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

Derya Kara *

Department of Chemistry, Art and Science Faculty, Balikesir University, 10100 Balikesir, Turkey

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 HNO_3 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.

© 2009 Published by Elsevier B.V.

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-

* Tel.: +90 266 612 10 00; fax: +90 266 612 12 15.
  E-mail address: dkara@balikesir.edu.tr.

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 ($18.2\,M\Omega\,cm$) 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 SpectrAA 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 $25 \pm 0.1\,^{\circ}C$ 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].
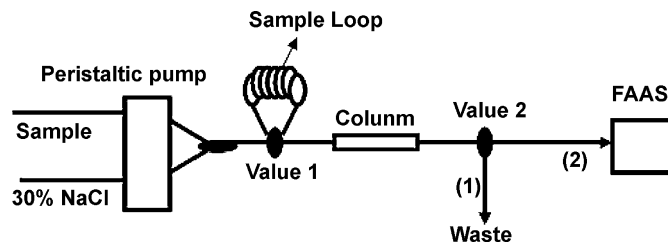

Fig. 1. The diagram of the flow injection micelle-mediated extraction. (1) Sample loading step and (2) elution and analysis step.

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 ($\bar{n} - p$[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 HNO$_3$ 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, de-ionised 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.