Flotation and Spectrophotometry: Thorough Investigation and Application to the Determination of the Total Amounts of Lanthanum and Yttrium in Natural Samples

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The extraction and preconcentration of a metal complex via surfactant-mediated phase separation was studied. A sensitive, selective and low-cost methodology for the determination of microamounts of Lanthanum and Yttrium, using alizarin red sulfonate (ARS) with a flotation step prior to absorptiometric determination was developed. The precipitate in the scum layer was quantitatively collected, stripped with 10% HNO_3 and measured by spectrophotometry at 650 nm. Stripping of La(Ⅲ) and Y(Ⅲ) from the scum layer was carried out in one step with different mineral acids. The stripping efficiency was found to be quantitative in the case of HNO_3. Excess ARS was used to nullify the interfering effects of various foreign species. The proposed procedure has been applied to the determination of La and Y spiked in natural water samples and real ore samples. Additionally, the mechanism of flotation of the metal chelate was proposed to be due to a physical interaction between the metal chelate and the oleic acid surfactant through the van der Waal force.

Lanthanum and yttrium are increasingly used in high-technology applications, such as in superconductors, supermagnets, lasers and alloys.[1] They occur in low concentrations of few μg/g in many rock formations and their major minerals, which are used economically to supply most of lanthanum and yttrium, are bastnaesite $[La(Y),Ce](CO_3)F$, monazite $(La,Ce,Nd,Th,Y)PO_4$ and xenotime (YPO_4).[2] These minerals occur in concentrations of 5–10% in carbonatites formations, iron ores and phosphate rocks.[3] From an industrial extraction point of view La and Y can also be obtained as by-products of other mineral processing methods, such as apatite mining and uranium tailings. Due to lanthanide contraction, La(Ⅲ) and Y(Ⅲ) have a similar chemistry and are almost identical. Therefore, it is very difficult to separate these elements in the pure state from their natural compounds. Among several preconcentration techniques, interactions based on chelate formation have received considerable attention due to their simplicity and ability to attain high enrichment.[4,5] Spectrophotometric determinations of La(Ⅲ) and Y(Ⅲ) in media of diverse origin using different complexing reagents have been reported.[6–9] Much attention has been given to the preconcentration and separation of heavy metals from environmental, biological and pharmaceutical samples by flotation techniques.[10–14] In this respect, the adoption of a flotation methodology has been shown to give accurate and reproducible results, together with simple, rapid analytical processing and low chemical blanks.

In the same context, alizarin red sulfonate (ARS), has widely been used for the direct spectrophotometric determination of many cations and some anions.[15–18] Recently, ARS has been applied to the separation flotation of Zr from Hf prior to their spectrophotometric determinations in real samples.[19]

The aim of the present work is an attempt to adopt the reagent ARS for the determination of La(Ⅲ) and Y(Ⅲ) by spectrophotometry. The reagent reacts with La and Y to form a water-insoluble precipitate, which can easily be floated using an oleic acid (HOL) surfactant at ambient temperature. The proposed procedure has been successfully applied to the determination of La and Y in granites and in natural water samples spiked with known amounts of both analytes.

Experimental

Reagents. All reagents, unless specified otherwise, were of analytical-reagent grade, and doubly distilled water was used throughout. Stock solutions of La(Ⅲ) and Y(Ⅲ) ($1.0\ \mathrm{mg\,mL^{-1}}$) were prepared by dissolving appropriate amounts of their oxides (specpure) in hydrochloric acid. Dilute solutions were prepared from these stock solutions. An oleic acid (HOL) stock solution, $6.3 \times 10^{-2}\ \mathrm{mol\,L^{-1}}$, was prepared from the food grade product with sp.gr. 0.895 (from J.T. Baker chemical Co.) by dispersing 20 mL of oleic acid in 1 L of kerosene.

Solutions of other foaming reagents (0.05%) were prepared by dissolving appropriate amounts of surfactant Triton X (TX 100) in water, cetyltrimethylammonium bromide (CTAB) in 95% ethanol and sodium palmitate (NaPL) and sodium stearate (NaST) in 99.7% propanol. A stock solution of ARS ($1 \times 10^{-2}\ \mathrm{mol\,L^{-1}}$) was prepared by dissolving 3.603 g of ARS in 1 L of bidistilled water. To make a formate buffer solution, 28 g of NaOH was dissolved in 60 mL of formic acid and diluted to 1 L with bidistilled water. Ore samples (202 83MAL NIM-G Granite and 203 83MAL NIM-L Lujavrite) were obtained from the National Institute of Metallurgy, South Africa. The pH of the solutions was adjusted using a $0.1\ \mathrm{mol\,L^{-1}}$ solution of HCl and/or 2.5 and 10% NaOH.

Apparatus. The flotation cell has already been described elsewhere.[12–14] Vigorous shaking of the flotation cell in the presence of a surfactant (HOL) creates bubbles in the solution, which enhance the floatability of the analytes-ARS complexes. The spectral data were recorded on Unicam 2100 UV/VIS and MATTSON 5000 FTIR spectrophotometers. The pH values of all solutions

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were measured using a Hanna Instruments 8519 digital pH meter.

Analytical Procedures. I. Recommended General Procedure i. Flotation–Separation Step: A 0.5 mL portion of 10^{-3} mol L^{-1} of the analytes La(Ⅲ) and Y(Ⅲ) and 2 mL of 10^{-2} mol L^{-1} ARS were mixed. The pH was adjusted at 3.0 using drops of diluted HCl. The mixture was then transferred quantitatively to the flotation cell and completed to 10 mL with doubly distilled water. The cell was shaken well to ensure complete complexation. To this solution, 3 mL of 2×10^{-4} mol L^{-1} HOL was added. The flotation cell was then inverted upside down twenty times by hand. After 5 min, the scum layer was separated, stripped with 2 mL of 10% HNO_3 and subjected to absorptiometric determinations.

ii. Spectral Detection Step: The absorbance of the resultant clear solution was measured at 650 nm in a 2-cm cell against a blank of the reagents, prepared identically, using 1 mL of 0.05% arsenazo Ⅲ and 2 mL of formate buffer.

The flotation efficiency was calculated from the relation

$$F = (C_s/C_i) \times 100\%, \tag{1}$$

where C_i and C_s are the concentrations of the analyte in the initial aqueous and scum layers, respectively.

II. Sample Procedure i. Granite Ores: A 0.25 g sample was weighed and dissolved in a Teflon beaker with a mixture of 45 mL HF, 15 mL conc. H_2SO_4 and 5 mL conc. HNO_3. After complete dissolution, the solution was evaporated until near dryness. The residue was dissolved in water. Into a flotation cell, was placed a 0.5-mL portion of that solution plus 4 mL of a 10^{-2} mol L^{-1} ARS solution. The same previous steps of separation, stripping and spectrophotometry were followed.

ii. Natural Water Samples (Recovery test): Drinking, Nile river and tank water samples were collected from the city of Mansoura and its neighborhood. Samples were filtered using a 0.45 µm pore size membrane filter to remove any suspended particulate matter, and immediately treated with a few milliliters of conc. HNO_3 to prevent the possible hydrolytic precipitation of some mineral salts.

Different concentrations of La(Ⅲ) and Y(Ⅲ) viz. 0.5 and 1×10^{-5} mol L^{-1}, were introduced to 20 mL aliquots of water samples, and 2 mL of 10^{-2} mol L^{-1} ARS was added. The same previous steps for flotation, metal stripping and spectrophotometry were carried out, and the recovery percentage was calculated.

Results and Discussion

Selection of pH. The dependence of the floatability of La(Ⅲ) and Y(Ⅲ) on pH was studied by floating a 20 mL solution containing 5×10^{-5} mol L^{-1} of each analyte individually, 5×10^{-4} mol L^{-1} ARS and 2×10^{-4} mol L^{-1} HOL at pH values ranging from 2.5 to 10. The results are presented in Fig. 1. It is clear that, in the absence of ARS (curve a), La and Y reach their maximum floatability (50%) in the pH range 4–7. On both sides of this range the separation percentage is low due to elution at low pH, and due to a change in the acidic nature of the surfactant at high pH.

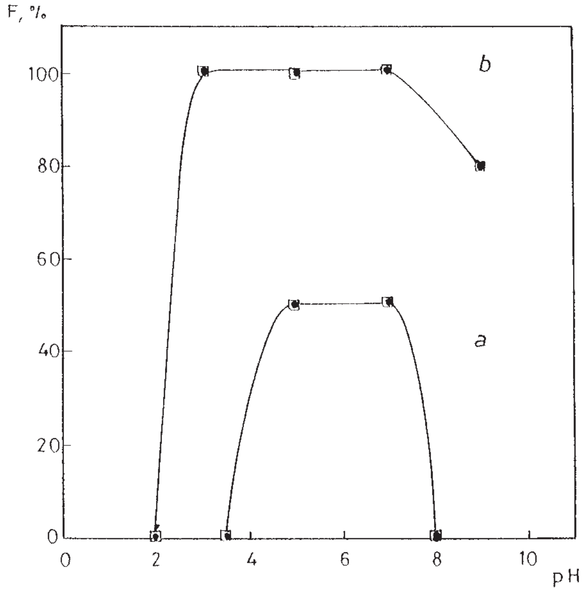


Fig. 1. Influence of hydrogen ion concentration on the floatability of 5×10^{-5} mol L^{-1} of La and Y using 2×10^{-4} mol L^{-1} HOL: a) in the absence of ARS, b) in the presence of 4×10^{-3} mol L^{-1} ARS.

In the presence of ARS, Fig. 1 (curve b), the floatability of La and Y rises from zero to nearly 100% in the pH range 3–7, above which it decreases. ARS forms complexes with La and Y, rendering them more hydrophobic and easily separated from the solution bulk. At a high hydrogen ion concentration, the decrease in the floatability can be attributed to the formation of a white emulsion, rendering the reaction to complete. In addition, excessive foams of sodium oleate enhance this postulation.

Selection of Surfactant. To select the most effective tenside among several cationic, anionic and non ionic surfactants, a series of flotation procedures under previously optimized conditions, were carried out (Table 1). The cationic surfactant CTAB, added to the system, foamed very well over the entire investigated pH range. Unfortunately, a copious white scum, which was formed at the top of the liquid phase in the flotation cell, made it impossible to collect quantitatively the sublate (collector with microelement in it). Flotation by the non-ionic surfactant TX 100 was also completely ineffective.

The anionic surfactants NaST, NaPL or HOL were more effective (Table 1). The data show that NaST and NaPL were less effective than HOL. Among all of the surfactants investigated, the recoveries obtained by oleic acid (HOL) were the highest. HOL, therefore, was selected as the most appropriate surfactant for the proposed flotation procedure.

Influence of HOL Concentration. The concentration of HOL is an important parameter; up to a limit the separation

Table 1. Applicability of Diverse Foaming Reagents for Precipitate Flotation of La and Y with ARS (pH = 3, ARS = 5×10^{-4} mol L^{-1}, La; Y = 5×10^{-5} mol L^{-1}, temp. = 25 °C)

Cationic surfactant	Anionic surfactants F/%			Nonionic surfactant
CTAB	NaST	NaPL	HOL	TX100
Foam, without flotation	94.2	92.3	100.0	Foam, without flotation

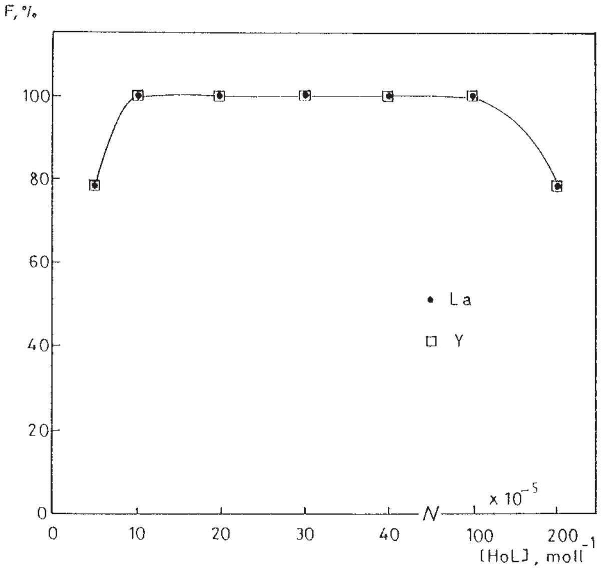


Fig. 2. Influence of HOL concentration on the floatability of 5×10^{-5} mol L^{-1} of La; Y, at pH 3 in the presence of 4×10^{-3} mol L^{-1} ARS.

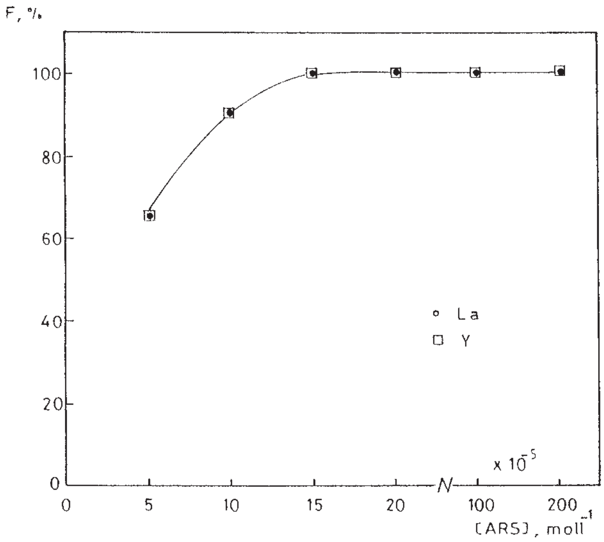


Fig. 3. Influence of ARS concentration on the floatability of 5×10^{-5} mol L^{-1} of La; Y at pH 3 in the presence of 2×10^{-4} mol L^{-1} HOL.

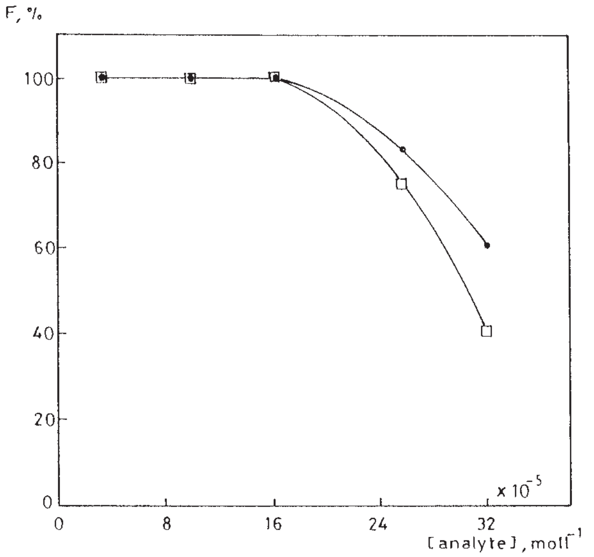


Fig. 4. Floatability of different concentrations of La; Y at pH 3 using 2×10^{-4} mol L^{-1} HOL in the presence of 5×10^{-4} mol L^{-1} ARS.

percentage increases as the concentration of surfactant increases. Figure 2 shows that the floatability of La and Y gradually increases as the concentration of HOL increases, reaching 100% at 1×10^{-4} mol L^{-1} HOL. The curve attains a plateau over a wide range of HOL concentrations. At a higher HOL concentration, there will be a concentration at which the surfactant molecules gather together to form a microball called, a *micelle*.[20] Micelles compete for the colligend molecules (metal-ARS), and since they stay in solution, they reduce the effectiveness of separation. The concentration of the surfactant also changes the bubble size, with the size becoming smaller as the surfactant increases. This makes creamier foam.[20]

Influence of ARS Concentration. To investigate the role of the sARS concentration on the floatability of La and Y, 2 mL of 2×10^{-4} mol L^{-1} HOL was added to 2 mL of 5×10^{-5} mol L^{-1} La and Y, each in a separate set of floatation cells. To each cell, different concentrations of ARS were added after adjusting the pH to 3. The process of flotation–separation was carried out, and the obtained data are given in Fig. 3. The data show that the floatabilities of La and Y are gradually increased as the molar concentration of ARS increased, reaching the maximum separation, ~100%, at molar ratio 1:3 (metal:ARS) for La and Y. The addition of excess ARS over the molar ratios has no adverse effect on the separation efficiency, thus facilitating the work in real samples with unknown analyte concentrations.

Influence of the Analyte Concentration on the Floatability of La and Y. The floatabilities of different concentrations of La and Y at pH 3 in the presence of a fixed concentration (2×10^{-4} mol L^{-1}) of ARS using 2×10^{-4} mol L^{-1} HOL were studied. Figure 4 shows that the floatabilities of La and Y reached their maximum value, 100%, at a concentration of less than 7×10^{-5} mol L^{-1} of La and Y. At higher concentrations of the analytes, the decrease in the floatability of La and Y is attributed to the insufficient quantity of ARS required for complete complexation of the analytes.

Influence of Temperature. The flotation efficiency of 5×10^{-5} mol L^{-1} of La and Y, under the previous optimized conditions of pH, ARS and HOL concentration, was studied at different temperatures. This was done by adding the recommended quantities of ARS and HOL quickly to the analyte solutions. The mixtures were introduced into flotation cells jacketed with 1 cm fiberglass insulation. The flotation procedure was then followed. Figure 5 shows that the floatability of La and Y was not affected by increasing the temperature up to 60 °C. Accordingly, the flotation procedure was carried out at room temperature, i.e. ~25 °C.

Induction Time (τ). The induction time (τ) is the time necessary for the incorporation of traces of the investigated

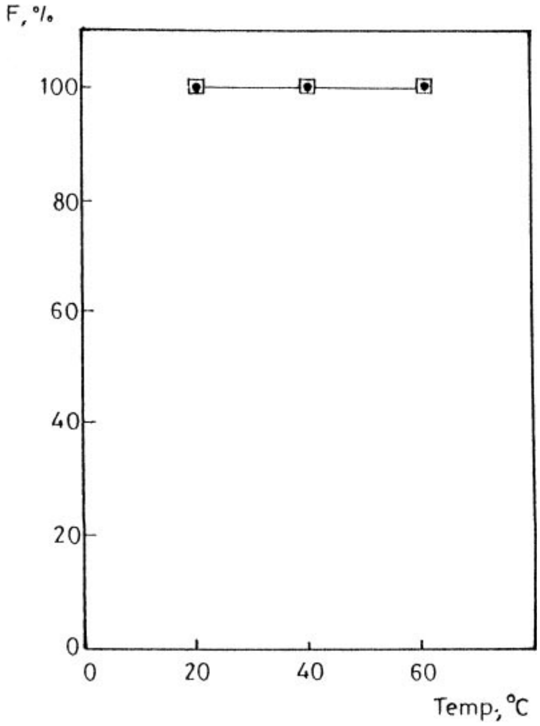


Fig. 5. Effect of temperature on the floatability of 5×10^{-5} mol L^{-1} of La and Y at the recommended conditions.

microelements in the collector precipitate. The experiment showed that, under the prevailing conditions, ARS could quantitatively collect La and Y during 1–5 min. However, in practice an induction time of 5 min was sufficient to perform the investigation.

Influence of Volume. A series of experiments was conducted to float different concentrations of La and Y from different aqueous volumes using suitable large flotation cells under the recommended conditions. The obtained results revealed that up to 400 µg of each analyte could be quantitatively separated from different volumes up to 800 mL. Accordingly, the detection limit of such a separation procedure is 0.5 ppm.

Influence of Various Mineral Acids on Stripping the Scum Layer. The effect of various mineral acids on the stripping of aqueous solutions containing two different concentrations of La and Y was studied. The experiments were carried out in two stages. First, after separation of an aqueous phase (25 mL) containing 0.5 ppm of La and Y, the scum layer was stripped with 2 mL of aqueous acid solutions including, HCl, H_2SO_4 and HNO_3. At the second stage, 25 mL of an aqueous solution containing 0.05 ppm of La and Y was separated by the recommended procedure; the scum layer was stripped with 2 mL of 10% HNO_3. The amounts of La and Y, each individually, in the aqueous phase after stripping the organic (scum) layer were determined by spectrophotometry, as mentioned before. The recovery percentage (R%) was calculated. For the preconcentration of 0.5 ppm of La and Y solutions, the highest recovery values, almost quantitative, were obtained with 3% HCl and 10% HNO_3. On the other hand, the use of 10% HNO_3 for stripping 0.05 ppm of La and Y yielded a recovery of ~100%. Accordingly, 2 mL of 10% HNO_3 was used for stripping.

Table 2. Influences of Foreign Species on the Separation and Determination of La and Y (pH = 3, La; Y = 5×10^{-5} mol L^{-1}, ARS = 2×10^{-4} mol L^{-1}, HOL = 2×10^{-4} mol L^{-1})

Foreign species*	Conc./ppm	Separation/%			
		La		Y	
		a	b	a	b
Ca, Mg, Cd, Li, Sr, Pb, Ag, Ba, Zn, Si, Hg, UO_2	1000	100	100	100	100
Th, Hf, Zr	100	60	100	60	100
V	20	79.0	99.8	79	99.8
Pt, Pd, Au	50	89.7	100	89.7	100
Mo, W, As	50	95	100	95	100
Al, Fe	100	87	100	87	100
Co, Cu, Ni, Mn, Cr, Sc	50	90	100	90	100

* Each individually or in combination.
a: $[\text{ARS}] = 3 \times 10^{-4}$ mol L^{-1}.
b: $[\text{ARS}] = 3 \times 10^{-3}$ mol L^{-1}.

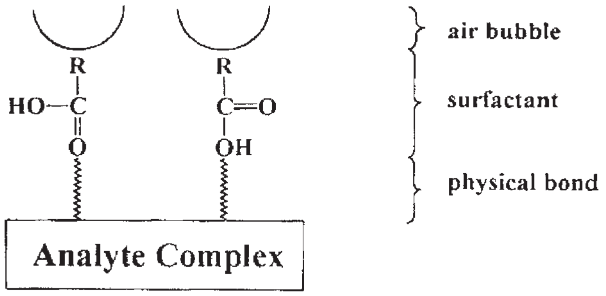
Interfering Effects of Various Ions. The interfering effects of various ions on the spectrophotometric determination of La and Y in aqueous solutions have been studied elsewhere.[4–7] The flotation of metal-ARS complexes into the HOL layer should avoid many of these interferences, especially those of calcium and magnesium, which are present at appreciable concentrations in many environmental samples. Aqueous solutions containing 5×10^{-5} mol L^{-1} of La and Y and ions, commonly found in water and real ore samples, were analyzed for La and Y, as described under the analytical procedure. The results are shown in Table 2. It has been found that as little as 5×10^{-5} mol L^{-1} of La and Y could be determined in the presence of excesses of Ca, Mg, Sr, Ba, Pb, Zn, Hg, Si, Cd, Ag, Li. Although the rest of the investigated foreign species interfere markedly, this effect could be completely eliminated by increasing the amount of ARS (4×10^{-3} mol L^{-1}) to cover the requirements for complexation of the foreign species.

Flotation Mechanism. In studies concerning separation via flotation, the role of the surfactant is of utmost importance.[12–14] The flotation mechanism may be either physical or chemical. The physical mechanism proceeds through a physical force viz. Van der Waal or hydrogen bonding between the hydrophilic part of the HOL and the active sites in the ligand complex. On the other hand, the chemical mechanism proceeds through an interaction between oleic acid and the complex formed in solution through a coordinate bond forming self-floatable species (Analyte–ARS–HOL). In either cases, the hydrophobic part of the surfactant attaches to air bubbles and floats, separating the analyte-containing species. In the present study, a physical mechanism of flotation, through the Van der Waal force, was proposed. The suggested proposal was based on the following observations and experimental findings: 1) Elemental analyses of the complexes isolated in both the absence and presence of HOL excludes HOL coordination for both La and Y. 2) The floated chelates

Table 3. Determination of La and Y in Real Ore Samples (pH = 3, ARS = 2×10^{-4} mol L^{-1}, HOL = 2×10^{-4} mol L^{-1})

Ore sample	La/ppm			Y/ppm		
	Certified	Found	R%	Certified	Found	R%
202 83MALI (NIM-G Granite)	109	108.6	99.63	143	142.4	99.58
203 83MALI (NIM-L (Lujavrite))	250	249.5	99.8	22	21.85	99.19

R% = Recovery%.



Scheme 1. Schematic diagram of the sublate.

have the same colour as that obtained in aqueous solution. 3) The infrared spectrum of La-complex isolated in aqueous solution is nearly identical with that in the HOL solution reflecting that no coordination or hydrogen bonding was formed between the La-ARS complex and HOL. In such a case, the separation may be suggested to be due to the formation of a physical force, ca. the Van der Waal force. In conclusion, the above-mentioned findings confirm that the separation of La and Y is most probably due to the physical interaction between the HOL surfactant and the metal-ARS complex. The schematic diagram of the sublate can be proposed, as in Scheme 1.

Application

Application to Real Ore Samples. The practical feasibility of the proposed procedure for the determination of La and Y was tested on Granite and Lujavrite ore samples (Table 3) with satisfactory results.

Application to Natural Water Samples. The developed procedure for the determination of La and Y using a flotation methodology and spectrophotometry was examined for several natural-water samples. The recoveries of spiked known additions to different water samples lay within the range 99.5–101%.

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