NOTE

Spectrophotometric Determination of Zirconium in Water Samples

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According to the property that in 2.40 mol L^{-1} nitric acid medium Zr(IV) can form a 1:3 blue complex nature with DBC-arsenazo (DBC-ASA), a new spectrophotometric method for the determination of Zr(IV) was established. The maximum absorption wavelength of the complex is 560 nm, Zr(IV) and absorbance in the range of 0-1.20 µg mL^{-1} obeys Beer's law. The apparent molar absorptivity of the method is $\varepsilon_{560 \text{ nm}} = 4.56 \times 10^4$ L mol^{-1} cm^{-1} and detection limit is 0.22 µg mL^{-1}. The method was used for the determination of zirconium in water samples. The relative standard deviation of 13 determination was 1.71-1.96 % and the recovery was 95.8-104.1 %.

Key Words: Zirconium, DBC-Arsenazo, Water sample, Spectrophotometry.

Zirconium is widely used in atomic energy, electronic engineering, metallurgy, chemical engineering, energy source and pharmaceutical field. Especially, in the industrial application of atomic energy it has an important position. At present the methods for determination of zirconium have spectrophotometry[1-3], emission spectrometry[4], inductively coupled plasma-atomic emission spectrometry[5], X-ray fluorescence spectrometry[6] *etc*. Among them the most simple spectrophotometric method is widely used[1-3]. Although some spectrophotometric methods for determination of zirconium using *m*-chloro-azoantipyrine, 2,3,7-trihydroxy-9-(3,5-dichloro-4- hydroxy) phenylfluorone have been proposed[1-3], selectivities of the methods especially for rare earths are poor and establishment of a new determination system is still needed. Dibromo-*p*-chloro-arsenazo[7] (DBC-ASA) is a type of asymmetric chromotropic acid diazo reagent with molecular formula $C_{22}H_{14}N_4O_{11}S_2AsBr_2Cl$. The structure is shown in Fig. 1. Fig. 1 shows that on the aromatic ring of DBC-ASA carry -OH, -SO$_3$H, -AsO$_3$H$_2$ and -N=N- multiligand containing N, O. Thus, the reagent has stronger coordination ability. It is found in present study that in 2.4 mol/L of nitric acid medium, colour reaction between Zr(IV) and DBC-ASA can occur, thus a new colour system for determination of trace zirconium was established. The method has been successfully used in the determination of zirconium in water samples with satisfactory results.

A 722S spectrophotometer (Shanghai Lingguang Technology Co. Ltd., China) was used for absorbance measurement. Zirconium standard solution: 0.3533 g ZrOCl$_2$·8H$_2$O

(Sinopharm Chemical Reagent Co. Ltd., China) was accurately weighed and dissolved in 5 mL of 2 mol/mL hydrogen chloride solution and diluted to 100 mL with water. 1 mg/mL Zr(IV) stock solution was obtained. Working solution was obtained by suitable dilution to be 4 µg/mL. DBC-Arsenazo solution (DBC-ASA, 0.2 % w/v): 0.2 g DBC-ASA (Shanghai Changke Research Institute of Reagent, China) was dissolved in 100 mL of water. Nitric acid solution: 8 mol/L. Unless otherwise stated, reagents used in this experiment were of analytically purity and water was distilled water.

In 10 mL flask, 3 mL of 8 mol/L of HNO$_3$ solution, 1 mL of 0.2 % (w/v) of DBC-ASA solution, 2 mL of 4 µg/mL of Zr(IV) working solution were in turn added. Water was used to dilute to the mark and then shaken. After 20 min, absorbance was measured with 1 cm cells at 560 nm using blank solution as reference.
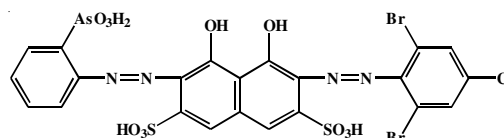

Fig. 1. Molecular structure of DBC-ASA

Absorption spectra: Zr(IV) forms blue coloured complex with DBC-ASA in nitric acid and the absorption curve results are shown in Fig. 2. Maximum absorption of reagent blank against water was at 506 nm. Maximum absorption of the complex against reagent blank produced at 560 nm, Thus, 560 nm was chosen as the measurement wavelength.

Sample	Found (n = 13) (μg/mL)	Average (μg/mL)	RS (%)	Added (μg)	Recover (μg)	Recovery (%)	Contrast method [a](μg/mL)
Lake water	0.336, 0.326, 0.350, 0.339, 0.336, 0.329, 0.343, 0.340, 0.345, 0.338, 0.335, 0.339, 0.330	0.337	1.96	1.00	1.04	104.1	0.337
Rain water	0.643, 0.658, 0.677, 0.660, 0.665, 0.681, 0.660, 0.639, 0.655, 0.662, 0.657, 0.663, 0.660	0.660	1.71	2.00	1.92	95.81	0.661

TABLE-1
ANALYTICAL RESULTS OF SAMPLES

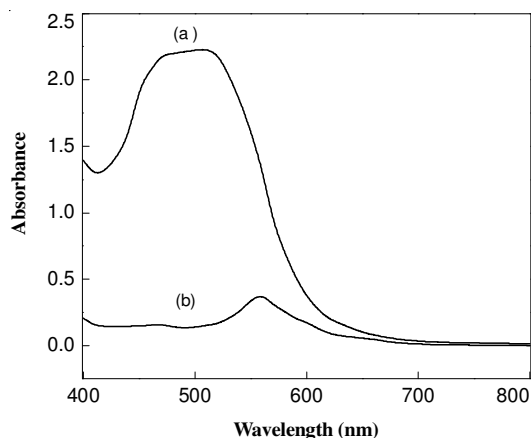[a]2,3,7-Trihydroxy-9-(3,5-dichloro-4-hydroxyl) phenyl fluorone spectrophotometric method[3]

Fig. 2. Absorption spectra: (a) reagent blank against water; (b) complex against reagent blank; $[Zr^{4+}] = 8.77 \times 10^{-6}$ mol/L; [DBC-ASA] = 2.37×10^{-4} mol/L; $[HNO_3] = 2.40$ mol/L

Amount of nitric acid: Acidity of solution directly influences the composition and stability species of metal and coloured complex. According to the standard procedure, effects of adding 0.5, 1.0, 2.0, 2.5, 2.8, 3.0, 3.2, 3.5, 4.0, 4.5, 5.0 mL of 8 mol/L nitric acid were tested. The results showed that as the amount of nitric acid added increased in 0.5-2.8 mL, the absorbance increased. In 2.8-3.2 mL, the absorbance was maximum. Over 3.2-5.0 mL with the increase of nitric acid added the absorbance decreased. Thus, 3 mL of 8 mol/L nitric acid were selected, at this time, nitric acid concentration in the system was 2.40 mol/L.

Effect of DBC-ASA dosage: Experiments showed that over the amount of 0-0.8 mL with the increase in DBC-ASA dosage the absorbance increased. Over 0.8-1.2 mL, the absorbance was maximum. Over the range of 1.2-1.5 mL, with increase in the amount of DBC-ASA the absorbance decreased. Thus, 1.0 mL of 0.2 % (w/v) DBC-ASA solution added was seleceed in the article. At this time, DBC-ASA concentration in the system was 2.37×10^{-4} mol/L.

Determination of complex composition and system stability: Zirconium(IV) and DBC-ASA produced the blue complex in the acidic medium. Equimolar ratio method and the equimolar continuous variation method was applied to measure the composition ratio of the complex and Zr(IV): (DBC-ASA) = 1:3 was obtained.

For the determination of 0.8 μg/mL Zr(IV), the absorbance value was stable and the complex formed completely after each solution was added for 20 min. Within 1.5 h time, the complex remained stable.

Linear range, sensitivity and detection limit: A standard curve was prepared under optimal conditions. The results showed that a good linear relationship lies in the range of 0-1.2 μg/mL. The regression equation was: A = 0.4730 C (C: μg/mL) + 0.0195, with a correlation coefficient of $\gamma = 0.9960$. The apparent molar absorption coefficient was calculated to be $\varepsilon_{660\,nm} = 4.56 \times 10^4$ L mol^{-1} cm^{-1}. The eleven parallel determinations of reagent blank were made and the relative standard deviation obtained was S = 3.42 %. According to the detection limit DL = 3 S/K (K: working curve slope), DL was calculated to be 0. 22 μg /mL.

Effect of coexisting ions: Under the optimal conditions, for the determination of 0.8 μg/mL zirconium(IV) the tolerant amount of coexisting ions was defined as the amount resulting in the error of $\leq \pm 5$ % and shown as follows (multiple of mass, m/m): SO_4^{2-} (2000); NH^+, Ba^{2+}, Si^{4+}, NO_3^-, SO_3^{2-}, CO_3^{2-}, PO_4^{3-} (200); Li^+, I^- (100); F^- (50); Sr^{2+}, Cr^{3+} (20); Mg^{2+}, Mn^{2+} (10); S^{2-}, NO_2^-, K^+, Na^+, Ca^{2+}, Al^{3+}, Cr^{6+}, Mo^{6+} (5); Cl^-, Zn^{2+}, Hg^{2+}, B^{3+}, W^{6+} (2); Cu^{2+}, Pb^{2+}, La^{3+}, Ce^{4+} (1); Fe^{2+}, Cd^{2+}, Hf^{4+} (0.2); Br^-, VO_3^-, Ag^+, Ni^{2+}, Sn^{2+}, Bi^{3+}, Fe^{3+}, Y^{3+}, Ti^{4+}, Th^{4+} (0.1).

Sample analysis: 100 mL of lake water or rain water sample was taken and placed into a 250 mL beaker. 15 mL of concentrated nitric acid and 5 mL concentrated hydrochloric acid were added, respectively. The solution was evaporated on an electric stove to near dryness, cooled. Then distilled water was added and the process of evaporation was repeated. The solution was transferred into a 10 mL volumetric flask and diluted to the mark with water. 1 mL of the testing solution was taken into a 10 mL volumetric flask and diluted with distilled water to the mark. Determination for zirconium was made according to the standard procedure. The results are shown in Table-1.

Conclusion

The optimum wavelength is at 560 nm using DBC-arsenazo spectrophotometric method for determination of zirconium. The good linearity is presented in the range of zirconium(IV) content 0-1.2 μg/mL with absorbance. Its linear regression equation is: A = 0.4730.C (C: μg/mL) + 0.0195 with a correlation coefficient of $\gamma = 0.9960$. The apparent molar absorption coefficient is $\varepsilon_{560\,nm} = 4.56 \times 10^4$ L mol^{-1} cm^{-1}. The detection limit of the method is 0. 22 μg/mL. The results were satisfied when the method was utilized to determine the zirconium content in the lake water and rain water.

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