



Dispersive liquid–liquid microextraction technique combined with UV–Vis spectrophotometry for determination of zirconium in aqueous samples

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ABSTRACT

Dispersive liquid–liquid microextraction coupled with UV–Vis spectrophotometry was applied for the determination of zirconium in aqueous samples. In this method a small amount of chloroform as the extraction solvent was dissolved in pure ethanol as the disperser solvent, then the binary solution was rapidly injected by a syringe into the water sample solution containing Zr(IV), xylenol orange and cetyltrimethylammonium bromide (CTAB). The formed ion-associate was extracted into the fine chloroform droplets. The detection limit for Zr(IV) was $0.010 \mu\text{g mL}^{-1}$. The precision of the method, evaluated as the relative standard deviation obtained by analyzing of 10 replicates, was 2.7 %. The practical applicability of the developed method was examined using natural waters and ceramic samples.

1. Introduction

Zirconium is used in the nuclear industry as a fuel rod cladding, as a catalyst in organic reactions and, additionally, in the manufacture of water repellent textiles, in metal alloys and in dye pigments and ceramics [1, 2]. Most of zirconium compounds have low solubility and as a result have low toxicity. However, chronic exposure to the soluble compounds of zirconium such as zirconium tetrachloride may cause skin and lung granulomas [3, 4]. Industrial wastewater can increase the amount of zirconium in the environment. Contaminated soil and water can expose humans to this metal. Therefore, extraction and determination of trace levels of zirconium is necessary.

Spectrophotometric methods are most commonly used for the determination of zirconium [5, 6]. However, the direct determination of zirconium at very low concentrations by traditional spectrophotometric techniques is difficult because of insufficient sensitivity of this technique as well as the matrix interferences occurring in real samples, and an initial sample pretreatment, such as preconcentration of the analyte and matrix separation, is often necessary. Several methods have been reported for the separation and preconcentration of metal ions, such as liquid–liquid extraction (LLE) [7], coprecipitation [8], solid phase extraction (SPE) [9, 10] and cloud point extraction (CPE) [11], but the disadvantages such as time-consuming, unsatisfactory enrichment factors, large organic solvents and secondary wastes, limit their applications.

Dispersive liquid–liquid microextraction (DLLME) is a modified solvent extraction method

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and provides the advantages of ease of operation, rapid extraction, and use of small volume of organic solvent [12, 13]. In DLLME, a water-immiscible organic extractant and a water-miscible dispersive solvent are two key factors to form fine droplets of the extractant, which disperse entirely in the aqueous solution, for extracting analytes. The cloudy sample solution is then subjected to centrifuge to obtain sedimented organic extractant containing target analytes. This method has been applied for the determination of trace organic pollutants and metal ions in the environmental samples [14-17].

Xylenol orange (XO) is a metal indicator, which is widely used for analytical determination [18, 19]. It can react with many metal ions in various oxidation states and the solution chemistry of its chelates is known to be complex [20]. However the utility of XO for extraction of metal ions is reported rarely. As the XO is a nonselective methallochromic indicator its complexes with the cited ion has severe spectral interferences and this makes the determination to be very difficult or practically impossible. For a successful determination a prior separation step is mandatory for elimination of the cationic interferences.

In the present study we introduce a simple and fast dispersive liquid-liquid microextraction (DLLME) method for the separation and preconcentration of trace amounts of zirconium, prior to spectrophotometric determination. The point of the present method is using of an accessible and inexpensive reagent, XO, with a cationic surfactant as a new extractant.

2. 2. Experimental

2.1. Reagents

All reagents were of analytical grade, purchased from the Merck Company. Standard stock solution (1000 $\mu\text{g mL}^{-1}$) of Zr(IV) was prepared by dissolving appropriate amounts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, in water. Stock solutions of diverse elements were prepared from the high purity salts of the cations (all from Merck, Germany). A solution of 1.0×10^{-3} mol L^{-1} xylenol orange was prepared by dissolving

appropriate amounts of this reagent in distilled water.

2.2. Instrumentation

A Perkin Elmer (Lambda 25) spectrophotometer with 10 mm quartz cells (500 μL) was used for UV-Vis spectra acquisition. A Metrohm model 744 digital pH meter, equipped with a combined glass-calomel electrode, was employed for the pH adjustments. A Hettich centrifuge model EBA 20 (Oxford, England) was employed for phase separation.

2.3. Dispersive liquid-liquid microextraction procedure

A 5 mL sample or standard solution containing Zr(IV) (pH 3.0), XO (3.0×10^{-5} mol L^{-1}), and CTAB (2.0×10^{-5} mol L^{-1}) was transferred in a 10 mL conical-bottom polypropylene centrifuge tube. Then 1.5 mL ethanol (disperser solvent) containing 120 μL chloroform (extraction solvent) was injected rapidly into the sample solution using a syringe and a stable cloudy solution (water, ethanol and chloroform) was formed. In order to separate the phases, the cloudy solution was centrifuged for 5 min at 3000 rpm and the aqueous phase was removed with a transfer pipette. Afterwards, the sedimented phase was dissolved in 500 μL of pure ethanol and transferred to a quartz cell and then the absorbance was measured at 592 nm.

2.4. Analysis of the real samples

A 5 mL of tap water, well water, and mineral water samples were filtered through 0.45 μm membrane filter, adjusted to the optimum pH and subjected to the recommended procedure for the preconcentration and determination of metal ions. To 1.0 g of ceramic samples in a platinum crucible, 10 mL of HF, 1 mL of H_2SO_4 , and 1 mL of HClO_4 were added and heated to 150 $^\circ\text{C}$ on a hot plate. The process was repeated three times. The residue was cooled and dissolved in 50 ml of 0.1 mol L^{-1} HCl and made up to 100 mL. Suitable aliquots were taken and subjected to preconcentration and determination by the procedure described above.

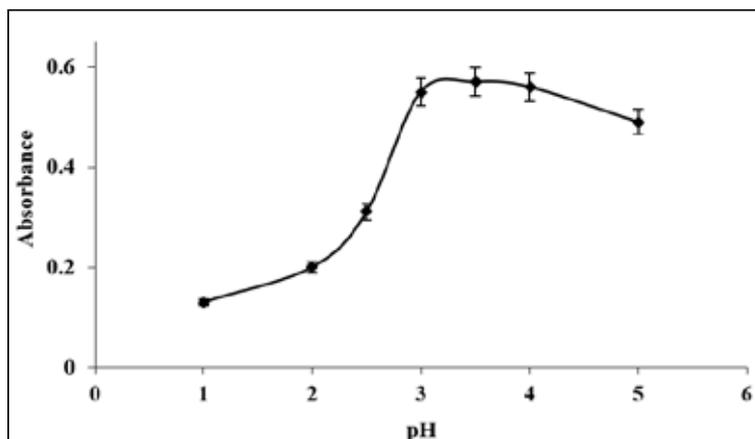


Fig. 1. Effect of pH on the absorbance of metal–xylenol orange complex.

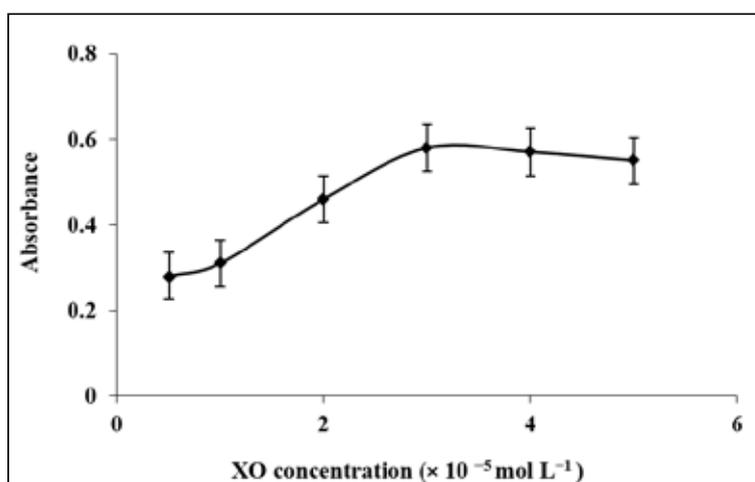


Fig. 2. Effect of xylenol orange concentration on the absorbance of metal–xylenol orange complex.

3. 3. Results and discussion

3.1. Effect of pH

The formation of metal chelate and its chemical stability are the two important influence factors for the extraction of metal ions, and the pH plays a unique role on metal chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of zirconium was studied in the range of 1.0–5.0 using hydrochloric acid or sodium hydroxide. As can be seen in **Fig. 1**, the highest signal intensity was obtained at pH 3.0–4.0. In more acidic or more alkaline solutions, absorbance decreased because of

incomplete complex formation and hydrolysis of the complex. Therefore, pH 3.0 was selected for further study.

3.2. Effect of xylenol orange concentration

The effect of xylenol orange concentration on the absorbance was studied, and the results are shown in **Fig. 2**. We investigated xylenol orange concentration in the range of 5.0×10^{-6} to $5.0 \times 10^{-5} \text{ mol L}^{-1}$. Maximum absorbance was obtained at a concentration of $3.0 \times 10^{-5} \text{ mol L}^{-1}$ of the ligand and after that, absorbance approximately stays constant.

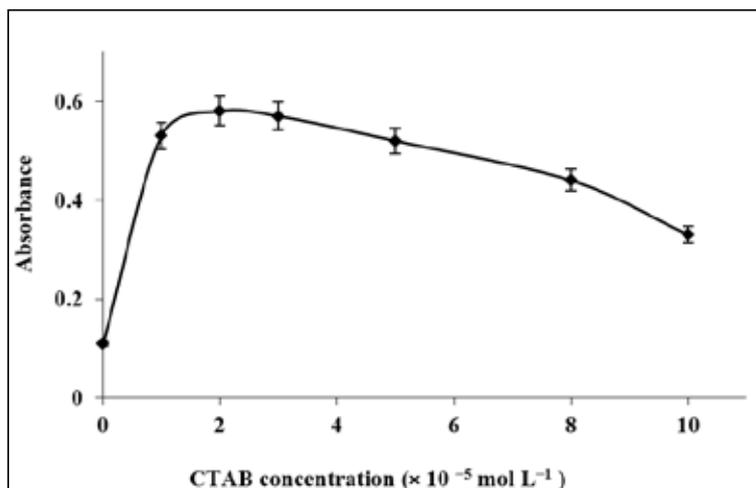


Fig. 3. Effect of CTAB concentration on the absorbance of metal-xylenol orange.

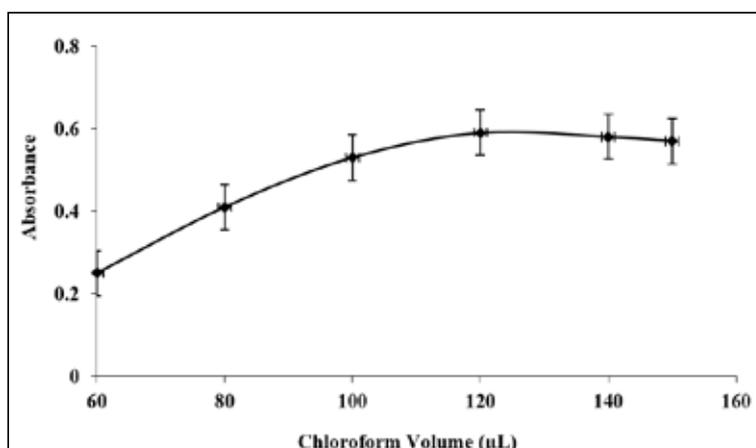


Fig. 4. Effect of amount of chloroform on the absorbance of metal-xylenol orange.

3.3. Effect of CTAB concentration

Effect of CTAB concentration on the extraction and determination of zirconium was investigated in the range of 0 to $1.0 \times 10^{-4} \text{ mol L}^{-1}$. The results are shown in **Fig. 3**. The amount of the absorbance for sample increased by increasing CTAB concentration. The blank signal also increased by increasing CTAB concentration. This is due to more extraction of xylenol orange by increasing CTAB concentration, but the difference between the sample and blank signals increased by increasing CTAB concentration up to 2.0×10^{-5}

mol L^{-1} and decreased at higher concentrations. Therefore, $2.0 \times 10^{-5} \text{ mol L}^{-1}$ CTAB was chosen as the optimum.

3.4. Effect of type and volume of the extraction solvent

Selecting the extraction solvent by paying attention to its characteristic properties is very important. Chloroform and carbon tetrachloride were compared in this extraction and obtained recoveries were higher for chloroform. To examine the effect of the extraction solvent volume, 1.5 mL of ethanol

containing different volumes of chloroform in the range of 60–150 μL were subjected to the same procedures. According to **Fig. 4**, increasing the volume of chloroform, initially increases the absorbance until at 120 μL it reaches the maximum amount. Thereby, the 120 μL of chloroform was employed to extract the zirconium from the aqueous samples.

3.5. Effect of type and volume of the disperser solvent

The main criterion for the selection of the disperser solvent is its miscibility in the extraction solvent and aqueous solution. In addition, the type of disperser directly influences the viscosity of the binary solvent. Thus, this solvent can control droplet production and extraction efficiency. To study this effect, two different solvents such as acetone and ethanol were tested. A series of sample solutions were studied using 1.5 mL of each disperser solvent with 120 μL of chloroform as the extraction solvent. The obtained enrichment factors for these two dispersers show no statistically significant differences between them; however we selected ethanol as the disperser because it was cheaper and more accessible than acetone. The effect of the volume of ethanol on the extraction recovery was also studied. The different volumes of ethanol (0.50, 1.00, 1.50, 2.00 and 2.50 mL) containing 120 μL chloroform were examined. For the first two tests, the droplets were big and the surface area was low, so the droplets rapidly settled at the bottom of the tube and low extraction efficiencies were obtained. Maximum extraction was observed when the disperser solvent volume was 1.5 mL. Thus 1.5 mL of ethanol was chosen as the proper amount.

3.6. Effect of diverse ions on the recovery

In order to assess the possible analytical applications of the recommended procedure, the effect of common coexisting ions in natural water samples on the preconcentration and determination of zirconium was studied. In these experiments, 5.0 mL solutions containing 0.10 $\mu\text{g mL}^{-1}$ of zirconium and various amounts of interfering ions were treated according to the recommended procedure. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding $\pm 5\%$ in the determination of investigated analyte. The results are summarized in **Table 1**. As it is seen, large numbers of ions used have no considerable effect on the determination of zirconium.

3.7. Analytical performance of the method

The linear working range of the method for determination of Zr(IV) was found to be 0.04–0.35 $\mu\text{g mL}^{-1}$. The limit of detection (LOD) of the proposed methodology was calculated as three times the standard deviation of 8 blank solution readings over the slope of the calibration graph. The LOD for the determination of Zr(IV) was found to be 0.010 $\mu\text{g mL}^{-1}$. The relative standard deviation (R.S.D) for analysis of 0.10 $\mu\text{g mL}^{-1}$ Zr (IV) ($n=10$) was 2.7 %.

3.8. Applications

The accuracy of the proposed method was tested by separation and determination of Zr(IV) ion in tap water, well water and mineral water samples. In order to validate the method, analytes were determined in spiked real samples. Also this method was applied to the determination of zirconium in ceramic materials. The results obtained are shown in **Tables 2 and 3**. The results demonstrated that the proposed method was suitable for the determination of Zr(IV) in real samples.

Table 1. Tolerance limits of some cations and anions on the determination of zirconium

Ion	Tolerance limit ($\mu\text{g mL}^{-1}$)
Li^+ , Na^+ , K^+ , Cl^- , NO_3^-	1000
Ca^{2+} , Mg^{2+} , Ba^{2+} , SO_4^{2-}	50
Co^{2+} , Cr^{3+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+}	5
Cu^{2+} , Hg^{2+} , La^{3+} , Ce^{3+} , UO_2^{2+}	2
Fe^{3+}	0.5

Table 2. Determination of zirconium in water samples (n= 3).

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water	0.0	< LOD	–
	50.0	45.8 ± 1.3^a	91.6
	100.0	93.2 ± 1.0	93.2
Mineral water	0.0	< LOD	–
	50.0	52.3 ± 0.45	104.6
	100.0	94.5 ± 1.5	94.5
Well water	0.0	< LOD	–
	50.0	54.1 ± 0.75	108.2
	100.0	93.7 ± 0.84	93.7

^a Standard deviation.

Table 3. Determination of zirconium in the ceramic samples (n= 3)

Sample	Proposed method (μg)	ICP-OES (μg)
1	456 ± 13.1^a	490
2	1098 ± 20.6	1140

^a Standard deviation.

4. Conclusions

In the present study, a novel method for the preconcentration and spectrophotometric determination of zirconium in water samples is proposed. Dispersive liquid–liquid microextraction is a sensitive, efficient, and simple method for preconcentration and separation of trace metals with the use of low sample volumes. The proposed preconcentration and determination method gives a low limit of detection and good R.S.D. values. The method can be successfully applied to the separation and determination of zirconium in real samples.

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