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부유 – 분광광도법에 의한 지르코늄의 극미량 측정

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Determination of Trace Amounts of Zirconium by Flotation – Spectrophotometric Method

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요약. 지르코늄의 부유-분광 광도의 측정에 대한 감도가 좋고 재현성 있는 방법이 기록되었다. 그 방법은 지르코늄과 자일렌 오렌지(XO)착물 형성에 기초하였고 그것은 격렬한 진탕에 의해 수용액 상과 n-헥산의 표면에 떠있게 된다. 수용액과 n-헥산을 폐기함에 따라 분리된 깔대기의 벽에 있던 흡착된 착물은 작은 부피의 메탄올 용액으로 해리되어진다. 그리고 그것의 흡광도는 429 nm에서 측정되었다. PH, HCl, XO의 농도, n-헥산 부유 용매의 부피, 지속시간과 진탕시간과 같은 다른 변수의 효과가 연구되었다. 보정곡선은 0.9991의 상관계수를 갖는 지르코늄의 7 ~ 120 ng/mL의 범위에서 선형이었다. 검출한계(LOD)는 58 ng/mL이었다. 지르코늄의 50과 110 ng/mL 의 7개의 분할척정에 대한 상대표준편차(RSD)는 4.4와 3.0%였다. 이 방법은 물 샘플에서 지르코늄의 측정에 성공적으로 적용되었다.

주제어: 부유-분광광도법, 지르코늄, 자일렌 오렌지

ABSTRACT. A sensitive and reproducible method for the flotation-spectrophotometric determination of zirconium is reported. The method is based on the complex formation zirconium and xylenol orange (XO) which is floated in the interface of aqueous phase and n-hexane by vigorous shaking. By discarding the aqueous solution and n-hexane, the adsorbed complex on to the wall of a separating funnel was dissolved in a small volume of methanol solvent and its absorbance was measured at 429 nm. The effect of different parameters such as pH, concentrations of HCl, and XO, and volume of n-hexane flotation dissolvent, standing and shaking time were studied. The calibration curve was linear in the range of 7-120 ng mL^{-1} of zirconium with a correlation coefficient of 0.9991. The limit of detection (LOD) was 5.8 ng mL^{-1}. The relative standard deviation (RSD) for seven replicate measurements of 50 and 110 ng mL^{-1} of zirconium were 4.4 and 3.0%, respectively. The method was successfully applied to the determination of zirconium in water samples.

Keywords: Flotation-Spectrophotometry, Zirconium, Xylenol orange

INTRODUCTION

Ion-associate complexes wherein positive charged ion (such as metal ions and quaternary ammonium salts) react with opposite charged ions such as colored dyestuff anions have aroused considerable interest in the past three decades. Flotation-spectrophotometry of such colored complexes probably provides the most sensitive, relatively simple and fast approach to trace metal analysis.[1,2] Acidic non-chelating dyes enjoy high popularity in spectrophotometric analysis due to a high molecular extinction coefficient (≈ 1 × 10^5 L mol^{-1} cm^{-1}). They are able to form extractable ion-pairs or ion-associates with monovalent or bivalent metal cation complexes leading to a variety of sensitive methods. Polyvalent cationic and/or anionic metal complexes also react with acidic and/or basic dyes but the reaction products cannot be extracted by slightly polar solvents. Instead, the compounds formed accumulate during shaking on the phase boundary or on the wall of the separating funnel. The precipitate can be separated off and dissolved in a polar solvent, producing an intensely colored solution that forms the basis of a flotation-spectrophotometric method of determination. Such complexes were made to be extractable from aqueous solutions in order to preconcentrate and determine trace amounts of metal ions.[1-3]

Determination of trace amounts of zirconium in environmental and industrial samples is interesting because of the high toxicity of its compounds. Different separation and preconcentration procedures such as extraction-spectrophotometry,[4-8] liquid chromatography,[9,10] solid phase extraction,[11-13] and cloud point extraction[14] are reported for determination of zirconium. Some of quantitative determination methods such as chromatography suffer from large solvent consumption. More investigation in this field could lead to a more sensitive method for trace zirconium determination.

In this paper, we present a sensitive flotation-spectrophotometric method for quantitative determination of zirconium, based on its complex formation with xylenol orange (XO) and its extraction into the interface between aqueous and n-hexane phase by flotation method. The proposed method has been successfully applied to the determination of zirconium in spiked water samples.

EXPERIMENTAL

Instrumentation

The absorption spectra were recorded on a JASCO model 7850 UV-Vis. recording spectrophotometer and a Perkin-Elmer model 550S spectrophotometer was used for absorbance measurements. A Metrohm model 632 pH meter with a combined glass electrode was used for pH measurements.

Reagents

All commercial reagents used were of analytical grades without further purification. 1000 μg mL^{-1} stock solution of zirconium was prepared by dissolving 0.368 g of $ZrOCl_2 \cdot 8H_2O$ (Merck) in freshly distilled water and diluting to the mark in a 100 mL volumetric flask. Working solutions were prepared by appropriate dilution of 1000 μg mL^{-1} stock solution of zirconium. Stock solution of 8×10^{-5} mol L^{-1} of XO was prepared by dissolving 0.0120 g of XO (Merck) in distilled water and diluting to 200 mL in a flask.

Recommended procedure

Transfer an aliquot of a sample solution containing not more than 12 μg of zirconium into a 100 mL volumetric flask, add 8 mL of 8×10^{-5} mol L^{-1} of XO, 0.5 mL of 1 mol L^{-1} of HCl solution, dilute to the mark with distilled water and let stand for about 15 min. Then transfer the flask content to a 100 mL separating funnel containing 9 mL of n-hexane and shake the mixture for 60 s and then allow standing for 6 min. The ion associate (colored solid) floats on the interface. After discarding the aqueous phase (below layer) add 2.5 mL of methanol to n-hexane solution containing adsorbed ion associate. The methanol phase extracts the solid ion associate from n-hexane phase and dissolves it completely. The absorbance of extracted colored ion associate was measured at 429 nm in 1 cm glass cells against a reagent blank. All the experiments were carried out at room temperature. The blank solution was also run under the same conditions without adding any zirconium.

RESULTS AND DISCUSSION

The preliminary investigation on the interaction of zirconium with different dyestuffs such as alizarin red, alizarin yellow, methyl thymol blue and xylenol orange, indicated that zirconium forms an ion-pair with xylenol orange (XO) which is insoluble in aqueous and highly non polar organic phases, but soluble in some polar organic solvents such as methanol. The absorption spectrum of the dissolved Zr-XO ion-pair in methanol recorded against a reagent blank in the range of 350 - 550 nm showed that maximum absorbance occurs at 429 nm. Therefore, this wavelength was selected as λ_{max} for spectrophotometric measurements.

Among organic solvents tested (methyl ethyl ketone, carbon tetrachloride, benzene and n-hexane) n-hexane showed good characteristics as a flotation dissolvent. Since the ion associated solid floats at the n-hexane-water interface and adheres on the funnel wall, the aqueous phase can be easily discarded and the n-hexane in the separating funnel can be immediately used cyclically without any treatment.

Among organic solvents (Acetone, ethanol, methyl ethyl ketone, THF and methanol) examined to dissolve the adhered ion associates from the wall of the separating funnel, the dissolution of the ion associate in methanol is almost complete. 2.5 mL of methanol was used as optimum extracting solvent volume.

The influence of HCl concentration on the flotation of Zr-XO ion-pair was studied by varying the concentration of HCl in the aqueous solution, before the organic phase addition. As it is seen from *Fig*. 1 the maximum extraction of floated Zr-XO ion-pair is achieved when HCl concentration is 0.005 mol L^{-1} in the final solution. This may be due to formation of single charged XO (XO^+) by protonation of three of four carbonate groups in XO structure. The protonation of all XO carbonate groups at higher concentrations of HCl (> 0.005 mol L^{-1}) causes lower extraction of ion-pair and decreases the absorbance.

The effect of XO dye concentration used for the flotation of zirconium was examined by varying the amounts of XO. The absorbance increased with increasing XO concentration up to 5.6×10^{-6} mol L^{-1} of XO in the final solution and then levels off. The XO concentration of 6.4×10^{-6} mol L^{-1} in the

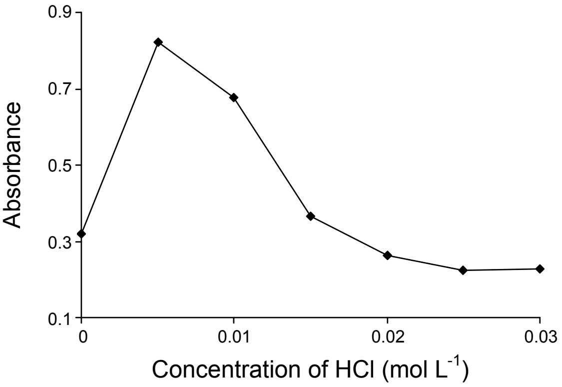

***Fig*. 1.** The influence of HCl concentration on the flotation of Zr-XO ion-pair for 100 ng mL^{-1} of zirconium and 6.4×10^{-6} mol L^{-1} of XO.

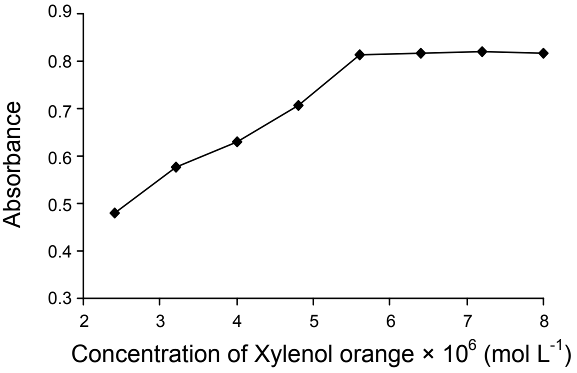

***Fig*. 2.** The effect of XO dye concentration on the flotation of Zr-XO ion-pair for 100 ng mL^{-1} of zirconium, HCl; 0.005 mol L^{-1}.

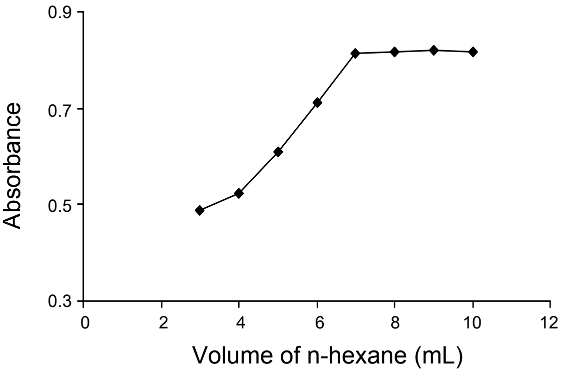

***Fig*. 3.** The effect of the n-hexane volume on the flotation of Zr-XO ion-pair in the range of 3-15 mL for 100 ng mL^{-1} of zirconium, HCl; 0.005 mol L^{-1} and 6.4×10^{-6} mol L^{-1} of XO.

final solution was chosen as the optimum XO concentration for ion-pair flotation process (*Fig*. 2).

The effect of n-hexane volume on the flotation process was examined in the range of 3 - 15 mL and the results showed that by increasing the n-hexane volume the absorbance of extracted ion-pair increases upto volumes of 7 mL of n-hexane and volumes more than 7 mL have no influence on the determination process of zirconium (*Fig*. 3). Therefore, 9 mL of n-hexane was chosen for further work.

The effect of standing time on the ion associate formation was studied over the time period of 5 - 30 min for 100 ng mL^{-1} of zirconium and 6.4×10^{-6} mol L^{-1} of XO concentrations at optimum HCl concentration and flotation and extraction process using optimum n-hexane and methanol volumes and then by measuring the absorbance at 429 nm. The results indicated that the maximum absorbance is obtained after 15 min standing time.

The effect of electrolyte concentration on the ion association of zirconium with XO was examined by varying the amounts of 0.1 mol L^{-1} of NaCl solution. The results showed that electrolyte concentration has no considerable effect on the flotation process of zirconium.

The flotation of the ion associate may also be influenced by the shaking time, because of increase in the surface of the gas-liquid interface. Maximum absorbance was obtained at 60 s shaking time.

Effect of interferences

In order to study the influence of various cations and anions on the determination of Zr, a fixed concentration of zirconium100 ng mL^{-1} was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of ± 5% with respect to the absorbance difference for the Zr solution was considered tolerable. Tolerance ratios are as follows: Cl^-, NO_3^-, Na^+, NH_4^+, ClO_4^-, SCN^-, SO_4^{2-}, Cu^{2+}, HPO_4^{2-} (1000 folds); Ca^{2+}, Ba^{2+}, K^+, Li^+, Mn^{2+}, (500 folds); Sr^{2+}, Hg^{2+}, Ag^+, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+}, Mg^{2+}, CO_3^{2-}, MoO_4^{2-}, WO_4^{2-}, (100 folds); Zn^{2+}, Al^{3+}, (5 folds); Th^{4+}, F^-, (1 fold). The results show that most of the cations and anions used have no considerable effect on the determination of zirconium.

Analytical performance

A calibration graph for the determination of zirconium was constructed under optimum experimental conditions described above. Beer's law was obeyed over the concentration range of 7 - 120 ng mL^{-1} of zirconium with a correlation coefficient of 0.9991 at 429 nm. The regression equation obtained by the least square method is $A = 4.49 \times 10^{-3}C_{Zr} + 0.378$, where A is the absorbance and C_{Zr} shows the concentration of zirconium in ng mL^{-1}. The limit of detection (LOD) based on $3S_b$ [15] was 5.8 ng mL^{-1}. With regard to the preconcentration factor of the process (40 fold, i.e., from 100 mL aqueous solution to 2.5 mL of methanol), and

***Table* 1.** Determination of zirconium spiked to the tap water samples

Sample No	zirconium (ng mL^{-1})[a]		%Recovery
	added	found[b]	
1	-	-	-
2	10	10.3 ± 0.7	101.5
3	20	20.6 ± 0.4	103.0
4	30	29.0 ± 0.4	96.7

[a]Average of three determinations. [b]$x \pm ts/\sqrt{n}$ at 95% confidence (n = 3).

a path length of 1 cm the conditional molar absorptivity was 6.9×10^5 L mol^{-1} cm^{-1} at the above wavelength. The relative standard deviation (RSD) for 50 and 110 ng mL^{-1} of zirconium were 4.43% and 2.98% (n = 10), respectively. The method exhibits a good repeatability.

APPLICATION

The proposed method was applied to the determination of zirconium content of Ahvaz tap water using standard addition method. The results are shown in *Table* 1. As it is seen, the results of the proposed method show good recovery values.

CONCLUSION

The proposed method is simple, reproducible and sensitive and can be applied to the determination of zirconium in water samples. The method shows good sensitivity due to high molar absorptivity character of xylenol orange dye and gave a wide linear dynamic range with respect to similar reported methods.[4-12] The proposed procedure is an easy and inexpensive methodology for separation and determination of trace amounts of Zr. The use of an inexpensive instrument is the main advantage of floatation spectrophotometric measurement over sophisticated and expensive instruments such as ICP-OES and ICP-MS.[16] In the case of working with large sample volume solutions of about 100 mL and also small extracting solvent volume (methanol) of 2.5 mL; a forty fold enrichment factor is achieved. The method compares favorably in sensitivity and selectivity with most of the published methods for the determination of zirconium.[5]

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REFERENCES

1. Cabellero, M.; Cela, R.; Perez-Butamante, J. A. *Talanta* **1990**, *37*, 275.
2. Rao, T. P.; Reddy, M. L. P.; Pillari, A. R. *Talanta* **1998**, *46*, 765.
3. Hosseini, M. S.; Y. Naseri, T. P. *Anal. Sci.* **2003**, *19*, 1505.
4. Argawal, Y. K.; Sudhakar, S. *Sep. Purif. Technol.* **2002**, *27*, 111.
5. Agrawal, Y. K.; Sanyal, M.; Shrivastav, P.; Menon, S. K. *Talanta* **1998**, *46*, 1041.
6. Xu, B.; Yao, J. *Yegin Fenxi* **1990**, *13*, 37.
7. Zai, Q. Z. *Analyst* **1994**, *119*, 1895.
8. Li, J.; Shi, H. *Fenxi Huxue* **1985**, *8*, 418.
9. Oguma, K. *Talanta* **1969**, *16*, 409.
10. Alimarin, I. P.; Fadeeva, V. I.; Kudryavtsev, G. V.; Lokutova, I. M.; Tikhomirova, T. I. *Talanta* **1987**, *34*, 103.
11. Wang, Z. P.; Shi, L. L.; Chen, G. S.; Cheng, K. L. *Talanta* **2000**, *51*, 315.
12. Oszwaldowski, S.; Jakubowska, J. *Talanta* **2003**, *60*, 643.
13. Yoon, J. I.; Choi, H. S. *J. Korean Chem. Soc.* **2009**, *53*, 27.
14. Shariati, S.; Yamini, Y. *J. Colloid. Interf. Sci.* **2006**, *298*, 419.
15. Miller, J. C.; J. N. Miller, S. *Statistics for Analytical Chemistry*; Ellis Horwood: Chichester, England, 1984.
16. Yang, X. J.; Pin, C. *Anal. Chim. Acta* **2002**, *458*, 375.