was devised on the basis of differential kinetics in the hydrolysis of the two compounds (yielding nitrite as a product) followed by their colorimetric determination using 4-aminothiophenol (4-ATP)–modified gold nanoparticles (AuNPs) and naphthylethylene diamine (NED) as coupling agent for azo-dye formation. Recently, selective and sensitive electrochemical determination of TNT, DNT, RDX, and HMX with AuNPs/poly(carbazole-aniline) film–modified glassy carbon electrode imprinted for molecular recognition of nitroaromatics and nitramines was performed. The developed electrochemical sensor could be efficiently used in analyzing nitroaromatics and nitramines in military explosives (i.e., comp B, octol, and comp A5)\(^1\). An easy-to-use AuNPs-based colorimetric sensor was developed for the determination of nitroaromatic explosives (TNT and tetryl), capable of analyte detection at picomolar levels. The sensor nanoparticles were synthesized by functionalizing the negatively charged thioglycolic acid (TGA)-modified AuNPs with positively charged (±)-trans-1,2-diaminocyclohexane (DACH) at a carefully calculated pH. The working principle of the sensor was CT-interaction between the electron-rich free amino (-NH$_2$) group of DACH and the electron-deficient -NO$_2$ groups of TNT/tetryl, added to possible nanoparticle agglomeration via electrostatic interaction of TNT-Meisenheimer anions with more than one cationic DACH-modified AuNPs\(^2\).

**Keywords:** Explosive detection, TNT, RDX, colorimetric probes, electrochemical sensors

**References:**
State of the art in Mass Spectrometry-based Proteomics: Post-translational Modifications, Imaging and Ion Mobility

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Mass spectrometry-based proteomics studies provide vital knowledge for in-depth characterization of proteins and their complexes in their intact forms. Post-translational modifications such as phosphorylation, glycosylation and ubiquitination at the level of modified peptide could be examined by mass spectrometry. In the case of glycosylation, released glycan sequence analyses are also possible in details for the early stage diagnosis. Post-translational modification studies led to discover novel biomarkers for most diseases and understand their progress in cellular systems. Although the advantages of modern mass spectrometries in the chemical analyses, prior to mass spectrometric analysis still enrichment and purification steps play a crucial role for the efficient analysis of post-translational modifications by mass spectrometry. Recently, beside the proteomics studies mainly need Electrospray Ionization-Mass Spectrometry (ESI-MS) and Matrix-assisted Laser Desorption/Ionization-Mass Spectrometry (MALDI-MS), a new mass spectrometric technique namely Ion Mobility-Mass Spectrometry (IM-MS) has been used widely to determine the conformational changes of biomolecules. This is used very efficiently to get more information about the fine structure of the biomolecules. In the proteomics area, recent fascinating application of MALDI-MS is to use MALDI-MS as a probing tool especially for tissue imaging or surface chemical analyses.

In this communication, several proteomics applications of MALDI-MS/MS, nano LC-ESI-MS/MS and IM-MS/MS for the analyses of some post-translational modifications after fast, efficient and user friendly specific enrichment of targeted biomolecules using sol-gel materials which have different hydrophilicity, surface morphology and surface pKa will be discussed. Also some mass spectrometric analyses will be discussed for analytical performance of new generation therapeutic drugs. Final part of the communication is about the measurement of conformational changes and the imaging of tissue samples by mass spectrometry.

Keywords: Proteomics, Post-translational modifications, MALDI-MS, ESI-MS, IM-MS.

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Recent developments in separation of enantiomers using high-performance liquid chromatography

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Enantiomers of chiral biologically active compounds are commonly characterized with different taste, smell, pharmacokinetics, metabolism and pharmacodynamics. Due to this reason separation of enantiomers on analytical and preparative scale is one of the hot topics of contemporary chemistry. High-performance liquid chromatography (HPLC) represents one of the major methods for separation of enantiomers and polysaccharide derivatives belong to the most successful group of chiral stationary phases (CSP) for HPLC. A CSP has to meet certain requirements in very competitive environment in order to be widely accepted and applied. The major requirements are universality not only from the viewpoint of coverage of various chiral analytes but also from the viewpoint of applicability in various above mentioned modes and compatibility with various type of mobile phases, stability, robustness, versatility and availability. This presentation summarizes our current attempts in order to implement chemo- and enantio-selectivity in the same CSP, to create stable and robust CSPs by covalent attachment of a chiral selector onto silica and creating CSPs with favorable kinetic properties by using superficially porous silica. In the presentation our strategy for obtaining extremely high separation factor ($\alpha > 100$) in HPLC separation of enantiomers, as well as baseline separation of enantiomers on a few-second timescale will be also demonstrated.

References:
Introduction

Nowadays, Alzheimer Disease (AD) becomes a leading cause of death throughout the World. Indeed, it is estimated that the number of AD patients will reach up to 130 million by 2050 in global scale. Then again, no exact pharmacological or non-pharmacological therapy options are still available. The current and best treatment options confer only a few conventional oral medications, which are found to be abortive to preventing or slowing down the AD progression. The current pharmacological options also exhibit considerable limitations related to solubility, absorption, bioavailability and ability to pass blood brain barrier (BBB) as well as adverse effects. At this point, nanotechnology brings prominent advantages for competing these limitations. Nanoparticles (NPs) give an opportunity to controlled drug release and site-specific effective delivery in biological systems due to their smaller size (0-100 nm). After the application of nanotechnology into medical practices triggered the generation of various nanoparticle-mediated drug delivery systems (nano-DDS). In the beginning, nano-DDS development strategies were focused mainly to across BBB as well as amyloid cascade and cholinergic impairment targets. In time developed nano-DDS were comprised other targets that related to AD pathogenesis such as oxidative stress, tau aggregation and bio-metal dyshomeostasis etc. Finally nano-DDS were endowed with desired features involving stable, biodegradable and non-immunogenic properties.

From NPs to Nano-DDS

When nanotechnologists spread on effort to develop Nano-DDS, it is very crucial to selection of NPs type for the first stage. From the previous data on nano-behaviors of the potential particles, it is appeared that every NPs may not serve as DDS. Therefore, several properties of NPs must be evaluated in detail before introducing them as effective DDS. These properties embrace inflow (circulation time, stability, lipophilicity, binding patterns, permeability, etc.), fundamental (biocompatibility, biodegradability, sustained release, cytotoxic and immunogenic responses etc.) and esoteric (interactions with biomolecules, precision targeting, etc.) characteristics.

Nano-DDS approaches for the treatment of Alzheimer Disease

Until today, different DDS platforms involving (I) polymeric nanoparticles, (II) solid lipid nanoparticles, (III) nano-spheres, (IV) nano-emulsion, (V) carbon nanotubes and (VI) super-paramagnetic nanoparticles were introduced in the literature. Polymeric NPs were used to deliver...
poorly soluble anti-Alzheimer agents with greater efficacy and attenuated cytotoxic damages on central nervous system (CNS). N-butylecanoacrylate, chitosan, chitosan–poly(ethylene glycol) (PEG), Poly-lactide-co-glycolide (PLGA) are the most preferred and promising NPs in DDS development targeting the CNS. Similar to these polymeric NPs, solid lipid nanoparticles potently considered as nano-DDS due to their remarkable advantageous such as enhancing circulation time of NPs, escaping from reticulo-endothelial system and interactions with BBB. Although the presence of their limited drug loading capacity and unenviable release performance, nano-spheres execute great potentials as nano-DDS. Nano-emulsions, as the combinations of different drugs, additives and emulsifiers, are being investigated in both drug delivery and imaging purposes. The use of different types of carbon nanotubes such as single-walled carbon nanotubes and multi-walled carbon nanotubes bring significant advantages via their desired superior electronic, thermal, encapsulating, penetrating and biocompatibility features. Super-paramagnetic nanoparticles are functioned effectively not only in drug delivery but also gene transfection studies4,5.

Conclusion and future directions
The current statistical analysis proved that death rates due to Alzheimer’s disease have increased over the recent 20 years, distinctly. Alzheimer brings serious social and economic insults along with its physical and psychological impacts due to therapeutics challenges. In fact, the satisfactory treatment options are not available yet. At this point the advances in nanomedicine allow to scientists for achieving these challenges in therapy. However, the literature scanning from Scopus database revealed that insufficient numbers of investigations (<300) were performed on Nano-DDS and Alzheimer treatments, up until now. Thereof, this field seems to be as newborn scientific area. To be able to move the nano-DDS to the central point of coping strategies against challenges of Alzheimer therapy, the below directions are propounded:
- The interdisciplinary approach encapsulated fields like neurology, pharmacology and toxicology, immunology, molecular biology, material science should be followed for each development stages of any nano-DDS.
- Along with the efficacy profiles, the safety issues of nano-DDS especially from the viewpoint of neuro-toxicology should be deciphered definitively.
- New experimental chronic exposure models should be developed for realistic modeling of chronic effects of applications with nano-DDS.
- The technological opportunities for transforming general nanomedicine into personalized nanomedicine in the near future should be considered more carefully.
- Along with the drug delivery targeting, the novel nano-DDS serving to early diagnosis or to neural regeneration should be invented for effective fight against Alzheimer disease.

References
Use of Tandem Mass Spectrometry in Fatty Acid and Sfingolipid Measurements

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Fatty acids are structures consisting of a hydrocarbon chain having a carbonyl group (C=O) at one end and a methyl group (-CH3) at the other end. They are classified as saturated and unsaturated fatty acids. Unsaturated fatty acids containing two or more double bonds in their structure are called polyunsaturated fatty acids (PUFA). PUFA are important cell membrane components and regulate a wide range of events in the body such as blood pressure, blood clotting, development and function of the brain and nervous system. Furthermore, they play important roles in the regulation of inflammatory response through the production of eicosanoids. PUFA are classified as omega-6 (n-6) and omega-3 (n-3) fatty acids according to the location of the last double bond in the hydrocarbon chain near the terminal methyl group of the molecule. In mammals, desaturation and elongation pathways of n-3 and n-6 fatty acids occur mainly in the liver. Eicosanoids derived from n-6 PUFA such as arachidonic acid (AA, C20: 4n6) have proinflammatory and immune regulation function, whereas eicosanoids derived from n-3 PUFA such as eicosapentaenoic acid (EPA, C20: 5n3) and docosahexaenoic acid (DHA, C22: 6n3) exhibit anti-inflammatory properties and inhibit the formation of n-6 PUFA derived eiconosanoids (1).

Sphingolipids are also structural elements of cell membranes. Recent studies have shown that sphingomyelin (SM) causes the formation of various lipid mediators. Ceramides (CERs) are centrally located in the metabolism of sphingolipids and are formed by the incorporation of serine and palmitoyl-CoA. Ceramides can also be formed by the hydrolysis of sphingomyelin by the sphingomyelinase enzyme. After ceramide is formed, it is converted to ceramide-1-phosphate by the ceramide kinase enzyme or used for the synthesis of sphingomyelin. Ceramide can also be broken down into sphingosine by ceramidase enzymes. Sphingosine can be converted to sphingosine-1-phosphate by sphingosine kinases. Phosphorylated sphingolipid metabolites ceramide-1-phosphate and sphingosine-1-phosphate are highly effective bioactive mediators and have recently been shown to play an active role in inflammatory response (2).

Levels of AA, C20:4n6, dihomo-gamma-linolenic acid (DGLA, C20:3n6), EPA, C20:5n3 and DHA, C22:6n3 can be determined by an optimized multiple reaction monitoring (MRM) method using ultra fast-liquid chromatography (UFLC) coupled with tandem mass spectrometry (MS/MS). Similarly, levels of C16-C24 SMs, C16-C24 CERs and sphingosine-1-phosphate (S1P) can also be measured by an MRM method using UFLC-MS/MS. Advantages of the use of MRM and MS/MS in estimating fatty acid and sphingolipid metabolites are accuracy, the use of complex mixtures and minimum run to run variability.

Key words: polyunsaturated fatty acid, sphingomyelin, ceramide, tandem mass spectrometry

References:
IS9- Solid Phase Microextraction Strategies in the Determination of Organic/Inorganic Analytes

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There are many sources of environmental contamination such as anthropogenic activities, and the risk of contamination gets higher due to the increase level of production and consumption of the variety of contaminants. Different organic and inorganic contaminants have several health concerns even at trace Levels. They could easily enter to human body and accumulate in different organs [1]. Hence, sensitive analytical strategies are needed to perform accurate, sensitive and precise determination of contaminants in variety of environmental and biological samples. Different microextraction strategies (liquid and solid phase microextractions) have been used in literature to preconcentrate analyte(s) of interest to make the trace/ultratrace determinations possible for variety of instruments [2]. Microextraction strategies have advantageous due to their preconcentration abilities in addition to reduction of the interference possibilities coming from the matrices. Solid phase microextraction (SPME) strategies have been most commonly used for organic/inorganic analytes as sample preparation extraction/preconcentration methods prior to determination in atomic/molecular sensitive detectors. Magnetic particles based DSPME are very popular due to their easy separation from sample matrices by a simple magnet supplying external magnetic field. Analyte selective solid phase adsorbents having high surface area have been also synthesized for efficient and accurate determination of analyte(s).

Keywords: Solid Phase Microextraction, Environmental Contaminants, Detection, Endocrine Disrupters.

References

Hyphenated techniques for the large scale speciation analysis of metals and metalloids in a biological milieu

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Metals and metalloids which occur in biological systems at trace (sub-µg/g) and ultratrace (sub-ng/g) concentrations play an important role in a number of processes essential for life. This role is played not by the metal itself but in association with its coordination environment constituted of proteins and small molecular mass (<1000 Da) ligands. The number of metals and the number of ligands present demand analytical approaches to the analysis of all the metals and the related ligands ensemble within the range of their thermodynamical stability and linking them with the organism’s genome. The development of suitable methods for this purpose is referred to as large scale speciation analysis or metallomics [1].

The classical approach in ultratrace metal speciation analysis consists in the coupling of a chromatographic or electrophoretic separation technique with inductively coupled plasma mass spectrometry (ICP MS). The choice of the latter is due to its outstanding features in terms of detection limits, multi-isotopic capability and matrix. The molecular selectivity is conferred by the separation technique [2] allowing the differentiation of species according to their physicochemical properties on-line prior to their detection. Advances in couplings of different separation mechanisms (e.g. HILIC) and formats (e.g. nanoHPLC) to ICP MS have been continuously proposed.

The advent in mid-90ties of electrospray MS indicated the potential of this technique to become the ultimate tool for speciation analysis. However, strong matrix dependent effects have been responsible for massive false negatives. The number of successful applications of electrospray MS/MS for speciation analysis has increased considerably since the development of ICP-MS-controlled multidimensional HPLC approaches [3]. In this way, the mass balance of the metal eluted from the column could be precisely controlled, the sequential use of different separation mechanisms lead to the chemically pure peaks enabling metal species cartography and, in most cases, their ESI MS analysis.

The concept of ICP-MS-controlled species purification for ESI MS has been integrated into canonical metalloproteomics and metabolomics protocols allowing the extraction of metal-related information on the entire proteome or metabolome scales. The progress in ESI FT MS, offering high resolution and accuracy of mass measurement and intrascan dynamic range has considerably facilitated structure elucidation of metal species [4,5].

The lecture discusses the recent advances in ICP MS–assisted electrospray MS for the discovery of new metal-containing molecules in bacteria, yeast and plants. The role of analytical chemistry in multidisciplinary studies aimed at the elucidation of the function of these molecules will be highlighted.

References
The most important methods of conducting polymer synthesis will be overviewed, during this presentation. These methods include electrochemical [1], chemical [2] and biochemical [3-6] formation of conducting polymer based layers. The applicability of conducting polymer based functional layers in the design of various types of electrochemical biosensors will be discussed [6]. Significant attention will be focused on the development of glucose biosensors based on conducting polymer layers. Advantages and disadvantages in the application of glucose oxidase (GOx) will be discussed. During the enzymatic reaction the GOx is forming hydrogen peroxide, which is able to initiate the polymerization of some conducting polymers. In some our researches, it was shown that this method is suitable for the synthesis of polypyrrole [3], polyaniline [4], polytiophene [5] and some other conducting polymer based layers and nanostructures. It was demonstrated that both dissolved and immobilized enzymes could be successfully applied in the enzymatic synthesis of conducting polymer-based nanoparticles and other structures. Enzymatic synthesis of nanostructures based on conducting polymers can be assigned to so called ‘green synthesis’ because except the monomer, which is required for the formation of conducting polymer any other environmentally harmful materials are applied in above mentioned enzymatic polymerization process. We also have demonstrated that formed nanostructures and nanoparticles shows good biocompatibility with living cells and when they were injected in living mice peritoneum. We have demonstrated that during such kind of synthesis of nanoparticles and/or nanostructured layers the enzymes becomes entrapped within conducting polymer layer. In some other our researches it was shown that redox processes that are part of metabolism of living cells can be applied for the synthesis of conducting polymer – polypyrrole (Ppy), and formed Ppy nanoparticles could be entrapped within cell wall of yeast cells [6]. Therefore, such nanoparticles and nanostructured layers are suitable for the design of amperometric glucose biosensors, biofuel cells and some other bio-devices. Formation of conducting polymer based molecularly imprinted polymer layers will be discussed during this presentation.

Keywords: Glucose Biosensor, Conducting Polymer, Polypyrrole, Polytiophene, Polyaniline

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References:
Current scientific investigations have evidenced that plants and other natural sources may have supreme contribution for the promotion of health and treatment of diseases. Particularly, proper or improper or speculative interpretations are published in visual or printed press related to these data, highly increase demand for natural products reaching to hundreds of billions of dollars of market sale yearly worldwide. However, since these products are commonly considered food supplements no official measurements have been applied on their quality assessment by the authority. On the other hand, market inspections which are carried out by the voluntary institutions or individual studies give cause of apprehension about the quality of these products, not only from the view point of lack or insufficient content of active components, but also presence of possible toxic ingredients.

Among a broad spectrum of analytical techniques which could be applied for quality assessment of natural medicines, High Performance Thin Layer Chromatography (HP-TLC) has recently been considered as one of the most useful tools in this area. HP-TLC provides rapid and reproducible results for both qualitative and quantitative analysis of natural products, enable comparative quality analysis of many samples in one go. Correspondingly, HP-TLC have also been frequently practiced identifying adulteration and fraud in herbal medicines, either in crude herbal materials (i.e., flower, leaves, roots, etc.)¹,², their extracts or in herbal medicinal products³ with single or multiple plant components.

**Keywords:** High performance thin layer chromatography, herbal medicines, quality control

**References:**
Food safety and food quality are important parameters for human health and quality life from the production to consumption in food industry. Due to that, producers have an attention on rapid and reliable, eco-friendly technologies to follow the food processes and final products. Also, consumers demand to be informed about the composition, origin and quality of food and they should choose their diet according to this information. However, food fraud is worldwide problem due to economic gain. Detection of fraud require analytical tools is increasing day by day to investigate the foods. At this respect, different analytical methods have been developed for monitoring food safety and quality which have main technological challenges. Majority of them depends on DNA, proteomics and isotopic analysis. Which are time-consuming, lab-scale methods and require certain hazardous chemicals, rigorous pre-processes and specialized person. Despite that, rapid, basic and practical on-line analysis in food industry gain popularity by the development in the spectroscopic analysis. LIBS and Raman spectroscopy are one of the most popular elemental composition and molecular structure detection system with high potential for rapid and accurate food analysis. In our studies, we showed the potential of Raman spectroscopy for different applications such as detection of ethanol/methanol in distilled alcoholic beverages, sugar in honey, label free bacteria detection and determination of purities of tea varieties. In elemental analysis, LIBS system was used to determine the food adulteration and quality parameters such as determination of meat species, determination of whey adulteration in milk powder and determination of NaCl, ash and protein content of cereal products. Alongside with the promising results of LIBS and Raman spectroscopy on food safety and quality determination, future applications fields, at-line and portable systems were discussed in the studies.

**Key words:** LIBS, Raman, Milk adulteration, Bacteria detection, NaCl measurement, Ash analysis, Meat adulteration.
Antioxidants are found in certain food and biological systems and may prevent some of the damage caused by free radicals by neutralizing them. Also, they can increase shelf life of food, medicine and pharmaceutical products by retarding of lipid peroxidation process, which is one of the major reasons for deterioration of these products during storage processing. An antioxidant molecule has been defined as any substance when found in low concentrations compared to that of an oxidisable substrate significantly delays or inhibits of oxidation. The major antioxidant compounds are especially phenolics and flavonoids, which are responsible for their health benefits.

On the other hand, carbonic anhydrases (CAs) are metalloenzymes that participate in the conservation of pH homeostasis in the cells by catalyzing the reversible hydration of water and carbon dioxide (CO$_2$) to protons (H$^+$) and bicarbonate ions (HCO$_3^-$). They had distinct and diverse families including α-, β-, γ-, δ-, ζ-, η- and θ-CAs. So far, sixteen isozymes of α-CA have been recorded in mammal cells. They differ in their catalytic activity, subcellular localization, and susceptibility to various types of inhibitor compounds. Between these isozymes, the human cytosolic hCA I and II isozymes are ubiquitous in the human body and are participate in the secretion of electrolyte cells in a plenty of tissues, such as the cerebrospinal fluid, as well as maintain pH and CO$_2$ homeostasis all over the body or the HCO$_3^-$-rich aqueous humor in the anterior chamber of the eyes. Hence, perturbation of activity of hCA I, and II in tissues give rise to pathologic situations, such as edema or glaucoma. Therefore, hCA I, and II became goals for anti-glaucoma, diuretic, and anticonvulsant drugs. Alzheimer’s disease has no cure, and the illness is an outcome of dementia caused by the reduction in the transition of nerve impulses. Thus, the real therapies are based on drug compounds that leverage the transition of electrical impulses. One method to improve nerve transition is to decrease or inhibit the activity of the acetylcholinesterase enzyme (AChE). AChE plays a key role in acting up of cholinergic neural pathways. AChEIs are clinically used for the treatment of Alzheimer’s disease, which increase cholinergic functions, by elevating ACh quantity in cholinergic synapses. Nowadays, the most commonly used synthetic AChEIs are tacrine, donepezil and physostigmine. However, these AChEIs are associated with a number of adverse effects such as gastrointestinal complaints and hepatotoxicity. α-Glycosidase is essential for carbohydrate digestion. This enzyme hydrolyzes polysaccharides and disaccharides to glucose units in small intestine. The inhibition act of α-glycosidase enzyme reduces the mechanism of carbohydrate digestion and avoids postprandial hyperglycemia, which is a main reason of chronic diabetes-associated complication.

This presentation consists of two main sections. The first section is devoted to main phenolic antioxidant compounds in the foodstuffs and beverages. The second general section is about some definitions of CA I, hCA II, AChE, and α-glycosidase inhibitory effects of the some phenolic compounds used for antioxidant activity. It was found that the phenolic compounds had marked inhibition effects against indicated metabolic enzymes. This class of compounds may lead to enzyme-selective inhibitors targeting.

**Keywords:** Antioxidant, phenol, carbonic anhydrase, acetylcholinesterase, α-glycosidase

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Some ordeals/memories in environmental analysis

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Environmental issues are the common arena of applications for chemical analysis. In this presentation, I will try to convey some incidents that took place in my research group. Being in the field of atomic spectrometry for determination of toxic elements and related chemical species, my research group has faced several interesting problems while we were trying to contribute to both research and direct daily applications.

In one of these cases, my PhD student, Sezgin Bakırdere was working on selenium speciation. The method was based on the use of HPLC-ICPMS. Although the main sample was chicken meat, the method was also applied on supplement pills in market to compare the claimed and the real contents regarding Se species. In some of the cases, the labels did not reflect the reality where in some cases they were fairly accurate according to our results1.

Using the analytical facilities in our laboratory, we tried to help some researchers studying the effects of boron on health and environment through collaborative work for determination of elements in various samples such as water, soil, food, blood and urine. Among these scientists were Mehmet Korkmaz from Celal Bayar University and Yalçın Duydu from Ankara University. Water samples were obtained from several sources near Bigadiç, Balıkesir in order to determine the daily boron uptake for people. Arsenic determination was also performed and high levels were observed. The local authorities were warned about the issue. The presence of arsenic of geologic origin especially in western Turkey has well been documented2.

In following years, another colleague, Sema Burgaz from Gazi University wanted to collect water samples from locations with high As content. We provided the locations of the water supplies where we had found high As concentration. It was observed that most of these wells were closed by the authorities.

In 2007, Ankara Municipality decided to use water from Kızılırmak river. This source contains relatively high levels of iron and arsenic. Some initial chemical analyses were performed in our laboratory. A new water treatment plant was built to remove undesired contents before the water is supplied to city of Ankara. The plant was working on the principle of coagulation and flocculation using aluminum sulfate. As the surface charge was positive, it was possible to remove negatively charged mono and di-hydrogen arsenate ion at a pH of about 7.00. However, arsenious acid with first pKₐ of 9.2 has no charge and thus was not removed. This could be easily explained by Pourbaix (potential-pH) diagrams of the related species.

**Keywords:** Boron, arsenic, supplement pills, city water.


**Acknowledgment:** I would like to thank all my students and colleagues, in particular professors Sezgin Bakırdere, Mehmet Korkmaz, Yalçın Duydu and Sema Burgaz.
Disposable Electrode Materials and Their Applications to Biosensing Systems

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Abstract: Disposable electrodes are the latest innovation in electrochemical biosensing systems, providing a new level of reproducibility and ease of use. They are less expensive than conventional, non-disposable electrodes and can be replaced more often without electrode reconditioning by polishing and other methods. More frequent replacement of working electrodes results in more predictable and reproducible electrochemical detection. In addition, the use of disposable electrodes can simplify troubleshooting. These kind of electrodes also make it possible to immobilize biological materials as bioreceptors onto their surface effectively. In this study different disposable electrode materials are discussed in terms of their analytical performances as working electrodes in biosensing systems.

Keywords: Biosensors; disposable electrodes; single-use electrodes; ITO

Introduction
The pioneering study of Clark and Lyons, more than four decades ago, shed light on some analytical researches in designing of biosensors, which perform as economical and fast tools for clinical, chemical, environmental, and pharmaceutical studies. Because of its simple use and portability in relatively complex samples, biosensors offer a potential alternative to advanced bioanalytical systems. Biosensors are employed in applications such as disease monitoring, drug discovery, and detection of pollutants, disease-causing microorganisms and markers that are indicators of a disease in bodily fluids (blood, urine, saliva, sweat). A typical biosensor is represented in Figure 1; it consists of the following components.

![Figure 1. General structure of a biosensor](image)

In all of these biosensor systems the main and the most important part is “the working electrode”. There is a simply two classes of these electrodes as disposable and reusable ones. In this study, a general introduction to disposable electrodes used in biosensors and biosensing technologies, introducing key developments in the field biosensor using disposable electrodes.

Materials and Method
Disposable working electrode materials are introduced. For this purpose, chip based systems, screen-printed electrodes, carbon paste and pencil graphite electrodes, paper based devices, and indium-tin oxide (ITO) based electrodes are discussed. First, a brief information about all of these kind of electrode materilas are given. Following this, different samples of biosensing strategies using disposable electrodes the point in question are given. Finally the pros and cons of disposable electrode materials used in biosensing strategies are concluded.

Results and Discussion
Chip-based systems are generally fabricated by using microfluidic technologies. Glass, paper, polymer, or silicon are used as a substrate in the microfluidic devices. For example analysis of chronic mylogenous leukemia, a DNA biochip was reported. Moreover, a microfluidic biochip was also designed by our research group, which was shown in Figure 2, below.

![Figure 2. A microfluidic biochip design.](image)

Screen printed electrodes (SPE) are another class of disposable working electrodes widely used in biosensor applications. They are used in many biosensors for the determination of biological and chemical targets. The most important advantage of SPEs is their compatibility with portative electrochemical analyzers. Paper based devices have attracted interest due to their friendly user formats, short assay times, little interferences, low costs, and being easy by operated by non-specialized personnel. This technique is based on biochemical interaction of antigen-antibody or probe DNA-target DNA hybridization. Moreover, paper based biosensing systems play an important role in detecting several compounds by obtaining results in a short time with minimal labor. A general construction for paper-based devices is given in Figure 3.

![Figure 3. A general construction for paper based devices](image)

ITO is an excellent material, which has been extensively utilized in biosensor studies owing to its unique properties such as good optic transparency, wide working window, high electrical conductivity, substrate adhesion, low capacitive current, and stable electrochemical and physical features. Owing to these unique features, it can be used in electrochemical researches. ITO based biosensing strategies have especially been reported for important cancer biomarkers. A smart
immobilization procedure made on ITO have represented in Figure 4. This biosensor was used for the determination of TNF-α which is an important cancer biomarker.

Figure 4. Immobilization of an antibody onto flexible PET substrate covered by ITO

Conclusion
As a conclusion, disposable electrode materials have important advantages such as low cost, good repeatability and reproducibility, acceptable linear determination ranges. There is no time consuming and surface destructive cleaning procedures unlike reusable working electrodes. They are generally could be integrated with portative analyzers. Also they could allow to be miniaturized.

References

Acknowledgment
I would like to thank TUBİTAK, TÜBA-GERIP, and ÇOMÜ-BAP for the financial supports.
Anticancer drug development is of immense importance because management of cancer is still poor due to ineffective therapy modalities although recent progress in immunotherapy seems to dramatically improve it. Therefore, new chemotherapeutics are still desirable. The success in drug development mainly relies on preclinical phase. If this phase is tightly controlled and standardized with quality assurance protocols, then the clinical phase may yield better outcome. The duration of a anticancer drug development is conventionally known to be about 15 years but recent developments in in silico designs accelerates the time. The first stage of the conventional preclinical phase is the initial screening. At this phase, a number of compounds are tested against 4-6 cell lines of different cancer types at the dose of 10-15 micromolar. Those inhibiting 50% (or higher) of viability are considered successfully for the initial screening, thereby they can be progressed into the further stages where the various doses (0.01 to 100 micromolar) are tested against desired cancer cell types. The next stage could be the evaluation of cell death mode or mechanism of action using various assays (e.g. NCI-60 cell lines protocol). The morphological evaluation (e.g. double staining with fluorochromes or electron microscopy) is also important for the elucidation of cell death mode (apoptosis, necrosis or autophagy). The further stage for the promising candidates that passes the in vitro phase is in vivo experiments (e.g. zebra fish assay, c.elegans assay, or more reliably xenografts). Finally, acute or chronic toxicity assays on small and big animals are performed, following pharmacokinetic and pharmacodynamic studies. In this talk, novel Pd(II)-based compounds synthesized by our group will also be discussed in comparison with other Pd(II)-based compounds in vitro and in vivo.
Since its inception, gas chromatography has been the method of choice for the analysis of volatile analytes due to its high separation efficiency and relative speed. Nonetheless, scientists have always strived for improving both the speed and the efficiency of gas chromatographic separations, which, however, are mutually dependent so that increasing the one typically means to reduce the other parameter. Skilful optimization of chromatographic parameters (e.g. mobile phase flow rate, column dimensions, phase ratio) allows to gain speed while not sacrificing too much of the chromatographic resolution, however, not beyond a certain extent\(^1\).

In order to overcome the speed/efficiency limitation, conceptually new approaches have to be realized. We will discuss some of these approaches that we have implemented in our laboratory, as well as have been proposed in the literature and assessed their suitability for achieving a maximum of information (which in most cases means a maximum separation efficiency) in a minimum of time. It is clear that these approaches do no longer rely only on the optimization of chromatographically relevant parameters, but are based on

\(a\) operating the GC column at vacuum outlet conditions,

\(b\) using directly heated capillaries for ultrafast gradients,

\(c\) multiplexing injections to increase the time resolution of classical chromatography,

\(d\) running comprehensive two-dimensional separations to improve productivity in terms of resolved peaks per time unit, or

\(e\) performing chromatography with stationary thermal gradients\(^2\).

The relative merits of these approaches, as well as their limitations will be critically discussed and supported mainly by examples from the field of environmental analysis.

It will be seen that none of the approaches is capable of removing the fundamental limitations of gas chromatography in terms of speed, efficiency and speed, however, all of them are highly versatile and allow extending the applicability of gas chromatography beyond the current commercialized state of the art.

**Keywords:** (ultra) fast gas chromatography – chromatographic theory – optimization – comprehensive multi-dimensional chromatography – vacuum outlet GC

**References:**


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ORAL PRESENTATIONS (OP)

OP1: A sensitive novel electrochemical biosensor based on a silane agent modified disposable electrodes for cardiovascular disease biomarker

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Abstract: Cardiovascular diseases (CVD) are one of the causes of death worldwide. In these types of diseases, which may occur due to many different factors, the systems developed for early diagnosis play a critical role. In this work, we designed a novel biosensor with disposable graphite paper (GP) electrodes for creatine kinase (CK) detection. CK has a critical role for myocardial infarction which is one of them cardiovascular disease. The immobilization process of immunosensor was characterized cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS) techniques. However, the optimization and analytical studies of biosensor were done. Finally, the proposed biosensor was measured in real serum samples.

Keywords: Creatine kinase (CK), graphite paper (GP), biosensor

Introduction

The cardiovascular disease (CVD) is considered as a major threat to global health. Accordingly, there is a growing demand for a range of portable, rapid and low cost biosensing devices for the detection of CVD. Biosensors can play an important role in the early diagnosis of CVD. Creatine kinase (CK) is a myocardial- specific isoenzyme and is the basis standard method for the diagnosis of acute myocardial infarction (AMI) in several laboratories. Moreover, it, one of the oldest biomarkers in this field, was introduced as a biochemical marker for myocardial damage in 1965. CK has a clinical sensitivity of 90% for the diagnosis of AMI.

The cost of used materials biosensors is an important problem for the biosensor system. Therefore, disposable, lower cost electrodes more accurate for the sensitive biosensor systems. Thanks to its excellent flexibility and roughness, the graphite paper is very useful because electrochemical energy conversion and storage devices such as redox can be used on a larger scale, such as the battery microbial fuel cells and the super capacitor.

Materials and Method

Impedance, cyclic voltammetry and square wave voltammetry measurements were taken with Gamry Potentiostat/Galvanostat (Reference 600, Gamry Instruments, Warminster, PA, USA) connected with a computer via an EChem Analyst software throughout the entire study. PURELAB flex 3 & 4 Ultrapure Water Purification System (ELGA LC 134 model ) was used during the preparation stages of all immobilization and incubation of the immunosensor. All the chemicals, biorecognition materials (anti-CK antibody, CK antigen and BSA protein) were purchased from Sigma-Aldrich (St. Louis, M.O., USA). The whole proteins were formed by using phosphate buffer (50 mM, pH 7.0) and were kept at -20 oC. Also, 5 mM [Fe(CN)6]4/5 mM [Fe(CN)6]3 (1:1) which is a redox probe solution containing 0.1 M KCl, was prepared. Using three - electrode system has a Ag/AgCl (saturated with KCl) as a reference electrode and a platinum wire as a counter electrode, except for the working electrode ( GP ) in this study. Reference electrode and counter electrode were purchased from BASi (West Lafayette, IN, USA). All measurements were performed at 25 °C in 15 mL of 5 mM [Fe(CN)6]4/5 mM [Fe(CN)6]3 solution which is ferricyanide/ferrocyanide redox probe.
Results and Discussion

EIS is a valuable method that is largely used in different areas of investigations\(^3\). Definition of samples, biosensor characterization and preparation could be efficiently observed by EIS\(^3,4\). Traditionally CV, which characterizes the steps of the immunosensor, is a very important device to investigate the electron transfer rate of the modified electrodes.

![Figure 1. Schematic presentation of the proposed biosensor](image)

![Figure 2. EIS and CV responses of immobilization steps for the proposed biosensor](image)
**Optimization studies**

In the optimization studies of the proposed biosensor, the concentration effect of 3-GOPE agent was examined. Accordingly, three different concentrations of 3-GOPE material, 1%, 1.5% and 5% were used. Each optimization step was characterized by impedance and voltammetric techniques which are strong tools for studying the measurement stages of immobilization during the immunosensor preparation. Belonging to the data obtained with the $R_{ct}$ values in the EIS, standard curves were drawn.

Figure 6. Standard curves obtained by different 3-GOPE concentrations.

**Conclusion**

In this study, a stable, sensitive and quite repeatable CK biosensor with a disposable, cost and practical GP working electrode is prosperously constructed. The constructed biosensor could determine the PAK 2 antigen at sub-picogram concentrations.

**References**


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OP2- A disposable and low-cost biosensor system for sensitive determination of leptin, a biomarker of obesity

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The incidence of obesity, which is defined as the increased amount of fat in the body, varies according to sex, age and race. Leptin, a protein product of the obesity gene, plays a key role in regulating energy intake and energy expenditure. In this study, a disposable GP (graphite paper) based biosensor was designed to determine leptin. After the immobilization process was carried out, all the immobilization steps were optimized in order to develop a precise and stable biosensor. For determining the immobilization steps and optimization of the biosensor, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were utilized. Afterwards, the analytical characterization of the proposed biosensor was determined.

Keywords: leptin, biosensor, graphite paper electrode

Introduction
Obesity, which is defined as abnormal or excessive accumulation of fat in the body by the World Health Organization (WHO), has quickly become one of the most important health problems recently. Obesity has affected children and adolescents as well as affecting adult age groups. The identification and analysis of potential biomarkers associated with obesity, which negatively affect living conditions, is very important and necessary for the early diagnosis of the disease1. Leptin is an ob gene product that is synthesized in adipose tissue and released into the plasma. Leptin is a hormone of 167-amino acids. Leptin performs several roles in endocrine and immune systems such as, hematopoiesis, wound healing, and glucose homeostasis. The level of leptin is relative to body fat and is closely associated with obesity2. Electrochemical impedance spectroscopy (EIS) is an effective method for monitoring the change in interface properties between electrode and electrolyte induced by antibody-antigen interaction, DNA hybridization or enzyme-substrate catalysis using ferri ferro cyanide as an indicator3. In this study, it is aimed to develop a biosensor using appropriate modification methods for early determination of childhood obesity.

Materials and Method
All measurements for the designed biosensor were taken from Gamry Potentiostate / Galvanostate, Reference 600 (Gamry Instruments, Warminster, USA) connected to a computer with Cyclic Voltammetry, Chronoimpedimetry and Electrochemical Impedance Spectroscopy software (Gamry Instruments, Warminster, USA). Graphite paper electrode, 3 M Ag/ AgCl saturated with KCl and platin wire were used as a working electrode, a reference electrode and a counter electrode, respectively. All chemicals used in this research were purchased from Sigma-Aldrich (St. Louis, MO, USA). GP electrode was purchased from Xiamen Tob New Energy Technology Co. Ltd. All electrochemical measurements were taken in ferri ferro cyanide. In this study, anti-leptin was immobilized onto the surface after the GP electrode was modified (Figure 1). Anti-leptin concentration was optimized to construct a sensitive biosensor.

Results and Discussion
Electrochemical impedance spectroscopy (EIS) is an unlabeled and successful method used to determine a number of biomarkers. The main components of the EIS spectrum are the semi-circle at higher frequencies representing the charge transfer resistance and the Warburg impedance at low frequencies.
Optimization studies

The optimization of anti-leptin concentration is very necessary and important step for constructing a stable, repeatable and sensitive biosensor. For this reason, the GP electrodes were immobilized with different concentrations of anti-leptin (18.5 ng/mL, 37 ng/mL, 74 ng/mL, 111 ng/mL). Calibration graphs were plotted using the impedance curves obtained by changing the anti-leptin concentrations.

Figure 3 shows the calibration graphs of biosensors prepared with different anti-leptin concentrations.
Figure 3. The calibration graphs of the biosensors prepared with A) 18.5 ng/mL anti-leptin, B) 37 ng/mL anti-leptin, C) 74 ng/mL anti-leptin and D) 111 ng/mL anti-leptin

Figure 4. The effect of anti-leptin concentration on biosensor responses

**Conclusion**

In this study, a disposable GP-based biosensor was constructed to detect the leptin, obesity biomarker. This biosensor system has a lot advantages such as low-cost, repeatability and usability to clinical field.

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*Acknowledgment: This work was funded by TÜBİTAK (The Scientific and Technological Research Council of Turkey, Project number: 113 Z 678) whose assistance is greatly acknowledged.*
Abstract - The identification and validation of biomarkers for diagnosing Alzheimer’s disease (AD) and other forms of dementia are increasingly important. Alzheimer’s disease is a neurodegenerative disorder that affects large areas of the cerebral cortex and hippocampus and progresses unceasingly. The late diagnosis of AD causes the delay of the treatment period. Early diagnosis may also allow individuals to make changes in their lifestyle to slow the progression of the disease.

This paper demonstrates the ITO-based single-use biosensing system for the precise and selective determination of Tau protein, which has an important role in the pathology of AD, has been designed. To monitor immobilization, optimization and analytical performance steps of biosensor, cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS) techniques were applied. To achieve selective biosensor system, some parameters such as antibody concentration, were optimized.

Keywords: biosensor, Alzheimer’s disease, EIS

Introduction
AD, the most common cause of dementia, is a chronic disease that presents cognitive symptoms, behavioral and psychological symptoms, and thus leads to difficulty in performing one’s daily living activities. One of the main pathologies in Alzheimer's disease is the intraneuronal accumulation known as Neurofibrillary Tangle, the main component Tau protein. It is believed that these accumulations disrupt the basic skeleton of the cell, leading first to the degradation of axonal conduction and then to the death of the cell. Cognition and especially memory problems become clinically detectable when neuron death threshold is exceeded. Total Tau and phosphorylated Tau levels in CSF are significantly higher in Alzheimer's disease. CSF tau levels are a useful biomarker for monitoring neuronal destruction and Neurofibrillary tangle formation.

Nanomaterials are unique in producing high performance systems and devices due to their wide range of physical and chemical properties. Graphene and graphene oxide, integrated with metallic nanostructures (Pd, Pt, Au and Ag) and semiconductors (TiO2 and ZnO), have been appealing candidates in applications related to many fields, i.e. catalysis, sensors, optical and electronic devices, and so forth.

A biosensor is an analytical device which converts a biological response into an electrical signal and the use of materials such as graphene in the design of biosensors provides many advantages.

Materials and Method
The reference electrode and counter electrode were purchased from BASi (West Lafayette, IN, USA), disposable ITO-coated PET films (The transmittance and surface resistivity are 550 nm (> 79%) and 60 Ω/ square, respectively and geometry area 0.25 cm2 ) Standard anti-Tau and Tau antigen, rGO and gold salt were acquired from Sigma Aldrich. All electrochemical experiments were carried out in an electrochemical cell (three electrode system), consist of a sheet of ITO film as a working electrode, a platinum wire as a counter electrode and a silver/silver chloride as a reference electrode which has a volume of 10 mL 1 M KCl, 5 mM [Fe(CN)6] 4− and 5 mM [Fe(CN)6] 3− redox probe. All the electrochemical measurements, including electrochemical impedance spectroscopy, were performed by a Potentiostat/Galvanostat (Gamry Interface 1000 Gamry Instruments, Warminster, USA). The measurements were checked by a personal computer running the electrochemical software program of Gamry Instruments (Echem Analyst) for data collection, monitoring of optimization parameters, and processing.
Results and Discussion

Electrochemical Impedance spectroscopy provides detailed information on the change of surface properties of modified electrodes. The semicircular diameter at high frequencies corresponds to the electron transfer resistance (Rct), while the linear part at low frequencies corresponds to the diffusion process.

Optimization studies

In the optimization studies, the effect of anti-Tau concentration on the nanomaterial additive biosensing system was investigated. For this purpose, neuro-biosensors were prepared with anti-Tau (10 ng/mL, 50 ng/mL, and 100 ng/mL) at different concentrations for 60 minutes at room temperature. The change in the charge transfer resistance was monitored by the calibration curves obtained from EIS data due to the change in anti-Tau concentrations and the change in the specific Tau concentrations with the neuro-biosensor, which kept the other parameters constant.
Analytical performances of biosensing system
The kinetic behavior of the immunocomplex between anti-Tau and Tau was evaluated by monitoring the changes in impedance and phase angle at constant frequency in non-pharyngeal environment.

Figure 4. Single frequency impedance data of neuro-biosensing.

Single frequency impedance analysis is an EIS technique used to reduce the complexity of a fixed frequency, signal acquisition and processing, making it a suitable, simple and inexpensive analysis technique. Thus, it provides opportunities such as rapid response, low cost and high analysis power for both clinical and field experiments.

Conclusion
In this study, a nanomaterial based disposable biosensor system for measuring Tau protein, an important biomarker of AD, was developed. This electrochemical based system has high reproducibility and regeneration capacity.

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OP4- Electrochemical immunosensor for sensitive detection of p53 cancer biomarker based on benzaldehyde substituted poly(phosphazene) modified disposable ITO electrode

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Abstract-In this study, we aimed to develop a benzaldehyde substituted poly(phosphazene) modified disposable immunosensor for p53 antigen detection. Anti-p53 antibodies were used as biorecognition elements to detect p53 antigens with high specificity. Electrochemical and morphological characterizations of electrode modification steps were performed by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) and atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively. To obtain high sensitivity and wide detection range, experimental conditions were optimized.

Keywords: immunosensor, cancer, EIS

Introduction
Cancer is a group of diseases characterized by the development of abnormal cells that divide uncontrollably and have the ability to infiltrate and destroy normal body tissue. Cancer often has the ability to spread throughout your body. The detection of cancer cells, before the occurrence of metastasis, the chance of survival of patients is increased. Biomarkers are measurable indicators of some biological state or conditions. Protein p53 is an important biomarker in tumor suppressing process and effects the cellular functions such as cell growth and proliferation, DNA repair, and apoptosis. When it losses function, tumor induction and gene mutation forms. The gene mutations form tumor. After destruction of tumor cells, p53 protein is released from cancer cells and penetrates into the circulation. The level of p53 protein is ranged from 0.52 ± 0.23 ng/mL to 1.03 ± 0.59 ng/mL in serum samples from cancer patients. For the determination of p53 biomarker a lot of techniques such as enzyme linked immunosorbent assay (ELISA), high performance liquid chromatography (HPLC), surface plasmon resonance, surface enhanced Raman spectroscopy, immunohistochemical method, Western blotting have been utilized. ELISA technique is mostly preferred technique for biomarker analysis. Although ELISA is a successful technique for the determination of p53 antigens, it requires a lot of time to perform the analysis procedure and also expensive devices1.

Electrochemical impedance spectroscopy (EIS) is a label-free and effective technique that is utilized in the determination of a number of biomarkers. The specific binding of biorecognition elements to their desired molecules causes variations in capacitance or charge-transfer resistance. By using this method several analytes are detected 2.

The basic stage of the biosensor development is the formation of immobilization interface for biosensing molecule. Immobilization interface is important to obtain stable and robust biosensor and it should fix the activity of biosensing molecule on the electrode surface and protect the structure of the biosensing molecule during the experiments. Spin coating is a simple method to form uniform thin films on flat surfaces. The principle of this method is based on the deposition of a small drop of a fluid onto the center of a material and then spinning of the material at high speed 3.

Materials and Method
Indium tin oxide (ITO) electrodes (5 mm × 20 mm, 60 Ω/cm²), monoclonal anti-p53 antibody, p53 human recombinant antigen were obtained from Sigma-Aldrich. Anti-p53 antibody, recombinant human p53 and bovine serum albumin (BSA) solutions were prepared using phosphate buffer (PBS 50 mM, pH 7.0) and stored at −20 °C. Ferri-ferro solution contained 1 M KCl, 5 mM [Fe(CN)₆]⁴⁻ and 5 mM [Fe(CN)₆]³⁻ in PBS and was utilized as redox probe. All electrochemical experiments were carried out in a conventional three-electrode cell containing a disposable ITO electrode, a platinum wire and Ag/AgCl as a working electrode, a counter electrode and a reference electrode, respectively. Electrochemical studies were carried out in the presence of [Fe(CN)₆]³⁻/⁴⁻ as redox couple and a Gamry Potentiostat/Galvanostat (Reference 1000,
Gamry Instruments, Warminster, PA, USA) was used for EIS and CV measurements. The applied potentials for cyclic voltammograms were between −0.5 V and 1 V. EIS experiments were carried out in the frequency range from 0.5 to 50,000 Hz. The spin-coating process was performed using a traditional spin-coater (MTI VTC-50) at 1000 rpm for 60 s.

Results and Discussion

The immunosensor preparation process is schematically illustrated in Scheme 1. First of all, benzaldehyde substituted poly(phosphazene) film was constructed by using spin-coating technique. Then, these electrodes were immersed into solution containing anti-p53 antibodies for 45 min, so they were immobilized onto ITO electrode via covalent bond formation. The free functional groups of polymer were blocked by incubating electrodes in BSA solution for 1 h to prevent nonspecific interaction which could be formed between free ends and p53 antigen and other proteins. Afterwards, proposed biosensor got ready to measure p53 antigen.

Scheme 1. Schematic presentation of immunosensor

EIS is widely utilized to validate the layer-by-layer deposition of materials onto a sensor surface because it is a very powerful tool for surface interface characterization and detection of changes formed onto biosensor surfaces. Here, impedance measurements were carried out at each stage of the assembly. The EIS spectra were analyzed using Gamry Echem Analyst software.

Figure 1. EIS responses obtained during immobilization steps
**Optimization studies**

To obtain high sensitivity for p53 antigen detection, the experimental conditions were optimized such as antibody concentration. Therefore, 0.4 ng/mL, 2 ng/mL and 4 ng/mL antibody concentrations were utilized. The change in the charge transfer resistance was monitored and the calibration curves of these were drawn.

![Graph showing the optimization results of antibody concentration](image)

**Figure 2.** Optimization results of antibody concentration

**Conclusion**

An electrochemical immunosensor was developed for p53 antigen detection using a disposable ITO electrode. By using spin-coating technique, a homogenous film was formed on the ITO electrode surface and this film was efficient for covalent binding of anti-p53 antibodies. The CV and EIS techniques were utilized to follow the individual steps of modified electrode fabrication and antibody-antigen interaction at the electrode surface. The fabricated immunosensor had good sensitivity for p53 antigens.

**References**


OP5- Electrochemical Determination of Catechol-Orto-Methyltransferase Inhibitor using NH$_2$- Functionalized Multi Walled Carbon Nanotubes based nanosensor

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Abstract: Electrochemical examination of antiparkinson drug Entacapone (ENP) using NH$_2$ functionalized multi walled carbon nanotubes (NH$_2$fMWCNT) on glassy carbon electrode (GCE) is investigated. The studied conditions were optimized for the electrochemical determination of ENP. Scanning electron microscopy armed with EDX analysis is used to characterize the surface of the nanosensor NH$_2$fMWCNT/GCE. The influence of interfering agents, pH, scan rate, model drugs were further studied. The designed nanosensor is applied to determination of ENP in real samples i.e., tablet, human serum and urine. Recovery studies from tablet, serum and urine samples with RSD values of less than 2% were also conducted.

Keywords: Entacapone; biomedical applications; multi walled carbon nanotubes; voltammetry; drug analysis

Introduction: Entacapone (ENP) is an antiparkinson drug used in the treatment of Parkinson’s disease as an adjunct to levodopa and carbidopa therapy$^{1,2}$. In last years, nanotechnology has become useful in multidisciplinary research topics, such as biochemistry, biotechnology etc. Hence carbon-based nanomaterials also found their place in the nanotechnological researches$^{3-5}$. Among all nanomaterials carbon-based nanomaterials have been extensively used in preparation of electroanalytical nanosensors due to their small size, increasing surface area. Carbon-based nanomaterials can supply nanosensors many properties such as stability, repeatability and sensitivity. Functionalized carbon-based nanotubes (fCNTs) have become vital because of their chemical and physical properties. In recent years, widespread researches have been conducted using these nanomaterials$^{3-5}$. In the present work an electrochemical nanosensor has been developed for detection and determination of ENP using NH$_2$fMWCNT/GCE.

Materials and Method: Prior to use, the GCE with diameter of 3 mm was polished and cleaned with 0.05 µm alumina slurry over a rubbing pad. NH$_2$fMWCNT suspension was prepared by dissolving 1mg NH$_2$fMWCNT in DMF and 10 µL of this suspension dropped on to GCE. NH$_2$fMWCNT/GCE was allowed to dry in a vacuum oven at a temperature of 45 °C. 1.0×10$^{-3}$ M ENP with a constant 20% (v/v) methanol was used as the stock solution of ENP. All other supporting electrolytes and buffer solutions were prepared in ultra-pure water. Electrochemical characterization of electrode was done prior to each reading using cyclic voltammetry. The three electrode system containing a bare glassy carbon GC (Φ=3.0 mm) as working electrode, a platinum wire as a counter electrode and an Ag/AgCl (BAS; 3 M KCl) as a reference electrode was allowed to dry in a vacuum oven at a temperature of 45 °C. 1.0×10$^{-3}$ M ENP with a constant 20% (v/v) methanol was used as the stock solution of ENP. All other supporting electrolytes and buffer solutions were prepared in ultra-pure water. Electrochemical characterization of electrode was done prior to each reading using cyclic voltammetry. The three electrode system containing a bare glassy carbon GC (Φ=3.0 mm) as working electrode, a platinum wire as a counter electrode and an Ag/AgCl (BAS; 3 M KCl) as a reference electrode was used. The differential pulse voltammetry (DPV) conditions such as; step potential: 0.005 V; modulation amplitude: 0.025 V; modulation time: 0.05 s; interval time: 0.5 s were used. For pharmaceutical analyses, ten pharmaceutical tablet sample was grind in mortar and pestle in order to obtain fine powdered samples. From this powder, 1.0 mM standard solution of tablet was prepared and used for analyses.

Results and Discussion: The electrochemical investigation of ENP was conducted in 0.5 M H$_2$SO$_4$ where the NP has highest peak towards other pH values with a scan rate of 100 mV$s^{-1}$. Using NH$_2$fMWCN/GCE, oxidation peak of ENP has increased nearly 5 time as compared to bare electrode when followed by cyclic voltammetry. Moreover, oxidation peak potential of ENP was
shifted to less positive potentials indicating the catalytic effect of NH$_2$/MWCNT as shown in figure 1.

![Graph](image)

Figure 1. Differential pulse voltammograms of 40µM ENP

Since the electrochemical mechanism is suggested as adsorption controlled, as the slope of the log I and log v is close to 1, adsorptive stripping differential pulse voltammetry technique was used for the determination of ENP. The accumulation potential and time were optimized and found as 0.6 V and 240 s, respectively. Approximately 25 times increase in current response was obtained using NH$_2$/MWCNT/GCE by adsorptive stripping differential pulse voltammetry. The suggested nanosensor was further used for determination of ENP in tablet, human serum and urine. The recovery studies real that the suggested nanosensor was useful for the determination of ENP with recovery percent values between 98 and 101 with RSD% values less than 2%.

**Conclusion:** NH$_2$/MWCNT/GCE was developed for the determination and detection of antiparkinson Entacapone. All parameters effecting the nanosensor, such as pH, scan rate, accumulation potential and time were optimized. Using the suggested nanosensor limit of detection value was found as 1.453x10$^{-11}$ M. It can be concluded that the suggested nanosensor can be used for practical application of ENP detection and determination.

**References**


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A novel electrochemical nanosensor based on NH2-Functionalized Multi Walled Carbon Nanotubes Decorated with ZnO Nanoparticles and Graphene Quantum Dots for Pimozide Assay

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Abstract-In this study, a novel and sensitive electrochemical nanosensor for the determination of antipsychotic drug Pimozide (PZ) is proposed using NH2 functionalized multi walled carbon nanotubes (NH2fMWCNT) decorated with ZnO nanoparticles (ZnONPs) co-catalyzed by graphene quantum dots (GQDs). Electrochemical impedance spectroscopy (EIS) employed to investigate the electron transfer capability and cyclic voltammetry (CV) technique was used to successfully compare the redox response of PZ with modified and unmodified electrode. The designed nanosensor response was linear between 6.25×10−11 and 1.20×10−7 M concentration range of PZ with 1.02 ×10−11 M detection limit. The influence of interfering agents was further studied to examine the selectivity of the designed sensor. A rapid screening of PZ as is required in pharmaceutical and biological samples underscores the paramount importance of nanomaterial based electrochemical sensor for its sensitive and selective detection.

Keywords Pimozide; CNT; Quantum Dots; ZnO Nanoparticles; Electrochemical Nanosensors

Introduction
Pimozide (PZ; 1-{1-[4,4-bis(4-fluorophenyl) butyl]piperidin-4-yl} -2,3-dihydro-1H-1,3-benzodiazol-2-one) is an antipsychotic drug of diphenylbutylpiperidine class which is primarily used to treat schizophrenia, but it is also effective in other psychotic and manic states.

Figure 1. Molecular structure of Pimozide

Electrochemical techniques are currently the leading probes for sensing and monitoring of pharmaceuticals1-3. Subsequently, the significant step in the electrochemical determination of PZ is the fabrication of an ideal sensor. Carbon nanotubes (CNTs) and graphene quantum dots (GQDs) are two most important carbonaceous materials4,5 that have been explored for electrochemical sensor fabrication and its applications in pharmaceutical analysis. In this manner, as working electrode surface modifiers, ZnONPs has caught prolific attention of scientists and a lot of research in this direction has been conducted in the previous decades. Hence, due to excellent electrochemical activity, high surface to volume ration and good chemical stability of ZnONPs, they are viewed as worthy candidates for electrochemical sensing applications. In this regard, NH2fMWCNT, GQDs and ZnONPs are the effective, robust and reliable options as electrode modifiers.

The present work is focused on fabrication of novel electrochemical nanosensor for the sensitive detection of PZ by modification of glassy carbon electrode (GCE) surface with NH2fMWCNT, GQDs and ZnONPs.

Materials and Method
The voltammetric experiments were performed with a Palm Sense 4 running with PSTrace 5.3 software. For electrochemical impedance spectroscopy studies AUTOLAB FRA32M, FI20-Integrator running with FRA (Frequency resonance analyser) software was used. A conventional three electrode cell system was used in all experiments consisting of Ag/AgCl (3M KCl solution), platinum wire and glassy carbon electrode (GCE) with active surface area of 0.071cm² as the
For preparation of modification agents, 1 mg.mL\(^{-1}\) suspension of NH\(_2\)MWCNT and 1 mg.mL\(^{-1}\) suspension of ZnONPs were prepared by ultrasonication for 1 hours in DMF, separately. A stock solution of \(1.0 \times 10^{-3}\) M PZ was prepared in methanol. A specific amount (10 \(\mu\)L of the NH\(_2\)MWCNT (1 mg.mL\(^{-1}\)) was carefully drop coated onto the polished GCE followed by vacuum drying. This was followed by a layer-by-layer casting of 5 \(\mu\)L ZnONPs and 5 \(\mu\)L GQDs in a sequence on the surface of NH\(_2\)MWCNT/GCE and allowing it to dry in vacuum. NH\(_2\)MWCNT/ZnONPs/GQDs/GCE electrode was thus obtained. Standard solutions of human serum derived from human male AB plasma (Sigma-Aldrich) were prepared and standard solution of urine was prepared after collection of human urine sample from healthy volunteer to test the validation of the sensing method. Recovery experiment were performed in order to verify the accuracy of the proposed method and to check whether the excipient used in the pharmaceutical dosages form show any interference.

**Results and Discussion**

Electrochemical impedance spectroscopy (EIS) can differentiate between the electronic transduction behavior of bare and modified electrodes. For a quantitative estimate EIS measurements were performed at the unmodified and NH\(_2\)MWCNT, ZnONPs and GQDs modified working electrodes using 5 mM potassium ferricyanide solution as the redox probe. Change in EIS parameters revealed that the modified electrode offered less resistance to the redox probe. Thus, NH\(_2\)MWCNT/ZnONPs/GQDs/GCE behaved as a better sensor compared to other sensing surfaces.

In this study, different kinds of modification agents such as COOH group functionalized multi walled carbon nanotubes (COOH/MWCNT), Graphene QDs, TiO\(_2\)NPs, AgNPs, AuNPs, ZnO, PtNPs, or surfactants such as tween 20, polyethylene glycol, were used to find best nanosensor toward PZ detection. In these modification agents, NH\(_2\) functionalized MWCNT generates a higher peak current than bare GCE. GQDs and NH\(_2\)MWCNT modified electrode in comparison with the NH\(_2\)MWCNT/GCE showed higher peak current due to the high surface area resonating well with a pronounced effect of MWCNT and GQDs in increasing electroactive surface area of the electrode. In contrast, NH\(_2\)MWCNT/ZnONPs/GQDs nanocomposite modified electrode with regards to other modified electrodes showed a further increase in current which implies a faster rate of electron transfer due to synergistic effect of GQDs, MWCNT and ZnONPs (Figure 1.).

The amount of modifier on the signal of PZ was probed for evaluating the best sensing platform. Maximum current response was obtained with 10 \(\mu\)L NH\(_2\)MWCNT (1 mg.mL\(^{-1}\)), 5 \(\mu\)L ZnONPs (1 mg.mL\(^{-1}\)) and 5 \(\mu\)L GQDs. Hence, further experiments were performed using modified electrode with an optimized 10:5:5 \(\mu\)L of NH\(_2\)MWCNT, ZnONPs and GQDs. The investigation of pH effect was performed in order to select the best pH media regarding peak shape, sensitivity and reproducibility for differential pulse voltammetric determination of PZ. Thus in succeeding experiments, a solution of 0.1 M \(H_2SO_4\) at pH 1.0, was chosen as the optimal experimental value as an effective supporting electrolyte. In order to investigate whether the process of PZ oxidation at the surface of modified GCE is diffusion or adsorption controlled, scan rate studies were conducted.
Figure 2. DPV and Cyclic Voltammograms of 40 µM solution of PZ on bare GCE and NH2MWCNT/ZnONPs/GQDs/GCE

It was observed that the peak current of PZ is proportional to with the scan rate. Moreover, in order to suggest a possible oxidation mechanism for Pimozide, other group members of piperidine drugs, Benperidol and Droperidol were studied as model drugs. Hence, it can be suggested that Pimozide oxidation is related to the piperidin moiety. Selectivity of the designed electrochemical nanosensor for the assay of PZ was investigated using 500-fold higher concentration of interfering species such as uric acid (UA), ascorbic acid (AA), dopamine (DA), paracetamol (PA), sucrose and magnesium phosphate with the help of DPV. In order to check the viability of the proposed method for the determination of PZ the relationship between the anodic peak current and the concentration of PZ was studied using DPV under optimum conditions. A linear relationship was observed between the $I_p$ and concentration of PZ in the range of $6.25 \times 10^{-11} - 1.20 \times 10^{-7}$ M with correlation coefficient of 0.998. The designed sensor was successfully applied for detection of PZ in concentration range of $3.3 \times 10^{-10} - 3.0 \times 10^{-8}$ M and for serum and urine samples.

Conclusion

Electrochemical techniques are currently the leading probes for monitoring pharmaceutical analytes. Nanomaterials play the different roles in the process of the construction of the nanosensors for their different composition, morphology and size. In this study, we aimed to create more sensitive nanosensor for the selective detection and sensitive determination of PZ.

References


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Fabrication of A Novel Surfactant Based Electrochemical Nanosensor for Esmolol Determination


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Abstract: Esmolol (ESM), is a cardio selective beta-adrenergic blocker in class II antiarrhythmic that used in the treatment of acute supraventricular tachycardia, arrhythmias and severe hypertension. The overdose of ESM can cause both cardiac and central nervous system side effects such as bradycardia, cardiac arrest, respiratory depression and coma. For this reason, it is very important to determine ESM levels in biological fluids such as human serum, urine and pharmaceutical preparations. In this study, the electrochemical behavior of ESM was investigated in a wide pH range using square wave voltammetric technique at glassy carbon electrode. Maximum current was observed in the pH 6.0 acetate buffer by square wave voltammetry (SWV). As a result of scan rate studies, diffusion-controlled mechanism was occurred. Interference and modification effects were investigated. The optimum effect of modification was obtained by sodium dodecyl sulphate and platinum nanoparticles. A linear relationship was plotted between ESM concentrations and the current response. The proposed method has been extensively validated according to ICH Guidelines. The developed electro-chemical method is also used for the determination of ESM in spiked human serum.

Keywords: Esmolol, Nanosensor, Square Wave Voltammetry, Nanoparticles

Introduction:
Esmolol, an ultra-short-acting beta-blocker, is used to reduce blood pressure in hypertension and increase exercise tolerance in angina. Esmolol is used in the treatment of aortic cross-clamping related hypertension and tachycardia, and it has been found useful in the postoperative period for abdominal aortic surgery. Ultra-short-acting β-blockers, which have beneficial effects of β-blockers, do not have the deleterious effects of long-acting agents. Esmolol may produce systolic hypotension as a side effect, but this is usually seen in high doses. The most common side effects associated with the use of esmolol are hypotension, confusion, bradycardia and phlebitis. Therefore, it is important that Esmolol is precisely and rapidly detected in biological fluids and pharmaceutical preparations. Electrochemical methods are very simple, less expensive, less time consuming, and a thorough pre-treatment of samples is not required. Voltammetry is a kind of electrochemical techniques in which the current in the working electrode is evaluated as a function of the potential applied to this electrode. Square wave voltammetry is among the most commonly used voltammetric methods. The voltammogram of square wave voltammetry displays excellent sensitivity and efficient analysis.

Materials and Method:
Electrochemical investigations including Electrochemical Impedance Spectroscopy (EIS) and voltammetric experiments including cyclic voltammetry (CV), and square wave anodic stripping voltammetry (SWASV) were performed by using PalmSense trace 5. All the electrochemical experiments were performed by using three electrode system.

Results and Discussion:
The electrochemical behavior of ESM was investigated in a wide pH range using square wave voltammetric technique at glassy carbon electrode. SDS/Pt has been successfully used as a sensor for determination of esmolol as the modified electrode greatly increased the current signal of the peak as compared to the unmodified electrode and from the experimental and theoretical study all results suggest that SDS/Pt greatly facilitate the sensing behavior of esmolol. This sensor delivers remarkable applicability for the detection of esmolol in serum samples and relative standard deviation was less than 2 % by using supporting electrolyte (Britton-Robinson buffer at pH 6.0).
Conclusion:
The sensitivity of the proposed method was found to be 115.0 µA/M with limit of detection 60 pM for square wave voltammetry in serum. Insignificant effect of other interfering agents was observed. Interaction energy calculated from computational study compliment the experimental work. Hence SDS/Pt is good for electro analysis and also very economical.

References:
**OP8- A Nanostructured Composite System for the Electrochemical Quantification of Aspartame**

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**Abstract**-In this study, an electrochemical sensor was developed for the detection of aspartame using square wave voltammetry (SWV). To this end, modifying a paper electrode was modified with zinc oxide nanoparticles (ZnONPs) dispersed over multiwalled carbon nanotubes (MWCNTs) in chloroform. The modified electrode surfaces were characterized by energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) techniques and by cyclic voltammetry (CV) in the presence of redox probes. The modified electrode was able to oxidize aspartame at a potential of 1.014 V in a phosphate buffer of pH 2.0. The current response showed a linear dependence on the aspartame concentrations in the range of 5.0 µM to 40.0 µM and the correlation coefficient (R²)=0.9991, and the detection limit (LOD) was calculated as 1.39×10⁻⁹ M. Improved voltammetric behaviour, long-time stability and good reproducibility were obtained for aspartame at the proposed electrode. Accurate and precise quantification of aspartame makes the proposed electrode system of great interest for the detection of food additives.

**Keywords:** Aspartame, nanocomposite, sensor.

**Introduction**
Since the first application of aspartame, the debates have been ongoing whether aspartame contains genotoxic and carcinogenic risks for humans⁴. As aspartame has a peptide structure and is digested in the body, it is hydrolyzed to amino acid, aspartic acid, phenylalanine and methanol². Being a lethal neurotoxin, methanol may cause permanent blindness. Phenylalanine and aspartic acid, which are other hydrolysis products of aspartame, also cause seizures and increase neurological defects when they reach high concentrations. In addition, aspartame is converted into a carcinogen, a neurotoxin (a poison with harmful effects on the nervous system) and an exotoxin (a toxic substance that kills nerve cells) after getting into the human body³,⁴. Considering all these, accurate and reliable determination of aspartame is important.

**Materials and Method**

**Chemical Reagents and Instrumentation**
NaOH and Na₂HPO₄ were purchased from Sigma-Aldrich. Chloroform and acetonitrile were obtained from VWR, and KH₂PO₄ from Merck. MWCNTs, aspartame, neotame, acesulfame-K, saccharin were purchased from Sigma. The solutions were prepared with ultrapure water. An Interface 1000B Potentiostat/Galvanostat/ZRA was used for the application of cyclic voltammetry and square wave voltammetry techniques in the electrochemical characterization and electrochemical application experiments.

**Preparation of ZnONP+MWCNTs/GC Electrode**
GC electrode was cleaned with 0.05 µm and 0.30 µm of alumina powder. The MWCNTs were functionalized in an acid mixture of HClO₄ + HNO₃ (3:7, v:v). The functionalized MWCNTs and ZnONPs were sonicated for 1 hour in chloroform⁵. This obtained suspension was dropped on the cleaned GC electrode and ZnONPs+MWCNTs/GC was prepared by drying at the room temperature.

**Optimization of Modified Electrode**
The experimental results showed that the best results were obtained by mixing MWCNT and ZnONPs mixture in 10.0: 1.0 ratio in 5 mL chloroform for 50 min. Furthermore, the composite layer on the GC electrode surface showed a clear peak formation for aspartame when the amount of ZnONPs+MWCNT suspension was 5 µL . Because when higher amounts of this suspension were added to the GC electrode surface, a significant reduction in sensitivity and repeatability was observed.

**Voltammetric Quantification of Aspartame**
The sensitivity of aspartame to different concentrations (0, 0 µM, 5, 0 µM, 10, 0 µM, 15, 0 µM, 20, 0 µM, 30, 0 µM) on ZnONPs+MWCNTs/GC surface was examined by applying square wave voltammetry (Frequency: 25 Hz Step potential: 100 mV/s Amplitude: 50 mV/s).
Results and Discussion

Characterization of MWCNTs/GC and ZnONPs+MWCNTs/GC Electrode Surfaces

To obtain information about the morphology of the modified electrode surfaces, the characterization was performed using the SEM. As presented in Fig 1a, MWCNTs were homogeneously distributed on the electrode surface and there was no agglomeration. It was observed that ZNONPs were distributed to the structure of MWCNTs to form a composite structure as presented in Fig 1b. It was observed that C, O, N and Zn were present in the EDX analysis of ZnONPs+MWCNTs/GC electrode surface as demonstrated in Fig 1c. In addition to these characterizations, voltamograms of the ferrocene and ferricyanide redox probes of bare/GC, MWCNTs/GC, ZnONPs/GC and MWCNTs+ZnONPs/GC electrodes were recorded and compared to each other. It was observed that this modified electrodes allowed the transfer of electrons for the reduction-oxidation reactions of the ferrocene redox probe as demonstrated in Fig 2a. On the other hand, maximum electron transfer was obtained on the composite electrode surface (32.01 µA). When the voltamograms given in Fig 2b are examined, it can be observed that the redox reaction of the ferricyanide redox probe is reversible and more catalyzed in ZnONPs+MWCNTs/GC (11.01 µA) electrode.

![SEM images of a) MWCNTs/GC b) ZnONPs+MWCNTs/GC the electrode surfaces c) EDX analysis of ZnONPs+MWCNTs/GC electrode surface](image)

**Fig1.** SEM images of a) MWCNTs/GC b) ZnONPs+MWCNTs/GC the electrode surfaces c) EDX analysis of ZnONPs+MWCNTs/GC electrode surface

![CV of a) 1.0 mM of ferricyanide in BR buffer, pH 2.0 b) 1.0 mM of ferrocene in TBATFB at Bare/GC, MWCNTs/GC, ZnONPs/GC ZnONPs+MWCNTs/GC surfaces. Potential sweep rate was 100 mV/s.](image)

**Fig2.** CV of a) 1.0 mM of ferricyanide in BR buffer, pH 2.0 b) 1.0 mM of ferrocene in TBATFB at Bare/GC, MWCNTs/GC, ZnONPs/GC ZnONPs+MWCNTs/GC surfaces. Potential sweep rate was 100 mV/s.

Quantification of Aspartame

The SWV technique was applied on the ZnONPs+MWCNTs/GC electrode surface for the quantification of aspartame and the experimental results are given in Fig3a and Fig3b. The peak currents of aspartame with the equation $I_{pa}(\mu A) = 0.8685C(\mu M) + 0.6331$ at ZnONPs+MWCNTs/GC electrode surface was observed to be linear in the range 5.0 µM~40 µM and the correlation coefficient ($R^2$) = 0.9991. The LOD of the molecule of aspartame was calculated using $C_m=3S_b/m$ and was found to be $1.39 \times 10^{-9}$ M. These results show that the reproducibility of the GC electrode modified with ZnONPs+MWCNTs/GC is excellent.
Fig3. a) SWV at various concentrations of Aspartame on ZnONPs+MWCNTs/GC electrode surface (Support Electrolyte 100 mM PBS, Frequency: 25 Hz Step potential: 100 mV/s. Aspartame Concentrations: a) 0.0 sM; b) 5 µM; c) 10 µM; d) 15 µM; e) 20 µM; f) 30 µM; g) 40 µM. b) Calibration graph of peak currents recorded against increasing concentrations of different Aspartame.

**Conclusion**

Fast, economical and reliable detection of aspartame molecule was performed on the proposed ZnONPs+MWCNTs/GC electrode surface. In addition, this electrode surface suggested a good stability, selectivity and reproducibility in determining the appropriate amount of harmful molecules formed as a result of the hydrolysis of aspartame to prevent the effects on human health.

**References**

4- Vale, A., Ethanol, Medicine, 35.11 (2007), 615-616.

**Acknowledgment**

I would like to thank the Research Foundation of Nevşehir Hacı Bektaş Veli University for their financial support to this research under the project number 162F20.
OP9- Evaluation of Antimicrobial Effect of Simvastatin on *E. Coli* with Metabolomics Analysis

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Abstract
Statins are most important drug class for cholesterol treatment. In recent years, statins have been emerged as an antimicrobial agents against various pathogens. In this work, we investigated antimicrobial effect of simvastatin over *E.coli*. We used GC-MS based metabolomics approach to understand mode of antimicrobial action of simvastatin. Principal component analysis showed that simvastatin effects global metabolic profile of *E.coli*. We found 22 differentially altered metabolites between control and simvastatin treated group. The significantly altered metabolites were evaluated in bioinformatics platforms. Finally, we found that simvastatin is very effective on energy metabolism and DNA replication processes. All these results showed that simvastatin affects cellular processes in various pathways and shows antiproliferative effects over *E.coli*.

**Keywords:** Metabolomics, GC/MS, Simvastatin, Antimicrobial effect

Introduction
Statins (HMG-CoA reductase inhibitors) are class of drugs used to lower cholesterol levels by inhibiting the conversion of HMG-CoA to l- mevalonic acid and subsequently inhibit cholesterol synthesis in the liver. Today, statins are used commonly around the worldwide. In recent years it has been shown that stains possess many effect on individual physiology without anti LDL (Low density lipoproteins) effects. Several studies showed that statins prevent against chronic diseases like diabetes and cancer¹,². Also antimicrobial effect of statins has been studied extensively. Results showed that statins, especially simvastatin, exhibits high antimicrobial effect on various pathogens³. Although solid evidences of antimicrobial effect of statins on various bacteria types, there is no detailed study to clarify their antimicrobial action mechanism. In this study we used GC/MS based metabolomics approach to understand action mode of simvastatin on *E. coli*.

Experimental
Antimicrobial activity analysis
*E. coli* ATCC 25922 was cultured on Tryptic Soy Agar. Standard broth microdilution was performed according to the method reported by Clinical Laboratory Standards Institute (CLSI) in order to determine minimum inhibitory concentration (MIC) of simvastatin against *E. coli* [1]. For Metabolomics experiments, MIC50 value of simvastatin was used. *E. coli* ATCC 25922 was cultured on Mueller Hinton Broth (MHB) and incubated under 37°C until the log phase achieved. The bacterial suspension was prepared with MHB containing the MIC50 value of simvastatin to obtain a concentration of 5x10⁵ cfu/mL bacteria. As control experiments the same amount of bacterial culture was also prepared without simvastatin. Flasks were incubated at 37°C for 20 h. Experiments were performed triplicate.

Metabolomics analysis
Following chemical disruption of bacterial cells, 100 µL of cell lysate is extracted with 900 µL methanol:water (8:1, v/v) mixture at ambient temperature, followed by spin-down of samples and transfer of 900 µL supernatant to an eppendorf tube with complete drying in vacuum centrifuge concentrator. Then samples were methoximated and derivatized using N-methyl-N-trimethylsilyltrifluoroacetamide with 1% trimethylchlorosilane (MSTFA + 1% TMCS, Pierce) and analyzed by GC-MS. The data files from GC-MS analyses were deconvoluted using MS-DIAL is used to list and track metabolite peaks. Two sample T-test was used to determine
differentially regulated metabolites between control and treated groups (p<0.05). PCA analysis was performed to understand overall effect of simvastatin over *E.coli* metabolome.

**Results and Discussion**
The MIC value of simvastatin against *E. coli* ATCC 25922 was found as 128 μg/mL. Thus, the MIC50 value of 64 μg/mL was used for further metabolomics study. Results showed that simvastatin is very effective over cellular processes. PCA analysis showed that simvastatin is very effective on global metabolome structure of *E. coli* (Figure 1).

![Figure 1. PCA analysis of control (red) and treated (blue) groups.](image)

We used two-sample t-test and found that 22 metabolites were differentially regulated (p<0.05). We analyzed these proteins in Metaboanalyst platform to find simvastatin-induced pathways (Figure 2).

Pathway analysis showed that simvastatin is effective on butanoate metabolism. These results showed that simvastatin induces energy metabolism in *E.coli*. In addition we observed that simvastatin effects glutamate metabolism. Glutamate metabolism is very important for nucleic acid biosynthesis. We can conclude that simvastatin is also very effective on DNA replication. DNA replication is general target for many antibiotic drugs.

**Conclusion**
In this study, we observed that simvastatin possesses antimicrobial effect over *E.coli*. GC/MS based metabolomics analysis showed that simvastatin affects energy and DNA replication process in *E.coli*. These results are very important to identify statins mechanism as an antimicrobial agent. In further experiments simvastatin will be analyzed with antibiotics for more efficient treatment against pathogens. We believe that our results will contribute evaluation of statins as antimicrobial agent.
Figure 2. Pathway analysis of differently regulated proteins

References
**Abstract**—In this study, structural and antibacterial properties of undoped hydrogel, nano-TiO$_2$ doped hydrogel and ZnO nano-flowers deposited on nano-TiO$_2$ doped hydrogel were investigated. According to their superior antibacterial property, nano sized TiO$_2$ and ZnO were chosen. Nano-TiO$_2$ particles have been incorporated in polymeric matrices in order to provide antimicrobial activity to the biodegradable hydrogel. Then ZnO nano-flowers have been deposited on the surface of the hydrogel to improve antimicrobial activity. At the reaction time of 60 minutes, nano-flowers were fully developed. Zn content of hydrogel was 35.89 at. %, Ti content of hydrogel was also determined as 0.16 at.%. In respect to antibacterial activity tests results, *Escherichia coli* were more resistant to hydrogel and ZnO nanoflower than *Staphylococcus aureus*.

**Keywords**: nano-TiO$_2$, flower-like ZnO, hydrogel, antibacterial activity

**Introduction**

Hydrogels are three dimensional (3D) polymeric networks which made of both natural and synthetic materials dominating high number of flexibility. Superior swelling property of hydrogels makes them an ideal material for variable applications. Some characteristic properties of hydrogels can be listed as desired functionality, reusability, reversibility, sterilizability and biocompatibility ($^{1,2}$). Inorganic nano-materials can be doped to hydrogels to provide opportunity for development of nanoparticles for use as antibacterial agents. Nano-particles have unique properties in comparison with their bulk size counterparts. Among all nano-particles nano-TiO$_2$ can be widely used in biomedical applications such as biosensors, drug delivery systems and cancer therapy in recent years ($^{3,4}$). The antimicrobial activity of metals such as silver (Ag), copper (Cu), gold (Au), titanium (Ti), and zinc (Zn), each having various properties, has been applied for centuries ($^5$). In this study, firstly nano-TiO$_2$ doped hydrogels were produced and then ZnO nano-flowers were grown on the hydrogels to enhance the antibacterial property of material.

**Materials and Method**

In the first part of the study, acrylic acid (AA) hydrogels were synthesized by free radical polymerization technique using with a radicalic initiator (ammonium persulfate) and a crosslinking agent (N,N’-methylene-bis-acrylamide). Nano-TiO$_2$ were used as a dopant to produce nano-TiO$_2$ doped hydrogel. In the second part of the study ZnO nano-flowers on hydrogels were deposited by chemical bath deposition technique (CBD) at different deposition times (15-30-45 and 60 min). Characterization studies were examined Fourier Transform Infrared Spectroscopy (FT-IR), Field Emission Scanning Electron Microscopy (FESEM). Elemental amounts of TiO$_2$ and ZnO nano-flowers were shown by Energy Dispersive X-Ray Spectrometer (EDX). After that, the antibacterial activity tests were carried out in accordance with ASTM E2149 (Determining the Antimicrobial Activity of Antimicrobial Agents Under Dynamic Contact Conditions) with the bacteria *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* ATCC 8739.

**Results and Discussion**

According to the images of nano-flowers obtained using 15, 30, 45 and 60 minutes deposition time, the nano-flower structures become more apparent as the reaction time increases (Fig.1). When the deposition time of 60 minutes, it was observed that nano-flowers were fully developed.
SEM-EDX results of nano-flowers obtained at 60 min was given in Fig. 2. Zn content of hydrogel was 35.89 at.%, Ti content of hydrogel was also determined as 0.16 at.%. Antibacterial activity tests were conducted on hydrogel, nano-TiO$_2$ doped hydrogel and flower-like ZnO deposited on nano-TiO$_2$ doped hydrogel. The results were given in Table 1. *Escherichia coli* were more resistant to hydrogel and ZnO nanoflower than *Staphylococcus aureus*.

**Figure 1.** Nano-flowers obtained at (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min.

C: 29.37 at.%  
O: 34.58 at.%  
Zn: 35.89 at.%  
Ti: 0.16 at.%

**Figure 2.** SEM-EDX results of nano-flowers obtained at 60 min.

**Conclusion**  
In this study, synthesized hydrogels were used as substrate to deposit ZnO nanoflower by chemical bath deposition technique. Deposition time plays a key role to obtain nano-ZnO particles in flower-shape. Significant differences of morphological characteristics were observed by
applying deposition time. Moreover, the deposited ZnO nanoflower on biodegradable hydrogel exhibited high activity against *Escherichia coli* and *Staphylococcus aureus*.

**Table 1.** Antibacterial activity test results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bacteria</th>
<th>Count in the control sample after 24 hours</th>
<th>Count in sample after 24 hours</th>
<th>Decrease (%)</th>
</tr>
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<td>Hydrogel</td>
<td><em>Staphylococcus aureus</em></td>
<td>530000</td>
<td>108915</td>
<td>79.45</td>
</tr>
<tr>
<td>Nano-TiO$_2$ doped hydrogel</td>
<td><em>Staphylococcus aureus</em></td>
<td>530000</td>
<td>51064</td>
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<td><em>Staphylococcus aureus</em></td>
<td>530000</td>
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<td><em>Escherichia coli</em></td>
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<td>210553</td>
<td>57.03</td>
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<tr>
<td>Nano-TiO$_2$ doped hydrogel</td>
<td><em>Escherichia coli</em></td>
<td>490000</td>
<td>94150</td>
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<tr>
<td>ZnO nano-flowers deposited nano-TiO$_2$ doped hydrogel</td>
<td><em>Escherichia coli</em></td>
<td>490000</td>
<td>12450</td>
<td>97.46</td>
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</table>

**References**


**Acknowledgement:** This work was financially supported by Scientific Research Project Commission of Bilecik Seyh Edebali University (project number is 2017-01.BŞEÜ.28-01). FTIR and SEM-EDX-Mapping measurements were performed in Bilecik Seyh Edebali University Central Research Laboratory. TGA measurements were performed in Hacettepe University Advanced Technologies Application and Research Centre. The antimicrobial activity tests were performed at Ege-MIKAL Environmental Health Laboratory.
**OP11- Detection of Alkaline Phosphatase Enzyme Activity with Different SERS Platforms**

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**Abstract**- In this study, three different nanoplasmonic platforms; rod-shaped gold nanoparticles (Au-NRs), spherical silver nanoparticles (AgNPs) and silver nanoparticle linked Au slides (Au-AgNPs) were developed using surface-enhanced Raman spectroscopy (SERS) for detection of alkaline phosphatase (ALP) activity on 5-bromo-4-chloro-3-indolyl phosphate (BCIP) as a substrate. After 1 hour reaction time ALP hydrolyzes BCIP to the SERS-active product; 5-bromo-4-chloro-3-indole (BCI). A good linearity was established between the specific SERS intensity of BCI at 600 cm⁻¹ and ALP concentration after enzymatic reaction. The coefficient of determination (R²) was calculated for Au-NRs, Au-AgNPs, AgNPs and found to be 0.988, 0.978 and 0.927, respectively.

**Introduction**

Alkaline phosphatase (ALP) is a hydrolase enzyme that removes phosphate groups of biomolecules. It is involved in many metabolic and biochemical reactions in the body. ALP is also found in human serum and assayed in clinical tests, thus, it is important to detect ALP activity or content in body fluids for diagnosis of bone and physiological disorders. Enzymatic activity of ALP is high stability and high sensitivity. Hence, monitoring ALP activity has great advantages on immunoassays, bacteria detection and affinity sensing methods for protein, nucleic acids and other analytes1,2.

It is important to develop a rapid and ultrasensitive ALP activity detection methods. Surface-enhanced Raman scattering (SERS) techniques could obtain a fingerprint of the target molecule in a mixed sample. This allows detecting the activity of ALP at very low concentrations. 5-bromo-4-chloro-3-indolyl phosphate (BCIP) is a chromogenic substrate of ALP. It is reported that ALP hydrolyzes BCIP and produces 5-bromo-4-chloro-3-indole (BCI) and inorganic phosphate³. SERS signal of BCI dimers at 600 cm⁻¹ could be obtained in the presence of metallic nanoparticles. In this study, different SERS platforms of plasmonic nanoparticles and surfaces developed for detection of ALP activity.

**Materials and Method**

**Materials:**
Hexadecyltrimethyl ammonium bromide (CTAB), gold (III) chloride solution (HAuCl₄), sodium borohydride (NaBH₄), silver nitrate (AgNO₃), L-ascorbic acid (AA), alkaline phosphatase, 5-bromo-4-chloro-3-indolyl phosphate disodium salt (BCIP), 1,4-dithiothreitol (DTT), sodium hydroxide (NaOH), hydroxylamine hydrochloride (NH₂OH-HCl), Tris-HCl were purchased from Sigma-Aldrich (Darmstadt, Germany).

**Methods:**
Rod-shaped gold nanoparticles (Au-NRs) and spherical silver nanoparticles (AgNPs) were synthesized according to Temur et. al and Leopold et. al procedures, respectively4,5. UV-Visible spectrophotometry and Transferred electron microscopy (TEM) used for characterization of nanoparticles. Synthesized nanoparticles are used as SERS nanoparticle platforms.

AgNPs were linked on Au slides after formation of self-assembled monolayer via DTT. AgNPs covered Au slides are used as SERS surface platform (Au-AgNPs).

ALP enzyme prepared and diluted in 0,05M and pH 9,8 Tris-HCl buffer and mixed with its substrate 0,3 mg ml⁻¹ BCIP for enzymatic activation.

**Instrumentation:**
DeltaNu Examiner Raman Microscopy system (Deltanu Inc., Laramie, WY) with a 785 nm laser source and a cooled charge-coupled device (CCD, at 0 °C) detector were used for ALP activity detection. The optimized parameters were determined as 100 mW laser power, and 20 s acquisition time.
**Results and Discussion**

The applicability of the developed SERS platforms for accurate measurement of ALP activity is directly related to enzymatic hydrolyses of BCIP. Figure 1. displays the specific SERS signal of BCI nearly at 600 cm$^{-1}$ were obtained in the presence of Au-NRs, Au-AgNPs and AgNPs platforms.

![Figure 1. SERS spectra of BCI (product); a) Au-NRs, b) Au-AgNPs surface, c) AgNPs platforms](image)

**Figure 2.** Correlation between A) Au-NRs, B) Au-AgNPs, C) AgNPs SERS signals and logarithmic ALP concentration

ALP enzymatic activity was studied that concentrations between $10^{-11}$–$10^{-15}$ M in the presence of a constant amount of BCIP (0.3 mg ml$^{-1}$). SERS measurements were performed in order to test developed nanoplatfroms for ALP activity detection. Results are shown for Au-NRs, Au-AgNPs and AgNPs platforms in Figure 2. A good linearity was obtained for developed SERS platforms.

**Conclusion**
In conclusion, three different methods were used to develop SERS-based platforms that make use of ALP enzymatic activity. ALP-BCIP enzymatic interaction takes 60 min. and SERS measurements less than 2 mins. SERS active substrates for enzymatic reactions were useful to develop new analytical methods.

References


OP12 - Metal Based Drug Candidate Molecules in Chemistry

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Abstract
A disease is a particular abnormal condition that negatively affects the structure or function of part or all of an organism, and that is not due to any external injury. The most known and used classification of diseases is the World Health Organization's ICD. Some diseases, such as most (but not all) forms of cancer, heart disease, and mental disorders, are non-infectious diseases. Many non-infectious diseases have a partly or completely genetic basis and may thus be transmitted from one generation to another. Various drug groups are used in the treatment of such diseases. These are metal based drugs which have an important place among them. A significant growing demand for metal-based anticancer, antimicrobial and anti-inflammatory drug candidates has been observed in the field of medicinal science. In this presentation, the advantages of well-known, newly synthesized and tried-and-tested Metal Based Drug Candidate Molecules in medicine and pharmacy will be emphasized.

Keywords: Metal Based Drugs

Introduction
We all talk about complexization reactions under Analytical Chemistry. Complexation reactions are widely used in inorganic, analytical and bioanalytical chemistry. Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or ligand, must have at least one pair of unshared electrons available for bond formation. Complexization reactions led to the emergence of coordination chemistry as an important discipline. An estimated 30% of proteins contain metal ions. Examples include the intensely colored vitamin B12, the heme group in hemoglobin, the cytochromes, the chlorin group in chlorophyll, and carboxypeptidase, a hydrolytic enzyme important in digestion. Another complex ion enzyme is catalase, which decomposes the cell's waste hydrogen peroxide. The approval of cisplatin for use in testicular and ovarian cancers by the US Food and Drug Administration on 19 December 1978 was directed to synthesizing metal-containing drugs. Investigation of metal complexes of pharmaceutical compounds is an important and active research area in bioanalytical/bioinorganic chemistry, because of the synergistic effect of the beneficial effects obtained from the ligand and the activity of the metal can provide an increased activity of drugs. Many metal-based compounds using drugs as ligands are available in the literature.

Materials and Method
In the synthesis of new metal based drugs, classical sedimentation reactions (reflower systems) and hydrothermal synthesis methods are used. In determining the analytical conditions; The effects of temperature, pressure, dwell time, ligand: metal coupling rates are investigated. Chloride or acetate salts of all metals (Pt(II), Cu(II), Zn(II), Mn(III), Ru(III), Au(II)) are used. Characterization of new products is done by various analytical and spectrophotometric methods such as melting point, TLC, elemental analysis, Uv-Vis, IR, Mass, NMR and x-ray etc.

Results and Discussion
Pharmacological and therapeutic efficiencies of drugs have often improved upon attachment with metal ions with organic compounds, i.e., metal complexes. Furthermore, it also depends on the arrangement of the donor ligands because different types of arrangement of ligands display diverse pharmacological properties to the drugs. Approximately thirty-two elements in the periodic table are believed to be essential or beneficial to life. The remainder of the elements is adventitious, having been introduced by local dietary or environmental sources. Some of these elements are derived from pollutants present in water or food. Elements necessary for good health, food being by far the largest source, read H, C, N, O, S, Na, Mg, P, Cl, K and Ca as major elements and V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo, B, F, Si, Ru(III), Au(I/II) and I as minor species. Newer trace elements possibly having a health role include Sr, Ba, W, Cd, Sn, As and Br. In the last two decades, studies have shown that metal-based compounds formed with these elements
are used in the treatment of diseases. The following Table lists some metal-based drugs that are in clinical use or in the trial phase.

Table. Some metal-based drugs and candidates in clinical use or trial

<table>
<thead>
<tr>
<th>Company Name</th>
<th>Drug Name</th>
<th>Disease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kocal A.S</td>
<td>Cis-platin</td>
<td>Cancer</td>
</tr>
<tr>
<td>Smith &amp; Nephew</td>
<td>Silver Eluting Dressing</td>
<td>Antimicrobial</td>
</tr>
<tr>
<td>Solasia Pharma K.K.</td>
<td>Darinaparsin</td>
<td>Cancer</td>
</tr>
<tr>
<td>Sanofi</td>
<td>Ferroquine</td>
<td>Antimalarial</td>
</tr>
<tr>
<td>Cornell University</td>
<td>Tetrathiomolybdate</td>
<td>Cancer</td>
</tr>
<tr>
<td>Mayo Clinic</td>
<td>Auranofin</td>
<td>Cancer</td>
</tr>
<tr>
<td>Prana Biotechnology</td>
<td>Hydroxyquinoline</td>
<td>Alzheimer</td>
</tr>
<tr>
<td>Ceva</td>
<td>Cu(^{2+}) indomethacin</td>
<td>Anti-inflammatory</td>
</tr>
<tr>
<td>University of Texas Health</td>
<td>Bi(^{3+}) compounds</td>
<td>Anti-inflammatory</td>
</tr>
<tr>
<td>Lilly</td>
<td>Hg(^{+}/^{2+}) compounds</td>
<td>Antibacterial</td>
</tr>
<tr>
<td>Molecular Insight Pharm.</td>
<td>99mTc-MIP-1404</td>
<td>Cancer</td>
</tr>
<tr>
<td>OHSU Knight Cancer Institute</td>
<td>Ferumoxytol MRI</td>
<td>Cancer</td>
</tr>
</tbody>
</table>

**Conclusion**

When I searched the web of science with the keyword "metal complex", there were 306,099 studies. The clinical and commercial importance of medical uses and applications of metals and metal complexes is increasing day by day. This result shows that the clinical and commercial importance of the applications of metal complexes is increasing day by day.

**Acknowledgement**

This study was supported by the Scientific Research Projects Unit of Istanbul Technical University (Project No: TGA-2017-40917).

**References**

1- https://en.wikipedia.org/wiki/Disease
Spectroscopic and voltammetric studies of anticancer drug Fludarabine bound to fish sperm double-stranded deoxyribose nucleic acid (fsdsDNA)

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Abstract
In this study, the interaction between fsdsDNA and anticancer drug fludarabine (FLD) was investigated using UV-Vis, IR, fluorescence and voltammetry (CV, DPV and OSW) techniques. In addition, the denaturation studies of the FLD-DNA pair were carried out by examining the change in the absorbance values of the specific wavelength versus the increasing temperature.

Keywords: Fludarabine, Drug, DNA binding

Introduction
DNA is a basic bio-molecule containing the molecular information necessary for the regular development of organisms, sustainability in life and reproduction. The first study between deoxyribonucleotides and a drug was carried out by different researchers about thirty years ago. Actinomycin is the first drug to be studied using different nucleotides. Since then, the investigation of interactions between small molecules and deoxyribonucleotides (especially deoxyribonucleic acid, DNA) has become the focus of the study. Recognition and characterization of these interactions is extremely important because valuable information is obtained on the development of therapeutic agents and on the control of gene expression.

Fludarabine, sold under the brand name Fludara among others, is a chemotherapy medication used in the treatment of leukemia and lymphoma. These include chronic lymphocytic leukemia, non-Hodgkin's lymphoma, acute myeloid leukemia, and acute lymphocytic leukemia. In this study, the interaction between fsdsDNA and anticancer drug fludarabine (FLD) was investigated using UV-Vis, IR, fluorescence and voltammetry (CV, DPV and OSW) techniques. In addition, the denaturation studies of the FLD-DNA pair were carried out by examining the change in the absorbance values of the specific wavelength versus the increasing temperature.

Materials and Method
Fludara was obtained from Sanofi pharmaceutical company in response to the request. fsdsDNA fsdsDNA was purchased from Sigma. The solutions used in the study were prepared daily by diluting the stock solutions with Tris-HCl/NaCl buffer (5mM Tris-HCl (Sigma-Aldrich, 99%), 50 mM NaCl (Sigma-Aldrich, 99%), pH = 7.2). Deionized water was used in the studies. Stock solutions were stored at 4 °C in the refrigerator. All binding studies were performed at room temperature.

Results and Discussion
In dsDNA-FLU binding studies with electronic absorption spectroscopy, the maximum absorbance value of the FLU at 263 nm was measured. UV-Vis, IR, fluorescence and voltammetry teknikleri kullanılarak FLU’nun fsdsDNA’ya bağlanma sabitleri (K₆, K₉ ve Kᵥ) hesaplanabilmistiştir. When the binding activity of FLU to fsdsDNA was evaluated by thermal denaturation method, information was obtained about fsdsDNA binding species by looking at the calculated ΔTₘ values of FLU.

Conclusion
Interaction between FLU and fsdsDNA was studied by several techniques. From the results obtained, the binding mode of FLU with fsdsDNA was determined and it was concluded that there was one binding site per drug molecule. The binding constants were obtained from different methods that were consistent in the binding mode found. Thermodynamic calculations revealed that these binding forces were involved in interaction.

Acknowledgement
This study was supported by the Scientific Research Projects Unit of Istanbul Technical University (Project No: TGA-2017-40917).

References
3- https://en.wikipedia.org/wiki/Fludarabine
In Vitro Controlled Release of an Anticancer Drug Epirubicin from pH Sensitive Hydrogel Systems

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1 Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, 34469, Maslak, ISTANBUL
2 Eskişehir Osmangazi University, Faculty of Science and Letters, Department of Chemistry, 26480, Meşelik, ESKİŞEHİR
*E-mail: adimcilar@itu.edu.tr

Abstract
Desired and specific release profile for each drug and treatment procedure can be achieved by designing novel drug release systems. In our study, epirubicin release from hydrogels in different media was investigated by using UV-Vis Absorption spectroscopy technique. Epirubicin is a drug used as a chemotherapeutic agent for cancer treatment nowadays. For this purpose, methacrylic acid-based hydrogels were prepared and by using methylene bisacrylamide as crosslinker a known amount of epirubicin was loaded into the gel structure. The release kinetics of epirubicin was investigated in different solutions with changing pH values which represent different body fluids. Also, the swelling abilities of the gels in different media were investigated. It is found that in high pH values swelling and the drug release was considerably high compared to the acidic pH values.

Keywords: Epirubicin, controlled release, hydrogel, UV-Visible Spectroscopy

Introduction

The drug delivery systems for sustainable release of some drugs was first introduced in the year of 1952 and the interest on the topic was gradually increased within the years. The studies on the controlled drug delivery systems were aimed to control or sustain the concentration of the drug in the blood or at the targeted tissues. Each system has its own kinetics and its properties depend on some modifications such as drug under study, type of polymeric material used and the release mechanism1. Designing biopolymer assisted release systems offers many advantages such as decreasing cytotoxicity of the drugs or increasing the efficacy of the treatment.2 Epirubicin, similar like doxorubicin but less toxic, is an anthracycline structure chemotherapeutic agent used for treating cancer patients mainly breast; but also in some cases of ovarian, lung and other cancer types. The action mechanism of the drug depends on the blocking of DNA replication and the process of transcription thus specific and controllable release system can increase the efficiency of the drug.3 In the literature, there are only few studies on epirubicin release based on graphene oxide incorporated hydrogels and dual phase transition systems where each system has its own properties.4-5 Thus novel systems should be designed and optimized for better treatment and in this study the objective was to prepare a system for controllable release of epirubicin at targeted tissues in body.

Materials and Methods

Preparation of the Hydrogels
In order to prepare polymeric matrices in aqueous phase, the certain amounts of acrylic acid and the drug were dissolved in water and methylene-bis-acrylamide were mixed in water. For the polymer without drug was prepared with same procedure without addition of the drug in water. For polymerization, an initiator which was ammonium persulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) was added on to the mixture. The free radical polymerization took place and the drug-loaded gels and empty hydrogels were obtained.
In vitro Release Studies
In vitro release of the drug epirubicin from polymeric matrices were performed by taking certain amounts of hydrogels with a known amount of drug loaded. The hydrogels were then immersed in 50 mL of solutions represents each medium and the solution was stirred during the experiment. The release was monitored at room temperature by taking equal amounts of solution each certain periods of time intervals at the same time fresh buffer solution was added into the vessel and the absorbance was measured by using UV-Vis spectrometer (PG Instruments T80 + UV-Vis spectrometer) at 232 nm.

Swelling Abilities of the Gels
The different pH values directly affect the release ratio of the drug due to the pH dependence of the swelling behavior of polymeric matrices. The swelling behavior of the gels were investigated in each medium studies with gravimetric method. For this purpose, pre-weighed non-drug loaded gels were immersed in same amount of solutions used in release experiments. The swelling ratios of the gels under study were calculated for certain period of times by weighing gels after blotted with filter paper to remove the water on them with the equation given below.

\[ \text{Swelling Ratio} = \frac{W_t - W_0}{W_0} \times 100 \]

Wt is the weight of the gel at time t and W0 is the initial weight of the gel under study.

Results and Discussion
The drug release behavior of epirubicin was investigated in different solutions with changing pH values which represent different body tissues. Stimulated intestinal and gastric fluids pH of 7.4 and 1.2 respectively and phosphate buffered saline solution (PBS) represents body fluid at pH 7.4 were studied for simulating treatment procedures of EPR in different cancer types. The release profile of the drug was monitored at least for six hours. It was found that the release behaviors of the prepared gels were differed by the variation in the pH. The negatively charged units on the polymer matrix dominates the swelling of the gel in basic media which also increases the drug release from the gel structure. As a result, in high pH values, the drug release was found to be higher and faster compared to the release in SGF solution. The cumulative release of each medium was given in Figure 1. Swelling of the gels was also studied and the results were in accordance with the release results. In high pH, the hydrogels were swelled and their volumes were increased, while in low pH the swelling was very small and the swelling ratios in PBS and SIF solutions were calculated 100% and 149 % higher than in the SGF solution respectively after 24 hours and the results were given in Table 1. More controllable release profile can be obtained by changing the properties of the gel especially the amount of crosslink density. Changes in the crosslink density affect the swelling ratio.
Table 1. Swelling Ratios of the prepared gels.

<table>
<thead>
<tr>
<th>Media</th>
<th>3 hours SR%</th>
<th>24 hours SR%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS</td>
<td>130.52</td>
<td>445.24</td>
</tr>
<tr>
<td>SGF</td>
<td>23.18</td>
<td>4.46</td>
</tr>
<tr>
<td>SIF</td>
<td>111.17</td>
<td>667.78</td>
</tr>
</tbody>
</table>

### Conclusion

Preparation of novel drug release systems on widely used anticancer agent epirubicin was studied for designing new and promising curing procedure with the controllable release of the drug. After the proposed system optimized it promotes a good alternative for injectable formulations and it may reduce the risk of some undesired side effects and also it may be more effective and less toxic.

### References

OP15 - Phenolic Contents and Bioaccessibility of Some Elements in Tea (*Camellia sinensis* L.) Samples Commonly Consumed in the Turkish Market

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**Abstract.** This study evaluates the amounts of Cu, Co, Ni, Zn and the phenolic contents of black, green, and earl grey teas. Total levels of elements were determined after microwave digestion. Bioaccessibility of elements were achieved using in vitro methodologies that mimic simulated gastrointestinal conditions. Time dependent leachability of the elements into tea infusions were found using three different infusion times of 2, 5, and 10 min. Addition of lemon juice, sugar, milk, calcium, tannic acid, and citric acid to bioaccessibility was studied. Inductively coupled plasma-mass spectrometry was used for elemental determinations. Total phenolic contents were determined using the Folin–Ciocalteu assay after brewing of tea samples in two different ways. Statistical evaluations between the elemental and polyphenolic contents were surveyed. The bioaccessibility from tea samples were found to be reached to 100% at a maximum level for some samples while phenolic contents were varied depending on tea type and infusion time.

**Keywords:** Tea (*Camellia sinensis L.*), total phenol, element, consumption habit, ICP-MS

**Introduction**

Food and beverages are the main sources of trace elements in the diet, while their contents are important for risk assessment studies related with consumption. Among all beverages, tea is the most popular non-alcoholic beverage next to water and prepared from the leaves of the tea plant. When teas are brewed, elements are differentially extracted into infusions, and become a dietary source of major and minor elements. Thus, the regular consumption of tea may contribute to the daily dietary requirements of elements. Beyond their complex chemical composition, this study evaluates the total amounts and bioaccessibility of Cu, Co, Ni, Zn and the phenolic contents of black, green, and earl grey tea samples. Statistical significance between the total phenolic contents in tea brews and the bioaccessibility and/or total elemental levels were studied.

**Materials and Method**

A multi-element standard solution (Merck 110580), certified reference material (GBW07605 tea leaves), suprapure quality acids (Merck), digestive enzymes (pepsin, pancreatin, and bile extract, Sigma-Aldrich), sodium hydrogen carbonate (Carlo Erba), 0.45 µm hydrophilic polyvinylidene fluoride (PVDF) syringe filters (Milliplex-HV), and ultrapure water (18.3 MΩ.cm) were used for sample preparations. Elemental levels determined using an Elan 9000 ICP-MS (PerkinElmer Sciex). The optimum instrumental conditions were detailed elsewhere. Nine different brands of tea samples, black, black with bergamot aroma and green three of each were purchased from local markets in Bursa-Turkey. A total of 100 g samples were mixed and homogenized. Samples were digested using microwave digestion equipment (Microwave Labstation MLS 1200 mega) and infused for 2, 5, and 10 min separately in closed centrifuge tubes after filtering through PVDF filters. 5 mL of the each infusions were subjected to an enzymatic in vitro method. One of the infused samples (5 min.) were evaluated after adding lemon juice, table sugar, skimmed milk, calcium, or tannic acid for bioaccessibility. After brewing of tea samples with two different mass to water ratio and brewing time detailed in results and discussion part, total phenolic contents were determined using the modified Folin–Ciocalteu assay. The absorbance was measured at 765 nm by UV-VIS spectrophotometer and the results are expressed in mg gallic acid/100 g of sample.
The data obtained from bioaccessibility studies as well as total contents and phenolic contents were analyzed by ANOVA, using IBM SPSS Statistics for Windows (Version 22.0, IBM Corp.).

Results and Discussion

Two certified reference materials have been analyzed to confirm the accuracy of elemental determinations. Measured levels of 0.19±0.02, 20.7±0.9, 52.7±1.5, and 3.7±0.1 mg kg⁻¹ for Co, Cu, Zn, and Ni were compatible with the certified values of 0.22±0.02, 18.6±0.7, 51±2, 3.4±0.3 mg kg⁻¹ for the mentioned elements, in respectively. Bioaccessibility of the selected elements were found to be increased with increasing infusion times, in generally. This tendency could be seen among black, black with bergamot aroma (earl grey) and green tea samples. Total polyphenol contents of teas were shown in Table 1. It can be seen that polyphenolic contents were also increased depending on infusion time. But, at the 3rd min and under the used preparing conditions (1 g of sample infused in 12 mL of water during 3 min) black teas and green teas showed similar tendency in terms of polyphenolic contents. When traditional infusion type that is generally used in Turkey (16 g of sample infused in 500 mL of water during 15 min) total polyphenolic contents were decreased in the following order: green, black, earl grey.

Table 1. Total phenolic contents of teas

<table>
<thead>
<tr>
<th></th>
<th>3 MIN</th>
<th>15 MIN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BLACK</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tea-1</td>
<td>147.6±9.6</td>
<td>206.3±5.5</td>
</tr>
<tr>
<td>Tea-2</td>
<td>114.1±3.2</td>
<td>178.9±2.6</td>
</tr>
<tr>
<td>Tea-3</td>
<td>179.2±3.9</td>
<td>204.6±3.0</td>
</tr>
<tr>
<td><strong>EARL GREY</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tea-4</td>
<td>142.4±4.2</td>
<td>163.2±5.5</td>
</tr>
<tr>
<td>Tea-5</td>
<td>126.7±8.1</td>
<td>211.8±4.7</td>
</tr>
<tr>
<td>Tea-6</td>
<td>132.1±5.5</td>
<td>165.8±4.4</td>
</tr>
<tr>
<td><strong>GREEN</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tea-7</td>
<td>127.9±3.8</td>
<td>152.2±1.2</td>
</tr>
<tr>
<td>Tea-8</td>
<td>105.2±5.9</td>
<td>189.0±0.2</td>
</tr>
<tr>
<td>Tea-9</td>
<td>199.6±2.6</td>
<td>313.3±11.6</td>
</tr>
</tbody>
</table>

Conclusions

This study assess the amounts of selected elements from tea samples with their polyphenolic contents and bioaccessible levels. Although recommended dietary allowance levels could be used for risk assessment studies, the influence of the commonly used consumption habits have to be taken into account for more realistic evaluations. There is still much to learn about fractionation and speciation studies on metals and its statistical evaluations. Nevertheless, our results indicate that the contribution of studied elements from tea samples to systematic circulation will be important in healthcare as well as translational applications.

References

3- Erdemir, US, Contribution of tea (Camellia sinensis L.) to recommended daily intake of Mg, Mn, and Fe: An in vitro bioaccessibility assessment, J Food Compost Anal., 69, 71-77.


Acknowledgments
The Commission of Scientific Research Projects of Uludag University (project number F-2008/25) is also gratefully acknowledged for providing ICP-MS. The authors thank the Scientific and Technological Research Council of Turkey/Bursa Test and Analysis Laboratory (TUBITAK-BUTAL) for their technical support for total phenolic assessments.
OP16- Comparison of Multivariate Calibration Methods to Determine Tahini Adulteration

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*E-mail: ihb@hacettepe.edu.tr

Abstract—Three different multivariate calibration methods, namely partial least squares (PLS) analysis, principal component regression (PCR), and multiple linear regression (MLR) were used for analysis of data obtained from synchronous fluorescence spectroscopy (SFS). SFS data were collected at 20, 40, 60 and 80 nm wavelength intervals. Additionally, wavelength selection feature of the chemometric software was used. Developed calibration models with and without wavelength selection mode were evaluated in terms of their potential to determine the adulteration of tahini oil with sunflower oil. Root mean square error of calibration (RMSEC), root mean square error of cross validation (RMSECV) and root mean square error of prediction (RMSEP) values were compared. Limit of detection (LOD), limit of quantification (LOQ), relative standard deviation (RSD) and relative error of prediction (REP) values were calculated from calibration and prediction models.

Keywords: Synchronous fluorescence spect., chemometrics, multivariate calibration, food adulteration

Introduction

Containing high amounts of vital minerals, phytosterols, polyunsaturated fatty acids, tocopherols and lignans like sesamin, sesamolin, sesamino1 and sesamolinol, sesame oil is high-quality edible oil produced from sesame seeds (Sesamum indicum). Abovementioned compounds bring sesame oil anti-inflammatory, anti-viral, anti-fungal and antibacterial properties and provide many purposes of usage in nutraceutical, pharmaceutical and food industries1. These advantages of sesame oil make it prone to adulteration practices mainly to increase profit. Hence, development of rapid methods for determination of sesame oil adulteration is required to protect consumer rights and provide legal compliance. In the present study, usability of synchronous fluorescence spectroscopy (SFS) for this purpose was investigated. In SFS, excitation and emission wavelengths are scanned simultaneously and during this scan a constant wavelength difference is maintained between them2. Three different multivariate calibration methods namely partial least squares (PLS) analysis, principal component regression (PCR), and multiple linear regression (MLR) were applied to collected SFS data. Results of the established calibration and validation methods were evaluated based on different quality parameters such as root mean square error of calibration (RMSEC), root mean square error of cross validation (RMSECV), root mean square error of prediction (RMSEP), limit of detection (LOD), limit of quantification (LOQ), relative standard deviation (RSD) and relative error of prediction (REP) values. Effect of wavelength selection mode was also evaluated to determine the optimum range of each dataset collected at Δλ=20, 40, 60 and 80 nm wavelength intervals.

Materials and Method

Oil Samples and Oil Extraction: Sunflower oil from five different brands and tahini oil from six different brands were used. By mixing these samples in equal amounts by weight, sunflower and tahini oil blends were prepared. Adulterated tahini oil samples were prepared from 0%, 2%, 5% to 100% with 5% increments of sunflower oil. Cyclohexane (50 ml) was used to extract oil from tahini samples (150 g). Mixture of oil and hexane centrifuged at 15485 g for 15 min and finally passed through filter paper to remove impurities. Solvent was evaporated at 50°C water bath by purging with N2 gas. Obtained pure tahini oil samples were stored at room temperature in the dark until further analysis.

SFS Measurements: Varian Cary Eclipse Spectrophotometer (Agilent Technologies Inc, Santa Clara, CA) equipped with a xenon flash lamp source was used to acquire fluorescence spectra. Excitation and emission slit width was 5 and 2.5 nm. Excitation wavelength ranged between 250 and 600 nm with 1 nm increments. Wavelength interval between excitation and emission monochromators varied from 10 nm up to 370 nm with 20, 40, 60 and 80 nm interval.
Data Analysis: Multivariate analysis was performed using PLS, PCR and MLR of Stand-alone Chemometrics Software (Version Solo 6.5 for Windows 7, Eigenvector Research Inc., Wenatchee, WA). The collected data set was divided into a calibration and a validation subset. Prediction models were validated with Venetian blind cross validation. Interval size was three hundred and fifty-one in wavelength selection mode.

Results and Discussion

SF spectra of sunflower and tahini oil blend at different $\Delta \lambda$ are shown in Fig.1. The band at 348-355 nm was observed in both oil samples and assigned to the tocopherol content. The other intense band at 266-291 nm was only observed for tahini oil and assigned to phenolic compounds. In the present study, this band majorly allowed the differentiation of these two oil samples.

High dimensional data obtained from SFS was analyzed by using three different regression methods. Below, Table-1 shows the wavelength intervals recommended by the chemometric software for each $\Delta \lambda$. It can be seen that for larger $\Delta \lambda$ values, programme offers same intervals while different intervals are recommended for $\Delta \lambda=20$ nm. Out of numerous preprocessing techniques, normalization and detrend were used in the present study for all regression methods. Table-2, 3 and 4 show results for calibration and validation methods with and without wavelength selection. Quality parameters showed that in terms of REP values, PLS and PCR methods showed similar results while MLR resulted with relatively higher REP values. This results and the minimized RMSEC values could be explained by the over-fitting problem of the MLR model. Compared to PCR result, RSD values were lower for PLS calibration models. LOD values were similar for PCR and PLS models while MLR models would be insufficient to determine possible adulteration practices below 10%. With high reproducibility and low error values, PLS would be the method of choice between these three regression methods.

A generalized effect of wavelength selection mode on RMSEC, RMSECV and RMSEP values were observed in all regression methods while no recurrent effect was observed on LOD, REP and RSD values.

Conclusion

Tahini adulteration with sunflower oil was successfully determined by using SFS in the present study. Capabilities of three regression methods to determine tahini adulteration were compared. Application of wavelength selection mode affected quality parameters of regression methods in different ways.
Table 2. PLS and PLS* calibration and validation models acquired at different wavelength intervals
(Δλ=20, 40, 60 and 80 nm)

<table>
<thead>
<tr>
<th>Model</th>
<th>LOD</th>
<th>REP</th>
<th>RSD</th>
<th>RMSEC</th>
<th>RMSECV</th>
<th>RMSEP</th>
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<tr>
<td>PLSR20</td>
<td>0.86</td>
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<td>3.15</td>
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<td>PLSR20*</td>
<td>0.50</td>
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<td>6.15</td>
<td>2.67</td>
<td>2.86</td>
<td>2.71</td>
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<tr>
<td>PLSR40</td>
<td>0.63</td>
<td>20.29</td>
<td>0.87</td>
<td>0.65</td>
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<td>3.1</td>
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<td>3.02</td>
<td>1.60</td>
<td>2.13</td>
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<tr>
<td>PLSR60</td>
<td>0.34</td>
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<td>0.84</td>
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<td>PLSR60*</td>
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<td>1.81</td>
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<td>PLSR80*</td>
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<td>6.49</td>
<td>1.66</td>
<td>2.25</td>
<td>2.03</td>
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</table>

Table 3. MLR and MLR* calibration and validation models acquired at different wavelength intervals
(Δλ=20, 40, 60 and 80 nm)

<table>
<thead>
<tr>
<th>Model</th>
<th>LOD</th>
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<th>RSD</th>
<th>RMSEC</th>
<th>RMSECV</th>
<th>RMSEP</th>
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<tbody>
<tr>
<td>MLR20</td>
<td>4.61</td>
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<td>0.85</td>
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<td>MLR20*</td>
<td>2.61</td>
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<td>2.71</td>
<td>0.00</td>
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<td>MLR40</td>
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<td>1.64</td>
<td>0.00</td>
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Table 4. PCR and PCR* calibration and validation models acquired at different wavelength intervals
(Δλ=20, 40, 60 and 80 nm)

<table>
<thead>
<tr>
<th>Model</th>
<th>LOD</th>
<th>REP</th>
<th>RSD</th>
<th>RMSEC</th>
<th>RMSECV</th>
<th>RMSEP</th>
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</thead>
<tbody>
<tr>
<td>PCR20</td>
<td>0.74</td>
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<tr>
<td>PCR20*</td>
<td>2.68</td>
<td>19.00</td>
<td>7.72</td>
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<td>3.90</td>
<td>3.83</td>
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<td>PCR40</td>
<td>0.34</td>
<td>27.89</td>
<td>3.68</td>
<td>1.44</td>
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<td>3.59</td>
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<tr>
<td>PCR40*</td>
<td>0.89</td>
<td>12.93</td>
<td>6.34</td>
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<td>PCR60</td>
<td>0.28</td>
<td>16.17</td>
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<td>2.41</td>
<td>1.96</td>
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<td>PCR60*</td>
<td>2.07</td>
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<td>4.30</td>
<td>3.56</td>
<td>3.79</td>
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<td>PCR80</td>
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<td>2.28</td>
<td>2.58</td>
<td>2.39</td>
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<tr>
<td>PCR80*</td>
<td>0.82</td>
<td>17.24</td>
<td>1.53</td>
<td>3.56</td>
<td>3.69</td>
<td>3.25</td>
</tr>
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</table>

References
OP17- Determination of Honey Adulteration Based on Volatile Profile using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) with Chemometrics

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Abstract-Honey is pleasantly preferable to the consumers for several reasons. Besides to its sweet taste, flavor is one of its most significant attributes. Environmental factors, diseases and beekeeping practices led to a decrease in global honeybee populations and honey production. Current regulations declare that producers are not allowed to add other substances. However, honey adulteration is rising. In order to determine the direct adulteration of honey, traditional analysis for chemical composition and physical properties are commonly used. These analysis techniques are routinely applied into the honey trade, but they are also relatively time-consuming. Therefore, it is important to establish efficient but fast quality control and detection of adulteration techniques. Selected ion flow tube mass spectrometry (SIFT-MS) is a new technique that quantifies volatile organic compounds (VOCs) simply and rapidly. Corn syrup is one of the most used adulterants and low cost sweeteners can be added to directly adulterate the honeys. The main purpose of this study is to identify adulteration of commercially available honeys using SIFT-MS with multivariate statistical analysis.

Key words: adulteration, honey, SIFT-MS, volatile compounds

Introduction
Honey is a natural food that produced by honey bees (Apis mellifera L.) from various secretions of plants. The chemical composition and characteristics of honey based on the botanical origin of the floral source, since the carbohydrates are the major components of honey. Two sugars, dextrose and levulose, are the main ingredients of honey1. Many minor components such as other carbohydrates and proteins, enzymes, amino and organic acids, lipids, vitamins, phenolic components and minerals are also available2. Besides to its sweet taste, flavor is one of its most significant attributes. Volatile organic compounds (VOCs) in honey are attained from diverse biosynthetic pathways. Environmental factors, beekeeping practices and processing, climatic conditions of the region and storage are main factors that effecting honey aroma.

According to Codex Alimentarius3, any kind of food additives or other additives are not allow to include to honey, if honey or honey products intended to use for human consumption. Even, honey is one of the widely used sweeteners in food industry, sale price is much expensive than refined or artificial sweeteners4. Nowadays, global honeybee populations are showed a decreasing trend due to increasing environmental pollution and spread of diseases5. The inequality between increasing consumption/demand and the limited availability of high quality honey supply has concluded in increase in price, as well as made it more prone to adulteration with cheap industrial sweeteners6.

Traditional analyses are routinely applied in the honey trade but these analytical methods are relatively time-consuming and require monotonous preparation of the samples as well as complex analytical equipment. Therefore, techniques for efficient quality control and detection of adulteration are of great importance to establish quality and safety. Selected ion flow tube mass spectrometry (SIFT-MS) is a new technique that quantifies volatile organic compounds (VOCs) simply and rapidly even in low concentrations (ppt) in short time. Corn syrup is one of the most used adulterants, which can be added to directly adulterate the honeys. The aim of this study is to identify targeted corn syrup adulteration of commercially available honeys using SIFT-MS with multivariate statistical analysis.

Materials and Methods
Pure honey and corn syrup (CS) were purchased from a local market in Columbus, OH. Adulterated samples were prepared by mixing CS with pure honey at different concentrations (1, 2.5, 5, 10 %). Pure and adulterated honeys were placed in an oven at 45°C to achieve better mixing. 24 adulterated samples were prepared in three batches (A, B, C).
Honey samples (10.02±0.2 g) were transferred into a 500 mL Pyrex bottle and capped with open top caps coupled to polytetrafluoroethylene (PTFE)-faced silicone septa. The samples were held in a temperature-controlled water bath (Precision, Jouan Inc., Winchester, V.I., U.S.A.) at 55°C for 60 min to allow equilibration of the volatiles which released from the samples into the headspace. A selected ion flow tube mass spectrometer (SIFT-MS, V200 Syft Technologies, Christchurch, New Zealand) was used to measure and quantify the volatile compounds in the headspace. The analysis was done using selected ion mode (SIM) and the concentrations of volatile compounds were calculated from their reactions with H2O+, NO+, or O2+ with known kinetic parameters. The scan duration was 2 min. Concentrations were measured in μg/kg in the headspace above the honey sample.

Multivariate statistical analysis provided by Soft independent modeling of class analogy (SIMCA) with Pirouette software for Windows Comprehensive Chemometrics Modeling, version 4.0 (Infometrix Inc., Bothell, Wash., U.S.A.) to identify distributions of volatiles in honey samples.

**Results and Discussion**

Based on the average concentration of measured volatile compounds (Table 1) multivariate statistical analysis was computed and the differences were determined between honey and corn syrup (Fig 1-A) or pure and adulterated honeys (Fig 1-B, C, D).

### Table 1. Selected volatile organic compounds to determine honey aroma

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Conc.(ppb) (min-max)</th>
<th>Compounds</th>
<th>Conc.(ppb) (min-max)</th>
<th>Compounds</th>
<th>Conc.(ppb) (min-max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E)-2-hexenal</td>
<td>3.20-15.32</td>
<td>chloroform</td>
<td>54.81-153.07</td>
<td>lemonol</td>
<td>0.95-8.84</td>
</tr>
<tr>
<td>(E)-2-methyl-2-butenal</td>
<td>1.31-35.11</td>
<td>cis-6-nonen-1-ol</td>
<td>6.35-15.01</td>
<td>lilac alcohol</td>
<td>3.75-9.25</td>
</tr>
<tr>
<td>(Z)-3-hexen-1-ol</td>
<td>1.97-14.66</td>
<td>coumarin</td>
<td>2.72-12.50</td>
<td>lilac aldehyde</td>
<td>1.72-18.76</td>
</tr>
<tr>
<td>1.3-butadienide</td>
<td>29.99-71.15</td>
<td>damascenone</td>
<td>2.82-8.26</td>
<td>maltol</td>
<td>14.80-59.36</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>3.82-7.29</td>
<td>decanal</td>
<td>2.30-8.98</td>
<td>menthol</td>
<td>5.29-18.62</td>
</tr>
<tr>
<td>1-octen-3-ol</td>
<td>7.53-39.09</td>
<td>dimethyl disulfide</td>
<td>1.47-10.02</td>
<td>methanol</td>
<td>90.81-2960.29</td>
</tr>
<tr>
<td>1-p-methen-9-ol</td>
<td>4.41-91.67</td>
<td>dimethyl sulfide</td>
<td>13.06-91.43</td>
<td>methyl anthranilate</td>
<td>0.58-3.74</td>
</tr>
<tr>
<td>2,3-butanedione</td>
<td>10.63-54.15</td>
<td>dimethyl trisulfide</td>
<td>26.92-69.00</td>
<td>nerolidol oxide</td>
<td>0.41-2.51</td>
</tr>
<tr>
<td>2-aminoacetophenone</td>
<td>0.62-22.34</td>
<td>dodecane</td>
<td>7.12-50.85</td>
<td>nerolidol</td>
<td>0.38-1.76</td>
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<tr>
<td>2-butanol</td>
<td>78.57-199.12</td>
<td>ethanol</td>
<td>363.66-14264.58</td>
<td>nonanal</td>
<td>14.51-73.89</td>
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<tr>
<td>2-cyclopenten-1,4-dione</td>
<td>15.70-181.81</td>
<td>ethyl acetate</td>
<td>21.42-189.94</td>
<td>nonane</td>
<td>10.54-25.89</td>
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<td>2-heptanol</td>
<td>3.58-7.75</td>
<td>ethyl benzoate</td>
<td>5.56-25.10</td>
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<td>10.46-20.92</td>
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<tr>
<td>2-hydroxyacetophenone</td>
<td>1.35-6.90</td>
<td>furfural</td>
<td>20.09-114.60</td>
<td>octanal</td>
<td>7.61-24.65</td>
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<td>2-phenethylalcohol</td>
<td>3.60-25.77</td>
<td>guaiacol</td>
<td>1.99-6.35</td>
<td>octanoic acid</td>
<td>10.48-20.92</td>
</tr>
<tr>
<td>3-methylbutanai</td>
<td>8.35-86.40</td>
<td>heptanal</td>
<td>5.90-16.22</td>
<td>p-cresol</td>
<td>1.04-4.93</td>
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<tr>
<td>4-methoxybenzaldehyde</td>
<td>1.34-6.84</td>
<td>heptane</td>
<td>37.20-73.12</td>
<td>p-isopropenyl tolueno</td>
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<tr>
<td>acetic acid</td>
<td>46.38-517.07</td>
<td>hexanal</td>
<td>9.04-19.41</td>
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<td>1.76-12.02</td>
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<td>acetoin</td>
<td>16.20-143.60</td>
<td>hexane</td>
<td>50.27-260.75</td>
<td>phenylacetaldehyde</td>
<td>9.11-54.86</td>
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<tr>
<td>acetic acid</td>
<td>38.93-259.64</td>
<td>hexanoic acid</td>
<td>18.26-36.41</td>
<td>phytic acid</td>
<td>0.86-5.55</td>
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<td>alpha-pinene</td>
<td>1.91-9.74</td>
<td>hotrienol</td>
<td>4.93-10.81</td>
<td>propanoic acid</td>
<td>17.21-65.05</td>
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<tr>
<td>benzaldehyde</td>
<td>9.33-55.85</td>
<td>hydroxymethylfurfural</td>
<td>17.34-41.18</td>
<td>propyl anisol</td>
<td>1.33-9.91</td>
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<td>benzyl alcohol</td>
<td>2.96-19.06</td>
<td>isoaamyl alcohol</td>
<td>18.53-123.59</td>
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<tr>
<td>beta-pinene</td>
<td>1.81-9.23</td>
<td>isobutyl alcohol</td>
<td>6.48-23.83</td>
<td>toluene</td>
<td>2.38-15.10</td>
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<td>butanoic acid</td>
<td>35.38-158.24</td>
<td>isopropyl benzene</td>
<td>18.98-72.62</td>
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Honey is a complex food material, and the adulterants may have similar chemical composition with the honey samples. For this reason, the differentiation of the adulterant (corn syrup) can be analyzed using chemometrics (Fig 1-A). Interclass distances (ICDs) of >3 indicates that samples are significantly different from each other. In this study the ICD between the corn syrup and the honey samples was 6.8, which indicates a significant difference among the groups (honey and corn syrup).

Adulterated honey exhibited a clear distinction compared to pure honey (Fig 1-B, C, D). Ethanol and methanol were one of the main differences between the pure honeys and the adulterant (corn syrup). Also, isobutyl alcohol, 2,3-butanedione, and dimethyl sulfide were some of the other
volatile compounds that causes the separation between pure honeys and the adulterant. The ICD between honey samples and the adulterant were 6.1 (Class B), 3.2 (Class C), 11.6 (Class D). Even though it was quite difficult to determine the exact amount of the adulteration agent added to the authentic sample based on volatile composition, with increasing amount of adulterant the ICD between classes were increased.

**Figure 1.** SIMCA 3D projection plots of data collected by SIFT-MS. For SIMCA plots, boundaries marked around the sample clusters represent a 95% confidence interval for each class. (A) Corn syrup and honey (B, C, D) Pure honey and adulterated honey

**Conclusion**

Our data supports the application of SIFT-MS for assessing corn syrup adulteration in honey samples based on their volatile profile. Ethanol and methanol were the main differences in volatile profile between the pure honeys and the samples were adulterated with corn syrup, besides isobuthyl alcohol, 2,3-butanedione, and dimethyl sulfide had effects on the composition differences. According to the results of study, SIFT-MS can be used as a valuable and a non-destructive quality control technique for commercial honeys along with savings in manpower and time.

**References**


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Determination of aflatoxin by HPLC in nuts and spices after post-column iodine derivatization

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Abstract-A method based on the use of immune affinity clean-up procedure for sample preparation before HPLC coupled with a post-column iodine derivatization and fluorescence detection was employed for the quantifications of the aflatoxin (AF): B1, B2, G1 and G2 in hazelnut, pistachio and spices collected from Diyarbakır, Turkey. Detection limits (LOD) of AFs were found to be 0.024, 0.06, 0.018 and 0.015 ng mL⁻¹ respectively for AFG1, AFG2, AFB1 and AFB2, and quantification limits (LOQ) were found to be 0.08, 0.02, 0.06 and 0.05 ng mL⁻¹. The recovery values were determined in the range of 92% - 98% for AF (B1, B2, G1 and G2). The results show that one of the red chilli pepper sample exceeds the maximum AF level determined by FAO/WHO Codex and Turkish Food Codex Regulation.

Keywords: Aflatoxin, Post Column Iodine Derivatization; HPLC

Introduction
Aflatoxins (B1, B2, G1 and G2) are secondary metabolites produced by members of the Aspergillus section flavi such as Aspergillus flavus, Aspergillus parasiticus, and Aspergillus nomius. Among 20 types of AFs only (AFB1), (AFB2), (AFG1) and (AFG2) play a vital role in divers foods and feeds. When feed products are contaminated with mycotoxins, there might be a health hazard for human and animals. AFB1 is categorized as a group 1 carcinogen, mainly affecting the liver. Numerous agricultural products such as peanut, corn, cottonseed, pistachio nut, fig, spices and copra may be contaminated with AFs. AFB1, AFB2, AFG1 and AFG2 are also classified as possible carcinogen to humans. In the last decade, studies focusing on AF contamination in foodstuffs, mainly cereals, nuts, and spices, have been reported from many countries, especially those in Asia and Africa. Based on FAO/WHO Codex (2001) food is not permitted to exceed 15 ng g⁻¹ of total AFs. Many countries regulate AF levels in their foods, to lower than 20 ppb in USA and EU (Europe Union) and 10 ppb in Korea and Japan. According to European Commission Regulation 1881/2006 peanut and dried figs are not permitted to exceed 2.0 ng g⁻¹ for AFB1 and 4.0 ng g⁻¹ for total AFs. Turkey is one of the major grain and spices producing countries in the world. Red ground pepper, the dried form of Capsicum annuum L. occupies a prominent place among the spices in Turkey consumed by the majority of people. The average daily consumption of grains and spices products by an average Turkish person is about two times as high as most western countries. For the analysis of AF, very sensitive and reliable analytical techniques have been developed, many of which based on solid phase extraction (SPE) or immune affinity chromatography in combination with reversed-phase HPLC and fluorescence detection with or without derivatisation. Therefore, this study has been undertaken to determine AFB1, AFB2, AFG1, and AFG2 levels in order to give insight on AF levels in some grain and spices, consumed in SE Anatolia of Turkey. Structures of some molecules of AF are given as follows.

Materials and methods
The approximately 25 g of dried and ground samples were weighed and placed into to the 250 mL flask. 5.0 g solid NaCl and 125 mL of mixture of methanol-water (v:v; 70:30) was added on the samples and stirred intensively by hand for 15-30 s and then for 30 min. at 500 rpm mixer (Ultra Turax T18 Basic). The mixture was filtered by using a filter paper (Whatman, 24 cm, Cat No: 1202240). Then, 15 mL of the filtered sample was added to 30 mL of water. This analysis
was performed with a Lab. Alliance HPLC system equipped with a Shimadzu RF-10A fluorescence detector at wavelengths of 365 and 430 nm for excitation and emission, respectively. The derivatization process of AFs, Lab. Alliance (Post Column Reactor) after column derivatization system was used and then an active agent for derivatising, iodine solution (100 mg L\(^{-1}\); dissolve 100 mg iodine in 2 mL methanol and completed with 1.0 L water), flow rate of 0.3 mL min\(^{-1}\) to be adjusted. Depending on the time of peaks, each analysis completed approximately 10 min.

**Results and Discussion**

In this study, a total of hazelnut, pistachio and 4 type spices samples collected from Diyarbakir local markets and bazaar were analyzed for the levels of AFB1, AFB2, AFG1, and AFG2 with an on-line immuno affinity chromatographic clean-up procedure by HPLC method (Table 1).

The recovery, LOD and LOQ were determined using AF standard solution based on a signal-to-noise ratio of 3:1 for LOD and 10:1 for LOQ. The detection limits (LOD) for analysis of the AF content were 0.024, 0.06, 0.018 and 0.015 ng mL\(^{-1}\) for AFG1, AFG2, AFB1, AFB2 and quantification limits (LOQ) for them were found as 0.08, 0.02, 0.06 as 0.05 ng mL\(^{-1}\). HPLC chromatograms of AF standard solutions for AFG2, AFG1, AFB2, AFB1 samples have well-separated peaks. The concentrations of AFs in the samples were calculated by using the calibration curves of peak area prepared for each AF standards separately. The obtained linearity showed correlation coefficients better than 0.998 for all AFs. Accuracy of the method was investigated by addition of the certified standard solutions of AFs (Mycotoxin Mix.) on the red chilli pepper, pistachio and hazelnut. The mean recoveries of AFs for AFB1, AFB2, AFG1 and AFG2 were found to be between 90% - 98%, respectively (Table 1). The results show that the recoveries of AF concentrations were within the satisfactory range, which indicates that the in-line IAC procedure is effective to use in the determination of AFs in food. The recoveries obtained for AFs in food were acceptable as set by European Regulation 401/2006 for AF determination methods. The results of an inter-laboratory study of AFB1 and total AF using off-line IAC, as organized by the European Communities, Standard Measurement and Testing Program in accordance with ISO 5725-2 (EU, 2007), exhibited recoveries of 90-109% of AFB1 and 81-92% of total AFs, 86% of AFB1 and 71-74% for total AFs for paprika powder, indicating that in-line IAC has a similar performance to off-line IAC. This fact revealed that the in-line IAC/HPLC used in this study was very specific to AFB1, AFB2, AFG1 and AFG2. The in-line immunoaffinity cleanup procedure provides clean chromatograms without any interference from other compounds. Furthermore, it leads to rapid, accurate and precise results.

As shown in Table 2, 6 AF samples were only found to be at a detectable level, while the other samples were found to be at an indetectable level. The results of this study demonstrate that the concentrations of AFB1 levels in only red chilli pepper samples were found to be higher than the legal limits of Turkish Food Codex (2002) and Commission Regulation (EC) (2002)\(^5\) (>5 μg kg\(^{-1}\)). Again, the results of this study revealed that AFB1 percentages of red chilli pepper samples were higher than the results in several other studies carried out in Turkey. In the perspective of the study, detection of AFB1 in powdered red pepper has shown that there is not enough precaution on production, transport, harvest, and storage of red pepper. Thus, one can conclude that the reason for high levels of AFB1 is a result of lying red peppers on soil and asphalt for

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Table 1. Accuracy assessment of analysis AFB1, AFB2, AFG1, AFG2 and AF standard solution

<table>
<thead>
<tr>
<th>Samples</th>
<th>AF standard, ng mL(^{-1})</th>
<th>Founded, ng mL(^{-1})</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>0.5</td>
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</table>


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drying, storage of the red peppers under relatively low humidity levels, and insufficient control of transport and shop conditions. The presence of AFB1 may give rise to high risks to human health because of their carcinogenic, mutagenic and teratogenic effects. As Turkey is one of the leading producer countries of red pepper, more precaution should be taken on hygiene controls in order to prevent microbiological and chemical hazards. Since red pepper is being used in most of traditional foods in Turkey, further studies should be conducted on the occurrence of AFB1 in traditional foods.

Table 2. Analysis of AF(B1,B2,G1,G2) with HPLC of spice and grain samples

<table>
<thead>
<tr>
<th>Spice samples</th>
<th>Source</th>
<th>Analysis of the AF (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>B1</td>
</tr>
<tr>
<td>Red chilli pepper</td>
<td>Bazaar</td>
<td>5.61 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>Market</td>
<td>4.32 ± 0.06</td>
</tr>
<tr>
<td>Black chilli pepper</td>
<td>Bazaar</td>
<td>2.13 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Market</td>
<td>1.58 ± 0.02</td>
</tr>
<tr>
<td>Dust red pepper</td>
<td>Bazaar</td>
<td>1.85 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Market</td>
<td>0.96 ± 0.06</td>
</tr>
<tr>
<td>Black pepper</td>
<td>Bazaar</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Market</td>
<td>ND</td>
</tr>
<tr>
<td>Pistachio</td>
<td>Bazaar</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Market</td>
<td>ND</td>
</tr>
<tr>
<td>Hazelnut</td>
<td>Bazaar</td>
<td>4.1 ± 0.066</td>
</tr>
<tr>
<td></td>
<td>Market</td>
<td>1.8 ± 0.025</td>
</tr>
</tbody>
</table>

Conclusion
This study demonstrates that in-line IAC has a similar performance to off-line IAC, which revealed that the in-line IAC/HPLC employed in this study was very specific to AFB1, AFB2, AFG1 and AFG2. The in-line immunoaffinity clean up procedure provides clean chromatograms without any interference from other compounds. Furthermore, it leads to rapid, accurate and precise results.

References
OP19- The Performance Of Poly(Guanine) Modified Carbon Paste Electrode In Anionic Surfactant Media For Enhancing The Determination Of Codeine

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Abstract: In this study, the preparation of a carbon paste electrode modified with poly(guanine) as well as its novel application for the electrochemical oxidation and voltammetric determination of codeine are described. Using square-wave voltammetry, the compound yielded a well-defined voltammetric response in phosphate buffer (pH 4.0) containing $5\times10^{-4}$ M anionic surfactant (sodium dodecylsulfate, SDS) at +1.13 V (vs. Ag/AgCl). The process could be used to determine codeine in the concentration range from $2\times10^{-7}$ to $3\times10^{-6}$ M, with a detection limit of $1.3\times10^{-8}$ M. The suggested method was applied to pharmaceuticals.

Keywords: Codeine, Electrooxidation, Poly(guanine) modified carbon paste electrode, Sodium dodecyl sulphate, Pharmaceuticals

Introduction: Guanine, one of the four bases in nucleic acids, is a fundamental compound in biological systems and plays an important role in the storage of genetic information and protein biosynthesis. Although several analytical methods have been proposed in the literature for the determination of guanine, little attention has been paid to its usage to construct electrochemical sensor1,2. Keeping the above knowledge in mind, in the present study, a novel poly(guanine) (PGA) polymer film modified carbon paste electrode (CPE) was fabricated and used in surfactant media to get the synergetic effect for the sensitive voltammetric determination of codeine (3-methylmorphine), an analgesic and an antitussive agent belonging to the family of opiates naturally found in the poppy plant, which can also cause drug addiction and mental damage if abused and then may give rise to social problems.

Materials and Method: Standard stock solutions of codeine HCl ($1\times10^{-2}$ M) were prepared daily in water and kept refrigerated when not in use. Britton–Robinson (BR) and phosphate buffer solutions (pH 2.0-10.0) were used for preparing more diluted solutions of codeine. All electrochemical experiments including cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed using an Autolab PGSTAT 128N potentiostat (EcoChemie, The Netherlands) driven by a GPES software version 4.9 (EcoChemie) in connection with a personal computer. Measurements were carried out using bare or modified CPE, a platinum wire auxiliary electrode, and an Ag/AgCl (3 M NaCl, Model RE-1, BAS) as reference, in a 10 mL one-compartment electrochemical cell, at a laboratory temperature.

For the fabrication of the modified electrode, the bare CPE was subjected to electropolimerization of guanine monomer by cyclic scanning of potential for ten times from ‒0.2 to +1.4 V at a scan rate 100 mVs$^{-1}$ in phosphate buffer (pH 10.0) containing $5\times10^{-4}$ M guanine. The obtained electrode was noted as PDA/CPE.

Results and Discussion: In order to understand the oxidative pathways of codeine, a detailed voltammetric study was carried out over the pH interval 2.0 to 10.0 at bare and modified CPE using CV and SWV. The results obtained showed that the anodic oxidation of codeine follows a very complex mechanism that is pH dependent. The sensitivity of the voltammetric measurements was significantly increased at PDA/CPE in comparison to CPE. Besides, a further increase in the detecting sensitivity of codeine could be obtained in the presence of anionic surfactant, SDS (Fig.1). After the optimization of experimental and instrumental parameters, SWV curve at +1.13 V (vs. Ag/AgCl) for codeine in phosphate buffer equal to pH 4.0 in the presence of $5\times10^{-4}$ M SDS was carried out by adding successive aliquots of codeine concentrations ranging from $2\times10^{-7}$ M to $3\times10^{-6}$ M. From the data obtained by the analytical curves, the limit of detection (LOD) and limit of quantification (LOQ) values were found as $1.3\times10^{-8}$ M (0.4 ng mL$^{-1}$) and $4.2\times10^{-8}$ M, respectively.
Next, to validate the practical applicability of the above-described methodology, the analysis of commercial tablet form containing codeine, paracetamol and caffeine was carried out. The results of the analysis of pharmaceutical product indicated that the PGA/CPE is highly selective towards codeine.

**Conclusion:** In addition to the practical application of the proposed method, the data based on PGA film-surfactant interaction obtained in the present study may be useful for *in-vivo* and *in-vitro* investigations in biomedical applications for future studies.

**References:**
OP20- Comparison of Corrosion Behaviors of Bare Ti and TiO\textsubscript{2}

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Abstract
In this study, titanium (Ti) surface was anodized by applying 60 volts for two hours to form titanium dioxide (TiO\textsubscript{2}) with anodization method. After anodization procedure, comparison of corrosion behaviors of the bare titanium and TiO\textsubscript{2} coated titanium was studied in 1 M KOH solution by using electrochemical methods such as anodic and cathodic current-potential curves and electrochemical impedance spectroscopy (EIS). According to obtained results, Ti surface was smooth and compact. However, surface structure of TiO\textsubscript{2} coated titanium was porous and nanotubes formed on the surface. This porous structure which has protective layer contributed to increase the corrosion resistance. Higher polarization resistance was obtained on porous TiO\textsubscript{2} than that of bare titanium. Besides, this protective layer bore good against the alkaline corrosion during long-term immersion.

Keywords: Corrosion, titanium, alkaline solution

1. Introduction
Titanium is widely used in many applications, from chemical industry to medical application due to its excellent corrosion resistance which is explained to the thin, stable and protective layer that forms spontaneously on its surface when expose to the natural environment\textsuperscript{1}. Its other important properties are good mechanical strength and high biocompatibility. Recently, many researchers have been investigating the optimization of Ti surface, particularly increasing the thickness of the oxide layer and modifying the surface morphology and crystal structure by using different methods to improve its corrosion resistance and to change chemical structure. Anodic oxidation method is one of the most used methods to build anodic films which are long, homogeneous, good electrical properties and porous at high voltages. This protective layer obtained by using anodic oxidation method prevents rapid dissolution of the underlying metal. Although there are much information of anodic oxidation of metals, less attention is available about corrosion of Ti metal or TiO\textsubscript{2} in strong alkaline solution. For this purpose, in this study, corrosion behaviors of bare Ti and TiO\textsubscript{2} obtained by using anodization method at high voltage were compared a series of electrochemical techniques in alkaline solution.

Ti disc (grade 2) which is surface area of 0.283 cm\textsuperscript{2} is used as a working electrode. Before the anodization procedure, Ti surface was polished with using emery paper. Polished Ti surface was modified by using anodization solution at constant potential of 60 V for 2 h. Anodization solution consists of 0.5 g NH\textsubscript{4}F, 2% (vol.) H\textsubscript{2}O and ethylene glycol rest. After anodic oxidation, Ti electrode with oxide layer was immersed in 1 M KOH solution for electrochemical measurements. Same experiments were done for bare Ti. Three electrode set-up was used for electrochemical measurements which contain Pt and Ag/AgCl as counter and reference electrodes, respectively. Anodic and cathodic current-potential curves were obtained separately after one hour immersion. Polarization resistances of electrodes were determined with EIS method after one hour and long-term immersions (30 days). Nyquist diagrams obtained from EIS were fitted by using Zview software.

3. Results and Discussion
Anodic(a) and cathodic(b) current-potential curves of bare Ti and anodized Ti electrode were given in Fig. 1. In the cathodic branch, only hydrogen evolution is seen on both electrodes. When Ti surface is modified with TiO\textsubscript{2}, open circuit potential shifted more positive values and higher hydrogen evolution current density is obtained. According to anodic branch, same behaviors are seen for both electrodes. TiO\textsubscript{2} formed naturally on bare Ti dissolved initial stage for bare Ti, after that, anodic current was constant until -0.584 V (Ag/AgCl). Very protective TiO\textsubscript{2} layer formed between these potentials\textsuperscript{2,3}. When compared with anodized Ti (TiO\textsubscript{2}), anodized Ti reduced the anodic current values. This reducing can be explained with existence of protective TiO\textsubscript{2} layer.
This protective oxide layer prevented the Ti surface against attacking of the corrosive alkaline solution. Nyquist diagrams and fitting parameters of bare Ti and anodized Ti are given in Fig. 1c and Table 1. Two time constant were obtained on bare Ti and anodized Ti after one hour immersion. Higher polarization resistance ($R_p$) which is nearly twofold was obtained on anodized Ti electrode. This high $R_p$ value proved the existence of the protective passive layer on Ti.

![Graphs showing current-potential curves and Nyquist diagrams](image)

Fig. 1. Anodic (a) and cathodic (b) current-potential curves and Nyquist diagrams (c) of bare Ti (●) and anodized Ti (□) in 1 M KOH solution.

Fig. 2 shows the Nyquist diagrams obtained different immersion time of bare Ti (a) and anodized Ti (b) in 1 M KOH solution. Suggested electrical circuits and fit parameters were given in the same figures as the insets and Table 1, respectively. Since anodized Ti had more porous structure than bare Ti, parallel connected electrical circuit was used\(^4\). It is seen from Table 1, $R_p$ of bare Ti reduced with increasing immersion time according to 2.day, however $R_p$ values of anodized Ti increased and decreased and then increased at 30.day due to protective passive layer. Here, CPE corresponds to constant phase element, $n$ is phase shift.

![Graphs showing Nyquist diagrams](image)

Fig. 2. Nyquist diagrams obtained 2(●), 12(△), 22(■) and 30(○) days immersion time of bare Ti (a) and 2(△), 12(●), 22(■) and 30(○) days immersion time of anodized Ti (b) in 1 M KOH solution. Suggested electrical circuits were given as the insets.
Table 1. Fit parameters determined from EIS

<table>
<thead>
<tr>
<th>Immersion time</th>
<th>Ti</th>
<th>Anodized Ti (TiO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R_p (Ω)</td>
<td>CPE1 (F cm⁻² x 10⁻⁵)</td>
</tr>
<tr>
<td>1. hour</td>
<td>36942</td>
<td>26.15</td>
</tr>
<tr>
<td>2. day</td>
<td>343991</td>
<td>18.23</td>
</tr>
<tr>
<td>12. day</td>
<td>203332</td>
<td>19.29</td>
</tr>
<tr>
<td>22. day</td>
<td>214704</td>
<td>20.64</td>
</tr>
<tr>
<td>30. day</td>
<td>263924</td>
<td>20.71</td>
</tr>
</tbody>
</table>

4. Conclusions

Naturally formed TiO₂ on Ti electrode can prevent the metal against the alkaline corrosion, but this thin layer dissolved in strong alkaline solution. Anodized Ti improved the polarization resistance of bare Ti due to existence of porous and protective TiO₂ layer in strong alkaline solution. This passive layer should be used in industrial applications to prevent bare Ti against corrosion.

References
OP21: Voltammetric Determination of Quercetin in Tea Samples

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Abstract: In this work, voltammetric determination of quercetine (QR) in tea samples was performed at glassy carbon electrode (GCE). Quercetin is one of the flavonoids naturally found in plant extracts. Due to the electroactivity of QR, electrochemical methods were used with great success in the determination of QR. The electrochemical behavior of QR was investigated. Quantitative amounts of QR in water and methanol extracts of green and black tea were determined at GCE in phosphate buffer solution at pH 5.0 by using square wave voltammetry (SWV), which were found to be 116.4 and 116.3 µg QR equivalent/g dry green tea and 27.5 and 26.1 µg QR equivalent/g dry black tea. The LOD and LOQ values for QR at the 0.01 - 100 µM concentration range were 7.7 nA and 25.6 nA, respectively. Very low amounts of QR were successfully determined by SWV technique with sensitively, selectively and effectively.

Keywords: Quercetin, voltammetry, glassy carbon electrode.

Introduction
Quercetin (2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxychromen-4-one) is one of the flavonoids naturally found in plant extracts. Quercetin is abundant in foods such as apples, fruits, grapes, blueberries, blueberries, blueberries, black plums, capers, red onions, Brassica vegetables, shallot, tomatoes, radicchio, cabbage, sweet potatoes, floods, tea, sorrel, radishes, dill, coriander, fennel, watercress, seeds and nuts. Quercetin is a biologically active substance with antioxidant, antibacterial, anti-inflammatory and antitumor properties and prevents cancer, heart and age related diseases. In addition, the cell acts as an anti-mutagen to reduce oxidative damage, and also protects human colonocyte DNA from in vitro oxidative attack. Besides, QR provides the ability to protect against cancer by clearing free radicals. Eventually, the determination of QR in food and medicinal plants is of great importance in the biological, pharmacological and life sciences fields. Due to the electroactivity of QR, electrochemical method was chosen in the determination of QR. In this study, it is aimed to determine the amount of QR in teas used in daily life by voltammetric techniques. Very low detection limit which couldn’t be obtained even at the modified electrodes used in the literature had been reached, was achieved by SWV at bare GCE.

Materials and Method
Reagents and apparatus
All chemicals used were analytical purity and were purchased from Merck or Sigma. Quercetin stock solution was dissolved in methanol and prepared in pH 5.0 PBS. All voltammetric determinations were performed on an electrochemical analyzer, Gamry Interface 1010B (Gamry, USA). The electrochemical performance was measured with a three-electrode system (BASi C3 Cell Stand) consisting of a silver-chloride reference electrode, a platinum wire auxiliary electrode and a GCE as the working electrode. The GCEs were cleaned mechanically and electrochemically as described in our previous works before they were used. During all experimental studies, nitrogen gas was passed through the solution for 5 min before the voltammetric measurements were performed.

Preparation of tea extracts
The analyzed tea samples were green tea (Lipton Green Tea) and black tea (Lipton Yellow Label), each one at nearly 1.5 g. During the preparation of tea infusions, 1 g of tea leaves was sonicated for 20 min into 10 mL freshly boiled water. In addition, while preparing methanol extracts, 10 mL of methanol was added to 1 g of tea leaves and then kept in an ultrasonic bath for 30 min. After cooling, the extracts were filtered. Then, 1 mL of these extracts were taken up to 10 mL with PBS (pH 5.0). Finally, QR in tea extracts were determined by SWV and the concentrations of QR were calculated from the calibration graph. Calibration equations were obtained from concentrations of QR versus oxidation peak currents.
Results and Discussion

The electrochemical characterization of QR was performed by cyclic voltammetry technique at GCE in PBS pH 5.0 and the scan rate was applied at 50 mV s\(^{-1}\). And, a reduction peak was observed at nearly 500 mV for QR at GCE by CV. Quercetin showed an irreversible character at GCE. In addition, differential pulse voltammetry (DPV) and SWV methods were applied to the voltammetric determination of QR.

In order to obtain the maximum response of the QR, the solution medium effect was investigated and for this, various electrolyte solutions were used as well as different pHs of PBS. The electrolyte effect was studied by DPV at GCE. Firstly, the electrolyte type was tested, and DPV measurements were taken in electrolyte solutions of 0.1 M NaCl, KCl, LiClO\(_4\), NaClO\(_4\), NaNO\(_3\), Na\(_2\)SO\(_4\) and PBS at pH 7.4. The highest peak current was obtained in 0.1 M NaCl. However, it was also studied at different pHs of PBS to make more accurate decisions. As shown in Fig. 1, the highest peak current was obtained at pH 5.0. Therefore, pH 5.0 was used as electrolyte solution in the following studies.

**Fig. 1.** pH effects of PBS on QR response at GCE by DPV.

SWV was adopted in order to enhance the sensitivity of GCE. In the absence of QR, the bare GCE was not produce any peak, while in the presence of QR, an observable peak was detected at nearly 350 mV. The peak currents increased in direct proportion to an increase in QR concentration from 0.01 µM to 84.19 µM. The peak currents had a linear relationship with the concentrations having excellent correlation coefficients (Fig. 2). The LOD was calculated as 0.0077 µM (S/N = 3).

In order to evaluate the presence of QR in tea samples, SWV technique was used to determine the QR concentrations in tea samples. The results are listed in Table 1.

Conclusion

The proposed method demonstrates the successful application of GCE for the determination of QR in real samples with excellent sensitivity (0.0085 µA/µM), LOD (7.7 nM) and selectivity. The obtained results at GCE was more sensitive than the previously reported methods.
Fig. 2. SWVs obtained increases the concentrations of QR in 0.1M PBS (pH 5.0) at GCE. The insets corresponding calibration plot of QR.

Table 1. Determination of QR in tea extracts at GCE by SWV (n = 3).

<table>
<thead>
<tr>
<th>Tea</th>
<th>Metanol Extract (µg/g)</th>
<th>Water Infusion (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>27.45 ± 0.25</td>
<td>26.10 ± 0.30</td>
</tr>
<tr>
<td>Green</td>
<td>116.36 ± 1.14</td>
<td>116.28 ± 0.74</td>
</tr>
</tbody>
</table>

References

OP22- Is It Possible To Use Pooled Plasma Samples For Large-Scale Human Metabolomic Studies? A Comparison Of The Metabolite Profiles Of Pooled Plasma Samples With Random Individual Samples Using Q-TOF LC/MS

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Abstract: Clinical metabolomic studies are primary focuses on finding biomarkers in disease conditions. Metabolome is in a dynamic range due to the fact that the environmental conditions like lifestyle, diet, drugs and even stress could affect the metabolism in a system of a body. In this situation, it is hard to define a global metabolite profile for a “healthy person”. Therefore, metabolite profiling studies for clinical biomarker discoveries are to find the differences of the concentration of metabolites in just the disease conditions but not the other conditions. Thus, the findings indicate the potential biomarkers in the disease conditions. If the number of samples are relatively high, using pooled samples is a good choice but it is suspicious whether the pooled samples represent the whole data, or not. In this study, it was compared the metabolite profiles of pooled plasma samples with random individual samples in a disease condition and a statistical evaluation was performed to understand the reliability of using pooled samples for patients and healthy subjects in clinical metabolomic studies.

Keywords: metabolomics, Q-TOF LC/MS, pooled plasma samples, biostatistics, metabolite profiling

Introduction
Metabolomics is the large-scale study of small molecules, commonly known as metabolites, within cells, biofluids, tissues or organisms. Collectively, these small molecules and their interactions within a biological system are known as the metabolome. In recent years, metabolomic has gained importance in support of post genomic studies especially in health field applications. At the moment when personalized medicinal applications are rapidly spreading, biomarkers determined for diseases have been taken into consideration at the metabolomic level, and important steps have been taken in the examination of the diagnosis, treatment and treatment response of diseases (1, 2). Metabolomic studies have become accessible and feasible through the development of advanced analytical techniques and data processing techniques (3). Nowadays the reproducibility and accuracy of the devices increases, and the quantities of metabolites belonging to different samples can now be compared with high accuracy within different groups in the semi-quantitative level. However, the variation from the samples itself and sample preparation technique plus instruments are still the cause of the variations in metabolite concentrations between patients and healthy subjects. In this study, we performed a metabolite profiling via Q-TOF LC/MS between the pooled plasma samples of 15 polycystic ovary syndrome in adolescents patients (Group T) with pooled plasma samples of 15 healthy subjects (Group C). The metabolites found to be changed more than 1.5 fold between the groups were focused on targeted metabolite analyzes for 6 random individual samples within the groups in order to evaluate the reliability of using pooled samples (4). Statistical analyzes were performed to compare the pooled sample results and the random sample results.

Materials and Method
Blood plasma samples were stored at -80 °C until the day of experiment. 200 µL of 15 plasma samples collected for the Group C were pooled in a 15 mL Falcon™ conical centrifuge tube from Fischer Scientific (New Hampshire, USA) and vortexed. Same process was also applied for Group T. Beside the pooled samples, six random samples within the Group C and T were used as random individual samples. Pooled samples and random individual samples were subjected to metabolite extraction by ultrafiltration using an Amicon® Ultra 0.5 mL Centrifugal Filters (Merck, Darmstadt, Germany). Mass spectrometry analysis were carried on Agilent 6530 LC/MS Q-TOF instrument (Agilent Technologies, 184 Santa Clara, CA). C18 column (Agilent Zorbax 1.8 µM, 50 x 2.1 mm) was used as the chromatography column. Mobile phases were water and acetonitrile and both of them consisting of %0.1 formic acid. Flow (0.20 mL min⁻¹) started with %90 H₂O
until 1st minute, the ACN ratio was raised up linearly to %90 ACN until 15th minute. The chromatographic conditions were later turned back to starting conditions linearly till 20th minute and 5-minute post run was applied for further injections. Scan range for MS device was 100-1700 m/z. After the analytical method validation procedure, there was a list of peaks statistically evaluated and validated having fold changes >1.5 where p<0.05. Reliability of these peaks were considered by comparison of the pooled sample results with random individual sample results. T-test and F-test were performed for the statistical evaluation.

Results and Discussion

The only differences between group C and group T pooled plasma samples should be the variation of the intensities of the metabolites if the method is accurate. 683 reliable peaks from raw data were considered to be evaluated on metabolite profiling. The peak areas were normalized to discard variations among injections and samples. After the normalization process, a statistical evaluation was performed to detect the peaks having fold changes >1.5 between the groups. Among 683 peaks 147 peaks had fold change more than 1.5 where R>0.90 and p<0.05. Figure 1 shows the distribution of the peaks having different fold changes for the groups.

![Figure 1. Fold change score graph for pooled plasma samples](image)

The high number of peaks having fold changes around 1 showed that the method was accurate and the only variation between the pooled sample groups was about the disease condition. Principal component analysis (PCA) is an exploratory statistical method for graphical description of the information present in large datasets. According to the PCA results, group C and T were found as statistically different. The PCA graph is shown in Figure 2. The comparison of pooled plasma samples is just a comparison of the average concentration of each peak between the groups after whole statistical process including peak normalization. In order to select potential biomarker peaks, T-test anf F-test were performed between pooled samples and random individual samples. The aim was to clarify even if the average concentration of a peak is different between the groups, its distribution within same group is statistically significant to indicate it as a biomarker, or not. Among 147 peaks found to be different in metabolome level between pooled C and T samples, 84 of them were statistically different (p>0.05) and could be used as potential biomarker according to Student t test results for comparison of pooled and individual random plasma samples injection for each group.
Conclusion
The results presented that polycystic ovary syndrome in adolescents patients could be identified by using 84 metabolites having fold changes at least 1.5 in comparison to healthy subjects. Using pooled plasma samples is a good strategy to validate the results but not a tool to identify potential biomarkers.

References
OP23- A new and simple method for copper determination in aqueous samples: Effervescence-assisted dispersive liquid-liquid microextraction based on deep eutectic solvent

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ABSTRACT-A new and simple effervescence-assisted dispersive liquid-liquid microextraction, EA-DLLME, method has been evolved for FAAS determination of copper traces in aqueous samples, for the first time. Extraction of copper ions was performed by using deep eutectic solvent (DES) as extraction solvent, which prepared by mixing choline chloride and phenol. In addition 1,5 diphenyl carbazide was used as complexing agent and tetrahydrofuran (THF) as dispersive solvent. During this study, a solid effervescent agent was added into samples to assist the dispersion of extraction solvent. The effervescent agent is environmentally friendly and only causes an increase in the ionic strength, which does not interfere with the extraction of the analytes. The parameters influencing the extraction efficiency such as pH, concentration of complexing agent, composition and volume of DES, amount of THF, composition and amount of effervescent agent were studied. Under optimized conditions: enhancement factor was 78, limit of detection was 2.9 μg L\(^{-1}\) and limit of quantification was 9.7 μg L\(^{-1}\). The relative standard deviations (intra-day) were calculated as 2.1% and 1.3% for Copper ion concentrations 10 and 50 μg L\(^{-1}\), respectively. The good linearity for the suggested method was found to be in the range of 10.0–100 μg L\(^{-1}\).

Keywords: Copper, effervescence-assisted, deep eutectic solvent, liquid-liquid microextraction, flame atomic absorption spectrometry

Introduction
In this study, an easy, rapid and sensitive extraction method called as effervescence-assisted dispersive liquid-liquid microextraction (EA-LLME) has been developed for preconcentration and flame atomic absorption spectrometric determination of copper ions in aqueous samples. For this purpose 1,5-diphenyl carbazide (DPC) was used as complexing agent to form stable and hydrophobic complex. DES was prepared by mixing choline chloride and phenol was used as extraction solvent. THF is a polar aprotic solvent that can be miscible with water. The use of THF reduces the interaction between water molecules and DES, allowing self-aggregation of DES microdroplets\(^1\)-\(^3\). The mixture of sodium dihydrogen phosphate and sodium carbonate was used as effervescence powder. Through the use of effervescent, the extraction solvent was dispersed without any need of energy and higher extraction efficiency was obtained. In order to improve the efficiency of the method several parameters, which affect complex formation and effervescence assistance, were optimized. The method was also applied to the determination of the copper ions in standard reference material and water samples. According to our literature survey there is no study on both copper microextraction by using DESs and no study on combining DESs and effervescence assistance for metal microextraction.

Materials and Method
Preparation of ChCl-Ph eutectic mixture
13.96 g choline chloride and 28.20 g phenol were mixed and magnetically agitated in a glass beaker until clear solution was achieved in 5 minutes at 50°C.

Effervescence powder preparation
0.3 g NaH\(_2\)PO\(_4\) (as a proton donor) and 0.1 g Na\(_2\)CO\(_3\) (as a CO\(_2\) source) were manually mixed in a porcelain mortar until homogenous powder formed. So, 0.4 g effervescence powder was obtained.

EA-DLLME Procedure
In the proposed EA-DLLME method, 0.4 g effervescence powder was introduced in a 50 mL conical bottom centrifuge tube; then analyte containing extraction solution which contains 25.0 mL of standard (50 μg L⁻¹) or sample solution of copper ions, 2 mL of pH 6.0 buffer, 500 μL of 1% (w/v) chelating agent DPC, 1000 μL of DES and 1000 μL of THF was added into the tube containing effervescence powder. Then effervescence occurred from the bottom to top of the tube immediately and the extraction solvent was homogeneously dispersed into the aqueous sample solution. After the effervescent reaction completed the mixture was centrifuged at 4020 × g for 3 min. By means of centrifugation DES phase collected at the top the tube and then aqueous phase was taken out using a pipette and the volume of DES phase remaining in tube was completed to 500 μL with 1% acidic ethanol. Finally, diluted DES phase was introduced into FAAS by direct nebulization for Cu²⁺ analysis and blank was also treated in the same way.

Results and Discussion
In order to obtain maximum extraction efficiency and highest enhancement factor several parameters influence the properties of effervescence agent, metal-ligand formation and the extraction conditions were studied. During this study a univariate optimization method was used in which one parameter was changed at a time and the others were kept constant. For all the optimization experiments 50 μg L⁻¹ of Cu²⁺ working solutions were utilized. After obtaining optimum conditions, Cu²⁺ content of certified reference materials and some natural water samples were determined by using these optimum conditions. A summary of optimum condition values obtained proposed EA-DLLME method was presented in the following Table 1.

Table 1. Optimum conditions of the proposed EA-DES-LLME method

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample volume</td>
<td>25.0 mL</td>
</tr>
<tr>
<td>Final volume</td>
<td>500 μL</td>
</tr>
<tr>
<td>pH</td>
<td>6.0</td>
</tr>
<tr>
<td>Composition of effervescence agent</td>
<td>Sodium dihydrogen phosphate:Sodium carbonate</td>
</tr>
<tr>
<td>Amount of effervescence agent</td>
<td>0.4 g</td>
</tr>
<tr>
<td>Amount of DPC</td>
<td>500 μL of 1% (w/v)</td>
</tr>
<tr>
<td>Composition of DES</td>
<td>ChCl:Ph (1:3 molar ratio)</td>
</tr>
<tr>
<td>Volume of DES</td>
<td>1000 μL</td>
</tr>
<tr>
<td>Volume of THF</td>
<td>1000 μL</td>
</tr>
<tr>
<td>Extraction temperature</td>
<td>40 °C</td>
</tr>
<tr>
<td>Extraction time (effervescence time)</td>
<td>3.2 min</td>
</tr>
<tr>
<td>Centrifugation rate</td>
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<tr>
<td>Centrifugation time</td>
<td>3 min</td>
</tr>
<tr>
<td>Diluent</td>
<td>1% acidic ethanol</td>
</tr>
</tbody>
</table>

By using optimized conditions statistical evaluation of the method was performed. Table 2 summarizes some analytical figures of the method. In order to prove the performance the proposed method a certified reference material (TM-61.2, fortified water) was used and recovery values were calculated. The certified copper concentration of CRM was 63.5 μg L⁻¹. After applying proposed method obtained copper concentration was 62.4 ± 0.3 μg L⁻¹ with the recovery of 98% ± 2.

For validation of the proposed method, experiments were performed by spiking tap water (Ankara, Turkey), and lake water (Ankara, Turkey) samples. During these studies different amounts of copper (10.0, 25.0 and 50.0 μg L⁻¹) were added to these water samples and optimized method was applied. Obtained results are given in Table 5. As could be seen from the table calculated recovery values for spiked water samples were always greater than 97%, and these results verify the validity of the proposed method.
Table 2. Some analytical features of the proposed EA-DES-LLME method

<table>
<thead>
<tr>
<th>Analytical Feature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enhancement factor (EF)</td>
<td>78</td>
</tr>
<tr>
<td>Limit of detection (LOD) (µg L⁻¹)</td>
<td>2.9</td>
</tr>
<tr>
<td>Limit of quantitation (LOQ) (µg L⁻¹)</td>
<td>9.7</td>
</tr>
<tr>
<td>Linear range (µg L⁻¹)</td>
<td>10.0-100</td>
</tr>
<tr>
<td>Precision (%RSD) (n = 9)</td>
<td>1.3 (for 50 µg L⁻¹ Cu²⁺)</td>
</tr>
<tr>
<td></td>
<td>2.1 (for 10 µg L⁻¹ Cu²⁺)</td>
</tr>
</tbody>
</table>

Table 3. Determination of copper ions several water samples (n = 3)*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (µg L⁻¹)</th>
<th>Found (µg L⁻¹)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>0</td>
<td>4.6 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>14.4 ± 0.2</td>
<td>99 ± 2</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>30.4 ± 0.1</td>
<td>103 ± 2</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>53.0 ± 0.2</td>
<td>97 ± 3</td>
</tr>
<tr>
<td>Lake water</td>
<td>0</td>
<td>3.7 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>14.2 ± 0.1</td>
<td>104 ± 2</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>28.8 ± 0.1</td>
<td>100 ± 1</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>54.1 ± 0.2</td>
<td>101 ± 2</td>
</tr>
</tbody>
</table>

*results were give as mean ± uncertainty at 95% confidence level

Conclusion
In this study effervescence-assisted dispersive liquid-liquid microextraction, EA-DLLME, technique was developed for preconcentration and determination of copper in aqueous samples. Here by using effervescence agent, homogeneous dispersion of extraction solvent into the aqueous sample was easily provided. Compared with conventional ultrasound or vortex assistance, effervescence is a simple, effective, energy free and does not need any special instrument. When all of the advantages are taken into account it could be concluded that effervescence-assisted dispersive liquid-liquid microextraction technique is promising to determination heavy metals in several water samples.

References
Abstract- RNA interference represents a promising therapeutic strategy for the silencing of specific target genes. Post-transcriptional gene silencing could be achieved by small interfering RNAs with sequence-specific binding to its complementary mRNA. Gene silencing is done by degradation of RNA into short RNA strands that are involved in activation of certain ribonucleases, which target homologous mRNA. However, efficient intracellular siRNA delivery strategies are urgently needed for its therapeutic use in cancer that is not still accomplished. By considering the complex nature and metabolic pathways on cancer, high target specificity and non-toxicity are desired for siRNA based gene silencing approaches. In addition, size and chemical degradability of siRNA under physiologically relevant conditions, viral and/or non-viral vectors are used to delivery of siRNAs to carry for their transfection into mammalian cells. Non-viral vector-based siRNA delivery strategies developed in our group for metastatic colorectal cancer and malignant pleural mesothelioma are discussed through the presentation.

Keywords: Theranostic, siRNA, non-viral vector, targeted cancer therapy, oncogene

Introduction

According to WHO-World Health Organization; the second largest cause of death in the world is estimated to be 9 million deaths in 2018 due to cancer. In our country, according to 2015 data, 167463 people were diagnosed with new cancer (459 cancer diagnoses per day) and the most common types of cancer in men were trachea (with bronchus and lung), prostate, collateral (colon and rectum), bladder and stomach in females, thyroid, colorectal (colon and rectum), uterine corpus and trachea (together with bronchus and lung)\(^1\). The use of anticancer drugs is another problem because of the insufficient efficiency of systematic distribution and development of multidrug resistance. Gene therapy, which aims to identify the gene that causes the tumor and silencing this gene, has become an important approach in recent years. From this perspective, siRNA is also an important component of targeted cancer research as it is prominent as an agent that specifically targets the biosynthesis of oncogenic proteins\(^2,3\). siRNA, 21-23 nucleotides is capable of silencing gene expression by binding to complementary RNA strands\(^4\). However, in a controlled and traceable manner, siRNA transport is an important factor that limits therapeutic approaches\(^5\).

Materials and Method

\(\gamma\)-Fe\(_2\)O\(_3\) used diagnostic core was synthesized by chemical coprecipitation. It was functionalized by adding of citric acid. \(\gamma\)-Fe\(_2\)O\(_3\):cholesterol:DSPE:biocompatible polymer at the volume ratio of 50:38.5:11.5 was designed for therapotic purpose in addition to bioconjuction reaction by EDC/NHS. Synthesize procedure was summarized in Fig. 1.

Results and Discussion

The synthesized non-viral vectors will be used for the delivery of siRNA for metastatic colorectal cancer and malignant pleural mesothelioma. k-RAS in metastatic colorectal cancer and FGFR1 and FGFR2 in malignant pleural mesothelioma were selected as oncotargets by considering the their roles in molecular pathways. Apoptosize on HCT116 and Caco2 cells will be measured in additon to antimicrobial and antioxidant activities, mutagenity, ROS production, mRNA measurement experiments.
Conclusion
We hope that theranostic non-viral vectors could find application to diagnostic and therapy of metastatic colorectal cancer and malignant pleural mesothelioma.

References

Acknowledgment: The present work was carried out under the financial support of University of Dicle – DUBAP (FEN.18.012, FEN.17.030). A.İ. Özkan and F. Çakmak were supported by Council of Higher Education with 100/2000 Priority Areas Scholarship ofr Ph.D.
OP25- Rosmarinic and Carnosic Acid Contents and Correlated Biological Activities of 15 Salvia Species from Anatolia

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²Bahcesir University, Department of Biology Education, Merkez, Balıkesir, Turkey  
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Abstract- Herbal medicine has been used worldwide as an alternative treatment. Salvia genus is one of the most remarked herb which is traditionally used in the treatment of many diseases. Therefore it is an important issue to reveal the chemical and biological profiles of different Salvia species. Rosmarinic and carnosic acid are the most well-known bioactive components generally accepted as the main antioxidant compounds in Salvia. They are also responsible of many biological activities against tumor, inflammation, and hepatitis. This study firstly aims the determination of rosmarinic and carnosic acid contents of 15 Anatolian Salvia species by a simple and rapid capillary electrophoresis method. The antioxidant activities and total phenolic contents of the Salvia samples were also investigated. Moreover, α-glucosidase enzyme inhibitory effects of the samples were tested with respect to their antidiabetic activities.

Keywords: Antidiabetic activity; Antioxidant activity; Capillary electrophoresis; Rosmarinic acid, Salvia

Introduction

The genus Salvia includes nearly 1000 species throughout the world. Salvia species are commonly used as tea. Especially Salvia officinalis (common sage) is a popular herb used in a variety of food preparations. However most of the studies on Salvia is based on sage, it is also important to reveal the chemical and biological profiles of endemic Salvia species. We have reported quantification of horminone and 7-O-acetylhorminone, ursolic and oleanolic acids in Salvia species, which are all bioactive components, before¹².

Rosmarinic acid is one of the most well-known diterpenoid found in the members of the genus Salvia. It has many biological activities against tumor, HIV-1, hepatitis and inflammation. Moreover it was investigated a strong correlation between the antioxidant activity and rosmarinic acid levels of Salvia in many reports. Together with rosmarinic acid, carnosic acid is another diterpenoid generally accepted as the most antioxidant compound in Salvia¹.

In this study, we quantified the rosmarinic acid and carnosic acid contents of 14 Salvia species, 12 of which are endemic. This is, to our knowledge, the first report in the literature on these compounds in studied Salvia species. Furthermore, the antioxidant and antidiabetic activities of the samples were also investigated.

Materials and Method

Rosmarinic acid, carnosic acid, Folin–Ciocalteu reagent, gallic acid, 2,2 diphenyl-1-picrylhydrazyl, α-glucosidase (EC 3.2.1.20), p-nitrophenyl- α-α-glucopyranoside (p-NPG), and genistein were purchased from Sigma Chemical Co (Germany). Methanol was from Merck (Germany). 15 Salvia samples were collected from 7 different regions of Anatolia.

Rosmarinic acid and carnosic acid analysis were performed with an Agilent 1600 capillary electrophoresis system (Waldbronn, Germany). Separations were carried out in silica capillaries with 50 μm i.d. (Polymicro Technology, Phoenix, AZ, USA). Injections were made at 50 mbar for 6 s. The UV detection was carried out at 210 nm. The total phenolic contents of the samples were measured by using the Folin-Ciocalteu method⁴. Folin–Ciocalteu's reagent (1.5 mL) and sodium carbonate solution (1.2 mL) were added into the 300 μL of extracts. After the mixtures were waited for 10 min at room temperature, the absorbance was measured at 760 nm.

The free radical-scavenging activity of the samples was tested using the DPPH assay developed by Blois⁵ (1958). 1980 μL of DPPH solution was added into 20 μL sample solutions. The absorbance was measured against the control at 515 nm after 30 min. α-Glucosidase enzyme inhibitory activities of extracts were evaluated according to the slightly modified method of Shai et al.⁶. 50 μL phosphate buffer (100 mM, pH:6.8), 10 μL alpha-glucosidase and 20 μL of extract solutions were incubated at 37 °C. The enzymatic reaction was initiated by the addition of...
20 μL of p-NPG (5 mM). The α-glucosidase enzyme inhibitory activity was found by monitoring the p-nitrophenol released from p-NPG at 405 nm using Microplate Reader.

Results and Discussion

Borate was selected as the optimum separation medium according to the literature with a little modification on the buffer concentration. Borate concentration was selected as 20 mmol L⁻¹ and pH was adjusted to 9.6. At these conditions, carnosic and rosmarinic acid migrates in 3.7 and 5.2 min, respectively.

The calibration curves were obtained in the range of 6-250 μg mL⁻¹ and 8-250 μg mL⁻¹ for rosmarinic acid and carnosic acid, respectively. The correlation coefficients of both rosmarinic and carnosic acid were 0.999. The precision of the method was performed in terms of intra-day and inter-day repeatability of corrected peak areas and migration times. The limit of detection (LOD) were 1.53 μg mL⁻¹ and 2.14 μg mL⁻¹ for rosmarinic and carnosic acid, respectively. The limit of quantification (LOQ) were 5.1 μg mL⁻¹ and 7.13 μg mL⁻¹ for rosmarinic and carnosic acid, respectively.

All the Salvia species contain rosmarinic acid in the range of 0.108 ± 0.001 (S. caespitosa) and 1.45 ± 0.12 (S. hypargiea) mg g⁻¹ dry weight (DW). However only one Salvia species namely S. fruticosa contain carnosic acid (1.09 ± 0.02 mg g⁻¹ DW). Total phenolic contents of the Salvia samples were changed between 17.75 ± 2.35 (S. caespitosa) and 232.2 ± 5.8 (S. Aramiensis) mg gallic acid equivalent (GAE) g⁻¹ DW. The samples inhibited the DPPH in the range of 3.76 ± 0.12 (%) (S. caespitosa) and 93.2 ± 4.6 (%) (S. hypargiea). The IC₅₀ values of the α-glucosidase enzyme inhibitory results were between 5.51 ± 0.89 (S. hypargiea) and 43.71 ± 2.86 μg mL⁻¹ (S. hedgeana). Higher IC₅₀ values indicate lower enzyme activity. The correlations between the bioactivities and rosmarinic acid contents were searched. The correlation between rosmarinic acid content and DPPH activity was 0.596. The antidiabetic activity and rosmarinic acid content was negatively high (r= -0.603).

Conclusion

This study evaluated the rosmarinic and carnosic acid contents in 15 Anatolian Salvia species. All the samples contained rosmarinic acid. Antioxidant and antidiabetic activities were well-correlated with the rosmarinic acid contents. Commercial use of Salvia by the food industry or alternative use as drug throughout the world can be provided.

References

Acknowledgment: We thank the Research Foundation of Istanbul Technical University, Department of Scientific Research Projects
OP26- Preparation of N-(Tris(hydroxymethyl)methyl) acrylamide hydrogel for removing of boron from water

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Abstract- Methacrylamide based hydrogel was prepared starting from N-(Tris(hydroxymethyl)methyl) acrylamide (0.90 mol) and Ethylene glycole (EGDMA) (0.10 mol) in water at 80 °C. The resulting hydrogel has been shown to be efficient in chelation with boric acid and shown to be appropriate for boric acid removal even at ppm levels. The gel has 1.57 mmol/g of boron loading capacity. The resulting hydrogel has been shown to be efficient in chelation with boric acid and shown to be appropriate for boric acid removal even at ppm levels.

Keywords: Boron removal; polymeric sorbent; N-(Tris(hydroxymethyl)methyl) acrylamide gel

Introduction
Boron contamination in aqueous media is a serious problem, severity of which is a rising concern according to the expanding usage of boron-compounds in many industries. Therefore, boron is harmful for plants and its concentration in water sources exceeds a certain amount ¹. Moreover, deficiency of boron is also harmful for plants since it is a micronutrient for animals, plants and human beings ². Consequently, boron amount in aqueous media should be maintained in such a level that both it is sufficient for healthy growth of plants and it does not exceed the toxic-border. Hence, a maximum boron amount of 2.4 mg/L was recommended in WHO regulations³⁴. Sorbents which have vicinal di- or tri- hydroxyl groups on them have a strong tendency to form bonds with boric acid that ends up with building neutral boron esters or anionic borate complexes since they enclose boric acid to create borate complexes even in aqueous media of ppm-level boron concentration, selectively.

In the present work, N-(Tris(hydroxymethyl)methyl) acrylamide (0.90 mol) and Ethylene glycole (EGDMA)(0.10 mol) was polymerized to obtain hydrogel. Boron sorption properties of this new material were investigated with respect to initial boron concentration and kinetic models were also studied.

Experimental
Materials
N-(Tris(hydroxymethyl)methyl) acrylamide, Ethylene glycol dimethacrylate (EGDMA), potassium persulfate,boric acid, carminic acid and sorbitol were provided from Sigma-Aldrich. All materials were analytical grade and used as obtained without further purification.

Preparation of poly (N-(Tris(Hydroxymethyl)Methyl) Acrylamide Hydrogel
3.0 g of N-(Tris(hydroxymethyl)methyl) acrylamide monomer (NTMAc), 0.092 g K₂S₂O₈ and 20mL of distilled water were taken into flask. Then, 0.36 mL of EGDMA was added to the mixture. The polymerization was carried out at 80°C until occurring gelation. After thrigorous washing, the hydrogel was dried at room temperature under vacuum. The yield was 3.05 g.

Boron Sorption Experiments
0.10 g of hydrogel was swelled and then mixed with 10 mL of H₃BO₃ solution (0.485 M). The mixture was stirred for 24 h at room temperature. For the determination of residual boric acid content of the filtrate, 2 mL of the filtrate was mixed with 10 mL of 0.50 M D-sorbitol solution and titrated with 0.10 M NaOH solution in the presence of phenolphthalein as a color indictor. Boron sorption capacities of the hydrogel were studied by using different boron concentrations.

Boron Sorption Kinetics of the Hydrogel
0.1 g of the hydrogel was soaked into 1 mL of water and left for 4 h. Then, 90 mL of H3BO3 solution (4.90×10⁻³ M) was added to the wetted sorbents at room temperature. The carminic acid method was used to determine boron content of the solution (λ=585 nm).

**Results and Discussion**

The hydrogel was prepared starting from N-(Tris(hydroxymethyl)methyl) acrylamide as monomer EGDMA as crosslinking agent and K₂S₂O₈ as initiator in the presence of water at 80°C (Scheme1). Two or more hydroxyl functions incorporated into the polymer structure act as chelating agent for boric acid, by forming boron esters. The synthesized hydrogel has three hydroxyl functions.

![Scheme1. preparation of the hydrogel](image)

**Boron Sorption experiments**

Boron sorption experiments were performed depending on different boron concentrations (Table 1). Maximum boron loading capacity of the hydrogel was found as about 1.57 mmol g⁻¹, in non-buffered conditions. According to Table 1, boron sorption capacity depends on boron concentration and loading capacity of the resin increases with increasing boron concentration.

<table>
<thead>
<tr>
<th>Initial Concentration (M)</th>
<th>Capacity (mmol / g hydrogel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0097</td>
<td>0.079</td>
</tr>
<tr>
<td>0.0242</td>
<td>0.180</td>
</tr>
<tr>
<td>0.0485</td>
<td>0.460</td>
</tr>
<tr>
<td>0.1213</td>
<td>0.840</td>
</tr>
<tr>
<td>0.2430</td>
<td>1.470</td>
</tr>
<tr>
<td>0.4850</td>
<td>1.570</td>
</tr>
</tbody>
</table>

**Boron Sorption Kinetics of the Hydrogel**

The kinetics of sorption is an important aspect of the process control of removal of pollutants. Figure 1 shows that the decrease of boron concentration reached up to 97% of the initial (initial=4.9×10⁻³ M) in 60 minutes.
Two kinetic models were used to analyze adsorption kinetics which are pseudo-first-order, and pseudo-second-order. The Lagergen first-order rate equation (1) is one of the most widely used equations for the sorption of solute from a liquid solution.

\[ \ln (q_{eq} - q_t) = \ln q_{eq} - k_1 t \]  

(1)

where \( k_1 \) is the rate constant of pseudo-first-order adsorption (min\(^{-1}\)) and \( q_{eq} \) and \( q_t \) show the amounts of adsorption (mmol.g\(^{-1}\)) at equilibrium and at time \( t \), respectively. According to experimental and theoretical kinetic data, the experimental results obtained for the adsorption of boron on the sorbent were found to obey first-order kinetics and rate constant was calculated as 0.0496 min\(^{-1}\).

**Conclusion**

A new hydrogel exhibits reasonable an alternative sorbent for removal of boron from water. The boron sorption capacity was found as 1.57 mmol/g sorbent. The results indicated that the sorbent demonstrates a potential for the boron removal from water.

**References**


**Acknowledgements**

*Istanbul Technical University Research Foundation is greatly acknowledged for financial support (project no: 40251).*
OP27- Investigation of the Solubility of Polyphenolic Compounds in the Presence of Lactic Acid Butylether PEG (200)

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Abstract - Polyphenolic compounds which are bioactive antioxidant compounds, have the disadvantage that their bioavailability is low due to their low solubility in water. In this study, lactic acid ester of butylether PEG (200) has been synthesized. PEG based polymer has been interacted with morin and curcumin to improve poor water solubility of these phenolic compounds. Lactic acid butylether PEG (200) compound, was found to be miscible with water and significantly improved the water solubility of curcumin and morin. A significant increase (about 400 times higher than raw curcumin and morin) has been obtained.

Keywords: Curcumin, morin, water solubility, lactic acid ester of butylether PEG (200)

Introduction
Many natural phenolic compounds found in plants have very beneficial effects on human health as well as their antioxidant capacity. Several studies have shown that polyphenols, which contain more than one phenolic group, have an important role in the reduction of lipid oxidation in tissues with antioxidant activities. It has also been shown to be effective in reducing the risk of developing some diseases. Majority of these are cancer, diabetes, heart diseases, cognitive disorder and neurological diseases [1-3]. Curcumin is an important polyphenolic compound which is the main active ingredient of turmeric which has an important place in Asian public health. In recent years, numerous studies have been carried out which characterize the pharmacological properties of curcumin. Curcumin, which has been in use for a long time in eastern medicine, has been shown to have strong pharmacological effects. Inflammation, which is believed to be the result of severe metabolic disorders caused by oxidative stress in the cells, has been demonstrated by in vivo and in vitro studies that prevent the development or development of diseases such as arthritis, cancer, parkinson's, and Alzheimer's [4]. Morin is a yellow polyphenolic bioactive compound found in some Central and South American plants and fruits (eg Osaga Orange). One of the most important features of morine is the inhibition of the formation of amyloid polypeptide, which is known to cause Alzheimer's disease, and the elimination of formed amyloid fibers [5]. Curcumin and morin are practically insoluble in water. Although they are alkaline soluble, they undergo rapid hydrolytic degradation at pH values above neutral. This low solubility in water limits the practical application of these valuable polyphenolic substances. Curcumin and morin structures are shown in Figure 1.

Figure 1. Structures of polyphenols a) Curcumin b) Morin

Experimental
Curcumin, morin hydrate, Poly (ethylene glycol) butyl ether, lactic acid, p-toluene sulfonic acid were provided from Sigma-Aldrich. All materials were analytical grade and used as obtained without further purification.

Esterification of Poly(ethylene glycol) butyl ether with lactic acid
10 g of Poly (ethylene glycol) butyl ether and 4.37 g (48.544 mmol) of Lactic acid and catalytic amount of p-toluene sulfonic acid were mixed and transferred into dean stark. The reaction mixture was heated removing of water at 180 °C for removing of water. Then, the viscose and yellow reaction content was cooled and put into 50 mL of hexane. The phase separation was observed and the esterfied PEG was dried under vacuum at 40 °C after removing of hexane phase. The yield was found about 12.50 g. The PEG-lactic ester is soluble in water and common organic solvents such as ethanol, acetone, ethyl acetate and DMF. Lactic acid ester of butylether PEG (200) has been synthesized according to the following scheme.

\[ \text{H}_3\text{C} - \text{O} - \text{H} + \text{H}_9\text{C}_4\text{O}_n\text{H} \rightarrow \text{H}_9\text{C}_4\text{O}_n\text{H} - \text{O} - \text{H}_3\text{C} \]

\[ \text{P-toluen sulfonic acid} \]

Results and Discussion
Curcumin and morin water solubility in the presence of Lactic acid butylether PEG -200
To investigate the solubility of curcumin in water in the presence of PEG, solutions in various curcumin / PEG ratios were prepared. In a total of 10 mL solution, 0.005 g of curcumin was kept constant and a series of solutions were prepared in which PEG amounts were increased. The amount of curcumin and morin dissolved in the prepared solutions were determined by using UV-visible spectrophotometric measurements. Absorbance measurements were performed at 425 nm for curcumin and 325 nm for morin. Almost 100% solubility was reached when the curcumin/PEG or morin/PEG weight ratios were 1/30. The curcumin PEG interaction mechanism which leads to increased solubility is as follows.

Conclusion
It has been shown that a novel PEG derivative synthesized in this study (Lactic acid butyl ether PEG -200 can be an alternative agent to increase the solubility of curcumin and morin in water. In the presence of PEG, the solubility of curcumin and morin in water increased approximately 300 times. The results showed a potential for increasing the solubility of polyphenolic substances in water.

References
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Acknowledgements: Istanbul Technical University Research Foundation is greatly acknowledged for financial support (project no: TGA-2017-40916).
OP28- Novel Drug Delivery Candidates: Sodium Dodecyl Sulfate Modified Calcium Alginate Beads

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Abstract
In this present study, alginate was incorporated with sodium dodecyl sulfate (SDS) and ionically cross-linked with calcium ions. To characterize Ca-ALG-SDS beads, scanning electron microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR), and swelling experiments were done. Then the obtained calcium alginate beads (Ca-ALG-SDS) were tested for their drug release behaviors. Bovine serum albumin (BSA) protein was chosen as a model drug in this study. SDS free Ca-ALG type beads were used as a control group in the release experiments. Following the encapsulation of BSA into Ca-ALG and Ca-ALG-SDS beads, in vitro release experiments were performed in simulated gastric fluid (SGF) and simulated intestinal fluid (SIF) solutions which were prepared without enzymes in acidic (pH 1.2) and basic (7.4) conditions, respectively. Modification of alginate with SDS significantly increased drug encapsulation efficiency for BSA. Results of the release experiments showed that Ca-ALG-SDS beads performed controlled and time efficient drug release.

Keywords: Alginate; Sodium dodecyl sulfate; Bovine serum albumin

Introduction
Biopolymers are naturally sourced polymeric biomolecules. Alginate (ALG) is a member of biopolymer family that is mainly produced from brown algae. Alginate hydrogels is produced generally by crosslinking chemically or physically. However, chemical crosslinkers such as glutaraldehyde are generally toxic. It is mostly preferred to produce alginate hydrogels via ionic gelation by divalent or three valent cations such as Ca$^{2+}$, Ba$^{2+}$, and Al$^{3+}$ 1,2. Different composite materials have been proposed to improve the physical properties of the alginate hydrogels. For instance, it has been shown by Kaygusuz et al. that the incorporation of sodium dodecyl sulfate (SDS) to alginate matrix improved the physical properties of the alginate beads3. Besides, the interaction of bovine serum albumin and SDS was studied in the literature4. Here, regarding the surfactant and protein drug interaction, calcium alginate-SDS-BSA composite beads were prepared and subjected to the release experiments in SGF and SIF media. One of our purpose is to increase the entrapment efficiency (EE%) of BSA. Since the drugs in the protein structure are easily degraded in acidic environment, it is secondly aimed to reduce the release in the stomach environment and release most of the drug in the intestinal environment.

Materials and Method

Chemicals
Sodium alginate (from brown algae; viscosity of 2% solution ~250 cP) was purchased from Sigma-Aldrich. Sodium dodecyl sulfate (SDS), Bovine serum albumin (BSA, fraction V), Coomassie® Brilliant blue G 250, and ethanol were from Merck. Orthophosphoric acid were purchased from Riedel-de Haën. Calcium chloride dihydrate (CaCl$_2$.2H$_2$O) was obtained from J.T. Baker).

Preparation of Ca-ALG and Ca-ALG-SDS Beads
Alginate was dissolved in deionized water in order to give a polymer solution. This solution was stirred to obtain a homogeneous solution. Alginate beads were formed by dropping polymer solution into CaCl$_2$ solution using a syringe. After incubating 5 minutes in the crosslinking solution, the beads were filtered and washed with deionized water. Ca-ALG beads were dried at room temperature. To prepare SDS doped alginate beads, SDS and ALG were dissolved in deionized water. Alginate and SDS solutions were blended in 1:1 volume ratio to produce a final mixture consists of 100 mM SDS and 2% (w/v) alginate concentration. Ca-ALG-SDS beads were formed in CaCl$_2$ solution as mentioned above. BSA was included into solutions of Ca-ALG and Ca-ALG-SDS beads in 1% (w/v) amount.
**Protein Release Experiments from Ca-ALG and Ca-ALG-SDS Beads**

Two type of beads loaded with BSA were put in vessels containing the release media (SGF or SIF). Beads were shaken in a temperature controlled water bath at 37 °C. At determined time intervals, the certain amount of release media was taken and BSA content in the samples was determined by Bradford protein assay.

**Results and Discussion**

SEM and FTIR analysis of Ca-ALG and Ca-ALG-SDS beads were performed to illuminate structural and morphological properties of beads. SEM showed that SDS modification has made a significant impact on the surface properties of the Ca-ALG beads. FTIR spectra provided structural information about BSA loaded Ca-ALG-SDS beads. Swelling experiments were conducted in SGF and SIF media to investigate the swelling profiles of beads in the release media. Both of Ca-ALG and Ca-ALG-SDS type beads did not swelled much in the acidic SGF solution. On the other hand, SDS free Ca-ALG beads swelled in basic SIF solution in an uncontrolled way. The SDS ensured fractional swelling until equilibrium time in SGF and SIF solutions. In addition to these result, SDS contributed an enhancement of the BSA encapsulation yield of Ca-ALG beads. Then, BSA release experiments were done by initially shaking the beads in SGF media for 2 hours and then carrying the beads in basic intestinal solution of pH=7.4. BSA loaded Ca-ALG beads delivered the drug in acidic media almost two times more than Ca-ALG-SDS beads. Moreover, Ca-ALG beads showed a faster and uncontrolled BSA release in a short time in basic media. The results of this study indicated that the Ca-ALG-SDS beads delivered BSA from SGF to SIF by performing controlled release behavior.

**Conclusion**

Consequently, SDS modified calcium alginate beads were developed, characterized and loaded with BSA. EE% of Ca-ALG-SDS beads showed almost total encapsulation for BSA. Protein release in acidic condition was decreased and the resistance time of calcium alginate beads in basic media was extended by the existence of SDS in the beads.

**References**


**Acknowledgment**

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OP29- Essential oils analysis of *Paeonia daurica* subsp. *macrophylla* by two different methods

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Abstract: Essential oils of the fresh root, scape, fruit and fruit bark of *Paeonia daurica* Andrews subsp. *Macrophylla* Albow (P. daurica), collected from Eastern Black Sea region, obtained by Hydrodistillation and SPME methods were investigated by using gas chromatography-mass spectrometry (GC-MS). Major constituents of the essential oil were salicylaldehyde, myrtanal, palmitic acid, methyl salicylate, myrtenal, terpineol-α, linalool, trans-myrtanol, cyclosativene.

Keywords: *Paeonia daurica*, essential oils, SPME, salicylaldehyde

1. Introduction

*Paeonia* is the monotypic genus of the Paeoniaceae family, which consists of 35 species with areas of maximum diversity in Greece western Asia, and in western China [1]. *Paeoniacea* family from aromatic plants produces a large number of secondary metabolites, namely essential oils (EOs) (terpenes, flavonoids, steroids, and paeonols) which have demonstrated several therapeutic properties mainly antioxidant, antifungal and anti-inflammatory ones [2]. However, only a few studies on many species of *Paeonia* genus have clarified the impact and safety mechanisms with chemical analysis of their volatile constituents and it is obviously required doing further research on the development of phytopharmaceuticals from these species [3]. In this study, we have reported the essential oils profiling the fresh root, scape, fruit and fruit bark of *Paeonia daurica* subsp. *macrophylla*.

2. Materials and Methods

2.1. Solid-phase Micro-extraction

*Paeonia daurica* was collected in Çeymakçur Plateau, Rize, stony places, in the northeastern part of Turkey, on September 17, 2015. Experiments were carried out at 55 °C for 10 minutes based on the optimization results. 0.2 g of fresh plant sample was placed in a 15 mL vial on heated block and SPME (Supelco SPME Holder, Manual, 57330-U) fiber was immediately introduced through septa of the vial for adsorption.

2.2. Isolation of Volatile Constituents by Hydro-distillation

100 g of the fresh plant sample was hydro-distilled in a Neo-Clevenger apparatus using cooling bath system at 5 hours. Obtained EO phase was dissolved in 0.5 mL HPLC grade n-hexane and kept at 4 °C until analysis. The amount of EOs were expressed as mL/100 g dried sample[3].

2.3. GC-MS Analysis of EOs

GC-MS analysis of the EOs were performed with a Shimadzu QP-2010 Ultra system with electron impact ionization mode produced at 70. Mass range (m/z) was from 40 to 450. Rxi-5MS capillary column was used with helium as a carrier gas at flow rate of 1.44 mL min⁻¹.

3. Results and Discussion

The essential oil compositions of SPME extracts were compared with those obtained by hydrodistillation. Essential oil yields (v/w) of the plant parts for hydro-distillation are 0.06%, 0.1%, 0.07% and 0.2% for fruit, fruit bark, scape, and root, respectively.

In all SPME extracts, salicylaldehyde is the major compound (≥32.45 %). *p*-hydroxy benzaldehyde was the second highest compound followed by myrtanal in the root (24.53% and
12.55%) and fruit bark (18.34 % and 6.12%). Fruit SPME extract has myrtanal as the second highest compound at 16.79% while scape SPME extract has methyl-salicylate as the second highest compound at 11.75%.

Essential oil compositions of the plant extracts obtained by hydro-distillation were quite different comparing with those obtained by SPME. The reason for these differences may be extraction time, extraction temperature, sample amount, solvent effect, and particle size.

Similar to SPME extract, only the root HD extract has salicylaldehyde as the major compound (30.47%). Root HD extract has also trans-myrtanol (15.61%) and 5-cyanotropilene (7.66%). Major constituents of the scape HD extract were terpine-α (20.73%), linalool (15.62%), 2-6 octadienoic acid (13.45%). Fruit HD extract has cyclosativene (20.36%), benzonitrile, 4-(dimethylamino)-(13.60%), β-patchoulen (9.87%) while fruit bark HD extract has terpine-α (53.91%), linalool (13.63%), dodecanoic acid (5.74%) as major compounds.

In the literature, Paeonia species were reported to have salicylaldehyde and/or myrtanalas the major volatile compounds[4,5]. Salicylaldehyde, myrtanal, and methyl salicylate were found as characteristic volatile compounds in the air-dried roots of three species of Paeonia (P. clusii, P. mascula and P. parnassica). Salicylaldehyde were similarly most abundant in the root SPME and HD extracts in P. daurica with the second highest compounds; p-hydroxy benzaldehyde in the root SPME and trans-myrtanol in the root HD extracts.

4. Conclusion
Although the common essential oils existence were expected in the extracts, quite different volatile compounds were found in them. Aldehydes were found as major essential oil class in SPME extracts above 59%, while terpenoids were found as the major class in HD extracts above 35%. It was concluded that the polar alcohols and low molecular-mass terpenes were not well adsorbed by the PDMS fiber used in SPME analysis. Because of the therapeutic properties of these essential oils such as their antioxidant, antifungal and anti-inflammatory effects, volatile compounds of P. daurica may have a potential for therapeutic candidate for infection diseases.

5. References
OP30 - Anthocyanidin profile of Stachys sylvatica extract and their antioxidant potentials

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Abstract: Anthocyanidin composition of Stachys sylvatica were analyzed by high performance liquid chromatography equipped with an ultraviolet detector (HPLC-UV). Total phenolic content of the anthocyanidin and phenolic extracts were determined with Folin-Ciocalteu’s phenol reagent. Antioxidant potential of all extracts were estimated with their radical scavenging activity against 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. Most abundant anthocyanidin were cyanidin in the extracts. Flower extract had 34.43 mg cyanidin and 5.55 mg apigeninidin per g extract while flower’s stem extract had 5.90 mg cyanidin and 0.79 mg apigeninidin per g extract. Leaf phenolic extract had the highest total phenolic content with the concentration of 649.34 mg trolox equivalent/g extract. All extracts exhibited potential DPPH radical scavenging activity. The highest scavenging activity was determined in hydrolyzed flower extract with \(SC_{50}10.79 \mu g.mL^{-1}\) and the lowest DPPH scavenging activity was in the flower’s stem extract with \(SC_{50}96.68 \mu g.mL^{-1}\).

Keywords: Anthocyanidins, Flavonoids, Quercetin, Caffeic acid.

2. Introduction

Stachys sylvatica, commonly called as hedge woundwort, belongs to Lamiaceae family. S. sylvatica is tall around 30-100 cm height, a hairy perennial herb with long-stalked, sharp-tipped, toothed, hairy, dark green leaves and white marked dark purple flowers. It grows in woodland, unhandled grassland and moist places. Plant doesn’t smell pleasant. The main centers of diversity for the genus are East Anatolia, Caucasus, Northeast Iran, North Iraq, and Balkan Peninsula. Members of this genus are known as medicinal plants using to treat fevers, diarrhea, sore mouth and throat, internal bleeding, genital inflammatory diseases, cough, ulcers, infected wounds, tumors, and sclerosis of the spleen for centuries (Gören, 2014). The studies on this genus have revealed that Stachys species have various bioactivity such as anti-inflammatory, antitoxic, antibacterial, antioxidant, anti-anoxia anti-nephritic and hypotensive activity and cytotoxic (Ebrahimabadi et al., 2010).

The scope of this study was identify and quantify the antioxidant compounds present in different tissue of S. sylvatica and determine the antioxidant activity of extracts. Although Various bioactivities and bioactive compounds of several Stachys species were reported in the literature, this is the first report for anthocyanidin and phenolic compounds of S. sylvatica.

2. Materials and Methods

2.1. Sample preparation

The aerial part of S. sylvatica was collected from sea level in Rize (Turkey) in June 2013. The identification of the plant was freshly performed by MsC Esra Demir from Department of Biology, RTEU in Rize, Turkey. For anthocyanidin extraction the method from Turumtay et al. 2015 was used with small modification; 0.52 g flower (FA), 1.52g flower’s stem (FSA) were extracted with 10mL of HCl:methanol:water (1:80:19) for 2 hours at 30ºC in ultrasonic bath. Hydrolysis was performed using 2 mL of anthocyanidin extracts with 4 mL of 2 N HCl at 100 ºC in for 2 hours. For phenolic compounds extraction; 1.18 g leaf (LP), 0.74 g flower’s leaf (FLP) and 1.02 g stem (SP) samples were extracted with 10 mL of methanol for 6 hours at 40 ºC in ultrasonic bath.

2.3. Determination of anthocyanidins by HPLC-UV

Anthocyanidins were separated on a reverse phase C18 column (50 mm × 2.1 mm id, 3 μm particle; Thermo) using a Thermo Finnigan Surveyor HPLC. Five anthocyanidin standards (delphinidin chloride, cyanidin chloride, apigeninidin chloride, pelargonidin chloride and malvinidin chloride) were analyzed at 520 nm. Gradient elution was used for HPLC analyses using two mobile phases as (A) 5% acetic acid in water and (B) 5% formic acid in acetonitrile. The injection volume was 2 μL, the flow rate was 0.150 mL.min⁻¹.
2.4. Determination of total phenolic content

The total phenolic content of plant extracts was analyzed with Folin-Ciocalteu's phenol reagent. Trolox, gallic acid and quercetin were used to generate a standard curve in a range from 0.015 and 0.5 mg.mL\(^{-1}\)\((r^2 = 0.998)\) (Singleton, 1985). The concentration of total phenolic compounds was calculated as mg of trolox equivalent (TE), mg of gallic acid equivalent (GAE) and mg of quercetin equivalent (QE), per g of dried extract (DE).

2.5. Scavenging of Free Radical (DPPH) Assay

Radical scavenging activity of methanol plant extracts against 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical was spectrophotometrically determined at 517 nm (Cuendet, 1997). Radical scavenging activity was compared to gallic acid and quercetin as standards. Results were given as \(SC_{50}\) values denote the concentration of sample, which is required to scavenge 50% of DPPH free radicals (\(SC_{50}: \text{mg sample per mL extract}\)).

3. Results and Discussions

3.1. Identification and quantification of anthocyanidins

Cyanidin and apigeninidin were observed and quantified in both flower and flower’s stem extracts of \(S. \text{sylvatica}\) (figure 1). The flower extract had the most amounts of anthocyanidins as expected. Flower extract had 34.43 mg cyanidin and 5.55 mg apigeninidin per g extract while flower’s stem extract had 5.90 mg cyanidin and 0.79 mg apigeninidin per g extract. Leaf phenolic extract had the highest total phenolic content with the concentration of 649.34 mg trolox equivalent/g extract. All extracts exhibited potential DPPH radical scavenging activity. The highest scavenging activity was determined in hydrolyzed flower extract with \(SC_{50} 10.79 \mu \text{g.mL}^{-1}\) and the lowest DPPH scavenging activity was in the flower’s stem extract with \(SC_{50} 96.68 \mu \text{g.mL}^{-1}\). While hydrolysis were caused that the amount of phenolic compounds decreased, the radical scavenging activities of the hydrolyzed extracts were increased. It can be because the phenolic compounds of hydrolyzed extracts turned into their more effective form for scavenging a radical. For instance, glycosidic form of anthocyanidins, anthocyanin, turn into their aglycone forms which may have higher antioxidant potential.

4. Conclusions

Anthocyanidin and phenolic compounds which are the plant secondary metabolites have potential for preserving foods from decay and contamination and/or preventing living tissues from various infections and diseases thanks to their biological activities such as antioxidant, antimicrobial and anticancer properties. Plants have been serving as medicines with these properties from the ancient time to date however each of them have their unique contents which must be illuminated for safely use. Several Stachys species were investigated for their bioactive compounds and bioactivities and they have showed strong antioxidant activities along with the several bioactivities. According to literature data, this is the first study on the anthocyanidins and antioxidant activities of the aerial parts of \(S. \text{sylvatica}\). The aerial parts of \(S. \text{sylvatica}\) have a potential as natural sources to develop free radical scavengers. Further investigations are certainly needed to isolate and identify radical scavenging components of the studied extracts.
Figure 1. HPLC-UV chromatograms of anthocyanidin mixture at 5 ppm, flower and flower’s stem extracts at 520nm.

5. References
OP31 - Investigation of Concentrations of Some Trace Element (Fe, Mn, Cu, Ni) in Spring Waters in Malatya (Turkey) Region

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Abstract - The impact of trace metals on groundwater causes serious concern worldwide. This study focuses on the selected some trace element analyses of spring waters in Malatya province of east Turkey. A total of 7 spring water samples have been collected in September 2015 and analyzed for trace element parameters (Fe, Mn, Cu, Ni). Water samples were analyzed with the ICP-MS device. The concentrations of trace element do not exceed a maximum permissible level as per the Turkish Standart (TSE, 2005) and the World Health Organization (WHO, 2011) standards. The results for trace elements; iron, manganese, copper and nickel concentrations in this study contain location based variability, ranging between 3.6 and 35.9 µg/L, 0.24 and 2.95 µg/L, 0.99 and 1.49 µg/L and 0.69 and 2.11 µg/L with a mean of 8.33, 0.46, 1.32 and 1.02 µg/L, respectively.

Keywords: Malatya, Spring, Trace Elements,

Introduction
Recently, trace metal contamination in groundwater has drawn attention owing to strong toxicity, persistence and high bio-accumulation [1]. Besides, some trace metals have been reported to have potential risk for ecosystem [2, 3]. For example, although some trace elements such as iron (Fe), manganese (Mn), copper (Cu) and nickel (Ni) are essential for living organisms at specific concentrations, toxic effects are reveal when concentrations increase [4]. Springs are an important source of groundwater for drinking and irrigation purposes. They are expressed as the water that discharges by itself from one or more locations in nature and its chemical structure could change by precipitation, geological formations and environmental conditions. Various natural and anthropogenic activities, for example, contaminate groundwater due to deep percolation from intensively irrigation, disposal of hazardous wastes from industries, sewage disposal [5]. Thus, it is important to analyzed the quantifying of trace element concentrations and to monitor possible changes [6, 7]. The present study was aimed at evaluating the levels of Fe, Mn, Cu and Ni in the spring water samples in the Malatya province.

Materials and Methods
Study area
Malatya province is located in the southeast part of Turkey. Its geographic coordinates is longitude 37°13' - 39°8' east and latitude 39°52' - 37°54' north. The study area is characterized by continental climate and the annual average rainfall is about 378.1 mm [8]. Geologically this region is covered by Permo-Carboniferous Malatya metamorphites, Tertiary and Upper Cretaceous limestones, and Quaternary units [9].

Sampling and Data Analyses
A total of 7 water samples were collected different from major springs of the Malatya province in Turkey. The water samples were taken in 1 L polyethylene bottles and preserved in a cool place (about +4°C). The total metal concentration of iron, manganese, copper and nickel were determined in µg/L level using to ICP-MS (Inductively Coupled Plasma – Mass Spectrometer) at the Bitlis (Turkey) University laboratory. Analysis results are compared with the safe limits set by national [10] and international [11] institutions.

Results and Discussion
Fe and Mn at low level is important for enzyme activity but at high level, it accumulates in muscle, liver and affects brain and central nervous system [12, 13].

The result for iron (Figure 1) shows that the values obtained for the spring water ranges from 3.6 to 35.9 µg/L which is far below the desirable limits set by Turkish Standards (2005) and World Health Organization (2011). The iron concentration was not detected only in S-5.

Manganese level ranges from 0.24 to 2.95 µg/L (Figure 2). These values are below the desirable limit for national (50 µg/L) and international (50 µg/L) standarts [10, 11]. From all the 7 sample of spring water studied, the manganese concentration was detected only in S-2 and S-7.
High concentration of Cu in drinking water can cause vomiting, abdominal pain, nausea, diarrhea, anemia and diseases like nervous system disorder, liver and kidney failure [12, 14, 15, 16]. Analysis results reveal the concentration of copper in all the spring water samples ranges from 0.99 to 1.49 µg/L which is below the Turkish standart (2005) and World Health Organization (2011) limit of 2000 µg/L (Figure 3).

Ni causes systemic toxicity, allergy, hair loss and anemia and damage to DNA [12, 17]. Nicel concentration levels ranges between 0.69 to 2.11 µg/L (Figure 3). The concentrations are below the maximum permissible limit of national (20 µg/L) and international standart (70 µg/L).

Conclusion
In that study, maximum concentrations of iron, manganese, copper and nickel was presented 35.9, 2.95, 1.49, 2.11 µg/L respectively. The results indicated that the concentrations of selected trace element were less than toxicity threshold limit in drinking water. Based on the results of the analysis, it is considered that the trace element concentrations of spring waters is caused by the specific geologic setting of the area. The studied area is located in irrigation and quarries region, groundwater of that district is not polluted by trace element. In despite of not finding of pollution in the spring waters, in order to prevent of pollution of groundwater in the future, it is suggested the determine of protection areas and construction of wastewater collection systems.

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**OP32-Synthesis and Preparation of Bionanosorbents for Cleaning of Polluted Wastewater by toxic metals**

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**Abstract:** In this work, the activated carbon obtained from chemically-modified biowastes including banana peel and peanut shells were studied to be prepared as both biosorbent and nanobiosorbent. The obtained sorbents were characterized using FTIR, SEM, and BET methods. The characterized adsorbents were used for removing of toxic metals. The optimization of conditions was performed using parameters such as pH, contact time and analyte/adsorbent. The measurements were carried out by inductively coupled plasma-mass spectrometry (ICP-MS). The obtained results were compared with the results published in literature.

**Introduction**  
Due to the widespread use of high-tech products, water pollution from toxic metals threatens the future of the world. After intensive studies on sorbents based different materials for preconcentration and determination of toxic metals, use of the adsorbents having high adsorption capacity for removing of toxic metals is a good approach. Particularly, the modified biowastes are candidate for these purposes due to their cheap and environmentally friendly (1-2).

**Materials and Method**  
The dried and milled banana peel and peanut shells samples were treated by citric acid and H2SO4, separately. After drying process, the samples were carbonized under nitrogen gas in an oven. The activated carbon obtained was used for preconcentration of toxic metals in model solutions as described elsewhere (3). Metal analysis were performed with a Perkin-Elmer SCIEX ELAN 9000 inductively coupled plasma mass spectrometer (ICP-MS) (PerkinElmer SCIEX, Concord, ON, Canada). Ultrapure water obtained from a water purification system (Millipore Direct-Q, Millipore Corporation, Bedford, MA, USA) was used for all samples and preparations of standard solutions. The prepared biosorbents were characterized by FTIR, SEM and BET. Related with statistically consideration, One-way analyses of variance (ANOVA) were conducted to test the equality of mean values for each plant species of interest. Statistical significance was considered when P was equal to=or higher than 0.05.

**Results and Discussion**  
The obtained typical FTIR spectrum belonging banana peel before and after chemically modifying by H2SO4 was given in Figure 1. It was observed that the functionally groups on banana before modifying were activated after modifying. For this purpose, the synthesized biosorbents were used to preconcentration of toxic metals in model solutions by changing pH values (between 3-6), contact time (between 15-90 min) and analyte/adsorbent. The obtained pH-recovery curve was given in Figure 2. It was found that the optimum pH for Pb is 6 when citric acid was used for modification. At low pH values, the decrease in biosorption levels could be explained by an increase of competition between hydrogen ions and metal cations for binding active sites of biomass. In this case, the biomass surface was more positively charged and biosorption rates decreased. On the contrary, when the pH increased, since biomass surface became more negatively charged, optimal metal uptake rates were acquired at around pH 6. It was found that 30 min is sufficient for contact time. After synthesized nanobiosorbent, the significant increases were not observed. This can be attributed to atom radius of the analyte and pore diameters of biosorbent. The obtained adsorbent capacities for Pb was higher in the reported values in the literature (1-4).
Figure 1: IR spectra of Banana peel before and after chemically modification by H2SO4.

Figure 2: Effect of pH on recovery of lead using Banana peel+citric acid-biosorbent

References
**OP33-Phospholipid Bilayer Formation on Metal Oxides and Application for Biosensing Toxins**

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Over the years biosensors based on phospholipid bilayer system had been well developed. The most popular system is based on using thiols anchors monolayer on gold substrates. Then using vesicle fusion method anchored phospholipid bilayer is formed. In this paper is presented a new system for phospholipid bilayer formation on fluorine doped tin oxide (FTO; commercially produced) and cadmium tin oxide (CTO; produced indoors) which was modified with alkyl silane monolayer. The main advantage of such system that it is cheaper than gold and it is not cytotoxic. To characterize the monolayer and bilayer, it was chosen to use contact angle and electrochemical measurements: cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Previously it was proven that it is possible to determine surface heterogeneity using EIS method. During this work, it was followed the same methodology to characterize substrate, monolayer and bilayer surface. At the end, achieved results for phospholipid bilayer formation on FTO, were as good as on alkane thiols on gold.

Next, bilayer application for sensing toxins was tested. Phospholipase A₂ is toxin which breaks the bond of phospholipid at glycerol sn-2 position, thus disrupting membrane. Such disruption is possible to detect with electrochemical methods. In presented experiments, complex capacitance is decreasing and therefore complex resistance is increasing which suggests that phospholipid membrane is compatible with biomaterials.

To sum up, phospholipid bilayer membrane was formed on metal oxide surfaces. Experimentation with toxins lead to conclusions that electrochemical phospholipid membrane based biosensor on metal oxide was developed.

**References**


The metabolic activities of living organisms can be observed via electrochemical pathways. Techniques including amperometric measurements, impedance spectroscopy and scanning electrochemical microscopy give us insight about the cell’s bioelectrochemical activity\(^1\). The electron transfer can be examined using mediators: hydrophilic and/or lipophilic and an electrochemical setup. In this study we modified Saccharomyces cerevisiae living cells with an electrochemically conductive polymer-polypyrrole and/or carbon nanotubes to increase the electrical conductivity of the cell’s wall and the surface area. Such an approach can be helpful in developing better microbial fuel cells and biosensors.

The main part of an electrochemical device is usually the anode. Various modifications can be employed for an enhanced overall performance, however in our study we focus on facilitating the electron transfer by in vivo encapsulating the cells with electrically conductive materials\(^2\). The cells were then tested with amperometric measurements, scanning electrochemical and impedance microscopy. Nanocomposite materials such as carbon nanotubes have been widely used and offer favorable possibilities for electrode modifications yet, for a more novel approach we also encapsulate the cells with a biocompatible and conductive polymer that has the ability to mediate the interaction between the cell’s surface and the electrode. By modifying Saccharomyces cerevisiae with these conductive materials we formed various biocomposites which were then tested in an electrochemical setup. Also, the electrochemical cell was tested in two discerning mediums: a single lipophilic and a double mediator system.

Such variations had different effects on the bioelectrochemical activity. Cyclic voltammetry presented differences in the extracellular electron transfer responses for different types of modified cells. The variations of bioelectrochemical activity of distinctive biocomposites will be discussed further in detail.

**Keywords**: polypyrrole, bioelectrochemistry, biocomposites, Saccharomyces cerevisiae, carbon nanotubes

**References:**


OP35- Application of ultra trace graphite electrode modified with graphene nanoplatelets in electroanalysis of metobromuron

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The most extensively used allotropes of carbon in electroanalysis is graphite. One of the representative of graphite-based electrode is an ultra trace graphite electrode (UTGE) which has been used so far for the voltammetric determinations of just a few analytes.

To increase the sensitivity of the voltammetric methods for the determination of biologically active compounds, modifications of the working electrodes surfaces with nanomaterials are very often applied. Graphene nanoplatelets (GNPs) have proved to be excellent modifiers due to their properties, such as an excellent conductivity, a large surface area and an electrocatalytic activity. GNPs have been successfully incorporated into electrochemical sensors.

The detection of pesticides with high precision is extremely important in order to monitor and analyze the permissible level. Metobromuron (Mbn, N’-(4-Bromophenyl)-N-methoxy-N-methylurea) is a selective, systemic, pre-emergence herbicide currently approved for use in the EU. Mbn is adsorbed by the roots and leaves of annual broadleaved weeds and grasses. It has a low mammalian toxicity but has a high potential to bioaccumulate. Mbn is applied in fields of common beans, potatoes, tomatoes, tobacco, maize and sugar beet.

In this work, unmodified UTGE and the UTGE modified with the GNPs (GNPs–UTGE) were considered as working electrodes. The comprehensive microscopic and electrochemical characterization of proposed unmodified UTGE and the UTGE modified with the GNPs was performed by atomic force microscopy (AFM), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). Both electrodes were further applied for the analytical purposes. The procedure for the determination of Mbn using bare UTGE and the GNPs–UTGE was developed using square–wave voltammetry (SWV). Analytical signal was obtained at potential about +1.2 V on both electrodes. The measurements were performed in Britton–Robinson buffer at pH 2.0 as a supporting electrolyte. SWV parameters, i.e. amplitude, frequency, and step potential, were optimized. The linear relationships between peak current vs. increasing concentrations of Mbn were defined using both electrodes, and the limits of quantification and detection were calculated. The obtained results showed that the GNPs–UTGE possess advantages in terms of linearity, sensitivity, and detectability when compared to bare UTGE.

**Keywords:** pesticide, metobromuron, ultra trace graphite electrode, voltammetry

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Nanoparticles composed of an inorganic core and shell composition can be synthesized in a way to be fluorescent, magnetic or radioactive, which offers an imaging agent with different modalities. (1) Combining different cores of these properties for multimodal imaging has gained great interest in the last decade. In this work, fluorescent folic acid (FA)-derived “Carbon Nano Dots” (CDs) with inherent folate receptor for cancer cell targeting were synthesized via a facile one-step hydrothermal approach by using the protocol of Haifang Liu et al. (2). After the characterization of the synthesized CDs with pendant functional groups, an inorganic core together with magnetic nanoparticles (MNPs) with an (3-Aminopropyl) triethoxysilane (APTES) shell were used to generate MNP-CD nanocomposites, which can have a potential of fluorescent and magnetic resonance imaging (MRI). In this case, different conjugation techniques were performed and characterized with the following cell culture applications to visualize cytotoxicity and imaging capabilities (fluorescent and MR imaging) of these nanocomposites. The synthesis of CDs was successfully performed with the hydrothermal carbonization with high temperatures. Spectrophotometric and other physicochemical characterization studies demonstrated that the FA-derived CDs have great fluorescence capabilities with a nano-sized structure. Concomitantly, conjugation between MNP-CDs was also achieved by varying different techniques. Finally, multifunctional composites like MNP-CDs were applied to cancer cells, which exhibit dual imaging features as MR and fluorescence imaging. The resulting multifunctional nanoparticles for dual-imaging might be a potential candidate for advanced diagnosis and advanced imaging modalities.

Keywords: Carbon Dots; Cancer Cell Imaging; Conjugation; Dual Imaging

References:

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Antineoplastic drugs are common agents that are given during chemotherapy treatment. Such drugs should be administered using specific intravenous equipment. There should be no interaction between drug and the container since it may cause allergic reaction or degrade the drug. Traditional intravenous equipment including tubing and plastic components can be affected or degraded by the drug itself. Intravenous chemotherapy drugs are mixed into the serum and given at various times and some of them may require long-term administration intravenously. During this administration it is crucial to demonstrate the effective use of the chemotherapy medicines. In order to be in safe line and the compatibility with the packages in the preparation and administration section should be proven by no interactions. 5-fluorouracil, Oxaliplatin, Cyclophosphamide are the most widely used chemotherapeutic drugs in various cancer cells like breast carcinoma, colorectal carcinoma, gastrointestinal cancers and leukemias, small cell lung cancer, ovarian carcinoma, respectively.

In this work, studies and results of the Ethylene Vinyl Acetate (EVA) bags, Oncocare Drug Preparation and Administration sets to evaluate their compatibility with 5-fluorouracil, Oxaliplatin, Cyclophosphamide are estimated. The effect of infusion bags, vial adaptors, preparation and administration sets on drugs are studied by HPLC (high pressure liquid chromatography) [1,2]. All analysis and chromatographic conditions have been performed according to the Pharmacopoeia monographs of European (EP) or United States (USP). Solutions of drugs in water for injection, in 5% dextrose injection and in 0.9% sodium chloride injection were prepared in six EVA bags and IV administration sets. All bags and sets were exposed with drug solutions during their administration infusion times for each medicines and additionally for 24 hours. All solutions were prepared in glass amber HPLC vials after requiring times and detected by UV detector immediately. The assay of the active pharmaceutical ingredients were compared by their initial concentrations. The availability and compatibility of drugs from solutions infused via infusion bags through administration sets have been examined in detail evolutions of chromatograms if any unknown/known impurity peak(s) could be observed. The results showed no significant drug loss (<2%) was observed during simulated infusions using EVA IV bags and administration sets over time periods used in hospital at room temperature and also for 24 hours at 4 °C. The study suggests that concentrations of 5-fluorouracil, Oxaliplatin, Cyclophosphamide chemotherapeutic drug solutions are compatible with Oncocare Drug Preparation and Administration sets.

**Keywords:** 5-fluorouracil, Oxaliplatin, Cyclophosphamide, HPLC, Cancer drug, Compatibility.

**References**

**Introduction:** The binding mechanism of some small molecules of interest in pharmaceuticals with DNA has been a key research topic for rational designing of new more effective targeted drugs. Electrochemical investigations have provided a simple tool to confirm the occurrence of interaction between drugs and dsDNA.

**Experimental:** The interaction between drug and DNA was investigated in solution and at the electrode surface by electrochemical methods. The surface confined interaction required a smaller volume of sample solution (i.e. 50 µL) compared to the interaction performed in solution phase (i.e. 1000 µL). In bulk incubation procedure, 100 µg mL⁻¹ ct-dsDNA and 10 µg mL⁻¹ NDP in solution form were mixed together in a pH 4.70 (0.1 M acetate buffer), and then incubated at room temperature with different time periods. The multi-layer ct-dsDNA-modified electrode was prepared by depositing three drops of 5 µL each containing 50 µg mL⁻¹ ct-dsDNA on the GCE surface.

**Results:** This study presents evaluation of the possible interaction mechanism between calcium channel blockers; Nifedipine, Amlodipine and calf thymus dsDNA. The interactions between Nifedipine-dsDNA was investigated by differential pulse voltammetry using two different interaction methods; at the dsDNA-electrochemical biosensor surface and in bulk incubated solution. In incubated solutions, the interaction was also compared with model drug, Amlodipine. The decrease in the peak current of guanine and adenine were used as an indicator for confirmation of the interaction event in acetate buffer of pH 4.70. In bulk incubated solution, after interaction with Nifedipine and Amlodipine the guanine signal was almost disappeared. At dsDNA biosensor, after interaction with Nifedipine, the peak currents of guanine and adenine were almost decreased by 100 to 24%.

The interactions between Nifedipine-dsDNA was further studied by UV-Vis absorption spectroscopy and molecular docking. The spectrophotometric studies indicate that the intermolecular interaction between Nifedipine and ds-DNA can be mainly through hydrogen bonding and van der Waals forces. The binding constants was found as 3.64×10³ for Nifedipine-dsDNA interaction. Molecular docking calculations shown that the AMP-1-2 and NDP having groove binding. Beside spectral data, docking studies elicited that AMP-1-2 and NDP complexes have different interaction and conformation trends to ctDNA.

**Conclusions:** This interaction studies by electrochemically, spectrophotometrically and molecular docking offer the opportunity to know about the effects of drugs in DNA structure and know about mechanism of interaction and it may be useful to design new drugs. Also, binding constant is a basic experimental parameter in many clinical studies, such as pharmacokinetic drug interaction.

**Keywords:** Biosensor, electrochemistry, dsDNA, nifedipine, amlodipine
OP39- Determination of Changes in Glutathione Reductase Activity Exposed to Imidacloprid and Thiamethoxam

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ABSTRACT- Glutathione reductase (EC 1.8.1.7) is an antioxidant defense enzyme. Glutathione reductase converts oxidized glutathione (GSSG) into reduced glutathione (GSH) in the presence of NADPH (β-nicotinamide adenine dinucleotide 2'-phosphate reduced). Imidacloprid and thiamethoxam are neonicotinoid insecticides. Neonicotinoid insecticides are a new class of neuroactive insecticides which are used in large quantities for protection crop. In this study, glutathione reductase from baker’s yeast (S. cerevisiae) exposed to 0, 25, 50, 100, 250 and 500 ppm imidacloprid and thiamethoxam. According to control activity or 0 ppm activity, no statistical changes were observed in glutathione reductase activities (p > 0.05). Imidacloprid and thiamethoxam don’t affect glutathione reductase activity in the range of 0 to 500 ppm.

Key Words: Glutathione Reductase, Imidacloprid, Thiamethoxam, Neonicotinoid Insecticides.

References:

OP40- Deep eutectic solvent based microextraction of tartrazine at trace levels

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Since the last decade microextraction techniques are very useful and popular for the pre-concentration-separation of inorganic and organic pollutants in environmental samples at trace levels. A deep eutectic solvent is prepared by mixing two safe ingredients together with ease to get a eutectic mixture. Deep eutectic solvents are generally obtained by using of combination of hydrogen bond donors and ammonium salts and which do not react with water.

In this study, a deep eutectic solvent microextraction method for traces tartrazine has developed for its the separation and preconcentration prior to determination by UV-VIS spectrophotometry at 430 nm. To obtain deep eutectic solvent, tetrabutylammonium chloride and decanoic acid was used. The important analytical parameters such as pH, deep eutectic solvent type, model solution volume, sample volume and matrix effect are optimized. Tartrazine was quantitatively extracted in the deep eutectic solvent phase at pH 4.0. The validation of the procedure was performed by using addition/recovery tests. The method was applied to the determination of tartrazine content of various water samples.

Keywords: microextraction, deep eutectic solvents, spectrophotometry

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Analytical Ammonium Ions Sensor Based on Electrochromic Properties of Prussian Blue

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Electrochromic properties is a unique feature of some materials caused by an electron-transfer (redox) process or by applied electrochemical potential. Prussian Blue (PB) exhibits such electrochemical and optical properties making it a promising material for development of electrochromic analytical sensors.

The objective of this work was to synthesize an electrochemically stable form of Prussian Blue on the surface of indium tin oxide (ITO) coated on a glass electrode (glass/ITO) and to investigate possible changes of glass/ITO/PB absorption spectrum at different ammonium ion concentrations. For this purpose an ITO coated glass (glass/ITO) plate was used as electrode, which was electrochemically modified with PB layer by potential cycling in electrochemical cell filled with solution containing 1 mM of FeCl₃ and 1 mM of K₃[Fe(CN)₆]. The interval of potentials used was between +0.4 V and +0.8 V vs Ag|AgCl|KCl sat. All optical measurements in KCl solution were accomplished by applying 0.2 V vs Ag|AgCl|KCl sat. After the optical measurement in NH₄Cl solution, glass/ITO/PB plate was regenerated by immersing it in 0.1 M KCl solution and applying 0.2 V potential vs Ag|AgCl|KCl sat. for 5 seconds.

A blue coloured PB film on the surface of glass/ITO/PB electrode was electrochemically stabilized by cycling in 0.1 M KCl solution until cyclic voltammograms gained steady-state values. The redox potential of PB calculated from voltammograms was equal to 0.18 V vs Ag|AgCl|KCl sat., so 0.2 V was used for further electrochromic effect based investigations. The optical spectra of glass/ITO/PB electrode were collected and analyzed in order to compare changes of optical absorption dependently on the concentration of NH₄Cl solution. Addition of ammonium ions in electrochemical cell caused the decrease in the intensity of absorption maximum and shifting of λ_max to longer waves. The obtained linear dependencies of absorption maximums and λ_max against concentration of ammonium ions could be very promising for developing electrochromic ammonium ions sensor based on variation of optical properties of PB.

Summarizing, the investigated glass/ITO/PB structure demonstrated fast electrochromic response towards ammonium ions indicating the applicability of glass/ITO/PB electrode for the electrochromic determination of ammonium ion concentration in aqueous solution.

Keywords: Prussian Blue; electrochromism; glass/ITO-electrode.

References

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OP42- Establishment of Primary Level Electrolytic Conductivity Measurement System and Uncertainty Estimation

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Measurement and control of electrolytic conductivity are essential in both industrial processes and research studies such as biochemistry, food science, chemical research and engineering, environmental research and pollution control and pharmaceutical industry. Hence there is a huge demand for traceable measurement results for electrolytic conductivity to ensure quality control and comply with the technical requirements.

In all of the above-mentioned fields, electrolytic conductivity is measured by conductivity meters or conductivity measuring systems. In Turkey, all laboratories (state, private or university laboratories) that are carrying out electrolytic conductivity measurements use reference conductivity solutions to calibrate their equipments and currently these solutions are imported from abroad. Therefore, production and certification of the reference conductivity solutions (CRM) are planned. Local supply of the buffer solutions will ensure measurement traceability chain through TUBITAK UME and the exchange spent for these solutions will be retained in the country.

Electrolytic conductivity measurements can be incorporated into the SI as they can be traced to measurements made using a method that fulfills the definition of primary methods of measurement. Due to all these objectives, the establishment of a primary level electrolytic conductivity measurement system, also called as jones cell, for measurement of electrolytic conductivity has been carried out under this project. Participation of international comparisons will be realized with the established system in order to ensure the compliance with the SI units system for conductivity measurements1,2. Traceability for these measurements will be disseminated through TUBITAK UME. Measurement uncertainty for primary level measurements is evaluated according to GUM principles3.

Keywords: Primary level measurement, conductivity, jones cell, CRM.

References
OP43- Voltammetric Determination of Molybdenum using Various Polymer Film Modified Pencil Graphite Electrodes

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A new indirect voltammetric method for determination of molybdenum using various polymer film modified pencil graphite electrodes was described¹⁻³. Poly eriochrome black t modified pencil graphite electrode (p-EBT/PGE), poly xylenol orange modified pencil graphite electrode (p-XO/PGE) and poly methyl red modified pencil graphite electrode (p-MR/PGE) were used for this purpose. These electrodes were characterized by EIS and XPS techniques. The method is based on measuring the oxidation current of tiron in the molybdenum-tiron complex at the polymer film modified PGE. The limits of detection (s/y) and analytical ranges for p-EBT/PGE, p-XO/PGE and p-MR/PGE were estimated as 70, 49, 33 μg/L and 232–900, 162–1000, 109–1000 μg/L, respectively. The selectivity studies were also performed for all electrodes. The method was applied to tap water and drinking water samples. The results obtained were compared with each other. The averages of RSD% values for low, medium and high molybdenum content were 5.46%, 6.30% and 4.69% for p-EBT/PGE, p-XO/PGE and p-MR/PGE, respectively.

Keywords: Molybdenum, tiron, polymer film modified electrode, voltammetry.

References
OP44- A Sensitive H$_2$O$_2$ biosensor based on cress (Lepidium sativum sub sp. sativum) POD and BiFeO$_3$ nanoparticles

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Biosensors are analytical tools that are capable of converting a biological response into a signal. Many types of biosensor are available in the literature such as; enzyme-based, tissue-based, immunosensors, DNA biosensors. The combination of stable, low-cost, homogenous mediators with the biological material is very crucial for biosensor construction and hence metal oxides are good candidates for this purpose$^1$. In this study BiFeO$_3$ was synthesized via hydrothermal method and characterized with FTIR, XRD and SEM techniques. XRD pattern of BiFeO$_3$ was shown in Fig.1. On the other hand, peroxidase (POD) enzyme was purified from cress by ammonium sulphate precipitation, gel filtration, and CM-Sephadex ion-exchange chromatographies and the obtained enzyme was further used for peroxide biosensor construction$^2$. The proposed sensor exhibited two linear concentration range 0.2 to 1.0 and 1.0 to 10 µM with correlation coefficients 0.9982 and 0.9876, respectively. The repeatability was found as 20.9 % for 2.10$^{-7}$ M. The sensor was then applied milk samples and satisfactory results were obtained.

Fig 1. XRD patterns of BiFeO$_3$ nanoparticles

Keywords: Hydrothermal method, BiFeO$_3$, amperometric biosensor

References
OP45- Flow Injection Amperometric Determination of H$_2$O$_2$ by Electrocatalytic Oxidation at a Cupric Neocuproine-Nafion Modified Pencil Graphite Electrode

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Among its wide range of applications, H$_2$O$_2$ has been widely used for the indirect determination of many compounds such as biosensing of glucose based on oxidase enzyme$^1$, peroxide-based explosives$^1$, etc. Thus, one of the most common ways to determine this important compound is the electrocatalytic oxidation and detection of H$_2$O$_2$ at modified electrodes with organic redox mediators. A literature research shows that CUPRAC, which was first developed by the Apak research group in 2004$^2$, was not used for the electrocatalytic oxidation of H$_2$O$_2$ at modified electrodes. In the proposed method, the CUPRAC reagent (cupric-neocuproine complex) was used as a redox mediator for the electrocatalytic oxidation of H$_2$O$_2$ and its amperometric determination in flow injection analysis (FIA) system for the first time. So, cupric-neocuproine was modified onto pencil graphite electrode (PGE) surface by using Nafion used as a cation-exchange membrane (having perfluorosulfonate groups) for adsorption of the copper-complex.

In the modified electrode preparation experiments, PGE was immersed into 0.75% of Nafion prepared in ethanol for 10 min, and then Nafion-adsorbed PGE was immediately immersed into CUPRAC reagent solution (0.40 mM of Cu$^{2+}$ and 0.80 mM of neocuproine prepared at pH 4.76 in 0.10 M acetate buffer) for 10 min. The used Nafion concentration and adsorption times were optimized based on the amperometric response of 0.1 mM H$_2$O$_2$ in the FIA system. Surface morphology of electrode surface was investigated by recording SEM images and EDX and XRD spectrum. The obtained results show that CUPRAC reagent was efficiently adsorbed onto PGE surface using Nafion. Fig. 1 shows cyclic voltammograms (CVs) of H$_2$O$_2$ at bare PGE and CUPRAC/PGE.

It can be seen that CUPRAC/PGE exhibited an excellent electrocatalytic activity toward oxidation of H$_2$O$_2$ due to shifting of peak potential to more negative direction and enhancement of peak current compared to bare PGE. Then, FIA of H$_2$O$_2$ was performed based on its electrocatalytic oxidation at CUPRAC/PGE using a previously constructed home-made flow cell for PGE. FI amperometric studies showed two linear calibration ranges (1.0-1000.0 μM (R$^2$=99.58) and 1000.0-10000.0 μM (R$^2$=99.02) with a limit of detection of 0.4 μM H$_2$O$_2$ which is considered good for electroanalytical determinations. The cupric-cuprous standard redox potential raised to 0.6 V in the presence of neocuproine greatly enhanced the electrocatalytic oxidation of hydrogen peroxide. To test the applicability of the developed FI amperometric H$_2$O$_2$ sensor, the determination of H$_2$O$_2$ was performed in some real samples.

**Keywords:** Hydrogen peroxide, CUPRAC, nafion, pencil graphite electrode, flow injection analysis

**References:**
A New Molecularly Imprinted Polymer for Purification of Cytochrome C from Blood Serum

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Molecular imprinting that first described in 19721 is a rapidly developing technique and has been attracted the attention of researchers for preparing polymeric sorbents for selective recognition and separation2.

In the present work, selective separation of cytochrome c (cyt c) in the presence of various competitive proteins by molecular imprinting technique was studied. For this purpose, after complexed of cyt c (as a template) with N-methacyrloylamido antipyrine (MAAP)-Ce(III) (as a functional comonomer), radical polymerization of 2-hydroxyethyl methacrylate and (MAAP)-Ce(III)-cyt (lanthanide-chelate complex) in the presence of MBAAm as crosslinker, TEMED as activator and ammonium persulfate (APS) as initiator agent was carried out. Cyt c imprinted-(HEMA-MAAP-Ce(III)) cryogel polymer has been synthesized by flushed out of bonded template molecule from polymer with 0.1 M Na2CO3 and NaOH mixture.

For comparison of binding capacity, the non-imprinted polymer (NIP) has also been prepared applying the above procedure in the absence of the template molecule. Prepared imprinted-cryogel has been characterized by ultraviolet-visible-near infrared (UV-NIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and swelling tests. Imprinted cryogel has been described how pH, initial cyt c concentration, flow rate, temperature and ionic strength affect the binding capacity. At the optimum conditions the cyt c binding capacity of the prepared cryogel was determined as 98.33 mg*g⁻¹. When purification of cyt c from blood serum using by MIP cryogel was compared with NIP, it was found that MIP displayed 92.78 % binding while the NIP displayed 23.96 % binding.

Keywords: Molecularly imprinted cryogels, Lanthanide-chelate, Cytochrome C, Selective separation

References
Capillary electrophoresis (CE) offers several advantages such as greenness due its requirement for low volumes of samples (in nL) and reagents (in µL), extremely high separation efficiency, and high versatility in terms of multiple separation modes. However, as compared to other separation techniques, it has not gained wide popularity due to low sensitivity caused by small path length particularly with UV detection. To overcome this problem, several on-line preconcentration strategies such as field-amplified sample stacking (FASS) and field-amplified sample injection (FASI) have been applied with organic and inorganic analytes. Despite its increasing prominence with many analytical instruments, there are still few reports on application of dispersive liquid-liquid microextraction (DLLME) prior to CE (< 2% of published work), which might be due to incompatibility of the final organic extract with CE. To overcome this problem, a rapid back-extraction step of ionizable analytes into an aqueous solution not only fulfills the instrument compatibility requirement but also gives a good control of the ionic strength in the final extract, which minimizes matrix effect and improves reproducibility.

This work illustrates the effectiveness of hyphenating DLLME with FASS/FASI in CE for determination of some organic analytes in complex matrices such as urine, milk and food (Table 1).

Table 1. DLLME-FASS/FASI-CE for the determination of organic analytes in various matrices.

<table>
<thead>
<tr>
<th>Analyte(s)</th>
<th>Matrix</th>
<th>Online Precon.</th>
<th>Dispersion solvent/volume (µL)</th>
<th>Extraction solvent/volume (µL)</th>
<th>LOD (µg mL⁻¹)</th>
<th>EF</th>
<th>%RSD</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol A</td>
<td>Human urine, FASS Human urine, FASI</td>
<td>1-Undecanol (90) 1-Undecanol (50)</td>
<td>Acetonitrile (1.0) Acetonitrile (1.0)</td>
<td>60 60</td>
<td>&gt;0.9992 &gt;0.9901</td>
<td>430 41-1046</td>
<td>&lt;1.2 5.5</td>
<td>[2] [3]</td>
</tr>
<tr>
<td>β2-agonists</td>
<td>Bovine urine, FASI</td>
<td>1-Undecanol (50)</td>
<td>Acetonitrile (1.0)</td>
<td>90 1.80-37.6</td>
<td>&gt;0.9915</td>
<td>46,229</td>
<td>6.2</td>
<td>[4]</td>
</tr>
<tr>
<td>NSAIDs</td>
<td>Bovine milk, FASS</td>
<td>Chloroform (150)</td>
<td>Acetonitrile (2.0)</td>
<td>120 3.0-13.1 (µg kg⁻¹)</td>
<td>&gt;0.9915</td>
<td>-</td>
<td>46-229</td>
<td>[4]</td>
</tr>
<tr>
<td>Parabens</td>
<td>Breast milk, FASS</td>
<td>Chloroform (200)</td>
<td>Acetonitrile (1.0)</td>
<td>&lt;120 0.1-0.2</td>
<td>&gt;0.9957</td>
<td>4.3, 10.7</td>
<td>&lt;3.5</td>
<td>[5]</td>
</tr>
</tbody>
</table>

Keywords: Capillary electrophoresis, Dispersive liquid-liquid microextraction, Field-amplified sample injection, Field-amplified sample stacking, Online preconcentration.

References:
**OP48** Synthesis, Characterization and Applications Of Antimicrobial Activity Of Silver Nanoparticles From *Juglans regia*

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**Abstract**-In the present study, nanotechnology has become a succesfull research field of new material science. were synthesized using peels *Juglans regia* as reductant by a simple and eco-friendly route. The aqueous silver ions when exposed to fruit peels *Juglans regia* were reduced and resulted in green synthesis of silver nanoparticles. The silver nanoparticles were characterized by UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM) analysis, Energy dispersive and X-ray analysis (EDAX). UV-visible spectrum of synthesized silver nanoparticles indicated maximum peak at 449 nm. SEM analysis revealed that the particles were spherical, hexagonal and irregular in shape and size ranging from 10 to 90 nm, the usability of nanoparticles at high temperatures was tested by using TGA-DTA (thermal gravimetric analysis) analysis and Energy dispersive X-ray spectrum confirmed the presence of silver metal. Synergistic antimicrobial potential of silver nanoparticles was evaluated with various commercial antibiotics against Gram positive (Staphylococcus aureus), Gram negative (Escherichia coli) bacteria and fungi (Candida albicans). The antifungal activity of AgNPs with antibiotics was better than antibiotics alone against the tested fungal strains and Gram negative bacteria, thus signification of the present study is in production of biomedical products. **Key words:** XRD, Antimicrobial activity, silver nanoparticles, *Juglans regia*

**OP49** A titania-glyco purification tip containing bioanalytical method for MS-based glycoproteomics and glycomics

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Glycosylation is the most ubiquitous post-translational modification (PTM) since it has significant roles in cellular pathways. Modern mass spectrometers including soft-ionization techniques are the most favored tools for glycosylation analysis. However, purification of native and derivatized glycans and glycopeptides is necessary for achieving efficient MS analysis of important glycoproteins such as immunoglobulin G (IgG)-based monoclonal antibodies that are used for the treatment of various cancers.

In the current study, titania-based material was synthesized using a facile sol-gel method and a bioanalytical approach was employed for the enrichment and purification of glycans and glycopeptides. Standard glycoproteins including IgG, transferrin, and fetuin was digested and the resulting glycopeptides were enriched by titania sol-gel material, and the enrichment performance of the material was evaulated comparing with commercially available TiO₂. It was found that titania sol-gel material had extremely better selectivity and sensitivity (femtomole level). Site-specific IgG glycosylation analysis was achieved by the enrichment of its glycopeptides using MALDI-TOF-MS. Finally, a facile bioanalytical tool containing a titania sol-gel packed pipette tip was developed and applied for the purification of 2-AA labelled N-glycans and native glycopeptides. Moreover, human plasma as a real-world complex sample was digested and analyzed by nLC-TIMS-TOF-MS/MS after applying an enrichment step using titania-glyco purification tip for the efficient analysis and N-glycoproteome profiling of human plasma. **Keywords:** glycosylation, glycoproteomics, glycomics, mass spectrometry.
Synthesis and Antibacterial Properties of Nitrogen or Carbon Doped Titanium Oxide Nano Films

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According to an analysis firms, antibacterial coatings market in 2024 will exceed US $ 7.4 billion [1]. US Centers for Disease Control and Prevention, allocated in 2016 fourteen million dollars in grants to the thirty-four research teams to create a protective coating against antibiotic resistant bacteria [2]. There is also a rising interest in antibacterial coating from the food industry [3]. The development of simple, inexpensive and effective antibacterial coatings is very important since the damage from harmful and stable microorganisms has become a serious social problem. The use of photocatalytic effect on nanoscale TiO₂ is conceptually simple and promising technology to mitigate bacterial contamination. However, the band gap of titanium dioxide is 3.0-3.2 eV, which means that it can be excited by UV radiation with a wavelength <380 nm, which is only 5% of the solar spectrum. One way to overcome this problem is to dope TiO₂ with carbon or nitrogen. This allows to engineer a material with a band gap less than 3.0 eV, which would support the photoactivity in low light conditions.

Over the years, numerous methods were developed to obtain nitrogen or carbon doped coatings. In this work atomic and molecular layer deposition (ALD and MLD) techniques were used to synthesize photoactive thin (<10nm) films. If ALD allows to deposit only inorganic coatings, using MLD one can deposit organic and hybrid organic-inorganic thin films. Unique features of these techniques as follows – atomic level thickness and composition control; high-level of film uniformity when deposited on membranes and nanoparticles. In ALD and MLD films deposited via sequential surface chemistry reactions. For this study, antibacterial ALD TiOₓNᵧ coatings were deposited using TiCl₄ and hydrazine (N₂H₄) chemistry. Carbon doped TiOₓCᵧ films were synthesized by pyrolysis of MLD titanium alocoxide thin films.

In this presentation, we will show our findings for photocatalytic distraction of stems of E. Coli and Staph. Aureus bacteria under exposure to artificial UV and ambient light sources for various TiOₓNᵧ and TiOₓCᵧ films.

References
Study on the Interaction between St. John’s Wort and Sertraline with Plasma Proteins and Cell-Culture Medium

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St. John’s Wort is herbaceous plant used as an antidepressant. Recent studies have supported that St John’s Wort is effective for treating depression but St. John’s Wort is considered dietary supplement by FDA and not regulated as prescription drug [1]. Sertraline is an antidepressant of the selective serotonin reuptake inhibitor (SSRI) class. Sertraline is used for major depressive disorder, obsessive–compulsive disorder, panic disorder, and social anxiety disorder [2]. Some studies indicate that both sertraline and St. John’s Wort increased serotonin level and combined usage of sertraline and St. John’s Wort causes serotonin syndrome but generally, antidepressant drug interactions have had not adequate explanation.

The aim of present study is determination of drug-herb interaction between St. John’s Wort and sertraline in BSA and cell-culture medium by using HPLC-DAD and LC-Q-TOF/MS systems. In this study, HPLC-DAD was used for quantification analyses of sertraline, and LC-Q-TOF/MS was used for determination of any changes occur in phenolic composition of St John’s Wort. However, to investigate the biological effects in the cell culture medium for drug-herb combination, relative cell viability was determined by colorimetric MTT assay and cytotoxicity activity were tested with (Uppsala 87 Malignant Glioma) U87 cell line.

As a result, in this study, drug-herb interaction was examined in two different ways. Drug-herb interaction in BSA and cell-culture medium were observed.

Keywords: Drug-Herb Interaction, St. John’s Wort, Sertraline, HPLC, LC-QTOF/MS, Cell-Culture

References:

Acknowledgment
This work was supported by Republic of Turkey, Ministry of Development (Project Grant No: 2010K120810) and EGE-MATAL chromatography laboratories were used in this study.
Conformational Characterization of Protein-Polyelectrolyte Complexes Using Trapped Ion Mobility Spectrometry–Time-of-Flight Mass Spectrometry

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Coupling of ion mobility spectrometry with mass spectrometry (IM-MS) enhances the detail of analytical data. Performing analyses using these type of hybrid instrumentation provides quite important data on conformational features of molecules besides highly accurate mass spectrometric information. Trapped ion mobility spectrometry (TIMS) hybridized with mass spectrometry is a recent development in the field of IM-MS. An electric field is applied in TIMS funnel to hold ions in a flow of a gas. Following the ion trapping event, the electric field is gradually reduced by decreasing voltage to allow sequential elution of trapped ions with ascending mobilities. High resolving power and speed of TIMS allow the detailed conformational characterization of large biomolecules such as proteins. TIMS provides advantages for structure elucidation to interpret changes in shapes of proteins caused by changes in their molecular structure. The interaction of molecules with their surroundings is the major fact for designation of their functional characteristics. Secondary and tertiary structures of proteins are regulated by noncovalent interactions so that proteins can attain their specific functions in the dynamic systems of organisms.

In this study, various types of polyelectrolytes were interacted with proteins to manipulate their conformations. Polyelectrolytes are molecules comprised of a large number of functional groups that are charged or could become charged under certain circumstances. Therefore, they have the ability to interact with charged biomolecules such as proteins. Biocompatible polyelectrolytes such as poly-L-lysine, polyacrylic acid, polyglutamic acid, and polystyrene sulfonate were used in the study. The changes in the conformations of proteins due to their interactions with polyelectrolytes were monitored using TIMS-TOF-MS. It was obtained that the changes in the charge state of protein molecules according to their interactions with polyelectrolytes in noncovalent nature cause dramatic change in their conformations.

Keywords: Trapped Ion Mobility Spectrometry, Mass Spectrometry, Conformational Characterization, Polyelectrolytes.
Post-translational modifications of proteins, such as phosphorylation, glycosylation, acetylation, ubiquitination and the other various post-translational modifications allow the regulation of many cellular functions and intracellular signaling events. Ubiquitination is a very common post-translational modification that plays a key role in the regulation and degradation of many protein groups. Analysis of ubiquitination and polyubiquitination is one of the most active study area in the field of proteomics. Ubiquitination is actively involved in the onset and progression of diseases such as cancer, metabolic syndromes, neurodegenerative diseases (Alzheimer, Parkinson, Huntington), inflammatory disorders, autoimmunity (the formation of antibodies against their own antigens in tissues), infection and muscular dystrophy. Identification of ubiquitination sites and enlightenment of the binding mechanisms for understanding the functions of ubiquitinated proteins are crucial in the development of diagnostic and therapeutic methods for diseases. Since the level of posttranslationally modified ubiquitinated proteins are very low in cells compared to their native forms, the detection of ubiquitination and ubiquitination sites is quite difficult. Analyzes needed for high sensitivity for the determination of ubiquitination sites are performed by using mass spectrometric techniques, where the most accurate and reliable results can be obtained in analyzes following a suitable enrichment method prior to the mass spectrometric analyses. In the scope of this study, a significant increase in the number of detected ubiquitinated proteins was observed after the enrichment studies performed with the immunoaffinity precipitation. Therefore, it was decided that an efficient enrichment method for ubiquitination detection assay is required for the trypsin digested peptides. Finally, enrichment studies of the monoubiquitinated Histon 2B peptide on potential surfaces that could be used to enrich the ubiquitinated peptides have been carried out. For further studies, the most suitable surface on which the signal of the ubiquitination site can be observed in the mass spectra has been determined.

**Keywords:** ubiquitination, proteomics, mass spectrometry, Histon 2B, peptide enrichment, surface
Factor VIII (FVIII) is a glycoprotein cofactor that serves as a critical component in the intrinsic blood coagulation pathway. Deficiency of FVIII causes hemophilia A, the most commonly genetic bleeding disorder. Although it is passed down from parents to children, about 1/3 of cases are caused by a spontaneous mutation, a change in a gene. aPTT is prolonged in the absence of FVIII. For this, it is used to diagnose factor deficiency. While this method is easy to implement, it is the disadvantage that it can detect low sensitivity and serious deficiencies of less than 5% only. Factor VIII activity is studied for the definitive diagnosis after determining aPTT extension and factor deficiency subject to this extension. Activity testing is mandatorily needed to demonstrate moderate and mild deficiencies.

The main medication to treat hemophilia A is concentrated FVIII product, called clotting factor, coagulation factor or simply factor. Recombinant factor products, which are developed in a laboratory with DNA technology. The use of recombinant factor in the world is increasing day by day. Regulatory bodies define different FVIII reference methods for product release testing in Europe (chromogenic method) and in the US (one-stage coagulation method) and yet FVIII reference methods have no global compatibility. Accurate determination of the amount of FVIII concentrates is important for calculating the dosage of the drug to be used by patients. Measurement of FVIII with a high sensitivity and reproducible method is also important for therapeutic drug monitoring in patients.

The main objective of this study is to develop a sensitive, reproducible and robust HPLC method to determine the dosage amount of the recombinant human coagulation FVIII. For the optimization of the method, four different columns (C4, C8, C18 and HILIC) were used with different mobile phase systems. The chromatographic method optimization parameters obtained will be shed light of other studies in order to measure FVIII level in plasma with high precision and accuracy.

**Keywords:** Recombinant human coagulation factor VIII, hemophilia A, HPLC

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**Acknowledgment**
This work was supported by Republic of Turkey, Ministry of Development (Project Grant No: 2010K120810) and EGE-MATAL Chromatography Laboratories were used in this study.
OP55- An Experimental Design Approach For The Solid-Phase Extraction Of Organophosphorus Pesticides From Water Samples

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Nowadays, organophosphorus pesticides used to increase agricultural yields are transported to underground and surface waters in various ways and pollute the water resources. These species, which are also present in the insecticide group, act as an acetylcholine esterase inhibitor. Because of the relatively high solubility of organophosphorus pesticides in water and their use in large, superficial or groundwater traces (µg / L), rapid, selective and accurate analytical techniques should be developed for their determination in water.

In this work, a solid-phase extraction (SPE) procedure using cartridges prepared from poly(divinylbenzene -N-methacryloyl-L-tryptophan methyl ester) poly(DVB-MATrp) microbeads was optimized for the extraction of organophosphorus pesticides from water. The poly(DVB-MATrp) microbeads synthesized by suspension polymerization were characterized by Fourier transform infrared spectroscopy (FTIR), elemental analysis, scanning electron microscopy (SEM) and swelling test. An experimental design was carried out for modelling SPE optimal extraction conditions of eleven pesticides. The three parameters studied were the flow rate, pH and adsorbent amount. Extracts were analyzed using gas chromatography equipped with a mass spectrometer (GC-MS). The optimal extraction conditions selected for the flow rate, pH and adsorbent amount were 4.6 mL/min, 6.3 and 0.365 g, respectively. The analytical procedure was validated for eleven pesticides. The linear range (1–50 ng mL⁻¹), correlation coefficients (0.9875–0.9997), detection limits (0.002–0.597 ng mL⁻¹), and precisions (0.69–4.27 % RSD, n=3) were determined. The technique was also applied to the enrichment of pesticides in environmental samples.

Keywords: organophosphorus pesticides, solid phase extraction, microsphere, GC-MS, preconcentration

References

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Scaling-Up of Dispersive Liquid-Liquid Microextraction for the Isolation of Piperine from Black Pepper

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Since its introduction by Assadi and his co-workers in 2006, dispersive liquid-liquid microextraction method (DLLME) has gained wide prominence among scientists due to its rapidity, simplicity, high recovery and environmental-friendliness [1]. In this study, DLLME was used for the extraction of piperine from black pepper followed by its determination using reversed-phase high-performance liquid chromatography with diode-array detector (HPLC-DAD).

Optimized DLLME conditions were scaled-up for preparative extraction of piperine from black pepper (i.e., 70 g). Optimum conditions were as follows: 1.0 mL of ACN (as a dispersive solvent), 200 µL of chloroform (as an extraction solvent), 8.0 mL of water, and 500 µL of 1.0 M NaOH. The mixture was sonicated for 10 min before it was divided into 15-mL portions for centrifugation (1 min at 6000 rpm) for phase separation.

Column chromatography was then performed for further purification of piperine from other matrix constituents in black pepper using silica gel as the stationary phase and manual gradient elution starting with 300 mL of toluene:ethyl acetate (90:10, %v/v), 200 mL (85:15), 200 mL (80:20), 100 mL (75:25), 200 mL (70:30), and 600 mL (60:40). A total of 130 fractions were collected and tested with thin-layer chromatography (TLC). In addition, HPLC chromatograms and UV Absorption profiles obtained with DAD were investigated to identify the analyte and the analyte-rich fractions. Those fractions (i.e., 46 to 63) were collected and evaporated to dryness using a rotary evaporator. A sample of the final yellow solid extract was analyzed using nuclear magnetic resonance (NMR) for characterization and structural elucidation of piperine using 1D-(1H- and 13C-NMR) and 2D-NMR (COSY, HSQC and HMBC).

The proposed scaled-up DLLME method followed by column chromatography resulted into 1.8 g of high-purity standard of piperine (>97%, w/w) as proven by NMR results. As compared with other conventional liquid-liquid extraction techniques commonly used for isolation of piperine, which include Soxhlet [2] and supercritical fluid [3] extractions, the proposed scaled-up DLLME method requires much smaller volume of organic solvents and extraction can be completed in a shorter time.

Keywords: Black Pepper, Dispersive liquid-liquid microextraction, Isolation, NMR, Piperine, Scaling-up.

References:

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A vortex assisted deep eutectic solvent based-liquid-liquid microextraction for the determination of caffeine in Turkish coffee samples by HPLC-UV

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Caffeine is a natural alkaloid widely used in food industry as the most favorable psychostimulant in beverages or foods for motor activation, mood changes, and cognitive/motor performances. Caffeine can have both positive and negative health effects. On the one hand, it is powerful stimulant of the central nervous system and also stimulates the cardiac muscle. On the other hand, its high amounts have noticeable irritation of gastrointestinal tract and might cause the “caffeinism” syndrome resulting anxiety, insomnia, irritability and headaches. Up to 300 mg of caffeine a day is considered safe for most healthy adults. It can be consumed daily with coffee, tea and energy drinks and also with pharmaceuticals. Therefore, the monitoring of caffeine's content in foods and drinks is an important challenge of food quality control.

The use of green solvents in different analytical applications minimizes or eliminates the environmental and health problems, which born of traditional toxic solvents as well as to decrease the process cost and evolve safety. Deep Eutectic Solvents (DESs) form by complexion of quaternary ammonium salt (usually choline chloride) together with a hydrogen bond donor (HBD). The formation of hydrogen bonding between the halide anion of choline chloride and functional groups of hydrogen-donor agent is responsible for the decrease in the freezing point of DESs in relation to the melting points of the individual components. DESs are superior in terms of the availability of materials, the ease of synthesis and the low toxicity.

In this study, a vortex assisted DES-based liquid-phase microextraction method for the determination of caffeine in Turkish coffee samples has been presented. Different DESs were prepared for determination of caffeine. This procedure involves the formation of DES by mixing choline chloride and phenol. Caffeine extraction into DES phase was detected by HPLC-UV. Some important parameters such as pH, DES volume and type, sample volume and vortex time were optimized to achieve maximum recovery. This developed method was demonstrated in the determination of caffeine in Turkish coffee samples.

References
The Role and the Benefits of Core-Shell Silica Particles in HPLC

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Core–shell silica particles are composed of a solid core and a porous shell. The core could be a single structure, linkage of group of spheres or even hollow shell filled in with small structures. The shell can be an uninterrupted layer or an aggregation of smaller spheres onto a bigger core sphere or aggregated core spheres. The idea of core-shell stationary phases was created by Horváth in 1967. He developed 40-50 µm particles covered by ion exchange resin, thus creating the first superficially porous packing material.

High performance liquid chromatography (HPLC) have been the most widely used tools for research and routine quality control of active pharmaceutical ingredients (API) both in academia and the industry. Generally, two different types of silica material preferred in HPLC based on their backbone. The fully porous silica particles comply with the essential criteria of analysis, but these particles show all the limitations of HPLC. One of the most challenging issue is the necessity of fast and efficient separation of the analytes in the mixture. However, in recent years, superficially porous silica particles have been increasingly used for highly efficient separation.

The current presentation included some of our recent studies that demonstrated the benefits of core-shell silica packing materials for the separation of drug active substances from their dosage forms and biological matrices from the perspective of column properties, system suitability test parameter results.

Keywords: Core-shell, HPLC, Pharmaceuticals, Validation

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Therapeutic drug monitoring (TDM) is the clinical practice of measuring specific drugs at designated intervals to maintain a constant concentration in a patient's bloodstream, thereby optimizing individual dosage regimens. It is used mainly for monitoring drugs with narrow therapeutic ranges, drugs with marked pharmacokinetic variability, medications for which target concentrations are difficult to monitor, and drugs known to cause therapeutic and adverse effects. Clozapine (CLZ) is classified structurally as a dibenzodiazepine derivative. It is known as an atypical antipsychotic agent and displays efficacy in management of schizophrenia and treatment of other psychotic disorders.

The aim of present work is to optimize, simple and rapid HPLC method for the determination of CLZ and its main metabolite norclozapine (NCLZ) from human plasma samples. Liquid–liquid extraction of the CLZ and NCLZ were easily performed through isoamyl alcohol-hexane mixture. In order to achieve the best extraction efficiency, the effective parameters involved were optimized. The optimal conditions used in the extraction process were provided with 8 mL of isoamyl alcohol-hexane mixture (5:95). The chromatographic conditions included a mobile phase consisted of buffer solution (%1 H₃PO₄, %1 (C₅H₅)₃N, pH 3.0), and acetonitrile (70:30) with a flow rate of 1.0 mL min⁻¹ with the detection wavelength of 260 nm. Under these optimum experimental conditions, the proposed LLE-HPLC-UV technique provided a good linearity for CLZ and NCLZ with the correlation coefficient (R²) higher than 0.998. The limit of quantification (LOQ) and limit of detection (LOD) were calculated as 11.5 – 14.6 ng mL⁻¹ and 3.8 – 4.8 ng mL⁻¹, respectively.

Keywords: Therapeutic Drug Monitoring, Clozapine, Norclozapine, HPLC, Validation

Acknowledgment: This study was supported by the Ankara University Research Projects Unit with the project number of 18L0217001
OP60- Pharmacokinetic profiles of metamizole metabolites in Horses

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Abstract-Metamizole (sodium N-[2,3-dimethyl-5-oxo-1-phenyl-3-pyrazolin-4-yl]-N-methylamino] methanesulphonate) (MS), also known as dipyrone, is a pyrazolone derivative. This is one of the strongest nonopiod analgesic drugs, used in both human and veterinary medicine for the treatment of pain and fever. The 4 major metabolites of metamizole are 4-methylaminoantipyrin (MAA), 4-amino-antipyrine (AA), 4-acetyl-amino-antipyrine (AAA) and 4-formyl-amino-antipyrine (FAA). According to the WADA’s (World Anti-Doping Agency), non-steroidal anti inflammatory drugs (NSAIDs) are not included in list enacting of doping substances and methods because of they have been abused in horse racing. So, restricted the use of non-steroidal anti-inflammatory drugs used in the treatment of injuries of racing horses (1-2). The aim of this study was to determine the pharmacokinetics of MS from NSAIDs in Arabian horses (Equus ferus caballus) which is a very important source for our country economy, by the intramuscular (IM) and intravenous (IV) route of the drug.

In this study; In total, 14 (7 female, 7 male) purebred Arabian horses were used in order to obtain a balanced balance. The horses received a single IM dose of 25 mg / kg metamizole and 30 day later, a single IV dose of 25 mg / kg metamizole. The analyses in blood plasma were determined by HPLC. The blood (10 mL) was collected via previously inserted catheters at assigned times at 0 minutes before the application and 15, 30, 45, 60, 90th minutes, 2, 3, 4, 6, 8, and 12th hours after the application. Pharmacokinetic parameters (EAA, C_{doruk}, t_{doruk}, OKZ, t_{1 / 2λz}.) were determined from plasma concentration-time graphs.

The used method was validated. Calibration for all metabolites; calibration graphs was linear between 0.01-100 μg/mL (r²≥0.999); the recovery values detectable between 82.7-98.5%; the detectable limit: 4.11-13.61 μg/mL. The pharmacokinetic parameters were calculated for the MAA metabolite in female horses following intravenous administration include C_{max}: 107.10 ± 5.55 μg/mL, t_{max}: 0.25 ± 0.00 hours, t_{1 / 2λz}: 6.81 ± 2.56 hours, OCS: 5.93 ± 0.69 hours and EAA: 194.42 ± 4.77 with μg/mL. As a result of all these evaluations; the pharmacokinetic parameters were compared after administration by IM and IV. Results were shown statistically significant differences (P<0.05). The effective metabolite MAA reached the highest concentration in plasma as soon as possible.

Keywords: Metamizol, Pharmacokinetics, Metabolite, Arabian Horses, HPLC

Acknowledgement: This study was supported by Inonu University BAP office with TYL-2018-1044 project number.

References


Different compounds of calcium phosphates are essential materials in medical implants because of its unique properties and hydroxyapatite (HAp) is the most widely used of the calcium phosphates. Its ability to accommodate defects and tendency to substitute Ca and P with other elements in the chemical structure leads to need accurate control of the chemical composition. One of the most important HAP quality indicators is the Ca/P molar ratio – a numerical value that is strictly fixed within a narrow interval. There is a great variety of methods for determining this ratio, both multi-element methods and individual detection methods. Each method has its own specifics, strengths and weaknesses, and, consequently, the effectiveness of different applications depends on the objective and the required accuracy of the HAp analysis. This is why the main goal of the current research was to develop new total reflection X-Ray fluorescence method for the fast and simple quantification of Ca and P in hydroxyapatites. TXRF method in practice was compared with most popular classical (gravimetry and titrimetry) and instrumental (inductively coupled plasma optical emission - ICP-OES, flame atomic absorption spectrometry – FAAS; wavelength dispersive X-Ray fluorescence – WD-XRF) methods.

Our study provides the framework for a new TXRF method for accurate and precise quantification of calcium and phosphorus in HAp. It was demonstrated that vacuum atmosphere for analyzed HAp sample drying on a quartz carrier provides a powerful tool in improvement of calcium and phosphorus quantification results in HAp by means of TXRF method. Internal standard method in its classical expression is not suitable for Ca/P ratio determination in HAp due to low sensitivity of phosphorus. Considerable insight in obtaining a high accuracy and precision of phosphorus mass fraction determination (up to ±0.018%) using TXRF method has been gained by a simultaneous use of internal standard method and standard addition method.

It can be concluded that developed TXRF method is sufficiently accurate and precise and could be applied for routine analyses in quality control of different HAp. Quantification results of TXRF analysis were in a good agreement and somewhat superior to other modern and classical analytical methods.

**Keywords:** hydroxyapatite, calcium, phosphorus, classical and instrumental analysis methods

**References.**


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OP62 - Distribution of Elements in Milk Samples: The Single Step Fractionation Approach

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Milk is one of the important dairy food for human and serves many nutrients including trace elements required for growth. In terms of prediction of element availability in food, fractionation analysis is helpful for understanding element distribution. In this purpose, a sequential but laborious separation procedure was suggested and applied, previously. In the present study, a single step analytical fractionation scheme was developed for minor and major element fractionation in milk samples prior to ICP-OES detection. The single step separation of lipid, protein and serum fractions were achieved using a mixture of ethyl ether, n-hexane and isopropyl alcohol. The suggested procedure was validated by the analysis of synthetic milk matrix and milk powder certified reference material (CRM). The recovery values for main constituents were between 95.9 – 103.6%. The suggested single step fractionation method was applied on various whole and semi-skimmed milk samples to determine minor and major elements.

Keywords: element fractionation, milk, ICP-OES

References

OP63 - Solid Phase Extraction of Cu$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$ using by N-N’-bis(5-methoxsalicylidene)-2-hydroxy-1,3 propanediamine modified silica gel

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Separation of matrix and trace element prior to analysis and preconcentration may be required to overcome detection problems of trace elements and to increase sensitivity. Recently, solid phase extraction (SPE) is generally used as rapid, easy, cheaper and eco-friendly preconcentration method. In this study, it is aimed solid phase extraction of Cu$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$ with N,N’-bis(5-methoxsalicylidene)-2-hydroxy-1,3 propanediamine modified silica gel resin from aqueous samples. In extraction studies, parameters such as contact time, pH of sample, sample flow rate, sorbent amount, sample volume, type and concentration of eluent and flow rate of eluent was examined and extraction conditions was optimized. The preconcentration studies were performed at pH 4.0 and the analytes were eluted with HNO$_3$ solution. Additionally, selectivity of the proposed method was tested with various anions and cations. The validity of the proposed method was tested with ERM-CA022a standard reference material. The developed method was suggested as alternative preconcentration method for Cu$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$ in various natural samples. The measurements were carried out by ICP-OES.

Keywords: multi element preconcentration, solid phase extraction, Schiff base, ICP-OES

References
**OP64- Removal of Cadmium (II) in the aqueous solutions by biosorption of *Bacillus licheniformis* isolated from soil in the area of Tigris River**

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**Abstract**-Biosorption by death bacteria is an alternative and effective method for the removal toxic elements from drinking water and waste water (1-2). The biosorption of Cd(II) from aqueous solutions was studied in a batch method by using death bacteria *Bacillus licheniformis* sp., extracted from soil in the area of Tigris River. The Cd element analysis was determined using ICP-OES. The maximum adsorption capacity of biosorbent was determined as 8.28 mg Cd/g, in the optimum condition pH 5.5, 90 min. at 25 °C, in 50 ml solution with 5.0 mg/L of initial concentration. The characterization of *Bacillus licheniformis* to describe behaviour of bacteria was determined such as adsorption isotherm, kinetic and thermodynamic data using FT-IR, TGA, DTA, SEM and EDX. The results suggested that the most equilibrium data of Cd(II) bioadsorption was best represented by the pseudo second order equation and Langmuir isotherm model at different time-temperatures. While ΔH° and ΔS° was obtained as 76.01 kj/mol and 239.11 kj/mol respectively, ΔG° had a low value (4.76 kj/mol). Therefore; the reaction mechanism of biosorbent was found to be endothermic from values of ΔG<0, ΔH>0 and ΔS>0. This study show that *Bacillus licheniformis* sp. having low cost can be used as an effective biosorbent for toxic element Cd(II) removal from drinking water and waste water.

**Key words:** *Bacillus licheniformis*, Biosorption, Tigris river

**References**
Palladium is one of the six metals in platinum group and had extensive usage area such as fuel cells, automobile, dental crowns and catalysts in drug synthesis\(^1\). In the consequence of its wide usage in various industries, the contamination having several effects on plants, animals, and human has raised in water sources and soils\(^2\). This study describes the selective and sensitive analytical method for the determination of palladium at trace levels with dispersive liquid-liquid microextraction prior to slotted quartz tube-flame atomic absorption spectrophotometry. N,N-dimethyl-4-[(1-naphtylimino) methyl]aniline was synthesized from the reaction of 4-(dimethylamino)benzaldehyde and 1-naphtylamine and used as a complexation reagent. All the experimental parameters that may affect the efficiency of extraction process were optimized step by step while the other variables was kept constant. After the optimization of complexation, extraction and instrumental parameters, the analytical performance of the analytical determination method was determined. Under the optimum conditions, limit of detection, limit of quantification and percent relative standard deviation were obtained as 0.009 mg L\(^-1\), 0.032 mg L\(^-1\) and 4.84\%, respectively. According to the detection limit of the conventional FAAS system, about 20 folds enhancement was obtained in detection power. In addition, accuracy and applicability of the developed system were tested with spiked recovery study on well, lake and tap water samples.

**Keywords:** Schiff base ligand; palladium; atomic absorption spectrometry; SQT; dispersive liquid-liquid microextraction

**References**

Iron is an important trace element for animals and plants affecting the photosynthesis, chlorophyll and carbohydrate formation for plants. For this reason, it is fundamentally important to determine iron at trace level. In order to improve the detection power of the system, some external attachments could be used. Slotted quartz tube increases the sensitivity of the flame atomic absorption spectrophotometry system by increasing the residence time of the atoms in the light path. A new method based on the combination of switchable solvent microextraction (SSME) and improved spectrophotometric detection (SQT) was proposed for the iron determination. A proper ligand was synthesized from the reaction of orto-fenilendiamin and 5-bromosalicylaldehye. All experimental variables were optimized to increase the extraction efficiency for iron. The calibration graph was linear in the range of 30.0-750.0 ng/mL and the percent relative standard deviation was 2.1%. Under the optimum conditions, limit of detection (LOD) and limit of quantification (LOQ) were 6.50 ng/mL and 25.0 ng/mL, respectively. Based on the LOD comparison with the conventional FAAS system, 35 fold enhancement was recorded. In order to check the accuracy of the developed method, recovery experiments were performed and satisfactory results in mineral spring waters were obtained.

**Keywords:** Iron; switchable solvent microextraction; flame atomic absorption spectrophotometry; slotted quartz tube

**References**
OP67- Sensitive and Accurate Determination of Butyltin Compounds in Fish and Mussel Samples by Vortex Assisted Dispersive Liquid-Liquid Microextraction-Gas Chromatography-Mass Spectrometry

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Organotin compounds possess several toxic properties even at trace levels for both aquatic organisms and human bodies. However, these compounds are used in various industrial areas causing contamination in marine life. In this study, a sensitive and selective analytical method for the determination of monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) compounds at trace levels has been developed. Sodium tetraethylborate (NaBEt₄) was used in the derivatization of the analytes in an aqueous solution and then dispersive liquid-liquid microextraction (DLLME) was employed to extract the derivatized analytes from the sample/standard matrix. Univariate approach was carried out to optimize some variables such as type of extraction solvent, type of dispersive solvent, volume of buffer solution, mixing period and derivatization period. In addition, experimental design was applied to determine optimum amounts of extraction solvent, dispersive solvent and derivatizing agent. Analysis of variance (ANOVA) was used to evaluate the significance of experimental variables and their interactions. Under the optimum conditions, the limits of detection for MBT, DBT and TBT were found to be 0.4, 0.6 and 0.5 µg/kg, respectively. The analytes were not found or below their detection limits in fish and mussel samples analyzed. The developed method was also applied to a mussel sample spiked at 5.0 ng/mL to investigate the accuracy/applicability of the developed method. Recovery results for the mussel sample were ranged between 94.9-112.6%.

Keywords: Monobutyltin; dibutyltin; tributyltin; dispersive liquid-liquid microextraction; GC-MS

References
Cobalt is known to be essential not only for human beings but also for numerous living organisms at trace levels. Cobalt deficiency results in some diseases including anemia, metabolic disorders, retarded growth and degeneration of nerve cells. In this study, preconcentration of cobalt was carried out with deep eutectic solvent based liquid phase microextraction for trace determination by a slotted quartz tube (SQT) attached flame atomic absorption spectrometry (FAAS) system (DES-LPME-SQT-FAAS). Choline chloride and phenol in a 1:2 ratio was used in the preparation of a green solvent to extract cobalt from the aqueous sample/standard solution. Key parameters that influence the extraction efficiency of cobalt were examined and optimized. Under the optimum conditions, linear dynamic range of the method was found between 5.0-50.0 µg L⁻¹, and the limits of detection and quantification (LOD and LOQ) were calculated as 2.0 and 6.6 µg L⁻¹, respectively. The detection power of the conventional FAAS was improved upon by 67 folds using the DES-LPME-SQT-FAAS method under the optimum conditions. The proposed method was successfully applied for the determination of cobalt in linden tea samples, and the recovery results obtained for different spiked concentrations were found to be very close to 100%.

**Keywords:** Cobalt; deep eutectic solvent; liquid phase microextraction; flame atomic absorption spectrometry

**References**
The using of laser ablation in combination with ICP–MS for the determination of major, minor and trace elements as well as isotopic ratios in solids and liquids has grown over the past decade. This sample introduction system, now mainly operating with UV laser light at different wavelengths, is one of the most versatile micro-analytical techniques currently available in the field of inorganic trace element analysis. There are several advantages using laser ablation as a sampling technique: Almost no sample preparation and no contamination from solvents and acids, less interferences due to the absence of solvents and acids, spatial resolution to as low as few μm (1-2 μm) are possible, elemental and isotopic information are obtainable, limits of detection are superior to other solid sampling techniques and the speed of data acquisition allows large quantities of samples to be analyzed within reasonable time. Although laser ablation has many advantages, the biggest disadvantages of this technique is quantitative analysis. Quantitative analysis by laser ablation ICP-MS is difficult to achieve for many sample types. This reflects a lack of suitable standards which ideally, though unobtainably, need to be identical to the sample both chemically and physically on all relevant spatial scales. Accurate results are generally obtained only when the sample and the standard are prepared in the same matrix. Various strategies have been investigated in order to obtain matches between samples and standards. However, still the most commonly used calibration standards are the NIST reference glasses. In this study, fusion discs are used as calibration standards. The prepared fusion discs were checked in terms of the homogenity and some important laser parameters; laser energy, laser frequency, scan rate, carrier gas flow and aperture size were optimized. The method has linear working ranges of 30-1000 mg/kg for Br and 120-1600 mg/kg for Sn. Method’s precision values were calculated as 6 % for Br and 12 % for Sn. The uncertainties of method were estimated as 20% for Br and 28% for Sn and then for 95% confidence interval, the reliability ranges of the method were found as 408-612 mg/kg for BFRs terms of Br concentration and 720-1280 mg/kg for OTCs terms of Sn concentration.

The results obtained have shown that this technique can be used for screening of plastics materials in terms of polybrominated flame retardants and organotin compounds which are under regulation by most of the countries especially in EU countries. Besides the LA-ICP-MS method can be used for heavy metals (Cr,Cd, Pb and Hg) analysis in platics with optimization of some laser parameters and also using LA as an extraction technique some plastic additives can be screened by GC-MS.

Keywords: plastic materials, flame retardants, organotin compounds, LA-ICP-MS, GC-MS

Acknowledgement: We are grateful to the management of TUITAK-BUTAL. In addition, we extend special thanks to Assoc. Prof. Dr.M. Akif ÇİMENOĞLU, Senior Researcher Anıl ÇETİNOĞLU and Dr.Peter WINSHIP for their valuable contributions.

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1- RoHS Restricted Substances, www.rohsguide.com/rohs-substances.htm-( access date:02/09/2015)
Mosquitoes represent one of the most significant threats to human and veterinary health throughout the world. The mosquito *Aedes aegypti* (L.) is a primary carrier of viruses causing dengue fever, dengue hemorrhagic fever and yellow fever in the tropical and subtropical regions of the world. Personal protection is one method to prevent viral transfer through mosquito bites. Monoterpenoids have been studied as candidate insecticides for many years; however, their mode of action is not yet fully understood. In this study, we investigated the repellent efficacy of three monoterpenoids (menthol, carvacrol and guaiacol) and their esters combined with amino acids (GABA and glycine).

Repellent activity of monoterpenoid esters (1-6) with neurotransmitter amino acids (GABA and glycine) was investigated against *Aedes aegypti* by using a “cloth-patch” assay and compared to reference standard *N*,*N*-diethyl-3-methylbenzamide (DEET). Monoterpenoid esters showed repellent activity with minimum effective dosages (MED) in the range of 0.031-0.469 mg/cm$^2$. The carvacrol ester of GABA (2, MED of 0.031 ± 0.008 mg/cm$^2$) exhibited the highest repellency of six monoterpenoid esters tested in comparison to the standard repellent DEET (MED of 0.009 ± 0.002 mg/cm$^2$); however, the repellent activity of carvacrol-glycine ester (5) decreased 4-fold compared to the carvacrol-GABA derivative (2). The repellent activities of menthol GABA (1, MED= 0.375 ± 0.000 mg/cm$^2$) and glycine ester (4, MED=0.312 ± 0.063 mg/cm$^2$) were similar. The guaiacol-glycine ester (6) was 3.75-fold more efficacious than the guaiacol ester of GABA (3). In the present study, we report repellent efficacy of prolonged exposure to GABA and glycine esters of menthol, carvacrol, guaiacol (1-6) as compared to the repellent activities of their monoterpeno moieties alone.

**Keywords:** terpenoids, GABA, repellent activity
Metabolomics Studies in Urine Samples Prepared by Thin Film Extraction Method

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For the early diagnosis of diseases, the biological matrix of blood, sweat, saliva and urine protein groups, tumor antigens, peptides, DNA and RNA and some genes expression, and metabolic products1 is monitored as a biomarker. The metabolomics studies of human body for biomarker selection is one of the popular studies in recent years. While the metabolomics studies in biological matrix are examined, biomarker groups are mostly analyzed by liquid and gas chromatographic techniques. The sensitivity of these techniques were improved using mass spectroscopic detectors (MS, MS / MS, QTOF, MALDI TOF) 2. However, the most important problem for the clinical use of these assays is the use of preconcentration and pre-separation methods that can lead to desired sensitivity, support the diagnosis in the biological environment and provide the reproducibility.

Present study describes thin film extraction procedure for eighteen including amino acids and organic acids in urine. Collected urine samples were placed in 96 well plates (96WP) system which contains a different structures of thin film plated blades to be executed on the adsorption of metabolites types of different chemical structures and polarities. Then the adsorbed metabolites were desorbed in a suitable solvent within a small volume and analyzed with LC-MS/MS system. Different surfaces of 96WP blades namely, multiwall carbon nanotube modified polyacrylonitrile (MWCNT-PAN), single wall carbon nanotube modified PAN (SWCNT-PAN), butylmethylchlorosilane (C4-PAN) oktyldimethylchlorosilane (C8-PAN) and octadecyldimethylsilane (C18-PAN) and silisyum dioxide modified PAN (SiO2–PAN) were utilized in fast microextraction of metabolites in urine.

Calibration curves were linear with correlation coefficients above 0.98. The RSD values were changed in the range of 5 – 17%. The detection limits were in the range 0.02-0.97 mg mL$^{-1}$. The accuracy of the method was tested with spiked urine samples.

Keywords: Metabolites, Thin film extraction, Urine

References:

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OP72- The Level Of Some Vocs In Breath Of Asthma Patients And Healthy Subjects


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Asthma is one of the most common causes of chronic airway disease in the community, and a fully controlled treatment of the disease depends on early diagnosis. Many studies have reported that VOCs exposure is an important cause of asthma, pneumonia, pulmonary edema, and other lung diseases (1). In fact, the concentration of certain volatile organic tracers (VOCs) in breath (so-called breath markers) can be related to physiological and pathological conditions (2). Breath analysis is an emerging field aiming for the next generation of hand-held and non-invasive medical diagnostic and monitoring devices.

The needle trap device (NTD) technique is a new microextraction method for sampling volatile organic compounds (VOCs) from various types of samples such as air, breath or urine. NTD technique is suitable for laboratory automation and on-site sampling compatibility with convenient coupling to analytical instrumentation.

In this study, NTD based sensitive analysis method was developed and applied for the analysis of volatile organic compounds in healthy subjects and asthma patients. The study includes approximately 50 healthy subjects and 100 asthma patients.

**Acknowledgement**: The authors gratefully acknowledge the Turkish Ministry of Science TUBITAK (116S196) and Ege University for financial support.

**References**
OP73 - Flow Injection Amperometric Sensor for the Determination of Formaldehyde based on its electrocatalytic Oxidation at Cu Nanoparticles Modified Graphite Pencil Electrode

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Studies on formaldehyde detection have been found a great attention in recent years, because it is a very important compound which is used in many industrial areas such as electroleless copper plating, textile, food, wastewater processing. In addition, its anodic oxidation has found high interest for fuel cell applications. On the other hand, exposure to formaldehyde can cause health risks in human due to its toxic and sensitizing properties [1]. Therefore, many sensors have been developed for formaldehyde detection in the last decades. One of the most widely used analytical methods to detect formaldehyde is the electrochemical sensors based on the electrocatalytic oxidation of formaldehyde. So, various types of electrodes modified with metal or bimetal nanoparticles such as Au, Pd and Cu-Pd have been efficiently used for amperometric or voltammetric determination of formaldehyde based on its electrocatalytic oxidation [2]. In this study, Cu nanoparticles (CuNPs) modified graphite pencil electrode (GPE) was used for electrocatalytic oxidation of formaldehyde and its amperometric detection in flow injection analysis (FIA) system. CuNPs were electrochemically deposited by recording 25 successive cyclic voltammograms of GPE in the presence of 0.01M Cu(NO₃)₂ and 0.1 M KNO₃ in the potential range from -0.7 to 0.8V with the scan rate of 25 mV s⁻¹ [3]. The recorded SEM images presented in Fig. 1A showed that CuNPs were successfully formed onto GPE surface. Fig. 1 B shows cyclic voltammograms (CVs) of formaldehyde at CuNPs/GPE in 0.1 M NaOH. It can be seen that an irreversible oxidation peak of formaldehyde was observed at about +600 mV at CuNPs/GPE and peak current increased by increasing of formaldehyde concentration. However, any peak was not observed at bare GPE for electrochemical oxidation of formaldehyde (data not shown). These results indicate that the CuNPs/GPE exhibits a good electrocatalytic activity toward oxidation of formaldehyde. In the final step, amperometric determination of formaldehyde was performed in FIA system under optimized conditions. Analytical figures of merit such as linearity range, limit of detection, sensitivity etc. were determined and compared with previously published studies.

Fig. 1. A) SEM image of CuNPs/GPE B) Cyclic voltammograms of CuNPs/GPE in the presence of various concentrations of formaldehyde (0.0 (a), 2.0 (b), 4.0 (c) and 6.0 (d) mM)

Keywords: Formaldehyde, electrocatalytic oxidation, Cu nanoparticles, graphite pencil electrode, flow injection analysis

References:
ABSTRACT- This work aims a review of voltammetric studies on the ophthalmic drugs of various clinical classes published in the last decade. The emerging new technologies add new drugs to the literature and electroanalytical chemistry offer new possibilities for the determination of these drugs. Ophthalmic drugs are widely used in clinical practice for both diagnosis and treatment. It is crucial to determine the trace amounts of ophthalmic drugs considering the usage of very low dosage. Thus, voltammetry as an analytical method offers significant advantages of low detection limit, high sensitivity, low cost and rapid determination. To achieve this goal, we searched literature for the ophthalmic drugs investigated via voltammetry and the keywords were limited to “determination, voltammetry, electrochemistry and electroanalytical methods”.

More than 145 articles were reviewed under seven major groups (antibiotics, antivirals, non-steroidal anti-inflammatory drugs, anti-glaucomatous drugs, steroidal drugs, local anesthetics and miscellaneous) for 33 drugs. The types of voltammetric techniques and electrodes, pHs, peak potentials, limit of detections (LOD), limit of quantifications (LOQ), linearity ranges, analytical samples and interference effects were compared for the electrochemical determination of these drugs.

Voltammetric techniques are also an important tool in the elucidation of electrode reaction mechanism and in this review, the electrode reaction mechanism of a number of ophthalmic drugs has been involved, as seen in the following proparacaine drug¹.

Keywords: Ophthalmology, Ophthalmic Drugs, Electrochemistry, Voltammetry

References:

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OP75- HPLC Method Development and Validation for the Simultaneous Analysis of Multivitamins in Pharmaceutical Dosage Forms: In Perspective of Industrial Requirements

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According to regulatory requirements, it is expected that the analytical methods, used for stability monitoring of pharmaceutical dosage forms, must accurately and precisely measure active ingredients (drug substance or drug product) and process or drug substance related impurities without interferences1,2. Such a method can allow monitoring results during stability studies and may guarantee safety, efficacy and quality of the pharmaceutical dosage forms. In this study, a fixed dose multi-vitamin tablet containing vitamin B1, B6, B12 and thioctic acid were formulated using a wet granulation process. The drug content, content uniformity, hardness, friability, disintegration time, thickness and in vitro dissolution tests were performed in order to evaluate in vitro quality parameters of the finished tablets. The content uniformity and in vitro dissolution profiles of the tablets must be also evaluated according to regulatory requirements. Therefore, we developed and validated two stability indicating HPLC methods for the analysis of vitamins in the tablets. The second method was used the analysis of vitamin B12 because of its low concentration. In order to show the suitability of the methods, forced degradation studies were performed at high temperature, acidic, basic, and oxidative conditions. In all cases, 5-15% degradation for each of the vitamins was obtained. The chromatographic conditions (column type, mobile phase pH and composition, gradient elution program, wavelength and injection volume) were optimized in order to achieve enough separation capability for requirements of the guidelines. The optimum chromatographic separations were achieved with ODS-3 C18 column (150 × 4.6 mm, 5 μ), using mobile phase containing acetonitrile and 50 mM phosphate buffer pH 2.5 in gradient elution profile. The flow rate was kept constant at 2 mL/min and eluent was detected at 220 nm (nm for B12). At the optimum conditions 4 vitamins and around 20 impurities (including forced degradation products) were successfully separated (resolution >1.5) from each other. Validation studies proved acceptable accuracy and precision of the method. Also, there was no interference of the excipients and degradation products at the retention time of vitamins, indicating the specificity of the methods. The robustness of the methods was tested using a statistical experimental design. Finally, the developed method was successfully applied for the content uniformity and in vitro dissolution tests of the tablets.

Keywords: Vitamin, HPLC, validation, forced degradation, stability indicating, dissolution, content uniformity

References:
**OP76- TLC based chiral separation of amino acids onto β-cyclodextrin incorporated glutaraldehyde cross-linked polyvinyl alcohol electrospun fiber stationary phase**

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Simpler and economical methods for chiral separations are always needed in synthesis, drug development, and as biomarkers besides many other useful applications. Cyclodextrins are chiral host molecules and have been used to separate number of chiral analytes, however, always used as mobile phase additives in thin layer chromatographic based applications. In this study, we have successfully prepared beta-cyclodextrin (β-CD) incorporated polyvinyl alcohol (PVA) electrospun based stationary phase and applied those in chiral separation of serine and histidine. As prepared sheets of β-CD incorporated GA cross linked PVA electrospun fibers were characterized by FTIR and SEM; then used for separation of amino acids. Amino acids were detected by spraying ninhydrin solution. Among various solvent systems employed, it was found that chiral separation of serine isomers with resolution of 1.6 was possible with mobile phase 4:5:5:0.5:1.5 (v/v/v/v/v) ethanol: butanol: ethyl acetate: water: acetone and histidine isomers with resolution 1.4 was possible with mobile phase in 4:5:4.5:0.5:1.5 (v/v/v/v/v) ethanol: butanol: ethyl acetate: water: acetone. However, the migration behavior and retention time was influenced by the morphology and thickness of fibers.

**Keywords:** Chiral separation; amino acid; thin layer chromatography; electrospun fibers; stationary phases
Determination of Ethylmalonic Acid in Urine by Capillary Electrophoresis with Capacitively Coupled Contactless Conductivity Detection

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Abstract - Ethylmalonic acid (EMA) is a biochemical metabolite for disorders that are seen in inborn error metabolism. This metabolite accumulates in blood or urine. We developed an inexpensive and simple capillary electrophoretic (CE) with capacitively coupled contactless conductivity detection (C\textsuperscript{4}D) method for the quantitative determination of EMA in urine samples. The electrophoretic conditions were optimized using 50 mM MES-Tris and 0.14 mM CTAB at pH of 6.5 as buffer solution. The separation was carried out at reversed polarity mode using a cationic surfactant as the buffer additive. Under these conditions urine samples were directly injected to the capillary without any pretreatment step. The analytical parameters of the method as linearity, precision, and detection and quantification limits were also investigated. The proposed method was applied to the determination of EMA in urine samples.

Keywords: Capillary electrophoresis, Contactless conductivity detection, Ethylmalonic acid, urine.

Introduction

The high amounts of EMA in urine is observed in patients with disorders of mitochondrial fatty acid oxidation, including short chain acyl-CoA dehydrogenase (SCAD) deficiency ethylmalonic encephalopathy syndrome, glutaric acidemia type II (deficiency of electron transfer flavoprotein). Besides muscle weakness, cardiomyopathy, and liver disease, many of these patients have neurological dysfunction with severe central nervous system involvement\textsuperscript{1}. The symptoms of these disorders are neurological dysfunction with severe central nervous system involvement, muscle weakness, cardiomyopathy, and liver disease. The present of EMA in urine can be result in death in first years of child because early diagnosis in newborn patients is important.

The determination of EMA in urine samples is usually performed by gas chromatography-mass spectrometry (GC-MS). However, the GC method needs a tedious sample pre-treatment step and the analysis is time consuming. CE is suitable method to monitor the metabolic inborn errors\textsuperscript{2,3}. The advantages of CE method are high separation efficiency, excellent resolution, short analysis time, and low electrolyte and sample consumption. CE -C\textsuperscript{4}D offers a simple and highly sensitive detection method for many types of analysis\textsuperscript{4}. In this study, a rapid, reliable and simple CE-C\textsuperscript{4}D method for the determination of metabolite EMA in urine samples was developed.

Materials and Method

2-(N-morpholino ethanesulfonic acid (MES), Tris(hydroxymethyl)aminomethane (Tris), EMA and cetyltrimethylammonium bromide (CTAB) was purchased from Sigma-Aldrich. All other chemicals were of analytical grade.

EMA analysis were carried out with a commercial CE system by Prince Technologies (BV, Emmen, Netherlands) coupled with TraceDec Contactless Conductivity Detector. DAx 8.0 Data Acquisition and Analysis software (Netherlands) was used for data processing. Separations were carried out with fused silica capillary obtained from Polymicro Technologies (Phoenix, USA) with 25 μm internal diameter and total and effective lengths of 65 and 52 cm, respectively. All solutions were prepared in pure water obtained by Elga PurelabOption-7-15 (High Wycombe, UK) model system.

Standard solutions were stored at 4 °C. The sample of patient urine was provided by the Cerrahpaşa Medical Faculty. The urine samples were maintained at -20 °C. The buffer solution was prepared from MES by dissolving in ultra-pure water and the pH was adjusted to 6.5 by addition of Tris. The separation voltage was -28 kV at 25 °C. Injections of sample were carried out with pressure of 100 mbar for 30 s. Injections were performed from the cathodic side. The capillary was flushed successively by 0.1 M NaOH for 10 min, water for 5 min, and buffer for 10
min at the beginning of every working day. A washing step of 2 min with NaOH and buffer between runs was applied. TraceDec detector was set to 100% gain and the voltage applied by actuator electrode was -18 dB.

**Results and Discussion**

For C4D in CE it is necessary to use a buffer solution of low conductivity in order to obtain good sensitivity and to minimize the electrophoretic current. According to previous studies we have chosen MES-Tris buffer system as background electrolyte. pH was adjusted with Tris in order to prevent increase in ionic strength of buffer solution.

EMA is a weak organic acid and has lack of UV absorbance property because C4D is convenient technique for detection of EMA. Negatively charged species such as anions of low molecular mass organic acids have high electrophoretic motilities and long analysis times. Therefore, electroosmotic flow (EOF) is reversed to leads to short analysis times. For this purpose, an EOF modifier such as CTAB was added in the buffer in order to reverse the EOF.

The effects of pH and concentration of buffer were investigated on resolution and peak height of the EMA. In addition, the influence of the concentration of CTAB was studied. Optimum separation conditions were obtained as 50 mM MES-Tris, 0.14 mM CTAB and pH 6.5. Under these conditions, the analysis time was less than 5 min with good peak shape. The analytical parameters of method were evaluated such as linearity, precision, detection limit (LOD) and quantification limit (LOQ). The linear regressions of the calibration curves indicated good linearity (R2>0.99). The relative standard deviation (RSD) values were 3.4% for the peak area and 0.9% for migration time. LOD (S/N = 3) and LOQ (S/N = 10) values for EMA were about 0.431 mg/L and 1.436 mg/L respectively. The proposed method was successfully applied to determine EMA in urine samples, with very simple preparation procedure of the real samples.

**Conclusion**

In this study, a rapid, reliable and simple CE-C4D method for the determination of EMA in urine samples was developed. Samples were only diluted with water before injections. The method can be applied for clinical analysis of EMA in patients.

**References**


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A magnetic nanocomposite, Fe\textsubscript{3}O\textsubscript{4}-functionalized and with glutaraldehyde cross-linked chitosan (Fe\textsubscript{3}O\textsubscript{4}-CH), was prepared as an efficient adsorbent to eliminate heavy metal (Pb (II)) [1] ions from aqueous solutions. Magnetic nano particles (Fe\textsubscript{3}O\textsubscript{4}) was synthesized using the in-situ chemical precipitation method of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} under alkaline pH conditions. Fe\textsubscript{3}O\textsubscript{4}-CH composite was successfully prepared by means of a crosslinking reaction using glutaraldehyde as cross-linker [2]. The prepared composite was investigated by techniques including FESEM, TGA and XRD techniques. The Pb(II) concentrations in the solution before and after nano composite treatment were determined by an inductively couple plasma-mass spectrometry (ICP-MS). Because of the excellent metal chelating capability of chitosan, the Fe\textsubscript{3}O\textsubscript{4}-CH nano particles showed better adsorption capacity and faster adsorption rate for Pb (II) than those of pure Fe\textsubscript{3}O\textsubscript{4}. The average crystallite size of Fe\textsubscript{3}O\textsubscript{4} was found to be 18 nm. The adsorption equilibrium time was almost 60 min and the maximum adsorption capacity was 40.6 mg/g at 297 K. All the above results provided some insights into the design of efficient adsorbents with a wide prospect of application for metal contaminated wastewater treatment.

**Keywords**: Heavy metal, Magnetic Nano Particles, Chitosan, inductively couple plasma-mass spectrometry

**References**


Does Aroma Ingredients Define the Origin of Citrus Honey? The Chemometric Approach of Aroma Compounds of Citrus Honey collected from Antalya

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Abstract

The aroma is one of the most appreciated properties of honey. Aroma is also one of the most important factors in honey characterization and is useful for determining the source of honey and quality control. The objective of the present study was to characterize the aroma compounds of citrus honey collected from Antalya using SPME-GC/MS technique and the chemometric analyses of the aroma data. Thirty-two aroma components were identified in citrus honey samples. The major compounds were elucidated as lilac aldehyde A, B, and D except the honey collected from Serik. The main components of the honey from Serik were cis-linalool oxide and phenyl ethanol. The chemometric technique; namely, principal component analysis was applied to the aroma components percentage amounts using Minitab programme. The honey from Serik which was collected from 150 m altitude and far to sea discriminated from the others.

Keywords: Aroma compounds; Citrus honey; SPME-GC-MS; Chemometry

Introduction

Citrus honey is produced during flowering period by Citrus species. The Citrus species (Citrus sinensis L.) are important sources of nectar for the production of citrus honey. The bitter orange (Citrus bigaradia L.), tangerines (Citrus reticulata) and lemons (Citrus limon) are contributed producing of the citrus honey, as well. This type of honey is distinguishable for its intense aroma, having a characteristic mild flavor, light amber color, crystallizing rather quickly. It is preferred by the people due to its aroma. In this study, we aimed to study the aroma compounds of citrus honey collected from 36 locations of 6 districts of Antalya. The goal of the study is to search the definition of origin of citrus honey samples.

Materials and Method

The citrus honey samples provided from 36 locations (Finike, Kumluca, Kumluca 150 m altitude, Manavgat, Serik 175 m and Konyaaltı district of Antalya/Turkey), which is produced under control within the scope of the project (TÄGEM-17/ARGE/13), has been chosen as the material of this study.

Aroma components of honey were determined using HS-SPME-GC/MS technique. In order to determine the aroma components of the honey, 10 grams of honey were diluted with 10 mL of distilled water and 1 gram of magnesium sulfate was added to the product to be homogenized by means of a magnetic stirrer. The mixture was maintained by ultrasonic bath extraction for 30 min. In SPME extraction, Divinylbenzene / Carboxen / Polydimethylsiloxane (DVB / CAR / PDMS) was used as the adsorbent. For GC-MS analysis; Varian Saturn 2100T (USA) coupled with ion trap mass spectrometer coupled with HP-5MS non-polar silica capillary column was used. Helium was used as carrier gas using electron ionization method. NIST07 library data, standard component comparison, peak area detection, retention times, etc. The oven temperature was kept at 60°C for 5 minutes. It was removed up to 200°C at 4°C / min and kept at 200 ° C for 5 minutes.¹

Results and Discussion

The aroma compounds of citrus honey collected from six different districts of Antalya were given in Table 1. Thirty-one compounds were detected and all of them were identified using, literature comparison, authentication compounds and Wiley MS spectral data library. The lilac aldehyde A, B, and D were the major aroma compounds in honey samples particularly collected at zero altitude. The cis-Linalool oxide was the major in the sample collected from Serik while Linalool
was in the sample collected from Kumluca (150 m altitude). The compounds more than 5% was highlighted in Table 1. Herein the main components look like very similar except the honey collected from Seric at 175 m altitude. The main compounds of the last one were cis-Linalool oxide and Phenyl ethanol.

**Table 1. Aroma compounds of citrus honey (%)**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Finike</th>
<th>Kumluca</th>
<th>Kumluca (150 m)</th>
<th>Manavgat</th>
<th>Serik (175 m)</th>
<th>Konyaalti</th>
<th>MAX</th>
<th>MIN</th>
<th>MEAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
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<td>0.87</td>
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<td>0.98</td>
<td>0.01</td>
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<td>0.43</td>
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<td>1.11</td>
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<td>4.11</td>
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<td>0.09</td>
<td>0.80</td>
<td>0.09</td>
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<td>0.72</td>
<td>0.01</td>
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<td>Phenyl acetaldehyde</td>
<td>1.52</td>
<td>5.10</td>
<td>2.76</td>
<td>5.78</td>
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<td>5.78</td>
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<tr>
<td>cis-Linalool oxide</td>
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<td>2.19</td>
<td>2.63</td>
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<td>2.19</td>
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<td>Linalool epoxide</td>
<td>0.49</td>
<td>0.23</td>
<td>0.77</td>
<td>0.23</td>
<td>0.66</td>
<td>0.09</td>
<td>0.77</td>
<td>0.09</td>
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<td>3.56</td>
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<td>Phenyl ethanol</td>
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<td>11.09</td>
<td>0.64</td>
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<tr>
<td>α-Iso phorone</td>
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<td>0.18</td>
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<td>0.86</td>
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<td>22.80</td>
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<td>18.36</td>
<td>28.52</td>
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<tr>
<td>Lilakdehyde D</td>
<td>8.87</td>
<td>8.05</td>
<td>12.86</td>
<td>11.57</td>
<td>1.05</td>
<td>8.52</td>
<td>12.86</td>
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<td>p-Mentha-1-en-9-al</td>
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<td>1.60</td>
<td>1.61</td>
<td>1.77</td>
<td>6.58</td>
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<td>6.58</td>
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<td>3,6-Dimethyl-2,3,3a,4,5,7a-hexahydro benzofuran</td>
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<td>4.02</td>
<td>4.59</td>
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<td>2.41</td>
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<td>0.22</td>
<td>0.00</td>
<td>0.01</td>
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<td>0.01</td>
<td>3.47</td>
<td>0.00</td>
<td>0.62</td>
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<td>Lilak alcohol C</td>
<td>1.45</td>
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<td>0.89</td>
<td>0.88</td>
<td>3.91</td>
<td>1.18</td>
<td>3.91</td>
<td>0.76</td>
<td>1.51</td>
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<td>p-Mentha-1,8-dien-7-ol</td>
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<td>0.57</td>
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<td>0.44</td>
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<tr>
<td>p-Mentha-1,8-dien-9-ol</td>
<td>1.98</td>
<td>1.50</td>
<td>0.45</td>
<td>1.18</td>
<td>4.40</td>
<td>1.40</td>
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<td>Myrtenol</td>
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<td>0.29</td>
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<td>1.76</td>
<td>0.65</td>
<td>1.76</td>
<td>0.29</td>
<td>0.78</td>
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<tr>
<td>Antranilic acid methyl ester</td>
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<td>5.01</td>
<td>0.88</td>
<td>3.70</td>
<td>9.24</td>
<td>5.81</td>
<td>9.24</td>
<td>0.88</td>
<td>4.47</td>
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<tr>
<td>Limonene diepoxide</td>
<td>0.59</td>
<td>0.09</td>
<td>0.23</td>
<td>0.96</td>
<td>0.08</td>
<td>0.09</td>
<td>0.96</td>
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<td>Jasnone</td>
<td>0.19</td>
<td>0.24</td>
<td>0.06</td>
<td>0.21</td>
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<td>0.49</td>
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<td>Geraniol acetone</td>
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<td>0.13</td>
<td>0.09</td>
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<td>Spathalenol</td>
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<td>0.15</td>
<td>0.09</td>
<td>0.18</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>trans-Nerolidol</td>
<td>0.09</td>
<td>0.09</td>
<td>0.06</td>
<td>0.21</td>
<td>0.28</td>
<td>0.18</td>
<td>0.28</td>
<td>0.06</td>
<td>0.15</td>
</tr>
</tbody>
</table>
PCA of 10 variables (36 samples) were carried out using Minitab 16.2.1 software. According to the results obtained from the analysis of 10 variables, the first five principal components explained 97.8% of the variation, with first two contributing 79.1% (Table 2). The 1st and 2nd component expressed 79.1% cumulative of all data. The dominant variables of 1st principal component were cis-linalool oxide, p-Mentha-1,8-dien-7-ol, α-terpineol, lilak alcohol C, and p-mentha-1,8-dien-9-ol. For the 2nd principal component the dominant variables were α-isophorone, lilak alcohol C, lilak alcohol D, p-mentha-1,8-dien-9-ol, and p-mentha-1-en-9-al. The p-Mentha-1,8-dien-9-ol and Lilak alcohol C were the common dominant compounds for PC1 and PC2. As for the 3rd principal component limonene epoxide, α-pinene epoxide, and trans-4,5-epoxy karen were the dominant components.

Figure 1 shows the score plot graphic for PC1 and PC2 for the means of 36 citrus honey samples. The means of every district were marked in the score plat graphic. The data were reduced enough to be seen easily. From the figure it can be concluded that the sea side productions gathered in the same area while the production for from the sea side grouped in different place. Briefly, it can be said that the means of principal component analyses indicated that the aroma compounds can be responsible to finds the origin of citrus honey.

Conclusion
The thirty-two compounds were elucidated in the citrus honey samples collected from 36 locations of six districts of Antalya city. Two groups are produced over 150 m altitude. The honey collected from Serik district discriminated from the others, distinctly. May be the altitude difference as well as the flower flora difference may affected this discrimination. It can be concluded that the aroma ingredients of honey are a good origin determiner for honey samples for citrus honey.

References

Acknowledgment The study is supported by TAGEM (Agricultural Research and Policy General Directorate) with the project number Tagem-17/ARGE/13. The authors thank to TAB (Turkish Association of Beekeepers) to provide the honey samples.
OP80- Anti-inflammatory Activity of Astragalus Honey Collected from Anatolia

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Muğla Sıtkı Koçman University, Koyceğiz Vocational School of Health Services, Department of Medical Services and Techniques, Köyceğiz-Muğla
*E-mail: tasmeltem@hotmail.com

Abstract- Turkey is one of the important countries in the world on beekeeping due to the biodiversity of medicinal plants. Astragalus honey takes its name from the abundant pollens of Astragalus plants. Due to the medicinal usage of honey, it is aimed to study the in vitro anti-inflammatory activity of Astragalus honey collected from 37 different stations from Kayseri, Niğde, Sivas, Diyarbakır, Elazığ, Tunceli, and Erzurum cities of Turkey. The anti-inflammatory activity was performed spectrophotometrically against cyclooxygenase-1 (COX-1) and cyclooxygenase-2 (COX-2) enzymes. The Astragalus honey collected from Niğde/Bor exhibited the highest COX-1 inhibitory activity (74.7% inhibition) while the honey collected from Diyarbakır/Karacadağ the lowest (47.1% inhibition) at 25% (w/v) honey concentration. As for against COX-2 enzyme the Astragalus honey collected from Niğde/Bor (55.0% inhibition) was the most active while the honey collected from Diyarbakır/Karacadağ (33.6% inhibition) was the least active one among the others at the same dilution.

Keywords: Anti-inflammatory activity; Astragalus honey; Anatolian honey

Introduction
Honey is phenomenal medicinal food which has been produced since ancient times. It contains mainly fructose, glucose, water, proteins. The minerals, vitamins and phenolics are the trace components. Honey can be classified as flowers and honeydew honey. Our country is rich in terms of flowering plants flora and endemic plant diversity. Due to geographical location and climate diversity, a wide variety of honey are produced depending on the origin in Turkey. The most exported honey types are pine, chestnut, citrus, clover, sunflower, cotton, corn, acacia and linden honey1,2. Astragalus honey is known as “Keven” in Anatolia and have a high source of energy that is quickly mixed into the bloodstream. In our country, especially in Central Anatolia, Eastern Anatolia and Southeastern Anatolia where the Astragalus plants are growing naturally, the Astragalus honey is produced. Since the beginning of humanity, honey has been used not only for nutrition, but also for therapeutic applications3. It is used against mouth, throat and bronchial infections with its antibacterial properties. Honey is also used as a nourishing and moisturizing cream against various ulcers, wounds and burn4,5. The Astragalus honey produced in Turkey has not been studied for its anti-inflammatory activity, yet. Therefore, it is aimed to be studied the in vitro anti-inflammatory activity of Astragallus honey against cyclooxygenase-1 (COX-1) and cyclooxygenase-2 (COX-2) enzymes.

Materials and Method
Honey samples provided from 37 locations (Kayseri, Niğde, Sivas, Diyarbakır, Elazığ, Tunceli, Erzurum), which is produced under control within the scope of the project (TAGEM - 17/ARGE/13), has been chosen as the material of this study. Anti-inflammatory activities of honey samples were evaluated according to COX-1 (Cyclooxygenase-1) and COX-2 (Cyclooxygenase-2) enzyme inhibition activity methods. For this purpose, spectroscopic measurements were performed using colorimetric COX (ovine) inhibitor assay kit (Cayman, No. 760111). The method is based on the measurement of absorption at 590 nm by oxidation of \(N,N,N',N'\text{-tetramethyl-phenediamine (TMPD)\). To the well plate 10 \(\mu\text{L\) honey samples dissolved with deionised water were added. Then 20 \(\mu\text{L\) of TMPD, a colorimetric test substrate solution, was added and then, 20 \(\mu\text{L\) of arachidonic acid was added quickly. The microplate was incubated for 5 minutes under continuous stirring. The absorbance was read at 590 nm after incubation using SpectraMax 96 well platter reader.

Results and Discussion
The in vitro anti-inflammatory activity of the Anatolian Astragalus honey performed by the spectrophotometric method are given in Table 1.
Table 1. Anti-inflammatory Activity of Astragalus Honey from Various Stations of Anatolia.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Stations</th>
<th>COX-1 Assay % inhibition (25% honey solution)</th>
<th>COX-2 Assay % inhibition (25% honey solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sivas/Yıldızdağ (4 station)</td>
<td>51.36 ±1.14</td>
<td>35.79 ±0.65</td>
</tr>
<tr>
<td>Niğde/Bor (3 station)</td>
<td>74.73 ±0.23</td>
<td>54.95 ±1.32</td>
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<td>Kayseri/Yahyalı (3 station)</td>
<td>60.67 ±1.15</td>
<td>47.29 ±0.36</td>
</tr>
<tr>
<td>Kayseri/Pınarbaşı (7 station)</td>
<td>62.94 ±0.96</td>
<td>51.09 ±0.55</td>
</tr>
<tr>
<td>Diyarbakır/Karacadağ (3 station)</td>
<td>47.07 ±0.45</td>
<td>33.61 ±1.13</td>
</tr>
<tr>
<td>Elazığ/Karakoçan (6 station)</td>
<td>59.78 ±0.19</td>
<td>39.34 ±0.74</td>
</tr>
<tr>
<td>Tunceli/Ovacık (6 station)</td>
<td>67.23 ±1.04</td>
<td>50.22 ±1.73</td>
</tr>
<tr>
<td>Erzurum/Tekman (5 station)</td>
<td>69.73 ±1.23</td>
<td>35.74 ±0.36</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The values expressed herein were the mean ± standard error meaning of three parallel measurements (\(p<0.05\)). The mean ± standard error meaning values followed by the different superscripts within the same column indicate significant difference statistically, between the extracts by Fisher’s test at \(p<0.05\).

The anti-inflammatory activities of the Anatolia (Kayseri, Niğde, Sivas, Diyarbakır, Elazığ, Tunceli, Erzurum) astragalus honeys were performed in vitro using COX-1 and COX-2 enzymes. The honey collected from Niğde/Bor exhibited the highest inhibitory activity (74.7\%) among the others against COX-1 enzyme, and followed by the that of collected from Erzurum/Tekman (69.7\%) and Tunceli/Ovacık (67.2\%). Among them the honey collected from Diyarbakır/Karacadağ indicated the least inhibitory activity (47.1\%). Even the honey collected from Diyarbakır/Karacadağ showed the least activity, the activity is very considerable. It can be said that the IC\textsubscript{50} of the inhibition activity is nearly 25\%. If the 15\% can be said that water, roughly, the IC\textsubscript{50} value could be said that 10-15\% diluted water. As for COX-2 inhibitory activity among the honey samples the highest activity was observed by the honey collected from Niğde/Bor (55\%), and followed by the that of collected from Kayseri/Pınarbaşı (51.1\%). The honey collected from Diyarbakır/Karacadağ was inhibited the lowest COX-2 inhibitory activity (33.6\%).

**Conclusion**
The Astragalus honey is one of the worthy foods that is produced in Turkey abundantly. The mean inhibitory values of the 25\% diluted honey samples were 61.7\% and 43.5\% against COX-1 and COX-2, respectively. The high anti-inflammatory activity results made it more special for medicinal usage and for food industry.

**References**

**Acknowledgment** The study is supported by TAGEM (Agricultural Research and Policy General Directorate) with the project number Tagem-17/ARGE/13. The authors thank to TAB (Turkish Association of Beekeepers) to provide the honey samples.
**OP81- Phenolic compounds of Anatolian Sunflower Honey with Chemometric Approach**

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**Abstract**—Honey is a special functional food produced by honey bees. It is called sunflower honey due to the containing abundant pollens of *Helianthus* species. In Turkey, sunflower honey is produced in Central Anatolia, Marmara, Black Sea and Mediterranean regions. The origin aspects of sunflower honey and the phenolic ingredients of Turkish sunflower honey has not been studied. The phenolic components of the 26 honey samples collected from Adana, Konya, Tekirdağ, Samsun and Tokat regions were screened using HPLC-DAD. The antiradical activity was performed for the honey samples by the DPPH and ABTS assays. 3,4-dihydroxy benzoic acid, 4-hydroxy benzoic acid, catechin, methyl-1,4-benzoquinone, caffeic acid, and ellagic acid were detected as common compounds. Among them 4-hydroxy benzoic acid was the major compound. The higher antiradical activity was observed in the samples collected from Tekirdağ/Hayrabolu and Tekirdağ/Malkara. The Principal Component Analyses study carried out using Minitab Programme discriminated the origins of honeys.

**Keywords**: Phenolic compounds; Sunflower honey; HPLC-DAD; Chemometry; Anatolian honey

**Introduction**

Honey is an important natural product that mainly contains glucose and fructose. The minor components are amino acids, enzymes, vitamins, proteins, organic acids, flavonoids and other phenolic compounds. Due to the minor constituents it is considered as medicinal. As published the polyphenolic compounds were responsible for health-promoting properties of honey. Sunflower honey is golden in color and can be produced in every region of our country where the *Helianthus* species are cultured. The sunflower honey looks like a cream and a unique taste and aroma. It explains the lovers who loves each other such worshipers. Every year, it is thought that more than 8,000 tons are produced in middle Anatolia and Trace Regions of Turkey. It crystallizes quickly. Therefore, it is not preferred in Turkey due to false belief. In contrast, according to science the natural honey crystalizes. The local people producing the sunflower honey used it against fever and to strengthen the immune system. The medicinal usage of sunflower honey and to promote the natural sunflower honey to the people, we have studied its phenolic compounds along with the antiradical activities. The chemometric technique; namely, principal component analyses (PCA) was applied to chemical data collected from analytical instruments.

**Materials and Method**

The sunflower honey samples provided from 26 locations (Adana, Konya, Tekirdağ, Samsun and Tokat regions), which is produced under control within the scope of the project (TAGEM - 17/ARGE/13), has been chosen as the material of this study. The phenolic compounds were screened using HPLC-DAD against 27 standard compounds. For the elution a gradient program was used. Solvent A contains 0.5% acetic acid in demineralized water while solvent B 0.5 acetic acid in methanol. A gradient elution was performed for the separation of phenolic compounds along with the antiradical activities. The chemometric technique; namely, principal component analyses (PCA) was applied to chemical data collected from analytical instruments.

**Results and Discussion**

The HPLC-DAD analyses of sunflower honey collected from 26 stations of 5 different cities afforded 6 common compounds; namely, 3,4-dihydroxy benzoic acid, 4-hydroxy benzoic acid, catechin, methyl-1,4-benzoquinone, caffeic acid, and ellagic acid (Table 1). The compound 3,4-dihydroxy benzoic acid is a general compound of honeydew honeys. It is very abundant in Tekirdağ/Suleymanpaşa 2nd station due to the oak trees. 4-hydroxy benzoic acid was ranged from 0.01 and 12.4 µg, while methyl-1,4-benzoquinone between 0.01 and 35.9; caffeic acid between 0.01 and 14.8; and ellagicacid between 0.01 and 37.3 µg/Kg honey.

**Table 1.** Phenolic profile results of sunflower honey (µg/1 Kg honey) and antiradical activity (IC₅₀; µg/mL)
Among the sunflower honey samples, the honey collected from Tekirdağ/Malkara exhibited the best DPPH free radical scavenging activity (IC₅₀: 25.4 µg/mL) while the honey collected from Tekirdağ/Hayrabolu the best ABTS cation radical scavenging activity (IC₅₀: 8.37 µg/mL). The antiradical activity IC₅₀ ranges were 25.4–40.0 µg/mL for DPPH assay and 8.37–37.4 µg/mL for ABTS assay. Normally, according to science, the IC₅₀ value lower than 50 is very remarkable. So the weakest one can be considerable as powerful antioxidant.

PCA of 10 variables (26 samples) were carried out using Minitab 16.2.1 software. According to the results obtained from the analysis of 10 variables, the first four principal components explained 72.8% of the variation, with first two contributing 48.1%. The results with bold character were more effective to explain the principal components than the others (Table 1). The dominant variable of 1st principal component was 3,4-dihydroxy benzoic acid. For the 2nd principal component the dominant variables were DPPH and ABTS activities. That the dominant components for the PCA2 was DPPH and ABTS due to the expressing of the antiradical data as...
IC$_{50}$ values. The lower IC$_{50}$ indicates the higher antiradical activity. As for the 3$^{rd}$ principal component, 3,4- dihydroxy benzoic acid, and methyl-1,4-benzoquinone were the dominant.

**Table 1.** The loading, eigenvalue, variance and cumulative variance values in principal component analyses

<table>
<thead>
<tr>
<th>Variable</th>
<th>PC1*</th>
<th>PC2*</th>
<th>PC3*</th>
<th>PC4*</th>
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<tbody>
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<td>3,4-Dihydroxy benzoic acid</td>
<td><strong>0.330</strong></td>
<td>0.265</td>
<td><strong>0.647</strong></td>
<td>0.186</td>
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<tr>
<td>4-Hydroxy benzoic acid</td>
<td>-0.636</td>
<td>0.041</td>
<td>-0.108</td>
<td>-0.241</td>
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<td>Methyl-1,4-benzoquinone</td>
<td>-0.360</td>
<td>0.106</td>
<td><strong>0.291</strong></td>
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<td>-0.240</td>
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<tr>
<td>Ellagic acid</td>
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<td>-0.681</td>
<td>0.552</td>
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<td>DPPH assay</td>
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<td>-0.030</td>
<td>0.209</td>
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<tr>
<td>ABTS assay</td>
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<td><strong>-0.613</strong></td>
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<td>0.119</td>
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<tr>
<td><strong>Eigenvalue</strong></td>
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<td>1.6539</td>
<td>1.0806</td>
<td>0.8744</td>
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<td><strong>Variance (%)</strong></td>
<td>30.1</td>
<td>23.6</td>
<td>15.4</td>
<td>12.5</td>
</tr>
<tr>
<td><strong>Cumulative (%)</strong></td>
<td>30.1</td>
<td>53.7</td>
<td>69.1</td>
<td>81.6</td>
</tr>
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</table>

*PC: Principal component

**Conclusion**

4-Hydroxy benzoic acid was the common component of Sunflower honey except Tekirdağ Süleymanpaşa-2 station. Additionally, the sunflower honey produced in Tokat Zile-2 station contained methyl-1,4-benzoquinone. 3,4-Dihydroxy benzoic acid, also known as protocatechic acid which is claimed to be the trace compound for oak honey and pine honey. So the compound may come from any oak trees during honey production.

**References**


**Acknowledgment** The study is supported by TAGEM (Agricultural Research and Policy General Directorate) with the project number Tagem-17/ARGE/13. The authors thank to TAB (Turkish Association of Beekeepers) to provide the honey samples.
Switchable-hydrophilicity solvents (SHS) have been recently introduced by Jessop P. et al. as a new class of extraction solvents for large-scale extractions [1]. The use of CO₂ to reversibly switch the polarity of an extraction solvent provides a promising tool for the design of environmentally benign analytical methods. The use of SHSs allows the extraction of analytes in a homogeneous medium without the need for a disperser solvent.

In this work, switchable-hydrophilicity solvent liquid-liquid microextraction (SHS-LLME) was applied prior to HPLC for the extraction of four non-steroidal anti-inflammatory drugs (NSAIDs) in human milk, saliva and urine. Optimum extraction conditions were achieved using 500 μL of switched-on N,N-dimethylcyclohexylamine (DMCA) (as an extraction solvent), by completing the extraction media to 13 mL with DI, and using 500 μL 20 M NaOH (as a phase separator). The extraction time was 30 s and there was no need for centrifugation. Direct injection of the final extract into HPLC showed superior advantages over the other sample introduction methods such as evaporation-to-dryness and back-extraction. Thus, it was adopted as the optimum introduction method.

Limits of detection (LOD) ranged between 2.73 and 3.78 mg L⁻¹ for the matrices analyzed. The method showed good linearity with coefficients of determination ($R^2$) higher than 0.9953 and percentage relative standard deviations (%RSD) ranging between 4.0 and 13.7%. Percentage relative recoveries (%RR) ranged between 95.4 and 106.9%.

The novel combination of the proposed centrifugeless SHS-LLME with direct injection into HPLC was proven to be a convenient method for the extraction and determination of NSAIDs in biological fluids.

**Keywords:** Biological fluids, Direct injection, HPLC, Non-steroidal anti-inflammatory drugs, Switchable hydrophilicity solvent liquid-liquid microextraction.

**References:**
**Poster Presentations**

**PP1** - A label-free electrochemical biosensor for direct detection of IL 1β by using star-shaped poly(glycidyl methacrylate) modified ITO based electrode

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**Abstract:** In this study, we developed a star shaped polymer modified disposable immunosensor for IL 1β antigen detection. Star shaped polymer utilized as an immobilization matrix material and anti-IL-1β antibody as a biorecognition element. Electrochemical and morphological characterizations of electrode modification steps were performed by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) and atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively. Some parameters such as antibody concentration were investigated to determine the optimum analytical performance of the immunosensor.

**Keywords:** immunosensor, cancer, EIS

**Introduction**

The early detection of biomarkers is important to monitor disease monitoring in the human body because change in the level of biomarkers is related to the disease. Biomarkers are secreted in body fluids and the concentration of biomarkers differs from fg/mL to g/mL. The determination of these low concentrations of biomarkers in human body requires an accurate detection technique. Interleukin 1β (IL-1β) is a protein which plays an important role in various biological activities such as defense system and immune responses. Macrophages are the largest producers of IL-1β. IL-1β is a biomarker in the human lung, colon, breast, oral carcinoma and skin melanomas. The level of IL-1 in biological fluids is very low and the concentration level is few pg/mL. Pfaffe et al. reported that the concentration of IL-1β was ∼212.8 pg/mL (in saliva) and <10 pg/mL (in serum) in healthy population while in unhealthy population, it was ∼753.7 pg/mL (in saliva) and >10 pg/mL (in serum). These low levels in serum and saliva require sensitive analytical methods to determine IL-1 concentration. For determination of IL-1, usually Enzyme-linked Immunosorbent Assay (ELISA) kits.

Electrochemical impedance spectroscopy (EIS) is a successful, non-destructive and informative technique for characterization of electrochemical properties of biological interfaces. A glass or polyethylene terephthalate (PET) coated indium tin oxide (ITO) thin film is used as a working electrode in electrochemical biosensors owing to its exceptional properties such as a good optical transparency, high electrical conductivity, wide electrochemical working window, and stable electrochemical properties. In several studies, self-assembled monolayers are usually utilized for immobilization matrix formation. Apart from this technique, spin coating technique provides uniform and reproducible immobilization matrix. Spin coating is a simple method to form uniform thin films on flat surfaces. The principle of this method is based on the deposition of a small drop of a fluid onto the center of a material and then spinning of the material at high speed.

**Materials and Method**

Indium tin oxide (ITO) electrodes (5 mm × 20 mm, 60 Ω/cm²), monoclonal anti- IL-1β antibody, IL-1β human recombinant antigen were obtained from Sigma-Aldrich. Anti- IL-1β antibody, recombinant human IL-1β and bovine serum albumin (BSA) solutions were prepared using phosphate buffer (PBS 50 mM, pH 7.0) and stored at −20 °C. Ferri-ferro solution contained 1 M KCl, 5 mM [Fe(CN)₆]³⁻ and 5 mM [Fe(CN)₆]⁴⁻ in PBS and was utilized as redox probe. All electrochemical experiments were carried out in a conventional three-electrode cell containing a disposable ITO electrode, a platinum wire and Ag/AgCl as a working electrode, a counter electrode and a reference electrode, respectively. Electrochemical studies were carried out in the presence of [Fe(CN)₆]³⁻/⁴⁻ as redox couple and a Gamry Potentiostat/Galvanostat (Reference 1000, Gamry Instruments, Warminster, PA, USA) was used for EIS and CV measurements. The applied
potentials for cyclic voltammograms were between 0.5 V and 1 V. EIS experiments were carried out in the frequency range from 0.5 to 50,000 Hz. The spin-coating process was performed using a traditional spin-coater (MTI VTC-50) at 1000 rpm for 60 s.

**Results and Discussion**

The whole procedure utilized for the fabrication of the immunosensor is shown in Scheme 1. First of all, star-shaped polymer film was constructed by using spin-coating technique. Then, these electrodes were immersed into solution containing anti-IL-1β antibodies for 45 min, so they were immobilized onto ITO electrode via covalent bond formation. Bovine serum albumin (BSA) blocked the remaining free and active epoxy groups. After all these steps, the immunoelectrode got ready to detect IL-1β antigen.

![Scheme 1. Schematic presentation of immunosensor](image)

EIS is a powerful and sensitive technique to monitor the charge transfer processes occurred between modified electrode and electrolyte solution. Here, impedance measurements were carried out at each stage of the assembly. The EIS spectra were analyzed using Gamry Echem Analyst software.

![Figure 1. EIS responses obtained during immobilization steps](image)


**Optimization studies**

To obtain high sensitivity for IL-1β antigen detection, the experimental conditions were optimized such as antibody concentration. Therefore, 0.25 ng/mL, 0.5 ng/mL and 1 ng/mL antibody concentrations were utilized. The change in the charge transfer resistance was monitored and the calibration curves of these were drawn.

![Figure 2. Optimization results of antibody concentration](image)

**Conclusion**

In this study, we designed a modified electrochemical immunosensor by using star-shaped polymer for IL-1β antigen detection using a disposable ITO electrode. By using spin-coating technique, a homogenous film was formed on the ITO electrode surface and this film was efficient for covalent binding of anti- IL-1β antibodies. The electrochemical signal changes caused by interaction between anti-IL-1β antibody and IL-1β antigen were measured by the CV and EIS methods. With high sensitivity and specificity, this sensor can be utilized as an incisive diagnostic tool with great potential.

**References**


Amino acid functionalized perylene bisimide for the sequential determination of mercury and biothiols

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Abstract - The determination of heavy metal ions has become a serious issue due to their toxic effects on human health and the environment. Among of them, mercury ion is one of the most dangerous heavy metal and its accumulations in the human body, may cause severe diseases such as motor disorders, neuropathy, and Minamata disease.

On the other hand, biological thiols (cysteine, glutathione and homocysteine) play important roles in protein synthesis, detoxification and cell growth. Abnormal level of biological thiols cause many diseases for example hair depigmentation, skin lesions, liver damage, cardiovascular and Alzheimer’s disease etc. Thiol group cause to reduce sulfur in a molecule bind to mercury. Due to the strong affinity between mercury and thiols can be allowed sequential determination of them. Herein, we designed and synthesized amino acid functionalized perylene which showed fluorescence emission “turn off” response for sequential detection of mercury ion and biothiols. The recognition behaviour of ligand was evaluated by UV-vis and fluorescence spectroscopy. The ligand showed rapid responses with good detection limits.

Keywords: Perylene, Fluorescence, Turn-off-on, Mercury, Biothiols.

Disposable and cost-effective ITO based biosensor system to analyse Melanoma antigen1

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The human MAGE-1 protein (46 kDa) is located in both the nucleus and cytoplasm. This gene is expressed in many tumors of several types, such as melanoma, head and neck squamous cell carcinoma, lung carcinoma and breast carcinoma, but not in normal tissues except for testes1. In this study, a biosensor based on indium tin oxide (ITO) electrode was designed to determine MAGE-1. To determine analytical characterization of the biosensor modified with 3-glycidoxypropyltriethoxysilane (3-GOPTES); linear range, repeatability, reproducibility, regeneration processes were studied. Moreover, Single frequency technique was used to understand the interaction between antiMAGE-1 and MAGE-1 and the designed biosensor was applied to real human serum. In optimum conditions, the linear range of the biosensor was determined as 0.01 pg-1.28 pg/mL. In conclusion, the applicability of the designed biosensor to the real serum sample indicates the potential for clinical use.

Keywords: biosensor, MAGE-1, ITO-PET electrode

References

Acknowledgment: This work was funded by TÜBİTAK (The Scientific and Technological Research Council of Turkey, Project number: 113 Z 678) whose assistance is greatly acknowledged.
A novel silanization agent based biosensor system: Analytical studies of a regenerative Melanoma Antigen-1 immunosensor by disposable indium tin oxide electrodes

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MAGE-1 (MAGE, for melanoma antigen), was identified by virtue of its processing and cell surface expression as a tumor-specific peptide bound to major histocompatibility complexes which was reactive with autolytic T cells1. Glycidoxypropyltrimethoxysilane (3-GPTMS) is frequently employed for the preparation of dense heterometal hybrid polymers which are used, e.g., for hard coatings of organic polymers and contact lens materials in the optical industry. In this study, we have improved a new immunological biosensor with indium tin oxide (ITO). Then, anti-MAGE-1 antibody was covalently immobilized with 3-GPTMS which formed a self-assembled monolayers (SAMs) on modified ITO electrodes. Analytical characteristics such as square wave voltammetry, linear determination range, repeatability, reproducibility and regeneration of biosensors are determined. All characterization steps are monitored by electrochemical impedance spectroscopy, cyclic voltammetry.

The developed biosensor has wide determination range (0.5 fg-15 fg/mL). To investigate long shelf life of the fabricated biosensor, the immunosensors were stored at 4°C for periods ten weeks. Furthermore, binding kinetics of MAGE1 to antiMAGE-1 is monitored by single frequency technique in real time. Additionally, Kramer’s-Kronig transform was used to understand whether the impedance spectra of biosensor system are affected from the variation that occurred because of external factor. Morphological characteristics of constructed biosensor were observed by scanning electron microscopy.

Finally, this biosensor was tried in real blood sample and that showed it could be utilized in clinical applications. A commercial ELISA kit was also used as a reference method to validate the results obtained by the biosensor. This biosensor can be preferred due to it has a wide linear range and it can be prepared easily.

Keywords: Indium tin oxide (ITO), Glycidoxypropyltrimethoxysilane (3-GPTMS), immunosensor

References

Acknowledgment: This work was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK, Project number: 113 Z 678).
PPS- Development of an ITO based disposable and highly reproducible biosensor to quantify C1-INH in real human serum samples

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Hereditary angioedema (HAE) is known as an autosomal dominant disease which can be fatal in the gastrointestinal tract and larynx, which is seen on the skin and mucosal surfaces. In this study, an ITO (indium tin oxide) based biosensor is configured to detect C1-INH. The ITO-PET electrodes were modified with NH$_2$OH / H$_2$O$_2$ / H$_2$O to form the hydroxylated electrode surface. Then, the ITO-PET electrode surfaces were modified with 3-Aminopropyltriethoxysilane (3-APTES). Then, gluteraldehyde was used as crosslinker. The 3-APTES concentration, anti-C1-INH concentration and incubation time, C1-INH incubation time were optimized. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used for immobilization, optimization and analytical studies. Linear range, repeatability, reproducibility, regeneration studies were investigated to characterize the proposed biosensor. The linear range of the immunosensor was determined as 2 fg / mL - 1500 fg / mL. The storage life of the biosensor was determined. Square wave voltammetry technique was applied to the biosensor. Single frequency technique was used to monitor the interaction between the anti-C1-INH and C1-INH. Finally, the designed biosensor was applied to real human serum.

Keywords: ITO-PET, C1-INH, 3-APTES, Biosensor, Electrochemical Impedance Spectroscopy

References
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Acknowledgment: This work was funded by TÜBİTAK (The Scientific and Technological Research Council of Turkey, Project number: 113 Z 678) whose assistance is greatly acknowledged.
Selective Separation of Hemoglobin from Blood Serum by Lanthanide-Chelate Based Molecularly Imprinted Cryogel

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Molecular imprinting is a technique that allows the design of synthetic adsorbents that provide selective and sensitive recognition of chemical and biological molecules including aminoacids, proteins, enzymes, DNA, drugs and metals¹. The aim of present study is to investigate selective recognition of hemoglobin (hgb) in human serum in the presence of various interferent proteins using a new lanthanide-chelate cross-linked molecularly imprinted cryogel polymer. In this regard, Hemoglobin has been complexed with lanthanide-chelate functional co-monomer N-methacryloylamido antipyrine (MAAP)-Ce(III). Hgb-imprinted cryogel polymer has been prepared by using free radical polymerization technique and characterized by ultraviolet-visible-near infrared (UV-NIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and swelling tests. The effect of various parameters such as medium pH, initial Hgb concentration, flow rate, temperature, ionic strength on binding capacity have been investigated for optimization of the binding conditions. The maximum binding capacity has been determined as 107.21 mg*g⁻¹ at pH 5.0 with flow rate of 1 mL*min⁻¹ at 25 °C. The selectivity of imprinted cryogel has been studied through on myoglobin and cytochrome c. The selectivity experiments proved that imprinted of Hgb on cryogel exhibited high selectivity towards competitive proteins.

Keywords: Molecularly imprinted cryogel, Lanthanide-chelate, Hemoglobin, Selective separation

References
A Novel colorimetric and fluorescence chemosensor based on coumarine derivate for the determination of copper(II) ion

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Copper ion is the essential transition metal ion in human body due to their significant roles in various physiological mechanism such as the growth and development of bones, free radical defense and the regulation of nerve impulse. However, the abnormal level of copper ion in the human plasma might cause anemia, Wilson’s, Parkinson’s and Alzheimer’s disease. Therefore, the determination of copper ion in the human blood and environment samples are very important. In this work, we report a novel fluorescent and colorimetric chemosensor by using 6,7-dihydroxy-3-(4-(trifluoromethyl)phenyl)-2H-chromen-2-one for the detection of copper ion. In the experimental results, copper ion is chelated with the chemosensor and the complex was evaluated by UV-vis absorption and fluorescence emission spectra. Probe showed a naked-eye and fluorescence turn off response in the presence of copper ion.

Figure 1. Structure of 6,7-dihydroxy-3-(4-(trifluoromethyl)phenyl)-2H-chromen-2-one

Keywords: Fluorescence, Copper, Chemosensor, Coumarine

Acknowledgment: The authors are grateful to the Research Fund of the TUBITAK for their support with the project No-116Z163
PP8- Primary Level High Precision Coulometry: Determination of HCl and KCl

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The techniques in which current passes through the electrochemical cell are dynamic techniques and coulometry also is a dynamic technique. Coulometry is based on a comprehensive electrolysis of the analyte. Comprehensively means that the analyte reacts completely with a reagent generated at the surface of working electrode. This also means that the analyte is thoroughly reduced or oxidized in the solution. Consuming the analyte completely equals 100% current efficiency. Coulometry is divided into two parts; controlled potential coulometry and controlled current coulometry. The applied potential is constant and the current is recorded as a function of time then integrated and charge is calculated at controlled potential coulometry (Eq.1). The applied current is constant and the period which is produced of titrant equivalent to analyte at controlled current coulometry (Eq.2).

\[ Q = \int_0^t i . dt \]  
(Eq.1)

\[ Q = i . t \]  
(Eq.2)

Q: Electrical Charge (Ampere.Second), I: Current (Ampere), t: Time (Second)

High precision coulometry is used in constant current mode. Analysis is formed of three steps; initial titration, main titration and final titration. Initial and final titrations are identical but using purposes are different. Both of them are applied low constant currents (\(I_{\text{initial}}\) and \(I_{\text{final}}\)). Titration end point is designated with high accuracy at initial titration (\(t_{\text{initial}}\)). Secondly the main titration is performed at high constant current (\(I_{\text{main}}\)) for a time (\(t_{\text{main}}\)) and is equivalent to 99.8% - 99.9% of the added sample. Final titration is also applied at constant low current, and remaining of the sample from main titration is titrated in this step. As a result, the sample weight or purity is given with high precision. These approaches were used for determination of HCl molality and KCl purity.

\[ n = \frac{1}{z.F.m} (I_{\text{init}}t_{\text{init}} + I_{\text{main}}t_{\text{main}} + I_{\text{final}}t_{\text{final}}) \]  
(Eq.3)

n: Amount Content (mmol/g), m: Sample Mass (g), z: Charge Number, F: Faraday Constant (96485.3365 coulomb/mol)

Measurement uncertainty for primary level high precision coulometry measurement is evaluated according to GUM principles. The uncertainty of high precision coulometry measurement was estimated by combining the standard uncertainties originating directly from the sample mass, buoyancy correction, voltage, resistance, time, current efficiency, incomplete rinsing, aerosol losses, electrolyte impurities, gas impurities and diffusion.

Keywords: High precision coulometry, coulometric titration, primary method, HCl, KCl.

References
Heavy metals are one of the most significant pollutants in aquatic ecosystems due to their toxicities, persistence and bioaccumulation potentials. It is well known that they pose significant health risks when human exposure dose exceeds safe consumption levels. They can accumulate in the tissues of organisms and may cause severe damage to the liver, kidney, central nervous system, mucus tissues, intestinal tract, and reproductive systems at high levels. Moreover, metals may be transferred to human body through the food chain, posing a potential health risk to human beings. Fish are commonly considered as bio-indicators for heavy metals in aquatic ecosystems. The content of toxic heavy metals in fish can counteract their beneficial effects\(^1,2\). Therefore, it is necessary to determine levels of trace elements.

Fish samples (\textit{Tinca tinca, Cyprinus carpio, Sander lucioperca, Esox lucius, Squalius cephalus, Copeata tinca, Silurus glanis and Oncorhynchus mykiss} species) were purchased from a fisherman in Kayseri, Turkey. A total of 0.20 g of fish samples was weighed and the samples were then digested in Berghofmws-4 microwave system. The concentrations of Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Hg and Pb in all digested samples were determined by ICP-MS. Accuracy of the analytical method was checked by certified reference material (DOLT-4, Dogfish Liver). Multivariate and univariate statistical techniques such as principal component analysis, cluster analysis, and correlation analysis were applied for the interpretation of the obtained data.

**Keywords**: ICP-MS, Fish, Heavy metals, Statistical analysis

**References**


Acknowledgements: This study was granted by the Scientific Research Project Unit of Erciyes University, Turkey (Grant No. TSA-2018-7757).
PP10- A New Magnetic Solid Phase Bio-extractor (*Anoxybacillus flavithermus* SO-17) for Preconcentration of Cu(II)

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Thermophilic *Anoxybacillus flavithermus* SO-17 loaded γ-Fe\(_2\)O\(_3\) magnetic nanoparticle was developed as a novel magnetic solid phase bio-extractor for the preconcentration and extraction of Cu(II) from real samples. The prepared magnetic solid phase bio-extractor was characterized by SEM and FT-IR. The Cu(II) analysis was performed by ICP-OES. The various factors affecting the magnetic extraction and preconcentration method were tested. The optimum conditions were found to be pH of 5.0-6.0, flow rate of 3.0 mL/min, 100 mg of *A. flavithermus* and γ-Fe\(_2\)O\(_3\) magnetic nanoparticle, 5 mL of HCl (1 mol/L) as the eluent and 400 mL for breakthrough volume. A good reusage (35 times) was obtained with the relative standard deviation (RSD) of 1.6%. In addition to these, new method was applied to determine Cu(II) ions in real samples.

**Keywords:** Magnetic solid phase extraction, pre-concentration, copper, thermophilic bacteria, *Anoxybacillus flavithermus*

PP11- Preconcentration of U(VI) by magnetized solid phase bio-extractor

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In this investigation, thermophilic *Bacillus cereus*-SO14 modified with γ-Fe\(_2\)O\(_3\) magnetic nanoparticles (MNPs) was successfully prepared for preconcentration of U(VI). It was characterized by Fourier transform infrared spectrometer (FT-IR), scanning electron microscope(SEM) and EDX before and after U(VI) extraction. Different experimental factors affecting MSPE of U(VI) such as pH, flow rate, eluent, sample volume, and co-existing ions were studied. Under the optimized conditions, the limits of detection (LODs) and limits of quantitation (LOQ) for U(VI) were 0.23 and 0.76 ng/mL, respectively. The biosorption capacities found as 51.8 mg/g. The accuracy of the proposed process was validated by analysis of a certified reference materials and the determined results demonstrated good agreement with the certified values. The novel MSPE process was also successfully applied for the preconcentration of U(VI) in environmental samples.

**Keywords:** Magnetized bio-solid phase extractor, preconcentration, Uranium, Thermophilic bacteria, *Bacillus cereus*.

**Acknowledgment:** This study was supported by Scientific Research Projects Unit of Mersin University (Project code: 2018-3-AP4-3092), Turkey.
Abstract: The pollution of water sources from industrial wastes is a major environmental problem. Therefore, the precise, sensitive and correct detection of metallic pollution in water is very important. The fluorimetric parameters of the new synthesized N,N'-bis (2,5-dihydroxybenzylidene)-4,4'-diamino diphenyl ether (DHDPE) and aluminum complex were determined in acetonitrile. The best fluorescence intensity of DHDPE-Al complex in acetonitrile medium was obtained at $\lambda_{ex} = 358.59$ nm and $\lambda_{em} = 482.51$ nm (excitation and emission wavelengths), (Fig. 1). The best pH, time and temperature were 4.0, 20 minutes and 35°C for optimal complex formation, respectively. [Al$^{3+}$]-F.I. calibration graphics were linear within 0.027-0.27 and 0.27-2.70 ppm aluminum concentrations. The fluorimetric aluminum determination method with the newly synthesized macro molecule Schiff base DHDPE which was used as the ligand, was applied to various water sources. As a result of the analysis, the Al content in water inlet to KOSKİ was double-fold compared to other water samples.

Keywords: Schiff bases, Aluminum, N,N'-bis(2,5-dihydroxybenzylidene)-4,4'-diamino diphenyl ether, N,N'-bis(2,5-dihydroxybenzylidene)-4,4'-diaminobenzene, Spectrofluorimetry.

Introduction

Aluminum in high concentrations can be toxic to the nervous system. Aluminum accumulation may increase the risks of neurological and bone diseases, e.g., Alzheimer’s disease, Parkinson’s disease, encephalopathy, and osteomalacia$^{1,3}$. Therefore, the evaluation of aluminum levels in biological fluids for prevention of aluminum overload has attracted considerable attention in the field of clinical chemistry. The pollution of water sources by toxic metals especially from industrial wastes is a major environmental problem nowadays. The precise, sensitive and correct detection of toxic metals in waste water, tap water and in fountain water in industrial regions is very important. Schiff bases and their metal complexes are becoming increasingly important as biochemical, analytical, industrial, and antimicrobial agents$^{4}$. Schiff bases play an important role as central ligands in main group and transition metal coordination chemistry. Fluorimetric methods are generally sensitive as an analytical technique for aluminum (III) determination at trace levels$^{5}$. In this work, the fluorimetric properties of a Schiff base, N,N'-bis (2,5-dihydroxybenzylidene)-4,4'-diamino diphenyl ether (DHDPE) and its complex formed with aluminum is studied and a development of a spectrofluorimetric method is aimed for the quantitative determination of trace aluminum. The method was also used to determine the aluminum levels in the water sources.

Materials and Method

Apparatus

The fluorescence spectra were obtained with Perkin-Elmer LS 55 Spectrofluorimeter. The slit width was fixed at 10 nm for excitation and 5 nm for emission monochromators. The pH of the experiment solutions were measured with METTLER TOLEDO pH-meter. A WiseCircu thermostatic bath with circulation was used to keep the temperature constant at 25°C.

Materials

The Schiff base (DHDPE) used in the experiments was synthesized according to the following reaction.
The aluminum (III) stock solution, 100 ppm was prepared from the standard 1000 ppm aluminum (Merck). Ammonium acetate (Merck) solution (20%) used to calibrate the pH of the experiment solutions. Interference ions and aluminum standard solutions were purchased from Merck. Selcuk University Faculty of Science Department of Chemistry Analytical Chemistry Laboratory tap water, Selçuklu district Musalla Bağları cemetery tap water, creek water in Meram district and inlet water to KOSKİ were used as a natural water sample for aluminum determination.

**Procedure**

1 mL of $10^{-4}$ M DHDPE, 1 mL of stock aluminum (III) solution (aluminum concentration range 0.027-2.70 ppm) and 1mL of 20% ammonium acetate solution were added into 10 mL calibrated flasks and then completed with ACN to 10 mL. The pH values of these solutions were adjusted to 4.0 with 1M HCl or 1M NaOH. Fluorescence measurements were performed to determine the optimum conditions. Fluorescence intensities of these solutions were measured at room temperature. Interference effects were measured. Al in natural water samples was performed by the method of standard addition method using a fluorimetric assay.

**Results and Discussion**

*Determination of Excitation and Emission Wavelength*

The optimum excitation and emission wavelength for DHDPE and DHDPE-Al complexes were determined by changing the excitation wavelength to 10 nm in the range of 200 to 400 nm. Accordingly wavelengths of the spectrum (Fig. 1) for DHDPE $\lambda_{ex} = 441.20$ nm, $\lambda_{em} = 542.25$ nm, for DHDPE-Al complex $\lambda_{ex} = 280.59$ nm, $\lambda_{em} = 391.26$ nm have been detected.

*Determination of the optimum experimental conditions*

The best pH, time and temperature were 4.0, 20 minutes and 35°C for optimal complex formation, respectively. [$\text{Al}^{3+}$]-F.I. calibration graphics were linear within 0.027-0.27 and 0.27-2.70 ppm aluminum concentrations.

![Emission spectra of DHDPE-Al in different Al concentrations](image)

**Fig. 1.** Emission spectra of DHDPE-Al in different Al concentrations. [$\text{DHDPE}$] = $10^{-4}$ M (F.I.= 20.20), [$\text{Al}^{3+}$]= 0.027 (F.I.= 40.68), 0.27 (F.I.= 85.11), 2.70 (F.I.= 124.96) ppm.
Determination of Aluminum in Water Samples

The developed fluorimetric method for aluminum determination applied in different water sources. In the water samples taken from four different sources, the aluminum concentrations found by the fluorimetric standard addition method applied in the optimum conditions are given in Table 1. Statistical parameters of the proposed fluorimetric method are given in Table 2.

<table>
<thead>
<tr>
<th>Water sample source</th>
<th>Aluminum concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selcuk University Faculty of Science Department of Chemistry, Analytical Chemistry Laboratory tap water</td>
<td>0.150±0.025</td>
</tr>
<tr>
<td>Selçuklu district Musalla Bağları cemetery tap water</td>
<td>0.175±0.015</td>
</tr>
<tr>
<td>Inlet water to KOSKI</td>
<td>0.360±0.020</td>
</tr>
<tr>
<td>Creek water in Meram district</td>
<td>0.170±0.039</td>
</tr>
</tbody>
</table>

Table 2. Statistical parameters of the proposed fluorimetric method.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DHDPE-Al complex</th>
<th>DHDPE-Al complex</th>
<th>S. U. Faculty of Sci. Dep. of Chem. Anal. Chem. Lab. tap water</th>
<th>Selçuklu district Musalla Bağları cemetery tap water</th>
<th>Inlet water to KOSKI</th>
<th>Creek water in Meram district</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear range, ppm</td>
<td>0.027-0.27</td>
<td>0.27-2.70</td>
<td>0.027-0.270</td>
<td>0.027-0.270</td>
<td>0.027-0.270</td>
<td>0.027-0.270</td>
</tr>
<tr>
<td>LOD</td>
<td>0.0066</td>
<td>0.068</td>
<td>0.008</td>
<td>0.002</td>
<td>0.018</td>
<td>0.007</td>
</tr>
<tr>
<td>LOQ</td>
<td>0.020</td>
<td>0.207</td>
<td>0.026</td>
<td>0.006</td>
<td>0.018</td>
<td>0.021</td>
</tr>
<tr>
<td>Slope (b)</td>
<td>139.6</td>
<td>19.25</td>
<td>169.7</td>
<td>152.9</td>
<td>142.6</td>
<td>267.1</td>
</tr>
<tr>
<td>Intercept (a)</td>
<td>43.36</td>
<td>31.41</td>
<td>25.98</td>
<td>26.93</td>
<td>51.50</td>
<td>44.68</td>
</tr>
<tr>
<td>Correlation coefficient (R²)</td>
<td>0.947</td>
<td>0.954</td>
<td>0.975</td>
<td>0.987</td>
<td>0.977</td>
<td>0.950</td>
</tr>
</tbody>
</table>

In this study, the newly synthesized DHDPE was first examined for fluorescence properties in various solvent media. Subsequently, the complex of DHDPE with aluminum was formed and the fluorescence properties of this complex was determined. The fluorimetric method developed for aluminum determination was applied to the water samples taken from various sources and appropriate results were obtained.

Conclusion

The newly synthesized DHDPE Schiff base is a suitable ligand for the fluorimetric determination of aluminum in natural waters. The developed method for aluminum determination using a newly synthesized Schiff base, can be proposed as an easy convenient method, inexpensive and determining aluminum in water in a very short time.

References

ABSTRACT Removal of toxic metal ions from aqueous solution have been interesting methods by using death bacteria recently. Removal of Cd(II), Cu(II), Pb(II), Fe(II), Ni(II) and Zn(II) from aqueous solution are investigated using batch method by death Bacillus licheniformis sp. isolated from soil in the area of Tigris River. The analysis of Cd(II), Cu(II), Pb(II), Fe(II), Ni(II) and Zn(II) were determined by using ICP-MS. Optimum conditions (pH, time, temperature, biosorbent dose) were studied to determine the adsorption capacity of each element with initial concentration 5 mg/L and solution volume 50 ml. The best optimum conditions required for maximum adsorption was found to be on average pH 6.0, temperature 25°C, time 60 min. and biosorbent dose 25 mg for all elements. This study included Bacillus subtilis ATCC 6051 (B1) strains for multi element ions and was evaluated using the bulk method in drinking water and wastewater. The results show that the bacteria are adsorbed better such as toxic elements Pb and Cd and the metal ions in the aqueous solution are determined removal in the range of % 70-98 respectively by bacteria (bacillus subtilis).

Keywords: Bacillus subtilis, drinkwater, wastewater, ICP-MS

INTRODUCTION

Contamination of water resources with toxic elements poses a serious threat to human health, living and ecological systems. Various methods are available for the removal of dissolved heavy metals, including ion exchange, precipitation, adsorption and biosorption. A large number of microbial biomass species were investigated in the biosorption studies. These include fungus, algae and bacteria. Bacillus can be isolated from food, soil, water and even eukaryotic organisms. Bacillus is a Gram-positive and rod-shaped bacterium grown under aerobic and facultative anaerobic conditions. The cell wall of Gram-positive bacteria is a highly complex network consisting mainly of peptidoglycan and teikoic acids. Among the various treatment methods, the biosorption method is widely used because of the distinctive characteristics of living and living microorganisms in the transformation and detoxification of inorganic pollutants. The use of non-living microorganisms may offer some advantages to the living organism, with a favorable concentration of toxic wastes, lack of need for continuous feeding, easy desorption and recovery, and long-term storage at room temperature. (Welasquez and Dussan. 2009).

MATERIALS and METHODS

Instrumentation and Standard Solutions
In this study; HNO₃, HCl, NaOH, Nitrate salt of Ni(II), Pb(II) Cd(II), Cu (II) and Fe(II) used were analytical grade obtained either from Merck, Germany. Stock solution for Cu (II), Ni(II), Pb(II) Cd(II), Zn(II) and Fe(II) was prepared 1000 μg/ml using Nitrate salt in double distilled water. Purified water was prepared using a Millipore Milli-Q (Direct-Q UV3, USA) water purification system. Different concentrations of Ni(II), Pb(II) Cd(II), Cu (II), Zn(II) and Fe(II) solutions (1-5μg/ml) were prepared by diluting the stock solution of 1000 μg/ml. Standard solution for ICP-MS was obtained from 1004 ± 4 μg/ml stock solution (Plasma CAL, SCP science, USA).
Analytical Sensitive and Accuracy of the Method For ICP-MS

In this study, the concentration of Cu, Cd, Pb, Ni, Zn and Fe elements was calculated using calibration curves for the analytical sensitive which were prepared from the 1004 ± 4 μg/ml stock solution (Plasma CAL, SCP science, USA). The limit of detection (LOD) and limit of quantification (LOQ) for Cu, Cd, Pb, Ni, Zn and Fe elements were determined by using analytical curves performed with 10 independent analyses of a blank solution spiked with the metal at a level of lower concentration. The LOD and LOQ were calculated from the standard deviation (Sd) of the determinations (LOD = X_{avr.} + 3 S_d and LOQ = X_{avr.} + 10 S_d) (Duz et al. 2012; Kilinc et al. 2012). The certified reference material (CRM) solution for wastewater (ERA A water Company Certificate of Analysis Lot No : P232740A) was used to assess the accuracy and precision of the method. The samples were analysed in triplicate by ICP–MS. The analytical results were in good agreement with the certified values (Table 1).

RESULTS and DISCUSSION

The effect of adsorption on multimetal (Ni(II), Pb(II), Cd(II), Cu (II), Zn(II) and Fe(II)) ions using Bacillus subtilis ATCC 6051(B1) such as pH, concentration, recovery of biosorbent, drinking water and wastewater were determined.

Bisorption studies

The optimum condition of adsorption on multimetal (Ni(II), Pb(II), Cd(II), Cu (II) and Fe(II)) ions using Bacillus subtilis ATCC 6051(B1) were determined. The best optimum conditions were applied to the solutions forming the mixture of Zn(II), Ni(II), Pb(II), Cu (II), Cd(II), and Fe(II)) ions at different pH. The calculations of biosorption were determined according to the following equation (1), The equilibrium sorption capacity (q_e) is the amount of metal ion sorbent at equilibrium (mg/g), C_0 initial concentration of metal, C_e equilibrium concentration, V volume of solution (L), m biomass dose and it can be expressed as follows:

$$ q_e = \frac{(C_0 - C_e) \cdot V}{m} $$

% Removal = $$ \frac{(C_0 - C_e) \cdot 100}{C_0} $$ equation (1)

Application of biosorbent (B1) in wastewater and drinking waters studies

In this study, the effects of biosorbent on water samples taken from different locations of Diyarbakır (Tigris river, wastewater) and Mardin dirinking water and CRM wastewater were investigated for removing trace elements from drinking and waste water. The best optimum conditions of biosorbent (B1) with 50 ml water were applied to the water samples forming the mixture of Ni(II), Pb(II), Cd(II), Fe(II), Cu(II) and Fe(II)) ions at the natural pH of water samples. As seen in the table 8 the elements of Ni(II), Pb(II), Cd(II), Zn(II), Cu(II) and Fe(II)) were well removed in different water and CRM (wastewater) by biosorbent (B1), especially Cd and Pb elements.

CONCLUSIONS

The Bacillus subtilis obtained from ATCC 6051(B1) isolated from soil in area east of Tigris River are observed similar adsorption capacities and characteristics. As a result of the studies carried out, it has been determined that it can be easily applied to water and wastewater treatments because of have a good morphological characteristics, recovery, temperature and water resistance. Because these bacteria are high metal binding capacity, low cost, high efficiency in dilute solution effluents, easily obtained in large quantities, water resistant and re-applicability.
Table 2. Removal of elements in different water and CRM waste water samples with B1 using ICP-MS (Initial concentration $C_o$, Equilibrium concentration $C_e$).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentrations (µg/L)</th>
<th>Drikingwater of Diyarbakır (pH: 7.6)</th>
<th>Drikingwater of Mardin (pH: 7.8)</th>
<th>Wastewater untreated (pH: 8)</th>
<th>Wastewater treatment (pH: 8.5)</th>
<th>Tigrisriver (pH: 8.2)</th>
<th>CRM Wastewater (pH: 5.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>$C_o$</td>
<td>156.0±13.80</td>
<td>99.74±2.99</td>
<td>24.0±0.81</td>
<td>14.25±0.50</td>
<td>30.30±0.25</td>
<td>744.0±0.001</td>
</tr>
<tr>
<td></td>
<td>$C_e$</td>
<td>81.30±2.60</td>
<td>42.56±2.10</td>
<td>11.04±1.34</td>
<td>7.02±0.11</td>
<td>13.97±0.15</td>
<td>407.8±0.004</td>
</tr>
<tr>
<td>Cd</td>
<td>$C_o$</td>
<td>0.970±0.00</td>
<td>2.26±0.08</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>13.37±0.06</td>
<td>184.0±0.005</td>
</tr>
<tr>
<td></td>
<td>$C_e$</td>
<td>0.240±0.00</td>
<td>0.44±0.02</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>13.37±0.06</td>
<td>184.0±0.005</td>
</tr>
<tr>
<td>Pb</td>
<td>$C_o$</td>
<td>0.660±0.00</td>
<td>2.34±0.36</td>
<td>1.13±0.30</td>
<td>0.96±0.02</td>
<td>5.16±0.98</td>
<td>631.0±0.046</td>
</tr>
<tr>
<td></td>
<td>$C_e$</td>
<td>0.130±0.00</td>
<td>0.67±0.01</td>
<td>0.29±0.00</td>
<td>0.21±0.01</td>
<td>1.29±0.07</td>
<td>59.3±0.004</td>
</tr>
<tr>
<td>Ni</td>
<td>$C_o$</td>
<td>35.80±0.80</td>
<td>9.76±0.95</td>
<td>30.66±2.20</td>
<td>14.90±1.26</td>
<td>22.30±1.45</td>
<td>1590±0.045</td>
</tr>
<tr>
<td></td>
<td>$C_e$</td>
<td>14.10±0.60</td>
<td>3.51±0.61</td>
<td>9.60±1.22</td>
<td>4.46±0.07</td>
<td>8.17±0.42</td>
<td>559.4±0.002</td>
</tr>
<tr>
<td>Zn</td>
<td>$C_o$</td>
<td>425.7±13.02</td>
<td>90.73±1.60</td>
<td>48.60±1.43</td>
<td>19.50±0.04</td>
<td>34.30±1.48</td>
<td>833.5±0.005</td>
</tr>
<tr>
<td></td>
<td>$C_e$</td>
<td>425.7±13.02</td>
<td>90.73±1.60</td>
<td>48.60±1.43</td>
<td>19.50±0.04</td>
<td>34.30±1.48</td>
<td>833.5±0.005</td>
</tr>
<tr>
<td>Fe</td>
<td>$C_o$</td>
<td>2.26±0.06</td>
<td>27.16±1.09</td>
<td>3.91±0.07</td>
<td>2.63±0.04</td>
<td>79.38±0.37</td>
<td>697.6±0.006</td>
</tr>
</tbody>
</table>

REFERENCES


Assessment with humic acid of trace elements by multivariate statistical methods of some agricultural soils in Diyarbakır area

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Abstract

The relationship between humic acid (HA) and some minerals provides important contributions in the soil (1-3). In this study, trace elements (Al, As, Ba, Be, Cd, Fe, Mn, Pb, Sb, Sn, Se, V, P) of some agricultural soil samples obtained from Diyarbakır are evaluated with some multivariate statistical analysis. The concentrations of elements were analysed by ICP-OES and the SRM (humik acid and element) was used for accuracy of method. The results were found to be in between 91.6% - 105.9%. Multivariate statistical analysis correlation, regression, HCA (Hyerarchical clustering analysis), PCA (Principle component analysis), as well as a difference in terms of humic acid between districts ANOVA (Analysis of variance) test was applied. The mean, minimum and maximum values of humic acid were found as 0.04 % - 2.340 %, respectively. CV (Coefficient of variation) value was found to be 143.63 % quite large variations between locations. Multiple regression analysis revealed significant regression model with Mn and P (P <0.01) when HA dependent variable was determined according to Stepwise method. According to Pearson's correlation coefficient, the negative correlation of HA with As; r = -0.282, P < 0.01, positive with Fe; r = 0.185, P < 0.05, positive with Sn; r = 0.242, P < 0.05, positive with Mn; r = 0.273, P < 0.01, positive with Se; r = 0.325, P < 0.05 and positive correlation with P r = 0.315, P < 0.01. The clustering and PCA analysis, HA, P , Mn and Fe were determined to be in the same group. The relationship in between humic acid and minerals of some territory in the region was found to be poor

Key Words: Trace element, Humic acid, Correlation, Regression, Cluster analysis

References

PP15 - Evaluation by multivariate statistical methods of relationship humic acid and some elements in agricultural soil

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Abstract: Humic acid and mineral matters are very important component and factor for regulation of plant nutrients in the soil (1-3). In this study, HA (humic acid) contents of soil samples taken from 12 different locations were determined by appropriate method. The concentration of elements in the remaining soil after extracting humic acid from soil samples and the elements passed to humic acid fraction were analyzed by ICP-OES. The organic matter (OM), pH, mineral matters, clay, silt and sand in the soil samples were determined. The relationships between all variables were evaluated by multivariate statistical analysis such as correlation, simple linear regression, PCA (Principal Component Analysis). Spearman rho coefficient was taken into consideration in the correlation analysis. Simple linear regression analysis showed that significant regression model between HA, OM, pH, the elements passed to humic acid fraction and in the remaining of soil. In the PCA analysis, 4 factors were found to explain 88.23% of the total change. In the correlation analysis of HA in the soil samples was significant negative with Be r = -0.786, P < 0.01, positive with Mn r = 0.918, P < 0.01, negative with Sn r = -0.700, P < 0.05, positive with Se r = 0.704, P < 0.05 and positive with P r = 0.700, P < 0.05 correlations were determined.

Keywords: Humic Acid, Regression, Correlation, ICP-OES

References
Reduction of Interferences of Ascorbic Acid, Uric Acid and Dopamine in Flow Injection Amperometric Glucose Biosensor at a Pt Nanoparticle Modified Pencil Graphite Electrode

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In the construction of amperometric glucose biosensor based on oxidase enzyme, either cathodic current of consumed O₂ or oxidation of enzymatically produced H₂O₂ can be monitored. Generally, the oxidation of H₂O₂ has been widely used for this aim and applying of high over potentials is mostly preferred to obtain high responses and sensitivities. But some biologically important and electroactive active compounds such as ascorbic acid (AA), dopamine (DA) and uric acid (UA) can cause positive interference effect at high overpotentials.¹ In this work, an insoluble pre-oxidant, sodium bismuthate (NaBiO₃), was used for the reducing of these interferences in Flow Injection Analysis (FIA) of glucose for the first time.

In the fabrication of biosensor, Pt nanoparticles were electrodeposited on the surface of p.PGE by recording of 30 successive cyclic voltammograms of H₂PtCl₆ in the 0.1 M KCl solution.² Then obtained Pt/p.PGE was immersed in GOx enzyme solution (40 mg mL⁻¹) containing 0.50 % chitosan (CT) for 1 h at +4.0 °C and dried for 15 min at the same temperature before use. The electrochemical characterizations of obtained electrode were performed by recording electrochemical impedance spectra. SEM, EDX and XRD measurements were also recorded for the examination of the surface morphologies of the electrodes.

In the flow injection amperometric glucose biosensor studies, applying potential and flow rate were optimized as +600 mV and 1.70 mL min⁻¹, respectively. Thus, FI amperometric current-time curves versus glucose concentration were recorded in the carrier stream of pH 6.0 Britton Robinson buffer solution including 1.0 M KCl under optimized conditions. Results show that the proposed FI amperometric glucose biosensor exhibits linear range between 0.01 and 10 mM glucose with a detection limit of 3.1 µM. In order to minimize the interference effects of AA, DA and UA on the FI amperometric glucose biosensor, these interferences were injected into FIA system using an injector which was filled with 1.0 g of NaBiO₃. Thus, AA, DA and UA were converted to their inactive oxidized forms before the reaching to the GOx-CT/Pt/p.PGE in the flow cell. FI amperometric studies show that the huge oxidation peak currents of AA, DA and UA decreased significantly in the working conditions of the biosensor, while glucose was not influenced by the pre-oxidant in the injector. The proposed biosensor was also applied to three different samples (Artificial Blood, Dextrose Serum and Glucose Tolerance Test Drink). Results approves that GOx-CT/Pt/p.PGE can be successfully applied to real samples.

Keywords: Glucose Biosensor, Pre-oxidant, Platinum Nanoparticles, Flow Injection Method, Electrochemistry.

References

Note: This study was produced from a part of the PhD thesis of Serkan Karakaya.
Scaled-up Dispersive Liquid-liquid Microextraction for the Isolation of Three Major Capsaicinoids from Cultivars of *Capsicum annuum* L.

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Dispersive liquid-liquid microextraction (DLLME) has gained widespread acceptance as a microextraction and preconcentration technique since its inception in 2006 by Assadi and co-workers [1]. This is due to its obvious strengths such as high speed, high extraction efficiency and low consumption of organic solvents. However, to the best of our knowledge, no attempt has yet been made to apply DLLME on a large-scale for preparative extraction of analytes for isolation of pure standards.

In this study, an optimized DLLME method was scaled-up for the extraction of three major capsaicinoids (i.e., capsaicin, dihydrocapsaicin and nordihydrocapsaicin) from fruit of cultivar of *Capsicum annuum* L. prior to their isolation by medium pressure liquid chromatography (MPLC). Optimum DLLME conditions were as follows: 100 μL chloroform (as an extraction solvent), 1.25 mL acetonitrile (as a disperser solvent), and extraction time of 30 s. The conditions were scaled-up by a factor of 150 for the large-scale extraction using 500 mL volumetric flasks in place of centrifuge tubes. The mixture was divided into screw capped centrifuge tubes for centrifugation at 6000 rpm for 3 min. MPLC conditions included a stepwise gradient elution starting with a constant composition of 20% (v/v) MeOH for 15 min, thereafter increased to 60% MeOH at 60 min, the composition was kept constant until 80 min, then finally increased to 85% at 120 min. A flow rate of 10 mL min \(^{-1}\) was employed.

Liquid chromatography-mass spectrometry (LC-MS) and nuclear magnetic resonance (NMR) were used for characterization and structural elucidation of the capsaicinoids using 1D- (1H- and 13C-NMR) and 2D-NMR (COSY, HSQC and HMBC). The results confirmed the structure of the isolated capsaicinoids with purity comparable to commercial standards (>98%, w/w).

This study demonstrated that scaled-up DLLME has great potential for preparative extractions due to its superior advantages over other existing methods such as rapidity, high selectivity and requirement of low amounts of organic solvents.

**Keywords:** Capsaicin, Capsaicinoid, Dihydrocapsaicin, MPLC, Nordihydrocapsaicin, Scaled-up dispersive liquid-liquid microextraction.

**References:**


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PP18- Effect of gold nanoparticles on the morphological changes in fish’s tissues and internal organs

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Abstract: The effect of gold nanoparticles on the morphological changes of tissues and internal organs of the European carp (Carassius carassius), which are characterizing their histological state, was studied. When entering of the gold nanoparticles into the fish body we observed the following morphological changes: (1) dystrophy of diffuse destruction of liver parenchyma; (2) karyopicosis and karyorexis of liver cells; (3) elements of dystrophy and outflow of glial cells of the spinal cord and medulla oblongata; (4) confluence of the olive cells; (5) dysplasia of the fibers of the medulla oblongata; (6) disorganization and fragmentation of muscle fibers; and (7) diffuse distribution of nucleus in muscle cells. Necrosis areas with nucleus lysis and myoplasma decay in fish heart tissues were observed, as well as we found the dark areas and dark inclusions in the form of speckles, which may be the result of necrotic processes of influence of gold nanoparticles. All of these may lead to pathology of the tissues and internal organs of the carp fish. If it is unambiguously proven that gold nanoparticles, with fairly small size, are capable of damaging cells, tissues and internal organs that provide vital activity of the body deeply and irreversibly, then this can be a serious obstacle to their widespread introduction the gold nanoparticles technology into the practice of daily life, especially in biomedicine.

PP19- Quercus alba Green and Amber Leaves Chemical Profile

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Quercus alba (white oak) do not develop complete abscission layer, in the leaf stem, in autumn to cause leaf foliage. White aok holds its dried leaves during the winter and leaf foliage occurs in spring, a phenomenon known under the name marescence. White oak chemical profiles, in green and amber leaves extracts, obtained by supercritical CO2 extraction were investigated. The extractions were done by supercritical fluid extraction at 30 MPa and 40°C with the CO2 flow rate 2.0 kg/h. The extracts obtained were analyzed by gas chromatography-mass spectrometry. The green leaves extract contained monoterpenes: limonene (21.52%) and 1,8-cineole (2.42%). In green leaves extract a diterpene phytol was present in 24.11%. In amber white oak leaves present were monoterpenes: α-pinene (2.70%), limonene (3.75%), anethole (7.99%) and β-eudesmol (3.61%). Phytol was not detected in amber leaves extract. There is no sufficient data to draw a conclusion, just it can be mentioned, diterpene phytol has been transfered from the leaves through leaves vascular cells or decomposed into another compound.

Keywords: white oak, supercritical fluid extraction, GC-MS
Prussian blue (PB) is a compound often named as “Artificial enzyme peroxidise”, because of its catalytic property of reducing hydrogen peroxide under low potential conditions. These conditions are thought to be the most progressive for development of oxidase – based biosensors. Glucose measurement becomes more accurate and sensitive because of low potential maintained during glucose measurement, and it also disables reduction of other electrochemically active materials occurring in blood. Multilayers created by coating the electrode with mixed layers of PB and other metals hexacyanoferrates exhibit some advanced characteristics in comparison with PB, for example: significantly increased stability in time and improved tolerance to alkaline conditions.

In this research simple, one – step based procedure for the modification of graphite electrode by composite layer based on polypyrrole (Ppy). Prussian blue and glucose oxidase (GOx) was developed. During electrodeposition of Ppy/GOx/PB composite layer, Prussian blue and Co or Ni hexacyanoferrates were entrapped within formed Ppy layer. The influence of temperature on the kinetics of enzymatic reactions in the range of 15-30°C was evaluated as well as Michaelis constant (K_M(app.)) and maximum velocity (v_max) of glucose biosensor based on Ppy/GOx/PB, Ppy/GOx/PB – NiHCF and Ppy/GOx/PB – CoHCF were investigated.

Optimal potential for the registration of amperometric response towards glucose was at +0.05V vs Ag|AgCl|KCl sat. The PPy/PB/GOx – modified graphite electrode was sensitive towards glucose in the range of 0.5 - 40 mM. The Ppy/GOx/PB – NiHCF electrode showed wider linear range of the calibration curve indicating this type of electrode being more sensitive to glucose concentration up to 100 mM of glucose. The temperature depends on the analytical results for the biosensor based on the Ppy/GOx/PB – NiHCF showed that optimal temperature range for the operation of suggested glucose biosensor are between 20°C and 22°C and calculated activation energy of enzyme catalysed reaction are 14.95 and 1.95 kJ mol\(^{-1}\) in line with glucose concentration of 18 mM and 4 mM.

In summary, we proposed simple and promising method of one – step based protocol for graphite electrode modification with bioselective layer of Ppy/GOx/PB. This method could be applied for the development of the enzymatic electrodes modified not only by glucose oxidase, but possibly by other oxidases too. The Ppy/PB/GOx – modified graphite electrode exhibited 1.0 - 1.9 \mu A cm\(^{-2}\) mM\(^{-1}\) sensitivity towards glucose in the range of 1.0 – 20 mM. Meanwhile, the Ppy/GOx/PB – NiHCF electrode enabled to increase sensitivity towards glucose up to 100 mM.

Keywords: Glucose Biosensor; Prussian blue; Hexacyanoferrates.

References
Food allergy is a common health problem for all around the world, and it is estimated that 2-3% of the world population has health problems due to food allergy[1]. Moreover, a lot of biosensors have been developed against the peanut allergen protein, but the investigations for a fast, reliable and inexpensive test kit is not available yet. This study suggest a test based on DNA aptamer which was selected against peanut allergen protein Ara h 1. Nucleic acid aptamers are capable of recognizing and binding to their target molecules with a high affinity and selectivity [2]. In order to meet the demand of food industry, a DNA aptamer based simple colorimetric test will be developed with this study. 5’ amine modified DNA aptamer is bound to tosyl activated magnetic beads. In this manner, aptamer coupled magnetic beads are capable of capturing allergen protein residues in food sample. N-terminal biotinylated recombinant Ara h 1 protein is competitor agent, and the colorimetric signal development is linked to interaction between biotinylated allergen protein and streptavidin-conjugated HRP. As a result, colorimetric signal decreases proportional to concentration of peanut allergen protein in food samples. Recombinant Ara h 1 protein was cloned to pET28a vector and it’s heterolog production was done in E. coli. Recombinant protein tested in the manner of correct folding, tertiary structure, allergenic activity and storage stability. Avi-tag fusion of Ara h 1 protein will be produced and purified in the context of this study. Biotin residue will be ligated to the N-terminal of Avi-tag fusion of Ara h 1 protein with BirA ligase enzyme catalysis. This biotinylated version of Ara h 1 will be used as a competitor agent for the test. DNA aptamer specific to Ara h 1 protein was synthesized and HPLC purified by Metabion, GmbH. As a result of colorimetric, fluorimetric and electromobility shift assay characterization of Ara h 1 aptamer, it was found that the aptamer is capable of binding to its target with a high affinity and selectivity. Fluorimetric and colorimetric tests were developed for the detection of peanut allergen residues in food samples in Our lab. This study is the further development of colorimetric test in order to meet the demand of simplicity, sensitivity, selectivity and reliability of an aptasensor. Protein extraction buffer, DNA aptamer/magnetic bead ratio, binding buffer, incubation time and competitor N-terminal biotinylated Ara h 1 protein amount will be optimized during this study. Antibody will not be used in the context of the method, so both the colorimetric test to be developed and the shelf life of the colorimetric test is longer than the antibody based ELISA kits. Furthermore, the test period is short due to the low number of processing steps and short duration of the process steps. To conclude, the technique will be sensitive, fast, low-cost and stable test which gives reliable results and it will be a potential product to provide a fast analytical tool for our country.

**Key words:** Ara h 1 protein, DNA aptamer, Colorimetric test, Food allergen, Biosensor

**References:**


Quantitation design of ephedrines by GC/MS – Multivariate optimization, validation of methods and applications in urines

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Introduction: Ephedrine and its derivatives belong to the family of amphetamines. They own various therapeutic properties. They are stimulant on the central nervous system. For this reason, some of them are used in alimentary supplements and in sport. They are wanted, mainly in anti doping control of sportsmen.

Methods: The goal of this work was, first to search the optimal conditions (resolution >1.5; short time test analysis) by GC/MS in the separation of seven compounds: ephedrine, pseudoephedrine, norephedrine, norpseudoephedrine, fenfluramine, fentermine and mephentermine (as internal standard). These molecules were studied after trimethylsilyl and trifluoroacetic derivatization. The software Nemrod-W was used in the building and the analysis of the experimental design, which allowed determining the optimal conditions for their separation.

Results: Optimal conditions were deduced: column HP5-MS, 30 m • 0.25 mm i.d. • 0.25 lm film thickness; Ti = 73_°C (1 min), 1st heating rate at 10_°C/min until 150_°C (0.5 min), then 2nd heating rate at 25_°C/min until 230_°C (5 min). The validation of the quantitation was applied to urines. Study was done after extraction and purification by a C18 adsorbent phase. Quantitation was done with the use of GC/MS with mode SIM (single ion monitoring) and with internal standard. The results of linearity, repeatability, precision, accuracy, sensibility, LOD, LOQ, yields of extraction, for these studied compounds (actives and urinary extracts) show the good validation of this analytical method GC/MS.

Conclusion: The study of seven ephedrine-like compounds was done successfully after realisation of the Nemrod-W experimental design, with the goal to separate them with good resolutions and short time analysis, followed by an application in urines.

**Keywords:** Ephedrines, derivatization., experimental design, optimization, validation

**References**


Dispersive Liquid-Liquid Microextraction of Caffeine from Turkish Coffee Prior to Its Determination by HPLC

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Since its introduction in 2006 by Assadi and co-workers [1], dispersive liquid-liquid microextraction (DLLME) has found wide acceptance as an outstanding sample preparation technique for its simplicity, cost-effectiveness and ability to provide high extraction efficiencies within a very short time due to the extensive surface contact between the droplets of the extraction solvent and the sample.

In this study, DLLME was used prior to high-performance liquid chromatography (HPLC) for the extraction and determination of caffeine in Turkish coffee samples. A reversed-phase column (Agilent Zorbax SB-Aq, 4.6 x 150 mm, 5 μm) was used for separating the analytes using a mobile phase consisting of 40% (v/v) methanol in water at 25 °C, a flow rate of 0.8 mL min⁻¹, and an injection volume of 20 μL. Caffeine was monitored using a diode array detector (DAD) at 273 nm.

Optimum DLLME conditions were as follows: 100 μL of chloroform (as extraction solvent), 500 μL of ethanol (as disperser solvent) and 60 s extraction time. Caffeine was back-extracted into 50.0 μL of 50/50% (v/v) methanol containing 50 mM NaOH solution within 60 s, which facilitated direct injection of the final extract into the reversed-phase column.

In order to examine the performance of the proposed DLLME–HPLC method with real coffee samples, matrix-matched calibration graphs were constructed by spiking pooled coffee samples with appropriate amounts of caffeine. Limit of detection (LOD), calculated based on a signal-to-noise (S/N) ratio of 3, was 1.1 mg L⁻¹ and limit of quantitation (LOQ), calculated based on an S/N ratio of 10, was 3.3 mg L⁻¹. Calibration graphs showed good linearity over the range of 3.3–60.0 mg L⁻¹ with a coefficient of determination (R²) higher than 0.9987 and relative standard deviation (%RSD) lower than 5.5%.

All of the 24 different brands of Turkish coffee samples analyzed contained caffeine at varying concentrations in the wide range of 0.89-15.40 μg g⁻¹. DLLME–HPLC was demonstrated to be a simple and rapid method for the determination of caffeine in coffee samples with percentage relative recoveries (%RR) in the range of 89.7–102.3%. The results proved that DLLME combined with a simple back-extraction step prior to HPLC could be of great interest in the determination of caffeine in foods and beverages in routine food analysis laboratories.

Keywords: Back-extraction, Caffeine, Dispersive liquid-liquid microextraction, HPLC, Turkish coffee.

References:

Acknowledgment:
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Investigation of the Combination of Fluoxetine and Clozapine on the U87 Cell Line

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Fluoxetine, an antidepressant agent belonging to the selective serotonin reuptake inhibitors (SSRIs), is used to treat depression, bulimia nervosa, premenstrual dysphoric disorder, panic disorder and post-traumatic stress. Clozapine is a tricyclic benzodiazepine, classified as an atypical antipsychotic agent. It binds several types of central nervous system receptors, and displays a unique pharmacological profile.

The adding another medication to treatment may increase the effectiveness of the primary treatment or reduce side effects. \textsuperscript{[1]} Some important measures to increase the therapeutic effect include the addition of serotonin reuptake inhibitors to the atypical, the addition of an atypical drug to serotonin reuptake inhibitors. \textsuperscript{[2]}

The aim of this study is to explain the effect of combination of fluoxetine and clozapine, which is different drug classes on the U-87 MG (abbreviation for Uppsala 87 Malignant Glioma). The drugs interact with each other and their neurotoxicity were investigated by MTT assay. In this study, combinations of drugs were analyzed quantitatively by using HPLC.

Cell viability was determined by MTT assay after incubating the cells with various concentrations of these two drugs and combination of these drugs. Cell viability was reduced according to the dose of combination of fluoxetine and clozapine. Cells were counted with a hemocytometer and appropriate dose-applied cells were applied to HPLC at regular intervals. Counting results and HPLC results were compared to find out changes according the time.

Keywords: Fluoxetine, Clozapine, Combination, U87MG

References

Acknowledgment
This work was supported by Republic of Turkey, Ministry of Development (Project Grant No: 2010K120810) and EGE-MATAL chromatography and cell-culture laboratories were used in this study.
Antidepressants, depression or dysthymia is used to relieve discomfort such as psychiatric drugs, nutrients or vegetable substances used for the term. Monoamine oxidase inhibitor, tricyclic antidepressant and selective serotonin reuptake inhibitor type of drug groups are called antidepressant drug groups. Antidepressants, which are popular today, are used by many people. In our study, we will consider ‘Venlafaxine and Sertraline’ as two agents that work as selective serotonin reuptake inhibitors. Venlafaxine is also used in the treatment of bipolar diseases, depression, and has been used to eliminate the depressions that occur after schizophrenia. Sertraline has the capacity to treat depression, anxiety and anxiety disorders in bipolar diseases. Compared with other antidepressants, side effects are very few and do not cause serious vital problems in case of overdose. The combination of these substances with the same effects is being investigated. Drug interactions are generally pharmacodynamic and pharmacokinetic interactions. Pharmacokinetic interactions can cause antagonistic pharmacological effects. Pharmacokinetic interactions can increase the effects of drugs and also have a negative effect. In pharmacokinetic studies, interactions between antidepressants have been investigated in clinical settings many times.

In this study, we investigated the release and interaction of two antidepressants (Venlafaxine and Sertraline) interacting with each other in the simulated gastric fluid with high performance liquid chromatography (HPLC). Limit of quantification (LOQ) of venlafaxine and sertraline are 4.55 ng/mL and 11.36 ng/mL, respectively. The simulated gastric fluid release results of the drug combination demonstrated the interactions of this combination.

**Keywords:** Venlafaxine, Sertraline, Drug Interaction

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**Acknowledgment**
This work was supported by Republic of Turkey, Ministry of Development (Project Grant No: 2010K120810) and EGE-MATAL chromatography laboratories were used in this study.
Determination of α-Tocopherol, Vitamin A and β-Carotene by using Molecularly Imprinted Polymers

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Biomedical researches of antioxidants have increased dramatically since the link between human diseases and oxidative stress was established.1 Molecularly imprinted polymers (MIPs) are synthetic porous polymers with the selective and specific recognition ability of the binding cavities to target molecules especially by non-covalent interaction such as hydrogen bonding, electrostatic interaction, π-π and hydrophobic forces.2 Separation technology plays an important role in the antioxidant components in the carrot industry as carrot provides highly valuable antioxidant substances including carotenoids, tocopherols and vitamin A. MIPs are used to separate or pre-concentrate bioactive substances from the matrix environment. In this study, MIPs were used to analyze α-tocopherol, which is the minor constituent in carrot. Besides α-tocopherol, β-carotene and vitamin A, which are major components of carrot, can also be analyzed with this MIPs. Thus, both the major components and the minor components of the carrot were analyzed by the same MIP-HPLC procedure. The analysis of the three bioactive components in the matrix was done by the simultaneous HPLC-DAD method. In addition, the binding efficiencies of MIPs were calculated using HPLC-DAD method.

MIPs were synthesized using α-tocopherol as template, methacrylic acid as functional monomer, ethylene glycol dimethacrylate as crosslinker and AIBN as initiator. The sorption of α-tocopherol, vitamin A and β-carotene was evaluated in acetonitrile and ethanol-water (6:4, v:v) and higher sorption efficiencies were obtained in ethanol-water (6:4, v:v) environment. Standard solutions were prepared such that the calibration interval for all analytes was 0.5 µg/mL -25 µg/mL. Limit of quantification (LOQ) of α-tocopherol, vitamin A and β-carotene are 68 ng/mL, 250 ng/mL and 447 ng/mL, respectively.

The MIP-HPLC procedure is practical, easy, fast, sensitive and selective for determination of α-tocopherol, β-carotene and vitamin A.

Keywords: α-tocopherol, β-carotene, vitamin A, Molecularly Imprinted Polymers (MIPs), High Performance Liquid Chromatography (HPLC)

References

Acknowledgment
This work was supported by Republic of Turkey, Ministry of Development (Project Grant No: 2010K120810) and EGE-MATAL chromatography and spectroscopy laboratories were used in this study.
Olanzapine is an antipsychotic drug used to treat schizophrenia and bipolar disorders. Olanzapine is generally classed with the atypical antipsychotics \(^1\). Sertraline is an antidepressant of the selective serotonin reuptake inhibitor (SSRI) class. Clinical trials indicate that using a combination of antipsychotic and antidepressant has better results than single usage of drugs when treating major depression \(^2\). The aim of present study is determination of plasma protein binding changes occur in the Bovine Serum Albumin (BSA) containing combination of these drugs with high performance liquid chromatography. HPLC method is developed for olanzapine and sertraline. Olanzapine and sertraline tablets are prepared in the BSA. The plasma protein binding rates were calculated based on the amounts reported in the original forms of the tablets. Analysis results are shown in Table 1.

<table>
<thead>
<tr>
<th>Drug/Drug</th>
<th>Sertraline (SER) (mg/mL)</th>
<th>Olanzapine (OLZ) (mg/mL)</th>
<th>BSA Binding Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sertraline (SER)</td>
<td>0.87</td>
<td>0.00</td>
<td>87.75</td>
</tr>
<tr>
<td>Olanzapine (OLZ)</td>
<td>0.00</td>
<td>0.76</td>
<td>24.28</td>
</tr>
<tr>
<td>1:1 Combination</td>
<td>1.10</td>
<td>0.66</td>
<td>110.09*SER:33.32 OLZ</td>
</tr>
</tbody>
</table>

Table 1. BSA Binding ratio of Drug-Drug Combination

Analysis of samples indicates that olanzapine and sertraline are interacted with each other. The results obtained from combined usage of olanzapine and sertraline in BSA could be useful for therapeutic drug monitoring studies of these drugs.

**Keywords:** Drug-Drug Combination, Olanzapine, Sertraline, HPLC

**References:**


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An in-vitro Study of the Interaction between Fluoxetine and Olanzapine in Protein Binding by HPLC Coupled with Ultrafiltration

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Olanzapine (OLZ) is a typical antipsychotic drug. It is used for the treatment of schizophrenia and other psychotic symptoms. This drug binds to dopamine, histamine H1, and serotonin type two (5-HT2) receptors. The antipsychotic activity of Olanzapine is likely due to a combination of antagonism at D2 and 5-HT2A receptors [1]. Fluoxetine (FLU) is used for therapy of major depression as selective serotonin-reuptake inhibitors (SSRIs). Metabolized to norfluoxetine, blocks the reuptake of serotonin at the serotonin reuptake pump of the neuronal membrane and increases in 5HT1A auto receptors the effects of serotonin [2]. Serum Albumin is a major carrier protein and its binding with drugs is important to examine the change in pharmacokinetic properties due to interaction amongst drugs. It is known that Olanzapine and Fluoxetine have 93% and 94.5% human serum protein binding capacity. However the protein binding ability of the co-administration of drugs is unclear. The combination of OLZ and FLU was chosen from the drug combination database for the present study which the tablets of OLZ and FLU has been used widely in combination therapy.

In the present study we have attempted to understand the relevant drug-drug interaction on protein binding between two antipsychotic drugs Olanzapine and Fluoxetine by High Performance Liquid Chromatography (HPLC-DAD) coupled with ultrafiltration. The chromatographic separations were achieved on C18 column (10 mm length, 4.6 mm ID with 3.5 µm particle size). Linearity and range, Limit of quantification (LOQ), Limit of Detection (LOD) and Precision (%RSD) was examined using pure drug active ingredient for both drugs before albumin binding studies. The serum albumin binding of OLZ and FLU and the various combinations of the OLZ with FLU were investigated using the tablet forms of these drugs. The results indicated that the protein binding ability was affected competitively therefore combined use of the drugs may alter the pharmacological effects of each drug. Furthermore in-depth studies are needed to understand the structural basis of the drug binding specificity of albumin and other serum proteins to evaluate the interactions.

Keywords: Antipsychotic, Albumin binding, Drug-drug interaction, HPLC

References

Acknowledgment-This work was supported by Republic of Turkey, Ministry of Development (Project Grant No: 2010K120810) and EGE-MATAL chromatography laboratories were used in this study.

212
Competition of Quetiapine and Fluoxetine in Binding to Serum Albumin in Combination Therapy

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Quetiapine is one of the most recent “atypical” antipsychotic drugs and Fluoxetine is an antidepressant of the selective serotonin reuptake inhibitor (SSRI)1. Combinations of antipsychotic and antidepressant drugs are commonly used in psychological disorders 2. According to drug combination database, quetiapine and fluoxetine interact with each other and used together. Drug protein binding phenomena can lead to some interesting drug-drug interactions when one drug displaces another in the binding site. The binding of drugs to plasma and tissue proteins is an important factor affecting their distribution and metabolism.

The aim of this in vitro study is to evaluate the competition between quetiapine and fluoxetine in binding with bovine serum albumin (BSA) in combination therapy. Studies of protein-binding capacity are of each drug was investigated by ultrafiltration coupled with High Performance Liquid Chromatography (HPLC-DAD).

The chromatographic separations were achieved on C18 column (10 mm length, 4.6 mm ID with 3.5 µm particle size). Linearity and range, Limit of quantification (LOQ), Limit of Detection (LOD) and Precision (%RSD) was examined using pure drug active ingredient for both drugs before albumin binding studies. The serum albumin binding of Quetiapine and Fluoxetine and the various combinations of the drugs were investigated using the tablet forms of these drugs. The results indicated that the protein binding ability was affected competitively therefore combined use of the drugs may alter the pharmacological effects of each drug. Furthermore in-depth studies are needed to understand the structural basis of the drug binding specificity of albumin and other serum proteins to evaluate the interactions.

Keywords: Quetiapine, Fluoxetine, Drug-Drug Combination, Albumin Binding HPLC

References:

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PP30- Determination of Adulteration in the Sunflower Oils Using Machine Learning Algorithms

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Adulteration of foods has a history dating back to ancient times. The demand for the use of vegetable oils is increasing day by day. In order to meet the market demands and to improve their profits, producers tend to blend cheap edible oils with edible oils of high economic value which is called economic adulteration. Especially, it is very common to mix edible oils to prepare adulterated products like addition of safflower oil into sunflower oil.

The main purpose of this study is to find out adulteration of sunflower oil with safflower oil using machine learning algorithms on 17 methyl esters of fatty acids obtained by GC-FID. For this purpose, 1%, 2%, 5%, 10%, 20%, 30% and 40% of safflower oil were added into the sunflower oil first. Then, fatty acid composition of adulterated sunflower oils were analyzed for all mixtures. Finally the obtained data was evaluated with Random Forest and Feature Selection algorithms using WEKA software. Feature Selection was performed to specify most important attributes for determining adulteration. Parameters used for Random Forest with 3-fold cross validation were 200 as iteration number and unlimited as maximum-depth. Also the method used for Feature Selection was CFSSubsetEval. The obtained accuracy value for the Random Forest classification algorithm was 97.53%. According to the Feature Selection algorithm, palmitoleic acid, oleic acid and linoleic acid were most effective attributes in finding adulteration. The accuracy value of Random Forest algorithm was increased to 98.77% after applying it on these attributes.

To conclude, fatty acid methyl esters compositions of sunflower oils and safflower oils are very close to each other. For this reason, it is difficult to determine adulteration at low percentages using fatty acid methyl esters with classic methods. However, it has been possible to determine adulteration using fatty acid methyl esters compositions of all mixtures with the Random Forest classification algorithm. The implementation of this multidisciplinary approach will provide the food industry with a new generation of quality and safety monitoring tools which are fast, efficient and easily implemented.

Keywords: Adulteration, Blending, Sunflower Oil, Safflower Oil, Machine Learning Algorithms

References

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This work was supported by Republic of Turkey, Ministry of Development (Project Grant No: 2010K120810) and EGE-MATAL chromatography laboratories were used in this study.
PP31 - Studies and Characterization of Fine and Coarse Particulate Matter from Fireworks.

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People are used that the fireworks are inherent tradition of the most public and national celebrations all over the world, giving an amazing visual enjoyment. There are historical evidences that fireworks originally were developed already in the second century B.C. But already at the beginning of the 21st century, scientists are beginning to draw public attention to air pollution that occurs directly during the firework episodes and in resent 5-7 years more and more studies are focused on the short term air quality degradation.

The burning of pyrotechnic devices is a huge source of gaseous pollutants as well as particulate matter, what may cause not only harmful health effects but seriously reduces visibility due to generation of dense, slowly disappearing clouds and affects the climate overall ¹,². Therefor PM₁₀ and PM₂.₅ aerosols were sampled in Riga, during the firework episodes of the Independence Day celebration on November 18th, 2017 and 2018 and during New Year celebration firework. The other set of PM₁₀ and PM₂.₅ were collected during usual everyday situation for background pollution control. The main purpose of the current research was to characterize chemical composition and the structure of coarse (PM₁₀) and fine (PM₂.₅) particulate matter fractions by the SEM, the TEM and the Raman Spectroscopy devices. It is known that spherical shaped particles mostly have been related to anthropogenic sources, while particles with regular morphological shape and a certain degree of symmetry have been related to natural sources. In all analysed samples both types of particles – spherical and regular shape are present, but in PM₁₀ samples more particles with regular symmetry were observed, while in PM₂.₅ aerosol samples more spherical and spheroidal particles as well as agglomerated particles were identified. The main observed difference between aerosol particles sampled during the fireworks and the usual pollution episodes was the amount of agglomerated particles. In images of aerosols from fireworks (both PM₂.₅ and PM₁₀) agglomerates were observed more, while in samples of aerosols obtained from the usual pollution episode, agglomerates were present only in fine fraction, but in a less extent. The EDS analysis showed that in aerosols from the usual pollution episode were detected: Na, Cl, Mg, K and Al, while aerosols from fireworks all samples contained Na, K, Cl, Al, S. K and Al were detected in all samples, but comparing results, aerosols from fireworks contain more than 10x and 50x higher concentrations respectively.

Mainly elevated concentrations could be explained by pyrotechnic additives KClO₄, Na₃AlF₆, Al powder, Ba, Fe, Ca salts and others. Unfortunately, the increasing number of publications regarding negative effects of fireworks has not diminished the frequency of them at least in Latvia.

Keywords: Firework emissions, air pollution, particulate matter.

References:

Acknowledgment
This study partially was supported by COST action nr. CA16109 - COLOSSAL - Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoL.
**PP32-** Determination of Polyaromatic Hydrocarbons in Drinking Waters

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**History of the subject**
The negative effects of polycyclic aromatic hydrocarbons (PAH) on human health have been determined in various studies. It has great important that methods of pre-treatment application to increase the concentration of PAHs before analysis especially in drinking water. On the other hand, the amount of chemicals, analysis time and cost to be used in separation procedures such as routinely solid phase extraction and similar pretreatments is exactly significant.

**Experimental**
Recovery studies were carried out with spike solutions for Fluorantene, Benzo (b) fluorantene, Benzo (k) fluorantene, Benzo (a) pyrene, Benzo (g, h, i) perylene and Indeno (1,2,3-c, d) pyrene via using appropriate SPE column and HPLC analysis steps.

**Results**
After modification of the method for six PAHs, totally 70 mL of chemical consumption is used and the recovery percent of modified method is calculated in respectively, Floranten 99.5%, Benzo (b) fluorantene 90.5%, Benzo (k) fluoranthene 84.8%, Benzo (a) pyrene 91.1%, Benzo (g, h, i) Perylene 75.9% and Indeno (1,2,3-c, d) pyrene 79.1%. Also the percentage of relative standard deviation results for repeatability from modified SPE method is given as Florentene 12.8%, Benzo (b) fluorantene 8.4%, Benzo (k) fluorantene 8.5%, Benzo (a) pyrene 8.0%, Benzo (g, h, i) perylene 12.2% and Indeno (1,2,3-c, d) pyrene is 17.5%.

**About conclusion**
In EPA 550.1, which is used as a standard analysis method for the analysis of PAHs in drinking water, poses problems in routine and multiple sample analyzes due to the long duration of analysis and high chemical consumption. The aim of this work to innovate the EPA 550.1 for specified of six PAHs in the method to save chemicals and time with specified yields and percent of relative standards deviation stated in the EPA 550.1.

**Keywords:** PAH, SPE, UHPLC, drinking water
Abstract—A novel type of green solvent of deep eutectic solvents (DESs) have been prepared and used as extraction solvents named ultrasound assisted deep eutectic solvent based liquid phase microextraction method (UA-DES-LPME) for the determination of Carmoisine. A deep eutectic solvent (DES) consist of tetrabutyl ammonium chloride-decanoic acid (1:3) as extraction solvent and tetrahydrofuran as emulsification agent were used for the microextraction of Carmoisine. Analytical parameters affecting the complex formation and microextraction efficiency such as pH, volume of tetrahydrofuran, type and amount of deep eutectic solvents and matrix effects and centrifugal time and speed have been studied in details. The quantitative recoveries were achieved at pH 3, 0.50 mL of deep eutectic solvent and tetrahydrofuran. Carmosine concentration in last volume was analyzed by micro-cuvette UV-VIS spectrophotometer at 517 nm. Carmoisine is used in food industry to obtain light red color. Commonly, Carmoisini is used cheese, baked products, condiments, ice cream, jelly crystals, dried vegetables and fruits, alcoholic beverages and drug additive. Accuracy and validity was verified by addition recovery studies for real sample.

Key-words: Deep eutectic solvents, Carmoisine, Liquid phase microextraction

References:
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Simultaneous Detection of Iron (II) and Iron (III) ions by a Flow Injection System

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Iron species as essential micronutrients are common contaminants of ground water. Accumulation of iron in the human body can increase the risks of cancer, arthritis, liver problems, and health issues. Spectroscopic techniques have been often used for the selective detection of Fe (II) in presence of Fe (III). A novel method for simultaneous detection of Fe (II) and Fe (III) species has been described by coupling Fe (II) and Fe (III)-selective electrodes as detectors in a flow injection analysis system. The potentiometric measurements were carried out by a lab-made computer controlled multi-channel potentiometer. The Fe (II) and Fe (III)-selective electrodes together with Ag/AgCl reference electrode were inserted into a custom-made flow cell and successfully used as potentiometric detectors in the flow injection potentiometric (FIP) system using pH 7 phosphate buffer (PB) as a carrier solution. Parameters of the FIP system such as mobile phase flow rate, sample injection volume and frequency were optimized. At a flow rate of 0.8 mL min⁻¹, linear working range and detection limit values were calculated as 0.1-100 ppm and 0.1-100 ppm for Fe(II) and detection limits 50 ppb for Fe (III) and 40 ppb for Fe(II) respectively in the FIP system. The electrodes as detectors displayed good sensitivity, selectivity, repeatability and rapid response towards Fe (II) and Fe (III) species. Lifetime of the electrodes was about at least two months in the FIP system. The results attained from FIP system were compared with the atomic absorption spectrophotometry (AAS) results and found in good agreement to each other.

Keywords: potentiometric analysis, flow injection, iron, ion-selective electrode

References

Acknowledgment: This work was financially supported by Research Fund of Yildiz Technical University [project number 2016-07-04-DOP03].
Nowadays, it has been theoretically shows that sandwich-type structures prepared by stacking metal nanoparticles in two graphene layers would have exceptional properties for practical applications. These sandwich structures designed by band gap engineering could lead to materials capable of being developed to meet industrial demands. In this study, copper nanoparticle (CuNP) islands decorated in sandwich-type single layer graphene have been designed as non-enzymatic sensor platform. Firstly, a single-layer graphene (SLG) has been synthesized on the copper foil by the CVD technique and transferred onto the FTO surface. Then CuNPs on this single-layer graphene have been prepared using inert-gas condensation method based on DC magnetron sputtering. Sensor platform based on sandwich-type hetero-structure (SLG/CuNP/SLG) has been constructed by transferring another single layer graphene onto the prepared CuNP decorated graphene layer (Fig.1). In this way, a unique sandwich structure has been obtained for further applications by stacking nanoparticles with have high stability, controlled size and regular particle distributions between impurity-free and large area single layer graphenes. The sensor properties of this sandwich structure to the saccharides have been compared with the single layer sensor platform (CuNP/SLG). In accordance with the theoretical studies in the literature, it has been found that the sandwich structure have improved greatly in sensor properties such as LOD, stability and response time. Furthermore, it has been observed that the CuNP islands, which has been decorated on a single layer of graphene, has formed dendrimer-like structures especially under the applied potential, whereas in the sandwich structure there has no such stacking. Thus, it was determined that sandwich structure as shielding layer has protected nanoparticles from electrochemical/optical and other environmental conditions. In this way, a very stable sensor platform has been obtained by providing long term stability of CuNPs. **Keywords:** sandwich type, single layer graphene, copper nanoparticle, nonenzymatic biosensor, glucose

![Figure 1. Preparation route of non-enzymatic sensor platform](image)
**References** (maximum 2 references) (10 punto, cited in the text as number exponentially 1, 2 or 3-5).


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**PP36**- VEGF Detection by a Disposable Biosensing System Based on VEGF-Receptor 1

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Nowadays, breast cancer is one of the most common types of cancer among women. Vascular endothelial growth factor (VEGF) could be used as a potential biomarker of this type of cancer which is an important regulator of angiogenesis and vascular permeability and is considered to be a powerful mitogen for endothelial cells¹. In this study, a novel biosensor was developed by using disposable indium-tin oxide-poly(ethylene terephthalate) (ITO-PET) electrodes as a working electrode for sensitive detection of VEGF. In the immobilization process, 3-Glycidoxypropyltriethoxysilane (3-GOPE) was used as surface modification agent with its chemically active glycidoxy groups, which were used for the immobilization of VEGF-R1 onto the ITO electrodes. All fabrication parameters of the biosensor such as the 3-GOPE and VEGF-R1 concentrations, VEGF-R1 and VEGF incubation periods were optimized. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) techniques were used for all optimization processes of the produced biosensor.  
**Keywords:** ITO-PET, VEGF-R1, 3-GOPE, Biosensor, Electrochemical Impedance Spectroscopy

**References**

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The Uses of Calcium Dobesilate as a Redox Mediator for Electrocatalytic Oxidation and Flow Injection Analysis of Hydrazine at Pencil Graphite Electrode

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Hydrazine is widely used in industry and agriculture as a reactant in fuel cells, a corrosion inhibitor in boilers, a rocket propellant, an antioxidant, a catalyst and a pesticide 1. Therefore, its sensitive, selective and fast determination has a critical importance in many fields. One of an affective determination way is its electrochemical detection based on its electrocatalytic oxidation at various modified electrodes 2. In this study, Calcium Dobesilate (CD) was used as redox mediator for the electrocatalytic oxidation of N2H4 and its amperometric determination in the Flow Injection Analysis (FIA) system for the first time.

Fig.1a and 1b show cyclic voltammograms CV of N2H4 (0.40 mM) and CD (0.050 mM) in the pH 9.0 Britton Robinson buffer (BRB) solution at Pencil Graphite Electrode (PGE), respectively. It can be seen that N2H4 oxidized irreversibly at high overpotential (about +800 mV), while CD has a well-defined reversible redox couple at a formal potential of 3 mV. In the CV of N2H4 in the presence of CD, the oxidation peak of CD at +30 mV increased significantly and shifted to +110 mV, whereas its cathodic peak current at -25 mV decreased. Thus, the peak potential of hydrazine oxidation shifts from +800 mV in the absence of CD to +110 mV in the presence of CD at PGE. These results indicate that the CD exhibits a good electrocatalytic activity toward oxidation of hydrazine in the solution media at the PGE.

Then, FIA of N2H4 was performed based on its electrocatalytic oxidation with CD using a homemade flow cell constructed for PGE. FI amperometric studies show that the linear calibration range and limit of detection values were found to be 5-750 µM (R²=0.993) and 1.5 µM hydrazine at PGE. The applicability of the developed FI amperometric hydrazine sensor to water samples has been tested and the obtained result showed that hydrazine added to tap water samples can be determined with a recovery of 98-102%.

Keywords: Hydrazine, Calcium Dobesilate, Mediator, Pencil Graphite Electrode, Flow Injection Analysis, Cyclic Voltammetry, Amperometry.

References
Purification and Mass Spectrometric Characterization of Protein-Polyethylene Glycol Conjugates

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Polyethylene glycol (PEG) chains are typically attached to proteins in various therapeutic drug production processes. The attachment of PEG units to proteins obviously increases the solubility and the stability of these biomolecules in the physiological medium. PEGylation, the covalent binding of PEG chains, prevents the rapid renal clearance of the therapeutic proteins by increasing their hydrodynamic radius and also shields them against immune system. Even though the PEGylation reaction itself might be controlled, the obtained product generally contains non-PEGylated protein and excess PEG chains besides the protein-polymer conjugates. Therefore, the products obtained from the conjugation process should be well-characterized prior to use in particular therapeutic applications. Mass spectrometry (MS) is now a primary analytical technique in the characterization of such protein-polymer conjugates by providing highly accurate data for both identification and quantification. However, highly complex nature of these samples arising from the presence of multiple conjugation forms for each protein and PEG molecule eliminates the advantage of mass spectrometry. The analytical performance of MS in the characterization of such samples can be enhanced by applying proper purification and separation strategies prior to instrumental analysis. The most crucial purpose of these analytical strategies is the removal of excess PEG chains and non-PEGylated protein from the mixture of conjugation medium. The fractionation of each conjugate group before the MS analysis is also helpful for reducing the heterogeneity of the sample and having more informative data. This purification is not only to have more information about the conjugated drugs but it is also to obtain the active form of the drug eliminating the expensive form of the therapeutic drug and the interference effect of free PEGs.

In this study, standard proteins and peptides are firstly PEGylated using end group-modified PEG chains having proper molecular weight. The samples obtained from the conjugation processes were used for testing the performance of developed purification and separation methods using various metal oxides. These methods are generally based on the separation of species according to their pKa values. The fractions were analyzed using various mass spectrometers having electrospray ionization and matrix-assisted laser desorption ionization capabilities. It was confirmed that the developed method was capable of removing excess PEG from the protein-polymer conjugates.

Keywords: PEGylation, Separation, Mass Spectrometry.

References:
1- Zhao C., O’Connor P.B., Removal of Polyethylene Glycols from Protein Samples using Titanium Dioxide, Anal Biochem., 365(2), 283–285.
Simultaneous Determination of Selected Drug Active Compounds in Wastewater Matrix by Binary Solvent Dispersive Liquid-Liquid Microextraction-LC-QTOF-MS/MS System

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In this study, binary solvent dispersive liquid-liquid microextraction (BS-DLLME) was combined with liquid chromatography quadrupole time-of-flight tandem mass spectrometry (LC-QTOF-MS/MS) for the simultaneous determination of selected drug active compounds. The optimization studies of the extraction parameters were carried out to obtain lower detection limits for seven drug active compounds. After the optimization studies, the limits of detection and quantitation values were calculated in the range of 0.01 – 6.1 and 0.05 – 20.0 ng mL⁻¹, respectively. Repeatability and reproducibility of the developed method were performed on the wastewater sample to figure out the precision of the method. Recovery studies in wastewater matrix were also performed to ensure that the applicability of the developed method is appropriate. The percent recovery values were found between 95-105 and 90-116% for 75.0 and 125.0 ng mL⁻¹ spiked samples, respectively. The recovery results obtained established the applicability of the method for the quantification of all analytes in the selected matrix. Results obtained showed that the developed method could be applied for the determination of selected analytes with high precision and accuracy.

Keywords: Dispersive liquid-liquid microextraction (DLLME); drug active compounds; LC-QTOF-MS/MS

An Accurate and Sensitive Reverse Phase High Performance Liquid Chromatography Method for the Determination of Arbutin in Blueberry Samples

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In this study, an analytical method based on high performance liquid chromatography (HPLC) was developed for the identification and quantification of arbutin in blueberry samples. Optimum conditions were investigated for qualitative and quantitative analysis of arbutin. 220 nm was selected as the most suitable wavelength in UV detection. The arbutin was separated with a mobile phase of water:methanol: 0.10 M hydrochloric acid (89:10:1, v/v/v) on a Zorbax SB C18 column. Analytical figures of merit were calculated under the optimum conditions by developing calibration plots in the concentration range of 0.010 – 250.0 mg/L for the analyte. The calibration plot of the HPLC method showed good linearity in a wide concentration range with a correlation coefficient of about 1.000 for arbutin. The LOD/LOQ values were found to be 1.98/6.60 µg L⁻¹, respectively. Spiked recovery tests were used to evaluate the applicability of the analytical method in different blueberry samples and the percent recoveries obtained ranged between 93.4 – 99.8%. The method has also been successfully applied for qualitative and quantitative determination of arbutin in different blueberry samples.

Keyword: High-performance liquid chromatography; arbutin; different arbutin samples
Determination of Lead at Trace Levels in Red Pepper Sample by Atomic Absorption Spectrophotometry Combined with Slotted Quartz Tube After Stearic Acid Coated Magnetic Nanoparticle Based Dispersive Solid Phase Microextraction

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Toxic metal contamination is one of the most important concern in environment. Lead is one of the major components of these contaminations in the consequences of its wide usage in several industrial area¹. On the other hand, even a small amount of lead intake/exposure may cause adverse effect on several organs such as kidney and lung functions, cardiovascular and reproductive system². In this study, a new analytical method was developed to determine lead at trace levels using stearic acid coated magnetic nanoparticles as solid sorbent in dispersive solid phase microextraction prior to slotted quartz tube equipped atomic absorption spectrophotometry. Iron MNPs were preferred due to their easy separation and fast application period. An experimental design was performed in the optimization of all extraction parameters. The results of the design were used to evaluate the variance analysis to determine the statistical significance of the fundamental factors of the extraction process and the interaction effects of these factors. The analytical performance values of the developed system were determined under the optimum conditions. The enhancement in detection power based on detection limit (10.3 ng mL⁻¹) comparision was found about 31 folds comparing to the conventional atomic absorption spectrometry. Spiked recovery study on red pepper sample was performed in order to determine the accuracy and applicability of the method. The percent recovery results were calculated for the samples spiked to 60 and 120 ng mL⁻¹ as final concentration as 106.6% and 102.6%, respectively. The obtained percentage relative standard deviation values below 5.0% for both concentrations verified that the developed method is suitable for the accurate and precise determination of lead in food samples.

Keywords: Stearic acid coated magnetic nanoparticles; atomic absorption spectrometry; lead; Box-Behnken design; dispersive solid phase microextraction

References
**PP42** - Sensitive Determination of Lead in Milk Samples Using Vortex Assisted Deep Eutectic Solvent Based Liquid Phase Microextraction-Slotted Quartz Tube-Flame Atomic Absorption Spectrometry System

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In this study, a deep eutectic solvent-based liquid phase microextraction (DES-LPME) method was developed for the accurate and sensitive determination of lead by slotted quartz tube-flame atomic absorption spectrometry (SQT-FAAS) after the preconcentration. Lead was extracted from the aqueous solution by using deep eutectic solvent as a green solvent. All instrumental and experimental parameters were optimized in order to lower the detection limit. Under the optimum experimental and instrumental conditions, the linear range of the proposed method was established between 50.0-1000 µg L⁻¹, and the limits of detection and quantitation (LOD and LOQ) were found to be 8.7 and 29.0 µg L⁻¹, respectively. A 48-folds improvement was observed in the detection power of the system using DES-LPME-SQT-FAAS method with respect to conventional FAAS system. In order to check the accuracy and the applicability of the developed method, recovery studies were carried out in raw milk samples and the percent recoveries obtained were between 102.5-103.2% for the spiked raw milk samples.

**Keywords:** Deep eutectic solvent; lead; liquid phase microextraction; flame atomic absorption spectrometry

**PP43** - Accurate and Sensitive Speciation of Chromium in Tap and Lake Water Samples by using HPLC-ICP-MS

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In this study, an accurate, sensitive and simple high performance liquid chromatography - inductively coupled plasma mass spectrometry (ICP-MS) system was developed for identification and quantification of chromium species. All the system parameters in separation and detection systems were optimized to lower the detection limits. The separation and quantification of the two chromium species was performed by using HPLC-ICP-MS system. The separation of Cr(III) and Cr(VI) was achieved on a anion exchange column (Hamilton PRP X100) using 80.0 mM NH₄NO₃ as mobile phase. The calibration plots of HPLC-ICP-MS method showed good linearity over a wide concentration range with close to 1.000 correlation coefficients for both analytes. The limit of detection/limit of quantification values for HPLC-ICP-MS were found to be 0.16/0.54 and 0.12/0.39 μg/L for Cr(III) and Cr(VI), respectively. Spiked recovery tests were used to evaluate the applicability of the analytical method in tap water and lake water samples, and the percent recoveries obtained ranged between 89-105.3% for both analytes. The method was also successfully applied for the qualitative and quantitative determination of both analytes in lake water samples.

**Keywords:** HPLC-ICP/MS; Cr (III); Cr (VI); speciation
PP44 - Simultaneous Determination of Four Endocrine Disrupting Compounds with Gas Chromatography-Flame Ionization Detector after Binary Solvent Liquid-Liquid Microextraction in Well and Hospital Wastewater Samples

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Endocrine disrupting chemicals cause several negative effects on endocrine system functions. These substances play important roles in the production, transport, metabolism and excretion of natural hormones. In addition, these substances may also produce similar or different effects on the target cell [1, 2]. This study describes the selective and sensitive analytical method for the determination of four endocrine disrupting chemicals with GC-FID after binary solvent liquid-liquid microextraction procedure. Experimental design was used to determine the optimum amount of binary solvent, mixing period, and dispersive solvent. The main effects of these parameters were assessed using variance analysis (ANOVA). Under the optimum conditions, limit of detection, limit of quantification and percent relative standard deviation were obtained in the range of 0.43 - 4.4, 1.4 - 15 and 0.7 – 8.2, respectively. Enhancements in detection powers for all analytes were recorded over 11 folds comparing the direct GC-FID determination. The accuracy and feasibility of the method was tested on well and hospital waste water samples. The recovery results were obtained vary between %90.8 - %112.9. These results demonstrate that the method can be used to determine the correct quantities of analytes in the both sample matrices.

Keywords: Endocrine disruptors; Pesticides; Multivariate optimization; Binary Solvent DLLME; GC-FID

References

PP45 - Determination of Anthocyanin Glucosides and Anthocyanidin Aglycones by HPLC-DAD and Validation Studies

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Anthocyanins are compounds belonging to the flavonoid family. Anthocyanins are called according to their binding position. Sugar species that are component of different regions of anthocyanins can be found in many fruits and vegetables. It was reported that these compounds have positive effects such as protection against liver injuries, suppression of proliferation of human cancer and strong anti-inflammatory and antimicrobial activities. Therefore, accurate and reliable analysis of these compounds is important. Various methods for separating anthocyanin glucosides and anthocyanidin aglycones by chromatographic methods are being developed. In this study, a method was developed to separate anthocyanin glucoside (delphinidin-3-o-glucoside, cyanidin-3-o-glucoside, pelargonidin-3-o-glucoside, malvidin-3-o-glucoside) and anthocyanidin aglycones (delphinidin, cyanidin, pelargonidin, malvidin) by using high-performance liquid chromatography-diode-detector (HPLC-DAD). For this aim, HPLC-DAD parameters such as injection volume, flow rate, column type and size, etc. were examined. Also, validation parameters including reproducibility (intraday and interday), limit of detection (LOD) and the limit of quantification (LOQ) were investigated for these compounds.

Keywords: Anthocyanin glucoside, anthocyanidin aglycone, validation, HPLC-DAD

References:
Copper is a metal of widespread use and frequently found in industrial wastewater. The major concern with heavy metals is their ability to accumulate in environment, and to cause heavy meal poisoning. Unlike some organic pollutants, heavy metals are not biodegradable, and cannot be metabolized or decomposed. Therefore, determination and removal/remediation of Cu ions in different matrices have become all the more necessary.

In this study, EDTA modified amorphous TiO$_2$ (EDTA a-TiO$_2$) was synthesized by sol-gel method in order to preconcentration of copper ions at low concentration in different matrices. Structural and physicochemical properties of the EDTA a-TiO$_2$ were determined by XRD, SEM, BET, FTIR, and zeta potential analysis. Effect of various factors such as pH, amount of adsorbent, adsorption time, initial concentration of Cu ions, desorption solutions, and effects of matrix on the uptake behavior of Cu$^{2+}$ ions from the aqueous solution was investigated.

Compared with bare amorphous TiO$_2$ (b-TiO$_2$) particles, the EDTA modified a-TiO$_2$ have a better activity in the Cu$^{2+}$ adsorption. The maximum adsorption capacity of EDAT modified a-TiO$_2$ is 4.81 mg/g. The results showed that 10 µg/L Cu$^{2+}$ ions with flow rate 0.1 mL/dk were strongly retained on the the 1.0 g of 3%(n/n) EDTA modified a-TiO$_2$ SPE column at pH 3 and were successfully desorbed by using 0.001 M NaOH solutions and the copper concentration in eluent was determined by flame atomic absorption spectrometer. The accuracy and validity of proposed method was confirmed followed by the implementation of developed method on certified reference materials (NIST 1547 peach leaves, IAEA 359 cabbage, GBW07605 tea leaves) and was evaluated by recovery test. The quantitative recovery 98% of certified reference materials was found by average of three replicates.

**Keywords:** Waste water, heavy metals, Cu$^{2+}$ ions adsorption, TiO$_2$, EDTA-modified TiO$_2$

**References**


**Acknowledgment:** İnönü University Scientific Research Projects Unit for supporting the study through the Project No ID 1377 is appreciatively acknowledged.
Insulin is a hormone that has important roles in the regulation of human metabolism. Insulin has a heterodimer containing A and B chains connected by disulfide bonds. It is secreted by beta cells in the pancreas and has a molecular weight of 5.8 kilodalton (kDa). The main functions of insulin are regulating glucose homeostasis, stimulation of glucose uptake from the systemic circulation, suppression of hepatic gluconeogenesis, and regulating glucose levels in blood. It is also involved in cellular processes such as, protein and fat synthesis, RNA and DNA synthesis, cell growth and differentiation. When the production of insulin in the pancreas does not occur, type 1 diabetes is observed and type 2 diabetes is seen in cases where the pancreas cannot produce enough insulin. According to the International Diabetes Federation, in 2040, 1 out of every 10 people worldwide will have diabetes. Blood glucose regulating pills are used in cases where insulin supplements are required to solve insulin-related problems in the functioning of metabolic events, or insulin injection is applied to the patient. However, these methods have disadvantage not only when the patient is negligent but also in the absence of medication or injection. In this study, experiments were carried out to develop bands which can supply controlled insulin release and, patient could easily stick them to his body in order to ensure that proper amount of insulin supplement can be taken on time. In this respect, the release of insulin-containing polymeric membrane, polyhydroxybutyric acid (PHB), which is compatible with the human body and which ensures long-term controlled release analysed by mass spectrometric methods. The effect of pH on insulin release due to diffusion of membranes and the amount of insulin obtained after membrane incubation with different salt solutions used in various concentrations were analyzed by mass spectrometry and information on insulin release parameters compatible with human body were obtained. In addition, amount of released insulin from polymeric membranes under different experimental conditions and optimization of the experimental parameters were determined according to quantitative data obtained by Electrospray Ionization Mass Spectrometry (ESI-MS) analysis. Finally the long-term insulin release parameters of the biocompatible polymeric material was determined.

**Keywords:** Insulin, membrane release, polyhydroxybutyric acid, mass spectrometry
ABSTRACT
By examining genes, proteins and metabolites as a whole, information about system biology can be obtained through mathematical modeling with bioinformatics approaches using new and advanced analytical techniques. The anticancer mechanism of some potential drug candidates nanoparticles on HEPG-2 liver cancer cell lines was determined by proteomic studies.

EXPERIMENTAL
The cell lines that were proliferated by applying drug candidates were used as treated cell lines and they were named as T group. The group which was not treated by any nanoparticles was used as a control group and it was expressed as group C. Proteins differentiated for group T and C groups were analyzed by Matrix Assisted Laser Ionization Mass Spectrometry (MALDI-TOF MS) following 2D gel electrophoresis separation and image analysis.

RESULTS
In this study, we observed different protein intensity values at image analyzes results for group T and C groups. The proteins over or under expressed by the treatment of nanoparticles were identified by peptide mass fingerprint analyzes. As result of proteomic studies, it was found significant changes in proteome level on cancer cell lines.

CONCLUSION
According to experimental data and identified proteins, they can be concluded that some of the applied nanoparticles could be used on liver cancer therapy. This data should be improved by further omic studies like transcriptomics and metabolomics.

Keywords: Nanotechnology, Nanoparticles, Proteomics, 2D Gel Electrophoresis, Mass Spectrometry.

References
Melatonin (MEL), is an endogenous hormone synthesized from tryptophan, mainly in the pineal gland. The role of MEL in the oral cavity is basically related to its antioxidant and anti-inflammatory effects. Hyaluronic acid (HA), a glycosaminoglycan, is an important compound that stimulates bone healing. MEL and HA acid have both favorable effects on soft and hard tissues of the oral cavity\(^1\)\(^2\). MEL and HA loaded carboxymethyl cellulose (CMC) hydrogel was prepared to produce a new synergistic system for therapeutic application in dental medicine. To examine characteristic properties of each component of MEL-HA loaded CMC hydrogel, UV-Vis spectrophotometry by applying at wavelengths 223 and 205 nm was established for the simultaneous determination of MEL and HA. Fourier transform infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, rheology and swelling measurements were used for the characterization of the hydrogel. In vitro release studies were performed by dialysis bag method. The pore size of the hydrogel matrice was found almost in the range between 300 nm to 6 µm. Melatonin showed good relase properties and compatibility with the hydrogel matrice as the the pores of the hydrogel matrice were smaller for melatonin. Consequently, the association of MEL, HA and CMC biomolecules could be used for obtaining a promising complex therapeutic agent with extensive applications in dental medicine.

**Keywords:** Melatonin, Hyaluronic acid, Carboxymethyl cellulose, Therapeutic agent, Hydrogel, UV-Vis spectrophotometry

**References:**
Pencycuron (monceren) is a new active ingredient from Bayer and is used as a fungicide to control plant diseases such as black scurf of potatoes, sheath blight of rice and ornamental plants and crop damping. The structural formula of pencycuron [1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea] is presented in the following Scheme.

In studies conducted previously, pencycuron in residue was determined by high performance liquid chromatography (HPLC-UV). Despite the determination of some fungicides by the square wave voltammetry (SWV), pencycuron determination has not yet been conducted by any voltammetric techniques. The electrochemical behavior of pencycuron was investigated by square wave stripping (SWSV) and cyclic voltammetric (CV) techniques by using glassy carbon (GC) or multi-walled carbon nano tube paste electrodes (MWCNTPE). Prior to analytical determinations, parameters such as pH, frequency, deposition time and deposition potentials were optimized. The oxidation peak potential of pencycuron fungicide was recorded +1156 mV (vs. Ag / AgCl) at pH 2.0 buffer solution and showed a good linear increments by standard addition. The peak potentials were pH-dependent in that they shifted to less positive values with increasing pH and showed a linear segment with a slope of 13.2 mV/pH.

\[ E (\text{mV}) = -13.2 \text{pH} + 1182.8(\text{mV}) \]

A new voltammetric method involving SWV together with glassy carbon or carbon paste electrodes was recommended to determine pencycuron content in agrochemicals or natural samples.

References:
PPS1- Low-Transition Temperature Mixtures Based on Amino Acids: Synthesis and Extraction Efficiency of Phenolics from Olive Mill by-Products

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Recently, consumers have become increasingly interested in new and safe added value products. Meanwhile, industry continues to confide in organic volatile solvents for the extraction of bioactive substances, contributing to environmental pollution and consumers health risk. Low-transition temperature mixtures (LTTMs) or deep eutectic solvents (DESs) is a relatively new class of solvents which usually is composed of polyols (H-donors) and organic salts (H-acceptors). Their main feature is low melting point compared to that of parent compounds. Additional properties that make them appealing as extraction solvents are; low toxicity, low vapor pressure, low cost, they are biodegradable and easily tailored. The purpose of this work is to synthesize deep eutectic solvents (DES) and to examine their efficiency as extraction media for the recovery of phenols, using as a substrate olive mill wastes. For this purpose, amino acids (L-Lysine, L-Arginine, L-Tyrosine) are combined with glycerol and lactic acid. The extractability of the chosen mixtures was optimised using response surface methodology.

Keywords: Olive; phenolics; deep eutectic solvents

PPS2- Elimination of hydrocarbon pollutants from water by adsorption using the coffee grounds activated by microwaves.

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Abstract: Removal of hydrocarbons substances from water by adsorption onto agro-food waste “coffee grounds” were studied. The novelty of this work is the use of a microwaves activated coffee grounds.

Performance of adsorption process depends on the chemical structure of organic components as phenol, initial concentrations, and the operating conditions.

Batch kinetic and equilibrium experiments were conducted to study the effects of initial concentration, activation time and activation power. Four different kinetic models, viz., pseudo-first-order, pseudo-second-order, intraparticulaire diffusion and Elovitch were used to fit the kinetics data. The pseudo-second-order model best described the experimental data. The equilibrium data were modeled by Langmuir and Freundlich. The Langmuir isotherm which provided the best correlation for phenol adsorption onto coffee grounds shows that the adsorption was favorable and the adsorption capacity found was equal to 11mg·g⁻¹.

Keywords: coffee grounds; polluted water; adsorption; Microwaves activation.
PPS3- Determination of Standard Glycosylated Proteins Using Borate Selective Electrode as a Detector in FIA System

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Glycosylated proteins, glycosylated hemoglobin (HbA1c) and glycosylated HSA (glucosylated albumin-fructosamine) are very important in the diagnosis and follow-up of diabetes. In the last 30 years; Chromatographic methods based on the charge difference between HbA0 and HbA1c, on the relation of phenylboronic acid-HbA1c and immunochemical tests based on the antigen-antibody relationship were developed for the detection of HbA1c. Chromatographic methods are expensive, require numerous preliminary procedures and professional users. Non-linear calibration curves and very perishable reagents were faced up in immunochemical tests. In the present study, a highly selective borate selective electrode that was applied as a detector in FIA system for the simultaneous detection of glycosylated proteins is described. The method can be maintained easily, economically and without the need of laborious pre-treatment and expert team. In the developed FIA method, the affinity of borate ions in the carrier solution to glycosylated proteins was utilized. The glycosylated hemoglobin and glycosylated HSA in the sample that were injected into the carrier solution reacted with the borate ions and the measurement of glycosylated proteins were performed following a reduction in the concentration of borate in the carrier solution. Potentiometric performance characterics of the borate selective electrode used in the study was examined. The electrode was revealed a linear behavior in the range of 1.0 * 10^-1 M and 1.0 * 10^-5 M borate solution in a repeated manner. On the other hand, the electrode was tested for chloride, bicarbonate, sulfate, nitrate, phosphate and chlorate ions as interferents and found selective with regular potential for only borate ion.

Key words: Biosensor, borate selective electrode, glycosylated protein assay, HbA1c determination.

PPS4- Fatty acid composition of sweet white lupin (Lupinus albus L.) seeds from Algeria

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Medicinal plants have been used in Algeria for centuries to treat different ailments. The seeds of L. albus L. are commonly used as raw to treat diabetes^1. Another effects of white lupin components are concerned in hypertension, obesity, cardiovascular diseases and colorectal cancer^2.

In this study the fatty acid composition of L. albus L. seeds was investigated by analyzing their methyl esters by GC-mass spectrometry. The major fatty acids were found as palmitic acid, oleic acid, linoleic acid and linolenic acid. Total lipid amount was determined as 11.75%.

The results were discussed in means of percentages and also ω3/ω6 ratio.

Keywords: Lupinus albus L., white lupin, fatty acid composition, Algeria

References
Evaluation of Drug-DNA Interaction Using High Performance Liquid Chromatography (HPLC)

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DNA is a nucleic acid that carries the genetic instructions necessary for all organisms and some viruses' vitality functions and biological developments. The main role of DNA is the long storage of information. Because it contains the information necessary for the construction of other components of the cell, such as protein and RNA, it is likened to a mold, template and recipe. Therefore, in order to understand the biochemical mechanisms of human disease prevention and treatment, great efforts have been made to investigate the interaction between DNA (especially dsDNA) and drug molecules¹. Furthermore, the interaction of nucleic acids with drugs is a fundamental issue in the life phenomenon. This process is directly related to the detection of bioactive substances such as molecular recognition, gene mutations, anticancer drugs, and the mechanism of action of some dsDNA-targeted drugs in dsDNA hybridization. Most known substances (e.g. ethidium bromide, daunomycin, doxorubicin, benzopyran diol epoxide, acridine derivatives, aflatoxin) that interact with DNA were shown the reduce the HPLC signal of free DNA in the chromatogram, in a reproducible dose-dependent manner². So, the aim of this study was evaluation of interaction mechanism of an atypical anti-Parkinson drug Carbidopa and dsDNA by using high performance liquid chromatography and identified the drug-DNA interaction mechanism easily, rapidly, more selectively, and safely.

Key Words: Carbidopa, DNA binding, HPLC

Reference

Synthesis of Advanced Titanium Oxide based Structures

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Titanium oxide is a very versatile material, which has a wide range of practical applications. It can be used in the design of sensors, biosensors, solar cells, waste water treatment systems, etc. Phase and crystal structure composition are especially important for successful application of Titanium oxide based structures. The application areas of Titanium oxide based structures is determined by surface morphology, band gap of formed Titanium oxide layer. Therefore, the synthesis of new titanium oxide structures with advanced properties is still on very high demand. Because advanced properties enable the extension of application areas of Titanium oxide based structures.

In this presentation methods of Titanium oxide formation will be discussed. Simple hydrothermal method enables the synthesis of controllable composition titanium suboxides from the aqueous solutions. By the variation of stoichiometry of titanium oxides some properties of formed Titanium oxide can be easily tuned. Such tuneable properties are significantly lower band gap and nanoplatelet-shaped surface morphology. The structure of formed titanium suboxides has been proved by EPR and XRD methods. Ellipsometry was applied to measure the thickness and to calculate dielectric properties and band gaps of the Titanium oxide based films. Depending on the oxide composition the band gaps varied from 3.2 eV to 1.29 eV (Fig 1). The porosity of titanium suboxide based films also varied in broad range, what enable to apply these films in the development of gas sensors.

Fig. 1. Tauc plots for indirect transitions of titanium monoxide nanoplatelet arrays

Keywords: Titanium oxide, Hydrothermal synthesis, Applications

References:
PP57 - Determination of the Change in Fatty Acid Composition During the Maceration of *Hypericum perforatum* L.

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Abstract

The aim of the study was to investigate the impact of maceration time on fatty acid composition of St. John’s wort (*Hypericum perforatum* L.) macerates in olive oil. Macerate was prepared according traditional method. The flowering tops of *H. perforatum* were macerated with extra virgin olive oil (plant/oil ration 1:4) under sunlight and 6 samples were taken with 10 days intervals from the same macerate during 50 days. Gas chromatography-mass spectrometry measurements were carried out to quantitate fatty acids in *Hypericum perforatum* macerate samples. GC-MS analyzes showed up to 13 fatty acids in oil extracts, abundantly covering oleic acid, linoleic acid, palmitic acid, stearic acid and elaidic acid. Fatty acid contents of these samples varied between macerate intervals. These results confirm that the fatty acid composition of the *Hypericum perforatum* L. oil macerate changes during the maceration time and should be monitored to obtain standardized preparations.

Keywords: *Hypericum perforatum*, Fatty acids, GC-MS, Maceration

1. Introduction

*Hypericum perforatum* L. is one of the most prominent and widely investigated medical plants during the last decades. Traditional use was characterized by external applications, mainly in the form of oils and tinctures. Some of external applications of *Hypericum perforatum* macerate are smaller wounds, sunburns, blunt traumata, ulcers, varicose, hemorrhoids, myalgia, rheumatism, keloid scars, and tooth extraction, based on folk tradition or medical experience 1-2.

The most commonly used external preparation of *H. perforatum* is its oily macerate made from fresh or dried flowers of the plant. For preparation of *H. perforatum* macerate in oil, the plant material is mixed (1:4) in vegetable oil (mostly olives, sunflowers, or others) in a white glass, the glass sealed and exposed to sunlight for about 4–6 weeks; during this time, the oil takes on an intense red color1,3.

There are studies in the literature related to the fatty acid composition of macerations made with *H. Perforatum* using different oils4 and changes in oil characteristics due to other environmental factors. However, no studies have been found related to the changes in fatty acid composition during maceration.

In this study, the change during the maceration time in fatty acid composition of *Hypericum perforatum* macerate prepared in olive oil was followed using GC/MS.

2. Materials and Method

In this study, samples were taken with 5 days intervals during 50 days of maceration of *Hypericum perforatum* (Fig. 1) and the variations in fatty acid composition was followed by GC/MS. 100 µL of the sample was weighed into a volumetric flask, then 9.80 mL of hexane was added. After vortexing for 1 min, 100 µL of 2N KOH dissolved in methanol was added and vortexed. After centrifugation at 4000 rpm for 10 min, the supernatant was removed for injection. An quadrupole mass spectrometer and J&W 112-88A7, HP-88 (60m x 250µm x 0.25µm) column were used for analyses. For GC/MS detection, an electron ionization system was used. Carrier gas was helium 29.901 psi at a flow rate of 1.8 mL/min. Injector and MS transfer line temperatures were set at 250 ºC. The oven temperature was held at 70 ºC for 1 min, and then increased up to 175 ºC with 10 ºC/min increments for 10 minute. Then, it was increased up to 210 ºC with 5 ºC/min increments for 5 min. Finally, increased up to 230 ºC with 5 ºC/min increments for 7.5 min. Diluted samples (1/25, w/v, in hexane) of 0.5 µL were injected automatically in the split mode. Split ratio was 50:1. Mass range was from m/z 50 to 650 amu.
The library search was carried out using NIST and Wiley 2008 (Gas chromatography-Mass spectrometry) GC-MS libraries. Supelco™ 37 components of (fatty acid methyl ester) FAME mixture (Catalog no: 47885-U) was used for the comparison of the GC chromatograms.

3. Results and Discussion
The chemical compositions of thirty seven fatty acids were analyzed using GC/MS. It was ensured by the qualification and evaluation of in the samples. A total of 37 fatty acids were identified and 13 of fatty acid were detected in Hypericum perforatum oil samples. Oleic acid (C18:1n9c), palmitic acid (C16:0), linolenic acid (C18:2n6t), myristic acid (C14:0), marginic acid ((C15:0), cis-10-heptadecenoic acid (C15:1), palmitoleic acid (C16:1), elaide acid (C18:1n9t), stearic acid (C18:0), cis-11-eicosenoic acid (C20:1), arachidic acid (C20:0), behenic acid (C22:0), lignoceric acid (C24:0) and squalene were detected in Hypericum perforatum oil after completion of maceration. The values were summarized in Table 1.

After 50 days of maceration, slight changes were detected in Hypericum perforatum oil in terms of fatty acid contents, myristic acid, palmitic acid, palmitoleic acid, elaide acid, cis-11-eicosenoic acid. However, during the maceration of Hypericum perforatum oil, the most frequent increase was found in marginic acid, cis-10-heptadecoenoic acid, stearic acid, arachidic acid, behenic acid and lignoceric acid contents. Additionally, oleic acid and linoleic acid contents were slightly decreased during the maceration of Hypericum perforatum oil. Besides, squalene content of the samples of Hypericum perforatum oil during the maceration was decreased dramatically.

Figure 1. Change in the appearance of olive oil during the H. perforatum maceration

Conclusion
Enhanced knowledge on the fatty acid composition of H. perforatum L. olive oil macerate would provide standardized industrial application of this plant and its value added products. The change during the maceration time in fatty acid composition of Hypericum perforatum macerate prepared in olive oil was examined using GC/MS.

References
Table 1. Changes in fatty acid methyl esters of *Hypericum perforatum* oil during maceration for ten days intervals

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<td>35</td>
<td>(C24:0)</td>
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<td>0.082</td>
<td>0.086</td>
<td>0.098</td>
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<tr>
<td>36</td>
<td>(C24:1)</td>
<td>&lt; nd</td>
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<tr>
<td>37</td>
<td>(C22:6n3)</td>
<td>&lt; nd</td>
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</tr>
</tbody>
</table>

nd: not detected
Development of immunosensors: immobilization of antibodies on different surfaces

Almira Ramanaviciene1,2*, A. Kausaite-Minkstimiene1,2, I. Morkvenaite-Vilkonciene1, A. Popov1,2, B. Brasliunas1, Arunas Ramanavicius1,3

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Immunosensor is an analytical device consisting of specific immune system molecules immobilized on the signal transducer. Upon analyte binding and immune complex formation the physicochemical changes on the surface are converted to a measureable signal proportional to the analyte concentration. Characteristics of an immunosensor such as sensitivity, stability, regenerability, depend on the type and amount of immobilized antibodies, on the remaining activity of antigen binding sites after immobilization and on the proper orientation on the sensing surface [1]. Although sensor surfaces prepared with antibodies immobilized in a random manner yield satisfactory results, site-directed immobilization of the sensing molecules significantly improves the immunosensor sensitivity [2,3]. Number site-directed antibody immobilization strategies are based on employing antibody-binding proteins, antibody fragments or oligosaccharide moieties present in antibody structure. Proper immobilization of antibodies is of considerable interest in many fields of interest, e.g. in clinical diagnostics (for the specific cancer biomarkers, different hormones detection), in food safety analysis or environmental monitoring [2-4].

In this work different antibody immobilization methods on plane gold, gold and ZnO nanostructures for the direct analyte detection are presented and compared. Advantages, disadvantages and analytical characteristics of immunosensors based on surface plasmon resonance, electrochemical and fotoluminescence signal transducers are discussed.

Acknowledgments
This work is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme – H2020-MSCA-RISE-2017 „Novel 1D photonic metal oxide nanostructures for early stage cancer detection“ (Project No 778157).

References:
Cytarabine (CYT) is a chemotherapy drug used to treat acute myeloid leukaemia (AML). It may also be used to treat other types of leukaemia and lymphomas. Absorption distribution metabolism excretion (ADME) studies are critical in modern drug discovery. Drugs are removed from the body by various elimination processes. Drug elimination refers to the irreversible removal of drug from the body by all routes of elimination. Drug excretion is the removal of the intact drug. Maximum plasma level of CYT is 26.3 µg/L. Less than 10% of a dose is excreted as unchanged drug in urine. Patients with severe renal insufficiency appear to experience a higher incidence of side reactions, in patients with renal failure is associated with an increase in toxic side-effects. Monitoring excreted urine drug level may help to renal insufficiency.

Spectrophotometric and chromatographic methods were developed for the determination of CYT from urine. First, a sensitive, simple and specific spectrophotometric method was developed for the determination of CYT from urine. Liquid-liquid extraction were used to separation of drugs from urine. UV detector was set at 278 nm. Calibration standard solutions of CYT were prepared within the 1.94 µg/mL and 4.86 µg/mL concentration range. A liquid chromatography (HPLC) method with MSMS detection was developed for determination of CYT from urine. The analysis was carried out using C18 (5 µm x 4.6 x 250mm) column with a mobile phase consisting of ACN and %0.5 Formic acid, at a flow rate of 0.5 mL/min. The developed methods were used to determine urine levels of CYT for excretion studies. Spectrophotometric method can be use for high dose application because of its sensitivity, for low level dose HPLC_UV method can be use.

References
Edible mushrooms are considered and consumed as valuable foods due to their unique flavor, nutritional properties and biological activities. Amongst all the edible mushrooms, the truffles have a number of distinctive characteristics. In addition to nutritional value, mushrooms have been used as food flavoring material in soups and sauces for centuries, especially because of their unique aromas. In this study, Tuber mesentericum mushroom was collected and its nutritional value was analyzed using various analytical methods. New extraction and sample preparation techniques were developed and phenolic compound profiles and free amino acid content were analyzed by UPLC-ESI-MS/MS. In addition, the antioxidant activities of hexane, ethyl acetate, alcohol and water extracts were analyzed using β-carotene bleaching, DPPH and ABTS assays. Moreover, fatty acids of T. mesentericum were determined by GC-MSD and mineral content was determined using ICP-MS.

As a result, T. mesentericum mushroom was found to be rich in phenolic compounds. In Tuber mesentericum, p-hydroxybenzoic acid (11.38±0.10 µg/g), protocatechic acid (9.01±0.12 µg/g) and caffeic acid (2.62±0.08 µg/g) were detected. Free amino acids of Tuber mesentericum were detected as 35.85±0.20 mg isoleucine, 49.35±0.18 mg leucine and 37.81±0.30 mg phenylalanine in 100 g of mushroom. Mineral content analysis of T. mesentericum, which is found to be rich in polyunsaturated fatty acid linoleic acid, has been analyzed with the ICP-MS and 20155.02±2.51 µg/g potassium, 901.47±1.56 µg/g phosphorus and 847.20±0.598 µg/g magnesium were detected. Nutritional content of T. mesentericum reveals its importance in the food and pharmaceutical industry. Chemical compounds which can be used as food additive with antioxidant activity were determined in study. Tuber mesentericum was found to be rich in minerals and free amino acids. Results were also provided valuable experimental data with new techniques and analytical methods.

Keywords: Phenolic profile, Amino acids, Tuber mesentericum, ICP-MS, UPLC-MS/MS

References

Acknowledment: We would like to thank Niyazi ULUÇOBAN, Chairman of the Board of Tuber Mushroom Promotion and Research Association, who worked with dedication in the process of making mushrooms collection.

This study has been granted by the Muğla Sıtkı Koçman University Research Projects Coordination Office through Project Grant Number: 17/289
Voltammetric Determination of Carboxin Fungicide Using Glassy Carbon Electrode

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Carboxin is a fungicide used to control plant diseases such as smut, rot and blight on corn, rice, cotton, barley, oats, and wheat [1]. The structural formula of carboxin [5,6-dihydro-2-methyl-1,4-oxathiine-3-carboxanilide] is presented in the following Figure.

In this study, square wave stripping (SWS) and cyclic voltammetric techniques (CV) are used to investigate electrochemical behavior of carboxin. In this sense, significant parameters such as pH, frequency, accumulation time and accumulation potential were optimized. The electro-oxidation peak potential of carboxin fungicide was recorded at +945 mV (vs. Ag/AgCl) and pH 2.0 H$_2$SO$_4$ solution. The electro-oxidation peak showed a good linear increment by standard addition. The cyclic voltammograms on glassy carbon electrode (GCE) at different potential scan rates exhibited that the peak potentials were shifted to more positive direction (Fig. 2).

In addition, the influence of some inorganic species and common pesticides on the determination of carboxin has also been studied. The voltammetric method was also applied for the determination of carboxin in commercial formulation.

Key Words: Pesticide, Carboxin, Voltammetry, Determination

Calcium is one of the most important elements for the growth and maintenance of human body. It is present in milk, meat, vegetables, etc., and it is accumulated in animals in the form of calcium phosphate in bones and teeth. In view of its importance, it is important to determine its concentration in biological and environmental samples. Thus, ion-selective microelectrodes are potential tools for studying with smaller amount of sample volumes. In this study, a calcium ion-selective microelectrode has been fabricated by comprising a PVC selective membrane matrix containing calcium ionophore “calimycin” (itself has antimicrobial activity against gram positive bacteria and fungi) coated on copper wire, previously covered with a solid-state contact mixture. We found that the calcium ion-selective microelectrode showed a Nernst characteristics in a concentration range of $10^{-1}$ to $10^{-6}$ mol/L. The selectivity coefficients over the main interfering ions of biological interest proved that the calcium microelectrode is highly selective. The short response time for Ca$^{2+}$ ions indicates its fast response characteristic (6s). The pH variation did not significantly modify the calcium microelectrode answer, being stable over the pH range (6.5-7.5) of interest. The calcium ion-selective microelectrode can be used over a period of two months with good reproducibility and sensitivity. The manufacture process of the ISE is easy and inexpensive. Also, it has reliable electrochemical response and can be, recommended as a solution for assessing the level of calcium ions of the gingival crevicular fluid and saliva.

**Keywords:** calcium, microelectrode, dental, medicine.

**References:**
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**Acknowledgement:** This research was supported by the scientific and technological research council of Turkey, TUBITAK, project number 9170032, MANUNET HAMELデン.
PP63 - Electrocatalytic Activity of Tungsten oxide Modified Electrodes Decorated with Platinum Nanoparticles towards Oxygen Reduction Reactions and Analytical Applications

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Transition metal oxides display unique electrocatalytic activities towards oxygen reduction reaction (ORR)\(^1\). Tungsten oxide (WO\(_x\)) modified electrode surfaces and their electrocatalytic activities are being popular recently owing to their remarkable electronic and catalytic properties depending on the synthesis procedure\(^2\). Catalytic activity can be further enhanced by decorating with noble metal particles due to the hypo-d and hyper-d interactions.

Present study describes the electrochemical synthesis of tungsten oxide film on glassy carbon electrode surfaces by pulsed deposition (PD) technique in comparison to the cyclic voltammetry (CV). The oxide film was further decorated with platinum nanoparticles (GCE/WO\(_x\)-Pt) from a 0.01 M sulfuric acid solution and obtained electrode surface has been characterized by using XPS and SEM measurements. The influence of experimental parameters was investigated by evaluating the ORR signal recorded in pH 5.0 BR buffer solutions. Solution characteristics (platinum to tungstate mole ratio, the medium pH) and operational parameters (potential range and scan rate for CV and pulse potentials and duration for PD) have been optimized.

Overall results have been summarized in Table 1. The modified electrode has displayed a high catalytic activity towards ORR and therefore, it can be considered as a good candidate for biosensor studies in which oxygen signal is monitored. The surface provides a platform for enzyme immobilization such as horseradish peroxidase.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Peak Current (µA)</th>
<th>Peak Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare GCE</td>
<td>11.5</td>
<td>-0.40</td>
</tr>
<tr>
<td>CV-GCE/WO(_x)-Pt</td>
<td>58.0</td>
<td>0.18</td>
</tr>
<tr>
<td>PD-GCE/Pt</td>
<td>33.57</td>
<td>0.20</td>
</tr>
<tr>
<td>PD-GCE/WO(_x)-Pt</td>
<td>40.0</td>
<td>0.34</td>
</tr>
</tbody>
</table>

**Table 1 Peak characteristics of ORR recorded at different electrodes**

**Keywords:** Tungsten oxide, ORR, pulsed deposition

**References:**


**Acknowledgement:** This study was supported by Ege University Scientific Research project no: 2018/FEN/036.
Bronchial asthma and chronic obstructive pulmonary disease (COPD) are among the most common chronic diseases\(^1\). Roflumilast is a novel, potent, selective and long acting phosphodiesterase 4 (PDE-4) inhibitor for the treatment of bronchial asthma and COPD. It has anti-inflammatory effects and it has been shown to reduce exacerbations and improve pulmonary function in patients with COPD\(^2\). In this study a square-wave stripping voltammetric method was developed and validated for the direct determination of roflumilast in pharmaceutical formulations. Optimization of the variables such as type and pH of supporting electrolyte and various instrumental parameters such as frequency, scan increment, pulse amplitude, accumulation potential and accumulation time were examined. The proposed method was based on electrochemical reduction of roflumilast at a hanging mercury drop electrode in 0.1 M K\(_2\)HPO\(_4\)-0.1 M Na\(_2\)B\(_4\)O\(_7\) (25:25, v/v) buffer at pH 5.0. Two reduction peaks were observed at -1150 and -1300 mV with 30 s of accumulation time and -850 mV of accumulation potential time versus Ag/AgCl reference electrode. The highest peak current values with the best peak definition were observed at the frequency of 50 Hz, scan increment of 5 mV and pulse amplitude 25 mV. The electrochemical behavior of roflumilast was investigated by cyclic voltammetry. The cyclic voltammogram of roflumilast exhibited two peaks and the reduction reaction was irreversible. The peak potential shifted to a more negative value on the increase of the scan rate, confirming the irreversible nature of the reduction process. A plot of log \(i_p\) (logarithm of peak current) versus log \(v\) (logarithm of scan rate) gave a straight line with a slope of 0.4791, which is expressed the diffusion-controlled electrode process. This equation was found to be: log \(i_p\) (\(\mu\)A) = 0.4791 log \(v\) (mV s\(^{-1}\)) - 2.0838, \(r = 0.9913\) (\(n = 6\)). The proposed method was validated by evaluating validation parameters such as linearity, sensitivity, repeatability, accuracy, precision, selectivity, recovery, robustness and ruggedness. Under the optimum conditions, square-wave stripping voltammograms recorded with increasing amounts of roflumilast showed that the peak current increased linearly with increasing concentration. A good linear correlation was obtained between the electrochemical response of roflumilast and its concentration in the range of 0.74 - 3.05 \(\mu\)g mL\(^{-1}\) under the optimum conditions. This method was applied successfully for the determination of roflumilast in tablet dosage form (Daxas\(^3\)) to assess active roflumilast content. **Keyword:** Roflumilast, Square-wave stripping voltammetry, cyclic voltammetry, Validation, Tablet analysis.

**References**

Drug active substances at ppm levels have the potential to cause negative effects for human and removal of these compounds through drinking and domestic water treatment processes is therefore emerging concern. Different kinds of sorbents, which are low-cost materials; such as natural clays, activated carbon, chitosan, alginate, microalgae biomass and others, to remove pharmaceutical compounds have been reported for the sorption process lately\textsuperscript{1,2}.

In this study, we present the synthesis of an efficient adsorbent, activated carbon/calcium alginate composites, \textit{via} a freeze-drying method using calcium chloride as a cross-linking agent between activated carbon and sodium alginate. The adsorption parameters of tetracycline onto the activated carbon embedded alginate were investigated through several parameters including pH, adsorbent dosage, the initial concentration of tetracycline, and agitation time. Also Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Halsey, Javanovic, Elovich, Harkins Jura adsorption isotherms were used to investigate the adsorption equilibrium. The kinetics of the adsorption process was determined using the adsorption kinetics were described using pseudo-first order, pseudo-second order, Weber–Morris, Elovich, and Bangham kinetic models.

**Keywords:** alginate, activated carbon, tetracycline, adsorption

**References**


**Acknowledgement:** This research was fully supported by Yalova University, Scientific research Project Unit under Project Number BAP-2018/YL/0013.
The Variation Of Acetic Acid Level In Breath Of Asthma Patients And Healthy Subjects

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Early intervention is recommended for preventing aggravation and progression of asthma. Breath is totally non-invasive and safe, making it much easier to collect than bio-fluids such as blood and urine. Because of these reasons, breath analyzers are very important and studies on this subject are increasing. One of the most studied biomarker groups in breath air analyzes is volatile organic compounds VOCs. In humans, VOCs are mainly released from cells that produce reactive oxygen species (ROS) in response to oxidative stress caused by activated leukocytes during inflammation [1].

Acetic acid is a kind of VOC and produced by metabolism of carbohydrates and fats in humans. The detection and characterization of acetic acid is highly important in many fields, including breath analysis and atmospheric monitoring. However, the concentration of free acetic acid in cells is kept at a low level to prevent the change of pH in the cell. Acetic acid can also be produced by certain bacteria. Some of studies reported that acetic acid can be used as biomarker for the diagnosis of cancer [2-3] and asthma. Thus, a sensitive method is required for the analysis of acetic acid.

In this study, NTD based sensitive analysis method was developed and applied for the analysis of acetic acid in healthy and asthma patients. The analysis was carried out in 100 asthmatics and 50 healthy patients. The higher acetic acid levels was obtained in asthma patient’s breath.

Acknowledgement: The authors gratefully acknowledge the Turkish Ministry of Science TUBITAK (116S196) and Ege University for financial support.

References
Dopamine (DA) is a chemical that is naturally produced in the body. In the brain, it acts as a neurotransmitter by activating dopamine receptors. Therefore, its determination is important as an attractive target for neuroscience research.

Present study presents a voltammetric method development for DA determination at a cobalt oxide/gold nanoparticle modified glassy carbon electrode (GCE/CoOx/AuNP) in BR buffer solutions. Cobalt oxide and gold nanoparticle were deposited with cyclic voltammetry on the GCE, consecutively in pH 4.0 chloroacetic acid/acetate buffer solution and then, 0.1 M HCl respectively. The electrode was transferred to the pH 2.0 BR buffer solution and the electrochemical behavior of DA was monitored by using cyclic (CV), differential pulse (DPV) and square wave voltammetry (SWV) techniques.

Table 1 summarizes the anodic and cathodic peak currents (\(I_{p,A}\) and \(I_{p,C}\)) and corresponding peak potentials (\(E_{p,A}\) and \(E_{p,C}\)). As can be deduced from the Table, best peak formation was obtained with GCE/CoOx/AuNP and used for further studies. Analytical characteristics of the method have been investigated by using DPV and SWV techniques and latter was found more sensitive allowing to attain submicromolar levels.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(I_{p,A}) (µA)</th>
<th>(E_{p,A}) (V)</th>
<th>(I_{p,C}) (µA)</th>
<th>(E_{p,C}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCE</td>
<td>6.9</td>
<td>0.57</td>
<td>6.2</td>
<td>0.37</td>
</tr>
<tr>
<td>GCE/Au</td>
<td>7.2</td>
<td>0.63</td>
<td>5.6</td>
<td>0.31</td>
</tr>
<tr>
<td>GCE/CoOx</td>
<td>10.1</td>
<td>0.51</td>
<td>8.4</td>
<td>0.41</td>
</tr>
<tr>
<td>GCE/CoOx/Au</td>
<td>21.6</td>
<td>0.49</td>
<td>17.2</td>
<td>0.44</td>
</tr>
</tbody>
</table>

**Keywords:** Dopamine, Cobalt oxide, Gold nanoparticle

**References**


Aptamer based biosensors have great attention because of sensitive and selective detection of various biological toxins such as OTA (Ochratoxin A)\(^1\). Transition metal oxides have exhibit unique electrocatalytic properties, large surface area, and strong adsorption ability of biomolecules for electrochemical biosensing applications\(^2\). In addition, these oxide films display strong interactions with noble metal nanoparticles deposited on the surface via several techniques including cyclic voltammetry (CV). Among them, Pulsed Deposition (PD) technique provides a high dispersion of the metallic NPs compared to other methods. Manganese oxide (MnO\(_x\)) can be deposited on the electrode surface in mixed valent form and its electrocatalytic performance can be further enhanced by decorating Pt nanoparticles on the oxide film\(^3\).

In this study, PGE/MnO\(_x\) electrode was prepared by both PD and CV techniques. dsDNA was immobilized onto PGE/MnO\(_x\) surfaces by covalent attachment and modified surfaces by different techniques were monitored by electrochemical impedance spectrometric (EIS) transduction of the \(R_{ct}\) in the presence of 5 mM [Fe(CN)\(_6\)]\(^{3−}/4−\). Label-free electrochemical aptasensor design for determination of Ochratoxin A (OTA) was performed. 5′ amino- OTA sensitive aptamer was immobilized onto PGE/MnO\(_x\) surfaces by immersing the aptamer solution for 3 hours. %1 BSA solution was used as a blocking agent for 1 hour. Aptamer modified surfaces was immersed into a OTA solution prepared in PBS buffer for 1h.

Electrochemical impedance measurements were carried out in the presence of 5mM [Fe(CN)\(_6\)]\(^{3−}/4−\). The effect of different deposition techniques on dsDNA adsorption ability was evaluated. An impedimetric aptasensor based on immobilized DNA aptamer onto PGE/MnO\(_x\) surfaces was developed. The binding interaction between the OTA and the DNA aptamer sequence was determined by the Electrochemical Impedance Spectrometry technique.

**Keywords:** Metal-metaloxide, aptamer, biosensor

**References**


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3- Ozdokur et al., Pyranose oxidase and Pt–MnO\(_x\) bionanocomposite electrode bridged by ionic liquid for biosensing applications, Sensors and Actuators B 197 (2014) 123–128
Formaldehyde, the smallest carbonyl compound, is a colorless gas with a penetrating odor, high volatility and reactivity at room temperature. Formaldehyde used in the various branches of industry such as leather tanning and finishing process. Because of its high chemical reactivity and versatility as a chemical intermediate, formaldehyde is considered a toxic substance, with irritant and local necrotic effects and potentially carcinogenic. Therefore, determination of its residue level on daily used leather and textile products is important. The standard method (TS EN ISO 17226-1) for the determination of formaldehyde in the leather is based on measuring with HPLC after derivatization with 2,4-dinitrophenyl hydrazine. However the analysis is of difficulties due to contamination risk during extraction procedure. The vapours sampled from headspace (HS) after being derivatized with o- (2,3,4,5,6-pentafluorobenzyl) -hydroxylamine (PFBHA) can be determined by HS/GC-MS method. The main goal of this study is to develop a sensitive method for the quantitation of formaldehyde in the leather samples. Chemometrics is a useful tool for providing maximum chemical information by analyzing data by using mathematical and statistical methods. Method optimization and experimental design can be achieved by this means. Screening experiments were carried out by using Plackett Burmann Design to reveal the factors effecting on the signal. The main effects of the factors were calculated in relation with the parameter of peak areas obtained from the chromatograms. According to these results the main factors have been determined as the sample volume, splitless purge flow, temperature of reaction cell and extraction cell and injection temperature. Then, the analytical characteristics of the method have been evaluated.

Key words: HS-GC/MS, Formaldehyde, PFBHA, Chemometric Approach

References
Variations in Cobalt, Zinc, and Iron Contents in the Roots of Some Native Plants Around Tungsten Contaminated Area

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Abstract. This study evaluates the elemental composition (Co, Zn, Fe, and W) of Marrubium astracanicum Jacq., Anthemis cretica, Trisetum flavescens, Plantago holosteum Scop., Dianthus leucaphaeus Sibth. var leucaphaeus, Erysimum pulchellum (Willd.) from an abandoned W mine work. Kjeldahl digestion was used for the decomposition of the soils of the selected species. Plant and surrounding soil samples were taken from the waste removal pools of an abandoned W mining area. The contents of these elements in soils may contribute the uptake characteristic in roots under W stress by showing their competitive and complementary effects.

Keywords: Element, native plants, tungsten mine, ICP-MS

Introduction
Tungsten (W) has been classified as an “emergent contaminant” by the Environmental Protection Agency. Although the concentration of tungsten in non-polluted soils generally ranges from 0.4 to 5 mg kg⁻¹,¹ this levels can be exceeded in the environment due to human activities, such as mining. The contamination of W on biological systems has not been clearly identified.² In terms of environmental studies about tungsten, more attention has been given to W mining sites, as these sites are the main source of tungsten contamination in natural environments.³ The production of tungsten in Turkey was mainly performed at the Etibank Tungsten Mine Work site on Uludağ Mountain (Bursa), and mining activity persisted for twenty years. In this study, native plants, Marrubium astracanicum Jacq., Anthemis cretica, Trisetum flavescens, Plantago holosteum Scop., Dianthus leucaphaeus Sibth. var leucaphaeus, Erysimum pulchellum (Willd.) were selected for elemental determinations. Zn, Fe, and Co levels were studied under elevated W concentrations.

Materials and Method
This study was performed around the Etibank Tungsten Mine Work, Uludağ Mountain, Bursa, Turkey. Surrounding soils of selected species were taken using vinyl gloves from each sampling site, separately (n=3). The depth of soil sampling was 0 to 15 cm and sampling was conducted on July 2015. Roots of the plant samples were removed and washed with ultrapure water using ultrasonic bath. A multi-element standard solution (Merck 110580), suprapure quality acids 0.45 μm hydrophilic polyvinylene fluoride syringe filters (Millex-HV), and ultrapure water (18.3 MΩ.cm⁻¹) were used for sample preparations. Elemental levels determined using an Elan 9000 ICP-MS (PerkinElmer Scienix). The optimum instrumental conditions were detailed elsewhere.⁴ A DK 20 Kjeldahl digestion unit (VELP Scientifica, Milan, Italy) was used for the soil samples. A total of 0.5 g of soil samples was digested by the method of Bednar et al. (2010)⁵ using nitric acid, phosphoric acid, and hydrogen peroxide.

Results and Discussion
Table 1 shows the W contents of soils. As the concentration of tungsten in non-polluted soils generally ranges from 0.4 to 5 mg kg⁻¹,¹ increased W contents of soils could be an indicator of W pollution mostly originating from mining activities. In our study, W levels were ranged from 883 to 2591 mg kg⁻¹. In addition to that, Table 2 showed the selected elemental contents of examined species. Only Co seemed to be in different characteristics which showed similar tendency among studied species depending on the absolute content and standard deviations. Variations among elemental contents except Co, may show species-specific uptake characteristics of elements.
Table 1. Total W contents in the soils of studied species

<table>
<thead>
<tr>
<th></th>
<th>M. astracanicum</th>
<th>A. cretica</th>
<th>T. flavescens</th>
<th>P. holosteum</th>
<th>D. leucaphaeus</th>
<th>E. pulchellum</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>2117±131</td>
<td>1379±672</td>
<td>1093±224</td>
<td>2591±112</td>
<td>2027±90</td>
<td>883±178</td>
</tr>
</tbody>
</table>

Table 2. Total elemental contents in the roots of studied species

<table>
<thead>
<tr>
<th></th>
<th>M. astracanicum</th>
<th>A. cretica</th>
<th>T. flavescens</th>
<th>P. holosteum</th>
<th>D. leucaphaeus</th>
<th>E.pulchellum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.05±0.01</td>
<td>0.03±0.01</td>
<td>0.05±0.02</td>
<td>0.05±0.01</td>
<td>0.04±0.01</td>
<td>0.10±0.05</td>
</tr>
<tr>
<td>Fe</td>
<td>19.0±1.6</td>
<td>26.4±18.5</td>
<td>29.1±11.8</td>
<td>23.4±10.1</td>
<td>20.67±2.92</td>
<td>52.6±33.4</td>
</tr>
<tr>
<td>Zn</td>
<td>264.2±27.3</td>
<td>144.2±18.5</td>
<td>196.1±69.5</td>
<td>535.7±148.4</td>
<td>45.95±8.47</td>
<td>96.9±49.6</td>
</tr>
<tr>
<td>W</td>
<td>11.6±2.37</td>
<td>9.3±0.4</td>
<td>8.3±0.8</td>
<td>27.8±5.2</td>
<td>3.77±1.04</td>
<td>21.2±12.7</td>
</tr>
</tbody>
</table>

Conclusions

Our findings contribute to the scientific information about the effect of tungsten on plants and ecosystems. Further studies may be conducted including statistical evaluations to reach more realistic complementary effects of elements.

References

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3- Wilson, B, Pyatt, FB. 2006, Bio-availability of tungsten in the vicinity of an abandoned mine in the English Lake District and some potential health implications, Sci Total Environ., 370, 401-408.

Acknowledgments

The Commission of Scientific Research Projects of Uludag University (project number F-2008/25 and F-2015/64) is gratefully acknowledged for this study.
Development of Magnetic Dispersive Microextraction Technique for Pesticide Analysis in Grape Juice Samples

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The use of pesticides in protection and product development in agriculture, causes pests to become more durable, decrease the quality of the product and cause acute and chronic poisoning of animals and humans. Product protection strategies and many health-related organizations have introduced rigid regulations in maximum residual amounts to maintain food quality and safety. For these reasons, the evaluation of pesticide residues is nowadays a priority objective for environmental, food and health scientists.

The most common and accepted method for determining the amount of pesticide residues is the chromatographic devices with different detector systems. However, the importance of preparing the samples for analysis in increasing the reliability and sensitivity of the results is becoming more and more evident nowadays. Efforts to develop methods for faster, easier and sensitive analysis of pesticide have started to be popular and green micro-extraction methods have been developed and used in different sample matrix.

Magnetic dispersive solid phase microextraction (MSPE) is one of the new procedure of micro extraction based on the use of magnetically modified adsorbents. This technique has gained much attention due to easy separation under an applied external magnetic field, minimum solvent consumption and the extraction efficiency. In this sample preparation method, a series of magnetic particles have been used for the extraction of organic pollutants including, nano iron oxide, iron oxide grafted with graphene and carbon nano tube.

In this work it was aimed to develop a novel magnetic surface for the extraction of pesticides from juice samples. For this purpose, Fe3O4/Ni/NiB nanocomposite magnetic adsorbent was synthesised and 3.0 mg of this nanocomposite particles were weighed transferred into the centrifuge tube containing 10.0 mL of grape juice sample (pH:4). The mixture was sonicated for 2 min and further stirred in a vortex stirrer for 30 min. Nano particles were isolated from the sample by placing a strong magnet at the bottom of the tube and the liquid phase was removed. The preconcentrated target analytes were desorbed with ethyl acetate and analysis was performed by GC-ECD system. The regression coefficients relating to linearity were at least 0.99. Under optimized conditions the linear range was found between 0.1 – 5 ng mL⁻¹, and the detection limits were calculated as above 0.03 ng mL⁻¹. Recoveries from spiked grape juice samples were calculated as above 80% and RSDs were no higher than 15%.

**Keywords:** Magnetic dispersive, green chemistry, Pesticide, Chromatography

**References:**

**Acknowledgment:** The authors gratefully acknowledge Ege University (2017FEN069) for financial support.
**PP72 - Effect Of Scopoletin On α-Glycosidase Enzyme**

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² Erzincan Binali Yıldırım University, Çayırlı Vocational School, Medical Services and Technics. Department, Erzincan
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**Objective:** The α-glycosidase enzyme is an important enzyme that converts glycogen to glycoside in metabolism. The α-glycosidase enzyme is an enzyme that increases the blood glucose level. The inhibition of the enzyme α-glucosidase is important because of the antidiabetic effect. In this study, the inhibitory effect of Scopoletin on α-glycosidase was examined and compared with Acarbose, a standard.

**Materials and Methods:** α-Glycosidase was used as substrate for β-NPG to determine enzyme activity. First, 250 mL of phosphate buffer (0.15 U / mL, pH 7.4) was prepared. Then 20 μL of enzyme in 5 μL sample was added. p-NPG (5 mM, pH 7.4) for 10 minutes at 35 ° C. Acarbose was used as a positive control. Absorbances were measured spectrophotometrically at 405 nm. An α-glycosidase unit was calculated based on the amount of enzyme catalyzing 1.0 molar substrate hydrolysis (pH = 7.4) per minute.

**Findings:** IC₅₀ values were calculated from the Scopoletin - Induced Activity (%) - [Scopoletin] graph and the Ki value was calculated from the Lineweaver-Burk graph.

**Conclusion:** In this study, the inhibitory effect of Scopoletin on α-glycosidase was examined. According to the results, the IC50 value of Scopoletin was 803.94 nM, while the mean Ki value was 572.88 nM. The results obtained are expected to make an important contribution to drug design and pharmacological applications.

**Key words:** Scopoletin, α-Glycosidase, enzyme inhibition

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**PP73 - Inhibition Properties of Teucroside, Arbutin, and Oleuropein on Carbonic Anhydrase and Acetylcholinesterase Enzyme Activity**

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³ University of Health Sciences, İstanbul Turkey
E-mail: ruyakaya17@gmail.com

Phenolic compounds are found in many plants and are the natural polyphenols. Various epidemiological research showed that flavonoids which are found in dietary supplements prevented some diseases and attenuated the side effects of various over the counter drugs.

Carbonic anhydrases (CAs) are a crucial enzyme including metal in the active site. These enzymes catalyze the reversible hydration of carbon dioxide (CO₂) to bicarbonate (HCO₃⁻) and proton (H⁺).

Acetylcholinesterase (AChE) are significant forms of cholinesterases in mammalian. It is characterized by very high concentrations in the placental tissue, brain, muscle, nerve cells, and erythrocytes. The objective of this study was to examine inhibitory effects of teucroside, arbutin, and oleuropein on CA and ACh E Enzyme activity.

IC₅₀ constants of teucroside, arbutin, and oleuropein were determined as 32.84, 93.15, and 34.14 nM for hCAI; 29.48, 70.50, and 43.31 nM for hCAII; 28.64, 38.08 and 48.46 for AChE, respectively.

Kᵢ constants of teucroside, arbutin, and oleuropein were determined as 32.60±7.40, 46.98±2.36, and 52.69±11.97nm for hCAI; 46.98±2.36, 13.63±1.64, and 52.69±11.97nm for hCAII; 14.95±0.99, 26.00±9.77, and 26.99±6.71 for AChE, respectively. These findings indicate that Teucroside, Arbutin, and Oleuropein could be useful in drug development studies.
Preconcentration of Lead Ions in Food Samples by Liquid Microextraction Based on Ultrasound-Assisted Deep Eutectic Solvent and Determination by Flame Atomic Absorption Spectrometry

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Abstract: One of green solvents named deep eutectic solvent (DES) have been considered alternatives to traditional organic solvents. In this study, a method based on deep eutectic solvents was developed for determination of lead ion in different food samples. In the proposed method, DES was selected as extraction solvent, ultrasound-assisted emulsification liquid phase microextraction (UA-ELPME) was used for extraction and atomic absorption spectrophotometer (AAS) equipped with flame atomizer was used for quantification. In this method, DES was synthesized with choline chloride and phenol at the molar ratio of 1:3. Meanwhile, several important parameters such as pH (6), complexing agent concentration (Dithizone, 3.0 x 10⁻⁵ Molar), volume of DES (1000 μL), volume of tetrahydrofuran (THF, 500 μL) and ultrasonication time (4 min) were optimized after performing proper experiments. Under the optimized conditions, the limits of detection and quantification of method were 6.21 μg mL⁻¹ (n=10) and 20.7 μg mL⁻¹ (n=10), respectively. The correlation coefficients of seven calibration curves are greater than 0.9998, relative standard deviation (RSD) of proposed method for seven repeated sample analysis was lower than 3.8%, and the mean recoveries were obtained for the certified reference materials were quite quantitative. The method was applied for the real food samples and high recovery values were able to obtain.

Keywords Lead, deep eutectic solvent, microextraction, food samples, atomic absorption spectrometry.

Introduction
Lead is one of the toxic heavy metals and its determination even at ultra-trace level is interesting analytical task. Because of its experimental rapidity, simplicity, and wide application, flame atomic absorption spectrometry (FAAS) is the one of the most widely applied methods for heavy metal analysis. Mostly, there is a pivotal need for the preconcentration and/or separation of trace elements before their analysis due to matrix interferences. Powerful methods to effectively enhance atomic absorption spectrometry’s sensitivity and selectivity are applying widely. Microextraction methods are good solution in this regard. Deep eutectic solvents (DES) are environmentally-friendly solvents with unique properties. The advantages of DES are used in this method. Therewithal, application of ultrasonic energy to a solution causes acoustic cavitations. Combination of microextraction processes with ultrasound energy accelerates the extraction step; as a consequence the efficiency of preconcentration improves. The combined technique is called as ultrasound-assisted emulsification liquid phase microextraction (UA-ELPME) and bears all the advantages of both methods.

Materials and Method
Reagent and Solutions: All chemicals were of analytical reagent grade and deionized water (Barnstead, 18.2 MW cm) was used throughout the experiments. The stock solution of Pb(II) were prepared by dissolving appropriate amounts of its nitrate salt (Merck, Darmstadt, Germany) in deionized water. Working standard solutions were obtained by dilution of the stock standard solutions. A buffer solution of pH 6 was prepared by using 0.1 M (8.204 g L⁻¹) of sodium acetate (Merck, Darmstadt, Germany) and 0.1 M of acetic acid (Merck, Darmstadt, Germany) at appropriate volumes. For DES solvent, choline chloride (ChCl) was used as quaternary ammonium salts, and phenol (Ph) were used as hydrogen bond donors were purchased from Sigma-Aldrich Germany. Tetrahydrofuran (THF) was used as aprotic solvent and purchased from Merck, Darmstadt, Germany. All other chemicals were prepared with proper amounts from their analytical grade chemicals.

Preparation of Choline Chloride-Phenol (ChCl-Ph) eutectic mixture: 13.96 g choline chloride and 28.20 g phenol were mixed and magnetically agitated in a glass beaker until clear solution was achieved in 5 min at 50°C.

Procedure: 25.0 mL of standard or sample solution of lead ions, 2 mL of pH 6.0 buffer, 750 μL of chelating agent Dithizone (taken from its 1 x 10⁻³ mol L⁻¹solution), 1000 μL of DES and 500
μL of THF was added into the tube. Then extraction occurred with the help of inserting tube in ultrasonic bath for the time of 4 minutes and applying 53 kHz power at room temperature. After extraction completed, the mixture was centrifuged at 4020 × g for 4 min. By means of centrifugation, DES phase collected at the top the tube and then aqueous phase was taken out using a pipette and the volume of DES phase remaining in tube was completed to 500 μL with 1% acidic ethanol. Finally, diluted DES phase was introduced into FAAS by direct nebulisation for lead analysis and blank solution was obtained in the same way.

Sample pretreatment: Real food samples and certified reference samples were digested with the help of CEM Mars 5 Microwave Digestion System according to the method proposed by manufacturer.

Results and Discussion
Optimization of Chemical Variables
1. pH: The pH is an important parameter for both metal complex formation and its extraction. Therefore, the effect of pH on the preconcentration of lead(II) ions was examined in the range of 3-11. The pH values of medium were adjusted the extraction by using 2 mL of different buffer solutions. The absorbance values for pH 5 and 6 were quite close to each other. However, the maximum absorbance value was obtained at pH 6. Therefore, the optimum working pH was chosen as 6 for the further experiments.

2. Effect of chelating agent: Extraction efficiency of the analyte depends on the distribution ratio of the metal chelate between the organic and the aqueous phases. At a constant aqueous phase pH, the distribution ratio and hence, the extraction efficiency increases with the increasing amount of the chelate. The influence of Dithizone (H₂Dz) amount on the extraction efficiency of lead was studied using different volumes of 1 x 10⁻³ mol L⁻¹ solution of Dithizone ranging from 100 μL to 1500 μL were added to sample solution. The absorption signal was increased with the increase of Dithizone volume up to 750 μL, and then remained constant between the values of 750 μL to 1000 μL. 1000 μL was choosen optimum value to ensure that enough amount of chelating agent was added.

3. Effect of tetrahydrofuran (THF) amount: THF behaves as dehydrating agent and DES becomes insoluble in the water-THF system. Effect of THF volume on extraction efficiency was explored in the volume range of 50–1500 μL. The maximum extraction efficiency observed between the ranges of 500–1000 μL. THF volume of 500 μL was determined as optimum value.

4. Effect of composition of DES: Several reagents, which act as hydrogen bond donor and salt, can be used for the preparation of various DESs. Different combinations like ChCl:Urea, ChCl:OA , and ChCl:Ph were tested as solvent pairs. For this study, choline chloride (ChCl) and phenol combination was chosen due to obtained quite higher absorption value. Since, (Ph) were chosen as a salt and a hydrogen bond donor, respectively. By using ChCl:Ph in different molar ratio (1:1, 1:2, 1:3, 1:4 and 1:5), mixtures were prepared and experiments were performed. Maximum extraction efficiency was achieved with ChCl:Ph having 1:3 molar ratio and this ratio was chosen as optimum.

5. Effect of volume of ChCl:Ph: Different amount of DESs (100–1500 μL) were added to the analyte solutions and maximum absorption value was obtained for 1000 μL addition volume.

6. Effect of ultrasonification and centrifugation time: Optimization of proper time for both ultrasonification and centrifugation time were tested in the range of 1-6 mins. For both processes 4 min was quite enough.

7. Effects of co-existing ions: Possible interference effects of some common co-existing ions were investigated. The tolerance limit was accepted as the amount of the interfering ion that caused more than a 5% absorbance change for analysis of 100 μg mL⁻¹ Pb(II) by the proposed method. According to the results, the Pb(II) determination was not interfered by many common ions can be found in food and water samples except aluminum. The amount of 5.0 mg L⁻¹ (500-fold of Pb amount) of Al(III) can expressed considerable interference effect. In addition, it is not likely for these metal ions to be found in nature at these levels. It can be said that this method has quite good tolerance regarding matrix interference.

8. Analysis of certified material: A certified reference food samples NCS ZC 73012-Cabbage and NCS ZC 73013 -Spinach were analyzed by the proposed technique in order to evaluate the
accuracy of the proposed method. There was good agreement with the certified values and obtained results.

9. Analytical features of the proposed method: Optimum conditions of the proposed method are summarized in Table 1. The analytical characteristics of the optimized method under these conditions can be seen in Table 2. The enhancement factor was calculated by dividing the slope of the calibration curve obtained by applying preconcentration to that obtained without preconcentration.

Table 1. Optimum conditions of the proposed method.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Sample volume</td>
<td>25.0 mL</td>
</tr>
<tr>
<td>Final volume</td>
<td>500 µL</td>
</tr>
<tr>
<td>pH</td>
<td>6.0</td>
</tr>
<tr>
<td>Amount of ditihzone</td>
<td>750 µL of 1 x 10^{-3} mol L^{-1}</td>
</tr>
<tr>
<td>Composition of DES</td>
<td>ChCl:Ph (1:3 molar ratio)</td>
</tr>
<tr>
<td>Volume of DES</td>
<td>1000 µL</td>
</tr>
<tr>
<td>Volume of THF</td>
<td>500 µL</td>
</tr>
<tr>
<td>Sonication time</td>
<td>4 min</td>
</tr>
<tr>
<td>Centrifugation rate</td>
<td>4020 × g</td>
</tr>
<tr>
<td>Centrifugation time</td>
<td>4 min</td>
</tr>
<tr>
<td>Diluent</td>
<td>1% acidic ethanol</td>
</tr>
</tbody>
</table>

Table 2. Analytical features of the proposed method.

<table>
<thead>
<tr>
<th>Analytical Feature</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enhancement factor (EF)</td>
<td>87</td>
</tr>
<tr>
<td>Limit of detection (LOD) (µg L^{-1}) (n=10)</td>
<td>6.21</td>
</tr>
<tr>
<td>Limit of quantification (LOQ) (µg L^{-1}) (n=10)</td>
<td>20.7</td>
</tr>
<tr>
<td>Linear range (µg L^{-1})</td>
<td>25.0-250</td>
</tr>
<tr>
<td>Correlation coefficient (R^2)</td>
<td>0.9998</td>
</tr>
<tr>
<td>Precision (%RSD) (for 100 µg L^{-1}) (n=7)</td>
<td>3.8</td>
</tr>
</tbody>
</table>

10. Analysis of real samples: In order to demonstrate the performance and applicability of the proposed UAE-SFODME, the method was applied to several environmental water samples for the determination of the lead ion. Quite good recovery values for real food samples (zucchini, purslane, Italian pepper, okra, celery leaf, cucumber, beans) could be obtained.

Conclusion

This study exhibits the successful application of (UA-ELPME) combined with FAAS that allowed for the analysis of lead ions present at low concentrations in food samples. It is an improved technique which benefits from ultrasonic radiation to increase the extraction efficiency of the procedure in the shortest possible time. Consumption of organic solvent is minimized by this technique. By the proposed method, lead analysis can be possible at reasonably mild conditions (pH: 6, room temperature) in a very short time. This method has a quite good LOD, limit of quantification and precision values. In addition, the method is linear over the range of 25–250 µg mL^{-1} of Pb(II). It has been possible to achieve a highly satisfactory enrichment factor. It has been possible to achieve a highly satisfactory enrichment factor. With all this, the main advantages of using DES also contribute to improve the method. The (UA-ELPME) methodology for the extraction and determination of lead has following features: Low sample consumption, minimal use of toxic organic solvents, short extraction time, resistance to matrix interference, simplicity, low cost and a high enhancement factor, green method. With the help of the proposed method, lead ion determination in food samples performed with high recovery values.

References


2- Arpa, Ç., Ardaşır, I., Ultrasound assisted ion pair based surfactant-enhanced liquid-liquid microextraction with solidification of floating organic drop combined with flame atomic absorption spectrometry for preconcentration and determination of nickel and cobalt ions in vegetable and herb samples, Food Chemistry, 284, pp. 16-22.

Sample preparation in analytical chemistry is the most important step affecting the reliability of the results including a number of process steps for preparing the actual example. These steps are (i) purification of the analyte (ii) removing the analyte into a suitable solvent without any degradation or conversion and (iii) reproducible and accurately detection at low levels. For this purpose, widely accepted methods in public and private analysis laboratories are chromatographic methods. The fact that clinical, environmental and food samples can be prepared quickly for analysis by using these techniques in less steps and with less solvent before measurement is critical for the reliability and sensitivity of the results.

The sample preparation step serves two main purposes; The first is to clean-up the analyte from the interferences in the sample matrix and to concentrate or enrich of the components in order to increase sensitivity. Liquid-liquid extraction and solid phase extraction techniques from conventional sample preparation processes are time-consuming, consuming large amounts of solvent. In the micro-extraction (SPME) technique of solid phase, the capacity problem of the fibers used as adsorbents comes to the fore. Problems can also be experienced in terms of repeatability. Therefore, there is a need for cheap and practical systems which may be an alternative to existing techniques.

An alternative novel sample preparation system has been created with thin film extraction blades (TFME) integrated into the 96-well well plate system to increase SPME sampling efficiency. The commercially available SPME fibers have low chemical and physical stability, low extraction efficiency for polar analytes, and a long-term stable use. In this study, to increase the extraction efficiency of SPME method, they improve the drawbacks by increasing the surface area of wire-shaped SPME fibers with small adsorption capacity. After the development of IFME sticks, many studies have been carried out for the extraction of organic substances.

In this study, the optimisation of an analytical method to determine five pesticides in surface water samples by extraction on polyaniline coated TFME blades followed by gas chromatography-electron capture detection was described. In the sample preparation step, the adsorption blades were immersed in 2 mL of water containing the target pesticides and the analytes were extracted for 60 sec. For the desorption step, the blades were then immersed in an appropriate solvent. These experiments were carried out in three parallel runs for each TFME blade. The parameters related to the extraction procedure namely; adsorption and desorption time, salt effect, desorption solution type were optimized. A linearity of 0.9957 and detection limits in the low-ppb level were found. The reproducibility was found to vary from 2.8% to %.

**Keywords:** Thin Film Extraction, Polyaniline, Pesticide, Chromatography

**References:**
Phenolic compound contents of olive oil has been the scope of many studies due to their antioxidant and antimicrobial effects.\(^1\) The levels of total and individual phenols in olive oil samples depend on agronomic factors, maturity of the olives, type of process, irrigation, packaging and storage. The phenolic compounds in olive oil are known to be strong antioxidants and radical scavengers. Phenolic compounds are also among the components most responsible for the nutritional and multiple pharmacological effects.\(^2\)

The main object of this study is to find out the effect of extraction techniques used in olive oil production on the phenolic compound composition. Phenolic content of olive oil samples different processes such as cold press, foot crashing, and several types of filtration methods were determined by LC-QTOF/MS technique and the data was evaluated by using principal component analysis (PCA). Locally collected samples were weighed to be 2.00 grams and then, diluted with hexane to be 5 mL and mixed with 5 mL of ultrapure water. The mixture was vortexed and stirred for one hour and then, the water phase was injected to LC/Q-TOF/MS system. The obtained results were analyzed by using Minitab program and the score plot was drawn. As shown in Figure 1, samples 1 and 2 extracted by applying pressure are separated from the other samples. Cold pressed samples (6 and 9) were not included in any group. Thermally processed sample 4 has discriminated from the others as also separated. Foot-crashed samples 5 and 10 have displayed different compositions from the others as well. Finally filtered samples (3, 7 and 8) were clustered together.

![Figure 1. Score plot of PCA Analysis for Olive Oils](image)

**Keywords:** Olive Oil, Extraction Process, Phenols, LC/QTOF/MS, PCA

**Acknowledgment:** Ege University Research Fund supported this work through the 15-EGEMATAL-002 project and EGE-MATAL chromatography laboratories were used in this study.

**References**


The Investigation Of Heavy Metal And Mineral Content Of Growing Cowers (G. Tournefortics) In The Siverek Region

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There are a number of factors in the concentration of heavy metals on and on the plants. These factors include climate, atmospheric accumulation, the nature of the soil grown on the plant and the degree of maturity of the plant at harvest time. The nature of the soil is one of the most important factors determining the heavy metal content of food plants. However, applications such as fertilizers, sewage water or wastewater and irrigation are other factors that can affect the heavy metal content in plants. Heavy metal contamination of agricultural soils can create long-term environmental problems and unhealthy effects.

Kenger (Gundelia tournefortii) Turkey, Central Anatolia, Eastern Anatolia, Southeastern Anatolia and the Mediterranean region grows. 20-100 cm height, spiny, perennial, milk and herbaceous plant. Young shoots are eaten and eaten from the root. Kenger (Gundelia tournefortii) This study was carried out on the 16th and 17th kilometers of the Siverek-Diyarbakır highway and on the 10th kilometer of the Siverek-Adıyaman highway. These samples were then dried and pulverized in the oven. Powdered kerners were added to the crucibles and 4 ml of a solution of 95% ethanol-5% H2SO4 was added. The samples added to the solution were burned in the ash oven at 550 oC for 3 hours. 4 ml of 3 N HCl was added to the ash samples. The filtrates were made up to 50 ml with pure water and measured in AAS.

Key words: Kenger, heavy metal, mineral

References
Yıldız S., 2014 Yüksel Fırat havzasında yetişen kenger (gundelia tournefortii l.), güllük (eremurus spectabilis m. bieb.) ve ışıkın (rheum ribes l.) bitkilerindeki polifenollerin ve bazı metallerin tayini, Yüksek Lisans Tezi Fırat Üniversitesi Fen Bilimleri Enstitüsü, Elazığ, 4.
Lead is an environmental pollutant found as organic or inorganic species as a result of both natural and anthropogenic events. Studies have shown that lead affects every system in the body and causes long-term health problems. Hence determination of lead in various samples are very important. Generally, preconcentration and separation step is required before the determination of lead to eliminate the effect of foreign ions and due to low concentration.

In this study, lemon peel powder (LPP) was successfully modified into a magnetic nanoadsorbent (LPP@Fe₃O₄) by co-precipitating it with Fe₃O₄ nanoparticles (MNP) for preconcentration of Pb. Concentration of lead was measured with inductively coupled plasma mass spectrometry (ICP-MS). The experimental parameters (adsorption time, pH of adsorption, volume of the eluent, and elution time, etc.) were individually optimized to achieve repeatable and reliable results. The quantitative determination of Pb was achieved for 1 µg/L Pb in 25 mL at pH 5 within 1 min as adsorption time and using 2.5 mL of 3% HNO₃ as eluent. The relative standard deviation was calculated as 4.7% for 1 µg/L lead concentration (n=5).

**Keywords:** Magnetic nanoparticles, Lead, solid phase extraction

References


Acknowledgment: Authors are fully grateful to Cumhuriyet University Advanced Technology Research Center (CÜTAM). This work is supported by the Scientific Research Project Fund of Cumhuriyet University under the Project number ECZ-064.
PP79- SYNTHESIS AND CHARACTERIZATION OF 4-AMINOANTIPYRINE DERIVATIVE OF HETEROCYCLIC NEW SCHIFF BASES AND AMIN COMPOUNDS

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Schiff bases are small molecules with azomethine (-C = N-) functional groups. It was first synthesized by Hugo Schiff; The primary amines are obtained by condensation reaction with aldehydes or ketones. [1]

Schiff base and complexes have variable applications according to their active groups. Industrial applications; There are pharmacology, biological activities, antimicrobial, antibacterial, anticancer activities and metallic enzyme preparations. [2]

In this study, a new heterocyclic Schiff base was synthesized from 4-aminoantipyrine with heterocycle 2-pyridine carboxaldehyde (1). The amine compound (2) was synthesized by reacting this compound with NaBH4 in room conditions. The synthesis procedure, unlike the conventional method, was added to the aldehyde reaction mixture for 2 hours. Thus, the formation of by-products from the heterocyclic of aldehyde was prevented. The structures of the synthesized compounds were confirmed by 1H NMR, 13C NMR and FTIR. In the following stages, the antibacterial and antioxidant effects of these Schiff bases will be examined.

Key words: Schiff base, amine, antibacterial, 1H NMR

References
Environmental approach of utilizing co-polymeric hydrogel: An application of dye removal

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Wastewater treatment with developing industrial activity is becoming the most important point today. Methylene blue dye is released into the water through textile industry. Higher dye concentration in water affect the aquatic life, negatively as it inhibits the photosynthesis process. In this study, polymeric and co-polymeric hydrogels were used as an adsorbent to removal of methylene blue. Acrylic acid and vinyl pyrrolidone monomers were selected to produce hydrogels by free radical polymerization technique. Synthesized hydrogels were characterized by various modern techniques such as FTIR, SEM-EDX-Mapping and TGA. The effect of hydrogel type, initial dye concentration and residence time on adsorption process were specified by batch adsorption experiments. According to the characterization and adsorption experiment results, adsorption process takes place second order kinetic model, which confirmed that it should be a chemical process. As conclusion, hydrogels have superior swelling property that provides it can be utilized successfully for the removal of methylene blue from aqueous solution.

Keywords: Adsorption, hydrogel, methylene blue, super adsorbent, swelling behaviour

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Voltammetric Determination of Ascorbic Acid Using Modified Solid Contact Electrode

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Abstract - Ascorbic acid is a water-soluble vitamin and is in fresh fruits and leafy vegetables. Large amount of deficiency of ascorbic acid causes some disease in the body such as swollen and inflamed gums, loss of hair and loosening of teeth. Therefore, the determination of ascorbic acid is very important.

In this study, platin wire, Ag/AgCl and solid electrode were used as counter, reference and working electrode, respectively. In order to determine the optimum conditions, the electrochemical experiments were performed in different potential ranges, solvents, scan rates and cycles.

The surfaces of the solid contact electrodes were modified with poly (L-cysteine) and o-phenyldiamine. The bare electrode and coated electrode surfaces were compared. These electrodes were used to determination of ascorbic acid

Keywords: Cyclic voltammetry, solid electrode, modification

1.Introduction

Ascorbic acid (AA) with chemical formula (C6H8O6) or vitamin C is a six-carbon compound structurally related to glucose. It consists of two transformable compounds. That is, L-ascorbic acid comprises a reducing agent and L-dehydroascorbic acid, the oxidized derivative. Its chemical name is known as 2-oxo-L-threo-hexono-1,4-lactone-2,3-endiol. Acute ascorbic acid deficiency in the body causes fragile blood vessels, connective tissue damage. This increases the risk of death. Ascorbic acid is one of the basic nutrients required for metabolic functions in humans. Ascorbic acid is a strong reductant. It has the ability to neutralize the potentially harmful free radicals produced in the body. It is a highly effective vitamin in the antioxidant defense system, strengthening immunity and resistance to infection. According to some studies, vitamin C prevents DNA mutations. This feature can be important in the treatment of cancer and chronic diseases. There are many methods used to identify ascorbic acid such as chromatography, titrimetry, voltammetry, potentiometry, etc. Ascorbic acid is an electrochemically active vitamin and its determination by using voltammetric method has attracted attention, because conventional electrodes have high overpotential, low repeatability and low sensitivity in ascorbic acid analysis.

2.Materials and Method

2.1.Chemicals, materials and instrumentation

All chemicals were provided from the Merck, Riedel, J.T. Baker and Sigma–Aldrich companies. Buffer solutions were prepared at different pHs for solutions to be used in the modification of the electrode surface and in the surface test.

Electrochemical measurements were carried out using an electrochemical cell with three-electrode system

The glassy carbon (GC) electrode model MF-2012 and the gold electrode model MF-2013 from BAS was used as the working electrode. Ag/AgCl in saturated KCl (Ag/AgCl/KClsat) model MF-2052 from BAS was used as the reference electrode in aqueous media and Pt wire was being used as the counter electrode. The cyclic voltammetry (CV) was applied using PHE 200 software and electrochemical impedance spectroscopy (EIS) was applied using EIS 300 software from Gamry Instruments.
2.2. Electrode modification procedure
Cleaning the working electrode before starting the modification process is important for accurate and reliable results. Primarily, the working electrode (Au) was cleaned by circular movements on the sandpaper. After, the gold electrode surfaces were polished with circular motions with 0.3 and 0.05 μm wet alumina powder. At second stage, the electrode was washed with water and was sonicated in pure water for 3 min. Electrode surfaces were cleaned as electrochemically about at 10 cycles in 0.1 M H₂SO₄ solution. Finally, the electrode was washed with pure water and again sonicated in CH₃CN for 3 min to get rid of impurities that cannot be removed with water.

The electrochemical behaviours of poly (L-cysteine) and o-phenyldiamine on cleaned the solid electrode surface were investigated at 25 cycles and the scan rate of 100 mV/s in different pH range.

Results and Discussion
The cyclic voltammetry curves of L-cysteine was occurred (Fig. 1). This figure shows the cyclic voltammograms of the solid electrode surface modified electrochemically with L-cysteine.

Fig. 1. The cyclic voltammograms on the gold electrode surface of L-cysteine dissolved in pH=7.02 phosphate buffer solution, (a) 1st, (b) 25th cycle. The scan rate is 100 mV/s vs.

Fig. 1 indicated that peak current (502.8 μA) was higher in the first cycle on gold electrode surface in the potential range −1.95 V and +1.9 V (the scan rate: 100 mV/s). However, the peak current (436.5 μA) is decreasing in the 25th cycle. There is also a sliding in peak potentials. For these reasons we can say that the material was coated on the electrode surface. It was concluded that the electron transfer was slow on the modified electrode surface. Additionally, modification of L-cysteine to the electrode surface was supported by surface tests with redox probes (Fig. 2).

Fig. 2. The cyclic voltammograms of 1.0 mM ferrocene in asetonitril containing 0.1 M of Tetrabütilamonymonium tetrafloroborat of (a) bare gold and (b) modified gold electrodes. At potential scan rate of 100 mV/s vs. Ag/Ag⁺(in 10 mM AgNO₃).
The figure shows us that the bare gold electrode surface allowed the transfer of electrons to Ferrosen, while the modified gold surface did not allow the transfer of electrons.

**Conclusion**

Electrochemical characterization of modified different electrode surfaces was performed and bare and modified electrode surfaces were compared using the obtained datas. Reduction of peak currents and sliding of peak potentials showed that these electrode surfaces were covered. These electrodes were used to determination of ascorbic acid.

**References**


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Investigation of Electrochemical Behaviours of Some Schiff Base on The Surface of Solid Contact Electrode Using Voltammetry

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Abstract - Schiff bases and their metal complexes have often been used for many years. Schiff base metal complexes have wide working areas such as antifungal, industrial, antibacterial, anticancer and herbicidal applications. In this study, platin wire, Ag/AgCl and solid electrode such as glassy carbon (GC) electrode were used as counter, reference and working electrode, respectively. In order to determine the optimum conditions, the electrochemical experiments were performed in different potential ranges, solvents, scan rates and cycles. Electrochemical behavior of Schiff base was investigated on electrode surface with cyclic voltammetry in aqueous solution media. The surface of the electrode was modified with Schiff bases. Modified electrode surface was investigated with cyclic voltammetry and electrochemical impedance spectroscopy techniques in the presence of Fe(CN)₆³⁻. The results were compared with each other using bare and modified electrodes. As a result we observed that there were differences in the current and resistance of the modified electrode.

Keywords: Glassy carbon electrode, electrochemical modification, Schiff bases

Introduction
It was in the 19th century that the German chemist Hugo Schiff discovered the preparation of Schiff bases. Since then, several methods have been used to synthesize imine. The classical synthesis made by Schiff requires the condensation of two compounds which are the carbonyl compound and the amine compound under azeotropic distillation. Elimination of water formed in the system made by molecular sieve¹. Several Schiff base ligands are "preferred ligands" because they are simply prepared by the condensation pathway between aldehydes and amines. Synthesis of Schiff bases are made by different solvents and reaction conditions. Schiff is prepared in ethanol which is the best solvent, depending on the reaction conditions at room temperature or at reflux. Generally, Schiff bases are stable compounds ²,³.

Electrochemical techniques specify the analysis of the material according to the oxidation or reduction properties. Thus these methods measure the electrical response of the electrode-solution system to give a measured response of the system. This answer informs us about the characteristics of the system. Generally electrochemical techniques have functionalities of current, potential and time depending on the functionalities specify the name of the technique. Thus according to the relation that exists between the potential-current functionalities; time-current and time-charge we will be able to determine the techniques used which are respectively the voltammetry; chronoamperometry and chronocoulometry ⁴.

Materials and Method

Chemicals, materials and instrumentation
All chemicals used as commercial from the Merck, Riedel and Sigma–Aldrich companies. Buffer solutions at different pHs and solutions of complex substances using these buffer solutions were prepared. The solution of mixture 1.0 mM Fe(CN)₆⁴⁻ / Fe(CN)₆³⁻ was prepared to use for electrochemical impedance spectroscopy in 1.0×10⁻¹ M KCl solution. Schiff Base was synthesized by Kurşunlu et al: An ethanolic solution of 2-amino-3-hydroxyypyridine (5g, 1 mmol) was added to the ethanolic solution of 2, 4-dihydroxybenzaldehyde (5.54 g, 1 mmol) in 250 ml round bottom flask. To this reaction mixture 3-4 drop of Conc. HCl was added with vigorous stirring. The reaction mass was refluxed on water bath at 80°C for 6 hour with constant stirring. The hot reaction mass was then quenched on crushed ice. Yellow crystals obtained were filtered, washed with hot water and recrystallized twice from distilled ethanol.
A electrochemical cell with three-electrode system was used in all electrochemical experiments. The glassy carbon (GC) electrode model MF-2012 from BAS was used as the working electrode. Ag/AgCl in saturated KCl (Ag/AgCl/KClsat) model MF-2052 from BAS was used as the reference electrode in aqueous solution media and Pt wire was being used as the counter electrode. The cyclic voltammetry (CV) was applied using PHE 200 software and electrochemical impedance spectroscopy (EIS) was applied using EIS 300 software from Gamry Instruments.

**Electrode modification procedure**
First stage, the working electrode(GC) was cleaned by circular movements on the sandpaper. After, the electrode surfaces were polished with circular motions with 0.3 and 0.05 ilem wet alumina powder. At second stage, the electrode was washed with water and was sonicated in pure water for 3 min. Electrode surfaces were cleaned as electrochemically about at 10 cycles in 0.1 M H$_2$SO$_4$ solution. Finally, the electrode was washed with pure water and again sonicated in CH$_3$CN for 3 min to get rid of impurities that cannot be removed with water. The electrochemical behaviour of (Z)-4-(((3-hydroxypyridin-2yl)imino)methyl)benzene-1,3-diol on cleaned glassy carbon electrode was investigated at 20 cycles in the potential range of −2.0 V/+2.0 V at the scan rate of 100 mV/s applied in pH=3.0 phosphate buffer solution.

**Results and Discussion**
The CV curves of (Z)-4-(((3-hydroxypyridin-2yl)imino)methyl)benzene-1,3-diol was occurred (Fig. 1). From Fig. 1 we know this complex structure has the peak. This figure shows the cyclic voltammograms of the glassy carbon electrode surface modified electrochemically with (Z)-4-(((3-hydroxypyridin-2yl)imino)methyl)benzene-1,3-diol.

![Cyclic voltammograms at the glassy carbon electrode surface of (Z)-4-(((3-hydroxypyridin-2yl)imino)methyl)benzene-1,3-diol in pH=3.0 phosphate buffer solution, (a) 1st, (b) 20th cycle. The scan rate is 100 mV/s vs.](image)

Fig. 1 indicated that peak current (76,19 μA) was higher in the first cycle on glassy carbon electrode surface in the potential range −2.0 V and +2.0 V (the scan rate: 100 mV/s). However, the peak current (23,81 μA) is decreasing in the 20th cycle. The reason of decrease in the peak current was that (Z)-4-(((3-hydroxypyridin-2yl)imino)methyl)benzene-1,3-diol was adsorbed on glassy carbon electrode surface. We can conclude that electrode transfer was slow because the surface was modified.

Modification of the complex material to the GC surface in aqueous media was supported by surface tests with redox probes (Fig. 2).
As shown in the figure, the bare GC surface allowed the transfer of electrons to Fe(CN)$_6^{3-}$, while the modified GC surface did not allow the transfer of electrons.

Conclusion

Electrochemical characterization of modified electrode surfaces was performed, the obtained data was compared with bare GC surface. In the first step of the modification, the peak in the first cycle seen in the voltamogram, later this peak was not seen in other cycles. It shows that the bare GC surface was covered by Schiff base in the first cycle.

References


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Comparative Assessment Of Selected Elements In The Scalp Hair And Nails Of Chronic Obstructive Pulmonary Disease And Controls

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With the growing speed of industrialization and urbanization worldwide, anthropogenic activities have considerably contributed to the discharge of a wide range of metallic pollutants in the environment. It has become undeniable that the imbalance in trace elements results in various health problems as they are deemed essential to keep the organs’ homeostasis. The imbalance may occur as a result of excess of toxic elements or a deficiency of essential elements. So far, concentrations of trace metals in different biological samples including whole blood, serum, plasma, and urine have been reported by many scientists and clinicians in an attempt to gather information about nutritional status for diagnosis of diseases, or to obtain indications on systemic intoxication or environmental exposure (1-3). While the blood gives transient concentrations and reflects recent exposure, the hair and toenail provides a more permanent record of trace and toxic elements associated with normal and abnormal metabolism and can reflect metabolic changes of many elements over a long period of time. Altered levels of essential elements and elevated levels of toxic elements have been linked to many physical and psychiatric disorders. High levels of Pb and Hg and low levels of Mg and Se were found in the hair of autistic children when compared to their normal peers. Higher levels of Cd and lower levels of Cr and Zn were also found in the hair of diabetes mellitus patients when compared to normal subjects. Recently, researchers analyzed some trace elements level in hair and nail of patients with stomach cancer, and compared with their level in healthy controls.

In this work, levels of Mn, Cu, Cr, Ni and Co have been determined in the hair and nail of Chronic Obstructive Pulmonary Disease (COPD) and healthy persons. The results obtained in persons with diseases were compared to in the controls as well as literature-based ‘background’ values. The samples were digested using microwave oven and the element determinations were measured by ICP-MS. It was found that Co levels are lower than the LOQ of ICP-MS.

Keywords: Trace elements, Epidemiology, ICPMS, hair, nail

References
Maruf Hursit Demirel, 126
Mehmet Atakay, 145, 221
Mehmet Emin Duru, 172, 175, 177
Mehmet GUMUSTAS, 151, 152
Mehmet Öztürk, 172, 175, 177
Mehmet Yaman, 126, 225, 269
Melek Avcı, 155
Melek GÜNER, 171
Meltem Taş, 172, 175
Mert AYGUN, 219
Merve Yasacan, 132
Metin Ak, 218
Minel AYAZMA, 211
Muhammet AYDIN, 53, 181
Munteha Nur Sonuc Karaboga, 50
Murat Celiker, 124
Mustafa Celebier, 66, 102, 228, 244
Mustafa Kemal Sezginturk, 39, 44, 47, 50, 53, 181, 184, 185, 186, 219
Mustafa Soyloğlu, 25, 134, 191, 216
Mutay Aslan, 31
N
Nagihan M. Karaaslan, 225
Najma Memon, 168
Nevin Oztekin, 169
Nikos Lydakis-Simantiris, 231
Nilay Kahya, 117
Nina Djapic, 202
Nur TARIMERI, 186
Nursu Aylin Kasa, 158
O
O. Yavuz Ataman, 38
Onur INAM, 166
Ozan Kaplan, 66, 102
Ozan MERT, 208
Ozer Unal Durisehvar, 232
Ozge Cansin Zeki, 132
Ozlem Tavukcuoglu, 242
P
Pelin SENEL, 77, 233
R
Resat APAK, 26, 139
Ruya Kaya, 253
Ryszard Lobinski, 33
S
S. Beniz Gündüz, 192
Sabriye Sel, 222, 224
Sadin Ozdemir, 191, 195
Sarah Albayati, 105, 254
Selen Ayaz, 220
Selim ERDOGAN, 153
Selvi ACER, 230
Sema Bağdat, 155
Sema Erdemoglu, 226
Seref Gucer, 82, 250
Serkan Karakaya, 200
Sevda Gültekin, 269
Sevinc Kurbanoglu, 56, 58
Seyda Kivrak, 235, 240
Sezen Sivrikaya, 150
Sezgin Bakirdere, 32, 158, 159, 160, 222, 223, 224, 225
Sezin Erarpat, 159
Sibel A. Ozkan, 56, 58, 61, 133
Simonas Ramanavicius, 234
Sławomira Szrypek, 130
Soykan Bicim, 269
Sukriye Nihan KARUK ELMAS, 184, 188
Ş
Şerife Tokaloğlu, 190
T
Tugba Yavuz, 164
Tugçe Unutkan, 160, 224
Tulay Oymak, 260
Tulin Bicim, 269
U
Ulku Guler, 146, 227
Umut Seven Erdemir, 82, 250
Umrot Ozerk ONKOL, 212
Usama Alshana, 141, 149, 180, 201, 206
V
Veselina Adımcılar, 79, 110
Y
Yasar Kaan EREN, 144, 210
Youcef Hadef, 205
Yunus Emre Unsal, 216
Yusuf Dilgin, 139, 200, 220, 225
Z
Z. Pinar GUMUS, 131, 144, 147, 207, 208, 209, 210, 211, 212, 213, 258
Zafer Yazıcıgil, 263, 266
Zuhre Senturk, 94