

Analysis of Germanium in the Ore Samples by UV-Visible Spectroscopy

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Abstract : A simple, rapid, reproducible and selective UV-Visible spectrophotometric method has been developed for determination of germanium in a weak acid medium (pH = 3.0) in the presence of mandelic acid (MA) and malachite green (MG). A single extraction in chlorobenzene was used for the analysis. The germanium-MA ion association complex exhibits an absorption maximum at $\lambda_{\max} = 618$ nm with MG as counter ion and has an apparent molar absorptivity of $1.313 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The values obtained by this UV-Visible spectrophotometric method are in good agreement with the values from inductively coupled plasma-mass spectrometer analysis.

Key words : UV-Visible spectroscopy, Germanium, mandelic acid, malachite green.

1. Introduction

Spectrophotometric methods, with varieties of complexants or color forming reagents, have been commonly employed for the determination of trace amount of germanium.¹⁻⁶ In the best known one phenylfluorone (9-phenyl-2,3,7-trihydroxy-6-fluorone; PF) was used as a complexing agent. This method suffers from problems related to poor selectivity, poor reproducibility and the slow formation of the Ge (IV)-PF complex. The PF method also requires the addition of gelatin, gum arabic or poly (vinylalcohol) as a dispersing agent because of the low solubility and stability of the complex in water. Alternatively, other color forming PF-derivatives in the presence of cationic surfactants have been tried for the

determination of germanium.^{7,8} These methods have to use highly acidic medium (15 M phosphoric acid or 6 M sulphuric acid) for forming stable complexes.

Methods using initial extraction of germanium and subsequent spectrophotometric determination have also been reported.⁹⁻¹² However, the major drawback in these studies is the tedious pre-extraction steps to separate the germanium from interfering ions. Flame atomic-absorption spectrophotometry cannot give reproducible results because of volatilization of GeO without undergoing atomization, on account of the high dissociation energy of the Ge-O bond.^{13,14}

α -Hydroxy-acids have been successfully tried as complexing agents, especially for metals which form oxo-ions in solution.¹⁵⁻²² It has been reported that germanium can react rapidly with mandelic acid (MA) to form a complex that could be extracted into chlorobenzene with malachite green (MG) as counter-ion, in weakly

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acidic media (pH = 2.5-3.5) at room temperature. The ion-association complex with MG is very stable. The complexation is very selective and the determination is reproducible, and less troublesome than previously reported methods.

It becomes important to find rapid and reproducible method for the determination of germanium from its ores. Further, the method should be free from using highly acidic conditions, additional dispersing agents (like gum Arabic) or surfactants. Hence, we employed a UV-Visible spectrophotometric method of determination of germanium in the ore by complexing with MA. A simple and single extraction procedure was adopted to isolate the Ge-MA complex by forming ion pair association with MG. The effectiveness of the Ge-MA complexation method for the determination of germanium was verified by comparing the data from inductively coupled plasma mass spectrometer (ICP-MS) analysis.

2. Experimental

2.1. Reagents

Malachite green (MG), mandalic acid (MA) and germanium ICP/DCP standard solution were purchased from Aldrich Chemical Co. Hydrofluoric acid, nitric acid, perchloric acid, sodium acetate and sulfuric acid were purchased from Duksan Pure Chemical Co. Ltd. Aqueous solutions were prepared using demineralized water.

2.2. Standard germanium solution and ore

Germanium ore samples obtained from various natural sources. Required concentration of germanium (1000 ppm) was obtained by suitable dilution of the standard Ge solution (0.1 mL) with demineralized water (10 mL).

0.3 g of ore the sample was taken in a PTFE beaker and treated with 5 ml of 4:1 v/v of nitric acid : perchloric acid, for 2 h. 5 mL of 4:1 v/v of hydrofluoric acid : perchloric acid was added to the mixture and heated at 60 °C. After cooling, required amount of the soluble salt was dissolved in demineralized water for complexation and extraction studies.

2.3. Complexation and extraction

A suitable volume of standard germination solution (containing up to 2.50 µg of germanium) was transferred into a 10 mL test-tube equipped with a stopper. 1.0 mL of acetate buffer, 0.6 mL of MA solution (1×10^{-2} M) and 1.0 ml of MG (2×10^{-3} M) were added to above solution. 4.0 mL of water and 4.0 mL of chlorobenzene were added and shaken well for 5 min. The phases were allowed to separate.

The amount of germanium in the ore samples was estimated using ICP-MS (VG Elemental Plasma Quad 3). The ore samples were treated successively with nitric acid : perchloric acid (4:1 v/v), hydrofluoric acid : perchloric acid (4:1 v/v) before making solution for analysis.

2.4. Apparatus

UV-Visible spectrophotometer (UV-240 Shimadzu, Japan) was used for absorbance measurements. The absorption spectra of chlorobenzene extracts of germanium-MA complex were recorded for the standard and core samples. ICP-MS (MLAN 6100), Perkin Elmer was used to estimate the germanium content in ore samples with an injection flow of 1.20 mL/min and under the pressure of 0.94 L/min.

3. Results and Discussion

3.1. Absorption spectra

By performing several trial experiments, the optimum conditions of experimental variables for the determination of germanium by complexation with MA in the presence of MG as counter ion were investigated. pH of the medium was controlled as 3.0 by employing an acetate buffer. While forming complexation and further extraction, a constant 5 min shaking time was maintained for ore and standard samples. The absorbance of chloroform phase was checked to be constant over a long period. This allowed use to measure the absorbance of chloroform extracts to determine the concentration of germanium.

The absorption spectrum of the ion association

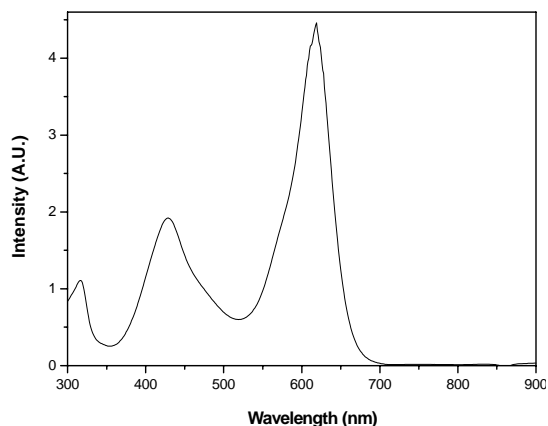


Fig. 1. UV-Visible absorption spectrum of the Ge-MA complex in chlorobenzene.

species formed between germanium-MA complex and the counter ion (MG) in chlorobenzene is presented in Fig. 1. An absorption peak was observed at 618 nm. The absorbance values of chlorobenzene extracts of germanium added samples increases with increasing concentration of germanium.

3.2. Calibration and molar absorptivity

Sequence of concentrations of germanium samples were made from the standard Ge sample and used to form complexation with MA in the presence of MG. Absorbances of chloroform extracts were followed at the wavelength corresponding to absorbance maximum. A calibration graph was obtained plotting the absorbance against concentration of germanium (Fig. 2). The calibration graph shows linearity over a range of germanium concentration. The apparent molar absorptivity of the germanium-MA complex was calculated as $1.31 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ from the slope of the linear region of calibration curve. The excess use of concentrations of MA and MG hinders the determination of exact composition of the complex by continuous various technique. Alternatively, the composition of the complex was inferred through the comparison of molar absorptivity values. It is to be noted that the molar absorptivity of the Ge-MA complex is two times higher than simple MG in aqueous solution. This suggested that

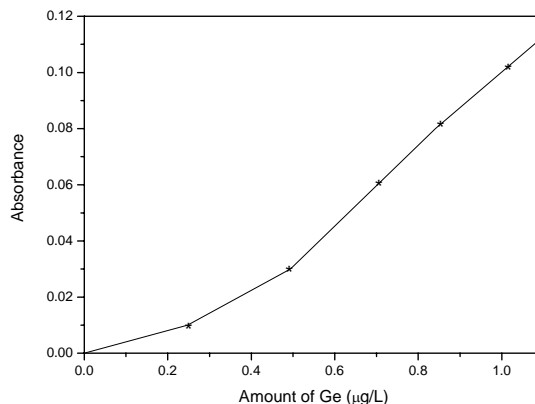


Fig. 2. Calibration plot showing the absorbance changes in Ge-MA ion association complex with concentration of germanium

MA = $1.5 \times 10^{-3} \text{ M}$, MG = $5.0 \times 10^{-4} \text{ M}$, pH = 3.0, Ge = 0.1-1.0 $\mu\text{g/L}$

molar ratio of MG to Ge in Ge-MA complex is 2:1. Hence, a doubly charged germanium complex of MA is expected to be formed.

Our main aim of the present study is to use this technique to find the germanium concentration in the ore samples. Hence, no attempt was made to know the stoichiometry of the Ge-MA complex. However, based on the charge of the complex and conditions of complexation, the complex is presumed to be $[\text{Ge}(\text{MA})_3]^{2-} \text{MG}^{2+}$.

3.3. Ore analysis

Ore samples (1-8) collected from various natural sources were used for the determination of germanium contents. Calculated portion of germanium ore sample (after chemical treatment as described in experimental section) was dissolved in water. A diluted solution of the germanium ore sample solution was used to make complex formation with MA in a similar conditions used for standard germanium samples. Few ore samples were analyzed for germanium content in them. The UV-Visible absorption spectra of Ge-MA complex corresponding to ore samples are presented (Fig. 3). The germanium content in the ore sample was calculated using the absorbance value of the ore sample

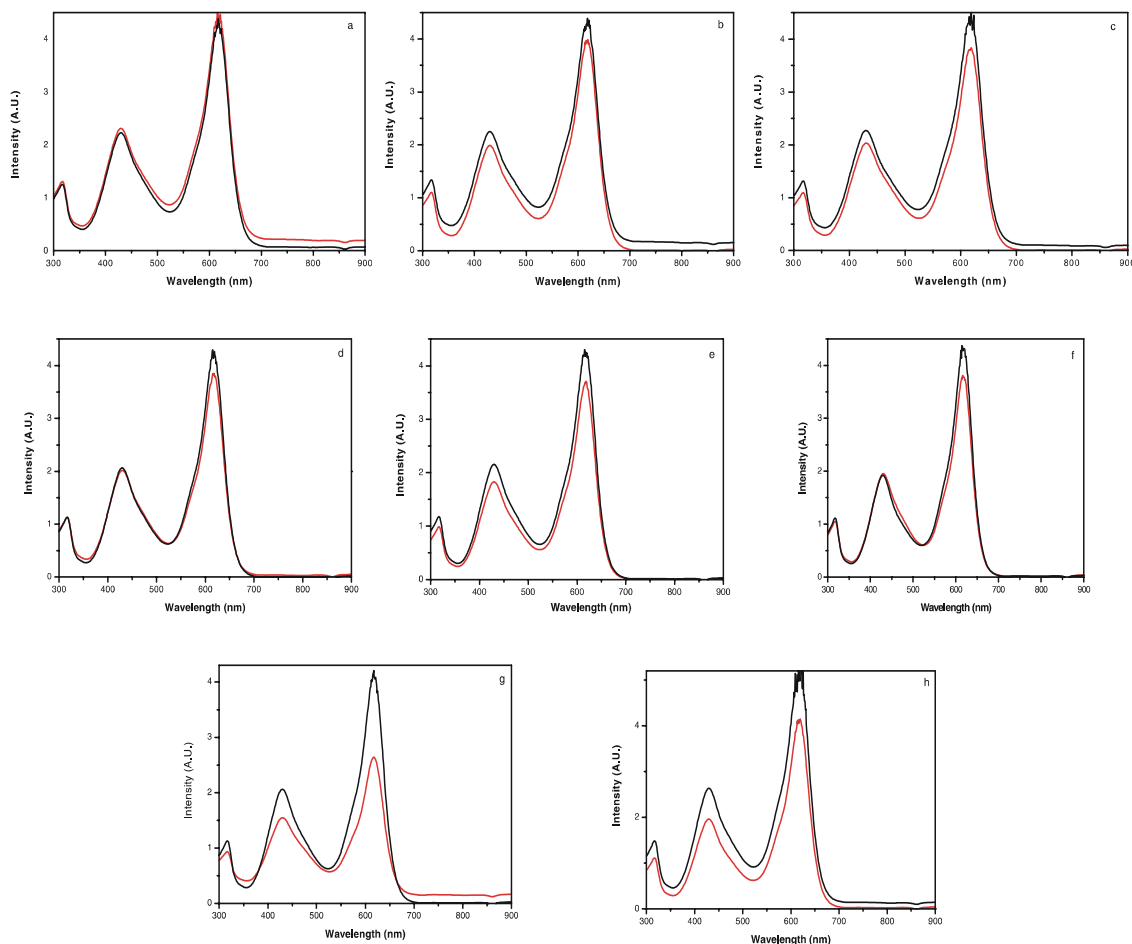


Fig. 3. UV-Visible absorption spectra of Ge-MA complex for the ore samples (a-h); MA = 1.5×10^{-3} M, MG = 5.0×10^{-4} M, pH = 3.0, Total volume used for complex preparation = 8 mL; Each ore sample was analyzed for two measurement with 0.1 mL (thick line) and 0.2 mL (dotted line) of Ge solution in the total volume.

and calibration curve of the standard samples.

The average value of the germanium contents of each ore sample is given in *Table 1*. To test the validity of this method of determination of germanium, the same ore samples were analyzed for germanium contents through ICP-MS method. The germanium content of the ore sample as determined by ICP-MS is presented in *Table 1*. The close matching of the values of germanium between ICP-MS and the UV-Visible spectrophotometric method validates the use of the Ge-MA complex method to follow the germanium content in germanium ore sample.

4. Conclusion

We developed a selective, rapid and reproducible method for determination of germanium in ore samples. The data obtained were compared by analyzing the sample by ICP-MS method. The results obtained were found to be highly satisfactory

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