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The use of a polymer inclusion membrane in flow injection analysis for the on-line separation and determination of zinc

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ABSTRACT

This paper reports the first use of a polymer inclusion membrane (PIM) for on-line separation in flow injection analysis (FIA) involving simultaneous extraction and back-extraction. The FIA system containing the PIM separation module was used for the determination of Zn(II) in aqueous samples in the presence of Mg(II), Ca(II), Cd(II), Co(II), Ni(II), Cu(II), and Fe(III). The Fe(III) and Cu(II) interferences were eliminated by off-line precipitation with phosphate and on-line complexation with chloride, respectively. The concentration of Zn(II) was determined spectrophotometrically using 4-(2-pyridylazo) resorcinol (PAR). The optimal composition of the PIM consisted of 40% (m/m) di(2-ethlyhexyl) phosphoric acid (D2EHPA) as carrier, 10% (m/m) dioctyl phthalate (DOP) as plasticizer and 50% (m/m) poly(vinyl chloride) (PVC) as the base polymer. The optimized FIA system was characterized by a linear calibration curve in the range from 1.0 to 30.0 mg L^{-1} Zn(II), a detection limit of 0.05 mg L^{-1} and a relative standard deviation of 3.4% with a sampling rate of 4 h^{-1}. Reproducible results were obtained for 20 replicate injections over a 5 h period which demonstrated a good membrane stability. The FIA system was applied to the determination of Zn(II) in pharmaceuticals and samples from the galvanizing industry and very good agreement with atomic absorption spectrometry was obtained.

1. Introduction

Liquid–liquid extraction is a powerful separation technique which has been frequently used in both industrial processes and chemical analysis [1]. It was introduced in flow injection analysis (FIA) by Karlberg and Thelander in 1978 [2] and since then it has been successfully implemented in both FIA and sequential injection analysis (SIA) for the determination of metallic and non-metallic analytes [3]. However, most of these analytical procedures involve complex operations such as the generation of a segmented flow pattern consisting of alternating aqueous and organic liquid segments with detection taking place either with or without phase separation. An alternative approach avoiding flow segmentation is based on the use of porous hydrophobic membranes separating the immiscible organic and aqueous phases [4]. The organic phase occupies the pores of the membrane and the actual extraction process takes place at the membrane/aqueous phase interface. This technique is often referred to as microporous membrane liquid–liquid extraction (MMLLE) [4]. In many cases it is advantageous to back-extract the analyte into an aqueous phase prior to its detection. To reduce the separation time, the extraction and back-extraction steps can be conducted simultaneously if a supported liquid membrane (SLM) is used. This membrane separates the two aqueous phases (i.e. donor and acceptor phase). An SLM can be constructed by impregnating the pores of a porous hydrophobic membrane (e.g. polytetrafluroethylene, polyvinylidene fluoride, and polypropylene) with an organic solution of a suitable extractant (e.g. Aliquat 336, Cyanex 272, di(2-ethylhexyl)phosphoric acid (D2EHPA)). The solid membrane acts as a support for the liquid phase retained in its pores by capillary forces. SLMs were introduced in FIA in 1986 by Audunsson [5] and they have played a key role in a number of flow analysis methods developed since then [6].

The main disadvantage of SLMs is the slow leaching of the membrane liquid phase into the donor and acceptor aqueous phases, thus reducing their lifetime [7].

Recent work on polymer inclusion membranes (PIMs) promises to provide more stable membranes for extraction and transport. Similarly to SLMs, PIMs incorporate an extractant, often called the carrier, in the membrane polymeric structure. In some cases the incorporation of plasticizers (e.g. 2-nitrophenyl octyl ether (2-NPOE); dioctylphthalate) is required to achieve homogeneity and sufficient flexibility of the membrane [7].

The structures of PIMs are currently being elucidated. Surface analysis results have suggested the presence of networks of nano-sized channels filled with the liquid extractant and diluent. The small size of these channels explains the facts that PIMs appear homogeneous at the macro level, and that the rate of loss of the liquid membrane phase is small compared to that in the case of

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SLMs [7]. The latter fact is responsible for the longer lifetime of PIMs which makes them an attractive alternative to SLMs. In addition, PIMs eliminate the need for the use of diluents, required in both liquid–liquid or SLM based extraction, while retaining the high selectivity associated with these two separation techniques.

Research on PIMs [7–13] has demonstrated that this type of extracting membranes offers considerable promise in the industrial and analytical separation of metallic species.

In this paper, we report to the best of our knowledge the first use of a PIM in a FIA system for the on-line extractive separation of the analyte. In order to provide proof of concept, we have chosen a poly(vinyl chloride) (PVC) based PIM with immobilized D2EHPA as extractant, which has been used for the solid phase extraction of Zn(II) [13]. D2EHPA is a common extraction reagent [1] and the PIM obtained using this extractant mimics the corresponding liquid–liquid extraction systems and shows high selectivity for Zn(II) in the presence of a number of frequently encountered metal ions (e.g. Cd(II), Co(II), Cu(II), Ni(II), and Fe(II)).

2. Experimental

2.1. Solution preparation

The commercial extractant D2EHPA and the plasticizer dioctyl phthalate (DOP) (both from Sigma–Aldrich) were used as received. High molecular weight PVC (Selectophore, Fluka, Switzerland) was used to prepare membranes. Tetrahydrofuran (THF) (Chem-Supply, Australia) was of analytical reagent grade and used as received.

A 0.20 mM PAR (4-(2-pyridylazo)resorcinol) solution was prepared in borate buffer (pH 9.3) using the monosodium salt hydrate of PAR (Sigma–Aldrich). The borate buffer was prepared by mixing 90 mL of a 0.05 M $Na_2B_4O_7$ (Chem-Supply, Australia) and 10 mL of 0.5 M H_3BO_3 (Ajax Chemicals, Australia) [14]. The acceptor solution was neutralized and buffered to pH 9.3 with a solution containing 1.0 M NaOH in the borate buffer outlined above.

Zinc(II) solutions (0–40 mg L^{-1}) containing 0.20 M sulfuric acid (Scharlau Chemie, Australia) and 0.20 M NaCl (Unilab, Australia), where necessary, were prepared daily from a stock solution of 1000 mg L^{-1} ($ZnCl_2$, Unilab, Australia). The solution pH was adjusted in the range of 1.5–2.6 with 3.0 M NaOH (Unilab, Australia). The same procedure was used for the preparation of standard Zn(II), Co(II), Cu(II), Cd(II), Ca(II), Mg(II), Ni(II), and Fe(III) solutions which were used in the interference studies. The corresponding analytical grade chloride salts ($ZnCl_2$, $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $CdCl_2{\cdot}1.5H_2O$, $CaCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, and $FeCl_3{\cdot}6H_2O$) were purchased from Unilab (Australia). Fe(III) was precipitated off-line by the addition of 0.5 M orthophosphate ($Na_2HPO_4{\cdot}2H_2O$, BDH, Australia).

The acceptor solution containing HCl was prepared by appropriate dilutions of the corresponding concentrated acid (Scharlau Chemie, Australia).

Deionised water (18 MΩ cm, Millipore, Synergy 185, France) was used in the solution preparation.

2.2. Instruments

Absorption spectra were recorded using a single-beam spectrophotometer (Model Libra S12, Biochrom, UK) with 10 mm fused-silica cells and a spectral bandwidth of 1.0 nm. The pH measurements were conducted with a combined pH/conductivity meter (Model SmartChem-Lab, TPS, Australia). The PIM thickness was measured along a cut edge using an optical microscope (Model LH50A, Olympus, Japan) with a calibrated lens (Carton Optical Ind., Japan).

Atomic absorption spectrometry was carried out using a polarized Zeeman atomic absorption spectrometer (Model Z-2000, Hitachi, Japan).

2.3. FIA manifold and experimental procedure

The FIA manifold employed in this study (Fig. 1) incorporated a rotary injection valve (Model 5020, Rheodyne, USA) with a 500 μL sample loop, Teflon tubing (0.5 mm i.d., Supelco, USA) and a home made membrane separation cell [15] with identical meander-shaped channels (length: 120 mm; width: 2.0 mm; and depth: 0.5 mm) separated by the PIM. The absorbance measurements were conducted at 491 nm in the flow-through cell (10 mm optical path, Starna, UK) of a UV-visible spectrophotometer (Model Libra S12, Biochrom, UK) connected via a data acquisition card (Advantech HG919, Taiwan) to a PC running a home-written in Microsoft Quick C® data collection program. Two mixing coils of 1 m length each facilitated mixing between the corresponding confluent streams (Fig. 1). Two peristaltic pumps (Minipuls 3, Glison, France) furnished with Tygon tubing (TACS, Australia) were used for propelling the donor, acceptor and reagent streams as shown in Fig. 1.

The analytical procedure involved injection of Zn(II) samples and standards into a 0.20 M H_2SO_4 donor stream (R_1, Fig. 1) adjusted to pH 1.5–2.6 by the addition of 3.0 M NaOH. In some cases the donor stream also contained 0.2 M NaCl. The results reported earlier by Kolev et al. [13] demonstrated that a 1.0 M HCl solution provided efficient back-extraction of Zn(II) from PVC/D2EHPA PIMs and therefore the same solution was used as the acceptor solution in the current study. The acceptor stream was stopped for a predetermined period of time (stop-time) after the sample/standard injection by switching off Pump 2. At the end of the stop-time Pump 2 was switched on and the acceptor stream was merged with a reagent stream (R_3) containing 1.0 M NaOH solution and the neutralized combined stream was merged with a second reagent stream (R_4) containing 0.20 mM PAR in borate buffer (pH 9.3). The absorbance of the resulting stream was continuously monitored at 491 nm corresponding to the absorption maximum of the orange coloured Zn(II)–PAR complex. The absorbance at the peak maximum was used as the analytical signal. After recording a FIA peak, the donor and acceptor solutions were allowed to flow continuously through the membrane separation cell for a predetermined period of time prior to the injection of the next sample or standard. This membrane reconditioning time was required for the complete removal of the Zn(II) ions remaining in the membrane at the end of the stop-flow period. All measurements were conducted in triplicate.

The flow rates in the FIA manifold channels were varied by the corresponding pump rate selectors while the exact values of these flow rates at each setting were determined by weighing the effluent collected over a 5 min period.

2.4. Membrane preparation and optimization

A wide range of PIMs with different concentrations of the base polymer (PVC), extractant (D2EHPA) and plasticizer (DOP) were prepared (Table 1) by dissolving the membrane components with a total mass of 400 ± 10 mg in 20 mL of THF and then pouring the solution into a 16.5 cm diameter glass ring sitting on a glass plate. The THF was allowed to evaporate slowly over 24 h at room temperature to yield a homogeneous, transparent, flexible and mechanically strong membrane. The membrane was then peeled from the glass ring. A 1 × 8 cm strip was cut out of its central section and fitted in the separation cell. The membrane thickness was controlled within 10% by varying the amount of THF solution used. The average thickness

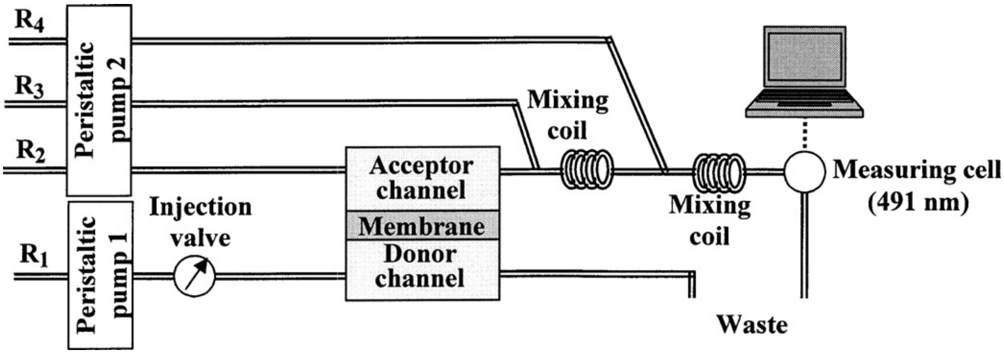

Fig. 1. Schematic of the experimental FIA system (experimental conditions—Table 2).

of the membranes studied was in the range between 40 and 22 μm.

Optimization of the membrane composition for Zn(II) extraction was carried out in triplicate as described previously [13]. The amounts of DOP and D2EHPA in the PIMs were varied from 0% to 25% (m/m) and 35% to 65% (m/m), respectively. Extraction experiments were carried out using 90 ± 4 mg of membrane with a surface area of 1.6×10^{-3} m^2 which was immersed in 100 mL of a solution containing 50 mg L^{-1} of Zn(II) and 0.20 M H_2SO_4, adjusted to pH 2.6 with 3.0 M NaOH solution. The solutions were shaken in a platform orbital shaker (Model OM 6, Ratek, Australia) at 125 rpm. Samples (0.40 mL) were taken at preselected time intervals, diluted with deionised water and analyzed for Zn(II) using AAS.

2.5. Interference studies

Solutions containing equal molar concentrations (5 and 10 mg L^{-1}) of each of the following ions: Zn(II), Cd(II), Co(II), Cu(II), Ca(II), Ni(II), Mg(II), and Fe(III) were prepared in 0.20 M sulfuric acid. The pH was adjusted to 2.6 by the addition of 3.0 M NaOH solution. The interference of Fe(III) was eliminated by off-line precipitation with orthophosphate [13]. These sample and standard solutions were treated with a solution of sodium orthophosphate in the mole ratio of Fe(III):NaH_2PO_4 of 1:3. The interference of Cu(II) was eliminated by addition of 0.20 M Cl^- in the solutions. The negatively charged Cu(II) chloride complexes could not be extracted into the PIM.

2.6. Analysis of real samples

The optimized FIA system was used to determine Zn(II) in two commercial pharmaceutical tablets and four galvanizing preparations. Prior to analysis each tablet was dissolved in a solution containing 0.20 M Cl^- and 0.20 M sulfuric acid adjusted to pH 2.6, as described above. The galvanizing samples were collected from industrial galvanizing plants located in Victoria (Australia) and analyzed after a 10,000-fold dilution with 0.20 M sulfuric acid adjusted to pH 2.6.

3. Results and discussion

3.1. PIM optimisation

PIMs suitable for extraction and transport must be homogeneous, flexible and mechanically strong [16]. In addition, for this FIA application, the PIMs need to be as thin as practically possible without compromising their mechanical strength. This will allow fast transport of Zn(II) from the donor to the acceptor solutions resulting in a reasonable sampling rate. Six of the membrane compositions studied (Table 1) produced flexible, homogenous and mechanically strong PIMs with the remaining membranes being either rigid or oily and thus not suitable for further study. With insufficient plasticization the polymer strands of PVC are closely packed and have high intermolecular forces resulting in rigid membranes. On the other hand, if the membrane is overloaded with plasticizer, an oily layer or droplets of the membrane liquid phase (D2EHPA and DOP) form on the membrane surface making it unsuitable for further use.

The six successful membranes were studied for their ability to extract Zn(II) in order to determine which membrane gave the highest initial flux [13].

$$J_{initial} = \frac{V}{S}\left(\frac{dC}{dt}\right)_{t=0} \approx \frac{V}{S}\left(\frac{C_0 - C_t}{t}\right) \qquad (1)$$

where V is the solution volume (m^3), C is the Zn(II) concentration (mol m^{-3}); t is time (s); S is the membrane surface area exposed to the solution (m^2), subscripts 0 and t refer to the initial concentration and the concentration at time t, respectively.

The corresponding flux values, calculated for $t = 300$ s, are shown in Table 1 and they suggest that the PIM with composition of 40% D2EHPA, 10% DOP (m/m) and 50% PVC (m/m) has the highest permeability to Zn(II). PIMs with this composition were used in the subsequent FIA experiments.

3.2. Optimization of the FIA system

The extraction of Zn(II) into a PIM containing D2EHPA and its transport across this membrane under batch conditions is influenced by four main parameters, (a) the acidity of the donor and

Table 1
Composition and physical description of the PVC-based PIMs developed and the initial flux values for the 6 successful membranes.

Concentration of DOP (%, m/m)	Concentration of D2EHPA (%, m/m) and $J_{initial}$ (mol m^{-2} s^{-1})						
	35	40	45	50	55	60	65
0		Rigid	Rigid	$J_{initial}$ 1.2×10^{-4}	$J_{initial}$ 1.5×10^{-4}	$J_{initial}$ 2.0×10^{-4}	Oily
5	Rigid	$J_{initial}$ 1.8×10^{-4}	$J_{initial}$ 2.2×10^{-4}	Oily	Oily		
10	Oily	$J_{initial}$ 2.4×10^{-4}	Oily	Oily			
15	Oily	Oily	Oily				
20		Oily					

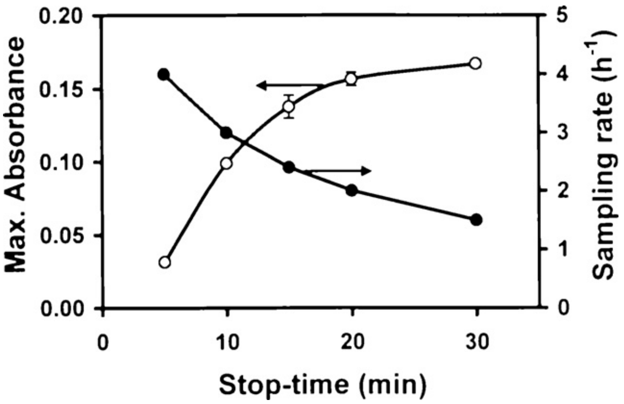

Fig. 2. Effect of acceptor stream stop-time on the sensitivity (●) and sampling rate (○) for the determination of 1.0 mg L^{-1} Zn(II) (experimental conditions—Table 2, membrane thickness—40 ± 4 μm).

acceptor solutions, (b) the initial Zn(II) concentration, (c) the thickness of membrane, and (d) the contact surface area of the membrane [13]. Under FIA conditions the membrane separation process is also dependent on the flow rates of the donor and acceptor streams and the stop-time of the acceptor stream when a stopped-flow approach is used. The variable FIA parameters affecting the on-line separation process which could be controlled in the present study were the flow rates and compositions of the donor and acceptor streams, the stop-time of the acceptor stream and the membrane thickness. The sampling rate was strongly dependent on the time required for the complete stripping of the Zn(II) ions remaining in the membrane when the acceptor stream was restarted at the end of the stop-flow period. This step in the FIA procedure was necessary for the elimination of 'memory effects'. A 10 min contact time between the membrane and the flowing donor and acceptor streams was found to be sufficient for successful membrane reconditioning. This 10 min period was included in calculating the sampling rate of the proposed FIA method.

3.2.1. *Acceptor stream optimization*

It has been demonstrated that efficient transport of Zn(II) across a PVC/D2EHPA PIM can be achieved if the acceptor solution contains 1.0 M HCl [13]. Hence in the proposed FIA method the acceptor stream was 1.0 M HCl solution.

Experiments were carried out at different donor and acceptor stream flow rates. It was found that substantially higher sensitivity could be achieved by stopping the acceptor stream for a predetermined period of time after sample/standard injection to allow the accumulation of a sufficient amount of Zn(II) in the static HCl solution located in the acceptor channel of the membrane separation cell. This is demonstrated in Fig. 2 which shows the effect of the stop-flow time on the analytical signal (maximum absorbance). A stop-flow time of 10 min appeared to provide an acceptable compromise between sensitivity and sampling rate. However, in most cases a stop-flow time of 5 min provided adequate sensitivity while ensuring a higher sampling rate. The flow rates of the acceptor steam (R_2) and the two reagent streams (R_3 and R_4) after restarting Pump 2 (Fig. 1) were maintained equal to 0.85 mL min^{-1}.

3.2.2. *Donor stream optimization*

Batch extraction experiments of Zn(II) into PVC/D2EHPA PIMs have shown that the rate of extraction increases with pH [13]. However, co-extraction of other metal ions sharply increases at higher pH. Therefore, a sulfuric acid donor solution of pH 2.6, adjusted by the drop-wise addition of 3.0 M NaOH solution, was selected as an acceptable compromise between sensitivity and selectivity for the determination of Zn(II). As discussed in the section on interferences, at this pH value the interference of other frequently encountered metal ions (i.e. Mg(II), Ca(II), Cd(II), Co(II), and Ni(II)) was found to be negligible.

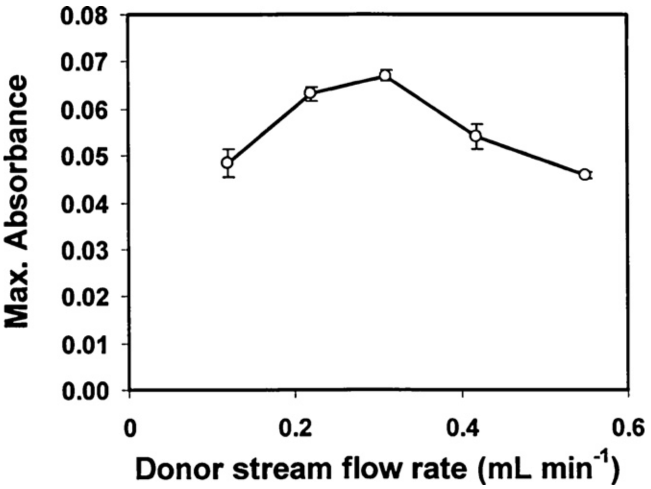

Fig. 3. Effect of the donor stream flow rate on the sensitivity for the determination of 1.0 mg L^{-1} Zn(II) (experimental conditions—Table 2, membrane thickness—40 ± 4 μm).

The amount of Zn(II) extracted from the sample zone into the PIM is strongly dependent on two factors: (1) the contact time between the sample zone and the membrane and (2) the degree of transverse mixing in the donor channel of the membrane separation module. The donor stream flow rate controls these 2 factors in a very different way. Lower flow rates ensure a longer contact time of the sample zone with the membrane while the transverse mixing is less efficient because it relies heavily on molecular diffusion. By increasing the flow rate transverse mixing can be expected to improve due to secondary flow in the meander shaped channel but the contact time between the PIM and the sample zone will decrease. To explore these effects on the analytical signal, the flow rate of the donor stream was varied between 0.10 and 0.55 mL min^{-1} in the case of a 5 min stop-time. Fig. 3 shows that the highest signal was achieved at 0.30 mL min^{-1} which has been chosen as the optimal donor stream flow rate.

3.2.3. *Membrane thickness and stability*

As mentioned above, the membrane thickness is another important factor affecting significantly both the sensitivity and sampling rate. The influence of this system parameter is illustrated in Fig. 4. As expected, a higher sensitivity and sampling rate were obtained

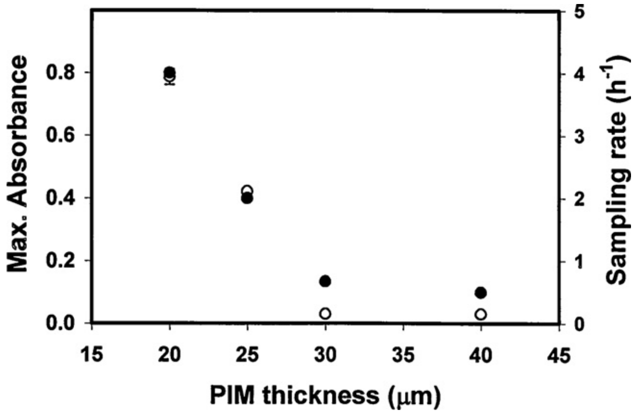

Fig. 4. Effect of PIM thickness on the sensitivity (●) and sampling rate (○) for the determination of 1.0 mg L^{-1} Zn(II) (experimental conditions—Table 2).

Table 2
Optimal conditions for the FIA method.

Parameter	Optimal value
R_1 (donor stream) composition	0.20 M H_2SO_4 and 0.20 M NaCl (pH adjusted to 2.6 with 3.0 M NaOH)
R_2 (acceptor stream) composition	1.0 M HCl
R_3 (reagent stream)	1.0 M NaOH in borate buffer[a]
R_4 (reagent stream)	0.20 mM PAR in borate buffer[a] (pH 9.3)
Flow rate of stream R_1	0.30 mL min^{-1}
Flow rate of streams R_2–R_4	0.85 mL min^{-1}
Sample volume	500 μL
Mixing coil length/diameter	1.0 m/0.5 mm
Stop-time	5.0 min
Membrane reconditioning time	10.0 min
Membrane thickness	22 μm

[a] 45 mM $Na_2B_4O_7$ and 50 mM H_3BO_3.

with thinner membranes which allowed faster transport of the analyte from the donor to the acceptor solution. The thickness of the thinnest membrane with acceptable mechanical strength that could be produced using the casting technique outlined earlier was 22 ± 2 μm. Its long term stability was tested by carrying out 20 repeated measurements of a 10 mg L^{-1} Zn(II) standard. No deterioration in the PIM performance was observed during these measurements and the standard deviation was 4.2%. A comprehensive study of the membrane stability is the subject of a second paper which is in preparation.

3.3. Interference studies

Many samples containing Zn(II) also contain other frequently encountered metal ions such as Mg(II), Ca(II), Cd(II), Co(II), Cu(II), Ni(II), and Fe(III) and so the interference from these was studied. In liquid–liquid extraction, D2EHPA has a high selectivity towards Zn(II) in the presence of all these metal ions except for Fe(III) at pH values less than 1.5 [1]. However, in the present work such low pH values lead to low transport of Zn(II) across the membrane and hence to low sensitivity (e.g. at pH 1.5 the sensitivity for Zn(II) was determined to be 6.7 times lower than that at pH 2.6). At pH 2.6 only Cu(II) and in particular Fe(III) were found to interfere significantly with the determination of Zn(II) which agrees with the known pH isotherms for metal ion extraction using D2EHPA [1]. After off-line precipitation of Fe(III) with orthophosphate and the addition of 0.20 M NaCl to the acceptor solution both interferences were completely eliminated. The analytical signals for solutions containing equal molar concentrations (5 or 10 mg L^{-1}) of each of the following ions: Zn(II), Cd(II), Co(II), Cu(II), Ca(II), Ni(II), Mg(II), and Fe(III) were within 0.3% of the analytical signals for solutions containing the same concentration of Zn(II) and no other metal ions.

3.4. Analytical figures of merit

Under optimal conditions (Table 2) the FIA system was characterized by a linear calibration range between 1 and 30 mg L^{-1} ($A = 0.0176C$, $R^2 = 0.991$, where A is the maximum peak absorbance and C is the Zn(II) concentration in mg L^{-1}). The relative standard deviation of the method based on 5 replicate measurements of 10 mg L^{-1} Zn(II) standard was 3.4%. The limit of detection (determined as three times the standard deviation of the blank) was found to be 0.05 mg L^{-1} and the sampling rate, including the 10 min membrane reconditioning time, was 4 h^{-1}.

3.5. Determination of Zn(II) in pharmaceutical and galvanizing samples

The optimized FIA system was used to determine Zn(II) in two commercial pharmaceutical tablets and four galvanizing preparations. The results are shown in Table 3 and compare well with the values obtained by AAS. The fact that the pharmaceutical samples which contained suspended particulate matter were analyzed without filtering indicates that a major advantage of this FIA method is that "dirty" samples can be determined directly without filtration.

Table 3
FIA and AAS results for Zn(II) in real samples.

Sample	Concentration of Zn(II) ± SD[a] (mg L^{-1})	
	FIA	AAS
Pharmaceutical 1	6.76 ± 0.13	7.45 ± 0.05
Pharmaceutical 2	19.6 ± 0.80	19.0 ± 0.1
Galvanizing sample 1	67.1 ± 0.7	67.8 ± 0.3
Galvanizing sample 2	53.9 ± 1.2	53.7 ± 0.2
Galvanizing sample 3	110 ± 3	115.0 ± 0.3
Galvanizing sample 4	54.7 ± 0.7	56.4 ± 0.4

[a] Standard deviation (SD) calculated on the basis of three replicate measurements.

4. Conclusions

A novel FIA system that uses a PIM for the on-line extractive separation and determination of Zn(II) in the presence of a range of other metal ions has been successfully developed. The system has been applied to the determination of Zn(II) in some pharmaceutical and galvanizing samples. It should be noted that the system can be used with "dirty" samples with minimal sample pre-treatment and so is applicable to a wide range of environmental samples.

The use in the PIM of D2EHPA to mimic the properties of the analogous liquid–liquid extraction system is an important development that can be extended to numerous other commonly used commercially extractants. PIMs have greater long term stability than SLMs and, once the composition has been optimized, do not suffer from appreciable leaching of the reagents from the membrane.

The sample throughput for the FIA system reported in this paper is 4 h^{-1} with a linear calibration curve up to 30.0 mg L^{-1} of Zn(II) and a detection limit of 0.05 mg L^{-1}. These parameters are largely determined by the kinetics of the transport of Zn(II) across the membrane. Due to the entangled nature of the PIM's structure, diffusion coefficients are not high and are set by the membrane composition. One factor that can be manipulated to give faster accumulation of Zn(II) in the acceptor phase is the membrane thickness. The thickness of the thinnest PIM that has been successfully prepared in this work is 22 μm which gives the analytical figures of merit mentioned above. However, we feel it is possible to prepare membranes thinner than 22 μm and work is in progress with this aim. Such membranes will lead to a higher sensitivity and lower detection limit and to a higher sampling rate.

Another commercial extractant we have studied extensively in PIMs is Aliquat 336 for the extraction and transport of Au(III)

[8] and Pd(II) [10] and for the separation of Co(II) and Ni(II) [12] and work is underway in our laboratory to incorporate PIMs containing this extractant in FIA systems utilizing extractive separation.

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