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Short communication

Determination of trace metal ions by ion-pair chromatography after enrichment using supported liquid membrane

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Abstract

A method for simultaneous trace determination of the metal ions Zn, Ni and Co at μg/l levels in river water using ion-pair chromatography (IPC) after supported liquid membrane (SLM) extraction is presented. The detection limits in reagent water for Zn, Ni, Co, Cd and Mn after 120 min enrichment time were 0.15, 0.15, 0.06, 0.3 and 0.12 μg/l, respectively ($n=5$).

Keywords: Trace analysis; Supported liquid membrane; Metal ions

1. Introduction

To determine trace elements in complex matrices, a separation of analytes from interferents in the matrix and a selective pre-concentration is frequently necessary.

Liquid–liquid extraction [1] or solid-phase extraction (SPE) using immobilised ligands or chelating resins [2] are frequently used for such purposes. The latter is gradually replacing the former due to its ease of automation via incorporation into flow systems and higher sample throughput. One of the main drawbacks of SPE columns is their inability to handle samples with high concentrations of particulate or organic matter without clogging and the risk of breakthrough in the presence of interferents at high concentration in the sample.

Supported liquid membrane (SLM) technology is an attractive alternative to these two ''traditional'' sample pre-treatment methods for metal ions due to its potential of selective enrichment of such ions from complex matrices. Although the method is now considered an important emerging technology for the removal of metals from feed solutions [3], its analytical application is relatively new. However application of SLM to analytical trace metal determination has been limited [4–6]. Recently, we reported the use of di-2-ethylhexyl phosphoric acid (DEHPA) extractant in an SLM-based procedure for the determination of some heavy metal ions in river water [7] and lead in urine [8]. In these cases, atomic absorption spectrometry (AAS) or inductively coupled plasma-mass spectrometry (ICP-MS) were used for the final determination.

In this paper we present a fast and inexpensive method for trace metal analysis in complex matrices using ion-pair chromatography (IPC) after SLM sample clean-up and pre-concentration.

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2. Experimental

2.1. Equipment

2.1.1. SLM equipment

The SLM device used was similar to the one previously presented from this laboratory [5]. Changes in pH in the acceptor channel were measured on-line using a custom-built wall-jet cell equipped with a pH electrode (Ingold, Switzerland) connected to a pH meter (Hanna Instruments, Singapore) [7].

2.1.2. Liquid chromatography (LC) separation and detection system

The LC equipment consisted of a high-pressure pump (HPLC pump 420 Kontron Instruments, Milan, Italy), a six-port injector valve (Valco, Houston, TX, USA) an analytical column (Techsphere, 250 mm× 4.6 mm I.D., particle size 5 μm, HPLC Technology, Cheshire, UK) and a variable-wavelength detector (HPLC detector 432, Kontron Instruments). Chromatograms were evaluated using a chromatographic data processor (Kontron DS-450-MT1) equipped with a plotter (plotter 800 Kontron Instruments). The eluted metal ions were detected with a post-column derivatization system. This consisted of a T-connector, which allowed the addition of a post-column reagent (PCR) to the column eluate.

A pressurised reagent vessel was used to deliver the PCR at a flow-rate of 0.7 ml/min.

2.1.3. AAS analysis

A Varian AA-1475 fitted with a Varian GTA-95 graphite tube atomizer was used for AAS measurements. Twenty μl samples were delivered to the furnace using a programmable auto-sampler. The furnace programme parameters were mostly those recommended in the application manual from the manufacturer. Pyrolytic graphite tubes were used exclusively.

2.2. Chemicals

All solutions were prepared either from suprapur or analytical-reagent grade chemicals and high-purity water was obtained from a Milli-Q RO4 unit (Millipore, Bedford, MA, USA). All glassware was cleaned with 2 *M* nitric acid for several days and finally rinsed with high purity reagent water just before use. The PCR was 0.2 m*M* 4-(2-pyridylazo)-resorcinol monosodium salt (monohydrate), (PAR) in 3 *M* ammonia and 1 *M* acetic acid filtered through a 0.22-μm filter.

2.3. Procedure

The configuration of the SLM set-up was similar to the one previously used [7] with minor modifications allowing elution of the enriched sample from the acceptor with a buffer instead of nitric acid. In a typical analysis, the acceptor side of the membrane, is first flushed with the acceptor solution (0.1 *M* HNO_3). The sample solution is then pumped through the donor side of the SLM unit at a flow-rate of 1 ml/min. After the enrichment, the enriched sample is eluted with buffer into a 2-ml vial in a fraction collector. The acceptor side is then rinsed with 0.1 *M* HNO_3 solution for 10 min and another enrichment cycle commences.

Normally, a volume of about 2 ml of eluent is used to pump out 1 ml of stagnant acceptor solution into the vial to ensure an almost complete transfer of the enriched sample into the vial. In the case where nitric acid is used as the acceptor solution, the enriched sample is eluted with a buffer resulting in an on-line pH adjustment procedure before sample injection into a C_{18} column.

3. Results and discussion

3.1. Optimisation of the SLM enrichment procedure

3.1.1. Choice of membrane liquid

Kerosene was found to be a good diluent for the extractant, di-2-ethylhexyl phosphoric acid (DEHPA) when using graphite-furnace atomic absorption spectrometry (GFAAS) for final analysis of the metal ions after SLM extraction [7]. However, during the course of the enrichment it was observed that the eluted sample was cloudy due to traces of kerosene leaking out of the SLM into the aqueous acceptor and hence being eluted with the sample. This caused severe peak broadening in the LC system especially

for the first few replicates. This problem was solved by dissolving the DEHPA in di-hexyl ether which we have successfully used previously as a diluent for Aliquat in SLM extraction of trace metals. Fig. 1 shows chromatograms after enrichment with an SLM containing 40% DEHPA in kerosene or dihexyl ether, respectively.

3.1.2. Acceptor solution

When using a weak organic acid such as DEHPA as an extractant in the membrane, the driving force for the extraction of the metal ions is the proton gradient between the donor and the acceptor side. With a strongly acidic acceptor solution, a pH adjustment is necessary before injecting the sample into a reversed-phase C_{18} column. This can be done off-line after sample elution from the SLM or on-line by pushing out the enriched sample from the acceptor side with a different solution from the one used for enrichment.

3.1.3. Eluent modification

The conditions normally used for eluting the metals from the SLM acceptor (0.1 *M* HNO_3), prior to final analysis using AAS or ICP-MS are not suitable for direct loading on a C_{18} analytical column. Therefore the acid sample must be neutralised before the chromatographic separation. This can be done off-line after sample elution using a base e.g., NaOH or buffer. This is however tedious and time consuming. The enriched sample (1 ml in 0.1 *M* nitric acid) was therefore pushed out with 1 ml of a 0.2 *M* solution of tartaric acid at pH 3 giving a solution with a pH of around 2.2 after mixing. This solution is suitable for direct injection into the analytical column. Normally, a volume of about 2 ml of eluent is used to pump out 1 ml of stagnant acceptor solution into the vial. This ensures an almost complete transfer of the enriched analyte species without excessive dilution of the sample.

3.2. Quantification

3.2.1. Calibration

Linear calibration lines were obtained for all the metal ions in the range 0–100 μg/l (five standards) The correlation coefficients were 0.999 and the intercepts did not deviate significantly from zero at

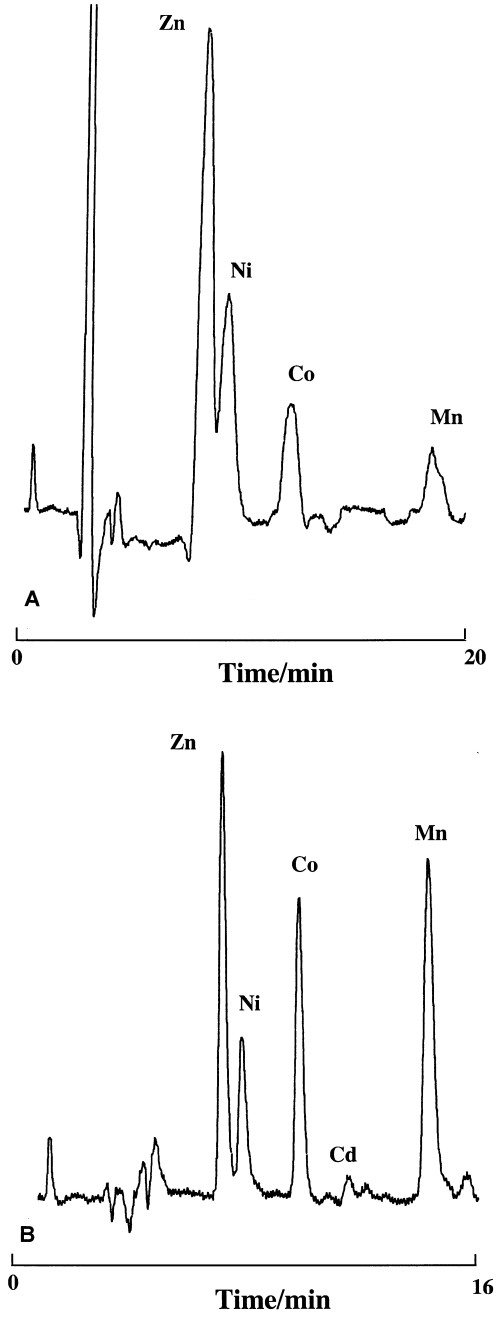

Fig. 1. Effect of the choice of solvent for the carrier DEHPA in the membrane on the separation of the metal ions Zn, Ni, Co, Cd and Mn. SLM with 40% of DEHPA in kerosene (A) or in di-*n*-hexyl ether (B). Mobile phase: 2 m*M* sodium octane sulfonate, 50 m*M* tartaric acid and 5% ACN at pH 3.2. Injection volume: 100 μl. Column: Techsphere 5 ODS 250×4.6 mm operated at a flow-rate of 1.0 ml/min. Detection: UV, 510 nm after post-column reaction with PAR.

the 95% confidence level except for Zn due to the a high value of the blank.

3.2.2. Limit of detection

Table 1 shows the extraction efficiencies and blank values obtained after enriching reagent water adjusted to pH 3.0.

As the risk of an interfering peak occurring on the chromatograms of Zn, Ni and Co is judged to be very small, the detection limits for these metals in real water samples will be about the same as those given in Table 1. Its not possible to determine Cd and Mn in river water at the moment because of the large interference peaks emanating from the enrichment of Ca and Mg (see Fig. 2).

3.3. Validation with GFAAS

Results from measurements of trace metals after SLM enrichment of the same samples using either IPC or GFAAS are shown in Table 2.

The measurements made with SLM–LC and SLM–AAS shown in Table 2 agree well with each other. Only in the case of Mn is there a significant difference between the values at the 95% confidence level. The reason for this difference is unclear. A typical analysis of a single element on the GFAAS with five standards and three replicates takes about 45 min. For five different elements the time sums up to 4 h. Corresponding analysis on the LC system can be performed in ca. 2.5 h. The LC system also offers

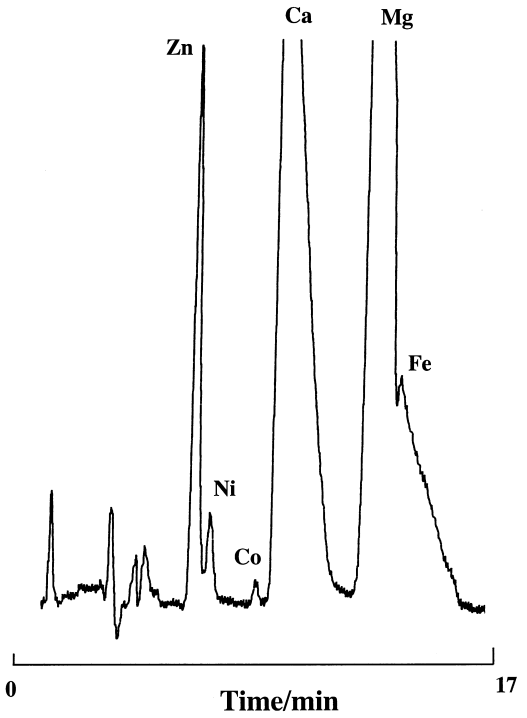

Fig. 2. Chromatogram of river water after a 2-h SLM enrichment. SLM: 40% DEHPA in dihexyl ether. Other conditions as in Fig. 1.

Table 1
Extraction efficiency (E), standard deviation (S.D.) and limit of detection (LOD) for a number of metals enriched by SLM technique

Metal	E (%)	S.D.	LOD (μg/l)
Zn	68	4.5	0.15[a]
Ni	64	4.5	0.15[b]
Co	65	1.5	0.06[b]
Cd	59	3.4	0.3[b]
Mn	69	5.1	0.12[b]

The E values were obtained using a membrane with 40% DEHPA in di-*n*-hexyl ether and metal concentrations of 5 ppb in reagent water at pH 3.0 as sample solution, enrichment time was 40 min. Detection limits obtained after a 2-h enrichment of an acidified reagent solution adjusted to pH 3.0. The acceptor solution was 0.1 M nitric acid. n =4.

[a] Determined as three-times the standard deviation (0.05) of the Zn peak.

[b] Determined from three-times the baseline noise in the regions where the different metals elute.

Table 2
Analytical results obtained by GFAAS or IPC of the trace elements Cd, Co, Mn and Ni in reagent water after 40-min SLM enrichment

Metal	AAS (μg/l)	S.D.	IPC (μg/l)	S.D.
Ni	57.2	3.0	55.7	2.5
Co	66.4	2.0	62.7	3.0
Cd	50.2	4.4	51.0	7.5
Mn	49.6	2.4	42.8	1.0

Donor: 5 μg/l metal solution adjusted to pH 3.0 with supra pur nitric acid, SLM 40% DEHPA in di-*n*-hexyl ether, acceptor 0.1 M nitric acid, eluting solution 0.2 M tartaric acid, pH 3.0, n=3.

lower operational costs and can provide, in a relatively short time a complete screening of the possible ions present in the sample.

3.4. Analysis of river water

3.4.1. Interferences

The extractant DEHPA used in the SLM does not extract alkali metals Na and K which are found in high concentrations in natural waters. However it extracts the alkaline earth metals Ca and Mg and also Fe [7]. Although the extraction efficiency for Ca and Mg is lower than that of the transition metals investigated, their concentration in river water is at the mg/l level or several orders of magnitude higher than the analytes.

Although this does not pose any breakthrough problems in the SLM extraction, it interferes with the LC determination of the two late eluting peaks of Cd and Mn. Cd elutes just before the Ca peak while Mn elutes close to the Mg peak. This is illustrated in Fig. 2, which shows a chromatogram obtained after a 2-h SLM enrichment of river water followed by a final determination using LC.

The broad Ca and Mg peaks mask the Cd and Mn peaks but Zn, Ni and Co can be determined. Attempts made to limit the interference due to occurrence of calcium in the samples by addition of a ligand oxalate, that forms calcium salts of very low solubility were not successful. Addition of oxalate to the sample did markedly decrease the Ca peak. Unfortunately this also resulted into a decrease of the analyte peaks probably due to co-precipitation thus limiting the use of this method for Ca removal.

3.4.2. Determination of Zn, Ni and Co

River water collected for trace metal analysis is normally passed through a 0.45-μm filter to reduce particulate matter and humic acids. In this way clogging is avoided when using packed columns. However, this increases the risks of contamination and possible losses of trace metals due to adsorption on the surface of the filters. A major advantage of using SLM methodology is that river water samples can be processed without any filtration and with very little risk of clogging. The only sample pre-treatment necessary after collection of the samples is acidification to a suitable pH (usually pH 3) to avoid losses due to adsorption on the container surface.

River water samples collected from a brook, about 100 m downstream from the discharge point of a municipal waste water treatment plant were analysed with IPC after a 2-h SLM enrichment. The concentrations of Zn, Ni and Co were 4.63, 0.22 and 0.16 μg/l, respectively with standard deviations of 0.23, 0.015 and 0.012, respectively. Only the free metal ions and those loosely bound to organic ligands or colloids can be broken at the donor–membrane interface and extracted by the DEHPA membrane. All the values are close to what would be expected in unpolluted river water, which shows that the purifying plant works efficiently.

4. Conclusions

We have shown that IPC is a powerful and cost effective method for trace metal determination after SLM pre-treatment which offers detection limits close to those of GFAAS for some metals. The method is particularly useful for handling complex matrices such as waste water and urine, where sample clean-up is necessary before the final analysis.

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