

## Preconcentration and Determination of $Zn^{2+}$ and $Fe^{3+}$ in Waste Water Samples by Cloud Point Extraction Method

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**Abstract :** A simple, low cost and highly sensitive method based on cloud point extraction (CPE) used for separation/preconcentration of zinc and iron has been described. After complexation with new ligand, Dithizone (DZ) followed determination of these ions by flame atomic absorption spectrometry. The ions are quantitatively extracted to the phase rich in Triton X-114 following centrifugation. The parameters which affecting the separation phase and detection process, were optimized such as pH, DZ, Triton X-114. Calibration graph showed linear trend in rang of 0.2-2.0  $\mu g\ l^{-1}$  for both analyts. The analyst were determined in petrochemical waste water sample which gave satisfactory results.

**Key words:** Cloud point extraction, zinc, iron, dithizone.

### Introduction

Determination of trace metals such as zinc and iron in environmental samples is a subject of considerable interest, because trace metals play important roles in biological processes both as essential components and as toxics<sup>1</sup>.

The metal elements exist in many environmental samples such as soil, water and plants. For these reason, establishing rapid and accurate methods for the determination of the cations for industrial process, quality and pollution control is important. Several analytical techniques such as flame atomic absorption spectrometry (FAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of trace zinc and, iron with sufficient sensitivity for most of applications<sup>2,3</sup>. However, the determination of trace metal ions in real samples is difficult due to various factors, particularly their low concentrations and matrix effects. Pre-concentration and separation such as liquid-liquid or solid phase extraction<sup>4</sup>.

The cloud point extraction (CPE) is an interesting and efficient alternative because reduces the consumption of and exposure to solvents, the disposal costs and the extraction time, and surfactants are not toxic, not volatile and not easily flammable<sup>5</sup>. The cloud point extraction (CPE) has been used for the extraction and pre-concentration of metal ions after the formation of sparingly water-soluble complexes and then determination the complex in the surfactant-rich phase by different spectrometric technique. In the present work, we report the results obtained in a study of the CPE for simultaneous and selective preconcentration of zinc and iron after the

formation of a complex with ligand, DZ and later analysis by flame atomic absorption spectrometry using Triton X-114 as surfactant. The proposed method is also applied to the determination of the analytes in some environmental samples such as waste water, samples which shown satisfactory results.

## Material And Method

### Reagents and solutions

All solutions were prepared with ultra pure water (obtained from HAMILTON, England) Laboratory glass was kept overnight in a 10% (V/V) HNO<sub>3</sub> solution and then rinsed with deionized water. All reagents were made from Merck.

The stock zinc and iron solutions (1000 mg l<sup>-1</sup>) were prepared by Merck standard solutions.

The nonionic surfactant Triton X-114, 0.3% (W/V) prepared by dissolving 0.30 gr surfactant Triton X-114 made up to 100 ml with distilled water. A solution of 1×10<sup>-1</sup> mol L<sup>-1</sup> DZ was prepared by dissolving 0.0249 gr of this reagent in 50 ml Ethanol. A buffer solution of pH 5 was prepared by using acetic acid and NaOH 0.1 M solution.

### Apparatus

A Varian 240 FS double beam atomic absorption spectrophotometer (AAS) with hollow cathode lamp operating at 5 mA was used for the determination of zinc and iron in the surfactant-rich phase, which were made at 213.9 and 248.3 nm respectively. An adjustable-capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomization. Deuterium lamp background correction was employed to correct for the non-specific absorbance. Operation in a double beam-background correction mode was imperative due to the complexity of the aspirated sample, which apart from the target metal and excessive chelating agent, causing a suppression of the signal. Measurements were performed in the integration mode.

A centrifuge (Hettich) was used to accelerate the phase separation process. A Methrohm model 780 pH-meter was used for pH measurements. An electronic analytical balance (AE 200 Mettler) was used for weighting the solid materials. A thermostated water bath (Memert) was employed to maintain the experimental temperature.

### Procedure

For the cloud point extraction, an aliquots of 10 ml of a solution containing zinc and iron, and 1 ml of buffer solution pH=5, 2 ml Triton X-114 0.3% (W/V), 0.2 ml of DZ 1×10<sup>-1</sup> mol l<sup>-1</sup> were placed in a centrifuge tube and heated in a thermostat water bath at 43°C for 15 min. After heated, the resultant solution was subjected to centrifugation at 4000 rpm for 10 min for phase separation, and then cooled in an ice-water for 10 min in order to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was easily decanted by simply inverting the tube. To decrease the viscosity of the surfactant phase and rich facilitate sample handling, 2 ml of methanol was added. The resultant solution was introduced into the flame by conventional aspiration.

### Preparation Of Real Samples

#### Waste water samples

Waste waters were collected from some Mahshar petrochemical industry (These locked in Mahshar city and is the important river in Khozestane province). They were filtered through Watman No. 42 and stored in glass bottles at 4°C. Then the samples were ready for purposed procedure.

## Results And Discussion

### Effect of pH

The pH plays a unique role on metal-chelate formation and subsequent extraction, and is proved to be a main parameter for CPE (6). The influences of pH of the aqueous solutions on the extraction yield of Zn (II) and Fe

(II) as DZ chelate were investigated in the pH range 1-11. For obtain better sensitivity pH values, several buffer agents such as phosphate, carbonate, boric acid / sodium hydroxide, and universal buffer were tested for pH adjustment, the best result was found for acetic acid/ sodium hydroxide buffer solution. Fig. 1 shows that the best recovery is in pH 5 on extraction of analytes complex.

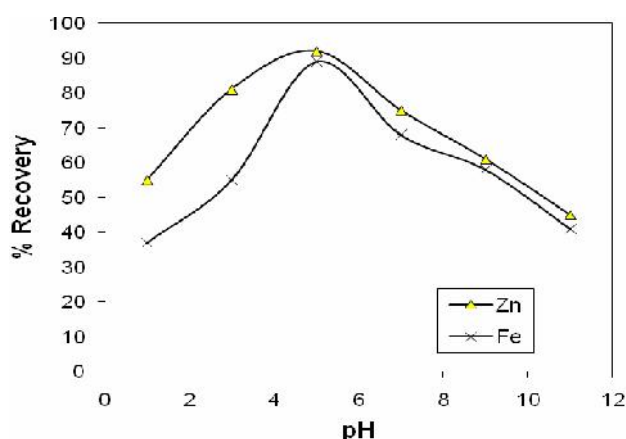
**Effect of DZ Concentration**

The amount of chelating agent is another important indicator as to whether the chelating action processed completely. The effect of DZ concentrations on the recovery were determined in the range of 0.01-0.30 ml of 0.1 M. As is shown in Fig. 2 on adding over 0.2 ml solution, the extraction efficiency were high at 0.2 ml of 0.1 mol l<sup>-1</sup> DZ solution in ethanol was chosen.

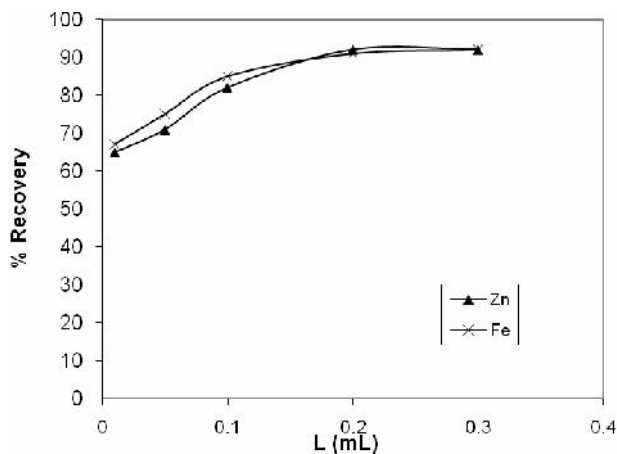
**Effect of Triton X-114 concentration**

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio (V<sub>org</sub>/V<sub>aq</sub>), thus improving the concentration factor.

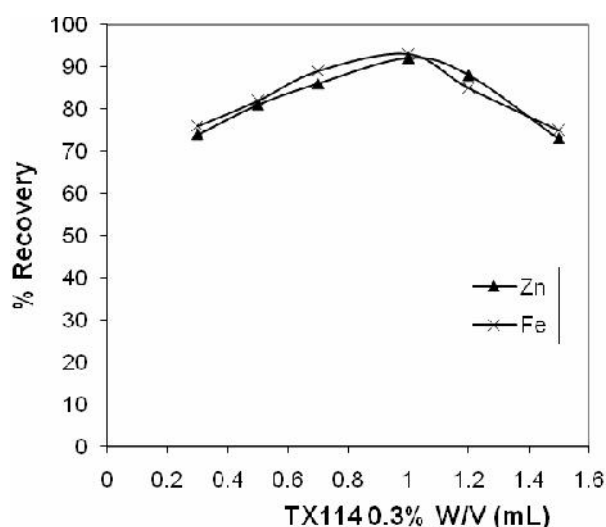
Fig. 3 has shown the effect of TritonX-114 concentration on the CPE pre-concentration of zinc and iron. The signals are increased as the Triton X-114 concentration increased from 0.30- 1.0% (W/V) when, Triton X-114 concentration was increased larger than 1.0% (W/V), the signals was decreased. Hence a low concentration of Triton X-114, 1.0% (W/V), was employed for the rest of this work.



**Fig. 1.** Effect of pH on recovery of analytes



**Fig. 2.** Effect of the DZ amount on the recovery of analyst ions.



**Fig. 3.** Effect of the Triton X–114 concentrations on the on the extraction recovery of the ions.

### Practical parameter

The dependence of extraction efficiency on equilibration temperature and time were studied within a range of 30 – 60 °C and 5–25 min, respectively. The results showed that an equilibration temperature of 43 °C and an equilibration time of 15 min are enough to get quantitative extraction of the ions. The effect of the centrifugation time on the extraction efficiency was also studied within a range of 5–25 min. A centrifugation time of 10 min at 4000 rpm was selected for the entire procedure, since analytes extraction in this time is almost quantitative.

### Figures of merit

Calibration graphs were obtained in optimum conditions and for Zn and Fe were linear from 0.2-2.0 mg l<sup>-1</sup> with a correlation coefficients of 0.9887 and 0.9963 respectively. The relative standard deviation (RSD, n=5) for 1.0 mg l<sup>-1</sup> concentration of zinc and iron were 1.5% and 1.4% respectively.

### Determination of zinc and iron in waste water:

In order to test the reliability of the proposed methodology suitable for the assaying of analyst in waste water samples. For this purpose, 10ml of each of the samples were pre-concentrated with 0.3% (w/v) Triton X– 114 and a 0.2 ml of DZ (0.01 M), following the proposed procedure. The results are shown in Table 1.

**Table 1.** Determination of Zn and Fe in waste water of Ghadir petrochemical samples.

Sample	Zn <sup>2+</sup> (µg L <sup>-1</sup> ) <sup>a</sup>		% Recovery
	Added	Found	
Waste water 1	-	ND	-
	40	45	113
	50	57	114
Waste water 2	-	ND	-
	40	42	105
	50	54	108

Sample	Fe <sup>2+</sup> (µg L <sup>-1</sup> ) <sup>a</sup>		% Recovery
	Added	Found	
Waste water 1	-	ND	-
	50	55	110
	100	103	103
Waste water 2	-	ND	-
	50	47	94
	100	104	104

a) After appropriate dilution

#### 4. Conclusion

This paper proposes a DZ ligand for the preconcentration and determination of trace levels of zinc and iron by CPE in waste water samples for their determination by flame atomic absorption spectrometry (FAAS). The methodology offers a simple, rapid, sensitive, low cost, good extraction efficiency and lower toxicity than those using organic solvents.

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#### References

1. Stanley E. Manahan Environmental chemistry, Pergamon Press: NewYork, 2002.
2. Koksai J., Synek V., Janos P., Talanta, 2002, 58:325.
3. Chen J., Teo K. C., Anal. Chim. Acta, 2001, 450, 215-222.
4. Shokrollahi A., Ghaedi M., Hosseini O., of Hazardous Materials, 2008,160:2-3, 435-440.
5. Thanasarakhan W., Liawruangrath S., Wangkarn S., Talanta, 2007, 71: 5,1849-1855.
6. Jeffery G. H., Bassett J., Mendham J., Denney R.C., Vogel's Textbook of Quantitative Chemical Analysis, 5th edition (November 1989), John Wiley & Sons Inc,1989.

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