

Extraction-Atomic-Absorption Determination of Gallium (III) with 2-hydroxy-5-T-butylphenol-4'-methoxy- azobenzene

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Abstract

The complexation of gallium with 2-hydroxy-5-T-butylphenol-4'-methoxy-azobenzene (HR) has been studied by atomic absorption and spectrophotometric methods. The optimal conditions for the formation and extraction of the complex were found. The maximum light absorption of the complex in n-butanol is in the range of 450 - 470 nm. The molar absorption coefficient is $(3.3 - 4.2) \cdot 10^4$. The stability constant of the gallium coordination compound in n-butanol is $\beta_1 = 4.2 \cdot 10^{10}$. The developed technique allows to determine the gallium content within $n \times 10^{-1} - n \times 10^{-4}\%$. The selective and sensitive technique for the extraction-atomic absorption determination of gallium in soils has been developed.

Keywords

Gallium, Complexing, Atomic Absorption Method, Extraction, Gallium in Soil

1. Introduction

The synthesis and research of new organic reagents, which minimize the determination of elements and increase the accuracy of the analysis, are actual tasks of spectrophotometry. In this aspect, azo compounds that contain nitrogen atoms are promising reagents for gallium ion in photometric and extraction-atomic absorption determination [1]-[7]. It is known that azo compounds based on para-tert-butylphenol and pyrogallol are promising reagents for the determination of several metal ions [8] [9]. This is because the hydroxyl group of

para-tert-butylphenol provides the possibility of complex formation with the direct participation of the nitrogen atom of the azo group forming metal-nitrogen bond. Therefore, the discovery of new analytical applications of azo compounds synthesized based on para-tert-butylphenol was practically interesting. The detection limit of gallium in various systems is reduced by using preconcentration. Especially gallium concentrates the extraction of its complexes with methyl isobutyl ketone or ammonium pyrrolidin-dithiocarbamate [5]. Despite the fact that gallium forms numerous complex compounds with organic ligands, the ligands that are used in its determination are still relevant [10] [11].

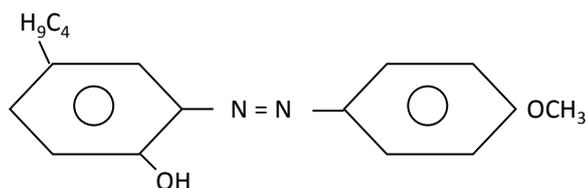
We studied the complexation of gallium with HR, as well as the conditions for the extraction preconcentration of gallium and its subsequent atomic absorption determination in soils.

2. Experimental Part

Reagents and equipment.

All chemicals used for getting a suitable medium, and solvents were commercially available chemicals from Aldrich. The initial gallium solution with a concentration of $1.2 \cdot 10^{-2}$ M was prepared by dissolving the calculated sample of metallic gallium according to the technique in [12]. More dilute gallium solutions were prepared by diluting the initial solution. HR solution with a concentration of $3.5 \cdot 10^{-4}$ M was prepared by dissolving an exact amount of HR in ethanol.

2-hydroxy-5-tert-butylphenol-4'-methoxy-azobenzene (HR) reagent was synthesized according to the procedure proposed in [13]. The reagent is a mono-basic acid and has a general structural formula as following:



The composition and structure of the reagent were determined by elemental analysis, as well as by IR and UV spectroscopy. It is a brown crystalline substance, soluble in methanol, ethanol, propanol, isopropanol, acetone and other solvents. Additional purification of the reagent was carried out by recrystallization from ethyl alcohol.

IR-spectrum 3400 cm^{-1} (O-H of aromatic ring); 2960 cm^{-1} (C-H of CH_3 group), 3060 cm^{-1} (C-H of aromatic ring); $1582, 1496, 1464 \text{ cm}^{-1}$ (C=C of aromatic ring), 1400 cm^{-1} (N=N), 1256 cm^{-1} (C-N), 1168 cm^{-1} (C-C), 1302 cm^{-1} (arom. NO_2).

The buffer solutions with ammonium acetate (pH 3 - 11) and fixanal HCl (pH 1 - 2) were used to set the pH of the medium; pH was controlled by EV-74. The ionic strength of the solutions ($\mu = 0.1$) was kept constant by KNO_3 solution.

Benzene, toluene, chloroform, carbon tetrachloride, dichloroethane, n-butanol and hexane were used as organic solvents.

The optical densities of the extracts were measured on a KФK-2 photoelectric colorimeter and on a CФ-46 spectrophotometer. Atomic absorption of gallium was measured on an atomic absorption spectrophotometer AAS-30 of Carl, ZEISS JENA Company. Standard hollow cathode lamps of the same company were used as sources of illumination. The optimal measurement conditions are given in **Table 1**.

The experimental technique.

The certain volume of a standard solution of gallium, 10 ml of a buffer solution with certain pH and 1 ml of a reagent solution have been introduced into a separatory funnel or ground stoppered test-tube, diluted with distilled water to 20 mL and extracted the formed compound with 10 ml of n-butanol, shaken for 1 min. After phase separation, the extract was sprayed into a flame of acetylene nitrous oxide and the atomic absorption of gallium was measured under optimal conditions (**Table 1**).

Technics of the determination.

A soil sample (2 - 4 g) was placed in a platinum cup, moistened with water, and 10 ml concentrated HNO₃, 10 ml of HF were added to it and three drops of 30% H₂O₂ were added dropwise. The contents were heated and filtered, the solution was evaporated to dryness, the residue was treated twice with 5 ml of concentrated HNO₃ and dissolved in 10 - 20 ml of hot water heating until dissolving the salts. The solution was transferred to a volumetric flask of 100 ml and diluted to the mark with water.

An aliquot (10 ml) of the solution was placed in a separatory funnel, the required acidity (pH 2) was adjusted with HCl, 1 ml of an ethanol solution of HR was added to it, latter was diluted with distilled water to 20 ml, and the obtained compound was extracted with 10 ml of n-butanol by shaking for 1 min. The organic phase was separated, the extract was sprayed into a flame of acetylene – nitrous oxide and the atomic absorption of gallium was measured. Gallium content was found according to the calibration curve.

The accuracy of the technique was tested on standard soil samples CII-1, CII-3. The results of the determination of gallium are given in **Table 2**.

3. Results and Their Discussion

Spectrophotometric study of the reaction.

When gallium (III) reacts with HR in hydrochloric acid solutions complexes

Table 1. The condition of atomic adsorption determination for gallium.

Wavelength, nm	Slit width, nm	Tube current, mA	Acetylene consumption, L/h	Nitrous oxide consumption, L/h
287.4	0.5	20	200	180

Table 2. The results of the extraction-atomic absorption determination of Ga (III) in standard soil samples (n = 5, p = 0.95).

Standard sample	Content, Ga, %		Sr
	According to the passport	Found	
CII-1	0.0010	0.0011 ± 0.0001	0.020
CII-3	0.0013	0.0014 ± 0.0001	0.016

are formed that are extracted with organic solvents. For the complete formation of the gallium complex, the optimum pH limit has to be 2 - 3 (**Figure 1**). The nature of the acid (HCl, H₂SO₄) almost does not affect on the reaction

The absorption spectrum of the complex.

Under optimal conditions, the absorption spectrum of the complex was recorded, the maximum of which is observed at 450 - 470 nm, and the maximum of the reagent is at 360 - 370 nm. Thus, complexation is accompanied by a bathochromic shift (**Figure 2**). The appearance of the absorption spectrum of the extract indicates that just one complex compound is formed.

Composition and physico-chemical properties of the complex.

The molar ratio of components in the complex, determined by the "straight line" method of Asmus and equilibrium shift, is 1:2 [14].

The stability constant of the complex in chloroform $3.8 \cdot 10^{10}$ and the equilibrium constant of the complexation reaction ($4.2 \cdot 10^4$ at pH = 2) were calculated by spectrophotometric data for chloroform and n-butanol solutions of the complex using the pH-dependence of the light absorption of solutions. The molar absorption coefficient of gallium, calculated by the Tolmachev method [14], is $(3.3 - 4.2) \cdot 10^4$. The calibration curve is linear within 1 - 10 µg/mL of gallium concentration. The effect of various ions on the results of gallium determination is shown in **Table 3**.

The influence of extraneous ions.

The selectivity of the extraction-atomic absorption determination of gallium with HR was studied. It has been established that large amounts of alkaline and alkaline earth elements and rare earth elements do not interfere with the determination of gallium.

Extraction of the complex.

The extractability of the complex was evaluated by the distribution coefficient and the degree of extraction. The equilibrium concentrations of gallium in the aqueous phase were differently found. During the single extraction with n-butanol, 96% gallium is extracted. An increase in the volume of the aqueous phase up to 30 ml does not significantly affect the optical density of the extracts in n-butanol. The maximum optical density of the solution is achieved by keeping the complex for 1 - 2 min. The complex is stable for two days. With increasing the concentration of the reagent, the optical density of the organic phase increases and reaches a plateau at a concentration of $3.5 - 4.2 \cdot 10^{-4}$ M of HR.

When spraying the extracts directly into the burner flame, the used organic

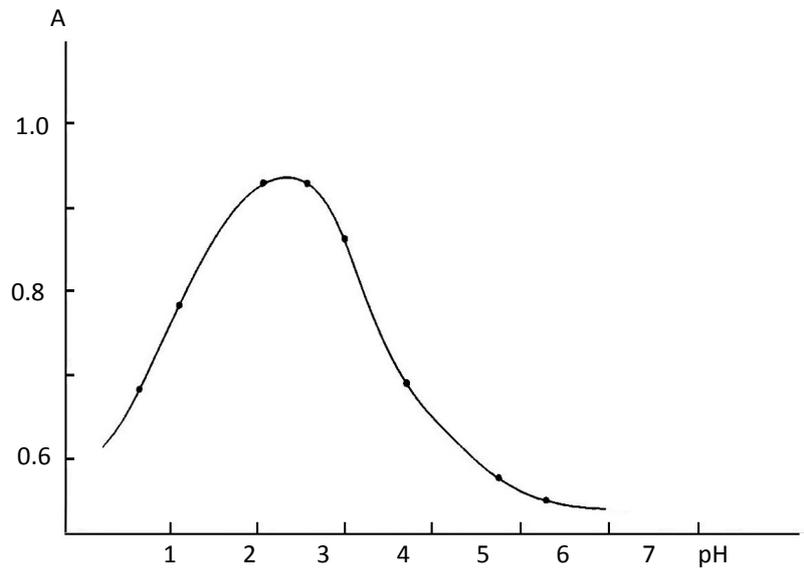


Figure 1. The effect of pH on complex formation of Ga(III). $C_{HR} = 3.5 \cdot 10^{-4}$ M, $C_{Ga} = 1.2 \cdot 10^{-2}$ M; $\lambda = 470$ nm; $V_{org} = 10$ mL; $l = 0.5$ cm; KФК-2, СФ-46.

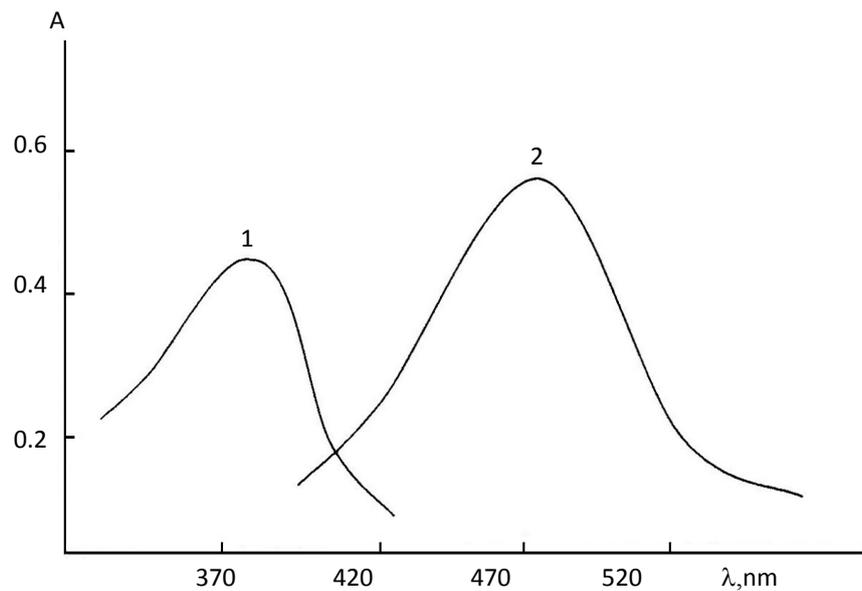


Figure 2. The adsorption spectrum of extracts of reagent (1) and Ga(III) complex (2); $C_{HR} = 3.5 \cdot 10^{-4}$ M; $C_{Ga} = 1.2 \cdot 10^{-2}$ M, $V_{org} = 10$ mL; $l = 0.5$ cm; KФК-2, СФ-46.

Table 3. The effect of extraneous ions on the results of determination of gallium (given 5 $\mu\text{g/mL}$ of gallium).

Concomitant ions	Permissible amount of concomitant ions, mg	Concomitant ions	Permissible amount of concomitant ions, mg
Na(I)	200	Fe(III)	15
K(I)	200	V(V)	10
Mg(II)	100	W(VI)	15
Ca(II)	50	Cl ⁻	4

Continued

Ba(II)	20	Br ⁻	5
Zn(II)	10	I ⁻	5
Cd(II)	10	SO ₄ ⁻²	10
Mn(II)	20	PO ₄ ⁻³	10
Co(II)	10	NO ₃ ⁻	0.5
Ni(II)	50	CO ₃ ⁻²	10
Cu(II)	10		
Pb(II)	15		
Al(III)	10		

solvents have to be inflammable. Atomic absorption of gallium is reduced when using halogen-containing solvents. A more suitable solvent for atomic absorption analysis was n-butanol. It does not change the mode of combustion of the flame and does not lead to the background in the region of the gallium analytical line, keeps stable combustion, which makes it possible to determine gallium direct spraying of the extract into the flame. For the first time, we applied the method for gallium ions of direct introduction of an organic extract into the flame to increase the sensitivity.

Preliminary extraction of gallium and the direct introduction of extracts into the flame makes it possible to increase the selectivity and sensitivity of the analysis.

The complete extraction of the gallium complex from the hydrochloric acid medium was almost used to develop the extraction-atomic absorption determination method for gallium in soils. A selective technique has been evolved for the extraction-atomic absorption determination of gallium in soils.

4. Conclusion

The complexation of Ga (III) with 2-hydroxy-5-T-butylphenol-4'-methoxyazobenzene (HR) was studied. For the first time, the coordination compound of gallium with synthesized azoreagents—HR has been obtained. It was established that including organic phase (of extract) directly into the flame increases the sensitivity of determination of gallium a few times. The optimal conditions for the complex formation and its extraction with chloroform and n-butanol are found. The molar absorption coefficient is $(3.3 - 4.2) \cdot 10^4$. The stability constant of the gallium complex in n-butanol is $\beta_1 = 4.2 \cdot 10^{10}$. Beer's law is observed within 1 - 10 mg/ml of gallium concentration. A technique of gallium determination in soils has been developed.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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