

Simultaneous Cloud Point Extraction and Determination of Zn, Co, Ni and Pb by Flame Atomic Absorption Spectrometry, Using 2-Guanidinobenzimidazole as the Complexing Agent

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A simple Cloud Point Extraction (CPE) method has been proposed for the simultaneous preconcentration and determination of Zn(II), Co(II), Ni(II) and Pb(II). The pH of the sample solution was adjusted to 9 with buffer solution and the cations were complexed with 2-guanidinobenzimidazole. Triton X-114 was added as a non-ionic surfactant. After the phase separation at $40 \pm 1^\circ\text{C}$, the surfactant-rich phase was diluted to 1.5 ml using an ethanolic solution of HNO_3 and the analytes were determined by flame atomic absorption spectrometry. The influence of variables, such as pH, ligand concentration, surfactant concentration, etc. upon the complexation and extraction, was studied. Preconcentration of a 50 ml sample solution in the 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. The dynamic linear range of concentration, relative standard deviation and enhancement factors are as follows: 8.8-80, 4.9-3000, 7.8-2000, 11-6000 ng mL⁻¹; 5.2%, 4.3%, 7.8%, 3.2% and 13, 15.5, 15, 29.6 for Zn, Ni, Co and Pb, respectively.

INTRODUCTION

The elements Zn, Ni, Co and Pb, which are commonly found together in most samples (ores, industrial wastes, etc.), are either essential or toxic for humans and plants in certain concentrations [1,2]. Hence, their simultaneous determination, especially in low concentrations, is of great interest.

Flame atomic absorption spectrometry has wide applications for this purpose as a powerful analytical tool, but, its sensitivity is not usually sufficient for low concentrations. Hence, preconcentration and separation of the metals are required prior to their determination by FAAS. Different methods and reagents have been reported for this purpose [3-5].

Separations and preconcentrations, based on cloud point extraction in the micellar solutions, using surfactants, are finding important applications in analytical chemistry. The principles and advantages of CPE have been well established in recent years. The use of CPE methodology offers an alternative to more conventional extraction systems and permits the design of extraction systems which are simple, cheap, highly efficient and of lower toxicity than LLE (Liquid-Liquid Extraction) systems [6-11]. 2-guanidinobenzimidazole (2-GBI) is an electron donating molecule. Recent studies have revealed that it can form a stable and selective 1:2(M(2-GBI)²⁺) complex with Co²⁺ and Zn²⁺ ions [12]. It has two nitrogen atoms located in such a position that allows each to form a covalent bond with M²⁺ ions. 2-GBI has been used for the solvent extraction of Co²⁺ [13] and solid phase extraction of Zn²⁺ and Co²⁺ [14]. Considering the advantages of CPE and extractive properties of 2-GBI, the authors decided to carry out the present work. To the best of their knowledge this is the first report on CPE of metal ions using 2-GBI.

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EXPERIMENTAL

Apparatus

A Varian model spectrAA 220 flame atomic absorption spectrometer with a Deuterium lamp background correction was used to measure Zn, Co, Ni and Pb in the surfactant-rich phase. The operating conditions were those recommended by the manufacturer. The measurements were performed in an air-acetylene flame. The acetylene flow rate was adjusted to obtain the maximum signal. A Metrohm model 692 pH /Ion meter was used for adjusting the pH of the solution. A Julabo MP5 open bath circulator was operated for controlling the temperature. The separation of phases was accomplished with a Herueus model Labofuge 300 centrifuge with the necessary rotor.

Reagents

The non-ionic surfactant, Triton X-114, was obtained from the Fluka chemical company and was used as received. 2-guanidinobenzimidazole (2-GBI), with analytical grade and stock standard solutions of Zn, Co, Ni and Pb, with concentrations of 1000 $\mu\text{g/ml}$, were obtained from Aldrich and Merck. Working standard solutions were prepared by appropriate dilution of the stock standard solutions. A stock buffer solution (0.1 M) was prepared by dissolving appropriate amounts of potassium hydrogen phthalate (Merck) and sodium tetra borate (Merck) in double distilled water and then adjusting to desired pH values by adding dilute HCl or NaOH solutions.

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

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

Procedure

A 50 ml aliquot of the solution containing Zn, Co, Ni and Pb (20 - 500 ng/ml), 2-GBI (1×10^{-3} M), sodium nitrate (1×10^{-2} M) as a counter ion source and Triton X-114 (0.05% V/V), whose pH was adjusted to 9 by using 1 ml of a sodium tetraborate solution, was subjected to Cloud Point Extraction (CPE). The mixture was heated in a thermostated bath at $40 \pm 1^\circ\text{C}$ for 10 mins. The two phases were separated by centrifuging the mixture for 10 mins. at 3200 rpm. On cooling in an ice-bath for 5 mins, the surfactant-rich phase became viscous and the upper aqueous phase was separated with the aid of a pipette. In order to decrease the viscosity and facilitate sample handling, the surfactant-rich phase was diluted to 1.5 ml using an ethanolic solution of HNO_3 (0.1 M) and then aspirated into the flame using conventional nebulization.

RESULTS AND DISCUSSION

Effect of pH and Buffer Concentration

Extraction yield depends on the pH at which complex formation is carried out. In order to investigate the influence of pH, the extraction was performed in different pH buffer solutions. As can be seen from Figure 1, the analytical signal for all cations increases after pH 6 and becomes constant after pH 8.5. Hence, pH 9 was chosen as an adequate pH value for further studies. In the meantime, it was observed that above 0.75 ml of buffer solution (0.1 M) added to the test solution caused no variation of extraction yield. Thus, 1 ml of buffer was added in all further experiments.

Effect of 2-GBI Concentration

The effect of ligand concentration on extraction yield was studied in the concentration range of $0 - 2 \times 10^{-3}$ M. Figure 2 shows that analytical signals become maximum at 1×10^{-3} M ligand, above which no considerable change of signal was observed. Hence, this concentration was selected as the optimum for further experiments.

Effect of Triton X-114 Concentration

The analytical signal variation, as a function of the Triton X-114 concentration, is expressed in Figure 3, when a 50 ml solution containing cations and all the reagents in the presence of various concentrations of Triton X-114, ranging from 0.01-0.5% (V/V), was extracted. The signal is maximum in the concentration range of 0.02-0.05(V/V) for Zn and 0.05-0.1% (V/V) for Pb, Co and Ni. At concentrations lower than these

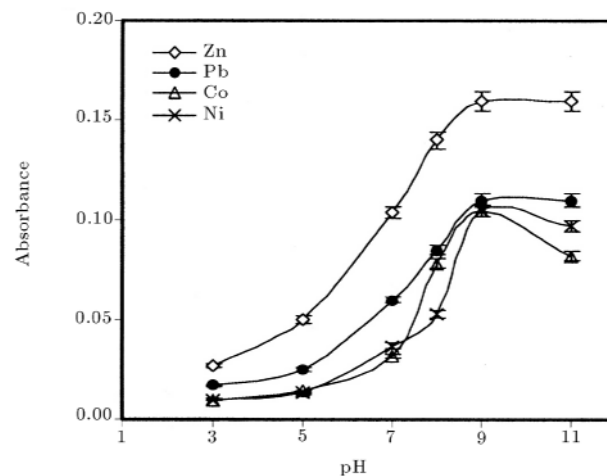


Figure 1. Effect of pH on the analytical signals of Zn (40 ngml^{-1}), Co, Ni and Pb (500 ngml^{-1} each). Conditions: 1×10^{-3} mol l^{-1} 2-GBI, 1×10^{-3} mol l^{-1} NO_3^- , 0.02% (VN) Triton X-114 at 40°C .

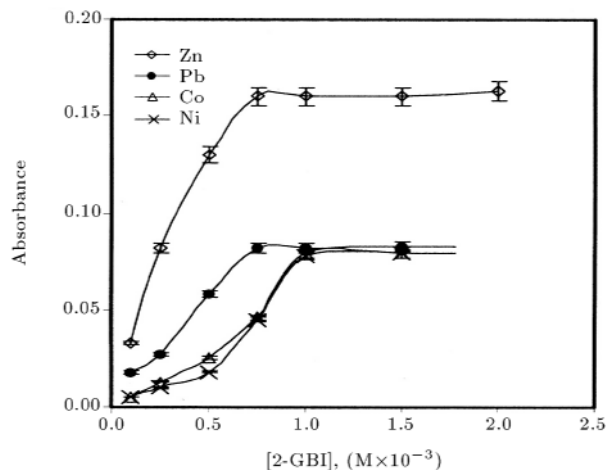


Figure 2. Effect of 2-GBI concentration on the analytical signals of Zn (40 ngml^{-1}), Co, Ni and Pb (500 ngml^{-1} each). Conditions: pH 9, $1 \times 10^{-3} \text{ mol l}^{-1} \text{NO}_3^-$, 0.02% (VN) Triton X-114 at 40°C .

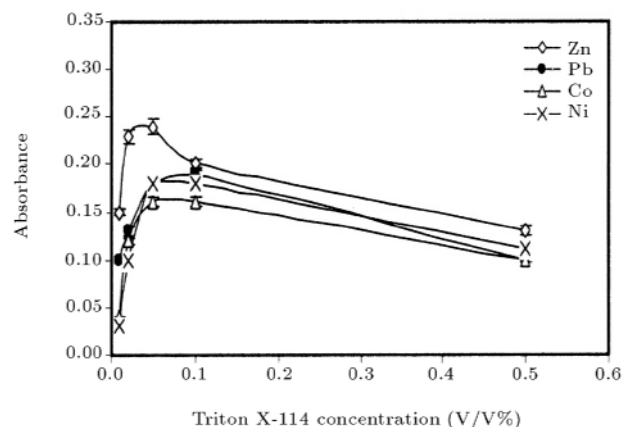


Figure 3. Effect of Triton X-114 concentration on the analytical signals of Zn (40 ngml^{-1}), Co, Ni and Pb (500 ngml^{-1} each). Conditions: pH 9, $1 \times 10^{-3} \text{ mol l}^{-1}$ 2-GBI, $1 \times 10^{-3} \text{ mol l}^{-1} \text{NO}_3^-$ at 40°C .

ranges, the extraction efficiency of the complexes was low, which may be due to the inadequacy of the assembly to entrap the complex. At concentrations higher than these ranges, the signals decrease slightly because of the increment in the volume and the viscosity of the surfactant-rich phase. Hence, a concentration of 0.05% (V/V) was chosen as optimum for further studies.

Effect of Counter Ion

Since 2-GBI forms a cationic complex, to achieve electroneutrality, which is necessary for extraction, some anion should accompany the cationic complex into the organic phase. In order to study the influence of the counter anion (type and concentration) associating to the cationic chelate, the experiment was carried out in the presence of different salts, such as NaClO_4 , NaNO_3 ,

Table 1. Effect of anion type on the signals.

Anion ($1 \times 10^{-2} \text{ mol l}^{-1}$)	Absorbance			
	Zn	Co	Ni	Pb
NO_3^-	0.5	0.13	0.18	0.3
ClO_4^-	0.56	0.15	0.2	0.35
CH_3COO^-	0.3	0.08	0.11	0.15
SCN^-	0.3	0.1	0.1	0.2

NaCH_3COO and KSCN , with a final concentration of $1 \times 10^{-2} \text{ M}$, while the other experimental variables remained constant. The obtained results are almost similar for NO_3^- and ClO_4^- , although nitrate has lower lipophilicity than perchlorate (Table 1). The reason for choosing nitrate as a counter anion is that it is reported to be more acceptable for AAS experiments [15]. Hence, the effect of nitrate ion concentration was investigated in the range of $1 \times 10^{-3} \text{ M}$ to $1 \times 10^{-1} \text{ M}$, while maintaining other parameters constant. Since the absorbance remained almost constant beyond $1 \times 10^{-2} \text{ M}$ nitrate solution, it was selected as optimum concentration (Figure 4).

Effect of Equilibration Temperature and Time

The effect of temperature and equilibration time on the analytical signal was investigated in the range of $30\text{--}90^\circ\text{C}$ and 5–35 min, respectively, while keeping all other parameters constant. The results are given in Figure 5. It is desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between the completion of extraction and efficient separation of phases. Thus, a temperature of 40°C and equilibration time of 10 min were selected.

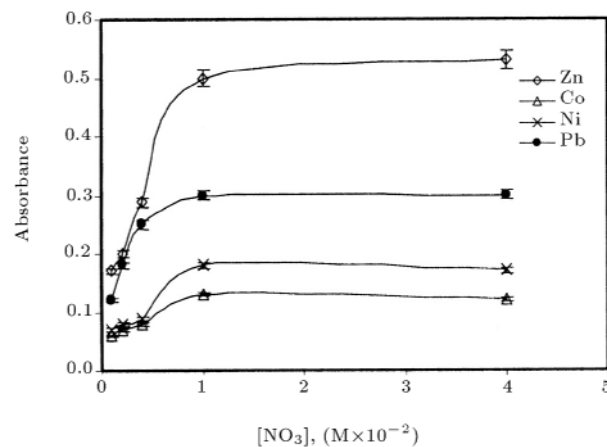


Figure 4. Effect of nitrate ion concentration on the analytical signals of Zn (40 ngml^{-1}), Co, Ni and Pb (500 ngml^{-1} each). Conditions: pH 9, $1 \times 10^{-3} \text{ mol l}^{-1}$ 2-GBI, 0.05% (VN) Triton X-114 at 40°C .

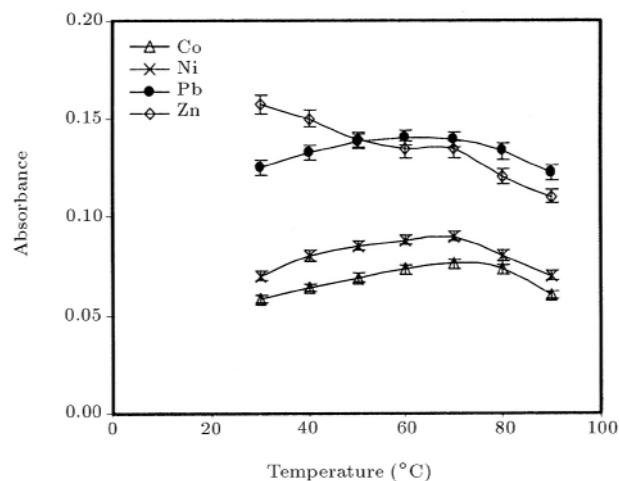


Figure 5. Effect of equilibration temperature on the analytical signals of Zn (20 ng ml^{-1} Co, Ni and Pb (300 ng ml^{-1} each). Conditions: pH 9, $1 \times 10^{-3} \text{ mol l}^{-1}$ 2-GBI, $1 \times 10^{-2} \text{ mol l}^{-1} \text{NO}_3$, 0.05% (VN) Triton X-114.

Effect of Centrifugation Time

The influence of centrifugation time on the separation of the phases was studied from 1 to 20 min with a speed of 3200 rpm. From the obtained results expressed in Figure 6, 10 mins was chosen as an appropriate time.

Analytical Performance of the Method

Calibration graphs were obtained by preconcentrating 50 ml of standard solutions containing all analytes under the optimum experimental conditions specified in the procedure. The relative standard deviations were obtained by eight replicate measurements and the limit of detection for each analyte was calculated as being three times the standard deviation of its blank signal. All results are shown in Table 2.

Enrichment Factor

Enrichment factor is defined as the ratio of absorbance of preconcentrated samples to the absorbance of unpre-

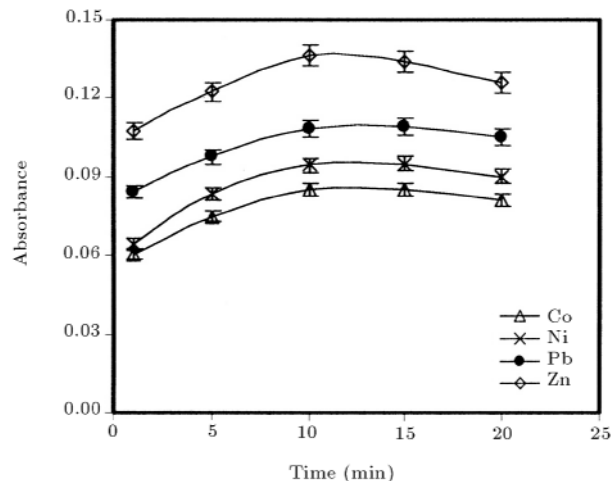


Figure 6. Effect of centrifugation time on the analytical signals of Zn (20 ng ml^{-1}), Co, Ni and Pb (300 ng ml^{-1} each). Conditions: pH 9, $1 \times 10^{-3} \text{ mol l}^{-1}$ 2-GBI, $1 \times 10^{-2} \text{ mol l}^{-1} \text{NO}_3$, 0.05% (VN) Triton X-114.

concentrated samples. Here, they were 13, 15, 15.5 and 29.5 for Zn, Co, Ni and Pb, respectively.

Interferences

In order to investigate the selectivity of the method a 10 ml of sample solution containing 20 ng/ml of Zn and 500 ng/ml of Co, Ni and Pb was extracted under the specified experimental conditions. The results given in Table 3 reveal that there is no significant interference by the diverse ions present at moderate concentrations.

Analysis of Real Samples

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

To prepare the sample solution, 0.1 g of each cake which was dried at 110°C , ground and homogenized, was taken separately and leached completely using aqua regia (1:3 HNO_3/HCl). The resulted solution

Table 2. Analytical performance of the method.

Element	Dynamic Range (ng/ml)	Regression Equation	R ²	RSD, % (n = 8)	LOD ^d (ng/ml)
Zn	8.8-80	$A^a = 1.4 \times 10^{-2} C^b + 0.053$	0.9895	5.2(20) ^c	8.8
Ni	4.9-3000	$A = 1 \times 10^{-4} C + 0.054$	0.9918	4.3(80)	4.9
Co	7.8-2000	$A = 3 \times 10^{-4} C + 0.012$	0.9963	7.8(80)	7.8
Pb	11-6000	$A = 8 \times 10^{-4} C + 0.0037$	0.9953	3.2(100)	11

^aA: Absorbance;

^bC: Concentration (ng/ml);

^c: Values in parentheses are the concentrations (ng/ml) of Zn, Ni, Co and Pb for which the RSD was obtained;

^dLOD: Limit of detection, calculated as three times the standard deviation of the blank signal.

Table 3. Effect of diverse ions on recovery of elements.

Ions	Concentration ($\mu\text{g/ml}$)	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
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.

Table 4. Determination of Zn, Co, Ni and Pb in Ni-Cd and Co filter 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
4) 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: nd: Not detected; d: Out of dynamic range.

after cooling was filtered and diluted up to 100 ml with distilled water. The proposed method was applied and the results, given in Table 4, show the applicability of the method for determination of the above mentioned elements in the Ni-Cd and Co filter cakes.

CONCLUSION

Cloud point extraction is proposed for the preconcentration of Zn, Co, Ni and Pb, as a step prior to determination of ng ml⁻¹ levels by FAAS. The difference between this work and earlier reports is the extraction by an ion-pair formation mechanism and simultaneous preconcentration of Zn, Co, Ni and Pb.

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