



Solid-phase extraction based on magnetic nanoparticles coupled with gas chromatography with flame ionization detection for the determination of low concentration of diazinon and malathion in aqueous samples

Mahmoud Ebrahimi*, Nafise Jafari, Amir Habibi Tamijani, Mohsen Aghamohammadhasan, Vahid Ghashamsham

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

Due to intensive use of pesticides, their residues have become an unavoidable part of the environment, and they are often detected in all environmental segments and therefore their monitoring has been frequently performed throughout the world [1]. Although separation chemical analysis involves several stages, sample preparation step can be marked as the most critical one [2]. Traditional sample preparation methods are laborious, time consuming, expensive, requires large amounts of organic solvents and usually involve many steps. As a result, modern sample preparation procedures have been developed [3]. As a promising sample pretreatment technique, magnetic solid phase extraction (MSPE) has caught much attention recently. In this study, a method for extraction and preconcentration trace amounts of two organophosphorus pesticides (diazinon and malathion) in environmental water was developed using magnetic solid phase extraction followed by gas chromatography with flame ionization detection (GC-FID). Fe_3O_4 nanoparticles were prepared via the modified coprecipitation method [4]. Various parameters, including the amounts of magnetic nanoparticles absorbents, extraction time, eluting solvent, eluting volume, and sample pH values were optimized. Under optimized conditions, method showed good linearity between 0.03–0.06 and 500 ng mL^{-1} with regression coefficients (R^2) of 0.997 and 0.998. Limits of detection were 0.010 and 0.018 ng mL^{-1} . The enrichment factors of this method were 560 and 445 and the analysis yielded good reproducibility with the RSD values 6.1% and 5.5% at the 10 ng mL^{-1} level ($n = 3$) for diazinon and malathion, respectively. Our procedure has been adopted and optimised for water samples and applied to surface water and river water samples from Mashhad (Iran). Average recoveries at three spiked levels were in the range of 88.2–94.2% with relative standard deviations below 9.1%.

References

- [1] M.G. Nillos, J.Gan, D. Schlenk, J. Chromatogr. B. 878 (2010) 1277–1284.
- [2] J. Pawliszyn, Anal. Chem. 75 (2003) 2543–2558.
- [3] R.M. Smith, J. Chromatogr. A. 1000 (2003) 3–27.
- [4] G.Guan, L.Yang, Q.Mei, K.Zhang, Z.Zhang, M.Y.Han, Anal. Chem. 84 (2012) 9492–9497.

Efficient separation of fluoride from aqueous solutions by grafting metalloporphyrin on Fe_3O_4 nanoparticles

Abouzar Zavareian^{1*}, Tahereh Poursaberi², Mostafa Hassanisadi², Yousefali Ghorbani² and Hassan Zavarmousavi¹

¹Department of chemistry, Semnan University, Semnan, Iran.

²Research institute of petroleum industry, Teheran, Iran.

*E-mail: Zavar2012abouzar@yahoo.com

High amount of fluoride in drinking water may cause serious health issues. World Health Organization (WHO) has adopted the guideline value of 1.5 mg/L as the acceptable level of fluoride [1]. Therefore fluoride contaminated waters must be treated properly to meet the regulations. Among several treatment technologies applied for fluoride removal, adsorption process has been explored widely [2] and magnetic nanoparticles has provided unique advantages in due course.

In this study, we have treated fluoride contaminated groundwater using magnetic nanoparticles. Therefore, we synthesis a new sorbent consisting of 3-aminopropyl triethoxysilane (APTES) coated magnetite nanoparticles functionalized with a Aluminum (III)-porphyrin complex Al(TCPP) [TCPP: 4,4',4''-(21H,23H-porphine-5,10,15,20-tetrayl) tetrakis (benzoic acid)] for the removal of trace amounts of fluoride ions from aqueous samples [3]. Fe_3O_4 nanoparticles were synthesized by co-precipitation of Fe^{2+} and Fe^{3+} in an sodium hydroxide solution [4] and then their surface was modified with APTES and AL (TCPP). The present study investigates application of this new sorbent for the removal of trace amounts fluoride ions from aqueous samples using ion chromatography (IC) [5]. The morphology and properties of the nanoparticles were examined by X-ray diffraction (XRD) Transmission Electron Microscopy (TEM), elemental analysis, Fourier Transform Infrared Spectroscopy (FT-IR) and Thermo-Gravimetric Analysis (TGA). The batch experiments showed that modified nanoparticles can effectively be used to remove fluoride from water. Under optimized conditions for a fluoride concentration of 10 mg L^{-1} , contact time: 20 min, pH: 6.5 and nanosorbents dosage: 25 mg, the percentage of the extracted fluoride ions was 98.0 ± 0.2 %. Furthermore, the addition of coexisting anions such as NO_3^- , NO_2^- , Cl^- , HClO_4^- , SO_4^{2-} , and CO_3^{2-} has no remarkable influence on fluoride removal efficiency. Regeneration of fluoride adsorbent material could be possible with NaOH and the reuse of the adsorbents is possible up to 6 cycles. The use of such a system can provide fast and efficient removal of the fluoride by using an external magnetic field.

Keywords: Metalloporphyrin; magnetite nanoparticles; wastewater treatment; surface modification; fluoride ion.

References

- [1] World Health Organization (WHO), Guidelines for Drinking Water Quality, vol.1, 2nd ed., World Health Organization, Geneva, 1993.
- [2] S. Kundu, A.K. Gupta, Chem. Eng. J. 122 (2006) 93–106.
- [3] V.K. Gupta, A.K. Jain, L.P. Singh, U. Khurana, Anal. Chim. Acta, 355 (1997) 33–41.
- [4] D. Maity, D.C. Agrawal, Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media, J. Magn. Magn. Mater, 308 (2007) 46–55.
- [5] E. Malinowska, L. Gorski, M.E. Meyerhoff, Anal. Chim. Acta 468 (2002) 133–141.

The competitive and selective transport of metal cations through bulk liquid membrane by 5,6,11,12-tetraphenyl-1,2,4,7,8,10-hexa azo-cyclododeca-4,6,10,12-tetra-N-9,4-ditione and new synthesized phosphorus-nitrogen compound, $(\text{CF}_3\text{C}(\text{O})\text{NH})(\text{C}_6\text{H}_{11}\text{NH})\text{P}(\text{O})[\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}]\text{P}(\text{O})(\text{NHC}_6\text{H}_{11})(\text{NHC}(\text{O})\text{CF}_3)$

Vahideh Ghaffari,* Razieh Sanavi Khoshnood^a, Fatemeh Karimi Ahmadabad^b, Mehrdad Pourayoubi, Hossein Eshtiagh-Hosseini

^aDepartment of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

^bDepartment of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

The competitive metal ion transport experiments of Co^{+2} , Cd^{+2} , Ag^+ , Pb^{+2} , Ni^{+2} and Pb^{2+} cations were carried by the title ligands using chloroform (CHCl_3), dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), nitrobenzene (NB), dichloromethane/1,2-dichloroethane (DCM/1,2-DCE) and dichloromethane/nitrobenzene (DCM-NB).

The $(\text{CF}_3\text{C}(\text{O})\text{NH})(\text{C}_6\text{H}_{11}\text{NH})\text{P}(\text{O})[\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}]\text{P}(\text{O})(\text{NHC}_6\text{H}_{11})(\text{NHC}(\text{O})\text{CF}_3)$ ligand was synthesized as the following procedure: to a solution of $(\text{CF}_3\text{CONH})\text{P}(\text{O})(\text{NHC}_6\text{H}_{11})(\text{Cl})$ (1.708 mmol) in dry chloroform, a solution of 2,2-dimethyl 1,3-propanediamine (0.854 mmol) and Et_3N (1.708 mmol) in dry chloroform was added at 273 K. After 5 h stirring, the solvent was removed and the product was washed with distilled water. In transport of metal cations, the source phase contained equimolar concentrations of the metal cations and buffer solution ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) at pH = 4.9 and the receiving phase



being buffered at pH = 3 by buffersolution (HCOOH/HCOONa). The organic phase consisted of the ligand as an ionophore. The obtained results show that the selectivity and efficiency of transport for these metal cations change with the nature of ligand. The highest transportation was observed for Cu^{2+} cation. The transport rate for copper (II) cation was changed as the sequence of $1,2\text{-DCE} > \text{CHCl}_3 > \text{DCM} > \text{NB}$. A non-linear relationship was observed for the variations of transport rate of Cu^{2+} cations with the composition of DCM/1,2-DCE and DCM/NB binary mixture for ligand 5,6,11,12-tetraphenyl-1,2,4,7,8,10-hexa azocyclododeca-4,6,10,12-tetra-N-9,4-dione. The influence of the nature of carboxylic acids (stearic, fumaric and maleic acids) as surfactant was also investigated in the membrane phase on the transport of metal cations [1].

Keywords: Transport, Extraction, liquid membrane, Metal cations

References

[1] G.H.Rounaghi, M.H. Arbab-Zavar and E.Fahmideeh-Rad, Asian journal of Chemistry, 21(2009) 1389-1399.

Determination of chlorpyrifos residues in pistachio oil using ion mobility spectrometry

Ali Sheibani*, Nasser Ghotbadini Bahraman, Amin Ashoori

Department of chemistry, Islamic Azad University, Yazd Branch, Yazd, Iran.

E-mail: alisheibani@ymail.com

Ion mobility spectrometry (IMS) is an analytical method with a low detection limit, fast response for determination of organic compounds [1, 2]. In this research, IMS was used for determination of chlorpyrifos in pistachio oil. An ion mobility spectrometer equipped with continuous corona discharge ionization source was used in this study. A drift tube installed in an oven, a needle for producing the corona, two high-voltage power supplies, a pulse generator, an analog to digital converter, and a computer to record spectra comprised the main components of the instrument. Under optimum conditions (Injection and cell temperature, carrier and drift gas, drift and corona voltage and pulse width), positive ion mobility spectrum of chlorpyrifos in air ambient pressure using IMS was obtained. The calibration curve was linear over two orders for determination of chlorpyrifos. Precision as relative standard deviation was lower than 10%. The ground pistachio kernels passed through a sieve with mesh size of 16 and dried at 70 °C to a constant weight. Then, pistachio oil was extracted with n-hexane using Soxhlet procedure. A QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method based on liquid-liquid partitioning followed by a clean-up step with dispersive solid phase extraction, was used for the extraction of analyte in pistachio oil [3]. The results were compared with other methods that demonstrate the capability of the proposed method in determination of chlorpyrifos in pistachio oil as a real sample.

References

[1] Eiceman G.A. Trends in Anal. Chem. 21 (2002) 259-275.

[2] Eiceman G.A Karapas Z. *Ion mobility spectrometry*. CRC Press, Boca Raton, FL (2005).

[3] Juan F. Garca-Reyes, Carmen Ferrer, M. Jose' Go'mez-Ramos, Antonio Molina-Di'az, Amadeo R. Fernandez-Alba. Trends in Anal. Chem. 26 (2007) 239-251.

Application of crown ether 18C6 as selective masking agent for improvement of transport-separation of Th(IV) and lanthanide(III) ions by DEHPA as carrier

H. Ahmadi*, A. A. Zamani, M. R. Yaftian^a

^aPhase Equilibria Research Laboratory, Department of Chemistry, Faculty of Science, Zanjan University, P.O. Box 45371-38791 Zanjan. yaftian@znu.ac.ir

One of the important processes in the management and storage of nuclear wastes is the intra- and inter-group separation of lanthanides and actinides [1]. To fulfill this need, several separation strategies have been studied and developed. Among them, liquid pertraction techniques are frequently investigated and used [2].

As a part of our research interests and following our studies on the separation of lanthanides and actinides [3], in the present communication we report on the application of a water soluble crown ether, named 18-crown-6 (18C6), as a masking agent in the feed phase of a bulk liquid membrane system. The membrane was formed by dissolving bis(2-ethylhexyl)phosphoric acid (DEHPA) in cyclohexane (or carbon tetrachloride). Parameters affecting the efficiency of the method for the transport of lanthanum ions such as feed phase pH values, 18C6 concentration in the feed phase, DEHPA concentration in the membrane, temperature, time dependency of the process, organic diluents of membrane, and stripping phase composition. Although a selective extraction was found towards thorium ions both in the presence and absence of 18C6 in the feed aqueous phase, the presence of this crown ether diminishes the extraction percentages of La(III) and Eu(III) ions into the membrane. This results an improvement in the selectivity during the extraction step of the transport process. The masking effect was more pronounced for lanthanum ions than that for europium ions. It is noteworthy that, a selective stripping augments the separation characteristics. In fact, no stripping values of thorium ions were found in the second interface. However, the stripping of La(III) and Eu(III) ions when 18C6 was used, significantly improved with respect to that in the absence of this crown ether in the feed phase.

The present study shows that the combination of chelating properties of acidic carriers and ion size selective masking effect of crown ethers, having opposite complexation tendencies, improves the separation of lanthanides. The crown ether 18C6 is more efficacious masking agent for lanthanum ions in comparison with europium ions while it has no interaction with thorium ions. By increasing the ionic radius in the series of rare earths, the transport of the ions moved to higher pH region. Consequently, the separation among the metal ions was markedly improved.

References

[1] K. L. Nash, Solvent Extr. Ion Exch., 11 (1993) 729-768.

[2] M. R. Yaftian, A. A. Zamani, S. Rostammia, Sep. Purif. Technol. 49 (2006) 71.

[3] see for example: (a) M. R. Yaftian, M. R. Razipour, D. Matt, Radioanal. Nucl. Chem. 270 (2006) 357-361; (b) N. Sehati, Z. Shiri-Yekta, A. A. Zamani, M. R. Yaftian, N. Noshiranzadeh, Sep. Sci. Technol. 47 (2012) 670-676; (c) Z. Shiri-Yekta, M. R. Yaftian, A. Nilchi, J. Iran. Chem. Soc. (in press DOI 10.1007/s 13738-012-0144-x).

Use of ionic liquid in sol-gel technique for preparation of novel solid-phase microextraction fiber for determination of Benzene, Toluene, Ethylbenzene and O-Xylene (BTEX) coupled to gas chromatography-flame ionization detector in water samples

Ali Sarafraz-Yazdi^{a,*}, Hossein Vatani^a

^a Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Iran

For the first time, novel SPME sorbents based ionic liquid mediated PDMS coating was fabricated via sol-gel technique. Ionic liquid is used to investigate the role of ionic liquid as a co-solvent on the extraction efficiency of SPME fibers. For this purpose, Three different coating fiber were prepared include: coating prepared from poly(dimethylsiloxane) (PDMS fiber), coating prepared from poly(dimethylsiloxane) in the presence of ionic liquid as co-solvent and conditioned at a higher temperature than decomposition temperature of ionic liquid (PDMS-IL-HT fiber) and coating prepared from poly(dimethylsiloxane)