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# APPLICATION OF 1-(2-HYDROXY-1-NAPHTOAZO)-2-NAPHTHOL-4- SULFO ACID IN AMPEROMETRIC DETERMINATION OF SCANDIUM ION


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**Abstract**: Scandium metal is widely used in the production of heat-resistant, corrosion-resistant optical objects, in the production of expensive instruments in industry and medicine. The article is devoted to the detection of scandium ion using 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfo acid on natural objects by electrochemical method. Optimum conditions for amperometric determination of scandium with 1-(2-hydroxy-1-naphthazo)-2-naphthol-4-sulfonic acid: at pH 2.58, voltage 0.6 V, reaction speed 3.7 seconds, participating 4 number of electrons on the electrode surface, and the Me:R ratio is 1:1 is found. Yb 3+ , Cd 2+ , Pb 2+ , Fe 2+ cations in a 1:1 mol ratio were found not to affect the determination of scandium. The accuracy of the developed method was 99.99 when using technological water analysis in the process of gold mining.



**Keywords:** amperometric titration, 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid, inductively coupled atomic emission spectrometry analysis.


**Introduction.** The price of scandium metal in the world market is increasing day by day. During the extraction of gold, copper and silver, scandium and rare earth metals are found as secondary elements, and their amount in technological solutions is less than $1 \cdot 10^{-5}$ mol. Therefore, adsorbents, extractors and separators are used to separate it. But the separation and identification of scandium from other ions presents some difficulties. Therefore, it is of particular interest to develop new analytical methods for its determination with high sensitivity, accuracy and a wide range of detected concentrations, and to improve existing analytical methods.

In the determination of rare earth metals, residues from the mining of precious elements such as rare earths and niobium are burned in NaCl-$Ca(OH)_2$-charcoal and then washing in hydrochloric acid and sulfuric acid [1], limonite laterite 50-100 (g/t) contains nickel, Co and Sc and extraction of Sc and Al ions was taken by nitric acid pressure washing (NAPL), homogenous precipitation of limonite laterite with $MgCO_3$ at 60°C pH=4.5 [2]. Solution of iminophenols 3,5-$but_2$-2-$HOC_6H_2CH$=NX (X = 8-$C_9H_6N$, 2-MeO-5-$MeC_6H_3$ va 2-$PhOC_6H_4$) in toluene was determined to form a complex compound with Sc (III) ions [3]. Th (IV), Fe (III) and Lu (III) ions do not destroy the determination of Sc (III) ion with bis(2,4,4- trimethylpentyl) phosphine acid H[BTMPP] in the sulfate acidic environment [4]. Separation of scandium (III) ion from the composition of Iranian Sarcheshmeh copper alloy was carried out using the ion exchange method. It was determined that the optimal conditions for the adsorption of $Sc^{3+}$ ions from the solution to the cathode resin are at room temperature and pH=1.5 [5]. Moreover scandium ion is heated from red mud with 2 M oxalic acid at 90°C in a microwave oven at 2 kW power for 7 minutes. [6], [7] in pH=4.5 environment solutions Algal/ Polyethyleneimine granules APEI and quartz Algal/ Polyethyleneimine granules with , watery solutions of $NH_4F$ and alcohols mixtures of $NH_4F$ ammonium scandium fluoride in case extraction so [8], [9] by using tandem quadrupole inductively coupled plasma mass spectroscopy method (IBP-MS/MS), in the hydrochloric acid environment 5-paraaminophenyl-1, 3, 4-oxadiazole-2-thione [10], [11] 30.25 °C, effect time : in 30 minutes 5 M NaOH , 1% $H_2O_2$ dissolve in 3 M HCl and red mud from a solution of 2 M HCl adding, 30 minutes at a temperature of 40-50 °C during heated , to adding of yielding solution 2 M $Ca(OH)_2$ effect bringing scandium (III) [12], from the remains of mountain - mine , running waters and industry the determination of Sc and other REEs with 1-(2-pyridylazo)-2-naphthol (PAN) are using [13], Sc (III) ion extraction from titanium pigment emissions with a concentration of 7 mol/l $H_2SO_4$ solution and 10% D2EHPA - 5% TBP - 85%, paraffin mixture [14], using tributyl phosphate (TBF) modified with activated carbon (FU) [15], detection within 30-40 minutes in media close to pH=4 using newly synthesized ionotropic calcium gel electrostatically interacting (ALPEI) granules [16], by Job's method the determination of Sc and Ce ions with calix(4)arene derivatives in acidic medium [17], by the extraction method with 1-(2-hydroxy-1-naphtoyazo)-2-naphthol-4-sulfocid solution [18], in the method of determining $Sc^{3+}$ ion from ferrocolumbite by separating it from Ta and Nb elements [19]: ferrocolumbite was determined by heating with $NH_4F{\cdot}HF$ in a ratio of 1:10 at 200°C during 60 minutes heating and using methyl isobutyl ketone (MIBK) in the presence of 16 M $H_2SO_4$, using polydentate hybrid phenol-aminopyridine polyligand $\{N^{Me2}NN^{Me2}C^{i\,Pr2}O\}H_2$ (1-$H_2$) [20] scandium (III) ion was determined.

Therefore, it is necessary to develop a technique with high sensitivity, precision and a wide range of detectable concentrations. In addition, these methods should be technically and methodologically simple, relatively quick to perform, and inexpensive to analyze.

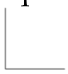
**Methods**. To determine the scandium (III) ion from the composition of the technological (AMMK) solution of the Almalyk Mining and Metallurgical Combine, add 5.0 ml of AMMK technological solution, 5.0 ml of 0.1 M solution of nitric acid solution, 10 ml of chloroform solution, 5.0 ml of a 0.1% solution of 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid reagent was added to a 50.00 ml separation funnel.

1-(2-Hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid used for analysis was purchased from Chem-Impex. A. 0.1% solution was prepared by studying the literature.

Preparation of background electrolytes. Universal buffer solutions with pH (1–12): mixture of 0.04 M ($H_3BO_3$ , $H_3PO_4$ , $CH_3COOH$) with 0.2 M NaOH solution [21].

The amperometric titration process was measured on an amperometric titrator Ekspert-001, Moscow, Russian Federation.

The amount of scandium was found from the graph of the titration curve of the dependence of the amount of current on the volume of the titrant, and the equivalent point was found.

**Results and discussion.** Amperometric titration of scandium ion with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid reagent was carried out, in which the oxidation of the reagent was first observed on the surface of two platinum electrodes. Due to the high reduction potential of scandium (III) ion, it is not reduced at the electrode and a curve of the form  is formed. It was applied to the analysis of scandium ion. The scandium titration procedure is given below.

It was carried out by amperometric titration of different amounts of scandium ion with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid solution using two platinum indicator electrodes. Each determination was repeated several times (at least 4 times) under optimal conditions based on information obtained from the literature: 1.0 ml of 0.04 M universal buffer solution (pH = 2.58) and up to 10.00 ml bidistilled water was added, 2 platinum microdisk electrodes were inserted into a cell with a volume of 50 ml, and amperometric titration was performed by applying different voltages. The obtained results are presented in Figure 1.

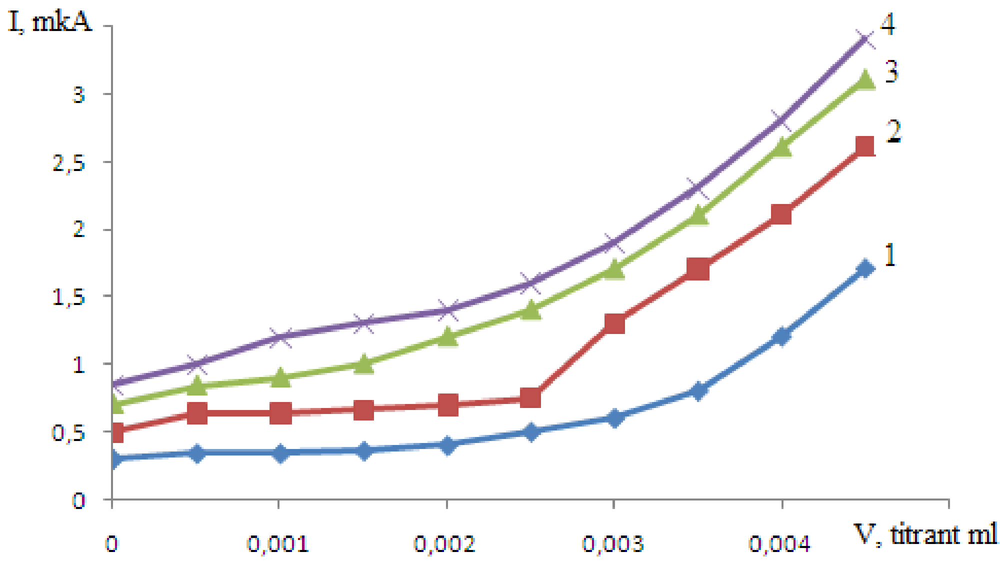



**Figure 1.** Amperometric titration graph of scandium ion with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfo acid in medium with pH=2.58 at different voltages: 1- 0.2 V; 2- 0.6 V; 3- 1.0 V; 4- 1.2 V.

As can be seen from Figure 1, it is possible to determine the equivalent point of scandium ion with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid at a voltage of 0.6 V in a buffer solution with pH=2.58.

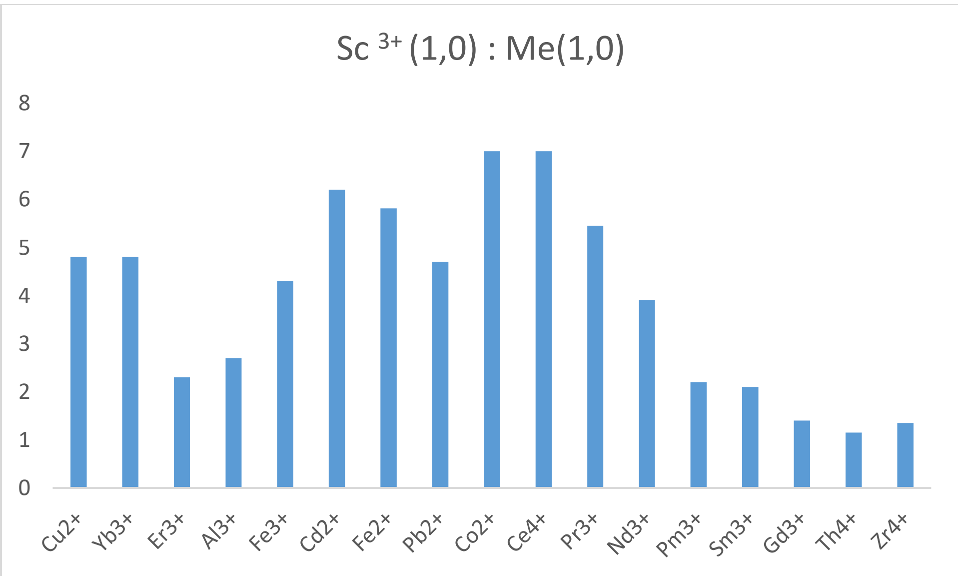
Based on the above result, the results of titration of various amounts of scandium with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid in a pH=2.58 buffer solution with a voltage of 0.6 V, the results of their processing according to the rules and methods in the literature and mathematical statistics were calculated based on the method of calculation [22] and are presented in Table 1.

**Table 1.** Results of amperometric titration of different amounts of scandium (III) with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid solution under optimized conditions

| № | Entered Sc (III), μg | Found Sc (III), μg ( $\bar{X}$ ±ΔX; R=0.95) | N | S | Sr |
|---|---|---|---|---|---|
| 1 | 0.45 | 0.44 ±0.06 | 5 | 0.05 | 0.1 |
| 2 | 0.9 | 0.89 ±0.1 | 5 | 0.08 | 0.08 |
| 3 | 1.35 | 1.33 ±0.12 | 5 | 0.10 | 0.074 |
| 4 | 1.8 0 | 1.79 ±0.14 | 5 | 0.12 | 0.06 |
| 5 | 2.25 | 2.24 ±0.19 | 5 | 0.15 | 0.06 |

It can be seen from the tables that the amperometric titration of scandium with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid corresponds to its entered content and does not deviate from the true range, and the relative standard deviation of this method (Sr) not exceeding 0.1 confirms the high accuracy of the method.

The effect of foreign ions was studied in evaluating the selectivity of the developed amperometric titration method. 20 μg/ml scandium ion was taken, foreign ions of different concentrations were added and amperometrically titrated with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid. In the amperometric titration of 20 μg/l scandium ion, the following foreign ions did not interfere with naphthoiazo in a 1:1 ratio: $Cu^{2+}$, $Cd^{2+}$, $Fe^{3+}$.




For the determination of scandium ion based on selectivity model mixtures consists of $Cu^{2+}$ (10.0), $Na^{+}$ (20.0), $Al^{3+}$ (20.0), $Fe^{2+}$ (10.0), $Pb^{2+}$ (10.0), $Ba^{2+}$ (10.0) were analyzed. The obtained results are presented in Table 3 .

**Table 3.** Results of determination of scandium (III) ions in artificial mixtures.

| Mixed components µg | The amount of scandium obtained is µg, | The detected amount of scandium $x_i$, µg | $\overline{X_i}$ | $x_i - \overline{x_i}$ | $(Xi - \overline{X})^2 \cdot 10^{-3}$ | S | Sr | ΔX |
|---|---|---|---|---|---|---|---|---|
| $Cu^{2+}$ (10) $Na^{+}$ (20) | 20.00 | 19.96 | 19.99 | -0.03 | 0.9 | 0.0308 | 0.0015 | 0.076 |
| $Al^{3+}$ (20 ) $Fe^{2+}$ (10) | | 19.98 | | -0.01 | 0.1 | | | |
| $Pb^{2+}$ (10) $Ba^{2+}$ (10) | | 20.02 | | 0.03 | 0.9 | | | |

The obtained results show that the developed method can determine scandium ions in artificial mixtures with an error not exceeding 0.0308. This allows the developed method to be used to determine the composition of natural objects.

**Table 4. Results of amperometric titration determination of scandium (III) ions from the composition of the technological water**

| Mixing components, µg | The amount of scandium found $X_i$, µg | Xi medium | S | $S_r$ | ΔX | $t_p$ account | F |
|---|---|---|---|---|---|---|---|
| Ca (20.6), Ce (9.32), Co (7.34), Cu (20.4), Fe (79), Mg (34,2), Pb (45), Th (4.06), cm (3.01), Dy (2.21), Y (4,12), Mn (11.45), Nd (2.87), Gd (4.97), Pr (5.69), In (5.41), Sc (6.76), Zr (3.22) | 6.5<br>6.4<br>6.4 | 6.4 | 0.07 | 0.01 | 0.2 | 0.08 | 0.44 |

The method of determination of scandium ion with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid was applied to a sample containing scandium in order to apply it to the analysis of natural objects. For this purpose, the technological water of the Almalyk Mining and Metallurgical Combine was chosen. Due to the large number of destructive ions in its composition, first the extraction process was carried out. Scandium ion was extracted from technological water. For determination of the scandium (III) ion from the composition of technological water 5.0 ml of the technological water of the Almalyk Mining and Metallurgical Combine, 5.0 ml of a 0.1 M solution of nitric acid, 5.0 ml of azapodand solution with TBP paraffin are added to a 50.00 ml separation funnel. The mixture was shaken in a separatory funnel for 60 min and then cooled. The organic layer was separated by a separatory funnel. It was re-extracted with sodium fluoride solution [23] and the amount of metal was measured by amperometric titration with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid reagent. The accuracy of the obtained results was compared with the ICP-AES method, and the absence of systematic errors was determined by the student's coefficients and Fisher's criterion and is presented in Table 4.

The correctness of the developed method and the correctness of the obtained results were proven by determining the pre-extraction and post-extraction solutions using the method of inductively coupled atomic emission spectrometry (ISP AES, Shimadzo ICPE9000) and the obtained results are presented in tables 5-6.

**Table 5.** ICP-AES analysis of the composition of the technological solution containing scandium (III) ion

| 396,847 (1) | 413,380 (2) | 228,616 (2) | 324,754 (1) | 259,940 (1) | 280,270 (1) | 220,353 (2) | 361,384 (2) | 274,716 (2) |
|---|---|---|---|---|---|---|---|---|
| **Ca** | **Ce** | **Co** | **Cu** | **Fe** | **Mg** | **Pb** | **Sc** | **Th** |
| 20.6 | 9.32 | 7.34 | 20.4 | 79 | 34.2 | 45 | 6.76 | 4.06 |
| 339,198 (1) | 334,881 (2) | 334,960 (2) | 335,085 (2) | 335,039 (2) | 411,729 (2) | 411,814 (2) | 411,853 (2) | 411,988 (2) |
| **Zr** | **Sm** | **Dy** | **Y** | **Mr** | **Nd** | **Mr** | **Pr** | **In** |
| 3.22 | 3.01 | 2.21 | 4.12 | 11.45 | 2.87 | 4.97 | 5.69 | 5.41 |

It can be seen from the results of the above inductively coupled atomic emission spectrometry analysis that the result of inductively coupled atomic emission spectrometry analysis before extraction of the complex formed by the reagent 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid with scandium (III) ion thorium, zirconium, and lead ions were presented, it can be seen from table 6 after the extraction that when the substance formed from the combination of $Sc^{3+}$ ion with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid reagent was purified from the mixture of ions, the concentration of $Sc^{3+}$ ion was high. This proves the sensitivity and selectivity of the method.

**Table 6.** ICP-AES analysis of the composition of the technological water containing scandium (III) ion after extraction.

| 396,847 (1) | 413,380 (2) | 228,616 (2) | 324,754 (1) | 259,940 (1) | 280,270 (1) | 220,353 (2) | 361,384 (2) | 274,716 (2) |
|---|---|---|---|---|---|---|---|---|
| **Ca** | **Ce** | **Co** | **Cu** | **Fe** | **Mg** | **Pb** | **Sc** | **Th** |
| 0.576 | 0.398 | 0.026 | 2.46 | 4.66 | 5.82 | 2.1 | 6.42 | 0.08 |
| 339,198 (1) | 334,881 (2) | 334,960 (2) | 335,085 (2) | 335,039 (2) | 411,729 (2) | 411,814 (2) | 411,853 (2) | 411,988 (2) |
| **Zr** | **Sm** | **Dy** | **Y** | **Mr** | **Nd** | **Mr** | **Pr** | **In** |
| **0.048** | **0.84** | **0.071** | **0.59** | **2.98** | **0.75** | **1.84** | **1.01** | **1.09** |

The developed method was compared with the ICP-AES method, and the Fisher values and calculated Student's coefficients were determined, and the determination method of scandium (III) ion with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid reagent was unable to detect all ions in one solution, but shows a high sensitivity even though it is not detectable.

**Conclusions.** It can be concluded from the research that scandium ion can be determined by amperometric titration with naphthazo reagent in acidic medium. From the results, the compatibility of the scandium (III) ion determination method with 1-(2-hydroxy-1-naphthoazo)-2-naphthol-4-sulfonic acid reagent to the determination of scandium ion in technological water was checked by ICP-AES method and proved that there are no the absence of systematic errors were determined by calculating the student's coefficients and Fisher's criterion were 0.08 and 0.44 respecticely.

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