

Spectrophotometric Investigation of Germanium Complex Solution with *o*-Chlorophenylfluorone and Determination of Trace Amounts of Germanium

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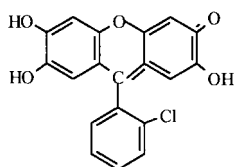
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A reaction between germanium (Ge) and the ligand, *o*-chlorophenylfluorone (*o*-CPF) has been carried out. The reaction sensitive at pH 4.5 in the presence of triton x-100 was selective in the presence of EDTA. The spectral correction technique was applied to the analysis of the reaction instead of single wavelength spectrophotometry because the absorption of excess of *o*-CPF was not negligible. An updated determination of the properties of the Ge(IV)-*o*-CPF complex is given, which involved the complex ratio, stepwise absorptivity and stability constant of the complex. In present work, the results show that the complex Ge(*o*-CPF)₃ was formed and its cumulative stability constant was 1.09×10^{16} . For sample analysis, the detection limit of germanium was 0.01 mg/L, and the recoveries were between 96.4% and 102%, with relative standard deviations of less than 6.5%.

Introduction

Germanium (Ge) is a rare element found mainly in geological material. It is a beneficial element to human health because its organic compounds can enhance the body's immunity and normal physiological functions. In addition, organic Ge compound has anticancer and health promotion functions so it is often used in medicines and nutriment.¹ For its conventional spectrophotometric determination the chromogenic agents: phenylfluorone,² *p*-nitrophenylfluorone,³ alizarine red S,⁴ etc are often used. The synthesis of *o*-chlorophenylfluorone (*o*-CPF) was earlier reported⁵ and its structure is given as:



o-CPF was earlier applied in the determination of trace amounts of Ga,⁶ W,⁷ etc in the present study. The reaction between Ge(IV) and *o*-CPF was sensitive at pH 4.5 in the presence of the non-ionic surfactant triton x-100. The solution changed to red from yellow, with the peak absorption of the complex product located at 530 nm and that of *o*-CPF at 460 nm. The Ge-*o*-CPF equilibrium solution contained Ge-*o*-CPF complex and free *o*-CPF. We found that the absorption of the free *o*-CPF took up a high fraction in its Ge solution. Therefore, it is impossible to investigate accurately the property of the Ge-*o*-CPF complex by ordinary spectrophotometry. The spectral correction method⁸ has been applied in the investigation of some metal complexes⁹⁻¹¹ instead of the ordinary method because the former can give the real absorption of the complex and that of the free *o*-CPF in solution. "Real" indicates the practical absorption in comparison with a pure water reference. It can not be measured directly but calculated only by measuring the absorbances of the Ge-*o*-CPF solution against the *o*-CPF solution reference

(containing no Ge). Here, we suggest that the molar absorptivity of the complex calculated from the "real" absorption is called "real" absorptivity, distinguishing it from "apparent" absorptivity. By means of the spectral correction technique, the characteristic constants of the Ge-*o*-CPF complex were determined easily for example, the composition ratio, stepwise absorptivity and stability constant. The recommended method was simpler in operation and more understandable than the classical methods such as molar ratio,¹² continuous variation,¹³ and equilibrium movement.¹⁴ We found that the non-ionic surfactant, triton x-100, increased the solubility of the complex, and that the masking agent EDTA may mask the other metal ions. In the present work, the complex is formed as follows: *o*-CPF: Ge is 3 : 1, its cumulative stability constant is 1.09×10^{16} and its molar absorptivity is $1.01 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 530 nm. The determination of several samples resulted in satisfactory recovery and precision.

Experimental Section

Apparatus and reagents. Absorption spectra were recorded with a Lambda 19 spectrophotometer (Perkin Elmer Co., USA) with 1.0-cm cell and the pH was measured with a Model PHS-2C acidimeter (Xiaoshan, China). The content of Ge in the samples was examined with a WFX-1F2 atomic absorption spectrophotometer (Beijing Sec. Opt. Instrument Works, China)

Standard Ge(IV) stock solution (1.000 g/L) was prepared by dissolving 1.000 g of high-purity germanium (>99.9%, Shanghai Chemical Reagents) in a mixture of 20 mL of concentrated hydrogen peroxide and 5 mL of 2 mol/L NaOH solution. Heat was applied to the mixture until the germanium dissolved completely. After cooling, the solution was neutralized with 2 mol/L HCl solution, and then volatilized the free hydrogen peroxide was volatilized. Finally, the solution was diluted to 1000 mL with non-ionic water. A standard Ge(IV) work solution (10.00 mg/L) was prepared daily with the above standard Ge solution.

The ligand solution (1.00 mmol/L *o*-CPF) was prepared by dissolving 0.3190 g of *o*-chlorophenylfluorone (*o*-CPF, Changke Reagents Institute, Shanghai) in 1000 mL of absolute alcohol (A. R., Shanghai Reagents). The ligand solution should be stored in a dark bottle and at less than 5 °C.

The buffer solution at pH 4.5 was prepared with acetate and acetic acid and used to adjust the acidity of the complex solution.

The non-ionic surfactant solution, 1% triton x-100 (Shanghai Chemicals), was used to increase both the solubility of the complex and the sensitivity of the reaction.

The masking agent was prepared by dissolving 5 g of EDTA-Na₂ (Kaifeng Chemical Reagents, China) in 100 mL of non-ionic water.

Recommended procedures. A known volume of a sample solution containing less than 30.0 μg of Ge(IV) was taken in a 25-mL volumetric flask. Next we added 2.5 mL of pH 4.5 buffer solution, 1 mL of triton x-100 solution, 0.5 mL of masking agent and 1.5 mL of *o*-CPF solution. The contents of the flask were diluted to 25 mL and mixed well. After 10 min, we measured absorbances at 460 and 530 nm against a reagent blank. We calculated the real absorbance (A_c) of the complex according to the following expression:⁸

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta}, \text{ where } \alpha = \frac{\epsilon_{ML}^{\lambda_1}}{\epsilon_{ML}^{\lambda_2}} \text{ and } \beta = \frac{\epsilon_L^{\lambda_2}}{\epsilon_L^{\lambda_1}}$$

The terms ΔA and $\Delta A'$ are the respective absorbances of the reaction solution at 530 (λ_2) and 460 nm (λ_1) against the reagent blank. The coefficients α and β are named correction factors. The terms, $\epsilon_{ML}^{\lambda_1}$, $\epsilon_{ML}^{\lambda_2}$, $\epsilon_L^{\lambda_1}$ and $\epsilon_L^{\lambda_2}$ are the molar absorptivities of the complex and ligand at 460 and 530 nm, respectively.

Results and Discussion

Absorption spectra. Figure 1 shows the absorption spectra of *o*-CPF and its Ge(IV) complex solution at pH 4.5. From curve 3, two wavelengths should be selected such that the two differences in absorbances between the *o*-CPF solution and the Ge-*o*-CPF solution reach the maximum: 460 (valley) and 530 nm (peak). The coefficient, β of the *o*-CPF solution is 0.224 calculated from curve 1. Using the same method, we calculated α of Ge-*o*-CPF complex to be 0.259 from curve 2. The A_c expression of complex is established as follows: $A_c = 1.06(\Delta A - 0.224\Delta A')$.

Effect of *o*-CPF concentration. Figure 2 shows the effect of the addition of *o*-CPF solution. From curve 1, it is difficult for the complex ratio of *o*-CPF to Ge to be calculated by the molar ratio method because its inflexion point can not be determined accurately. From curve 1, the addition 1.5 mL of *o*-CPF solution was used. The effective fraction (η) of *o*-CPF and the molar ratio (γ') of effective *o*-CPF to Ge are calculated according to the following expressions:⁹

$$\gamma' = \eta \times \frac{C_L}{C_M}, \text{ where } \eta = \frac{\alpha \Delta A - \Delta A'}{(1 - \alpha \beta) A_o'}$$

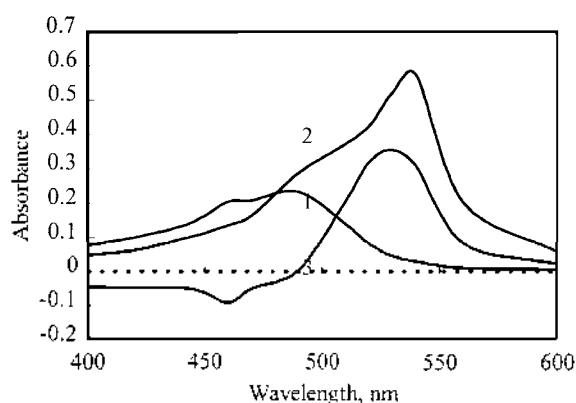


Figure 1. Absorption spectra of *o*-CPF and Ge-*o*-CPF complex solutions at pH 4.5 and in the presence of triton x-100: 1-1.00 μmol/25 mL *o*-CPF, 2-only Ge (0.40 mg)-*o*-CPF (0.25 μmol) complex solution; 3-Ge (10 μg)-*o*-CPF (1.00 μmol) reaction solution, both 1 and 2 against water and 3 against reagent blank reference.

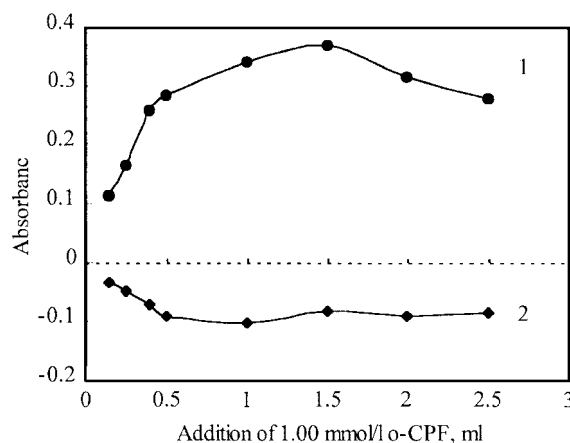
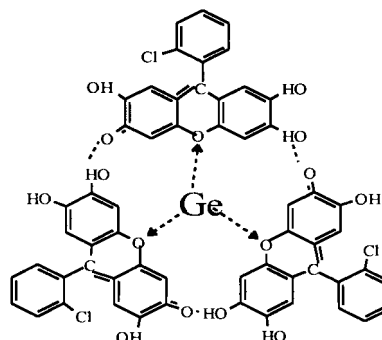


Figure 2. Effect of 1.00 mM *o*-CPF addition on absorption of Ge (10 μg) complex solution: 1- at 530 nm and 2- at 460 nm, both against reagent blank reference.

Here, the symbols C_M and C_L indicate the initial concentration (M) of Ge and *o*-CPF, respectively. The term A_o' is the absorbance of the blank reagent at 460 nm against water. Their curves are shown in Figure 3. From curve 2, γ' approaches to maximum and remains constant. 3, when the addition of *o*-CPF solution exceeds 0.5 mL. Therefore, Ge(*o*-CPF)₃ was formed here. Its possible structure is as follows:



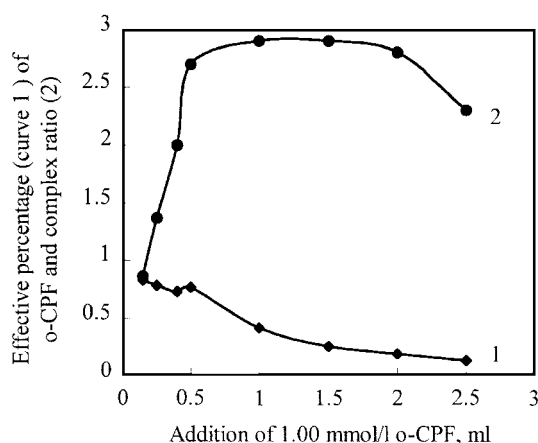


Figure 3. Effect of 1.00 mM *o*-CPF addition on η (%) of *o*-CPF and γ' of *o*-CPF to Ge.

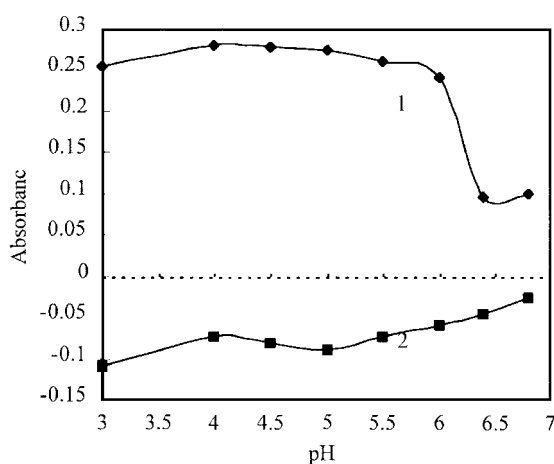


Figure 4. Effect of pH on absorption of Ge ($10 \mu\text{g}$)-*o*-CPF complex solution: 1- Δ 4 at 530 nm and 2- Δ 4' at 460 nm.

This structure shows a stable complex, with *o*-CPF linked by hydrogen bonds and the entire plane gives the closed circle. From curve 1 in Figure 3, the effective fraction of *o*-CPF is only 26% at the addition of the *o*-CPF solution, 1.5 mL. Excess *o*-CPF reaches 74%, maintaining the reaction equilibrium. Interference of free *o*-CPF in the measurement of the complex's absorption is inevitable.

Effect of pH. The effect on absorption of Ge-*o*-CPF solution by varying pH of solution is shown in Figure 4. We observed that the absorbances reached maximum at pH 3.0-6.0. In this study, a pH 4.5 buffer solution was used. In weak acidic solution, the protonation of *o*-CPF happened so as to adsorb easily on triton x-100 molecular micelle. Thus, the *o*-CPF concentration was very high in the micelle phase and Ge(IV) was modified easily on the adsorbed *o*-CPF molecules, resulting in the high sensitivity.

Effect of selection and addition of surfactants. The solubility of the Ge-*o*-CPF complex is negligible in aqueous solution and the use of surfactants may increase its dissolution. In addition, the micelle can adsorb *o*-CPF molecules then Ge(IV) is attracted to the micelle where *o*-CPF concentration is high. Thus, a Ge-*o*-CPF-surfactant ternary com-

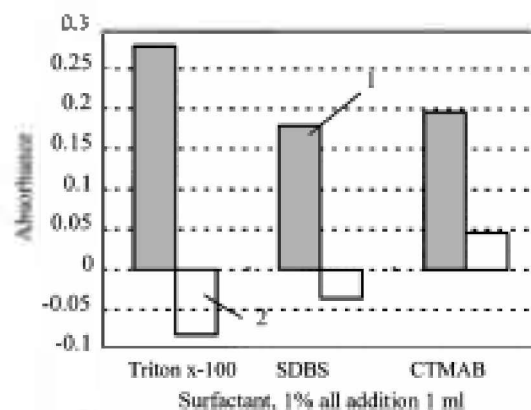


Figure 5. Effect of the different surfactant on absorption of Ge ($10 \mu\text{g}$)-*o*-CPF complex solution: 1- Δ 4 at 530 nm and 2- Δ 4' at 460 nm.

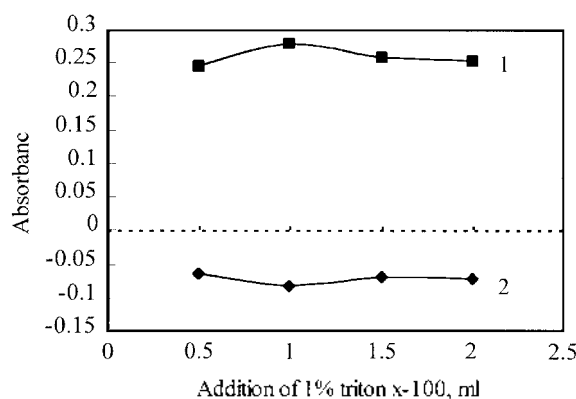


Figure 6. Effect of the addition of 1% triton x-100 on absorption of Ge ($10 \mu\text{g}$)-*o*-CPF complex solution: 1- Δ 4 at 530 nm and 2- Δ 4' at 460 nm.

plex was formed. From Figure 5, we observe that the various surfactants give different absorptions. This is because the different surfactant formed micelles different in size and different micelles have still different adsorption forces. Among them, the non-ionic surfactant, triton x-100, gives the highest peak and deepest valley absorption. Therefore, triton x-100 was used in this study. The effect of varying the addition of 1% triton x-100 on absorption of Ge-*o*-CPF complex solution is shown in Figure 6. The Ge-*o*-CPF complex solution approaches to maximum and remains almost constant while the addition of 1% triton x-100 is more than 0.5 mL. In this study, 1.0 mL of triton x-100 solution was added.

Effect of time. The effect of reaction time is shown in Figure 7. We find that the reaction is complete in 5 min. So the reaction between Ge(IV) and *o*-CPF is rapid at pH 4.5. In general, surface adsorption reaches equilibrium easily, giving rapid binding. At first, the *o*-CPF molecules are adsorbed on triton x-100 micelles then Ge molecules are modified and combined with the adsorbed *o*-CPF molecules. Therefore, the two-step reactions are both rapid. In addition, the color absorption remained almost constant for at least 2 hours. Therefore, the Ge-*o*-CPF complex is stable. This conclusion is the same for the above analysis in 'Effect of *o*-

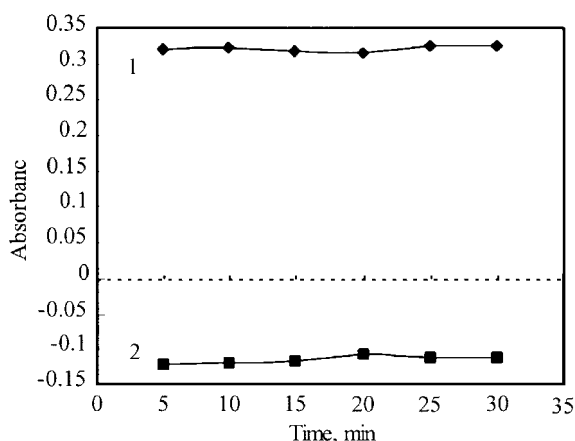


Figure 7. Effect of the reaction time on absorption of Ge (10 µg)-*o*-CPF complex solution: 1-ΔΔ at 530 nm and 2-ΔΔ at 460 nm.

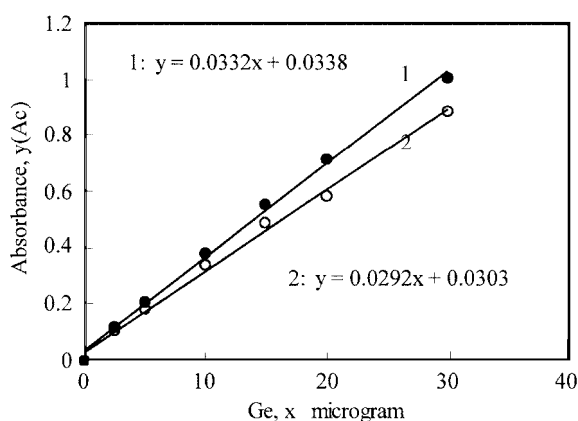


Figure 8. Calibration curves for the determination of germanium at 530 nm: 1-Δc, 2-ΔΔ.

CPF concentration

Determination of stepwise stability constant and real absorptivity. The stepwise stability constant (K_n), cumulative stability constant (K) and stepwise absorptivity (ϵ) of the complex can be calculated by the equations:⁹

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma' C_M)} \quad \text{and the cumulative constant (K)}$$

$$K = \prod_{n=1}^{\gamma} K_n \epsilon_{ML_n}^{\lambda_2} = \frac{A_c}{\delta C_M (\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n} \epsilon_{ML_{n-1}}^{\lambda_2}$$

The term n indicates the n -th complex and δ , the thickness of the cell. The molar ratio γ' should be between $n-1$ and n when preparing the mixed solution. The following solutions were prepared for the determination of the above stability constant and absorptivity of the complex: 10.0 µg Ge(IV) with 0.10, 0.30 and 0.50 µmol *o*-CPF at pH 4.5, at a temperature of 15 °C and in 0.001 ionic strength. Results were listed as follows: $K_{\text{Ge}(\text{o-CPF})} = 7.45 \times 10^5$, $K_{\text{Ge}(\text{o-CPF})_2} = 4.49 \times 10^5$, $K_{\text{Ge}(\text{o-CPF})_3} = 3.26 \times 10^4$, $\epsilon_{\text{Ge}(\text{o-CPF})} = 2.44 \times 10^4$, $\epsilon_{\text{Ge}(\text{o-CPF})_2} = 5.00 \times 10^4$ and $\epsilon_{\text{Ge}(\text{o-CPF})_3} = 1.01 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 530 nm. We observe that the next-step K is always less than the last-step

K . This agrees with the multi-stage chemical reaction law. On the contrary, the absorptivity of the next-step complex is always more than the last-step one because the increase of *o*-CPF content in complex strengthens certainly the absorption of complex. The cumulative stability constant of $\text{Ge}(\text{o-CPF})_3$ was calculated to be 1.09×10^{16} . The cumulative constant of Ge-o-CPF complex is high, so the complex is very stable.

Calibration graph. A series of standard Ge (0-40.0 µg/25 mL) solutions were prepared and the absorbance of each was measured. A_c of each solution was obtained. Calibration curves are shown in Figure 8. All measurement points around curve 1 are more linear at the range 0-30.0 mg Ge in 25ml of solution than those around curve 2, and the slope of curve 1 is steeper than that of curve 2. The linear regression equation of curve 1 is expressed as: $y = 0.0332x + 0.0338$ (x indicates Ge amount, mg and $y = A_c$, the correlation coefficient was 0.9995). Therefore, the accuracy and sensitivity of the recommended method are better than those of ordinary spectrophotometry.

Precision and detection limit. Six replicated determinations of standard solution containing 2.50 µg of standard Ge(IV) were carried out. Results are as follows: 2.45, 2.45, 2.54, 2.51, 2.48 and 2.57 µg, respectively. The relative standard deviation (RSD) is 1.8%. However, the RSD is 4.8% by ordinary spectrophotometry.

We used 0.010 of real absorbance (A_c) to calculate the detection limit of Ge: 0.30 µg/25-mL (0.01 mg/L).

Effect of foreign ions. Once the masking agent was added, none of the following ions affected the direct determination

Table 1. Determination of germanium in water and drink samples (*: mean of 2 determinations by AAS, drops Ge(IV) standard solution were added into samples 1 and 2)

Sample	Added, mg/L	Found, mg/L	Recovery, %
1 Wastewater	0.000	0.941, 0.938	102
		0.958, 0.953	
		0.934, 0.949	
		average 0.946 (0.981 *)	
		RSD 0.97%	
2 Hot spring water	0.000	1.20	96.4
		(average of 2 determinations)	
		0.538, 0.524	
		0.530, 0.565	
		0.547, 0.541	
		average 0.541 (0.529 *)	
		RSD 2.7%	
3 Drink	0.000	0.782	101
		(average of 2 determinations)	
		0.046, 0.043	
		0.046, 0.052	
		0.046, 0.049	
		average 0.047 (0.051 *)	
		RSD 6.5%	
3 Drink	0.250	0.300	101
		(average of 2 determinations)	

of 10.0 μg of Ge (<10% error): 1 mg of Cl^- , SO_4^{2-} , NO_3^- , F^- , PO_4^{3-} , NH_4^+ , Ca(II), Mg(II), Ba(II), Cu(II); 0.5 mg of Hg(II), Cd(II); 0.2 mg of La(III), Au(III); 0.2 mg of Ni(II), Co(II), Sn(II), Fe(II), Ag(I), Pt(IV), Cr(III), Zn(II), Mn(II), W(III), Al(III) and 0.05 mg of V(V), Ti(IV), In(III), Mo(IV); 0.02 mg of Zr and 0.005 mg of Sb(III).

Samples analyzed. To the method, Ge was determined in water and samples. The results are listed in Table 1. The RSDs are less than 6.5% and the recovery rate of standard Ge(IV) between 96.4 and 102%. In addition, to confirm the data obtained by the recommended method, we determined Ge content in the above samples by AAS. The results are listed in Table 1, too. By comparison, the data obtained by the two methods are identical, so the recommended method may give the accurate determination of micro amounts of Ge.

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