Simultaneous Determination of Iron and Cobalt using Spectrophotometry after Catanionic Mixed Micellar Cloud Point Extraction Procedure

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ABSTRACT

A new preconcentration method which utilises a mixture of cationic and anionic surfactants for separation and spectrophotometric determination of iron and cobalt simultaneously has been developed. The metal ions, iron and cobalt were complexed with thiocyante. The hydrophobic complexes of iron and cobalt were then extracted into catanionic mixed micelles of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS). Different parameters like concentration of HCl, concentration of thiocyanate, concentrations of the surfactants (CTAB and SDS), equilibration temperature and time were studied to get maximum efficiency. The linear ranges of Fe^{3+} and Co^{2+} were found to be $0.139 – 0.838$ µg mL^{-1} and $5.89 – 35.4$ µg mL^{-1}, respectively the detection limits obtained were 1.54 ng mL^{-1} and 6.18 ng mL^{-1}. The developed procedure has been employed for the retrieval of Fe^{3+} and Co^{2+} in water samples successfully (tap water and sea water). $98 – 107\%$ recoveries were obtained.

Keywords: Cloud point extraction, Catanionic mixed micelles, Iron and Cobalt.

INTRODUCTION

Iron and Cobalt are the most important metals in biological systems, as they are the constituent elements in haemoglobin and vitamin B_{12} (Cyanocobalamin). The deficiency of these analytes might lead to deadly diseases like anaemia while the high levels of iron might cause diseases like thalassemia. Excess of cobalt may result in cardiomyopathy or vasodilation in human beings. It is therefore important to determine the levels of iron and cobalt accurately.

Direct determination of these metals in water is a complex process, because of their very low concentrations and the high interferences from other components in the solution. Hence, reducing the matrix effects is an important task prior to their determination. The cloud point extraction is an environmentally favourable technique which follows green chemistry principles for extraction. When the surfactants are heated they separate into two different

phases at a particular temperature called cloud point temperature, the surfactant abundant phase and the water phase. solutes/metal ions can be removed into the surfactant phase. In cloud point extraction procedure, the two important factors for selection of surfactants is that the cloud point temperature should be close to room temperature and the other is extraction efficiency. The extraction of compounds is due to the hydrophobic and electrostatic interactions with the micelles. Maximum extraction efficiency is achieved by using two surfactants.

The method has been used for the extraction of metal complexes with ligands like APDC (ammonium pyrrolidine dithiocarbamate)[1–4], 8-HQ (8-hydroxyquinoline)[5,6], 2-GB (2-guanidino benzimidazole)[7], TAN (1-(2-thiazolylazo)-2-naphthol)[8,9], PMBP (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone)[10], PHBI (2-phenyl-1H-benzo[d] Imidazole)[11], MPMP (2-[(2-mercaptophenylimino) methyl]phenol)[3], Me-BTABr (2-[2-(6-methyl-benzothiazolylazo)]-4-bromophenol)[12], MPKO (methyl-2-pyridylketone oxime)[13], anthralin (1, 8-dihydroxyanthrone)[14] and ACDA (2-amino-cyclopentene-1-dithiocarboxylic acid)[15]. The addition of salts also influences the cloud point where the temperature decreases by salting out effect[16–18]. The retrieval of iron and cobalt in different matrices by cloud point extraction was reported in literature using expensive instruments like atomic absorption spectrometry with graphite furnace (GFAAS)[12,19], inductively-coupled plasma with OES (ICP-OES)[5,6].

In this paper we report the spectrophotometric determination of Fe^{3+} and Co^{2+} metal ions simultaneously in the presence of thiocyanate ligand using catanionic mixed micelles of CTAB and SDS. The surfactant phase of catanionic mixed micelles formed from CTAB and SDS have both positive and negative entities of the surfactants[20], which resulted in a strong synergistic effect(indicated by a negative interaction parameter between the two surfactants(β)[21,22] thereby increasing the efficiency of the extraction process. The factors affecting the extraction were optimised to get maximum efficiency and the developed system was used for the calculation of Fe^{3+} and Co^{2+} in different real samples of water.

MATERIALS AND METHODS

Instrumentation

A Shimadzu spectrophotometer was used for measuring absorbance. A systronics digital pH meter 335 was used for all pH measurements.

Reagents and solutions

Analytical grade reagents were used. Sigma-Aldrich make Cetyltrimethylammonium bromide, CTAB and (Sodium dodecyl sulfate, SDS) were used. Aqueous solutions of 10% (w/v) CTAB and 10% (w/v) SDS were made. Standard solutions of Fe^{3+} and Co^{2+} were made from ammonium ferric sulphate and cobaltous chloride respectively which are taken as stock solutions. An aqueous solution of the ligand, sodium thiocyante (NaSCN) obtained from Lobachemie, India. 5 mol L^{-1} solution of NaSCN was made.

Experimental procedure

In a graduated test tube, 0.15 mL of concentrated hydrochloric acid and standards of corresponding concentrations of analytes were added followed by 1.1 mL of 5 mol dm^{-3}NaSCN, 1.1mL of 10% (w/v) CTAB and 50 µL of 10% (w/v) SDS and made up to 10 mL with Milli-Q water. The mixture was then heated to 50°C for 15 minutes. After heating, two phases were observed. Phase separation was obtained completely after reducing the temperature of the system during a period of one hour. In this method surfactant rich phase was observed at the top and bulk aqueous phase was observed at bottom. The non-surfactant phase was decanted. Methanol was used to dissolve the surfactant phase containing the metal ions and absorbance was recorded at wavelengths of maximum absorbance (502 nm for Fe^{3+}–SCN– complex and 618 nm for Co^{2+}–SCN– complex).

RESULTS & DISCUSSION

To get maximum efficiency of the method, each reagent concentration was changed and keeping all other reagents constant and optimizing each reagent at a time.

Variation of % (v/v) of HCl

Three types of mineral acids (H_2SO_4, HNO_3 and HCl) were chosen for the initial study of the system. The recoveries of the analytes show that

hydrochloric acid is the best acid for the extraction of these metal complexes simultaneously. The effect of HCl concentration was varied from 0 % (v/v) to 10% (v/v). The extraction increases up to 1.5% (v/v) of HCl and thereafter decreases. Fig. 1 shows that the percentage concentration of HCl for the simultaneous extraction of Fe^{3+} and Co^{2+} is 1.5%(v/v).
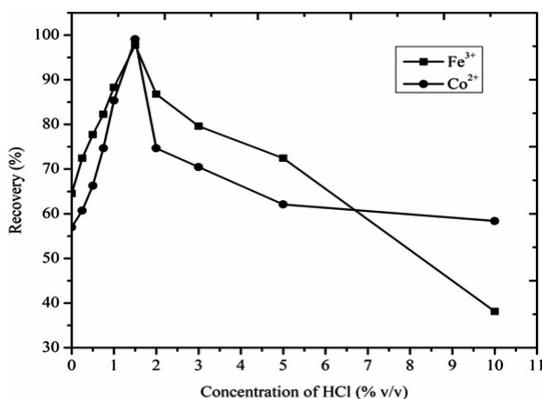
Fig. 1. Plot of recovery versus percentage concentration of HCl. Conditions: 0.55 mol L⁻¹ of SCN–, 1.1 % CTAB (w/v), 0.05% SDS (w/v), 50°C of equilibration temperature, 15 min of equilibration time

Variation of the amount of SCN

The concentration of the monodentate ligand, SCN– selected for complex formation with analytes Fe^{3+} and Co^{2+} was varied in the range (0.1 to 0.6) mol L⁻¹. The recoveries increase up to 0.55 mol L⁻¹ concentration of SCN- and then decrease for both the metals. Therefore, 0.55 mol L⁻¹ of SCN– was used for the rest of the study (Figure 2).
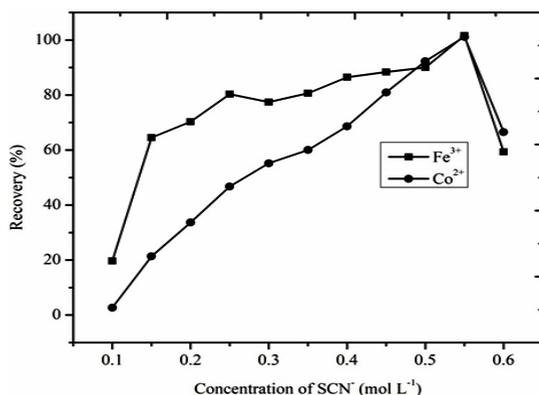
Fig. 2. Variation of amount of SCN–. Conditions: 1.5%(v/v) of HCl, 1.1% CTAB(w/v), 0.05% SDS(w/v), 50°C of equilibration temperature, 15 min of equilibration time

Variation of % (w/v) of CTAB

Percentage of CTAB was changed from

(0.1 to 1.2)%(w/v) and recovery of Fe^{3+} and Co^{2+} was studied. The metal retrieval increases up to 1.1% (w/v) of CTAB and then decreases (Fig. 3). 1.1% (w/v) CTAB was fixed for the rest of the study.
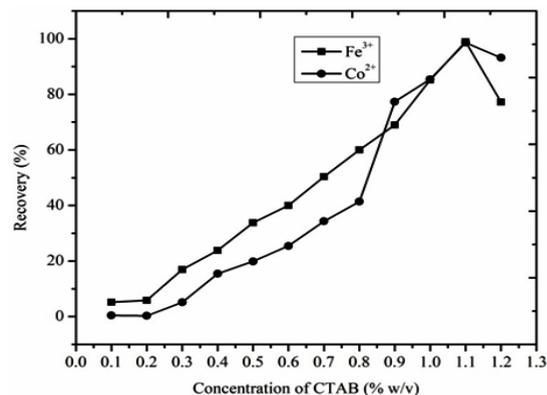
Fig. 3. Plot of recovery versus %(w/v) CTAB. Conditions: 1.5%(v/v) of HCl, 0.55 mol L⁻¹ of SCN–, 0.05%(w/v) of SDS, 50°C of equilibration temperature, 15 min. of equilibration time

Optimization of % (w/v) of SDS

SDS concentration was varied from (0-0.1)%(w/v) to get maximum recovery. The extraction of analytes increases till 0.05%(w/v) of SDS and decreases thereafter (Fig. 4). Therefore, 0.05%SDS concentration was used for maximum extraction of Fe^{3+} and Co^{2+}.
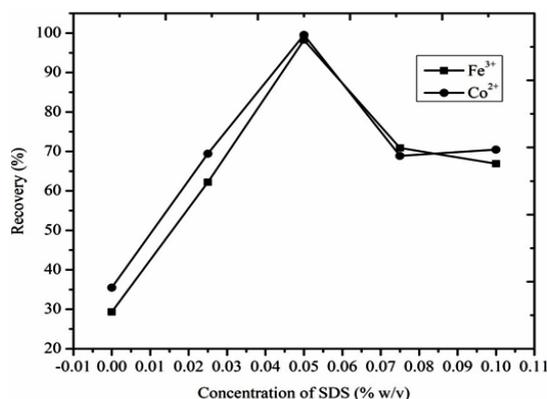
Fig. 4. Variation of %(w/v) of SDS. Conditions: HCl = 1.5% (v/v) , SCN- = 0.55 mol L⁻¹, CTAB = 1.1%(w/v) , equilibration temperature=50°C, incubation time = 15 minutes

The metal extraction mechanism in for the mixed micellar system of CTAB and SDS can be explained by the following mechanism. The monodentate ligand, SCN- and anionic surfactant, SDS, form a negative metal complex which is then form ion-pair complex with protons from strong acids or positive surfactant CTAB.

$$M^{n+} + nL^- + nDS^- \longrightarrow [ML_n(DS)_n]^{n-}$$

Metal ligand complex
(L= SCN$^-$, Cl$^-$)

$$[ML_n(DS)_n]^{n-} + nCTA^+ \longrightarrow [nCTA^+][ML_n(DS)_n]^{n-}$$

Ion pair between
complex and CTAB

$$[ML_n(DS)_n]^{n-} + nH^+ \longrightarrow [nH^+][ML_n(DS)_n]^{n-}$$

protons from
strong acids

Ion pair between
complex and protons
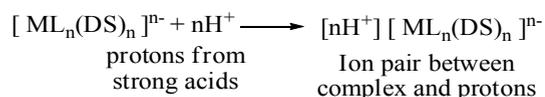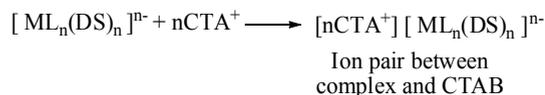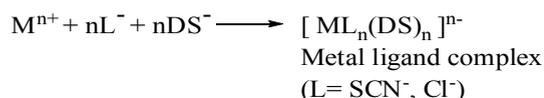
Optimization of incubation time and equilibration temperature

It is always advisable to have shortest incubation time and temperature close to room temperature along with maximum recovery of the method. In the present study the equilibration temperature was varied from 25 to 100°C and equilibration time was changed from 5 to 60 minutes. The optimum temperature was observed to be 50°C and optimum time was found to be 15 min respectively.

Analytical figures of the method

The analytical parameters of the developed method were determined. The observed linearity ranges of Fe^{3+} and Co^{2+} from the calibration graphs were found to be 0.139-0.838 µg mL^{-1} and 5.89-35.4 µg mL^{-1}, respectively. The equations obtained were A = 0.532446 [Fe^{3+}] + 0.004214 and A = 0.013357 [Co^{2+}] + 0.013000 with correlation coefficients of 0.9990 and 0.9934 for Fe^{3+} and Co^{2+}. The detection limits for Fe^{3+} and Co^{2+} were as low as 1.54 ng mL^{-1} and 6.18 ng mL^{-1}, respectively. The preconcentration factor and phase volume ratio of the method are 40 and 0.025, respectively Table 1. A comparison of the results obtained from the developed method with methods reported in literature for the retrieval of Fe^{3+} and Co^{2+} is given in Table 2.

Table 1: Analytical parameters for the two metals

Parameter	Fe^{3+}	Co^{2+}
λ_{max} (nm)	502	618
Linear range (µg mL^{-1})	0.13–0.84	2.9–35.4
Correlation coefficient (R^2)	0.9990	0.9934
LOD (ng mL^{-1})	1.54	6.18
Preconcentration factor	40	40
Phase volume ratio	0.025	0.025
Extraction efficiency(%)	98.26	100.76

Table 2: List of the details of the present method and previous methods

Analytes	Ligand	Surfactants	LOD	Technique	Matrix	References
Fe, Co and Ni	APDC	TX-114	19,5 and 11 µg L^{-1} for Fe, Co and Ni	FIA-FAAS	Waste, river, tap and sea water.	[9]
Fe	Ferron	TX-114	1.7 µg L^{-1}	FI-FAAS	Water and milk	[42]
Co	PAN	TX-114	0.6 µg L^{-1}	Spectrophotometry	Water samples	[14]
Co	Without	PONPE 7.5	10 ng L^{-1}	ETAAS	Drinking water samples	[37]
Co, Ni	ACDA	TX-114	7.5 and 10 µg L^{-1} for Co and Ni	Spectrophotometry	Natural and waste water samples	[33]
Fe, Co	SCN–	CTAB and SDS	1.54 and 6.18 ng mL^{-1} for Fe and Co	UV-Vis Spectrophotometry	Tap and sea water samples	Method developed in this paper

Validation of the method and analysis of real samples

The developed cloud point extraction method using CTAB and SDS mixed micellar system was employed for the simultaneous determination of Fe^{3+} and Co^{2+} in different water samples. 92–102% spike recoveries were found Table 3.

Table 3: Recovery values of Fe^{3+} and Co^{2+} in water samples along with spike recoveries

Samples	Spiked (µg mL^{-1})		Detected (µg mL^{-1})		Recovery(%)	
	Fe^{3+}	Co^{2+}	Fe^{3+}	Co^{2+}	Fe^{3+}	Co^{2+}
	-	-	0.0906±0.0023	1.733±0.06	-	-
Tap water	0.419	11.79	0.519±0.02	13.84±0.297	102.24±4.89	102.69±2.07
	0.698	23.57	0.783±0.04	25.62±1.09	99.2±5.65	101.34±4.36
	-	-	ND	ND	-	-
Sea water	0.419	11.79	0.403±0.02	11.27±0.36	96.18±5.18	95.59±3.05
	0.698	23.57	0.646±0.03	21.69±1.02	92.55±4.65	92.02±4.31

ND: Not Detected

CONCLUSION

A new cloud point extraction method based on catanionic mixed micelles of CTAB and SDS for the preconcentration of Fe^{3+} and Co^{2+} and their determination simultaneously using spectrophotometry in different water samples in the presence of thiocyanate as ligand was developed. This new method is much simple and accurate and for the determination of Fe^{3+} and Co^{2+} at ng mL^{-1} level.

Conflicts of Interest
The authors declare no conflict of interest.

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