



Preconcentration and determination of trace metals by flow injection micelle-mediated extraction using flame atomic absorption spectrometry

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ABSTRACT

Micelle-mediated extraction/preconcentration is incorporated on-line into a flow injection system used to determine low levels of Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) present in various samples. The analyte is complexed with HBDAP (N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane). Under optimal conditions, a solution of 30% (m/v) NaCl and a sample solution containing 2.5 mL of 1% (m/v) sodium dodecyl sulfate (SDS), 0.5 mL of 1.8×10^{-3} M HBDAP and 2.5 mL of pH 8.5 borate buffer solution in 25 mL were pumped through the cotton filled mini-column; onto which the surfactant-rich phase containing the complex is collected. A solution of 0.5 M HNO₃ in 50% acetone is used as the eluent. The limits of detection are (ng mL^{-1}) Cd=0.39, Cu=3.2, Co=7.5, Mn=3.0, Ni=3.4, Pb=17.9 and Zn=0.89 if the sample is allowed to flow for 30 s, but improved for extended preconcentration periods. Analysis of liquid and solid reference materials showed good agreement with the certified values. Complex formation constants between HBDAP and these metal ions were also determined potentiometrically.

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1. Introduction

Ionic surfactants get adsorbed from solution on to interfaces and aggregates in solution to form charged micelles through a cooperative association process. The micellar formation takes place above a certain surfactant concentration, the so-called critical micelle concentration (CMC), below which surfactant molecules are present as monomers [1,3]. Such self-assembled systems have been examined for several decades; the most extensively studied surfactant being sodium dodecyl sulfate [4,5]. It is thus not surprising that the effect of different kinds of electrolytes, both with inorganic and organic counter ions, on the critical micelle concentration (CMC), aggregation number (N_{agg}) and micellar transition for surfactants has been examined in detail [2,3]. Inorganic salts decrease CMC, increase N_{agg} and favour sphere-to-rod transitions due to the condensation of counter ions on the charged micelles.

Most of the developed preconcentration methods were based on the cloud point phenomenon where an aqueous solution of some surfactant becomes turbid and separates into two isotropic phases if some condition such as temperature or pressure is changed or if an appropriate substance is added to the solution. Non-ionic micelles have been used extensively for the cloud point extraction of metal ions [6–8]. Some of the cloud point extraction (CPE) procedures have been developed using the mixture of non-ionic and anionic

surfactants [9,10]. However, the use of only charged surfactants such as anionic surfactants is still rare for the preconcentration of metals [11–13]. There are, however, a few determination methods of metal ions based on to use of anionic surfactants [14,15].

The very small size and the dynamic properties of the micelle seem to promise the development of rapid and highly efficient micelle-based methodologies for concentrating analytes in water. In the literature, there are a few flow injection methods using micelle-mediated extraction and most of these methods are based on the cloud point extraction technique that uses non-ionic surfactants. Some of these methods are based on off-line merging of flow injection analyses. After the viscous surfactant-rich phase that contains metal chelates was decanted from aqueous solution, it is dissolved in an appropriate solution and delivered to the FIA stream of instrument [8,16–18]. Flow injection on-line cloud point extraction methods using non-ionic surfactants [19–21] or the mixture of non-ionic and anionic surfactants [9] have also been described in the literature. Furthermore, the on-line applications of CPE were described not only as a preconcentration scheme but also as an efficient way to deliver the sample to the detector device.

In this work, a flow injection on-line micelle-mediated extraction method has been developed to determine heavy metals in various samples using a chelating agent, N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane. Micelle media were produced using inexpensive anionic surfactant sodium dodecyl sulfate in aqueous solution. N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane has been used to preconcentrate metal ions by liquid–liquid extraction [22–26]. The micelle-mediated extrac-

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tion method has some advantages over liquid–liquid extractions. Included in these advantages is the fact that surfactants are used instead of harmful organic solvents. The degree of formation of the metal–ligand complex and the success of extraction systems may be understood by determining the stability constants of the HBDAP metal ion complexes. The stability constants of HBDAP metal ion complexes have been determined using a program developed by Martell and co-worker [27] for potentiometric titration or by manual calculation [28].

2. Experimental

2.1. Reagents and chemicals

A multi-element stock solution containing 200 mg L⁻¹ of Cu, Ni, Co and Mn; 50 mg L⁻¹ of Cd and Zn and 500 mg L⁻¹ Pb were prepared from 10,000 mg L⁻¹ stock standard solutions (BDH, Aristar, Poole, UK). From this solution, other diluted standard solutions were prepared daily. Buffer solutions were prepared using pure boric acid and sodium tetraborate (BDH).

All reagents used were of the highest available purity. Doubly de-ionized water (18.2 MΩ cm) obtained from a Primar water system (Elga, Buckinghamshire, UK) was used throughout. Nitric acid for sample digestion was obtained from BDH. 5-Bromo-2-hydroxybenzaldehyde, 1,2-diaminopropane and ethanol were purchased from Fluka (Gillingham, Dorset, UK). N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane was synthesised according to the procedure given in the literature [22,23]. Ligand (0.2 g) was dissolved in 25 mL methanol and then the solution was diluted to 250 mL using 0.1 M NaOH. Four certified reference materials were used in this study: a high purity standard (QCS-19) (High Purity Standard, Charleston, USA), a river water sample (SLRS-4), hay leaves (IAEA V-10) and poplar leaves (NCS DC73350). Each of the CRMs were analyzed using the proposed method under optimal conditions in replicate ($n = 5$). Perchloric acid solution, prepared by the use of double distilled water, was standardized by titration using primary standard sodium carbonate, potentiometrically. Sodium hydroxide solutions were prepared in a (50:50) ethanol/water mixture containing 0.1 M sodium perchlorate and were standardized against the potassium hydrogen phthalate and solutions by the potentiometric method, and they were kept under nitrogen atmosphere.

2.2. Apparatus

2.2.1. FAAS system

A Varian SpectraAA 50 atomic absorption spectrometer (Oxford, UK) furnished with a hollow cathode lamp, and an air–acetylene flame (9.0/3.0 L min⁻¹) as the atomiser was used as the detector throughout. The wavelengths (nm) selected for the determination of the analytes were as follows: Cd 228.8, Co 240.7, Cu 324.8, Mn 279.5, Ni 232.0, Pb 283.3 and Zn 213.9. The flow rate of the peristaltic pump was adjusted to be between 3.6 and 8.4 mL min⁻¹.

2.2.2. Potentiometric system

Potentiometric apparatus consisted of a water-jacketed glass reaction vessels as described in Ref. [29]. A solution of base (sodium hydroxide) was introduced into the measuring cell using a Titroline 96 automatic titrator; the solution in the measuring cell was stirred magnetically. The titration data were obtained in the form of milli-volts against milli-liters of base added. The temperature was maintained at 25 ± 0.1 °C and titrations were performed under nitrogen. Milli-volt values were recorded directly from the automatic titrator. The calibration of the cell used in the titrations was performed as described in the literature [30].

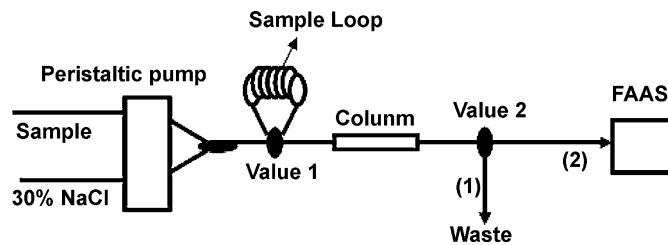


Fig. 1. The diagram of the flow injection micelle-mediated extraction. (1) Sample loading step and (2) elution and analysis step.

2.3. Measurement procedures

2.3.1. Determination of the complex formation constants of HBDAP metal ion complexes

The stability constants for the metal complexes were determined as described in the literature [31,32]. The analytical concentration of metal ion, perchloric acid, HBDAP and sodium perchlorate were 1.5×10^{-3} , 6×10^{-3} , 3×10^{-3} and 0.1 M, respectively. The stability constants were also determined by the use of formation curves ($\bar{n} - p[\text{HBDAP}]$) plotted by the use of potentiometric titration data [31] (\bar{n} = the average number of HBDAP bound to each metal ion).

2.3.2. On-line FI preconcentration and elution procedure

A schematic diagram of the on-line preconcentration system is presented in Fig. 1. The system consists of a Gilson Minipuls 3 peristaltic pump (Anachem Ltd., Luton, UK), a four-way valve and a mini-column (5 cm × 3 mm, Omnifit, Cambridge, UK), packed with cotton wool. The 30% (m/v) NaCl solution and a sample solution that contains 2.5 mL of 1% sodium dodecyl sulfate (SDS), 0.5 mL of 1.8×10^{-3} M ligand and 2.5 mL of a pH 8.5 borate buffer solution in a 25 mL volumetric flask were transported using the peristaltic pump. The tubing carrying these two solutions was connected using a T-piece connector, post-peristaltic pump. The other side of the T-piece was connected to the mini-column via the four-way rotary valve. This valve also had a loop fitted that could be filled with the nitric acid prepared in acetone–water mixture as an eluent. The mini-column was also connected to a second valve so that one orientation of this valve directs the flow to waste whereas the other way enables the flow to be directed to the FAAS instrument. Transport lines were made using the minimum length necessary of 0.3 mm id PTFE tubing.

The FI system was operated as follows: during the 30 s sample loading period, with the valve in the 'fill' position, the micelle solution was produced by mixing the 30% NaCl solution with a sample or blank solution containing 2.5 mL 1% sodium dodecyl sulfate (SDS), 0.5 mL of 1.8×10^{-3} M ligand and 2.5 mL of pH 8.5 borate buffer solution diluted to a volume of 25 mL. Mixing was achieved using the T-piece. Both the NaCl and the sample solutions were pumped at a flow rate of 8.4 mL min⁻¹ through the mini-column containing the cotton wool. The micelles containing the metal complexes were adsorbed on the cotton within the mini-column and the sample matrix was allowed to pass through to waste. After preconcentration, valve 2 was turned to orient the flow towards the FAAS instrument and the 500 μL loop on valve 1 was filled with 0.5 M HNO₃ in a 50% acetone–water mixture. On turning this valve, the eluent was pumped in a stream of water at a rate of 8.4 mL min⁻¹ by the peristaltic pump to the FAAS instrument. After measuring the metal ions, deionised water was passed at a flow rate of 8.4 mL min⁻¹ for 30 s through the mini-column to re-equilibrate it prior to the next sample.

Table 1
The stability constants for metal complexes of HBDAP.

	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta$
Cu(II)	20.7	14.6		35.3
Mn(II)	28.5	14.2	10.7	53.4
Cd(II)	16.2	6.7	5.9	28.8
Pb(II)	18.7	11.1	9.4	39.2
Zn(II)	21.6	11.2	10.4	43.2
Ni(II)	23.7	9.5	7.9	41.1
Co(II)	17.9	10.1	9.6	37.6

3. Results and discussion

3.1. Stability constants for metal complexes of HBDAP

Potentiometric measurements have been used to determine stability constants (K) for the metal complexes of HBDAP. The stability constants of HBDAP with metal ions were determined by the use of formation curves ($\bar{n} - p[\text{HBDAP}]$) plotted by the use of potentiometric data [28,33]. Test solutions containing suitable amounts of metal ions, HBDAP and perchloric acid stock solutions were titrated with sodium hydroxide solution until a precipitate or opalescence was just observed in the titration cell. The degree of formation, \bar{n} values were calculated, in order to find the number of ligands bound to each metal ion; then \bar{n} values were plotted versus $p[L]$ values that were found from potentiometric titration results; however it is known that \bar{n} cannot be deduced unless it reaches a limiting value metal:ligand system. The values of \bar{n} (the average number of HBDAP bound to each metal ion) and $[L]$ (the concentration of the anionic form of free uncomplexed of HBDAP) were calculated based on the potentiometric data. The stability constants, $\log K_1$, $\log K_2$ and $\log K_3$, of metal complexes of HBDAP were determined by the use of $p[L]$ values where $\bar{n} = 0.5, 1.5$ and 2.5 , respectively. The stability constants of the metal complexes of HBDAP were given in Table 1. As can be seen from Table 1, HBDAP produces very strong complexes with Cu, Cd, Co, Mn, Ni, Pb and Zn ions.

3.2. Analytical parameters of on-line micelle-mediated extraction system

Different experimental parameters (such as temperature, pH, ligand concentration, SDS and sodium chloride concentration, sample flow rate and elution flow rate) were investigated to determine the optimum conditions for the on-line micelle-mediated extraction system.

The most important parameter in the complexation reaction between the metal ion and a ligand is to select a pH at which the complexation rate is very high and very rapid. The effect of pH was studied using the flow injection system between pH values of 3 and 11. The concentrations of the analyte solutions were 2 mg L^{-1} for Cu, Co, Ni and Mn; 0.5 mg L^{-1} for Cd and Zn and 5 mg L^{-1} for Pb. These solutions were passed through the flow injection system shown in Fig. 1 at a flow rate of 7.2 mL min^{-1} . The adsorbed micelles on the mini-column were eluted using 0.5 M HNO_3 in a 50% acetone–water mixture at a flow rate of 7.2 mL min^{-1} . Absorbance signals for metals were recorded using the FAAS detector. The results indicated that the extraction ratio increased as the pH increased (Fig. 2). A similar result was found in previous work using the same reagent in a solvent extraction method [26]. Ionic surfactants such as SDS produce charged micelles that can attract ions. These experimental results also showed that metal complexes were produced at basic pH values and hence, have cationic charges. High absorbance signals were observed at pH 10. However, it was also noted that some precipitation reactions occurred at this pH. Since the aim of the work was to evaluate the complexation reaction effect of the ligand on the micelle-mediated extraction, pH 8.5 was selected as opti-

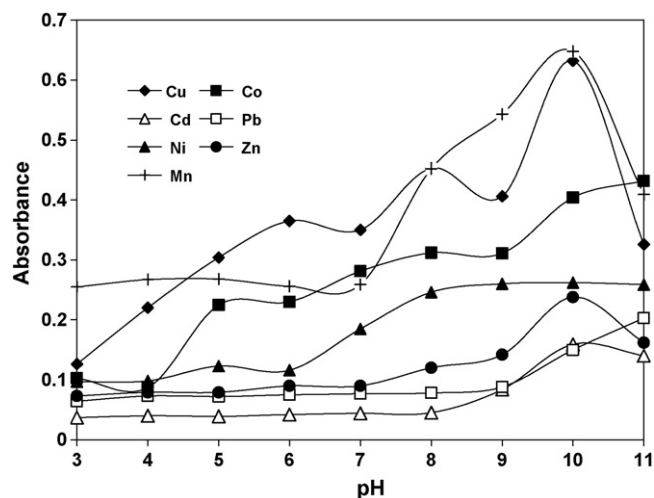


Fig. 2. The effect of the pH on the micelle-mediated extraction.

imum for all subsequent experiments. A borate buffer was selected to maintain the sample solutions at this pH.

Another analytical parameter requiring optimisation of the developed method is the concentration of the ligand in the solution. To determine the suitable ligand concentration, different concentrations of ligand up to $72 \mu\text{M}$ were used to prepare 25 mL of the solutions that also contain 0.3 ppm Cu, Ni and Co, 0.08 ppm Cd and Zn, 0.8 ppm Pb and 0.2 ppm Mn and analysed according to the procedure. As can be seen in Fig. 3, $36 \mu\text{M}$ of the ligand solution was sufficient to obtain maximum signal for all of the analytes. Since the extraction efficiency of the micelle-mediated extraction was highest using this concentration of the ligand, $36 \mu\text{M}$ was used for all subsequent experiments.

SDS was used to create the micelle media in the experiments and therefore the optimization of its concentration was also very important during the development of the method. Different volumes of 1% SDS were added to the 25 mL solution containing metal ions, buffer and ligand. The results showed that the highest signals were observed when the SDS volume was 2.5 mL. Greater volumes than this led to the absorbance signal decreasing slightly. In addition, when higher volumes of SDS were used, considerable foaming was produced and this caused some flow problems during the elution step of the flow injection system. Consequently a stable absorbance

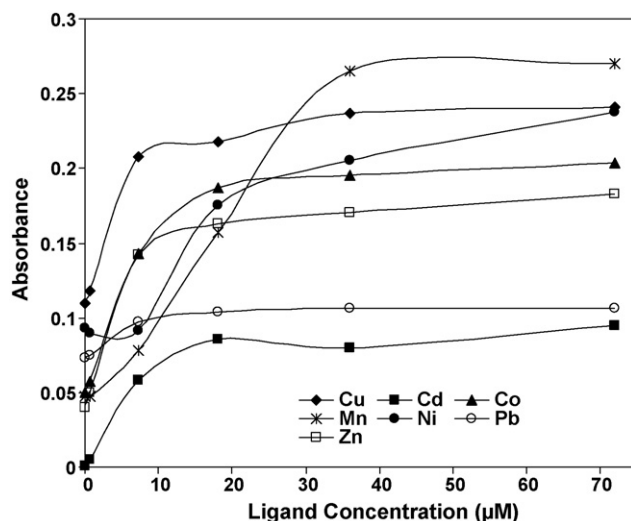


Fig. 3. The effect of ligand concentration on the absorbance signals of the metals.

signal could not be observed. For these reasons, the volume of 1% SDS used was 2.5 mL during subsequent experiments.

It is known that electrolytes such as NaCl decrease the critical micelle concentration. Addition of NaCl in the SDS solution facilitates micelle production to under the critical micelle concentration of the SDS solution alone. Different percentages of NaCl were therefore used in the flow injection system to find the optimal concentration. This solution was supplied separately via a peristaltic pump. The NaCl and the sample solution containing SDS were mixed using a flow system. This was possible because the micelles were produced very rapidly after the two solutions were mixed. Had they been mixed beforehand in a batch type system, some micelles and foam containing the metal chelates could stay within a volumetric flask and hence be lost analytically. Different percentages of NaCl were supplied to the system. The micelles adsorbed on the column were eluted and the absorbance signals were recorded. Absorbance signals were very low when the NaCl solutions were at 5 and 10%. This was attributed to low micelle formation. When the percentage of NaCl was increased, higher absorbance signals were observed as the micelle concentration increased. Subsequent experiments were performed using 30% NaCl solution. A higher percentage of NaCl was not tried because of the solubility problem of NaCl in water. Although a very high concentration of NaCl was used in these experiments, it is a very cheap and readily available chemical. It therefore does not increase the cost of the method significantly. In addition it is a chemical that can be obtained in very high purity, leading to low blanks and improved limits of detection.

The temperature effect on the micelle formation for sodium dodecyl sulfate was studied using sodium chloride that is used to decrease critical micelle concentration of sodium dodecyl sulfate. The experimental studies showed that the micelles of SDS which formed at room temperature rapidly disappear if the temperature increases. In addition, the critical micelle concentration was also found to increase as the temperature increased. Similar results have been found in the literature [34]. It is an advantage that the method can be optimised at room temperature with a low concentration of SDS. For these reasons, subsequent experiments were performed at room temperature.

Different eluents were tested to elute the metal ions from the cotton wool filled column. Different concentrations of nitric acid solutions in water (0.1, 0.5 and 1.0 M) as well as 0.5 M nitric acid in a 50% acetone–water mixture were used to determine the eluent that gives the highest desorption or absorbance values for

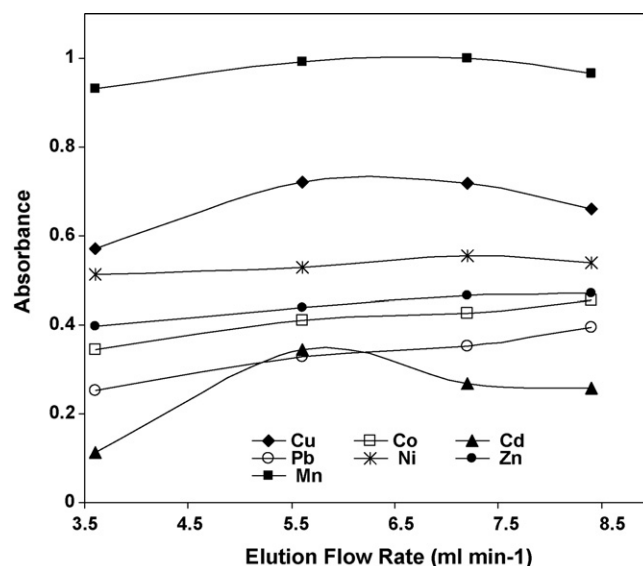


Fig. 5. The effect of the elution flow rate on the flow injection system.

the metal ions. As the concentration of the nitric acid increased, the absorbance signals did not change. The highest signals were obtained using 0.5 M nitric acid in 50% acetone. It is possible that the acetone helps to desorb the metal chelates from the cotton as well as increasing the absorbance signals for metals because of the improved transport efficiency associated with nebulisation of organic solvents.

Lastly, for flow injection analysis, the selection of the optimum flow rates is very important. Although the sample and elution flow rates should be rapid to increase sample throughput, they should not be too fast so that the adsorption and desorption characteristics become impaired. The effects of sample and elution flow rates were determined in the range between 3.6 and 8.4 mL min⁻¹. While the effect of sample flow rate was investigated, the eluent flow rate was kept constant at 7.2 mL min⁻¹. Similarly a constant flow rate of 7.2 mL min⁻¹ was used for the sample flow rate when the eluent flow rate was changed between 3.6 and 8.4 mL min⁻¹. Figs. 4 and 5 show that the highest flow rate of 8.4 mL min⁻¹ for both sample and eluent flows was suitable for obtaining higher signals for the required metal ions. Therefore, a cycle of preconcentration and elution was extremely rapid with the time required for one sample analysis being approximately 2 min.

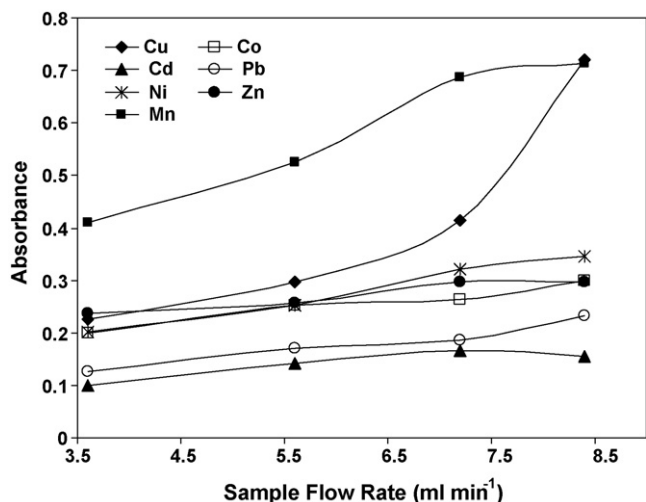


Fig. 4. The effect of the sample flow rate on the flow injection method.

Table 2

Effect of potentially interfering ions on the determination of Cd, Co, Cu, Mn, Ni, Pb and Zn using flow injection micelle-mediated extraction method by FAAS.

Ions	Tolerance limit of concentration (mg L ⁻¹)
Na ⁺ , K ⁺ , SO ₄ ²⁻ , PO ₄ ³⁻ , Cl ⁻	>10,000
Mg ²⁺	1300
CO ₃ ²⁻	>10,000 for Zn ²⁺ , Ni ²⁺ , Cu ²⁺ and Cd ²⁺ ; 5000 for Co ²⁺ , Mn ²⁺ and Pb ²⁺
NH ₄ ⁺	>10,000 for Zn ²⁺ , Mn ²⁺ , Pb ²⁺ , Cu ²⁺ and Cd ²⁺ ; 5000 for Co ²⁺ , Ni ²⁺
Ca ²⁺	500
Sn ²⁺ , Al ³⁺	100
Ag ⁺	100 for Zn ²⁺ , Ni ²⁺ , Cu ²⁺ , Co ²⁺ , Mn ²⁺ and Pb ²⁺ ; 25 for Cd ²⁺
Ba ²⁺	100 for Ni ²⁺ and Co ²⁺ ; 50 for Zn ²⁺ , Cu ²⁺ , Mn ²⁺ , Cd ²⁺ and Pb ²⁺
Cr ³⁺	100 for Zn ²⁺ , Cu ²⁺ , Cd ²⁺ and Pb ²⁺ ; 50 for Ni ²⁺ , Mn ²⁺ and Co ²⁺
Fe ³⁺	100 for Cu ²⁺ ; 50 for Cd ²⁺ , Zn ²⁺ , Ni ²⁺ , Mn ²⁺ , Pb ²⁺ and Co ²⁺

Table 3

The results for the certified materials.

Trace element	HPS		SLRS-4		IAEA/V-10 HAY		NCS DC73350		t_{exp}
	Certified value ($\mu\text{g L}^{-1}$)	Found value ($\mu\text{g L}^{-1}$)	Certified value ($\mu\text{g L}^{-1}$)	Found value ($\mu\text{g L}^{-1}$)	Certified value (mg kg^{-1})	Found value (mg kg^{-1})	Certified value (mg kg^{-1})	Found value (mg kg^{-1})	
Cd	30	29.7 ± 2.5	0.012 ± 0.002	<LOD	0.03	<LOD	0.32 ± 0.07	0.4 ± 0.1	0.68
Co	30	30 ± 1	0.033 ± 0.006	<LOD	0.13	<LOD	0.42 ± 0.03	0.4 ± 0.1	0.8
Cu	30	29.6 ± 0.7	1.81 ± 0.08	1.8 ± 0.1	9.4	9.4 ± 0.5	9.3 ± 1.0	9.7 ± 0.9	0.08
Mn	30	29 ± 1	3.37 ± 0.18	3.3 ± 0.6	47	N/A	45 ± 4	N/A	1.08
Ni	30	31 ± 2	0.67 ± 0.08	<LOD	4.2	4.6 ± 0.3	1.9 ± 0.3	2.1 ± 0.2	2.16
Pb	30	29 ± 3	0.086 ± 0.007	<LOD	1.6	1.7 ± 0.1	1.5 ± 0.3	1.6 ± 0.1	0.74
Zn	30	31.1 ± 0.5	0.93 ± 0.10	0.9 ± 0.4	24	N/A ^a	37 ± 3	N/A ^a	0.98

^a Not analysed because preconcentration was not necessary.

3.3. The effect of foreign ions

A list of tolerance limits for an assortment of foreign ions (expressed as mg L^{-1}) during the determination of the seven elements is given in Table 2. The effects of each potential interferent on every element were determined separately to make the study more complete. The concentrations of the analyte ions used during this experiment were 0.4 mg L^{-1} for Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} , 0.1 mg L^{-1} for Cd^{2+} and Zn^{2+} and 1.0 mg L^{-1} for Pb^{2+} . The only significant interfering element appeared to be Fe^{3+} and only then if the sample contains more than 50 mg L^{-1} . The results indicate that this method may easily be applied for the determination of these seven elements in water samples as well as acid digests of solid samples that contain less than 50 mg L^{-1} Fe. If the sample contains more than 50 mg L^{-1} Fe, a masking agent such as fluoride should be added to the sample before determination. The method may also be used to determine these seven elements in sea water that contains very high concentrations of Na, K, Cl, etc. since these ions do not cause any interference.

3.4. Analytical characteristics

In order to evaluate the performance of the developed method, the linearity and detection limits for the seven analytes were determined. The standards and blanks were passed through the FI manifold shown in Fig. 1 using the optimum flow and experimental conditions determined. All solutions were prepared using ultra-pure water. The correlation coefficients of the calibration curves for the seven metals were typically close to 0.999. The detection limits were calculated using $3s/\text{slope}$ ($n=15$ runs of the blank). The limits of detection for a 30 s period of preconcentration were $\text{Cd}=0.39 \text{ ng mL}^{-1}$, $\text{Cu}=3.2 \text{ ng mL}^{-1}$, $\text{Co}=7.5 \text{ ng mL}^{-1}$,

$\text{Mn}=3.0 \text{ ng mL}^{-1}$, $\text{Ni}=3.4 \text{ ng mL}^{-1}$, $\text{Pb}=17.9 \text{ ng mL}^{-1}$ and $\text{Zn}=0.89 \text{ ng mL}^{-1}$. However, these improved to $\text{Cd}=0.29 \text{ ng mL}^{-1}$, $\text{Cu}=2.1 \text{ ng mL}^{-1}$, $\text{Co}=3.8 \text{ ng mL}^{-1}$, $\text{Mn}=1.5 \text{ ng mL}^{-1}$, $\text{Ni}=1.97 \text{ ng mL}^{-1}$, $\text{Pb}=7.8 \text{ ng mL}^{-1}$ and $\text{Zn}=0.58 \text{ ng mL}^{-1}$ if the flow time, i.e. the preconcentration period, was doubled. These results were considered to be satisfactory considering the very short pre-concentration time.

3.5. Analyses of certified samples

The accuracy of the developed procedure was tested using certified reference materials. Two water certified materials, a high purity standard (QCS-19) (High purity standard, Charleston, USA) and a river water (SLRS-4) as well as two plant samples Hay (IAEA/V-10) and Poplar leaves (NCS DC73350) were analysed using the developed procedure. Acid digests of the vegetation samples were prepared by weighing material (0.25 g) into a pre-cleaned beaker, adding nitric acid (5 mL) and then heating on a hot plate. After an hour of boiling, the digests were allowed to cool and were then transferred quantitatively to clean 25 mL volumetric flasks. The other reagents (2.5 mL of 1% sodium dodecyl sulfate (SDS), 1.0 mL of $1.8 \times 10^{-3} \text{ M}$ ligand and 2.5 mL of pH 8.5 borate buffer solution) were then placed in the flask and the sample solution diluted to volume (25 mL) with water. The results of the analyses are given in Table 3. As shown in Table 3, the results obtained are in close agreement with the certified values. These results show that the method may readily be applied for the determination of these metals in water and vegetation samples. The iron concentrations are 177–190 and $274 \pm 17 \text{ mg/kg}$ in hay and poplar leaves, respectively. Therefore, the digested solutions contained less than 50 mg L^{-1} iron, which was below the concentration required to cause an interference.

Table 4

The results of the real natural water samples.

Analyte	Added value ($\mu\text{g L}^{-1}$)	River water ($\mu\text{g L}^{-1}$)	Recovery (%)	Sea water ($\mu\text{g L}^{-1}$)	Recovery (%)
Cu	–	11 ± 1		18 ± 1	
	60	72.6 ± 0.7	102.7	80 ± 4	103.3
Cd	–	–		–	
	16	15.3 ± 0.9	95.6	16 ± 2	100
Ni	–	3.0 ± 0.6		3.4 ± 0.8	
	60	64 ± 2	101.7	63 ± 3	99.3
Pb	–	–		–	
	160	163 ± 6	101.9	167 ± 3	104.4
Zn	–	5.4 ± 0.4		28 ± 1	
	16	21.5 ± 0.7	100.6	45 ± 0.6	106.2
Mn	–	6 ± 1		22 ± 0.6	
	40	48 ± 2	105	63 ± 1	102.5
Co	–	–		–	
	60	63 ± 3	105	61 ± 1	101.7

Table 5
Characteristics of Micelle-mediated extraction—flow injection method for determination of metal ions in different samples.

Reagent (surfactant type)	Detection method	Samples	Temperature (°C)	Analysed metals	Preconcentration factor	Detection limits	Ref.
Luminol – H ₂ O ₂ (SDS + Triton X114)	Chemiluminescence	Water	Room temperature	Cr	6	0.5 ng L ⁻¹	[9]
Dithizone (Triton X-100)	Spectrophotometer	Water	60	Hg	6	0.014 µg mL ⁻¹	[19]
2-(5-Bromo-2-pyridylazo)-5-diethylamino phenol (PONPE-7.5)	ICP-OES	Urine	Room temperature	Gd(III)	20	40 ng L ⁻¹	[20]
Pyrrolidine dithiocarbamate (APDC) (Triton X-114)	ETAAS	Biological	Room temperature	Pb	22.5	44.6 ng L ⁻¹	[21]
Chrome-Azurol-S (benzyltrimethyl tetradecyl ammonium chloride + PONPE-7.5)	Spectrophotometer	Parenteral solutions	Room temperature	Al	50	3.024 µg L ⁻¹	[36]
N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diamino propane (SDS)	FAAS	Water and biological	Room temperature	Cd, Co, Cu, Mn, Ni, Pb and Zn	8.4	Cd = 0.39 ng mL ⁻¹ , Cu = 3.2 ng mL ⁻¹ , Co = 7.5 ng mL ⁻¹ , Mn = 3.0 ng mL ⁻¹ , Ni = 3.4 ng mL ⁻¹ , Pb = 17.9 ng mL ⁻¹ , Zn = 0.89 ng mL ⁻¹	This work

Using the paired *t*-test, adopting the null hypothesis it is possible to determine whether or not there is a significant difference between the mean concentrations found using the proposed method and the certified values. The paired *t*-test was performed for every element and for each of the certified materials individually. The results show that the *t* values calculated using the equation $\bar{x}_d\sqrt{N}/s_d$, where \bar{x}_d , s_d and N show the mean difference, the standard deviation of differences and the number of samples, respectively, are smaller than the critical value of *t* at 95% confidence interval for all certified samples, indicating that there is no evidence of systematic error in the proposed method [35]. The critical values of *t* for 1, 2 and 3 number of degrees of freedom at 95% confidence interval are 12.71, 4.3 and 3.18, respectively. This confirms that the results obtained by the proposed method were in good agreement with the certified values.

3.6. Analysis of real samples

The proposed method was applied to river and sea water samples. The experiments were performed using river and sea water samples at natural analyte concentrations and with samples spiked with 16 µg L⁻¹ of Cd(II), 40 µg L⁻¹ of Mn(II), 60 µg L⁻¹ of Co(II), Cu(II) and Ni(II) and 160 µg L⁻¹ of Pb(II). The results of these spike/recovery experiments are given in Table 4. The recovery values obtained were very satisfactory. The procedure developed in this work is therefore an alternative method for the determination of very low concentrations of Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) in fresh and sea waters.

3.7. Comparison with other flow injection micelle-mediated extraction methods

In the literature, although there are numerous applications of the off-line micelle-mediated extraction to determine metal ions in different samples, only a few applications have been developed that have used on-line flow injection for the purpose of micelle-mediated extraction. Comparative data using on-line flow injection methods given in Table 5 show that all the previous applications reported data only for a single element. The method presented in this work was applied to the determination of seven elements in water and biological samples. In addition, the method

proposed here needs only one surface active material, SDS, and could be applied at room temperature. Most surfactant-mediated procedures use one surface active compound, generally non-ionic surfactants. The combination of surfactants such as non-ionic and cationic or anionic surfactants is another aspect and it is used depending on the target analyte. Room temperature extraction can also be achieved with non-ionic surfactants like Triton X-45 or Triton X-114 in the presence of salts in the literature. All the methods except this work are based on the cloud point phenomenon. However, since SDS is an anionic surface active material, the micelles disappear as the temperature increases whereas a polar surface active materials such as Triton X-100, Triton X-114, etc. gives a cloud point temperature above which the micelles are produced. There appear few applications in the literature that have used only an anionic surface active material in flow injection micelle-mediated methods. An advantage of the method is that the presence of excess chelating agent does not reduce the extraction efficiency as may occur with other reagents. Instead, the presence of an excess of reagent helps to compensate for the competition from other metals present within the sample. From this perspective, this work is a new application of the on-line flow injection micelle-mediated extractions.

4. Conclusions

A micelle-mediated FI-FAAS preconcentration method has been developed to determine very low concentrations of Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) in natural waters and foodstuffs. N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane (HBDAP) was used to complex Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) at pH 8.5. The limits of detection for a 30 s period of preconcentration were Cd = 0.39 ng mL⁻¹, Cu = 3.2 ng mL⁻¹, Co = 7.5 ng mL⁻¹, Mn = 3.0 ng mL⁻¹, Ni = 3.4 ng mL⁻¹, Pb = 17.9 ng mL⁻¹ and Zn = 0.89 ng mL⁻¹. However, these improved to Cd = 0.29 ng mL⁻¹, Cu = 2.1 ng mL⁻¹, Co = 3.8 ng mL⁻¹, Mn = 1.5 ng mL⁻¹, Ni = 1.97 ng mL⁻¹, Pb = 7.8 ng mL⁻¹ and Zn = 0.58 ng mL⁻¹ if the flow time, i.e. the preconcentration period, was doubled. These results were considered to be satisfactory considering the very short preconcentration time. The method is very fast, cheap and does not use any hazardous solvents. The analysis time for one sample is less than 2 min.

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