Analysis of the mixture of rare earth elements by atomic spectroscopy

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Abstract. The authors of this paper give the characteristic and the principle of operation of the ICPE-9000 spectrometer, proposed for the chamber residue analysis that is one of the products of ion flotation, for individual rare earth elements and their mixture content by atomic spectroscopy. The chamber residue was obtained by conducting the ion flotation from nitrate solutions, containing individual rare earth elements of the cerium group and their mixture. The results of the analysis of the solutions by optical emission spectroscopy are shown in the form of molar concentration. According to the obtained experimental data, a tendency for the change of distribution coefficients, separation factors and pH values of maximum recovery at the different values of equilibrium aqueous phase pH value was identified. The possibility of the most effective separation of rare earth elements of the cerium group at different concentrations of indifferent ions was revealed, as well as the forms of recovered compounds were determined.

1. Introduction

In the research of a more effective removal of various components scientists study rare earth elements (REE), ferrous, non-ferrous, and amphoteric metals; use different models (GANN, MLR, CCD and others); analyze composition and structure of extracted substances.

The articles of Jensen, Bond, Chiarizia described removal of different lanthanides and actinides. In the extraction of trivalent lanthanide (Sm$^{3+}$, Eu$^{3+}$) and actinide (Am$^{3+}$, Cm$^{3+}$) cations from nitrate systems into n-dodecane solutions of phosphinic acids (HC272, HC302, HC301) it is stated that in all cases the dependence of the distribution ratios on the total extractant concentration is approximately second power. The effect of aggregation is considered for every extractants, and the stoichiometries of the extracted complexes are M(H(C272)$_2$)$_3$, M(C302)$_3$, and M(C301)$_3$ [1].

The paper of Jensen et al. [2] is related to separating americium from curium and all the lanthanides by solvent extraction. The sterically constrained, macrocyclic, aqueous soluble ligand N,N'-bis (6-carboxy-2-pyridyl)methyl-1,10-diaza-18-crown-6 (H2BP18C6) was studied. Pairing H2BP18C6, which favors complexation of larger f-element cations, with acidic organophosphorus extractants that favor extraction of smaller f-element cations, solvent extraction systems with good Cm/Am selectivity, excellent trans-lanthanide selectivity ($K_{ex}$, Lu/$K_{ex}$, La = 10$^{8}$), but poor selectivity for Am against the lightest lanthanides was created.
The article of Lutskiy et al. analyzes the information on modern developments in the utilization of phosphogypsum demonstrating the possibility of using phosphogypsum as a raw material for obtaining rare-earth elements [3].

The papers of Götze J, Arsentyev V A [4, 5] describe using of the analytical combination of cathodoluminescence microscopy and spectroscopy, electron paramagnetic resonance spectroscopy for characterizing trace element compositions and defect structures in quartz samples.

The authors of the article [6] were determined the difference between zircons of the 1st, 2nd and 3rd group by contents of trace elements by electron microscopy, mass-spectrometry of secondary ions, Raman spectroscopy.

For ion flotation and extraction Hosenian and others have used the algorithms called GANN and MLR to remove Zn as well as Ni. Research related to REE encompasses various directions: ion flotation, liquid extraction, filtration and others. In their research modelling process of ion flotation of nickel is carried out [7]. The purpose of this study was to model the Zn(II) flotation using a hybrid neural network/genetic algorithm (GANN) and multivariate linear regression (MLR). The results showed that this model could be useful in predicting the Zn(II) removal in response to changes in the input parameters.

In another research [8] a new predictive model based on the hybrid neural genetic algorithm (GANN) was developed to predict the Ni(II) ion removal and water removal during the process from aqueous solutions using ion flotation. The input variables of the model were pH, collector concentration, frother concentration, impeller speed and flotation time. The outcomes revealed that the proposed GANN models could be used to predict the Ni(II) removal and water removal during ion flotation.

According to the articles [9, 10] ion flotation is a green and cost-effective technology where separation of molecules exploits the difference in surface affinity. In the work of Ghosh and others [11] a batch ion foam fractionation system was designed and optimized for the separation of trace Cr(VI) from aqueous solutions. The effect of surfactant head groups (collectors) on the adsorption dynamics was analyzed. Cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant demonstrated high efficiency for the removal of Cr(VI) from aqueous solutions. The experimental investigation of the effect of different operational parameters on the separation characteristics has been presented.

The effects of chemical conditions on the recovery of Zn(II) and water during the ion flotation process were assessed utilizing a central composite design (CCD) of response surface methodology [12]. The optimum effective parameters including pH, collector and frother concentration were determined. The results demonstrated that the pH and collector concentration were effective factors for the efficiency of Zn(II) flotation. The effects of collector and frother concentration on the characterization of sublate and the complexation of sodium dodecyl sulphate with Zn(II) were studied using scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX) spectroscopy and Fourier transform infrared (FTIR) spectroscopy.

Apart from researching ways of increasing effectiveness of chemical processes, the attention of researchers is focused on developing environmental accountability in different spheres of companies’ work, especially in the sphere of risk management [13, 14]. The article [15] demonstrates the effectiveness of employing case study analysis in English in order to teach would-be oil and gas engineers on environmental accountability.

Risks can be prevented by means of environmental integrated monitoring system in the stage of liquidation, reclamation of mining operations [16], the wastewater disposal system modernization by creating a recycled water supply [17]. Another way of monitoring system can be the one based on Unmanned Aerial Vehicles and utilized in air and water pollution [18], also the research of evaluation of the alluvial anthropogenic array - tailings storage of apatite-nepheline ores [19].
2. Materials and methods
All chemical reagents used in experimental studies of this paper are chemically pure and have quality certificates. The nitrate solutions of rare earth elements with concentration 0.01 M were prepared by the dissolution of rare earth elements with 99.9% purity in distilled water. All process solutions were prepared from this solution by dilution to 0.001 M concentration. The initial solution concentration was checked by sample trilonometry titration by EDTA solution with Xylenol orange indicator. Sodium dodecyl sulphate salt for biochemistry (NaDS, C_{12}H_{25}SO_4Na) manufactured by Acros organics (USA) with 99% purity was used as surfactant. During the test, a sample of NaDS was added to the working solution. Only fresh nitric acid and sodium hydroxide for adjusting the required pH value to the required value was used.

The recovery of rare earth elements from aqueous nitrate solution to froth pulp was carried out by using the ion flotation technique [20-23].

The diluted solution of individual rare earth elements with concentration of 0.001 M was used as an initial solution; its volume was set to 200 ml. Sodium dodecyl sulphate was added to the solution in accordance with a stoichiometry of the following reaction:

$$\text{Ln}^{3+} + 3\text{C}_{12}\text{H}_{25}\text{SO}_4 = \text{Ln} (\text{C}_{12}\text{H}_{25}\text{SO}_4)_{3}$$

and its concentration was 0.003 M. PH value was adjusted to the required value by a batchwise addition of NaOH 1 N alkaline solution or diluted nitric acid HNO_3 diluted. The aqueous solutions pH value was determined to an accuracy of 0.01 by using the "pH-150 MA" pH-meter. The flotation process was conducted on the mark 137 V-FL laboratory flotation machine with the cell volume of 1 dm³ and the agitator rotational speed of 1,000 RPM for 5 minutes. The selection of duration and rotational speed was conducted experimentally and determined by obtaining the highest process efficiency indices. The froth pulp was destroyed by 2 N solution of H_2SO_4.

3. The analysis of ion flotation products by AES
In the studies of Pusz, Picayo, Galico, Zapala and others XRD technique, simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC) were utilized for characterization of complexes. New solid lanthanide(III) (Ln) compounds of Tb(III), Ho(III), Er(III) and Yb(III) with sodium salt chrysin-4í-sulfonate (Nachsa-4í) were obtained [24]. Solid products showed Ln(OH)(Nachsa-4í)\(_2\)\(\Sigma\)\(n\)H_2O stoichiometry based on elemental analysis and thermogravimetric studies. The complexes were characterized in solution by UV/Vis and infrared as well as by the 

$$1^H \text{NMR spectroscopies.}$$

Understanding and optimizing the kinetics of rare earth separations represent a frequently overlooked approach to increasing the throughput of rare earth separations [25]. The kinetics of solvent extraction can be incredibly complex. In order to stimulate kinetic studies of rare earth separations, we provide an overview of liquid extraction chemistry relevant to rare earth separations, the equipment and methods for collecting kinetics data, and fundamental kinetic models for dealing with extractions controlled by diffusion or slow chemical reactions. Published kinetic studies available for rare earth extractions using the most viable and industrially applied systems are analyzed.

Thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), powder X-ray diffractometry (XRD), elemental analysis, complexometric titration, middle (MIR) and near (NIR) infrared region spectroscopy were used to characterize solid-state [La(Nap)3(H2O)], in which Nap is naproxen; the proposed stoichiometry is confirmed [26]. The experimental results provided information concerning the chemical composition, dehydration, coordination modes of the ligand, crystallinity of the sample, thermal behavior, thermal decomposition and polymorphism. Cyclic DSC and XRD in different temperatures showed that the complex presents five temperature dependent polymorphic forms. MIR spectroscopy suggest that the naproxen coordinates through the carboxylate group as a chelating ligand.

New binuclear complexes of La(III), Ce(III), Pr(III) and Nd(III) ions with N-phenylanthranilic acid were synthesized and characterized by elemental analysis, infrared spectroscopy, XRD technique and thermogravimetric analysis [27, 28]. The obtained results show that in complexes only the
The carboxyl group is involved in the coordination of the rare earth ions in the bidentate mode. The calculated dehydration enthalpies are low for all studied complexes what indicates that it is crystallization water. Moreover, the thermal stability and the decomposition path of these compounds depend on the metal ion and the used atmosphere. The EGA data allowed the identification and comparison of gaseous products evolved during pyrolysis and oxidative decomposition of the compounds which were considered.

The new ternary complexes of the formula Ln₂(nfa)(phen)(OH)·nH₂O (Ln = La(III), Ce(III), Pr(III) and Nd(III)) were synthesized and characterized by elemental analysis, complexometry, infrared spectroscopy XRD technique, simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC). Low values of the dehydration enthalpies indicate that dehydration is connected with the release of crystallization water [29]. Using the coupled TG–FTIR–MS techniques the decomposition pathways of the synthesized compounds were analyzed and the gaseous products released during pyrolysis and thermal oxidation of the complexes were identified.

New binuclear complexes of La(III), Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) ions with mefenamic acid were obtained in solid phase [30]. For all compounds considered, complexation occurs at pH 6-6.5. The analyzed complexes were characterized on the basis of chemical and elemental analyses, molar conductance, spectroscopies as well as thermoanalytical techniques. According to the research results, the molecular formula of the complexes is Ln₂(C₁₅H₁₄NO₂)₃(OH)₃×nH₂O, with the exception of the La(III) complex which has the formula La₂(C₁₅H₁₄NO₂)₅(OH). The received results give information on the composition, thermal stability, thermal decomposition, as well as the gaseous products that evolved during the thermal decomposition of the considered compounds.

The ion flotation products (chamber residue) was analysed for rare earth elements content by optical emission spectroscopy on ICPE-9000 spectrometer at the analytical research department of Saint Petersburg Mining University (SPMU).

The analysis of atomic emission spectral (AES) is based on the thermal excitation of atoms or ions that are in the vaporous or gaseous state, and the registration of optical spectres (qualitative analysis) or the measurement of the intensity of separate spectral lines of the determined elements (quantitative analysis).

The atomic spectres appear during the emission or absorption of electromagnetic radiation by free or weakly bound atoms (in gases and vapours) and consist of separate spectral lines.

Emission spectres are obtained when the atoms get excited. A lifetime of the excited state is short and is 10⁻⁷-10⁻⁸ seconds. During this time frame the atom losses the excess energy by emitting the electromagnetic radiation quantum.

The measured values of emission intensity are then compared with the values of the intensity of standards with known concentration to obtain the element concentration value in the unknown sample.

4. ICP burner and high-frequency generator
ICP is a plasma discharge that is excited in the argon flow and sustained by impact of high-frequency electromagnetic field on ionized argon.

The plasma temperature may reach 10,000 K. which ensures complete atomization of sample elements and minimizes chemical effects of interference.

The ICP burner consists of well-centred quartz tubes. The induction coil is connected to a high-frequency generator with a frequency of 27 - 56 MHz and an input power of several kW. The plasma-supporting argon gas is fed to the tubes with different velocity: the inner analyte aerosol carrying flow has a velocity of 1 l/min, the intermediate axial flow has a velocity of approx. 1 l/min. and the outer flow – 10 - 20 l/min. The outer flow is fed to the tube tangentially and forms vortexes when moving up. Originally under the impact of high-frequency spark the argon ionization occurs, after which the high-frequency generator is activated automatically and discharge is created at the expense of the electromagnetic field interaction with flowing gas, the electrical conduction of which is provided at the expense of a high degree of ionization. A plasma jet is blown outside. The burning of plasma is
sustained at the expense of induction heating of the gas. The aerosol carrying gas flow is supplied to the plasma base and passes through the toroidal high-temperature zone, forming a cooler jet over the bright plasma. For analytical purposes, a jet that is sustained at the specified height over the burner by an intermediate axial flow is used.

5. Optical system and spectrometer
Radiation emitted by the ICP carries the information about the elemental composition of the analysed sample. However, to retrieve the obtained information is possible only after the dispersion of spectrum or the separation of a narrow spectral range that corresponds with the analytical line.

![Figure 1. ICPE-9000 spectrometer](image)

The ICPE-9000 uses an optical echelle scheme and a CCD detector on solid-state semiconductor arrays (CCD – charge coupled device). It represents a two-dimensional array, consisting of photosensitive semiconductor p-n junctions (pixels) \( \leq 10 \text{ \mu m} \) in sizes that are isolated from each other. Under the impact of electromagnetic radiation the alternation of electrical charge at the p-n junction occurs, that is proportional to luminous flux intensity and exposure time. Information reading from the array is performed by using a computer.

6. Results and discussion. Ion flotation in the joint presence of samarium (III) and europium (III)
The results of the conducted studies of ion flotation in the joint presence of cerium group elements (samarium (III) and europium (III)) are specified in tables 1 and 2.

| pH | [Ln^{3+}] chamber residue, mmol/l | [Ln^{3+}] froth pulp, mmol/l |
|----|---------------------------------|----------------------------|
|    | Sm | Eu | Sm | Eu |
| 4.0 | 0.054 | 0.066 | 0.851 | 0.841 |
| 5.0 | 0.053 | 0.070 | 0.758 | 0.744 |
| 6.0 | 0.041 | 0.054 | 0.852 | 0.841 |
| 6.7 | 0.006 | 0.008 | 0.795 | 0.794 |
| 7.1 | 0.006 | 0.008 | 0.895 | 0.893 |
| 7.5 | 0.005 | 0.007 | 1.106 | 1.103 |
| 7.8 | 0.005 | 0.006 | 1.106 | 1.104 |
| 8.5 | 0.022 | 0.024 | 1.087 | 1.084 |
After analysing the experimental data in table 2 we came to the following conclusions. When floating the mixture of rare earth elements the samarium cations have the maximum distribution coefficient of 221.1 at pH 7.5-7.8 that is significantly higher than in the case of individual flotation recovery, at which the maximum $K_{distr}$ is 81.9 at pH 6.7. In the case of europium, the maximum recovery is observed during the individual flotation recovery and the pH of maximum recovery is shifted towards the smaller values range compared to the flotation of the mixture of rare earth elements. Thus during the flotation of the mixture, the maximum distribution coefficient for europium is 184.1 at pH 7.8. In the case of individual flotation the maximum $K_{distr}$ of europium is 208.9 at pH 7.1.

**Table 2.** Distribution coefficients of rare earth elements at their flotation in the joint presence

| pH | $K_{distr}^{Sm}$ | $K_{distr}$ | $K_{distr}^{Eu}$ | $K_{distr}$ |
|----|-----------------|-------------|-----------------|-------------|
| 4.0 | 15.8           | 14.1        | 12.7            | 5.0         |
| 5.0 | 14.3           | 11.5        | 10.6            | 10.2        |
| 6.0 | 20.8           | 15.1        | 15.6            | 16.6        |
| 6.7 | 132.5          | 81.9        | 99.2            | 204.1       |
| 7.1 | 149.1          | 81.5        | 111.6           | 208.9       |
| 7.5 | 221.1          | 81.5        | 157.6           | 194.0       |
| 7.8 | 221.1          | 81.6        | 184.1           | 182.6       |
| 8.5 | 49.4           | 92.0        | 45.2            | 176.8       |

The experimental data are shown in fig. 2 - 3.

**Figure 2.** Samarium (III) cations distribution coefficients as a function of pH of the solution for the cases of their individual flotation and in the joint presence

Thereby in the case of europium, the $K_{distr}$ and separation are decreased in the joint presence of cations, and in the case of samarium, the $K_{distr}$ and separation are on the contrary increased.
7. Conclusions
In the process of ion flotation of rare earth elements in the presence of indifferent ions, different trends of distribution coefficient changes are observed, and accordingly the recovery ratio and pH of maximum recovery as a function of the composition of the floating system.

When floating the mixture of rare earth elements by the example of cerium group elements (samarium (III) and europium (III)) it was determined that the distribution coefficient of samarium cations increased significantly in the case of rare earth elements flotation in the joint presence, and the pH of maximum recovery shifted towards the higher values range. In the case of europium cations, the relation is inverted. The maximum distribution coefficients are observed in the case of flotation of individual elements, and the pH of maximum recovery during the flotation of the mixture of rare earth elements also shifts towards the higher values range.

![Figure 3](image_url)

**Figure 3.** Europium (III) cations distribution coefficients as a function of pH of the solution for the cases of their individual flotation and in the joint presence.

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