Asian Journal of Chemistry Vol. 12, No. 2 (2000), 477–482

β-Correction Spectrophotometric Determination of Gallium with Alizarine Red S

HONG-WEN GAO* and HONG-LIANG SHI†
School of Chemistry and Chemical Engineering, Anhui University
Hefei-230039, PR China

The determination of gallium has been improved by β-correction spectrophotometry with alizarine red S (ARS). β-Correction spectrophotometry can eliminate completely the effect of excess ARS in its gallium colored solution to give out the real absorbance of Ga-ARS chelate. All of the analytical sensitivity, accuracy and precision were higher than those in the single wavelength method. By means of the β-correction principle the characteristic parameters of the chelate can be determined acceptably. Beer's law was obeyed over the concentration range 0–1.0 mg/L Ga and the detection limit of Ga is 0.015 mg/L. This method has been applied to the analysis of environmental materials with satisfactory results.

INTRODUCTION

Gallium (Ga) is one of the rare elements. It often exists in some environmental materials, for example, coal-gangue, ore, etc. The ordinary spectrophotometric determination of gallium includes triphenyl methane dyes[1, 2], trihydric fluorenone[3, 4], etc. The determination of trace amounts of gallium in environmental materials has been improved by β-correction spectrophotometry with the reaction of gallium(III) with alizarine red S (ARS) at pH 4, which is selective in the extraction procedure with butyl acetate to separate other metal ions. β-Correction spectrophotometric method is a new analytical method which is different from other dual-wavelength methods[5–10]. It can eliminate completely the effect of excess ARS in its gallium(III) coloured solution to give out the real absorbance of produced Ga-ARS chelate. The sensitivity, precision and accuracy are all increased. By means of this β-correction principle the Ga-ARS chelate's composition ratio, its practical molar absorptivity at 490 nm and its instability constant at pH 4 have all been determined. Especially, the complexation ratio is simpler in operation and more understandable in principle than that obtained by the usual molar-ratio method[11], equilibrium movement[12], continuous variation[13], etc. Recently, this method has been applied to the analysis of beryllium[14], aluminium[15], antimony[16], etc. Results show that Beer's law is obeyed over the concentration range 0–1.0 mg/L Ga and the detection limit of Ga 0.015 mg/L. The recovery of Ga was between 91.8 and 106% with the relative standard deviation less than 3.8%.

Principle

From the following expression the real absorbance (A_c) of a metal (M) complex (ML_γ) produced with a ligand (L) in solution is calculated.

---

†Huaibei Enviroment Monitoring Center, Huaibei-235000, PR China

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta}$$

where ΔA and $\Delta A'$ are the absorbances of the mixed solution of ML_γ and L measured at wavelengths λ_2 and λ_1 against the reagent blank (only L solution), respectively and both α and β are named correction factors which are calculated as follows.

$$\alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda_1}}{\varepsilon_{ML_\gamma}^{\lambda_2}} \quad \text{and} \quad \beta = \frac{\varepsilon_L^{\lambda_2}}{\varepsilon_L^{\lambda_1}}$$

where $\varepsilon_{ML_\gamma}^{\lambda_1}$, $\varepsilon_{ML_\gamma}^{\lambda_2}$, $\varepsilon_L^{\lambda_1}$ and $\varepsilon_L^{\lambda_2}$ are the molar absorptivities of ML_γ and L at wavelengths λ_1 and λ_2, respectively, whose ratio may be computed after the direct determination of L and ML_γ solutions.

The true not apparent molar absorptivity ($\varepsilon_{ML_\gamma}^{\lambda_2}$) and the amount ($\gamma'$) of L to coordinate M in reaction may be expressed as follows:

$$\varepsilon_{ML_\gamma}^{\lambda_2} = \frac{A_c}{\delta C_M}; \qquad \eta = \frac{A_c - \Delta A}{A_0} \qquad \text{and} \qquad \gamma' = \eta \times \frac{C_L}{C_M}$$

where η is the reacted ratio of ligand, C_M is the molar concentration (mol/L) of M in the beginning solution and δ is the thickness of the cell. C_L is the molar concentration (mol/L) of L in the beginning solution and A_0 is the absorbance of the blank reagent (only L) measured at wavelength λ_2 against water reference. While γ' reaches maximum we think that $\gamma = \gamma'$, where γ is a natural number to the named the complex number or stoichiometric ratio of the complex produced.

In order to obtain the instability constant (K) of chelate MR_γ, we discuss the following equilibrium from the reaction between 'b' mol/L R and 'a' mol/L M.

$$\gamma R + M \overset{K^{-1}}{\rightleftharpoons} MR_\gamma$$

At beginning	b	a	0	mol/L
At equilibrium	(b–γc)	(a–c)	c	mol/L

where c is the chelate's concentration and K is the instability constant of complex MR_γ. We may calculate K value from the following equation:

$$K = \frac{(a - c)(b - \gamma c)^\gamma}{c}$$

Because $\gamma c/b = \eta$, the instability constant of chelate MR_γ may be expressed by

$$K = \frac{b^{\gamma-1}(a\gamma - b\eta)(1 - \eta)^\gamma}{\eta}$$

EXPERIMENTAL

Visible spectra were recorded with Model 7230 spectrophotometer (Shanghai, China) in a 3 cm glass cell.

Standard gallium solution, 10.0 mg/L; ARS solution, 0.020% (Shanghai

Reagents); acetate buffer solution, pH 4; titanium trichloride solution, 15–20% (AR, Shanghai Chemicals); butyl acetate (AR, Shanghai Chemicals); hydrofluoric acid; hydrochloric acid; sodium citrate solution, 2% (AR, Beijing Reagents)

Recommended Procedure: Weigh 1.00 g of an environmental sample and burn into ashes at 600°C in a muffle furnace. Add 1 mL of hydrofluoric acid, 1 mL of 50% sulfuric acid and 3 mL of hydrochloric acid. Evaporate the excess acid at 250°C. After cooling, dissolve it in 5 mL of 6 mol/L hydrochloric acid and dilute to volume with distilled water in a 25 mL volumetric flask. To an aliquot of the above solution containing less than 0.025 mg of gallium, add 1 mL of titanium trichloride solution and 5 mL of 6 mol/L hydrochloric acid. After 20 min, the solution is transferred into a separating funnel and extracted with 10 mL of butyl acetate for 1 min. After separating the aqueous layer, gallium ions are stripped with 10 mL of distilled water and determined spectrophotometrically with ARS as follows: The above solution is taken in a 25 mL standard flask. 2 mL of acetate buffer solution, 1 mL of sodium citrate solution and 3 mL of ARS solution are added successively. Dilute to volume with water and mix well. After 20 min, measure the absorbance at 420 and 490 nm, respectively.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 1 shows the absorption spectra of ARS, Ga-ARS complex solution containing 0.020 mg of Ga(III) and only Ga-ARS chelate solution. From curve 2 two wavelengths should be selected such that the analytical sensitivity reaches maximum: 420 and 490 nm. From curve 1, β is calculated to be 0.148 and $\alpha = 0.332$ from curve 3.

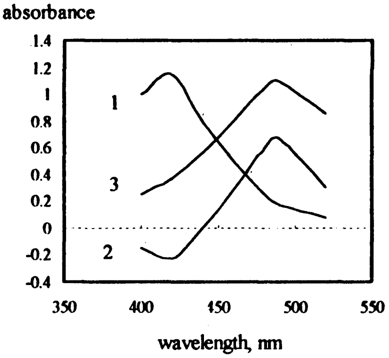

Fig. 1. Absorption spectra: 1. 24 mg/L ARS against water; 2. Ga (0.020 mg)-ARS solution against reagent blank; 3. Only Ga-ARS complex solution against water.

Effect of ARS Concentration: Fig. 2 shows the effect of ARS, in the presence of citrate, on absorbance of the reagent blank at 420 nm against water, that of the Ga(III)-ARS (containing 0.020 mg of Ga) solution at 420 and 490 nm against the reagent blank and that of the real absorbance of Ga-ARS chelate at 490 nm against water. It is difficult to calculate accurately the complex ratio of ARS to Ga from curve 3 by the molar ratio method because of the unclearness of the inflexion point.

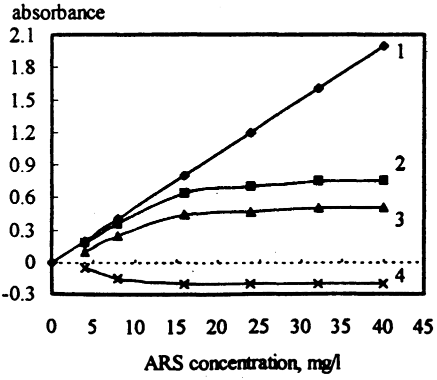

Fig. 2. Effect of ARS concentration on Ga complex solution. 1. ARS solution at 420 nm against water, 2. Ac of Ga (0.20 mg)-ARS complex solution at 490 nm against water; 3. Ga (0.020 mg)-ARS reaction solution at 490 nm against reagent blank, 4. Same as 3 but at 420 nm.

Determination of γ: From curves 1, 2 and 3 above, both the effective percentage (η) of ARS and its complex ratio (γ) to Ga at any ARS concentration may be calculated and their curves have been drawn in Fig. 3. We see that from curve 1, γ value remains constant to be 2 when ARS concentration is more than 16 mg/L. The complex ratio of Ga to ARS is therefore 1 : 2, which is expressed by GA(ARS)$_2$. At this concentration, η of ARS equals about 40% from curve 2 in Fig. 3. The excess of ARS occupies about 60% in this solution. It is indubitable that this excess will affect the measurement of the chelate's absorbance and the determination of the chelate's characteristic parameters. In other words, the single wavelength spectrophotometry may not give out the expected analysis.

Calculation of Instability Constant: In the determination of instability constant of Ga-ARS complex, we use $a = 1.15 \times 10^{-5}$ and $b = 1.12 \times 10^{-5}$ mol/L (to see principal section). We obtain that $\gamma = 2$ and $\eta = 65\%$. Therefore, K of the formed chelate was computed to be 3.32×10^{-11} at pH 4.

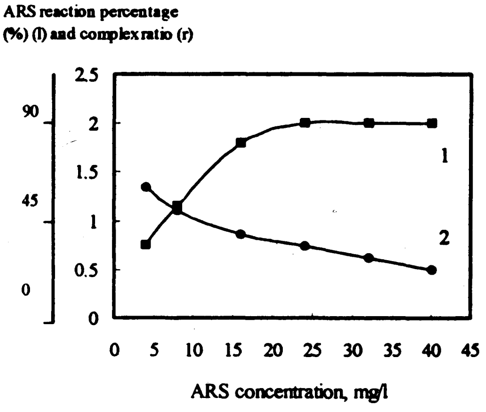

Fig. 3. Determination of ARS reaction percentage (η%) and its Ga complex ratio (γ): 1. γ., 2. η%.

Effect of Changing Other Conditions: The reaction between Ga(III) and ARS proceeds hardly when pH is less than 3 or more than 7, but fairly and rapidly at pH 4–5. The formation of the colored complex of Ga with ARS is complete in 10 min. Measurement of the absorbance was therefore carried out 20 min after the addition of ARS, the color of the complex remaining constant for at least 2 h.

Calibration Graph: A series of standard gallium solutions were prepared and the absorbance of each was measured and plotted. Two curves of Ac and ΔA with the concentration (x) of gallium were drawn in Fig. 4. From curve 1, Beer's law is obeyed over the concentration range 0–1.0 mg/L Ga Curve 1 is more linear than curve 2, which shows that the accuracy obtained by β-correction spectrophotometry is higher than that obtained by single wavelength spectrophotometry. From curves 1 and 2, the sensitivity of the recommended procedure is increased, as shown by the higher gradient. We can calculate the chelate's ε_p to be 1.97×10^4 L mol^{-1} cm^{-1} at 490 nm from curve 1 but its ε_a to be only 1.39×10^4 from curve 2.

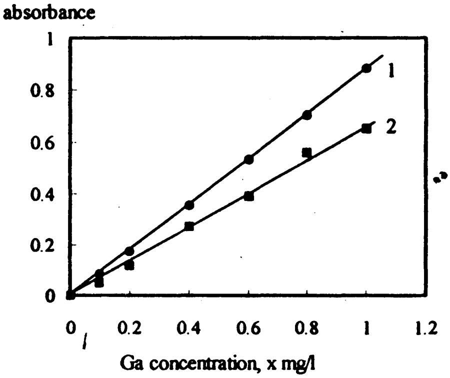

Fig. 4. Standard curves for determination of Ga at 490 nm. 1. Ac(x), 2. ΔA(x).

Effect of Foreign Ions: Once the extraction procedure is carried out and in the presence of sodium citrate, for 20 μg of gallium, up to 10 mg of Ca^{2+}, Mg^{2+}, K^+, Ti(IV), Al^{3+}, Fe^{2+}; 1 mg of Mn^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, As(III) and 0.2 mg of Sb^{3+}, Hg^{2+}, Co^{2+}, Ni^{2+} can be tolerated.

Precision and Detection Limit: Ten replicate determinations of a standard Ga solution containing 5.0 μg were carried out, the relative standard deviation (RSD) and the maximal relative error (MRE) being 3.4 and 7.6%, respectively. However, the RSD and MRE for the single wavelength method were 7.4 and 12%. Therefore, both the precision and accuracy obtained by β-correction spectrophotometry are higher than those obtained by ordinary spectrophotometry.

We use 0.010 of a real absorbance to calculate the detection limit of gallium to be 0.015 mg/L.

Samples Analyzed: As a test of the method gallium was determined in environmental materials, for example, wastewater (1) coal (2), gangue (3) and dust (4). The results have been listed in Table-1. The recovery was found to be between 91.8 and 106% with the RSD of less than 3.8%.

TABLE-1
DETERMINATION OF GALLIUM IN SEVERAL SAMPLES

Sample No.	Added, mg/kg	Found, mg/kg	RSD, %	Recovery, %
1.	0	0.045*	3.8	106
	0.05	0.098†		
2.	0	0.679*	2.8	106
	0.50	1.21†		
3.	0	0.992*	2.0	91.8
	1.00	1.91†		
4.	0	1.65*	1.6	94.0
	1.00	2.59†		

*Average of 6 determinations; †Average of 3 determinations

Conclusion

β-Correction spectrophotometry has determined accurately trace amounts of gallium and its complex ratio with ARS simple and easily using the reaction of Ga(III) with ARS at pH 4. According to the recommended procedure, almost all metal ions can be separated or masked to increase the selectivity. This method is suitable for the analysis of wastewater, ore, coal and other environmental materials.

REFERENCES

1. Y.X. Ci, *Scientia Sinica*, **3**, 209 (1985).
2. Y.D. Se, *Fenxi Ceshi Xuebao*, **5**, 42 (1986).
3. G.M. Li, *Phy. Test and Chem. Anal., Part B*, **16**, 43 (1980).
4. J.X. Wang, *Fenxi Huaxue*, **13**, 593 (1985).
5. H. Watanabe and H. Ohmori, *Talanta*, **26**, 959 (1979).
6. D. Chen, *Anal. Chim. Acta*, **222**, 205 (1989).
7. K.L. Ratzlaff, *Anal. Chem.*, **49**, 2170 (1977).
8. H.W. Gao, *Huanjing Kexue*, **14**, 80 (1993).
9. J.S. Wei, *Fenxi Huaxue*, **13**, 762 (1985).
10. H.W. Gao, Proc. 4th Asian Chem. Congress, Chin. Chem. Soc., Beijing, p. 372 (1991).
11. J. Yoe, *J. Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).
12. A.I. Laearev, *Zav. Lab.*, **41**, 534 (1975).
13. P. Job, *Ann. Chim.*, **9**, 113 (1928).
14. H.W. Gao and P.F. Zhang, *Anal. Proc.*, **31**, 85 (1994).
15. H.W. Gao and H.L. Shi, *Spectroscopy*, **8**, 47 (1994).
16. H.W. Gao and P.F. Zhang, *Analyst*, **119**, 2109 (1994).

(*Received*: 11 October 1999; *Accepted*: 27 November 1999) AJC-1932