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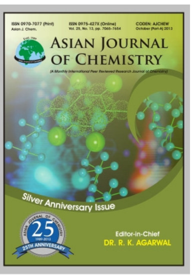

Spectrophotometric Determination of Micro Germanium(IV) with 5-(4-Carboxylphenylazo)-8-hydroxylquinoline as Colour Reagent

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The colour reaction of chromogenic agent 5-(4-carboxylphenylazo)-8-hydroxylquinoline with Ge(IV) was studied in the presence of micromulsion CTMAB-OP. A novel spectrophotometric determination of trace Ge(IV) with high sensitivity was established. The results showed that in the $Na_2B_4O_7$-NaOH medium of pH 9.8, 5-(4-carboxylphenylazo)-8-hydroxylquinoline reacted with Ge(IV) could form a red stable complex and the molar ratio of reagent:metal was 3:1. The maximum absorption peak of the complex was located at 558 nm with the apparent molar absorptivity of 2.5×10^5 L mol^{-1} cm^{-1}. In 10 mL of solution, 0.03-2.8 μg of Ge(IV) obeyed Beer's law and the detection limit was 0.1 mg/L. The colour reaction system could tolerate many interfering ions due to the existence of ammonia. This method was applied to determination of trace Ge(IV) in tea. The results are in consistency with the results obtained by atomic absorption spectrometric method. Recovery was also tested and values obtained were in the range of 102.5-103.6 % and the RSD (n = 6) of lower than 3.6 %.

Key Words: 5-(4-Carboxylphenylazo)-8-hydmxylquinoline, Spectrophotometric method, Ge(IV).

INTRODUCTION

The trace element Ge(IV) with physiological functions of anticancer, antiaging, improving the body's immunity has been used more and more in many areas,such as in medicine, clinical medicine, food health products, *etc*. So studies on the methods of determining Ge (IV) are of realistic sense. There are many methods for determination of germanium, such as atomic absorption spectrometry (AAS)[1], atomic emission spectrometry[2], polarographic analysis[3], inductively coupled plasma mass (ICP-MS)[4], spectrofluorimetry[5] and spectrophotometry. Now there have been some methods for the spectrophotometric determination of germanium such as rhodanine[6], porphyrin[7], fluorone[8], *etc*. The electron cloud structure changes its chromophore, make the colour change, determination of carboxyazo reagents have been used in copper, lead[9,10] and other heavy metal ions, but has not been reported for determination of Ge(IV). 5-(4-Carboxylphenylazo)-8-hydroxylquinoline has been used to determine the trace amount of mercury(II) and platinum(II). It was found that Ge(IV) could react with the reagent 5-(4-carboxylphenylazo)-8-hydroxylquinoline to form a stable blue complex (1:3) in pH range of 9.5-10.5, in the presence of hexadecyl trimethyl ammonium bromide,which has the maximum adsorption peak at 558 nm with an apparent molar adsorptivity of ε_{558} 2.5×10^5 mol^{-1} cm^{-1}. Beer's law is obeyed at the Ge(IV) concentration range of 0.01-2.8 μg/10 mL. Moreover, this colour system has excellent selectivity and stability. Most of the metal ions can be tolerated in considerable amounts without any masking reagents, especially large amounts of Mo and W which do not interfere with determination of trace germanium. Its selectivity was superior to other congener reagents. The proposed method is simple, fast and selective and has been applied to the determination of trace amount of germanium in tea and zinc concentrate samples with satisfactory results.

EXPERIMENTAL

UNICO WFJ 7200 spectrophotometer (Shanghai Analytical Instrument Factory V); pH-3C pH meter (Shanghai Precision kore Magnetic Co., Ltd.). Borax-NaOH ($Na_2B_4O_7$-NaOH) buffer solution: pH 9.80, 0.05 mol/L of $Na_2B_4O_7$ solution with 200 g/L NaOH solution tune to the required value in pH meter; 5-(4-carboxylphenylazo)-8-hydroxylquinoline solution: Weighed 0.05 g colour reagent, dissolved with ethanol into 100 mL volumetric flask, diluted with ethanol to scale and shake. Its concentration was 1.6×10^{-3} mol/L. A standard stock solution of Ge(IV) (1 mg mL^{-1}) was prepared as follow: weigh metal Ge 0.1 g in 250 mL beaker, add (1 + 4)

H_2O_2 20-30 mL, heating it in the water bath solution (dropping a few drops of $NH_3.H_2O$ can accelerate decomposition). Adding a few mL of hot water, using (1 +1) dilute HCl to acidify it and excessive 2-3 mL, boiled to drive hydrogen peroxide out, cooling, then transferred into 1000 mL calibrated flask, diluted with water to calibration, shaking. Then diluted the solution with distilled water to the concentration of 1 µg/mL; 5 g/L solution of hexadecyl trimethyl ammonium bromide (CTMAB) was used in the determination of germanium.

Reagents all above were of analytical grade, water used in the test was double distilled water.

Methods: 1 µg of Ge(IV) was transferred into a 10 mL calibrated flask, 1.5 mL pH 9.80 of buffer solution,1.2 mL of CTMAB solution and 1.5 mL of 5-(4-carboxylphenylazo)-8-hydroxylquinoline were added successively. Then it was diluted to the mark with water and mixed well and stood for 15 min. The absorbance of the coloured solution was measured at 558 nm in a 1 cm path length against a blank reagent solution.

RESULTS AND DISCUSSION

Absorption curve: The absorption spectra of the reagent 5-(4-carboxylphenylazo)-8-hydroxylquinoline (CPAHQD) and Ge(IV)-CPAHQD complex were shown in Fig. 1. It was evident that the maximum absorption of CPAHQD was at 490 nm while the Ge(IV)-CPAHQD and Ge(IV)-CPAHQD-CTMAB complex were separate at 550 and 558 nm. The contrast of the two peaks was 68 nm, which can be obviously distinguished. So the absorption peak 558 nm was chosen as the determination wavelength.

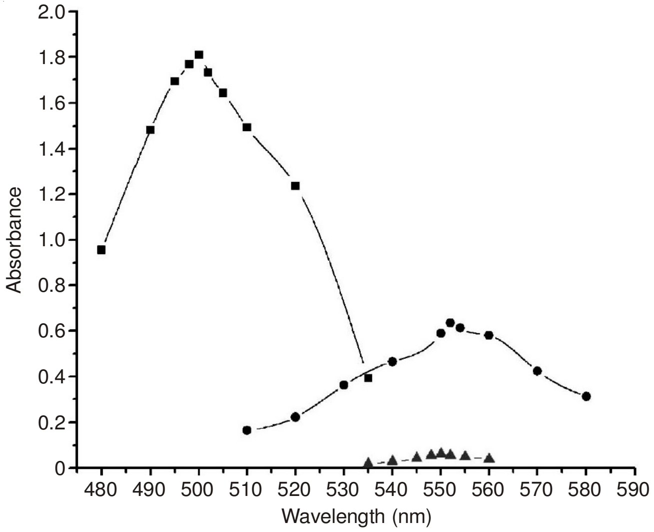

Fig. 1. Absorption spectra. 1. Reagent blank/water, 2. Ge(IV)-CPAHQD-CTMAB/reagent blank. 3. Ge(IV)-CPAHQD/reagent blank

Effect of system acidity: A series of solution with different values of pH were prepared to determine the influence of pH solutions (HCl, H_2SO_4, H_3PO_4, Na_2SO_3, NaOH, AcOH-NaOAc, H_3BO_3-NaOH, $NH_3 \cdot H_2O$-NH_4Cl, $Na_2B_4O_7$-HCl, $Na_2B_4O_7$-NaOH) on the absorbance of the complex. Results show that the complex was almost unchanged in the pH range of 9.5-10.5, therefore the buffer solution of $Na_2B_4O_7$-NaOH with pH 9.80 was selected. In the range of 1.0-1.8 mL, the absorbance of the complex was largest and kept constant. In this study, 1.5 mL was chosen as the reactive dose.

Influence of the colour reagent dosage: With the increase of the volume of CPAHQD solution, the absorbance increased rapidly, followed by remaining almost at a maximum and unchanged. the addition of 1.2-1.8 mL solution gave maximum and constant absorbance, thus an addition of 1.5 mL CPAHQD solution was recommended.

Surfactant types and the choice of the amount: After investigated different types of surfactants on the impact of the colour system,it was found that in the presence of 1.0-1.6 mL CTMAB the system gave the maximum and constant absorbance, thus an addition of 1.2 mL was recommended.

Influence of reagent adding order and colour reaction time and the stability of complex: Various adding order of reagents will affect the colour reaction. The results showed that the adding order of reagents according to the experimental method was the best. The system could finish colour reaction completely in 15 min at room temperature and stay stability for 7 h.

Determination of complex components: Molar ratio method and continuous change method determined the composition of complex was n(Ge(IV): n(CPAHQD) = 1:3 as shown in Figs. 2 and 3.

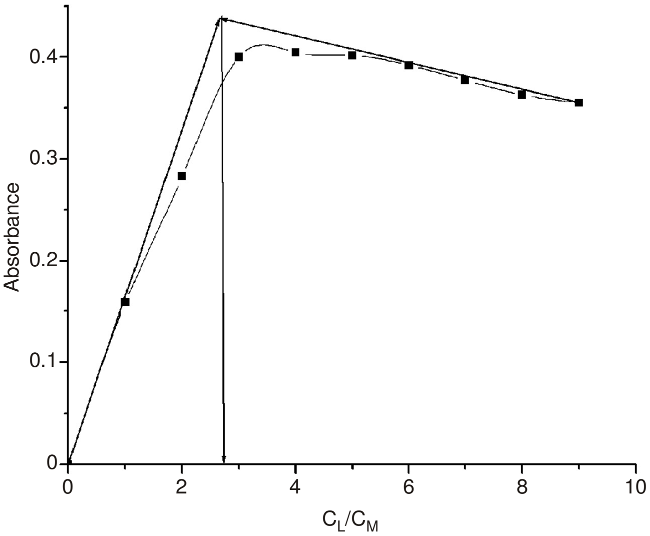

Fig. 2. Molar ratio method

Influence of coexisting ions: Measuring 1 mg Ge(IV) according to the experimental method, when the relative error is not more than 5 %, the maximum amount(mg) of coexistent ions was permitted as follows K^+ (30000); Na^+ (25 000); Ca^{2+} (1000); Mg^{2+} (800); Ba^{2+} (500); Al^{3+} (300); Ni^{2+} (250); Cd^{2+}(200); Cr(VII), Co^{2+} (150); Pb^{2+} (120); Pd^{2+}, Bi^{3+} (100); Mn^{2+} (80); Bi^{3+} (50); Fe^{3+}, Pt^{2+} (40); Rh^{3+} (10), Zn^{2+}, (18) Sr^{2+}; In^{3+} (35); Sb^{3+}(30); Mo^{6+}, Ti(IV) (25); Au^{3+}, Ag^+ (20); Os(III), Zr(IV) (15); W^{3+} (10); Sn^{4+} (5); Ru^{3+}, Ga^{3+}(3); V(V), Hg^{2+} (2); Nb(V), La^{3+}, Cu^{2+} (1); triethanolamine (2000) tartrate (1500) citrate (1000). Lots of EDTA can exist, EDTA can be use as the masking reagents improve other ions coexistent amount. SO_4^{2-}, PO_4^{3-}, NO_3^-, NO_2^- have no influence on the determination of Ge(IV). Experimental results showed that interference of 0.25 mg Cu^{2+}, 0.2 mg Fe^{3+}, 0.3 mg Hg^{2+} could be eliminated efficiently by addition of 05 mL 2 g/L EDTA. For the sample

TABLE-1
DETERMINATION RESULTS OF GERMANIUM(IV) IN TEA SAMPLE (n = 6)

Sample	Recommend (µg/L)	Method (µg/L)	Average (µg/L)	RSD (%)	Added Ge(IV) (µg)	Recovery (%)
Tea-1	6-25	6.22, 6.23, 6.24, 6.21, 6.23, 6.24	6.23	1.80	1	102.5
Tea-2	5-30	5.27, 5.28, 5.28, 5.29, 5.31, 5.32	5.29	3.60	1	103.6

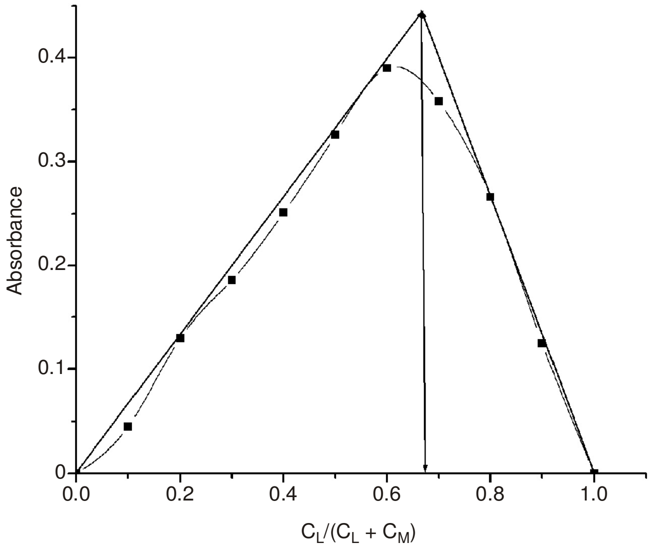

Fig. 3. Continuous change method

which contain more interferential ions (such as znic concentrate which contains lots of Zn^{2+}),we can use DDTC/CCl_4 extraction and water antiextraction,then determine by experimental methods.

Calibration curve and sensitivity: Adding a quantity of standard Ge(IV) working solution in a series of 10 mL calibrated flask, do the colour reaction etermination according to the experimental methods, when the quantity of Ge is from 0.03-2.8 mg, it obey the Beers law. The linear regression equation is: $A = 0.3600\ \rho(\mu g/10\ mL) + 0.0015$ with a correlation coefficient of 0.9999. The apparent molar absorptivity is 2.5×10^5 L mol^{-1} cm^{-1} and method detection limit was 0.01 mg/10 mL.

Sample analysis: Take a certain amount of tea in the oven, dry at 1000 ºC, ground, weighed 1 g sample in 100 mL conical bottle. Added 10 mL conc. HNO_3, after 2 h, heating at low temperature in distillation unit, circufluence and digest until solution clarified, remove the distillation, heating to volatile nitrate. When the solution remains 1-2 mL, add H_2O_2 by drop, when the solution is colourless, stop dropping, continue to heat until completely dry and cold to room temperature. After adding appropriate distilled water dissolve solids, add 15 mL 9 mol L^{-1} HCl, shake and add 10 mL CCl_4, oscillating 5 min and extraction, static delamination and separate CCl_4 in another funnels, add 10 mL of water and extraction after transfer to 25 mL calibrated flask, constant volume and shake, fetch 2 mL solution, determine by the experimental methods, the results were shown in Table-1.

Conclusion

The method has been used for the determination of trace germanium(IV) in tea with satisfactory results and the result was in accordance with that of the atomic absorption spectrometry method.

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