Development of 1-(2-pyridylazo)-2-naphthol-modified polymeric membranes for the effective batch pre-concentration and determination of zinc traces with flame atomic absorption spectrometry

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Abstract

The development of 1-(2-pyridylazo)-2-naphthol (PAN)-modified polymeric membranes for the effective batch pre-concentration and determination of zinc traces with flame atomic absorption spectrometry (FAAS) is described. The method is based on the chemical bonding of the metal species with a suitable ligand, which has been immobilized into a water-insoluble cellulose acetate (CA) membrane followed by simple rinsing of the chelating agent–metal complex with an acidified methanolic solution. The latter is directly aspirated to the nebulizer of a FAA spectrophotometer without any other treatment. As an analytical demonstration, trace concentrations of Zn(II) were successfully detected in real samples, such as seawater, river and lake water, wastewater as well as in a reference material, without any laborious and time-consuming treatment. Several working parameters were investigated. A pre-concentration factor of 100 was achieved by simple immersing of a circular piece of the CA–PAN membrane (0.6 cm diameter) in the tested samples for 30 min at room temperature. The analytical curve was rectilinear up to 30 \( \mu \text{g} \cdot \text{l}^{-1} \) zinc with detection limit of 0.7 \( \mu \text{g} \cdot \text{l}^{-1} \), a quantitation limit of 2.0 \( \mu \text{g} \cdot \text{l}^{-1} \) and a relative standard deviation lower than 2%. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Trace metal ion determinations are receiving at present particular attention due to their strong environmental impact. The direct determination of metal traces in various samples usually requires an efficient pre-concentration step in order to
bring the concentration of the analyte within the dynamic measuring range of the detector and additionally to eliminate matrix effects, interferences, which cannot be manipulated by the measuring device. Conventional separation and pre-concentration techniques such as co-precipitation, distillation, liquid–liquid extraction, ion exchange, absorbative columns etc. have been employed for the single- or multi-element extraction of almost every metal from their initial matrices [1–4].

For many years, solvent extraction has been the most widely applied method and numerous publications have been presented for the determination and speciation of various elements and in a wide variety of samples-matrices [5–7]. The most typical problem of the solvent extraction has been the large amount of sample and organic solvent volume required. A significant advancement in this filed represents the work of Delves et al. [8]. They extracted and determined eleven elements sequentially by means of selective extraction from 1 ml of sample.

Requirement for simpler and safer methods for the determination of metallic elements has triggered the development of alternative methods, which would marginalize the use of hazardous and volume consuming organic solvents. Techniques like co-precipitation, ion exchange [1–4] and more recently, cloud point extraction [9–11] have been successfully employed for a wide variety of metallic species. One problem related to most of these techniques is their lack of automation, which increases the experimental effort and the total time of analysis. Cloud point extraction, although generally simple to apply, it is still prone to the analyst’s efficiency [11].

In order to ensure the efficiency of the analysis, especially when high sample throughput is required for routine applications, on-line separation and pre-concentration techniques have been presented [12–14]. These techniques circumvent most of the problems mentioned above in the conventional batchwise procedures and make possible the determination of a wide variety of elements (and their species) by fully automated manifolds [13–16], however they suffer from poor reproducibility.

Alternatively, simple, rapid and precise batch pre-concentration methodologies, which overcome the above described problems are receiving particular attention and much research is currently ongoing [17,18]. Recently, solvent–soluble membrane filters have been proposed for pre-concentration of trace metal ions after pre-complexation with suitable ligands able to pair with species being oppositely charged and to be retained by the filters through electrostatic forces [17]. Cellulose-graft polymers, which can absorb ions from aqueous and non-aqueous solutions through coordinate chelation of the metallic ions with carbonyl oxygen and through ionic bonds with acidic groups in the polymer backbone, have also been described [18].

In the present study, a novel method is presented, for the extraction and pre-concentration of zinc from water samples. The method is based on the direct complexation of zinc with PAN, which has been immobilized into a cellulose acetate membrane. The reaction between zinc and PAN is well-established [19] and has been widely used for the determination of zinc in real samples [9]. Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility of obtaining the maximum extraction efficiency with minor sample treatment and minimum experimental conditions. Under these conditions a pre-concentration factor of 100 was achieved. The extracts obtained by the proposed methodology are directly subjected to analysis by FAAS yielding detection limits, which match those obtained by GF-AAS.

2. Experimental section

2.1. Materials

All reagents used were of analytical grade. Working solutions of the metallic species were prepared by appropriate dilution of the corresponding standard solutions 1000 mg l−1 (BDH, UK) with double distilled water. Cellulose acetate (approximately 40% acetyl) and polyvinyl acetate (PVA, MW 167 000 Da) were purchased from
Sigma (St. Louis, MO, USA) and Aldrich (Golling, Germany), respectively. Polyvinylchloride (PVC, high molecular weight) and dioctylphthalate (DOP) were also purchased from Aldrich. All other materials were of analytical grade from Sigma.

2.2. Casting of the CA–PAN membranes

CA–PAN membranes were prepared in our laboratory according to a previously described protocol [20] by dissolving 3.996 g cellulose acetate and 4 mg PVA in a mixture of 60 ml acetone and 40 ml cyclohexanone. Ten milliliters of the polymeric solution were then mixed with an equal volume of a 2–16 mM PAN solution in acetone. The mixture was well homogenized in a Vortex. The final concentrations were ranging from 1 to 8 mM PAN in a 2% cellulose acetate solution. CA–PAN films were cast after the evaporation of 12 ml of the mixture in a Petri-dish (110 mm diameter). The thickness of the membranes is about 20 μm [20]. The film (110 mm diameter) was peeled out by immersing the mould in a distilled water bath, and appropriate circular pieces of 6 mm diameter were cut with the aid of a puncher. Prior to use the membranes were left in a distilled water bath and, under the specified conditions, the membranes were stable for more than 6 months.

2.3. Apparatus

A GBC 2000 atomic absorption spectrometer with hollow cathode lamps operating at 5 mA was used throughout the measurements, which were made at 213.9 nm. An adjustable-capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomization. Operation in a double beam-background correction mode was imperative due to the complexity of the aspirated sample, which apart from the target metal contains cellulosic residues and excessive chelating agent, causing a suppression of the signal. For that reason optimization of the flame conditions was performed by a standard solution of zinc of approximately the same composition. The output signals were processed with a time constant of 1.0 s in the peak height mode.

2.4. Procedure

Typically, an aliquot of 50 ml of a solution (sample) containing zinc was adjusted to pH 3 by proper additions of diluted HCl (or NaOH). A round piece of CA–PAN membrane was added to the sample, which then was placed in a water bath shaker and thoroughly turbulated for approximately 30 min at ambient temperature. The membrane was removed and any remaining water on its surface was removed with the aid of a lens cleaning tissue (Whatman No.105). The metal–PAN complex was washed from the membrane surface by the addition of a methanolic solution in 1 mol l⁻¹ HNO₃. The mixture was left for about 5 min to ensure complete decoloration of the membrane and was directly aspirated into the flame of the AAS.

2.5. Application to real samples

Samples of wastewater, river water, seawater and lake water were collected from the Epirus region (Local Wastewater Treatment Plant, Louros River, Preveza Harbour and Pamvotis Lake). They were stored in glassware bottles and acidified for preservation. Recovery experiments were also conducted by spiking the samples with appropriate amounts of zinc in order to simulate real-life conditions. The certified water reference material IMEP-9 (acidified river water) obtained from the Institute for Reference Materials and Measurements (IRMM, Belgium) was analyzed without any further dilution to assess the accuracy of the method.

3. Results and discussion

Parameters affecting the proposed pre-concentration procedure were included in a univariate optimization experimental design procedure and the results are presented below. Absorbance val-
ues are expressed as relative percentages to that of a reference solution of 2 mg l\(^{-1}\) zinc in the same matrix in order to assess the efficiency of the method by employing the least required sample treatment. The reference solution was prepared by dissolving a membrane to 500 µl of a methanolic/HNO\(_3\) metal solution. Blank samples employed throughout all measurements were prepared by dissolving a membrane into the same volume of the methanolic–nitric acid solution. The construction of the calibration curve was made by using standard solutions of zinc ranging from 2 to 30 µg l\(^{-1}\). These solutions were then pre-concentrated according to the proposed procedure and the formed PAN–metal complex(es) was extracted with 500 µl of a methanol–1 mol l\(^{-1}\) HNO\(_3\) mixture.

3.1. Effect of experimental conditions

All optimization experiments were carried out in samples containing 20 µg l\(^{-1}\) Zn(II). The effect of the concentration of the immobilized chelating agent on the analytical response was the first parameter evaluated for the determination of zinc and the results are depicted in Fig. 1. As can be seen, the maximum enrichment factor could be attained with CA–PAN membranes bearing 6 mM PAN. At higher loadings lower efficiencies were observed. This behaviour was basically attributed to the heterogeneity of the surface of the resulted membranes. At loadings higher than 6 mM, leakage of the immobilized compounds to the sample solution was taking place, thus indicating the maximum membrane capacity for entrapping the specific compound (PAN). As a result of the vigorous turbulence, applied for uniform exposure of the membrane to the solution, this physically sorbed portion (not immobilized) was washed off (desorbed) from the membrane surface and was released into the metal containing solution. A part of the metal was then complexed with PAN, lowering the extraction efficiency and decreasing the reproducibility of the method.

The metal complexation on the modified membrane is graphically illustrated in Fig. 2. Probably, PAN is incorporated into the membrane by its phenolic rings leaving the hydrophilic moieties (oxygen and azo-nitrogens) available for metal complexation through the formation of one or even two coordination spheres leading to the respective stable five-member rings [21]. Once the metal has been complexed with PAN, the complex is retained in the surface due to its hydrophobicity and cannot be released into the solution unless an organic solvent is applied, where both PAN and the PAN-metal complex become soluble. For that purpose, water insoluble chelating agents, that provide also water–insoluble metal complexes, are applicable. It is important to note that the applied membrane should be strictly insoluble in water as well as in the extraction mixture, in contrast with the metal chelate that should be thoroughly soluble in the latter. In any other case, the membrane will be readily dissolved in the aqueous phase during its application, while dissolution of its material in the final eluent mixture would interfere during the determination with FAAS, as will be discussed below.
The effect of the working pH was also investigated. The results illustrated in Fig. 3 show that zinc was favourably extracted in a wide pH range of 2–8. Lower values were found to impair the quality of the analytical data due to the destruction of the membrane as well as of the zinc–PAN chelate. The same results were observed at alkaline media (pH > 9.5) due to hydrolysis of the membrane surface [20]. In both cases, evidence for the failure of the procedure was the leaking of PAN into the working solution, which resulted in the coloration of the sample.

The time required for the complete complexation of zinc was subsequently assessed. Fig. 4 highlights the effect of incubation (exposure) time on the analytical signal. It was proved that an incubation time of 30 min is sufficient for the completion of the complexion reaction. Longer time periods do not improve the pre-concentration efficiency while shorter incubation time result to partial complexation of Zn(II). These results are of significant importance, as they clearly demonstrate the simplicity of the method.

Another important feature of the proposed method is the quantitative extraction of the metal chelate by simple rinsing with an acidified methanol mixture (500 μl from a solution containing 3 ml concentrated nitric acid in 50 ml methanol), which would dissolve and decompose the complex. The remaining aqueous phase on the surface of the membrane was found to impair the efficiency of the extraction. It was proved that results within the experimental error are feasible by removing the remaining water with a Whatman paper, or even air-drying, in order to ensure complete rinsing of the PAN–metal complex from the membranes surface. The presence of water was found to inhibit the reproducible and complete rinsing of the PAN–metal complex resulting in significant decrease of the measuring signal.

Furthermore, complete dissolution of the membrane is not desired, as it interfered with the measurements possibly due to the high molecular weight of the membrane material. It was considered that the flame temperature was not adequate to ensure complete dissociation of the membrane material resulting in significant interference effects, which could hinder the absorption signal during the atomisation [22]. Heating or prolonged ultrasonication of the final solution, which could accelerate the extraction of the PAN–metal complex, was found to strongly deteriorate the analytical signal due to the extensive dissolution of the membrane. Exposing of the membrane piece to the extraction solvent for approximately 5 min was found to be adequate for the complete decoloration of the membrane causing minimal dissolution of the polymeric material. Nevertheless, double beam operation and background correction was found to be necessary in order to account for the chemical interferences induced by polymeric residues due to the partial dissolution of the membrane material, which could not be totally avoided.
The effect of different membrane material (PVC) on the performance of the system was also investigated. A PVC membrane was prepared for that purpose and was subjected to the same optimization procedure described above. Under the optimum experimental conditions a series of six solutions, each containing 20 \( \mu \text{g l}^{-1} \) of zinc, were pre-concentrated with both membranes (triplicate measurements for each membrane) and the results (relative to that of a standard solution) were compared. The PVC membrane extracted approximately half of the amount of zinc.

It is important to point out that the behavior of any polymeric material is strongly dependent on the way of its fabrication (solvent evaporation, spin-coated, electropolymerization) as well as by a number of parameters regarding its nature and composition (molecular weight, % content, nature and concentration of the plasticizer and solvent(s)). These parameters have a strong influence on the thickness and the porosity of the resulted membranes, which are the most important characteristics of a polymeric film, since they control its capacity to entrap a compound, the diffusion of various species from the solution towards its pinholes etc. However, all the observations reported in this work are referring to the specific membranes and cannot be generalized for other types. This fact opens a huge field of research for the study of the behavior of cellulose acetate and PVC membranes that are cast under different protocols.

### 3.2. Figures of merit

Calibration curves were obtained by pre-concentrating 50 ml of standard solutions with the CA membrane bearing 6 mM of PAN. Table 1 features the analytical characteristics of the method. Under the specified experimental conditions, the calibration curve was rectilinear up to 30 \( \mu \text{g l}^{-1} \). The pre-concentration factors obtained were of about 100. Compared to relevant studies, where pre-concentration is employed [10,15,17] it can be considered as quite satisfactory. The limit of detection was sufficiently low.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase volume ratio</td>
<td>0.01</td>
</tr>
<tr>
<td>Pre-concentration factor</td>
<td>100</td>
</tr>
<tr>
<td>Extraction concentration factor</td>
<td>( \sim 1 )</td>
</tr>
<tr>
<td>LOD (( \mu \text{g l}^{-1} ))</td>
<td>0.7</td>
</tr>
<tr>
<td>RSD (%) ((n = 5, 20 \ \mu \text{g l}^{-1}))</td>
<td>1.8</td>
</tr>
<tr>
<td>Regression equation</td>
<td>( A = 0.042 + 0.021C_{\text{Zn(II)}} )</td>
</tr>
<tr>
<td>Correlation coefficient ((r))</td>
<td>0.997</td>
</tr>
</tbody>
</table>

### 3.3. Interferences

PAN is a non-selective chelating agent and favorably reacts with many metal ions. In an ambience of competitive reactions of the chelating agent with various metallic species, a reduction of the extraction efficiency of the target metal species should be expected. In this respect, interfering studies were conducted to determine whether other trace elements or anions interfere with the determination of zinc during the proposed pre-concentration scheme. Various amounts of the potential interferants were added to a 20 \( \mu \text{g l}^{-1} \) Zn(II) solution, and the signals were compared to that of a solution containing only Zn(II). The metals examined were selected with respect to their alleged reactivity with PAN and the results of these studies are collected in Table 2. Calcium was also included in this study because of its high abundance in real samples. The tolerance limits were taken for a maximum error of 5%. As can be seen, the tested cations, at concentration levels higher than those usually present in real samples, were not found to impair the effectiveness of the proposed method. At higher concentrations a decrease in the signal of zinc was observed owing to the competition of these metals with Zn(II) for the binding sites of the ligand. It was proved that the requirement for additional binding sites could be fulfilled by the addition of a second membrane.

Various anions were also tested for their effect on the pre-concentration of zinc. Phosphates and organic matter in the form of humic acids (5 mg l\(^{-1}\)), citrates, tartarates, sulfide, oxalates, fluoride (8 mg l\(^{-1}\)) and nitrates (20 mg l\(^{-1}\)) were not found to impair the effectiveness of the proposed method.
Table 2
Interference effect of various metals

<table>
<thead>
<tr>
<th>Amount of metal added (µl⁻¹)</th>
<th>Signal for [metal+Zn(II)]/signal for Zn(II) Total Zn(II) = 20 µg l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.01</td>
</tr>
<tr>
<td>100</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 3
Recovery studies of Zn(II) in various real samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured (µg l⁻¹ Zn²⁺)</th>
<th>Spiked (µg l⁻¹ Zn²⁺)</th>
<th>Found (µg l⁻¹ Zn²⁺)</th>
<th>Recoveryb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>8.0</td>
<td>5.0</td>
<td>13.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>17.7</td>
<td>97</td>
</tr>
<tr>
<td>Lake water</td>
<td>10.0</td>
<td>5.0</td>
<td>14.9</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>19.9</td>
<td>99</td>
</tr>
<tr>
<td>Seawater</td>
<td>13.0</td>
<td>5.0</td>
<td>18.1</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>22.8</td>
<td>98</td>
</tr>
<tr>
<td>Wastewater (1:10)</td>
<td>35.0</td>
<td>5.0</td>
<td>39.9</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>45.1</td>
<td>101</td>
</tr>
<tr>
<td>IMEP-9</td>
<td>9.5</td>
<td></td>
<td>9.4</td>
<td>99</td>
</tr>
</tbody>
</table>

The standard deviation of the means ranges from 0.1 to 0.3 µg l⁻¹.

a All samples were analysed in triplicate.
b Estimated according to IUPAC recommendations.

3.4. Analysis of real samples

Samples of wastewater, seawater, lake and river water were analyzed in triplicate to assess their content in Zn(II). The analytical applicability and potential interfering effects were also assessed by recovery experiments, which were carried out by spiking the samples with appropriate amounts of Zn(II). The recoveries were found to lie in the range of 97–102%, indicating that the method permits the determination of zinc in the analyzed samples without matrix effects. The results given in Table 3 indicate that the proposed method can be reliably used for the determination of zinc in various natural samples of different matrixes. Recovery studies were also carried out at a river water reference material (IMEP-9) in order to further demonstrate the accuracy of the proposed method. As shown in Table 3, the recovery was 99%.

4. Conclusions

The proposed methodology offers a pre-concentration factor of 100 under minimum experimental requirements. It produces extracts representing samples at concentrations of the µg l⁻¹, which can be readily analyzed by flame rather than electrothermal atomic absorption. The overall procedure is simple and does not require any tedious and time-consuming steps for sample pre-treatment. As an analytical demonstration, trace concentrations of zinc were successfully determined in various real samples. Further work is underway in our laboratory to transfer this technique to electrothermal atomic absorption spectrometry in order to accomplish ultra low detection limits for the determination or even speciation of several metallic species. The use of chemically modified membranes for the speciation of metal species [Cr(III)--Cr(VI)] [10] is currently ongoing.
Especially when element specific techniques, like AAS are used, this method generates the ability of reliable pre-concentration of the target analyte at the place of sampling. Thus, the need for sample storage and handling, in the awe of analyte loss, contamination and variation in speciation is minimized. The target species can now be gathered on a small piece of plastic and remain stored and transportable for a long period, as solid-state reactions are unlikely to occur.

If selective reagents are considered as immobilized chelating agents the method can be applied in connection with other instrumental analytical techniques e.g. molecular absorption, potentiometry, polarography etc.

Acknowledgements

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References