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A Rapid Spectrophotometric Determination of Thorium with DBC-Arsenazo as a Chromogenic Reagent

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A simple, rapid and sensitive spectrophotometric method for the determination of trace amount of thorium(IV) has been developed using DBC-arsenazo (DBC-ASA) as a chromogenic reagent in a 1.0 mol L^{-1} hydrochloric acid solution. Absorbance was measured in 1 cm cell and the complex has the maximum peak of absorption at 622 nm. The complex of thorium thus formed, is stable for 1 h with constant absorbance. Beer's law is obeyed in the range 0-0.60 μg mL^{-1} of thorium concentration with an apparent molar absorptivity at $\varepsilon_{622\ nm} = 7.15 \times 10^4$ L mol^{-1} cm^{-1} at 25 ºC. The linear regression equation of the method is A = 0.032C-0.004 [C: μg Th(IV)/ 10 mL], the correlation coefficient $\gamma = 0.9991$. The stoichiometric composition of the Th-(DBC-ASA) complex is 1:2. A large excess of cations and anions do not interfere with the determination of thorium. The proposed method was directly applied to the determination of thorium in hairtail and dried shrimps samples with satisfactory results. The relative standard deviation of nine replicate determinations and the recovery were over the range of 1.45-2.95 and 99.3-101.1 %, respectively.

Key Words: Thorium(IV), Spectrophotometry, DBC-Arsenazo, Chromogenic agent.

INTRODUCTION

Because of increasingly serious environmental pollution, thorium element enters human body by food chain and harms the health of mankind. Thus, developing the analytical methods for thorium is of very interest. Although NAA, ICP-AES and ICP-MS methods, *etc*. can be used to determine thorium, they are difficult to be extended for use in a daily routine analysis due to instrument's expensive price and operation complexity. Spectrophotometry has a series of the advantages of operation simplicity, low instrument price, *etc*. It is more suitable for the routine determination of thorium. Some reagents have been reported for the spectrophotometric determination of thorium, including thorin[1,2], arsenazo-III[3,4], Eriochrome black T[5], 1-(2'-

thiazolylazo)-2-naphthol[6], 3-hydroxy-2(2'-thienyl)-4*H*-chromene-4-one[7], 5-(2-hydroxy-4,5 -dinitrophenylazo)-4-hydroxy-2,7-naphthalene disulfonic acid[8], *etc*. These reagents have their own characteristics as well as defects, such as low sensitivity, poor selectivity. In addition, some methods need extraction separation, *etc*. DBC-Arsenazo (DBC-ASA), 3-(2-arsonophenylazo)-6-(2,6-dibromo-4-chlorophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, has been a spectrophotometric chromogenic reagent of rare earths[9]. Here, we report on its use in a sensitive and highly specific spectrophotometric method for the trace determination of thorium. Compared with existing methods[1-8], the method has the distinct advantages with respect to sensitivity, selectivity, simplicity, accuracy, precision and ease of operation. The present method is based on the reaction of DBC-arsenazo with thorium(IV) in 1 mol L^{-1} hydrochloric acid to produce a blue-purple complex, followed by a direct measurement of the absorbance at 622 nm in an aqueous solution. The optimum experimental conditions for the colour reaction between DBC-arsenazo and thorium(IV) were established and the properties of the colour system were studied. This method has been succe-ssfully applied to the determination of thorium in hairtail and dried shrimps samples. The relative standard deviation of nine replicate determinations and the recovery were between 1.45-2.95 and 99.3-101.1 %, respectively.

EXPERIMENTAL

Absorption spectra and absorbance were recorded and measured with a 722S spectrophotometer using a 1 cm cell. All of the chemicals used were of analytical reagent grade and distilled water was used throughout the study.

Standard thorium(IV) solution: The standard stock solution of thorium was prepared by dissolving thorium nitrate tetrahydrate, $Th(NO_3)\cdot 4H_2O$, in a given volume of water and the solution was standardized by titration with EDTA. The working standard solution (10 μg mL^{-1}) was prepared by dilution.

DBC-Arsenazo (DBC-ASA) solution: 0.050 % (w/v) DBC-ASA solution was prepared by dissolving 0.050 g of DBC-ASA in 100 mL of water.

Hydrochloric acid: 5.0 mol L^{-1}.

General procedure: An aliquot of standard or sample solution containing 0-6.0 μg of thorium was transferred to 10 mL calibrated flask. Then, 1 mL of 0.050 % (w/v) DBC-arsenazo solution and 2.0 mL of 5.0 mol L^{-1} were successively added and diluted to the mark with water. After 20 min, the absorbance was measured at 622 nm in a 1 cm cell against a reagent blank prepared in the same manner.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of DBC-ASA solution and its thorium complex are shown in Fig. 1. DBC-ASA exhibits a maximum absorption peak at 526 nm, whereas the Th(IV)-(DBC-ASA) complex produces an absorption peak at 622 nm. Thus, in all instances the measurements were carried out at 622 nm against a reagent blank.

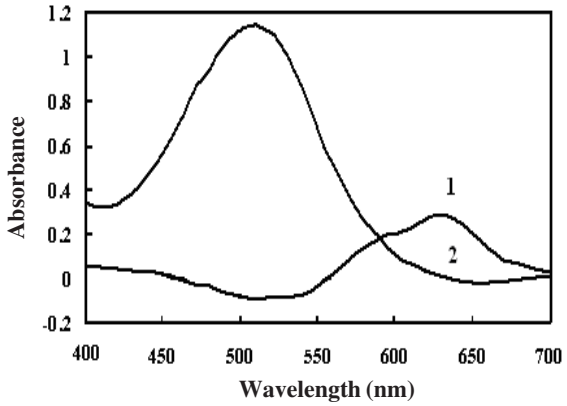

Fig. 1. Absorption spectra; (1) Th(IV)-(DBC-ASA) (against reagent blank); (2) reagent blank (against water); [Th(IV)] = 0.50 μg mL^{-1}, [DBC-ASA] = 50 μg mL^{-1}, [HCl] = 1 mol L^{-1}

Optimization of experimental variables: The experimental results showed that in a 25 mL of solution, the addition of 1.6-4.0 mL of 5 mol L^{-1} hydrochloric acid gave a maximum and constant absorbance. At this time the acidity of the system was 0.80-2.0 mol L^{-1}. Outside this range of acidity, the absorbance decreased. For all subsequent measurement, 5 mol L^{-1} hydrochloric acid (2 mL) was added. At this time, the acidity of the system was 1 mol L^{-1}.

Different molar excesses of DBC-ASA were added to a fixed thorium ion concentration and absorbance was measured according to the standard procedure. It was observed that at 0.50 μg mL^{-1} of thorium(IV), the addition of 0.50-1.5 mL of 050 % DBC-ASA solution produced a constant and maximum absorbance. For all subsequent measurements, 1 mL of 0.50 % (w/v) DBC-ASA reagent was added.

The absorbance of Th(IV)-(DBC-ASA) complex reaches a maximum value within 20 min at room temperature 25 ºC after diluting the solution to the final volume, which then remains stable for 1 h.

Composition of the complex: Job's method of continuous variation and the molar-ratio method were applied to ascertain the stoichiometric

composition of the complex Th(IV)-(DBC-ASA) (1:2) complex was indicated by both methods.

Calibration graph and sensitivity: A linear calibration graph was obtained for 0 to 6.0 μg of thorium(IV) in a final volume of 10 mL. The calibration regression equation is: A = 0.032C-0.004 [C: μg Th(IV)/10 mL]. The calibration graph has a correlation coefficient of 0.9991. The apparent molar absorptivity was calculated to be $\varepsilon_{622\ nm} = 7.15 \times 10^4$ L mol^{-1} cm^{-1}. The detection limit and quantitation limit of the determination of thorium were found to be 9.3 and 28.2 ng mL^{-1}, respectively. The reproducibility of the method was established by an analysis of 5.0 μg of thorium in a final volume of 10 mL. Eleven replicate determinations gave a relative standard deviation of 2.3 %.

Effect of coexisting substance: The effect of various potential interferences on the determination of thorium by the proposed method was examined. The tolerance limits of interfering species were established at the concentration required to cause not more than a ± 5 % error in the determination of thorium(IV) at 4.0 μg in a volume of 10 mL solution. The tolerance results are as follows(w/w): SO_4^{2-}, PO_4^{3-} (5×10^4); K^+, Na^+, Al^{3+}, NO_3^- (1.2×10^4); Ag^+ (5000), Co^{2+} (2500), Zn^{2+} (2000), Ca^{2+} (750), Cu^{2+} (500), Fe^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, W(VI) (250); EDTA (120), Pb^{2+}, Fe^{3+}, Cr^{3+}, V(V), Mo(VI) (50); Zr(IV) (25); Ti(IV) (5); La(III) (0.1), Ce(III) (0.05), Eu(III) (0.02).

Determination of thorium in hairtail and dried shrimps samples: 20 g of hairtail or dried shrimps sample was accurately weighed and placed into a ceramic crucible. The sample was carefully heated on an electric cooker for carbonization. Then it was placed into an oven at 550 ºC to incinerate for 5 h. After a complete ashing was made and the temperature decreased to room temperature, the sample was taken out and cooled to a room temperature. Along the wall of the crucible, 15 mL of concentrated nitric acid was added to dissolve the residue. It was evaporated to near dryness and transferred with water to a 25 mL calibrate flask and diluted to the mark with water. Mixed well, an aliquot of the testing solution was taken and transferred into a l0 mL of calibrate flask, then the general procedure was followed for the determination of thorium. The analytical results for the determination of thorium are given in Table-1.

From the Table-1, it can be seen that the analytical results of present method were excellent agreement with those obtained by arsenazo-III spectrophotometry. The relative standard deviation of nine replicate determinations was over the range of 1.45-2.95 %. The recovery of the present method was over the range of 99.3-101.1 %. The analytical results were fairly satisfactory.

TABLE-1
ANALYTICAL RESULTS OF SAMPLES

Sample	Found (n = 9, μg g^{-1})	Average (μg g^{-1})	RSD (%)	Added (μg)	Found (μg)	Recovery (%)	Contrast method [Ref. 3] (μg g^{-1})
Hairtail	9.98, 9.77, 10.33, 9.88, 10.12, 10.12, 10.33, 9.78, 9.88	10.12	2.95	1.00	0.993	99.3	10.10
Dried shrimps	9.75, 9.85, 9.93, 9.78, 9.75, 9.93, 9.85, 9.70, 9.75	9.80	1.45	1.00	1.011	101.1	9.80

Conclusion

A simple, rapid and sensitive spectrophotometric method for the determination of thorium with DBC-arsenazo was developed. The sensitivity, selectivity, precision and accuracy of the method are very good for the determination of thorium. The proposed method has been used to the determination of thorium in hair tail and dried shrimps with satisfactory results.

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