SIMULTANEOUS CLOUD POINT EXTRACTION AND DETERMINATION OF ZN, CO, NI, AND PB BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

A simple cloud point extraction method has been proposed for the preconcentration and simultaneous determination of Zn(II), Co(II), Ni(II) and Pb(II). The pH of sample solution was adjusted to 8.5 with buffer and the cations complexes with 2-guanidino benzimidazole. Triton X-114 was added as a non-ionic surfactant. After the phase separation at 65 ± 1°C the surfactant – rich phase was diluted to 1.5 ml using ethanolic solution of HNO_3 and the analytes were determined by flame atomic absorption spectrometry. The influence of variables upon the complexation and extraction such as pH, ligand concentration surfactant concentration etc. was studied. Preconcentration of 50 ml sample solution in presence of Triton X-114 (0.05% v/v) provided detection limits of 8.8, 4.9, 7.8 and 11 ng mL^{-1} for Zn, Ni, Co and Pb, respectively.

Dynamic linear range of concentration, relative standard deviation and the enhancement factors are as follows:

8.8-80, 4.9-3000, 7.8-2000, 11-6000 ngmL^{-1}; 5.2%, 4.3%, 7.8%, 3.2%;
13, 15.5, 15, 29.6 for Zn, Ni, Co and Pb respectively

Key words: Cloud Point extraction, 2-guanidino benzimidazole, atomic absorption, Zn, Ni, Co, Pb.

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1. INTRODUCTION

The elements Zn, Ni, Co, and Pb that together are commonly found in most of the samples (ores, industrial wastes etc) are either essential or toxic for the human body /1,2/. Hence their simultaneous determination, especially in low concentration, is important. Flame atomic absorption spectrometry has wide application and is a powerful analytical tool; however, its sensitivity is not sufficient for low concentration. Hence preconcentration and separation of these metals are required. Separation and preconcentration based on cloud point extraction in the micellar solution using surfactant are finding important applications in analytical chemistry due to its simplicity, low cost, and its being environmentally friendly /3-8/.

2. EXPERIMENTAL

2.1 Apparatus

A Varian SpectrAA 220 flame atomic absorption spectrometer, coupled with D2 lamp for back ground correction, was used to measure the concentration of Zn, Co, Ni and Pb in the surfactant – rich phase. A Metrohm model 692 pH /Ion meter, and Julabo MP5 open batch circulator were used.. The separation of phases was accomplished with Herueus Labofuge 300 centrifuge with necessary rotor.

2.2 Reagents

The non-ionic surfactant Triton X-114 from Fluka chemical company was used as received. 2-Guanidinobenzimidazole(2-GBI) with analytical grade and stock standard solutions of Zn, Co, Ni, and Pb, with concentration of 1000 μg/ml were obtained from Aldrich and Merck. Working standard solutions were prepared by appropriate dilution of the stock standard solutions.

All other reagents and chemicals were of highest purity (Merck) and all solutions were prepared in double distilled deionized water.

All the glassware was kept in choromic acid and washed thoroughly with distilled water before use.

3. PROCEDURE

50 ml aliquot of the solution containing Zn, Pb, Co, and Ni (20 – 500 ng/ml), 2-GBI (1×10^{-3} M), sodium nitrate (1×10^{-2} M) as a counter anion Triton X -114 (0.05% V/V) whose pH was adjusted to 8.5 by using concentrated NaOH solution was subjected to CPE. The mixture was heated in a thermostated bath at 65±1°C for 10 min. The two phases were separated by centrifuging the mixture for 10 min at 3200 rpm. On cooling in an ice-water mixture for 5 min, the surfactant – rich phase became viscous and the upper aqueous phase was separated with the aid of a pipette. The surfactant-rich phase was diluted to 1.5 ml using ethanolic solution of HNO_3 (0.1 M) and then aspirated into the flame for AAS measurements.

Ni – Cd and Co cakes preparation

0.1 g each of Ni, Cd and Co were mixed thoroughly and dried at 110 °C. The cake was ground, homogenized, taken separately and leached completely using aqua regia (1:3 HNO_3/HCl). The resulting solution was filtered and diluted up to 100 ml with distilled water.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

In order to investigate the influence of pH, the extraction was carried out in the pH range of 2 – 11. As can be seen from Fig. 1, the analytical signal for all cations increased after pH 6 and became constant after pH 8.5. Hence pH 8.5 was adequate for further studies.

3.2 Effect of 2-GBI Concentraion

The effect of ligand concentration on extraction yield was studied in the range of 0-2 × 10^{-3} M. Figure 2 shows that analytical signals are maximum at 1 × 10^{-3} M. Higher ligand concentration shows no considerable change, hence this concentration was selected as optimum concentration for experiments.

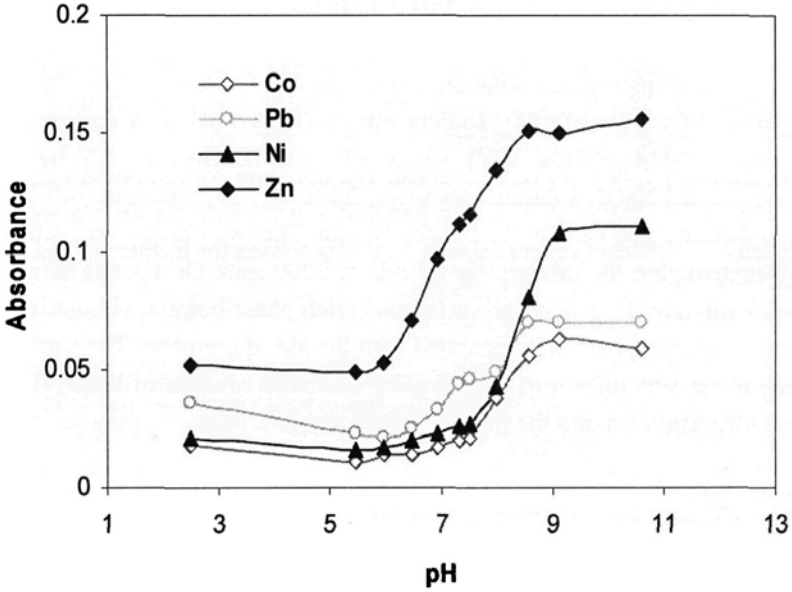

Fig. 1: Effect of pH

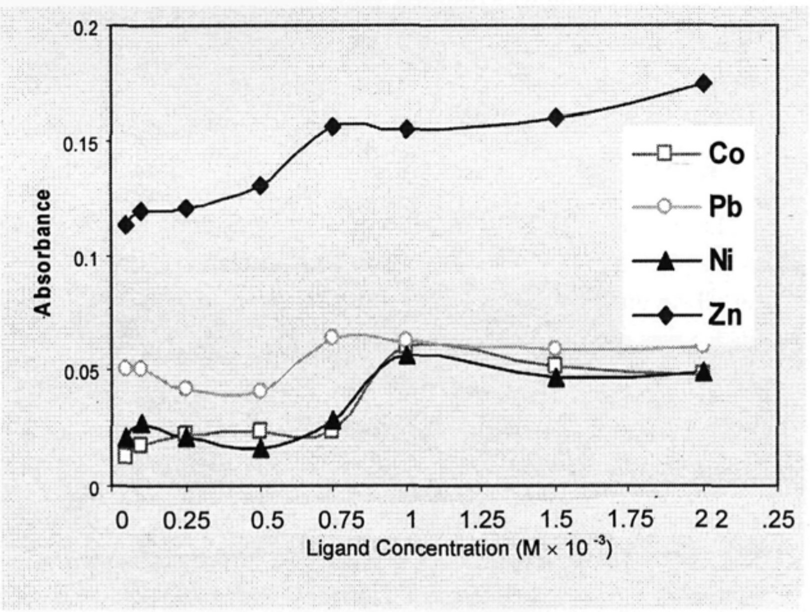

Fig. 2: Effect of 2-GBI concentration

3.3 Effect of Triton X-114 concentration

The analytical signal variation as a function of the Triton X-114 concentration is shown in Fig. 3, when a 50 ml solution containing cations and all the reagents in the presence of various concentrations of Triton X – 114 (from 0 – 1 % V/V) was extracted. The optimum concentration found in the range of 0 – 0.05% V/V for Zn and 0.05 – 0.1% V/V for Pb, Co and Ni, respectively. Concentration of 0.05% V/V was chosen for further studies.

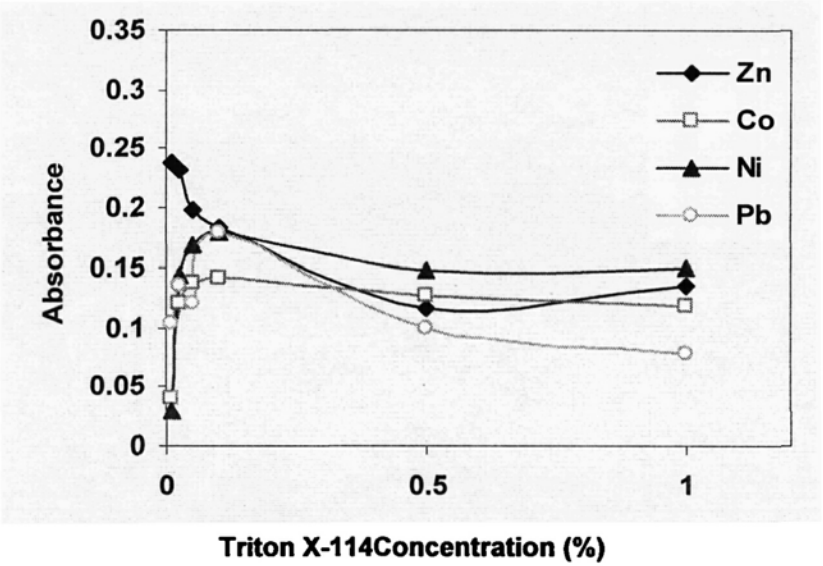

Fig. 3: Effect of Triton X-114 concentration

3.4 Effect of nitrate concentration

In order to study the effect of ionic strength and counter anion concentration - to chelate the experiment was carried out in the presence of a constant amount of all other reagents while varying the nitrate concentration from 1×10^{-3} to 1×10^{-1} M and finally 1×10^{-2} M was selected for further studies (Table 1). The absorbance remained almost constant beyond 1×10^{-2} M nitrate.

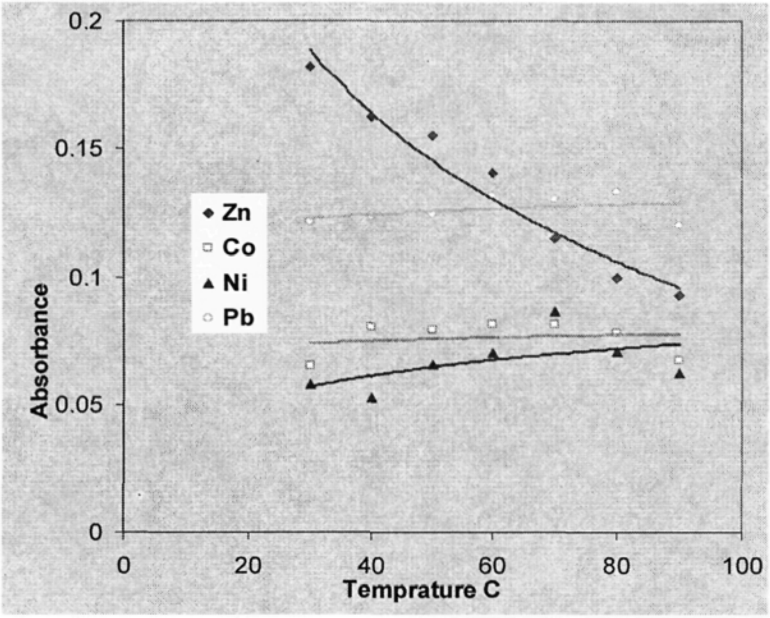

Fig. 4: Effect of equilibrium temperature

Table 1

Effect of nitrate concentration

NO_3^- (mol/L)	Absorbance			
	Zn	Co	Ni	Pb
1×10^{-3}	0.17	0.06	0.07	0.12
2×10^{-3}	0.20	0.07	0.08	0.18
4×10^{-3}	0.28	0.08	0.09	0.25
1×10^{-2}	0.50	0.13	0.18	0.30
4×10^{-2}	0.53	0.12	0.17	0.30
1×10^{-1}	0.50	0.13	0.16	0.32

3.5 Effect of equilibrium temperature and time

The effect of temperature and equilibration time on the analytical signal was investigated in the rang of 30 – 90 °C and 5 – 35 min, respectively, while keeping all other parameters constant. The results are given in Figs. 5 & 6. Since the shortest time and the lowest temperature is desired, the temperature of 65 °C and equilibration time of 10 min were selected.

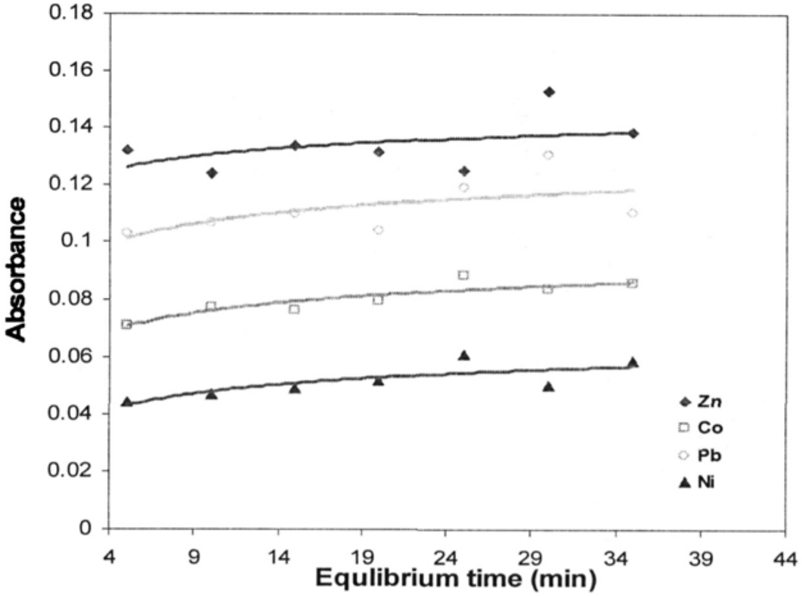

Fig. 5: Effect of equilibrium time

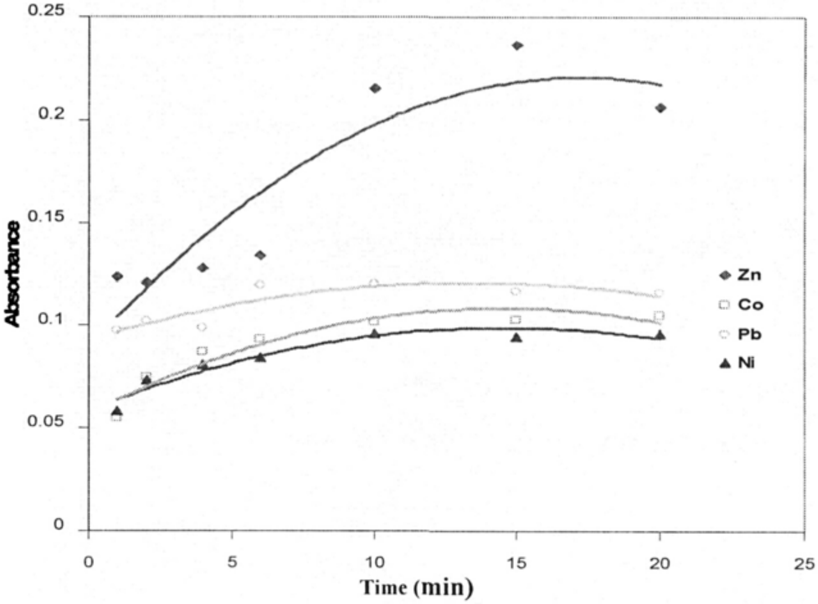

Fig. 6: Effect of centrifugation time

3.6 Effect of centrifugation time

The influence of centrifugation time on the separation of the phases was studied from 1 – 20 min with the velocity of 3200 rpm, 10 min was chosen as an appropriate time (Fig. 6).

3.7 Analytical performance of the method

Calibration graphs were obtained by preconcentrating 50 ml of standard solution with known concentration of analytes under the experimental conditions specified in the procedure. The results are shown in Table 1. The relative standard deviations were obtained by 8 replicate measurements. The limits of detection were calculated as three times the standard deviation of blank signals.

$$\mathrm{LOD} = S_B.k/m$$

3.8 Enhancement factor

This is defined as the ratio of absorbance of preconcentrated samples to the absorbance of unpreconcentrated samples were 29.5, 15.5, 15, 13, for Pb, Ni, Co, and Zn, respectively.

$$E_f = A_{pre}/A_{Unpre}$$

3.9 Interferences

In order to investigate the selectivity of preconcentration. a 10 ml sample of solution containing 20 ng/ml of Zn, 500 ng/ml of Co, Ni, Pb was extracted under the spesified experimental conditions. The results are given in Table 2 and reveal that there is no significant interference by the diverse ions present at moderate concentration.

4.0 ANALYSIS OF REAL SAMPLES

In order to evaluate the applicability of the proposed method it was applied for determination of Zn, Pb, Co and Ni in the Ni – Cd and cobalt filter cakes (the Zinc plant residues from Zanjan province).

Table 2
Analytical performance

Element	**Dynamics range (ng/ml)**	**Regression equation**	**R^2**	**RSD (%)**	**LOD[(4)] (ng/ml)**
Zn	8.8 – 80	$A(1) = 0.034C^{(2)} + 0.4534$	0.9895	5.2[(3)]	8.8
Ni	4.9 – 3000	$A = 0.0001C + 0.0544$	0.9918	4.3	4.9
Co	7.8 – 2000	$A = 0.0003C + 0.612$	0.9963	7.8	7.8
Pb	11 – 6000	$A = 8*10^{-5} + 0.3792$	0.9953	3.2	11

1: Absorbance
2: Concentration (ng/ml)
3: number of measurements is eight
4: limit of detection

Ni-Cd and Co cakes preparation

To prepare the sample solution, 0.1 g of each cake was dried at 110° C, ground and homogenized, taken separately and leached completely using aqua regia (1:3 HNO_3/HCl). The resulting solution after cooling was filtered and diluted up to 100 ml with distilled water.

The results given in Table 3 show that the method can be applied to determination of the above-mentioned elements in the real samples.

Table 3
Effect of diverse ions on recovery of elements

Ions	Concentration (μg/ml)	Recovery (%)			
		Zn	Ni	Co	Pb
Na^+	400	103.9	102.3	100.8	101.6
K^+	400	102.5	100.7	97.6	95.4
Ca^+	400	105.3	106.9	103.4	107.9
Mg^{2+}	400	107.1	106.5	106.4	98.1
Cr^{3+}	15	101.4	102.3	100.6	99.8

Table 3 (continued)

Fe^{3+}	15	100.4	94.7	96.3	98.7
Mn^{2+}	20	98.6	97.6	99.1	100.9
Cu^{2+}	15	92.4	94.2	100.0	95.7
Cd^{2+}	20	99.6	107.3	101.6	99.8
Pb^{2+}	20	98.9	102.6	100.7	---
Co^{2+}	5	91.8	93.6	---	98.8
Ni^{2+}	10	98.3	---	92.5	100.0
Zn^{2+}	10	---	100.7	101.6	95.1

Solution containing 20 ng/ml Zn, 500 ng/ml Co, Ni, Pb, 0.01 M sodium nitrate, 0.05 V/V Triton X-114, 1×10^{-3} M 2-GBI

5. CONCLUSION

We could extend the application of cloud point extraction to the simultaneous preconcentration of Ni, Co, Zn and Pb as a prior step to their determination at micrograms/ liter levels by FAAS. The method is simple, sensitive, inexpensive and nonpolluting.

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Table 4

Determination of Zn, Co, Ni & Pb in Ni-Cd and Co cakes

Samples	Spiked(ng/ml)				Measured (ng/ml)				Recovery			
	Zn	Pb	Co	Ni	Zn	Pb	Co	Ni	Zn	Pb	Co	Ni
1) Ni-Cd Cake[a]	---	---	---	---	249	nd[c]	nd	nd	---	---	---	---
	20	500	500	500	273	500	489	488	110	100	97.8	97.6
2) Ni-Cd Cake[b]	---	---	---	---	over[d]	nd	127	over	---	---	---	---
	---	500	500	---	---	500	631	---	---	100	100.6	---
3) Co Cake[a]	---	---	---	---	52.8	nd	nd	nd	---	---	---	---
	20	500	500	500	70.6	452	500	473	96.9	90.4	100	94.6
3) Co Cake[b]	---	---	---	---	over	720	1927	830	---	---	---	---
	---	500	500	500	---	1251	2432	1373	---	102.5	100.2	103.2

a: 0.1 ml of sample solution in 50 ml final volume

b: 5 ml of sample solution in 50 ml final volume

c: not detected

d: over of dynamic range