Separation and preconcentration methods in trace species in environmental samples: from solid phase extraction to microextraction

Mustafa Soylak

Erciyes University, Faculty of Science, Department of Chemistry, 38039, Kayseri-Turkey
E-mail: soylak@erciyes.edu.tr
Personal web page: www.soylak.net
TRACE HEAVY METALS

- Metals such as iron, copper, zinc and manganese are essential metals since they play an important role in biological systems.

- The main roles of these elements can be described as functional and structural.

- Some trace metals like lead, cadmium, arsenic, mercury are the heavy metals playing toxic role human life.

1/11/2019
Sigaradaki Zehirleri Hiç Merak Ettiniz mi?

Sigara Dumanında
Bunlardan Başka
4000'den Fazla Zehir Var !...

- SİYANÜR
  (Çok Güçlü Zehir)
- TOLUİDİN
  (Kanser Yapar)
- AMONYAK
  (Yer Temizleyici)
- ÜRETAN
  (Kanser Yapar)
- ARSENİK
  (Çok Güçlü Zehir)
- METANOL
  (Körlük Yapar)
- NAFTİLAMİN
  (Kanser Yapar)
- PİREN
  (Kanser Yapar)
- KARBONMONOKSİT
  (Zehiri Gaz-Egzoz Gazi)
- NAFTALİN
  (Güve Zehiri)
- KADMIYUM
  (Ateroskleroz ve Kanser Yapar)
- NİKOTİN
  (Alışkanlık Yapar, Zehir)
- BENZOPİREN
  (Kanser Yapar)
- VINİL KŁORİD
  (Kanser Yapar)

Kendinize Bir İyilik Yapın
SİGARAYI
BIRAKIN

Afiş Haritaları: Dr. Mükrrem Er, Göğüs Hastalıkları Uzmanı, Ankara Güven Hastanesi, Şimşek Sk. No: 29, Kavaklidere/Ankara
Web adresi: http://yunus.hacettepe.edu.tr/muer
E-Mail: muer@hacettepe.edu.tr
Choose Fish Low in MERCURY

Fish You Buy

Atlantic Salmon
Low
Mercury Level
High

Shellfish
Low
Mercury Level
High

Flatfish & Flounder
Low
Mercury Level
High

Hake, Haddock, Pollock, Cod
Low
Mercury Level
High

Canned ‘Light’ Tuna
Low
Mercury Level
High

Canned ‘White’ Tuna
Low
Mercury Level
High

Tuna
Low
Mercury Level
High

Hallibut
Low
Mercury Level
High

Swordfish
Low
Mercury Level
High

Shark
Low
Mercury Level
High

Fish You Catch

Atlantic Mackerel
Low
Mercury Level
High

Brook Trout
Low
Mercury Level
High

Landlocked Salmon
Low
Mercury Level
High

Striped Bass
Low
Mercury Level
High

Brown Trout
Low
Mercury Level
High

Lake Trout
Low
Mercury Level
High

Largemouth Bass
Low
Mercury Level
High

White Perch
Low
Mercury Level
High

Smallmouth Bass
Low
Mercury Level
High

Pickerel
Low
Mercury Level
High

Fish is good for you - Eat fish low in mercury!

Take this brochure for our Safe Eating Guidelines.
SELENYUMLU YUMURTA


55-65 gr 10 adet


<table>
<thead>
<tr>
<th>ŞİRİN YUMURTA BESİN DEĞERİ 50 gr için</th>
<th>SELENYUMLU YUMURTA BESİN DEĞERİ 50 gr için</th>
</tr>
</thead>
<tbody>
<tr>
<td>SELENYUM = 0,0072 µg SE/g</td>
<td>SELENYUM = 0,0159 µg SE/g</td>
</tr>
<tr>
<td>Enerji = 70 kcal</td>
<td>Enerji = 70 kcal</td>
</tr>
<tr>
<td>Protein = 6 gr</td>
<td>Protein = 6 gr</td>
</tr>
<tr>
<td>Doymuş Yağ = 1,5 gr</td>
<td>Doymuş Yağ = 1,5 gr</td>
</tr>
<tr>
<td>Karbonhidrat = 1 gr</td>
<td>Karbonhidrat = 1 gr</td>
</tr>
<tr>
<td>Kalsiyum = 2 %</td>
<td>Kalsiyum = 2 %</td>
</tr>
<tr>
<td>Sodyum = 63 mg</td>
<td>Sodyum = 63 mg</td>
</tr>
</tbody>
</table>

+8°C ile +12°C arasında saklayınız. Son kullanma tarihi, üretim tarihinden sonra 21 gündür.

Üretim Tarihi > Son Kullanma Tarihi

T.C. Tarım ve Köy İşleri Bakanlığı
24-01-2003 Tarih G 19.0093.00001

Sayılı izniyle üretilmiştir.

Üretici Firma: Corum Yumurta Üretim Pazarlama A.Ş.
Adres: Ankara Asfalt 4. Km No: 206 Corum
ALO CORUM YUMURTA HATTI: (0364) 235 01 63 (Pbx)
www.corumyumurta.com.tr
7088
Gas-Phase Chemiluminescence-Based Analyzer for Waterborne Arsenic

7071
On-Line Drug Metabolism in CE; Glucuronidation Using Rat Liver Microsomes

7078
Visualizing Ion Electromigration during Isotachophoretic Separations with Capillary ITP-NMR

http://pubs.acs.org/ac
Toxicity from dietary intake of arsenic—up to 60 µg/day daily—is relatively low. Intakes of higher amounts of arsenic on a chronic basis may cause hyperkeratosis, especially of the palms and soles, skin pigmentation, eczematous or follicular dermatitis, edema (especially of the eyelids). Chronic-high arsenic ingestion has been associated with various cancers, such as basal cell carcinoma and bladder, liver and lung cancers. The nail changes associated with arsenic toxicity are known as Mees' lines or transverse striate leukonychia.
Good intentions gone awry. Villagers drill a tubewell in Bangladesh (left). Encouraged as a solution to pathogenic contamination of surface waters, such wells have resulted in exposure of millions to arsenic, leading to the need for alternative water sources (above).
PROBLEMS IN DIRECT DETERMINATION OF TRACE SPECIES

**PROBLEM**

Very Low Concentration of Analyte in Samples

Large Amount of Matrix Components in Samples

**SOLUTION**

Preconcentration of Analyte

Separation of Analyte
PRECONCENTRATION-SEPARATION METHODS

- Solid Phase Extraction and Solid Phase microextraction
- Coprecipitation
- Cloud Point Extraction
- Solvent Extraction
- Flotation
- Electrochemical deposition
- Atom traps
- Microextraction techniques
- Magnetic separations
Flow Chart for SEPARATION-PRECONCENTRATION

Trace Species

Directly or Convert into a suitable form

Separation-Preconcentration Stage

Determination by instrumental techniques
( HPLC, GC, MS, GC-MS .... AAS, ICP-OES, ICP-MS etc.)

It is a long story for me from solid phase extraction to microextraction for 30 years and with many experiences…
Solid Phase Extraction

• Solid phase extraction is the one of the separation-preconcentration method for the traces analyte ions in the various materials including natural waters, ores, biological samples etc.

• Solid phase extraction has several advantages:
  • Sensitive
  • Fast
  • Economic
  • Large preconcentration factors
  • Simplicity of phase separation
  • Suitability for automation
STRUCTURE OF AMBERLITE XAD RESIN SERIES

Polystyrene-divinyl benzene (PS-DVB)

Polyacrylic acid ester (PAA-E)

Preconcentration of trace metals in river waters by the application of chelate adsorption on Amberlite XAD-4

L. Elci, M. Soylak, and M. Dogan
Department of Chemistry, Faculty of Art and Science, Erciyes University, TR-38039 Kayseri, Turkey

Received February 12, 1991; revised March 26, 1991

Adsorbent: Amberlite XAD -4
Ligand: APDC
Adsorbent Amount: 500 mg
Eluent: 1M HNO3 in acetone
Sample volume : 1000 ml
Eluent volume: 5 mL
Preconcentration Factor: 200
Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column

İbrahim Narin a, Mustafa Soylak b,*, Latif Elçi b, Mehmet Doğan c

a Niğde University, Faculty of Art and Science, Department of Chemistry, 51100 Niğde, Turkey
b Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey
c Hacettepe University, Faculty of Art and Science, Department of Chemistry, 06532 Ankara, Turkey

Received 24 January 2000; received in revised form 15 May 2000; accepted 22 May 2000

Abstract

A simple preconcentration method is described for the determination of Cu, Mn, Co, Cd, Pb, Ni and Cr in water samples by flame AAS. Trace metal ions in water were sorbed as pyrocatechol violet complexes on activated carbon column at the pH range of 4–8, then eluted with 1 M HNO3 in acetone. The effect of major cations and anions of the natural water samples on the sorption of metal ions has been also investigated. The concentration of the metal ions detected after preconcentration was in agreement with the added amount. The present method was found to be applicable to the preconcentration of Cu, Mn, Co, Cd, Pb, Ni and Cr in natural water samples with good results such as R.S.D. from 3 to 8% (V = 10) and detection limits under 70 ng L−1. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Preconcentration; Activated carbon column; Trace metal; Natural waters; AAS
Impregnation – physical interaction between adsorbent and ligand

The uses of 1-(2-pyridylazo) 2-naphtol (PAN) impregnated Ambersorb 563 resin on the solid phase extraction of traces heavy metal ions and their determinations by atomic absorption spectrometry

Ibrahim Narin\textsuperscript{a}, Mustafa Soylak \textsuperscript{b,*}

\textsuperscript{a} Department of Chemistry, Faculty of Art and Science, Nigde University, Nigde 51100, Turkey
\textsuperscript{b} Department of Chemistry, Faculty of Art and Science, Erciyes University, Kayseri 38039, Turkey

Received 26 September 2002; received in revised form 7 January 2003; accepted 10 January 2003

Abstract

1-(2-pyridylazo) 2-naphtol (PAN) impregnated Ambersorb 563 resin was used as solid phase extractor of copper, nickel, cadmium, lead, chromium and cobalt ions in aqueous solutions prior to their atomic absorption spectrometric determinations. The parameters including pH, sample volume, matrix effects were also investigated. The relative standard deviation (R.S.D.) of the combined method of sample treatment, preconcentration and determination with atomic absorption spectrometry is generally lower than 10%. The limit of detection was between 0.21 and 1.4 μg l\textsuperscript{-1}. The results were used for preconcentration of analyte ions from natural water samples. The method was also applied to a stream sediment standard reference material (GBW7309) for the determination of Cu, Ni, Cd, Pb, Cr and Co.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Ambersorb 563; Impregnation; PAN; Preconcentration
Aluminium determination in environmental samples by graphite furnace atomic absorption spectrometry after solid phase extraction on Amberlite XAD-1180/pyrocatechol violet chelating resin

Ibrahim Narin\textsuperscript{a}, Mustafa Tuzen\textsuperscript{b}, Mustafa Soylak\textsuperscript{c, *}

\textsuperscript{a} Department of Chemistry, Faculty of Art and Science, Niğde University, 51100 Niğde, Turkey
\textsuperscript{b} Chemistry Department, Faculty of Science and Arts, Gaziosmanpasa University, 60250 Tokat, Turkey
\textsuperscript{c} Department of Chemistry, Faculty of Art and Science, Erciyes University, 38039 Kayseri, Turkey

Received 29 August 2003; received in revised form 26 October 2003; accepted 6 November 2003

Abstract

A chelating resin, pyrocatechol violet (PV) immobilised on an Amberlite XAD-1180 support, was prepared and its use for the atomic absorption spectrometric determination of aluminium was investigated. The XAD-1180-PV resin was characterised by infrared spectrometry and thermal gravimetric analysis. The optimum pH value for quantitative sorption is 8–9, and desorption can be achieved by using 5.0–10.0 ml of 2 M HCl. The effects of diverse ions on the sorption and recovery of aluminium have been studied. The capacity of sorbent was 6.45 ± 0.59 mg g\textsuperscript{-1} Al XAD-1180-PV. Recoveries for aluminium from water samples were in the range 95–105%. The accuracy of procedure was confirmed by aluminium determination in certified reference materials. The method developed was applied with varying results to the analysis of natural water, haemodialysis fluids and microwave digested red wine samples from Tokat City.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Chelating resin; Preconcentration; Amberlite XAD-1180; Pyrocatechol violet; AAS
Biosorption of copper(II), lead(II), iron(III) and cobalt(II) on *Bacillus sphaericus*-loaded Diaion SP-850 resin

Mustafa Tuzen, Özgür Dogan Uluoğlu, Canan Usta, Mustafa Soylak

*Gaziosmanpaşa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey*
*Gaziosmanpaşa University, Faculty of Science and Arts, Biology Department, 60250 Tokat, Turkey*
*Erzyes University, Faculty of Science and Arts, Chemistry Department, 38039 Kayseri, Turkey*

Received 30 June 2006; received in revised form 18 August 2006; accepted 22 August 2006
Available online 26 August 2006

**Abstract**

The biosorption of copper(II), lead(II), iron(III) and cobalt(II) on *Bacillus sphaericus*-loaded Diaion SP-850 resin for preconcentration–separation of them have been investigated. The sorbed analytes on biosorbent were eluted by using 1 mol L\(^{-1}\) HCl and analytes were determined by flame atomic absorption spectrometry. The influences of analytical parameters including amounts of pH, *B. sphaericus*, sample volume etc. on the quantitative recoveries of analytes were investigated. The effects of alkaline, earth alkaline ions and some metal ions on the retentions of the analytes on the biosorbent were also examined. Separation and preconcentration of Cu, Pb, Fe and Co ions from real samples was achieved quantitatively. The detection limits by 3 sigma for analyte ions were in the range of 0.20–0.75 μg L\(^{-1}\) for aqueous samples and in the range of 2.5–9.4 ng g\(^{-1}\) for solid samples. The validation of the procedure was performed by the analysis of the certified standard reference materials (NRCC-SLRS 4 Riverine Water, SRM 2711 Montana soil and GBW 07605 Tea). The presented method was applied to the determination of analyte ions in green tea, black tea, cultivated mushroom, boiled wheat, rice and soil samples with successfully results.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** *Bacillus sphaericus*; Diaion SP-850; Biosorption; Preconcentration; Trace metal; Atomic absorption spectrometry
Speciation of Cr(III) and Cr(VI) by solid phase extraction

Natural Water (Cr^{3+}, Cr^{6+})

Cr^{3+} + (excess) H_{2}O_{2} 
Cr^{6+}-DDTC Chelate (pH 2.5)

Amberlite XAD–2010 Column Procedure

FAAS Total Cr

Total Chromium Conc. – Chromium(VI) = Chromium(VI)^{+}

Natural Water (Cr^{3+}, Cr^{6+})

pH 2.5
Cr^{6+} - DDTC Chelate

Amberlite XAD–2010 Column Procedure

FAAS Cr^{6+}

Speciation of Cr(III) and Cr(VI) after column solid phase extraction on Amberlite XAD-2010

V.N. Bulut\textsuperscript{a}, C. Duran\textsuperscript{b}, M. Tufekci\textsuperscript{b}, L. Elci\textsuperscript{c}, M. Soylak\textsuperscript{d,∗}

\textsuperscript{a} Karadeniz Technical University, Giresun Faculty of Science and Arts, Department of Chemistry, 28049 Giresun, Turkey
\textsuperscript{b} Karadeniz Technical University, Faculty of Science and Arts, Department of Chemistry, 61080 Trabzon, Turkey
\textsuperscript{c} Pamukkale University, Faculty of Art and Science, Department of Chemistry, 20020 Denizli, Turkey
\textsuperscript{d} Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey

Received 26 July 2006; received in revised form 31 August 2006; accepted 31 August 2006
Available online 6 September 2006

Abstract

A speciation procedure for Cr(III) and Cr(VI) based on column solid phase extraction on Amberlite XAD-2010 and flame atomic absorption spectrometry combination. Cr(VI) was quantitatively recovered on Amberlite XAD-2010 resin at pH range of 2.0–3.0 as its diethylthiocarbamate complex, while the recoveries of Cr(III) was below 5%. The influences of the various parameters including amounts of the reagents, eluent type and its volume, sample volume, etc., on the quantitative recoveries were examined. The interference of matrix and coexistent elements for method were studied. The detection limit (corresponding to three times the standard deviation of the blank) and the enrichment factor for Cr(VI) were found to be 1.28 μg/L and 25, respectively. To verify the accuracy of the method, drinking water certified reference material (CRM-TMDW-500) was analyzed and the results obtained were in good agreement with the certified value. The proposed method has been successfully applied to the speciation of Cr(III) and Cr(VI) in water samples and preconcentration of total chromium in environmental samples.

© 2006 Elsevier B.V. All rights reserved.
Carbon based nanomaterials

- Carbon nanotubes
- Grafene and grafene oxide
- Nanodiamond
Fullerene $C_{60}$  SWCNTs  MWCNTs  Graphene

Graphite  
\[
\text{Oxidation} \quad \text{Graphite oxide} \quad \text{Sonication} \quad \text{Hybrid material} \\
\text{Reduction} \quad \text{Graphene oxide} \quad \text{Chemical functionalization with other material}
\]

Graphite  Fullerene  Carbon nanotube  Graphene

Just one side available for sorption  Both sides available for sorption
Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes

Mustafa Tuzen a, Kadriye O. Saygi a, Mustafa Soylak b, *

a Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey
b Erzies University, Faculty of Science and Arts, Chemistry Department, 38039 Kayseri, Turkey

Received 22 December 2006; received in revised form 12 March 2007; accepted 11 July 2007
Available online 17 July 2007

Abstract

Multiwalled carbon nanotubes (MWNTs) were used as solid phase extractor for Cu(II), Cd(II), Pb(II), Zn(II), Ni(II) and Co(II) ions as ammonium pyrrolidine dithiocarbamate (APDC) chelates, in the present study. The influences of the experimental parameters including pH of the solutions, amounts of MWNTs, amounts of APDC, eluent type and volume, sample volume etc. on the quantitative recoveries of analyte ions were investigated. The effects of matrix ions of natural waters and some transition metals on the recoveries of the analyte ions were also examined in the model solutions. Tests of addition/recovery for analyte ions in real samples were performed with satisfactorily results. The detection limits (3σ) for the analyte ions were in the range of 0.30–0.60 μg l−1. The concentrations of analytes in standard reference materials (NIST RM 8418 Wheat gluten, LGC 6010 Hard drinking water and NIST SRM 1515 Apple leaves) pretreated by the presented method were measured with FAAS and the analytical values were well agreed with the certified values and the reference values without the interference of major components. The presented method has been applied to the determination of analytes in food and environmental samples with satisfactory results.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Multiwalled carbon nanotubes; APDC; Metal ions; Solid phase extraction; Atomic absorption spectrometry
Solid phase extraction of Cd(II), Pb(II), Zn(II) and Ni(II) from food samples using multiwalled carbon nanotubes impregnated with 4-(2-thiazolylazo)resorcinol

Zeid A. ALOthman · Mohamed Habila · Erkan Yilmaz · Mustafa Soylak

Abstract Multiwalled carbon nanotubes were impregnated with 4-(2-thiazolylazo)resorcinol and used for the separation and preconcentration of Cd(II), Pb(II), Zn(II) and Ni(II) ions from food samples. The analytes were quantitatively recovered at pH 7.0 and eluted with 3 mol L$^{-1}$ acetic acid. The effects of pH value, flow rate, eluent type and sample volume on the recoveries, and the effects of alkali, earth alkali and transition metals on the retention of the analytes were studied. The method was validated using the standard certified reference materials SRM 1570A (spinach leaves) and IAEA 336 (lichen), and the results were found to be

Introduction

The accurate and precise determination of metal ions at trace levels is an important field in analytical and environmental chemistry [1–4], because of their roles in the human body and environment. Inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES), graphite furnace (GFAAS) and flame (FAAS) atomic absorption spectrometry are the main analytical instruments used currently [5–7]. Element concentrations those are low relative to the detec-
Nanocomposites are materials formed by the dispersion of particles in a matrix at the nanometer scale.

- Nano Komposzitler
  - metal / seramik
  - metal / metal
  - seramik / seramik
  - polimer / seramik
  - inorganik / polimer
  - polimer / polimer
Polypyrrole/multi-walled carbon nanotube composite for the solid phase extraction of lead(II) in water samples

Ertugrul Sahmetlioglu a, Erkan Yilmaz b, Ece Aktaş a, Mustafa Soylak a,b,*

a Nigde University, Faculty of Sciences and Arts, Chemistry Department, S1100 Nigde, Turkey
b Erciyes University, Faculty of Sciences, Chemistry Department, 38039 Kayseri, Turkey

A R T I C L E  I N F O
Article history:
Received 14 August 2013
Received in revised form
10 November 2013
Accepted 15 November 2013
Available online 27 November 2013

Keywords:
Conducting polymer
Multi-walled carbon nanotubes
Nanocomposite
Lead
Solid phase extraction

A B S T R A C T
A multi-walled carbon nanotubes-polypyrrole conducting polymer nanocomposite has been synthesized, characterized and used for the separation and preconcentration of lead at trace levels in water samples prior to its flame atomic absorption spectrometric detection. The analytical parameters like pH, sample volume, eluent, sample flow rate that were affected the retentions of lead(II) on the new nanocomposite were optimized. Matrix effects were also investigated. Limit of detection and preconcentration factors were 1.1 μg L⁻¹ and 200, respectively. The adsorption capacity of the nanocomposite was 25.0 mg lead(II) per gram composite. The validation of the method was checked by using SPS-WW2 Waste water Level 2 certified reference material. The method was applied to the determination of lead in water samples with satisfactory results.

© 2013 Elsevier B.V. All rights reserved.

Adsorbent: PPY/CNT nano composite
Adsorbent Amount: 200 mg
Eluent: 3M nitric acid
Sample volume: 200 ml
Eluent volume: 1 mL
Preconcentration Factor: 200
Preparation and characterization of magnetic allylamine modified graphene oxide-poly(vinyl acetate-co-divinylbenzene) nanocomposite for vortex assisted magnetic solid phase extraction of some metal ions

Mansoor Khan a,b, Erkan Yilmaz a, Basak Sevinc c, Ertugrul Sahmetlioglu c, Jasmin Shah b, Muhammad Rasul Jan b, Mustafa Soylak a,⁎

⁎ Erciyes University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri, Turkey
b Institute of Chemical Sciences, University of Peshawar, Peshawar, Pakistan
c Niğde University, Faculty of Sciences-Arts, Department of Chemistry, 51240 Niğde, Turkey

ARTICLE INFO
Article history:
Received 17 June 2015
Received in revised form 12 August 2015
Accepted 15 August 2015
Available online 18 August 2015

Keywords:
Magnetic solid phase extraction
Preconcentration
Magnetic nanocomposite
Flame atomic absorption spectrometry
Trace metal ions

ABSTRACT
Magnetic allylamine modified graphene oxide-poly(vinyl acetate-co-divinylbenzene) (MGO-DVB-VA) was synthesized and used for magnetic solid phase extraction of Pb(II), Cd(II), Cu(II), Ni(II) and Co(II) prior to their determination by flame atomic absorption spectroscopy. The adsorbent surface functional group was characterized by using FT-IR and Raman spectroscopy. XRD pattern was used to determine the layers of GO. Surface morphology and elemental composition of the adsorbent were evaluated by using SEM and EDX analysis. Various parameters, effecting adsorption efficiency like initial solution pH, adsorbent dose, type and volume of eluent, volume of sample and diverse ions effects were optimized. The preconcentration factor (PF) is 40 for all the metals and the limits of detection for Pb, Cd, Cu, Ni and Co are in the range of 0.37–2.39 μg L−1 and relative standard deviation below 3.1%. The method was validated by using the method for certified reference materials (Tobacco Leaves (INCT-OBTL-5), Tomato Leaves (1573a), Certified Water (SPS-ww2) and Certified Water (TMDA 64-2)). The method was successfully applied for natural water and food samples.
Solid phase extraction of uranium(VI) on phosphorus-containing polymer grafted 4-aminoantipyrine

Mustafa Soylak¹ · Mansoor Khan¹,² · Rasim Alosmanov³ · Jasmin Shah² · Mohammad Rasul Jan²

Abstract Phosphorus-containing polymer grafted 4-aminoantipyrine has been synthesized and used for solid phase extraction of U(VI) prior to its UV–Visible spectrophotometric determination by using arsenazo(III). The adsorbent was characterized by using FT-IR and SEM analysis. The influence of parameters including pH, adsorbent dose, amount of complexing reagent, sample volume and matrix effect have been optimized. The detection limit was determined as 1.4 μg L⁻¹ with pre-concentration factor of 30 and RSD of 1.4 %. The accuracy was checked by the analysis of GBW07424 soil and TMDA-64.2 environmental water certified reference materials. The method was applied to natural water and soil samples.

Keywords Solid phase extraction · Spectrophotometry · Determination · Uranium · Arsenazo(III)
Fig. 1 Graphical representation of the proposed solid phase extraction of U(VI)

Fig. 4 Effect of pH on the recovery of U(VI). (Experimental conditions; amount of PhCP-AAP: 100 mg, amount of arsenazo(III): 30 µg, volume of sample: 10 mL N = 3)
Preparation and characterization of magnetic carboxilated nanodiamonds for vortex-assisted magnetic solid-phase extraction of ziram in food and water samples

Erkan Yılmaz, Mustafa Soylak*
Erciyes University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri, Turkey

Abstract
A simple and rapid vortex-assisted magnetic solid phase extraction (VA-MSPE) method for the separation and preconcentration of ziram (zinc dimethyldithiocarbamate), subsequent detection of the zinc in complex structure of ziram by flame atomic absorption spectrometry (AAS) has been developed. The ziram content was calculated by applying stoichiometric relationship between the zinc and ziram. Magnetic carboxilated nanodiamonds (MCNDs) as solid-phase extraction adsorbent was prepared and characterized by Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD) spectrometry and scanning electron microscopy (SEM). These magnetic carboxilated nanodiamonds carrying the ziram could be easily separated from the aqueous solution by applying an external magnetic field; no filtration or centrifugation was necessary. Some important factors influencing the extraction efficiency of ziram such as pH of sample solution, amount of adsorbent, type and volume of eluent, extraction and desorption time and sample volume were studied and optimized. The total extraction and detection time was lower than 10 min. The preconcentration factor (PF), the precision (RSD, n=7), the limit of detection (LOD) and limit of quantification (LOQ) were 160, 7.0%, 5.3 μg L⁻¹ and 17.5 μg L⁻¹, respectively. The interference of various ions has been examined and the method has been applied for the determination of ziram in various waters, foodstuffs samples and synthetic mixtures.

© 2016 Elsevier B.V. All rights reserved.

- Adsorbent: magnetic carboxilated nanodimons
- Analyte: Ziram
- Adsorbent Amount: 25 mg
- Eluent: 0.25 M HNO₃ in acetone
- Sample volume : 40 ml
- Eluent volume: 1 mL
- Preconcentration Factor: 40
One step hydrothermal synthesis and characterization of moss like MWCNT-Bi$_2$S$_3$ nanomaterial for solid phase extraction of copper

Zainab Manzoor Memon$^{a,b}$, Erkan Yilmaz$^a$, Mustafa Soylak$^a$,*

$^a$ Erciyes University, Fen Fakultesi Kimya Bolumu, 38039 Kayseri, Turkey
$^b$ Institute of Biochemistry, University of Sindh, Jamshoro, Pakistan

ARTICLE INFO

Keywords:
Moss like MWCNT-Bi$_2$S$_3$ nanomaterial
Solid phase extraction
Copper
Tobacco
Food
Flame atomic absorption spectrometer

ABSTRACT

The present work was designed with the aim to one step simple hydrothermal synthesis of moss like MWCNT-Bi$_2$S$_3$ nanomaterial as solid phase extraction sorbent for separation, preconcentration and determination of copper in tobacco and food samples. Cu(II) ions was strongly retained on the MWCNT-Bi$_2$S$_3$ nanomaterial at the pH 7.0 and was successfully desorbed by using 1.5 mL of 4 M HNO$_3$. The copper concentration in eluent was determined by flame atomic absorption spectrometer. The certified reference material (NC SZC 73033 Scallion) was analyzed for the verification and accuracy of the proposed method. This work was interpreted statistically and found the analytical performance of the proposed method which consist of preconcentration factor (20), limit of quantification (13.1 µg L$^{-1}$) and relative standard deviation (2.2%), respectively. It was concluded that this method was applied for the detection of copper from different types of tobacco and food samples successfully.
A magnetic MoS$_2$-Fe$_3$O$_4$ nanocomposite as an effective adsorbent for dispersive solid-phase microextraction of lead(II) and copper(II) prior to their determination by FAAS

Neda Baghban$^{1,2}$ • Erkan Yilmaz$^1$ • Mustafa Soylak$^1$

Abstract The authors describe the preparation of a nanocomposite (mag-MoS$_2$-Fe$_3$O$_4$) that was prepared from molybdenum disulfide (MoS$_2$) and magnetic Fe$_3$O$_4$ nanoparticles by a hydrothermal method in an inert atmosphere. The composite is shown to be a viable magnetic adsorbent for dispersive solid phase microextraction of lead(II) and copper(II) ions from water and plant samples. The nanocomposite was characterized by FT-IR, Raman spectroscopy, XRD, SEM, and BET methods. The factors affecting the extraction recovery of the analytes, including the pH value, type of dispersive solvent, sample volume, type and volume of eluent solution, and interfering ions, were optimized. Flame atomic absorption spectrometry was then used for quantitation. Figures of merit of this method include a preconcentration factor of 50 for lead(II) and 35 for Cu(II), LODs of 3.3 µg L$^{-1}$ for lead(II) and of 1.8 µg L$^{-1}$ for Cu(II), and RSDs of 4.9 and 1.5%, respectively. The method was used to preconcentrate the analytes from plant and water samples prior to their determination by FAAS. It was then validated by analyzing certified reference materials (water and plant), and this resulted in good accuracy.
Nanodiamond/MoS$_2$ nanorod composite as a novel sorbent for fast and effective vortex-assisted micro solid phase extraction of lead(II) and copper(II) for their flame atomic absorption spectrometric detection

Neda Baghban $^{a,b}$, Erkan Yilmaz $^a$, Mustafa Soylak $^{a,*}$

$^a$ Faculty of Sciences, Department of Chemistry, Erciyes University, 38039 Kayseri, Turkey
$^b$ Young Researchers Club, Shahr-e-Qods Branch, Islamic Azad University, Tehran, Iran

This study is a report on the synthesizing nanodiamond/MoS$_2$ nanorod composite using the hydrothermal method and its application as adsorbent in micro solid phase extraction of lead(II) and copper(II) prior their determination through flame atomic absorption spectroscopy. The nanodiamond/MoS$_2$ nanorod composite was characterized using Raman spectroscopy, BET surface analysis and scanning electronic microscopy (SEM). The optimal conditions including amount of used adsorbent, pH, vortex time, elution condition and volume investigated. Quantitative recoveries for both analytes were obtained at pH 3.0. The preconcentration factor is 35, and the sorption capacity of synthesized adsorbent for lead(II) and copper(II) is 19.87 and 49.33 mg g$^{-1}$. The relative standard deviation is 0.9 and 1.5% for lead(II) and copper(II) at a level of 200 µg L$^{-1}$ ($n = 6$), and the detection limit is 42 and 22 µg L$^{-1}$ for lead(II) and copper(II), respectively. The procedure accuracy was proved via analyzing the standard reference materials (SPS-WW2 Waste water Level 2 and TMDA-53.3). The presented procedure was applied for the determination of copper and lead contents of the water samples from Turkey.

©2017 Elsevier B.V. All rights reserved.
Vortex assisted solid-phase extraction of lead(II) using orthorhombic nanosized Bi₂WO₆ as a sorbent

Neda Baghban¹,² • Erkan Yilmaz³ • Mustafa Soylak¹

Received: 22 July 2017 / Accepted: 9 November 2017
© Springer-Verlag GmbH Austria, part of Springer Nature 2017

Abstract
Nanosized single crystal orthorhombic Bi₂WO₆ was synthesized by a hydrothermal method and used as a sorbent for vortex assisted solid phase extraction of lead(II). The crystal and molecular structure of the sorbent was examined using XRD, Raman, SEM and SEM-EDX analysis. Various parameters affecting extraction efficiency were optimized by using multivariate design. The effect of diverse ions on the extraction also was studied. Lead was quantified by flame atomic absorption spectrometry (FAAS). The recoveries of lead(II) from spiked samples (at a typical spiking level of 200–400 ng·mL⁻¹) are >95%. Other figures of merit includes (a) a detection limit of 6 ng·mL⁻¹, (b) a preconcentration factor of 50, (c) a relative standard deviation of 1.6%, and (d) and adsorption capacity of 6.6 mg·g⁻¹. The procedure was successfully applied to accurate determination of lead in (spiked) pomegranate and water samples.
A new magnetic nanodiamond/graphene oxide hybrid (Fe₃O₄@ND@GO) material for pre-concentration and sensitive determination of sildenafil in alleged herbal aphrodisiacs by HPLC-DAD system

Erkan Yılmaz a, d, Halil İbrahim Ulusoy b, *, Özge Demir b, Mustafa Soylak c

a Erciyes University, Faculty of Pharmacy, Department of Analytical Chemistry, Kayseri, Turkey
b Cumhuriyet University, Faculty of Pharmacy, Department of Analytical Chemistry, Sivas, Turkey
c Erciyes University, Faculty of Sciences, Department of Chemistry, Kayseri, Turkey
d Nanotechnology Research Center (ERNAM), Erciyes University, 38039, Kayseri, Turkey

ARTICLE INFO

Keywords:
Sildenafil citrate
Magnetic hybrid material
Magnetic solid phase extraction
Graphene oxide
Nanodiamond
High performance liquid chromatography
Herbal products

ABSTRACT

A sensitive analytical methodology was investigated to concentrate and determine of sildenafil citrate (SLC) present at trace level in herbal supplementary products. The proposed method is based on simple and sensitive pre-concentration of SLC by using magnetic solid phase extraction with new developed magnetic nanodiamond/graphene oxide hybrid (Fe₃O₄@ND@GO) material as a sorbent. Experimental variables affecting the extraction efficiency of SLC like; pH, sample volume, eluent type and volume, extraction time and amount of adsorbent were studied and optimized in detail. Determination of sildenafil citrate after magnetic solid phase extraction (MSPE) was carried out by HPLC-DAD system. The morphology, composition, and properties of the synthesized hybrid material was characterized by Fourier transform infrared spectrometry (FT-IR), Raman spectrometry (Raman), X-ray diffraction spectrometry (XRD), scanning electron microscopy (SEM), mapping photographs, zeta potential analyzer, and BET surface area analysis. Under optimized conditions, linear range was ranged from 5.00 to 250.00 ng mL⁻¹ with R² of 0.9952. The limit of detection (LOD) was 1.49 ng mL⁻¹ and the recoveries at two spiked levels were ranged from 94.0 to 104.1% with the relative standard deviation (RSD) < 7.1% (n = 5). The enhancement factor (EF) was 86.9. The results show that the combination MSPE with HPLC-DAD is a suitable and sensitive method for the determination of SLC in real samples.
Comparison SPE and SPME techniques

<table>
<thead>
<tr>
<th>parameter</th>
<th>Classical Solid phase extraction</th>
<th>Solid phase microextraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of adsorbent</td>
<td>500 mg</td>
<td>20-50 mg</td>
</tr>
<tr>
<td>Sample volume</td>
<td>100 ml</td>
<td>10 ml</td>
</tr>
<tr>
<td>Time</td>
<td>At least 30-60 min per sample</td>
<td>10 min per sample</td>
</tr>
<tr>
<td>Organic solvents</td>
<td>Too much</td>
<td>limited</td>
</tr>
</tbody>
</table>
Nanomaterial's based chromium speciation in environmental samples: A review

Muhammad Balal Arain a, b, Imtiaz Ali a, Erkan Yilmaz c, d, Mustafa Soylak b, *

a Department of Chemistry, Abdul Wali Khan University, Mardan, 23200, KPK, Pakistan
b Department of Chemistry, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey
c Department of Analytical Chemistry, Faculty of Pharmacy, Erciyes University, 38039 Kayseri, Turkey
d Nanotechnology Research Center (ERNAM), Erciyes University, 38039, Kayseri, Turkey

ARTICLE INFO

Article history:
Available online 28 March 2018

Keywords:
Chromium
Speciation
Nanomaterials
Instrumental detection
Environmental samples
Food samples
Biological samples

ABSTRACT

To investigate critical health effects, a supporting speciation analysis is often matter of concern in order to identify figure of the bioconcentration or biomagnification of elements like chromium. Chromium speciation study requires high capacity separation and high sensitivity detection because chromium naturally exists in small quantities. Scientific literature supports chromium speciation at trace levels by using different nanomaterials and methodologies. Nanoparticles adsorbent based speciation technique is a current state-of-art technique due to its exceptional surface area chemistry, maximum mechanical strength, optical, magnetism, unique electrical, catalytic and photonic properties. The present review is aimed to discuss significance of chromium speciation and specific properties of different nanoparticles as adsorbent and also explore the new possible nanomaterials for chromium speciation. All data used for chromium speciation with various kind of nano adsorbent has also been tabulated with their analytical figure of merit.

© 2018 Elsevier B.V. All rights reserved.
Fig. 2. The milestones in the development of adsorbent for adsorption based chromium speciation methods.
Green chemistry

- Safe chemicals
- Safe solvents and auxiliary reagents
- Renewable materials
- Reduction of waste
- The use of a safer method for the prevention of accidents
- Monitoring and analysis of the prevention of pollution
- The using of microsized methods
- Less harmful chemical processes
- Waste measures
- Energy efficiency design
- Waste measures
New Generation Separation-Preconcentration Methods

- Ionic liquids
- Supra molecular solvents
- Deep eutectic solvents
- Switchable solvents

New generation solvents

- Organic solvents
- Liquid phase microextraction
- Solid phase microextraction
- Magnetic solid phase extraction

Apparatus
- Ultrasonication
- Vortex
- Microwave
- Magnetic stirring

New Generation Preconcentration Methods
Why is Microextraction…?

- To use minimum amounts of solvents and reagents
- Simplificty of steps
- High preconcentration factors (from 20 ml to 100 microliter)
- Green methods green chemistry (green solvents like ionic liquids)
- Less harmful or harmless than a process with simple step
- Lower cost
- High yield
- Time saving
- Low risc

*
Addition of microextraction solvent

Model solution → Cloudy phase

Centrifuge

Extractant phase

Phase separation
- Classical Solvents

- New generation solvents
  ✓ Ionic Liquids
  ✓ Supramolecular Solvents
  ✓ Deep eutectic solvents
  ✓ Switchable solvents
Classical Organic Solvents

CCl₄, CHCl₃, CH₂Cl₂, CS₂, ….

Advantage:
✓ Phase stability
✓ High preconcentration factor
✓ Simple phase separation
✓ High mass transfer

Disadvantage:
○ Toxic
○ Some of them are prohibited chemicals
○ Expensive
Dispersive liquid–liquid microextraction of cadmium(II) for preconcentration prior to flame atomic absorption spectrometric detection in water

M. Soylak* and Y.E. Unsal

Faculty of Sciences, Chemistry Department, Erciyes University, 38039 Kayseri, Turkey

(Received 14 December 2011; final version received 29 July 2012)

A dispersive liquid–liquid microextraction procedure for cadmium(II) as its 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol chelate is presented. Carbon tetrachloride and methanol were used as extraction and dispersive solvents, respectively. After phase separation, the preconcentrated-separated cadmium(II) is determined by flame atomic absorption spectrometry with a microinjection technique. The factors which affected the extraction efficiency, i.e. the pH of the sample solution and the volumes of reagent and sample were investigated. The effects of some alkali, alkali earth, and transition metal ions, and of some anions on the recovery of cadmium were also studied. A preconcentration factor of 250 was obtained for a sample volume of 50 mL under optimum conditions. The method was validated by analysis of certified reference materials and applied to some water samples from Turkey.

Keywords: preconcentration; cadmium(II); 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol; dispersive liquid–liquid microextraction; flame atomic absorption spectrometry; natural waters
Technical Note

Cr speciation in water samples by dispersive liquid–liquid microextraction combined with total reflection X-ray fluorescence spectrometry

Z. Bahadir a, V.N. Bulut b, M. Hidalgo c, M. Soylak d, E. Marguí c, * 

a Department of Chemistry, Giresun University, Giresun, Turkey
b Macka Vocational School, Karadeniz Technical University, Macka, Trabzon, Turkey
c Department of Chemistry, Faculty of Sciences, University of Girona, Girona, Spain
d Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri, Turkey

ARTICLE INFO

Article history:
Received 9 September 2015
Accepted 9 November 2015
Available online 14 November 2015

Keywords:
Total-reflection X-ray fluorescence spectroscopy (TXRF)
DLLME
Cr species
Water sample

ABSTRACT

A novel method based on dispersive liquid–liquid microextraction (DLLME) and total-reflection X-ray fluorescence spectrometry (TXRF) is proposed for the determination and preconcentration of inorganic Cr species (Cr(VI) and Cr(III)) in water samples.

Parameters affecting the extraction procedure for Cr speciation (pH, sample volume, disperser solvent, complexing agent, organic solvent, temperature) and TXRF conditions (sample volume, drying mode, measurement time, internal standardization) have been carefully evaluated to ensure the highest sensitivity for Cr determination. It was found that the minimum Cr content that can be detected was 0.8 μg L⁻¹. This value is significantly lower than the maximum Cr content permissible in drinking waters and it is better or comparable with those obtained in other published works based on the use of solid phase extraction or liquid phase microextraction in combination with atomic absorption spectrometry techniques. A good linearity (R² = 0.9937) was obtained in the range of 5 to 4000 μg L⁻¹ demonstrating the suitability of the DLLME + TXRF for both the analysis of drinking and waste water samples.

Additional advantages of the DLLME-TXRF systems include the use of very small amount of reagents and the simplicity and low cost of operation of the benchtop instrument used (no cooling media and gas consumption are needed).
Ionic liquids refers to liquid organic salts which may be below the 100 °C. Simple ionic liquid consists of an anion and cation. Cations are usually found in larger and anions are the smaller alkyl chain.
Benefits:
✓ Anions and cations of the ionic liquid can be changed by forming properties can be synthesized in different ways and for specific processing
✓ Density, melting point, viscosity and so on. properties can be achieved by changing the structure of the ions in a suitable solvent to the process
✓ Flammability and low vapor pressure
✓ The solubility of organic and inorganic components
✓ Thermal stability
✓ Phase stability
✓ High preconcentration factor
✓ Simple phase separation
✓ High mass transfer

Disadvantage:
Expensive
Ionic liquid dispersive liquid–liquid microextraction of lead as pyrrolidinedithiocarbamate chelate prior to its flame atomic absorption spectrometric determination

Mustafa Soylak a,b,*, Erkan Yilmaz a

a Erciyes University, Faculty of Science, Department of Chemistry, 38039 Kayseri, Turkey
b King Saud University, Riyadh, Saudi Arabia

ARTICLE INFO

Article history:
Received 21 January 2011
Received in revised form 1 March 2011
Accepted 3 March 2011
Available online 25 March 2011

Keywords:
Lead
Flame atomic absorption spectrometry
Ionic liquid
1-Hexyl-3-methylimidazolium hexafluorophosphate
Ammonium pyrrolidinedithiocarbamate
Natural waters

ABSTRACT

A novel separation–preconcentration procedure based on ionic liquid dispersive liquid–liquid microextraction of traces lead as pyrrolidinedithiocarbamate chelate has been developed. 1-Hexyl-3-methylimidazolium hexafluorophosphate as ionic liquid was used for extraction of lead pyrrolidinedithiocarbamate chelate. After phase separation, the enriched analyte in the final solution is determined by flame atomic absorption spectrometry (FAAS). The effects of pH, amounts of ligand, amounts of 1-hexyl-3-methylimidazolium hexafluorophosphate, sample volume etc. on the recoveries of lead ions were investigated. The influences of some cations and anions on the recoveries of lead were also examined. The preconcentration factor was calculated as 40 at the sample volume of 20 ml. The detection limit for lead ions was 1.5 μg/l. The validation of the presented method was performed by the analysis of TMDA-51.3 fortified water. The method was applied to natural water samples.

© 2011 Elsevier B.V. All rights reserved.
Supramolecular solvents

Supramolecular solvents is obtained by mixing have long carbon chain such as hydroxyl solvent (OH) and carboxylic acid (COOH) with tetrahydrofuran and tetrabutyl ammonium species.

1-Decanol-THF amphiphiles formation
Advantages of supramolecular solvents

✓ Supramolecular solvents in the extraction study are alternative environment-friendly solvent to the resultant organic solvent.

✓ Supramolecular solvents is obtained by changing some effect such as pH, temperature, and ionic strength and the resulting effects of the colloidal solution with surfactants, water immiscible solvent dispersed in a continuous phase.

✓ In the extraction operation, i.e. amphiphilic supramolecular linking group of solvents consisting of high concentration, a very small volume (50 to 1000 µL) solution is obtained by adding high yield of extraction media.
Development a novel supramolecular solvent microextraction procedure for copper in environmental samples and its determination by microsampling flame atomic absorption spectrometry ☆

Erkan Yılmaz, Mustafa Soylak *

Erciyes University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri, Turkey

ARTICLE INFO

Article history:
Received 12 January 2014
Received in revised form 20 March 2014
Accepted 21 March 2014
Available online 29 March 2014

Keywords:
Supramolecular solvent
Copper
1-Decanol
Tetrahydrofuran
Flame atomic absorption spectrometry
Sodium dimethyl dithiocarbamate

ABSTRACT

A supramolecular solvent (SS) made up of reverse micelles of 1-decanol in tetrahydrofuran (THF): water was used for the fast and selective microextraction of Cu(II) prior to its determination by microsampling flame atomic absorption spectrometry (FAAS). Cu(II) was complexed with dimethyl dithiocarbamate (DMDC) to obtain hydrophobic complex and extracted to supramolecular solvent phase. The influences of some analytical parameters including pH, type and volume of supramolecular solvent, amount of complexing agent, ultrasonication and centrifuge time and sample volume were investigated. The effects of matrix components were also examined. The detection limit (LOD) and the quantification limit (LOQ) were 0.52 μg L⁻¹ and 1.71 μg L⁻¹ respectively. An preconcentration factor was obtained as 60 and the relative standard deviation was < 3%. The accuracy of the developed method was evaluated by the analysis of the certified reference materials (TMDA-64.2 water, SRM 1568 A Rice Flour and 8433 Corn Bran) and addition-recovery tests. The presented supramolecular solvent based liquid–liquid microextraction (SS-LLE) procedure was applied to the determination of copper in food and water samples with satisfactory results.
Deep Eutectic Solvents

Deep eutectic solvents (DESs) show physical properties similar to ILs such as tunable miscibility, low volatility, high conductivity and good thermal stability.

DESs eliminate the disadvantages of ILs such as dangers to health and the environment and high price.

Some DESs are drinkable and are prepared by simply mixing two safe components together, they are easily accessible, cheap, biodegradable, renewable, non-flammable and nonvolatile.

The preparation facility of hydrophobic or hydrophilic DESs is the most important property of DESs in extraction studies and provides a suitable extraction medium for different polarity analytes.

Formation of DESs.
DES 's the most important aspect of having very low freezing point and that they are liquid below 150 °C. DES 's is the most liquid at between room temperature and 70 degrees.

- Chlorine chloride (Vitamin B4) due to cheap, durable and low toxicity, urea, glycerol as an organic salt is usually used in the preparation of DES.

- DES's eliminates the disadvantage of organic solvents being expensive, flammable and toxic effects.

- DES 's are inert to water, and they can be prepared without requiring any special equipment or techniques in laboratory conditions.

- DES 's have been used in the field of organic chemistry, biochemistry, electrochemistry, catalysis processes and preparation of new materials.

- Hundreds of different kinds of DES 's can be prepared with different properties, such as pH, freezing point, viscosity, conductivity and so on.
Ultrasound assisted-deep eutectic solvent extraction of iron from sheep, bovine and chicken liver samples

Erkan Yilmaz, Mustafa Soylak*

Erciyes University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri, Turkey

ARTICLE INFO

Article history:
Received 19 October 2014
Received in revised form
13 December 2014
Accepted 21 December 2014
Available online 30 December 2014

Keywords:
Deep eutectic solvent
Choline chloride
Lactic acid
Extraction
Iron
Flame atomic absorption spectrometry
Liver

ABSTRACT

A green, novel and effective ultrasound assisted-deep eutectic solvent (DES) extraction (UA-DES-E) procedure was developed for extraction of iron from sheep, bovine and chicken liver samples. The analytical parameters including type and composition DES, volume of DES, ultrasonication time and ratio of sample to DES were optimized by using 50 mg of the NIST SRM 1577b bovine liver certified reference material. The limit of detection (LOD) and the limit of quantification (LOQ) were found as 0.026 μg mL⁻¹ and 0.085 μg mL⁻¹, respectively. The relative standard deviation (RSD) as a result of 7 replicates of 50 mg of certified reference material was 1.4%. The accuracy of proposed method was checked by the addition/recovery tests to NIST SRM 1577b bovine liver and a sheep liver. The extraction method was applied to extraction of iron from bovine, sheep and chicken liver samples retail from markets at Kayseri, Turkey with satisfactory results (recoveries higher than 95%).
Ultrasound assisted-deep eutectic solvent based on emulsification liquid phase microextraction combined with microsample injection flame atomic absorption spectrometry for valence speciation of chromium(III/VI) in environmental samples

Erkan Yılmaz, Mustafa Soylak*

Erciyes University, Faculty of Sciences, Department of Chemistry, Kayseri, 38039 Turkey

**Abstract**

A new type of deep eutectic solvents (DESs) have been prepared and used as extraction solvents for ultrasound assisted-deep eutectic solvent based emulsification liquid phase microextraction method (UA-DES-ELPME) for the determination and speciation of total chromium, chromium(III) and chromium (VI). The chromium concentration in DES rich phase (extraction phase) was determined by using microsample injection flame atomic absorption spectrometer (FAAS). The detection limit (LOD), the quantification limit (LOQ), preconcentration factor and relative standard deviation were found as 5.5 μg L⁻¹, 18.2 μg L⁻¹, 20 and 6%, respectively. The accuracy of the developed method was evaluated by the analysis of water the certified reference materials (TMDA-53.3 Fortified environmental water and TMDA-54.4 Fortified Lake Water) and addition-recovery tests for water samples.
Fig. 1. Graphical representation of the UA-DES-ELPME method.
Switchable solvents have two form polar and non-polar form, which they show differences in terms of their physical properties.

A switchable polarity solvent (SPs) is a solvent that creates water-miscible hydrophilic form in the presence of an atmosphere of CO$_2$ at 1 bar, however separates from water and creates hydrophobic form when CO$_2$ is removed with a phase transition trigger such as bubbling air, argon, nitrogen or other inert gas under heating and addition of acids and bases.
The formation of switchable solvents based on the protonation of apolar secondary, and tertiary amines, with water in the presence of CO$_2$ at 1 atmosphere pressure. The basis of this reaction is exothermic and is based on the protonated amines involves an alkyl amine bicarbonate or carbonate salts.

The reaction of ammonium bicarbonate or alkyl carbonate solvents resulting switchable polar solvents form that is miscible with water. However creates hydrophobic form when CO$_2$ is removed with a phase transition trigger such as bubbling air, argon, nitrogen or other inert gas under heating and addition of acids and bases.

Besides being switchable in this reaction, all of the components react readily available, they are not toxic and is cheaper to build Another important advantage of the use of these solvents.
Presence of $\text{CO}_2$

$\text{NR}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons ^+\text{HNR}_3 + \text{HCO}_3^-$

Removing of $\text{CO}_2$
Addition of acid or base
Passing $\text{N}_2$ or Ar gas
Heating
Switchable polarity solvent for liquid phase microextraction of Cd(II) as pyrrolidinedithiocarbamate chelates from environmental samples

Erkan Yilmaz, Mustafa Soylak

Erzurum University, Faculty of Sciences, Department of Chemistry, 38039 Kayseri, Turkey

HIGHLIGHTS
- Switchable polarity solvent was synthesized from triethylamine (TEA)/water/CO₂.
- The switchable polarity solvent has been used for the microextraction of cadmium(II).
- The important factors were optimized.
Switchable Solvent Based Liquid Phase microextraction
Switchable solvent-based liquid phase microextraction of copper(II): optimization and application to environmental samples

Erkan Yılmaz and Mustafa Soylak*

A switchable solvent-based liquid phase microextraction (SS-LPME) procedure has been established for the preconcentration of copper prior to its determination by microsampling flame atomic absorption spectrometry (FAAS). Triethylamine (TEA) was adopted for the study as a green and cheap switchable solvent. The Cu(II)-(2-pyridylazo)-2-naphthol (PAN) complex was extracted into the TEA phase by converting the protonated carbonate (P-TEA-C) to TEA. The experimental conditions have been comprehensively studied and optimized. The limit of detection (LOD) and repeatability (RSD%) of the method were 1.80 µg L⁻¹ and 3.8%, respectively, and its accuracy was assessed against certified reference materials (TMDA-64.2 fortified water, TMDA-53.3 fortified water, TMDA-51.3 fortified water, 1573a tomato leaves, INCT-OBLT-5 oriental basma tobacco leaves and NCS ZC 8100 2b human hair), and by addition-recovery tests. The SS-LPME-FAAS method was also applied for the determination of trace amounts of copper in water, food and hair samples.
Switchable solvent based liquid phase microextraction of uranium in environmental samples: a green approach

Mustafa Soylak,*a Mansoor Khanab and Erkan Yilmaza

This paper describes a new and green approach for the preconcentration and separation of U(Ⅵ) by switchable solvent based liquid phase microextraction (SPS-LPME) and its UV-vis spectrophotometric determination. 1-(2-pyridylazo)-2-naphthol (PAN) as complexing agent was used. Conversion features of triethylamine (TEA) and protonated triethylamine bicarbonate (P-TEA-BC) as a green and cheap switchable solvent pair were used in the presented work. Protonated triethylamine bicarbonate (P-TEA-BC) as the polar form of the switchable polarity solvent (SPS) was successfully synthesized from triethylamine (TEA) via a proton transfer reaction and used for microextraction of the hydrophobic U(Ⅵ)-PAN complex at pH 9.0. The relative standard deviation was 2.5% for five repeated determinations of model solutions containing 6 μg L⁻¹ of U(Ⅵ). The limit of detection (LOD), the limit of quantification (LOQ) and enhancement factor were 0.3 μg L⁻¹, 1.0 μg L⁻¹ and 40, respectively. The accuracy of the method was evaluated by analyzing certified reference materials and addition-recovery tests. The method was successfully applied to the determination of uranium in water, sediment, soil and rock samples.
Switchable solvent-based liquid phase microextraction of copper(II): optimization and application to environmental samples

Erkan Yılmaz and Mustafa Soylak*

A switchable solvent-based liquid phase microextraction (SS-LPME) procedure has been established for the preconcentration of copper prior to its determination by microsampling flame atomic absorption spectrometry (FAAS). Triethylamine (TEA) was adopted for the study as a green and cheap switchable solvent. The Cu(II)-1-(2-pyridylazo)-2-naphthol (PAN) complex was extracted into the TEA phase by converting the protonated carbonate (P-TEA-C) to TEA. The experimental conditions have been comprehensively studied and optimized. The limit of detection (LOD) and repeatability (RSD%) of the method were 1.80 µg L⁻¹ and 3.8%, respectively, and its accuracy was assessed against certified reference materials (TMDA-64.2 fortified water, TMDA-53.3 fortified water, TMDA-51.3 fortified water, 1573a tomato leaves, INCT-OBTL-5 oriental basma tobacco leaves and NCS ZC 8100 2b human hair), and by addition-recovery tests. The SS-LPME-FAAS method was also applied for the determination of trace amounts of copper in water, food and hair samples.
Nowadays works and Future planning...

- Quantum dots in the solid phase extraction
- Thin film preconcentration
- Novamene: A new class of carbon allotropes
- Mg/Al layered double hydroxide (LDH)
- Metal Organic Frameworks (MOF),
- Covalent Organic Frameworks (COF)
- Nanoextraction and solid phase nanoextraction ...
- Nanoengines.... Nano membranes, Microfactories ???
Collaborations and thanks

- King Saud University- Suudi Arabistan
- Sindh University Pakistan
- University of Peshawer - Pakistan
- Yasouj University- Iran
- Baku State University - Azarbeycan
- Universidade Federal da Bahia, Brezilya
- National Research Centre, Mısır
- University of Girona, Girona, Spain
- University of Pavol Jozef Safárik, Slovakya
- Erciyes Üniversitesi
- TÜBİTAK
- Hacettepe Üniversitesi
- Pamukkale Üniversitesi
- Karadeniz Teknik Üniversitesi
- Gaziosmanpaşa Üniversitesi
- Nevşehir Hacı Bektaş Veli Üniversitesi
- Niğde Üniversitesi
- Gümüşhane Üniversitesi
- Çanakkale 18 Mart Üniversitesi
- Van Yüzüncü Yıl Üniversitesi
- Siirt Üniversitesi
- Cumhuriyet Üniversitesi
Thanks for your attention

Soylak Research Group

www.soylak.net

To get signal 50 or 100 microliter of sample is enough.
The reproductive and developmental toxicity of nanoparticles: A bibliometric analysis

Zengjin Wang, Tongchao Zhang, Fengyan Huang and Zhiping Wang

Abstract
Because of the advantages of nanoparticles (NPs) in a variety of industrial, biomedical, and consumer applications, they are intentionally (such as in medicine) or unintentionally (environment exposure) introduced into the human body. However, to date, the detrimental effects of NPs are still unclear, especially in reproductive and developmental toxicity. In this study, we researched 266 articles related to the reproductive and developmental toxicity of NPs from 2006 to December 2016 based on the database of the Web of Science. According to the bibliometric analysis, we found that China and the United States were the leading countries in this field and the major research trends might focus on the pathogenesis of NPs, such as oxidative stress, inflammation, and DNA damage. By this analysis, we provide new insights into the research trends and characteristics of the field.

Keywords
Nanoparticles, reproductive and developmental toxicity, bibliometric analysis, oxidative stress

Received 11 September 2017; Revised 7 October 2017; Accepted 17 October 2017
Toxicity of carbon nanotubes: A review

Arul Prakash Francis and Thiyagarajan Devasena

Abstract
Carbon nanotubes (CNTs) are widely used in the aerospace, automotive, and electronics industries because of their stability, enhanced metallic, and electrical properties. CNTs are also being investigated for biomedical applications such as drug delivery systems and biosensors. However, the toxic potential of CNTs was reported in various cell lines and animal models. The toxicity depends on diverse properties of the CNTs, such as length, aspect ratio, surface area, degree of aggregation, purity, concentration, and dose. In addition, CNTs and/or associated contaminants were well known for oxidative stress, inflammation, apoptosis, pulmonary inflammation, fibrosis, and granuloma in lungs. The increased production of CNTs likely enhanced the possibility of its exposure in people. Studies on the toxicity of CNTs are mainly focused on the pulmonary effects after intratracheal administration, and only a few studies are reported about the toxicity of CNTs via other routes of exposure. So, it is essential to consider the chronic toxicity of CNTs before using them for various biomedical applications. This review focuses on the potential toxicities of CNTs.

Keywords
Carbon nanotubes, aggregation, intratracheal, granuloma, inflammation

Received 21 August 2017; Revised 31 October 2017; Accepted 13 November 2017