

Extraction and Atomic-Absorption Determination of Scandium (III) with 2-Hydroxy-5-T-Butylphenol-4'-Nitroazobenzene

Aydin Pashajanov

Academician M.Nagiyev Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences, AZ 1143 H.Javid Ave. 113 Baku, Azerbaijan

Abstract

Complexation of scandium 2-hydroxy-5-T-butylphenol-4'-nitroazobenzene (HR) was studied by atomic-absorption and spectrophotometric methods. Optimum conditions of formation and extraction of the complex were found. Maximum light absorbance of a complex in n-butanol is in the range of 470÷480 nm. Molar absorption coefficient equals to $(2.0-2,5) \cdot 10^4$. Stability constant of scandium in n-butanol is $\beta_{11}=3,8 \cdot 10^{10}$. Selective and sensitive techniques of extraction-atomic absorption determination of scandium in soils were developed.

Keywords: scandium, atomic-absorption method, extraction, complexation.

1. Introduction

Synthesis and study of new organic reagents that can reduce the duration of determining elements and increase the accuracy of analysis are actual tasks of spectrophotometry. In this regard promising reagents on scandium ions for photometrical and extraction-atomic-absorption determination are nitrogen containing azo-compounds [1-5]. It is known that azo-compounds based on para-tret-butylphenol and pyrogallol are prospective reagents for determination of ions of a number metals [6, 7]. This was caused by the fact that hydroxyl group of para-tret-butylphenol creates the possibility of forming the complexes with direct involvement of nitrogen atom of azo group caused by metal-nitrogen bond. That's why the discovery of new analytical possibilities of azo-compounds synthesized on the basis of para-tret-butylphenol was of practical interest. Preconcentration is applied to reduce the detection limit of scandium in different objects. Scandium is especially often concentrated by extraction of its complexes with methylisobutylketone or ammonium pyrolidiniumthiocarbamate [5].

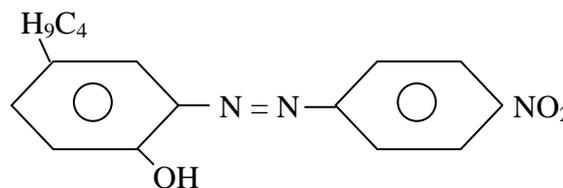
We studied the complexation of scandium with HR, as well as extraction concentration conditions of scandium and following atomic-adsorption determination in soils.

2. Experimental part

Reagents and instruments. Primary solution of scandium with concentration of $1.2 \cdot 10^{-2} \text{M}$ was prepared by dissolution of accurate weight of metallic

scandium by technique [8]. More diluted solutions of scandium were prepared by diluting the primary solution. The solution HR with concentration of $3,5 \cdot 10^{-4} \text{M}$ was prepared by dissolution of accurate weight of HR in ethanol.

Reagent 2-hydroxy-5-T-butylphenol-4'-nitroazobenzene (HR) was synthesized by technique [9]. Reagent is a monoacid, it has general structural formula.



The composition and structure of the reagent were determined by elemental analysis, as well as by methods of IR-, UV-spectroscopy. This is a brown colored crystalline substance which is dissolved in methanol, ethanol, propanol, isopropanol, acetone and other solvents. Additional purification of the reagent was conducted by recrystallization from ethyl alcohol.

IR-spectrum 3400 cm^{-1} (O-H arom.); 2960 cm^{-1} (C-H from CH_3), 3060 cm^{-1} (C-H arom.); 1582 , 1496 , 1464 cm^{-1} (C=C arom.), 1400 cm^{-1} (N=N). 1256 cm^{-1} (C-N), 1168 cm^{-1} (C-C), 1302 cm^{-1} (arom. NO_2). For creation of necessary values of pH we used ammonium acetate (pH 3–11) and fixanal HCl (pH 1–2) buffer solutions; pH was controlled by EV-74. Ionic strength of solutions ($\mu=0,1$) was supported with constant solution of KNO_3 . We used benzene, toluene, chloroform, carbon tetrachloride, dichloroethane, n-butanol and hexane as organic solvents.

Optical density of extractants was measured on photoelectrometer KFK-2 and spectrophotometer SF-46. Atomic absorption of scandium was measured on atomic-absorption spectrophotometer AAS-30 Carl, ZEISS JENA. As light sources standard hollow cathode lamps were used. Optimum measurement conditions are listed in Table 1.

Table 1. Conditions of atomic-adsorption determination of scandium

Wavelength, nm	Slot width, nm	Lamp current, mA	Acetylene flow, l/h	Consumption of nitrogen oxide, l/h
390,7	0.5	20	200	180

Technique. A certain amount of standard solution of scandium, 10 ml of buffer solution with certain pH, 1 ml of reagent solution were poured into a separatory funnel or stoppered tubes, diluted with distilled water to 20 ml, and resulting compound of 10 ml n-butanol was extracted and mixed one minute. After complete separation of phases extract was sprayed into the flame of acetylene-nitrogen oxide and atomic-absorption of scandium was measured under optimum conditions (table 1).

3. Results and discussion

Spectrophotometric study of the reaction. During the interaction of scandium (III) with HR in hydrochloride solutions the complexes are formed which can be extracted with organic solvents. The limit of pH 2-3 is optimum for full formation of a complex of scandium (Fig.1). The nature of acids (HCl, H₂SO₄) do not almost influence on the reaction.

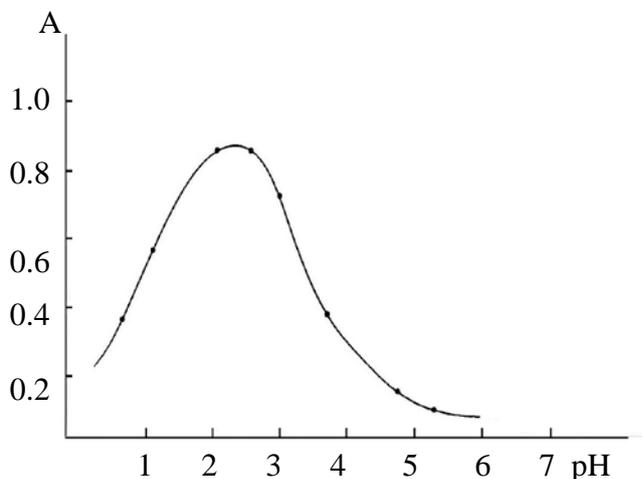


Figure 1. Influence of pH on complexation of Sc(III). $C_{HR}=3.5 \cdot 10^{-4}M$, $C_{Sc}=1.2 \cdot 10^{-2}M$; $\lambda = 470 \text{ nm}$; $V_{org}=10 \text{ ml}$; $l=0,5 \text{ cm}$; KFK-2, SF-46.

Absorption spectrum of the complex. Under optimum conditions we have taken absorption spectrum of the complex the maximum of which is observed at 450–470 nm, but maximum of the reagent is observed at 360–370 nm. Thus, the complexation is accompanied by bathochromic shift (Fig.2). View of absorption spectrum of extractant indicates the formation of one complex.

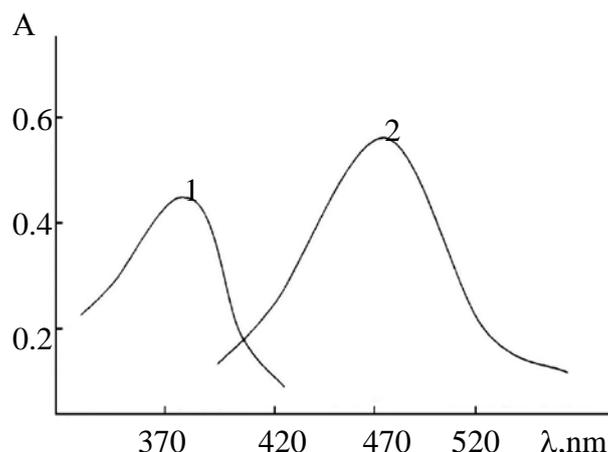


Figure 2. Absorption spectrum of extractants of reagents (1) and complex Sc(III); $C_{HR}=3.5 \cdot 10^{-4} M$; $C_{Sc}=1,2 \cdot 10^{-2}M$, $V_{org}=10 \text{ ml}$; $l=0,5 \text{ cm}$; KFK-2, SF-46.

Composition and physical-chemical properties of the complex. Molar ratio of components in the complex which was established by straight-line method of Asmus and equilibrium shift, equals to 1:2 [10]. Stability constant of the complex in chloroform $3,8 \cdot 10^{10}$ and equilibrium constant of complexation reaction $3,2 \cdot 10^4$ at pH=4.0 were calculated by spectrophotometric data for chloroform and n-butanol solutions of the complex by using dependence of light absorbance of solutions on pH.

Molar absorption coefficient of scandium, calculated by Tolmachev method [10] equals to $(2,0-2,5)10^4$. Calibration chart is linear at concentrations of scandium $1.0 \div 10.0 \text{ mkg/ml}$.

The influence of different ions on the results of determination of scandium is shown in table 2.

Influence of foreign ions

Selectivity of extraction-atomic absorption determination of scandium was studied with HR. It was established that large amount of alkali alkali-earth elements and rare-earth elements do not interfere with the determination of scandium.

Table 2. Influence of accompanying ions on the results of determining scandium (5 mg/kg of scandium was added)

Accompanying ion	Permissible amount of accompanying ion, mg	Accompanying ion	Permissible amount of accompanying ion, mg
Na(I)	200	Fe(III)	15
K(I)	200	V(V)	10
Mg(II)	100	W(VI)	15
Ca(II)	50	Cl ⁻	4
Ba(II)	20	Br ⁻	5
Zn(II)	10	J ⁻	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		

Extraction of the complex. Extractibility of the complex was evaluated by distribution coefficient and extraction degree. Equilibrium concentration of scandium in aqueous phase was found by difference. 96% of scandium is extracted with single extraction with n-butanol. Increase in volume of aqueous phase up to 30 ml does not essentially influence on optical density of extractants in n-butanol. Maximum optical density of the solution is achieved during keeping the complex 1-2 minutes. The complex is stable within two days. When the concentration of the reagent increases optical density of organic phase is enhanced and achieves plateau at the concentration of $3,5-4,2 \cdot 10^{-4}$ M HR.

When spraying directly the extracts into burner flame, organic solvents must be fuel. Atomic absorption of scandium is reduced during the use of halogen containing solvents. N-butanol was turned to be more suitable for atomic-absorption analysis. It does not change burning regime of a flame and does not create background in the field of analytical line of scandium, supports stable burning which allows us to determine scandium in direct spraying of extractant into flame. For the first time we used direct input of organic extractant into flame for scandium ions to increase sensitivity.

Preliminary extraction of scandium and direct input of extractants into flame allow us to increase selectivity and sensitivity of the analysis.

Practically full extraction of the complex of scandium from hydrochloride medium was used for development of extraction-atomic-absorption determination

of scandium in soils. Selective technique for extraction-atomic-absorption determination of scandium in soils was developed.

Determination. Soil sample (2–4 g) was put into platinum dish, wetted with water, 10ml conc. HNO₃, 10 ml HF were poured and 30% H₂O₂ was added drop by drop. The content was heated and filtered, the solvent was evaporated dry, the residue was treated twice with 5 ml conc. HNO₃ and dissolved in 10–20 ml hot water with heating till dissolution of salts. The solution was placed into 100 ml measuring flask and diluted with water to the mark.

Aliquot (10 ml) part of solvent was placed into separatory funnel, necessary acidity (pH 2) was created by HCl, 1 ml of ethanol solution HR was added, was diluted with distilled water to 20 ml and formed compound of 10 ml n-butanol was extracted by mixing 1 min. organic phase was separated, extractant was sprayed into flame of acetylene-nitrogen oxide and atomic absorption of scandium was measured. The content of scandium was found by calibration chart.

Correctness of the technique was tested on standard samples of soil SP-1, SP-3. Results of determining scandium are given in the table 3.

Table 3. Results of extraction-atomic-absorption determination of Sc(III) in standard samples of soils (n=5, p=0,95).

Standard sample	Content, Sc, %		Sr
	By name-plate	found	
SP-1	0.0012	0.0012±0,0001	0.020
SP-2	0.0014	0,0014±0,0001	0.016

4. Conclusions

Complexation of Sc(III) with 2-hydroxy-5-T-butylphanol-4'-nitroazobenzene (HR) was studied. Optimum conditions of formation of the complex and its extraction with chloroform and n-butanol were found. Molar absorption coefficient equals to $(2,0-2,5) \cdot 10^4$. Stability constant of the complex of scandium in n-butanol is $\beta_{sc}=3,8 \cdot 10^{10}$. Beer's law is observed at concentrations of scandium 1-10 mg/ml. Determination technique of scandium in soils was developed.

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