Cloud point extraction with mixed micelles of TX-114/DOSS and derivative spectrophotometry for simultaneous determination of Fe\textsuperscript{2+} and Co\textsuperscript{2+} using 2,2′,6′,2″-terpyridine

K Ravi Kumar & P Shyamala*
Department of Physical and Nuclear Chemistry & Chemical Oceanography, School of Chemistry, Andhra University, Visakhapatnam 530 003, Andhra Pradesh, India

Email: shyamalapulipaka06@gmail.com

Received 24 August 2016; revised and accepted 5 December 2016

A new cloud point extraction procedure with derivative spectrophotometry for the simultaneous preconcentration and determination of Fe\textsuperscript{2+} and Co\textsuperscript{2+} has been developed. In this method both the Fe\textsuperscript{2+} and Co\textsuperscript{2+} metal ions are simultaneously complexed with 2,2′,6′,2″-terpyridine at a pH of 3.8. The complexes of Fe\textsuperscript{2+} and Co\textsuperscript{2+} are then extracted into mixed micelles of surfactants (Triton X-114 and docusate sodium salt). Various parameters such as pH, concentration of the ligand, concentrations of the surfactant, concentration of salt (Na\textsubscript{2}SO\textsubscript{4}), equilibration temperature and time have been optimized. Under optimum conditions, the linear ranges of Fe\textsuperscript{2+} and Co\textsuperscript{2+} are found to be 3.14–18.86 \mu g mL\textsuperscript{-1} and 0.373–2.42 \mu g mL\textsuperscript{-1} respectively. Their corresponding limits of detections are found to be 0.498 ng mL\textsuperscript{-1} and 4.54 ng mL\textsuperscript{-1}. The proposed method has been successfully applied to the determination of Fe\textsuperscript{2+} and Co\textsuperscript{2+} in tap water and sea water. The recoveries were found to be in the range of 98–107%.

Keywords: Analytical chemistry, Derivative spectrophotometry, Cloud point extraction, Mixed micelles, Surfactants, Iron, Cobalt, Terpyridine

Direct determination of iron and cobalt in natural waters with sophisticated instruments is a complicated process due to their very low available concentrations and high matrix effects. Hence, minimising the matrix effects is a prerequisite task for their determination. Preconcentration techniques like dispersive liquid-liquid microextraction, solid phase extraction, co-precipitation and cloud point extraction are generally used for minimising matrix effects. Amongst these preconcentration schemes, cloud point extraction is an environmental friendly technique which is in agreement with green chemistry principles and requires less toxic surfactants as extracting agents. The surfactants used in the cloud point extraction procedures are mostly of non-ionic type like Triton X-114 (TX-114), Triton X-100 and PONPE 7.5\textsuperscript{9,10} since these surfactants have cloud point temperatures at around room temperature. However, one of the limitations of cloud point extraction (CPE) with non-ionic surfactants like TX-114 is the lower extraction efficiencies of hydrophilic inorganic and polar organic compounds. To overcome this limitation, an ionic surfactant can be added so that a neutral species is formed with hydrophilic charged compounds\textsuperscript{11,12} which can be easily extracted into the neutral surfactant like TX-114. This facilitates the extraction of compounds with different charges\textsuperscript{13-15}.

In the present work the mixed micelles of TX-114 and docusate sodium salt (DOSS) have been used for simultaneous preconcentration of iron and cobalt. The anionic surfactant, DOSS, reacts by ion-pair formation with the cationic metal complex. This makes extraction into the neutral surfactant, TX-114, easier. Further, another reason for the use of DOSS is its low hydrophile-lipophile balance (HLB) value as compared to other surfactants, indicating its high hydrophobicity, which is required for extraction. DOSS increases the CP temperature to > 100 °C, while TX-114 has a cloud point temperature around 25 °C. The mixed micelles in the presence of Na\textsubscript{2}SO\textsubscript{4} have a CP temperature around 20 °C and actual phase separation was observed at 50 °C, which is convenient for extraction procedure.

Cloud point extraction procedures have been successfully applied to the extraction of inorganic analytes, where the metals form complexes with ligands such as APDC (ammonium pyrrolidinedithiocarbamate)\textsuperscript{16-19}, PAN (1-(2-Pyridylazo)-2-naphthol)\textsuperscript{10,24}, 5-Br-PADAP (2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol)\textsuperscript{25,29} and 8-HQ (8-hydroxyquinoline)\textsuperscript{30,31}. However, 2,2′,6′,2″-terpyridine (TPY) has not been used as a ligand for the determination of iron and Cobalt using cloud point extraction procedures so far. Hence, we have chosen TPY for the extraction of the Fe\textsuperscript{2+} and Co\textsuperscript{2+} in the presence of mixed micelles of TX-114 and DOSS. Moreover, Fe\textsuperscript{2+} and Co\textsuperscript{3+} gave intense coloured complexes with TPY at \lambda_{\text{max}} of 559 and 514 nm in first derivative spectrophotometric method respectively.
Experimental

All reagents used were of analytical grade. Stock solution of 10% w/v Triton X-114 (polyethylene glycol tert-octylphenyl ether) (Sigma-Aldrich, USA) was prepared in doubly distilled water and 10% w/v DOSS (docusate sodium salt) (Fluka, USA) was prepared in methanol. Stock solution of Fe$^{2+}$ (2x10$^{-2}$ mol L$^{-1}$) was prepared by dissolving 0.7843 g of ammonium ferrous sulphate (Merck India) in doubly distilled water with an overall concentration of 1% sulphuric acid and standardised. Stock solution of Co$^{2+}$ (2x10$^{-2}$ mol L$^{-1}$) was prepared by dissolving 0.4759 g of cobaltous chloride hexahydrate (Merck India) in doubly distilled water and standardised. Working solutions of Fe$^{2+}$ and Co$^{2+}$ were then prepared by diluting the stock solutions with doubly distilled water. 2,2',6,2''-terpyridine (TPY) (Sigma-Aldrich, USA) solution (2x10$^{-3}$ mol L$^{-1}$) was prepared by dissolving 0.04665 g of the compound in doubly distilled water and an overall concentration of 0.1% HCl was maintained in the solution.

All absorbance values and spectra were recorded with a double beam UV-vis derivative mode spectrophotometer (UV-1800, Shimadzu, Japan). All pH measurements were carried out using systronics digital pH meter 335. A Remi R-24 was used for centrifugation of samples.

In the CPE procedure, acetate buffer at pH 3.8 was taken in a 15 mL vial and an aliquot of the solution containing the analytes in concentrations ranging from 0.373–2.42 µg mL$^{-1}$ of Fe$^{2+}$ or 3.14–18.86 µg mL$^{-1}$ of Co$^{2+}$ was added. Then, 1.2 mL of 2x10$^{-3}$ mol L$^{-1}$ TPY, 1.2 mL of 10% w/v DOSS, 1.2 mL of 10% w/v TX-114 and 0.8 mL of 30% w/v Na$_2$SO$_4$ were added and volume was made up to 10 mL with doubly distilled water. Heating at 60 ºC for 25 minutes, resulted in two phases. Subsequently, complete phase separation was obtained through centrifugation and cooling for 10 minutes in an ice bath. The supernatant aqueous phase was then decanted. The surfactant-rich phase was dissolved in 20% methanol to decrease the viscosity and the homogenized surfactant rich phase was analyzed spectrophotometrically at corresponding wavelengths (514 nm for Co-TPY complex and 559 nm for Fe-TPY complex) of the analytes complexes.

Results and discussion

The ligand TPY forms coloured complexes with the analytes, Fe$^{2+}$ and Co$^{2+}$, at a pH of 3.8. These complexes were extracted into mixed micelles of TX-114 and DOSS in the presence of sodium sulphate. For maximum extraction efficiency, the parameters affecting the cloud point extraction were optimized.

The zero order spectra of Fe$^{2+}$ and Co$^{2+}$ in their single and binary mixtures show that there is strong overlapping of peaks and lacks accuracy (Fig. 1a). Hence, the first derivative spectrophotometry method was used for the determination of Fe$^{2+}$ and Co$^{2+}$ simultaneously with the ligand TPY. Figure 1(b) shows the variation of first order derivative absorption spectra of Fe$^{2+}$ and Co$^{2+}$ complexes with TPY. The absorption maxima ($\lambda_{max}$) for Fe$^{2+}$ and Co$^{2+}$ complexes were observed at 514 nm and 559 nm.
For optimization of pH, buffers in the pH range from 2–8 were used. To maintain pH in this range, KCl/HCl, CH₃COONa/CH₃COOH and NaH₂PO₄/Na₂HPO₄ buffers were used. Maximum recoveries were observed for acetate buffer (CH₃COONa/CH₃COOH) at pH 3.8 (Fig. 2(a)). Therefore, pH 3.8 was chosen for the determination of Fe²⁺ and Co²⁺ in subsequent experiments.

The recoveries of the analytes were studied in the concentration range from 0.4×10⁻⁴ mol L⁻¹ to 4×10⁻⁴ mol L⁻¹. As the concentration of TPY increases, the recoveries increase up to 2.4×10⁻⁴ mol L⁻¹ and then decreases for both analytes. Therefore, 2.4×10⁻⁴ mol L⁻¹ of TPY has been chosen for the further experiments (Fig. 2(b)).

The recoveries of Fe²⁺ and Co²⁺ were studied varying the concentration of TX-114 in the range of 0.2%–2% (w/v). The recoveries of Fe²⁺ and Co²⁺ increased up to 1.2% (w/v) of TX-114 and then decreased. Thus, the optimum concentration of

![Image](image_url)
TX-114 was taken as 1.2% (w/v). The positively charged analytes Fe$^{2+}$ and Co$^{2+}$ react with the chelating agent TPY and form positive complexes. The concentration of DOSS was optimized in the range 0.3%–2% (w/v). The recovery increased up to 1.2% (w/v) of DOSS and then decreased. Thus, the optimum concentration of DOSS was 1.2% (w/v) (Fig. 2(c)).

The surfactant mixture, TX-114 and DOSS, which was used for the extraction of analytes has a cloud point temperature around 90–100 °C. To reduce the cloud point temperature and to achieve the phase separation of mixed surfactants, a salting out agent was used. The addition of Na$_2$SO$_4$ to the mixture of TX-114 and DOSS reduced the cloud point temperature up to 25 minutes and then decreased. Hence, the optimum concentration of Na$_2$SO$_4$ was found to be 2.4% (w/v) as shown in Fig. 2(d).

The phase separation was not observed below 50 °C and the recoveries increased with increase in temperature up to 60 °C and then decreased. In the study of equilibration time, the recoveries increased up to 25 minutes and then decreased. Hence, the optimum equilibration temperature and time were taken as 60 °C and 25 minutes, respectively.

The analytical characteristics of the proposed method were evaluated under the optimized conditions. Calibration graphs were drawn for both Fe$^{2+}$ and Co$^{2+}$ under the optimum conditions, from which the observed linearity ranges were 0.373–2.42 µg mL$^{-1}$ for Fe$^{2+}$ and 3.14–18.86 µg mL$^{-1}$ for Co$^{2+}$. The calibration equations obtained were $dA/d\lambda = -0.005466C_{Fe^{2+}}-0.000301$ and $dA/d\lambda = -0.000300C_{Co^{2+}}+0.000130$ with correlation coefficients of 0.9996 and 0.9985 for Fe$^{2+}$ and Co$^{2+}$, respectively. The limits of detections of Fe$^{2+}$ and Co$^{2+}$ were 0.498 ng mL$^{-1}$ and 4.54 ng mL$^{-1}$, respectively.

The proposed mixed micellar cloud point extraction method was successfully applied for the simultaneous determination of Fe$^{2+}$ and Co$^{2+}$ in tap and sea water samples. The spike recoveries were found to be in the range from 98–107%.

In the present study, the mixed micellar cloud point extraction method was successfully employed for the simultaneous preconcentration of Fe$^{2+}$ and Co$^{2+}$ and their determination with derivative spectrophotometry in different water samples using mixed micelles of TX-114 and DOSS and TPY as complexing agent. The proposed cloud point extraction method is sensitive, sensitive, low cost and accurate, which allows the simultaneous determination of Fe$^{2+}$ and Co$^{2+}$ at ng mL$^{-1}$ level using derivative spectrophotometry.

**Acknowledgement**

The authors are grateful to the Department of Science and Technology (DST-SERB), India, for financial support under the major research project, SB/SI/IC-35/2013.

**References**

NOTES