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Determination of Germanium with Phenylfluorone by β-Correction Sectrophotometry

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The determination of trace amount of germanium with phenylfluorone using β-correction new spectrophotometry was studied. At pH 4.5, the germanium complex exhibits an absorption maximum at 540 nm, whereas that of the reagent is at 510 nm. Beer's law was obeyed over the concentration range of 0–12.5 μg of germanium per 25 mL of final solution. The method has been applied to the determination of trace amount of germanium in water and coal with satisfactory results.

INTRODUCTION

Germanium has been determined with phenylfluorone (abbreviated as PF), nitrophenylfluorone and disulfophenylfluorone[1]. PF is commonly used as a sensitive spectrophotometric reagent for determining germanium. Hence in this paper, the colored reaction of germanium with pH 4.5 AcOH-NaOAc buffer solution using β-correction spectrophotometric method was studied. The absorbance due to small excess of PF can be deduced and thus the analytical sensitivity is increased. Beer's law was followed in the concentration range of 0–12.5 μg/25 mL for germanium. The method is sensitive, accurate and reproducible and has been applied to the determination of trace amount of germanium in coal and water with satisfactory results.

EXPERIMENTAL

Visible spectra were recorded with a spectrophotometer, Model 722, 1-cm glass cell; PHS pH-meter equipped with glass and calomel electrodes was used for pH measurements.

Standard germanium solution, 1 mg/mL: dissolve 0.1000 g of germanium powder in 5 mL of 1 mol/L NaOH and acidify the solution slightly with hydrochloric acid, and dilute to the mark in a 100 mL volumetric flask with distilled water. Prepare a 5 μg/mL working standard by dilution with distilled water. Sodium sulfite solution: 20% (m/v) water solution. Gelatin solution: 1% (m/v) water solution. Phenylfluorone solution; 0.03% (m/v) ethanolic solution. pH = 4.5 AcOH-NaOAc buffer solution.

Recommended Procedures

In a 25-mL calibrated flask, pipette an aliquot of the sample containing *ca.* 12.5 μg of germanium and add with swirling 1.0 mL of 20% sodium sulfite

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solution, 1.0 mL of 1% gelatin solution, 5 mL of pH 4.5 AcOH-NaOAc buffer solution and 1.2 mL of 0.3% phenylfluorone ethanolic solution. Dilute to volume with distilled water and mix well. After 30 min, measure the absorbances (A and A′) at 510 nm and 540 nm, respectively, in a 1-cm cell against a reagent blank (absorbance was adjusted top 0.500) and calculate A_β from equation (2).

RESULTS AND DISCUSSION

β-Correction principle and absorption spectra: The absorption spectra of both PF and Ge(IV)-PF complex are shown in Fig. 1. From Fig.1, we can see that the absorbance of Ge(IV)-PF at its maximum absorption wavelength (λ_{max}) should be equal to MO but not MN. In order to make $A_\beta = MO$, that is called β-correction absorbance, the $A_\beta > \Delta A$ ($\Delta A = MN$), so the analytical sensitivity of β-correction spectrophotometry is higher than that of the single wavelength method. A_β is computed from references 2 and 3 and is expressed by the following equations:

$$\beta = A_0/A_{0m} \qquad (1)$$

$$A_\beta = (A - 0.5) - \beta(A' - 0.5) \qquad (2)$$

Here A, A′ are the absorbances at wavelengths λ_{max} and λ^0_{max}, respectively which are determined after the blank absorbance was adjusted to 0.500. A_0 and A_{om} are the absorbances of the blank at λ_{max} and λ^0_{max} for distilled water as the reference, respectively. Usually, β is a constant. The relation between A_β and germanium concentration (x) gives a linear curve and is expressed by the following equation:

$$A_\beta = kX + b \qquad (3)$$

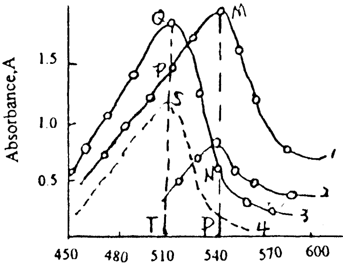

Fig. 1 Absorption spectra:
1. Ge(IV)—PF against water;
2. Ge(IV)—PF against blank;
3. PF against water;
4. Reagent blank of remainder PF against water.

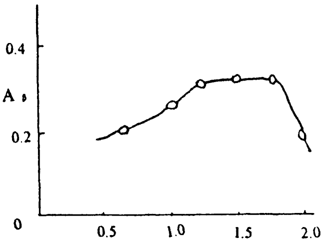

Fig.2. Effect of PF concentration

Here both k and b are constants calculated from germanium standard solution.

Also, from Eqn. (2), it can be seen that $(A' - 0.5) < 0$ and $(A - 0.5) = \Delta A$; therefore $A_\beta > \Delta A$. In consequence, the analytical sensitivity of this method is increased.

The absorption spectra of PF and its germanium complex at pH 4.5 in the presence of gelatin are at 510 nm (λ^0_{max}) and 540 nm (λ_{max}), respectively.

Effect of pH: The reaction between germanium and PF proceeds slowly in acid solution (pH 0–1), but fairly rapid (1–2 min) in acetate-buffered solution (pH 4–5). Hence, all studies were carried out at pH 4.5 with sodium acetate buffer.

Effect of PF concentration: The absorbance values at pH 4.5 of a test solution containing 12.5 μg of germanium and increasing amounts of PF showed that the absorbance remained constant after addition of PF in amounts from 1.1–1.8 mL. Therefore, 1.2 mL of the reagent solution was used in all studies (Fig. 2).

Effect of time and stability of the complex: The formation of the colored complex of germanium with PF is fairly rapid. However, a 30-min standing period was allowed for equilibration. Measurement of the absorbance was therefore carried out 30 min after the addition of PF and thereafter the color of the complex remained virtually constant for at least 1 h (Fig. 3).

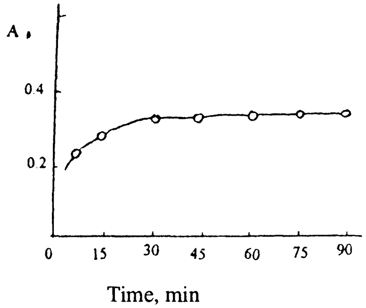

Fig. 3 Effect of the reaction time and stability of the complex
1. $A_\beta - x$; 2. $\Delta A - x$

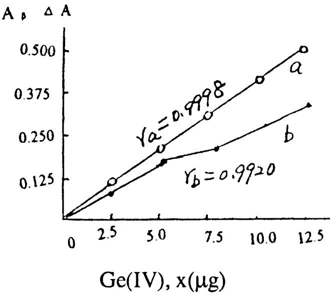

Fig. 4. Standard curves of A(x)

Standard Curve [A(x)]: A series of standard germanium solutions were prepared and the absorbance of each was measured and plotted. Beer's law was obeyed over the concentration range of 0–12.5 μg of germanium in 25 mL of final solution (Fig. 4 and Table-1). Two curves of $A_\beta(x)$ and $\Delta A(x)$ were drawn at wavelength of 560 nm. From Fig. 4, we can see that the linearity of the curve [$A_\beta(x)$; r = 0.9998] is better than that of the curve [$\Delta A(x)$; r = 0.9920]. Hence, the sensitivity of the recommended procedure is increased due to higher oblique rate k. Consequently, $A_\beta(x)$ and ΔA can be expressed by the following regression equations:

$$A_\beta(x) = 0.0394x - 0.001 \quad (4)$$

$$\Delta A(x) = 0.0275x + 0.012 \quad (5)$$

TABLE-1
ANALYTICAL RESULTS OF GERMANIUM STANDRD SOLUTION

Germanium, x (μg)	0	2.5	5.0	7.5	10.0	12.5
Absorbance at 510 nm	0.500	0.472	0.292	–0.020	–0.065	–0.550
Absorbance at 540 nm	0.500	0.588	0.642	0.733	0.806	0.833
Correction Absorbance	0	0.092	0.200	0.298	0.391	0.490

Effect of foreign ions: PF also forms colored complexes with multivalent metals [*e.g.*, Sn, Sb, Ti, Fe, Nb and Ta]. Preliminary separation of germanium as $GeCl_4$ by extraction with CCl_4 and striping germanium from CCl_4 phase with water renders the PF method specific for germanium.[4]

Composition of the complex: The composition of the complex was determined by continuous variation method and the molar-ratio method. A ratio of germanium to PF of 1 : 2 in the complex molecule was obtained by both methods.

Precision and determination limit: Replicate (7 times) determinations of three standard germanium solutions of 2.5 μg, 5 μg and 12.5 μg were made; the relative standard deviations (RSD) were 0.5%, 0.2% and 0.1%, respectively. However, the RSD's of single wavelength spectrophotometry were 2.8%, 2.4% and 2.2%, respectively, by working exactly the same replicate (7 times) determinations of three standard germanium solutions. Therefore, the precision of the method by β-correction spectrophotometry is also higher than that of the ordinary spectrophotometry. Replicate (20 times) determinations of reagent blank showed that the standard deviation of A_β values was Sb = 0.00328. Hence, the detection limit of germanium calculated from the equation $L_{min} = 3Sb/S$ was found to be 0.25 μg.

Samples analyzed: The results obtained for the recovery of known amounts of germanium added to three samples of mineral water, river water and gangue are listed in Table-2 and the recovery was found between 98.2–99.8%. Replicate (7-fold) determination on mineral water sample gives an RSD for 2.4%.

TABLE-2
RESULTS OF ANALYSES BY PRESENT METHOD IN COMPARISON WITH SINGLE WAVELENGTH METHOD

β-correction spectrophotometric method				Single wavelength method	
Sample		Germanium		Recovery %	Germanium found, μg
Name	Amount taken	add, μg	found μg		
Mineral water*	1 mL	0	6.73	99.8	6.68
		5	11.70		
River water†	1 mL	0	6.92	99.7	6.89
		5	11.90		
Gangue‡	1 mL	0	3.32	98.2	3.27
		1.5	4.610		

* Produced in Huaiyuan native mineral water refinery of Anhui.

† Suixi river water added to germanium standard solution.

‡ Taken from Xiangcheng Colliery of Huaibei Coal-Mineral Bureau and the test solution of sample was prepared according to the procedure given by reference 5.

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