Simultaneous Preconcentration Flotation-Separation and Spectrophotometric Determination of Thorium, Lanthanum and Yttrium in Some Geological and Environmental Samples

A.M. Abdallah, M.A. Kabil, M.A. Akl*, D.S. Ismael

Department of Analytical Chemistry, Faculty of Science, Mansoura University 35566, P.O. Box 70, Mansoura, Egypt

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 micro amounts of thorium, lanthanum and yttrium ions, using Eriochrome Cyanine R (ECR) with a flotation step prior to spectrophotometric determination was developed. The precipitate in the scum layer was quantitatively collected, stripped with 4 ml of 3% HCl and measured spectrophotometrically at 540 nm for Th(IV) and at 650 nm for both La(III) and Y(III). The stripping of Th(IV), 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 HCl. An excess amount of ECR was used to eliminate the interfering effects of various foreign species. The proposed procedure was applied to the determination of Th(IV), La(III) and Y(III) spiked in natural water samples and in some 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 Waals force.

Key words: Thorium, Lanthanum, Yttrium, Flotation, ECR, Oleic acid, Spectrophotometry, Ores

INTRODUCTION

Thorium and its compounds are seriously hazardous [1]. Because of environmental pollution, the determination of thorium is becoming increasingly important. Lanthanum and yttrium are used in high technology applications, such as in superconductors, supermagnets, lasers and alloys [2]. They occur in low concentrations of few μg g^{-1} in many rock formations. Their major minerals, which are used economically to supply most of lanthanum and yttrium, are xenotime (YPO_4), bastnaesite [La(Y), Ce](CO_3)F and monazite (La, Ce, Nd, Th, Y)PO_4 [3]. These minerals occur in concentrations of 5-10% in carbonatite formations, iron ores and phosphate rocks [4]. From

an industrial extraction point of view, Th, La and Y can also be obtained as by products of other mineral processing methods, such as apatite mining and uranium tailings. Thorium, lanthanum and yttrium often coexist in minerals, by products and even in wastewater. Due to their similar behavior, the determination of Th, La and Y is a problem in analytical chemistry. Various methods such as isotopic dilution mass spectrometry (ID-MS) [5], instrumental neutron activation analysis (INAA) [6], inductively coupled plasma mass spectrometry (ICP-MS) [7] and inductively coupled plasma atomic emission spectrometry (ICP AES) [8] are available for the determination of Th or La and Y. These methods require costly equipments or a reactor facilities (for INAA); most of the laboratories in the developing countries are not equipped with these instruments. Moreover, some of

---

* Corresponding author. E-mail: magdaakl_59@hotmail.com

the interferences to which these methods are subject are poorly understood and continue to cause problems [1]. Therefore, spectrophotometric determination of Th or La and Y remains to be of great interest. Spectrophotometric determination of Th(IV) [9-12], La(III) and Y(III) [13-16] in media of diverse origin using different complexing reagents has been reported. However, these methods lack sensitivity and/or selectivity. Among several preconcentration techniques, interactions based on chelate formation have received considerable attention due to their simplicity and ability to attain high enrichment factor [17,18]. Much attention has been given to the preconcentration and separation of heavy metals from environmental, biological and pharmaceutical samples by flotation techniques [19-24]. 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, Eriochrome Cyanine R (ECR) has been used widely for the direct spectrophotometric determination of many elements [25-28]. Recently, ECR has been applied to the separation of Zr from Hf by flotation prior to their spectrophotometric determinations in real ore samples [29].

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

EXPERIMENTAL

Reagents

All reagents, unless specified otherwise, were of analytical-reagent grade. Doubly distilled water (DDW) was used throughout.

The standard stock solution of Th(IV) was prepared from $Th(NO_3)_4.5H_2O$ in 100 ml volumetric flask. 2 ml of conc. HNO_3 was added and diluted to the volume with DDW and the solution was standardized by EDTA titration.

The standard stock solutions of La(III) and Y(III) (1.0 mg ml^{-1}) were prepared by dissolving appropriate amounts of their oxides (spectroscopic grade) in hydrochloric acid. The solutions

were then standardized by EDTA titration with xylenol orange as indicator. Diluted solutions were prepared from these stock solutions.

A stock solution of ECR (1×10^{-2} mol l^{-1}) was prepared by dissolving 5.363 g of ECR in 1 l of DDW. An oleic acid (HOL) stock solution, 6.3×10^{-2} 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 the oleic acid in 1 l of kerosene. Solutions of other foaming reagents (0.05%) were prepared by dissolving appropriate amounts of surfactants Triton X (TX 100) in water, cetyl trimethylammonium bromide (CTAB) in 95% ethanol, sodium palmitate (NaPL) and sodium stearate (NaST) in 99.7% propano1. A tartaric acid solution (10%) was prepared by dissolving 10 g of tartaric acid in 100 ml of DDW. To make an arsenazo(III) (0.05 %) solution, 0.05 g of arsenazo(III) was dissolved in 100 ml of DDW. A formate buffer solution was prepared by dissolving 28 g of NaOH in 60 ml of formic acid and diluting to 1 l with DDW.

Ore samples 202 83 MAL NIM-G Granite and 203 83 MAL NIM-L Lujavrite were obtained from the National Institute of Metallurgy, South Africa.

The pH of the solutions was adjusted using a 0.1 mol l^{-1} solution of HCl and/or 2.5% and 10 % of NaOH solution.

Instrumentation

Two types of flotation cells were used throughout this study as it has already been described [21-24]. The flotation cell (a) is a cylindrically graduated glass tube of 16-mm inner diameter and 290 mm length with a stopcock at the bottom. Such a cell was used to study the experimental variables affecting the efficiency of flotation. Flotation cell (b), on the other hand, is a cylindrical tube of 6-cm inner diameter and 45 cm length with a stopcock at the bottom and a quick fit stopper at the top; this cell is used to separate the investigated analytes from 1 l of different water samples. 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-ECR complexes. The pH values of all solutions were measured using a Hanna Instruments model 8519 digital pH meter.

The spectral data were recorded on Unicam model 2 100 UV/Vis and MATTSON 5000 FTIR spectrophotometers. The UV/Vis spectrophotometer was calibrated with multi-

element rare earth (La and Y) standard stock solutions (MSC) [9,30-32].

Analytical Procedures

Flotation–separation step. A 0.5 ml portion of 10^{-3} mol l^{-1} of the analytes Th(IV), La(III) and Y(III) and 2 ml of 10^{-2} mol l^{-1} ECR were mixed. The pH was adjusted to 7.0. The mixture was then transferred quantitatively to the flotation cell and its volume was adjusted to 10 ml with DDW. 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 4 ml of 3% HCl and subjected to spectrophotometric determination.

Spectral detection step. The resultant clear solution was divided into two portions. To the first portion, 1 ml of 0.05% thorin plus 2 ml of 10% tartaric acid and 2 ml of 1% ascorbic acid were added. The absorbance was measured at 540 nm [12] for the spectrophotometric determination of Th in a 2-cm cell against a reagent blank. The concentration of Th was determined from the standard calibration curve previously constructed for Th. On the other hand, the absorbance of the second portion was measured spectrophotometrically for both La and Y at 650 nm using 1 ml of the 0.05% arsenazo(III) and 2 ml of the formate buffer [33]. The concentrations of La and Y are determined using the MSC standard calibration procedure [9,30-32].

The flotation efficiency was calculated from the relation

$$F = (C_s/C_i) \times 100\%$$

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

Ore sample analysis. A 0.25 g sample was weighed and dissolved in a Teflon beaker with a mixture of 45 ml HF, 15 ml concentrated H_2SO_4 and 5 ml concentrated HNO_3. After complete dissolution, the solution was evaporated nearly until dryness. The residue was dissolved in 10 ml DDW. Into a flotation cell, was placed a 0.5 ml portion of that solution plus 4 ml of a 10^{-2} mol l^{-1} ECR solution. The same previous steps of separation, stripping and spectrophotometry were followed.

**Natural water sample analysis (recovery test).** Drinking water, Nile river water and tank water samples were collected from the city of Mansoura (Mansoura is an agro-industrial area located in the Nile delta of Egypt) 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 few milliliters of concentrated. HNO_3 to prevent the possible hydrolytic precipitation of some mineral salts.

Different concentrations of Th(IV) or La(III) and Y(III) *i.e.* 0.5×10^{-5} mol l^{-1} and 1×10^{-3} mol l^{-1} were introduced into 20 ml aliquots of water samples and 2 ml of 10^{-2} mol l^{-1} ECR was added. The same previous steps of 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 Th(IV), La(III) and Y(III) on the pH was studied by floating a 20 ml solution containing 5×10^{-5} mol l^{-1} of each analyte individually, in the presence of 4×10^{-3} mol l^{-1} ECR and 2×10^{-4} mol l^{-1}
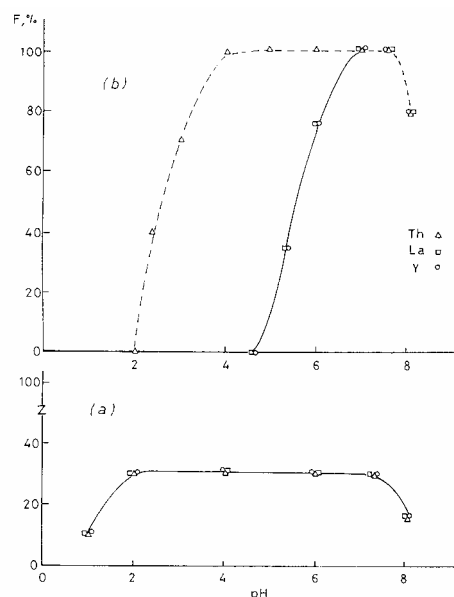
Fig. 1. Influence of pH on the floatability of 5×10^{-5} mol l^{-1} of Th, La and Y using 2×10^{-4} mol l^{-1} HOL: (a) in the absence of ECR and (b) in the presence of 4×10^{-3} mol l^{-1} ECR.

HOL, at pH values ranging from 2.0 to 10.0. The results are presented in Fig. 1. Figure 1a shows that, in the absence of ECR, the floatability of Th, La and Y reaches its maximum value (30%) in a pH range of 2-7. This separation percentage is considered unsatisfactory from the analytical point of view.

Figure 1b shows that, in the presence of ECR, the floatability of Th sharply rises from zero to nearly 100% at pH 4 and remains constant up to pH 7.5, and then it decreases. On the other hand, the floatability of La and Y rises from zero to nearly 100% in the pH range 7-7.5; above pH 7.5, it shows a decrease in floatability. ECR forms complexes with Th, La and Y, rendering them more hydrophobic and easily separated from the solution bulk. At higher pH values the decrease in the floatability can be attributed to the formation of a white emulsion, rendering the reaction incomplete. In addition, excessive foams of sodium oleate enhance this postulation. All further measurements were carried out at pH 7.

Selection of Surfactant

To select the most effective reagent among several cationic, anionic and non ionic surfactants, a series of flotation procedures were carried out, under previously optimized conditions. 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. The data obtained revealed that NaST and NaPL were less effective than HOL. Among all of the surfactants investigated, the recoveries obtained by the HOL were the highest. Therefore, HOL 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 percentage increases with increasing concentration of the surfactant. Figure 2 shows that the floatability of Th gradually increases with the concentration of HOL, reaching 100% at 1×10^{-4} mol l^{-1} HOL. The curve attains a plateau over a wide range of HOL concentrations until its critical micelle concentration (CMC) is reached. For La and Y,
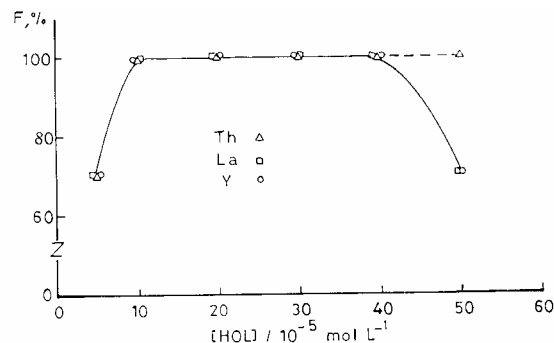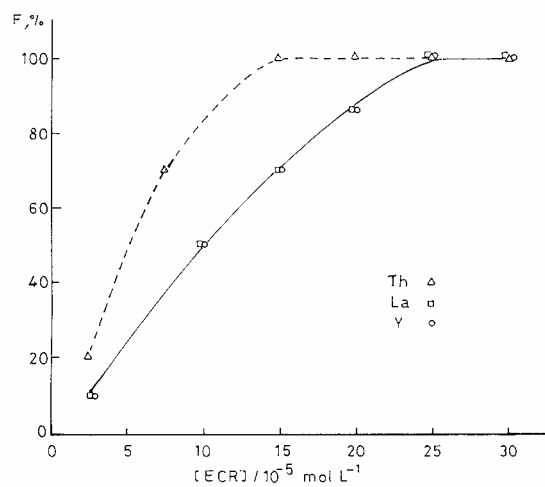

Fig. 2. Influence of HOL concentration on the floatability of 5×10^{-5} mol l^{-1} of Th, La and Y, at pH 7 in the presence of 4×10^{-3} mol l^{-1} ECR.

the same behavior was observed but at a somewhat lower concentration of HOL. The floatability of La and Y starts to decrease at 4×10^{-4} mol l^{-1} HOL. At a higher HOL concentration, there will be a concentration at which the surfactant molecules gather together to form a microball, called micelle [34]. Micelles compete for the colligend molecules (metal-ECR) 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 getting smaller as the surfactant increases. This makes creamier foam [34]. A suitable concentration (2×10^{-4} mol l^{-1}) of HOL was selected throughout this work.
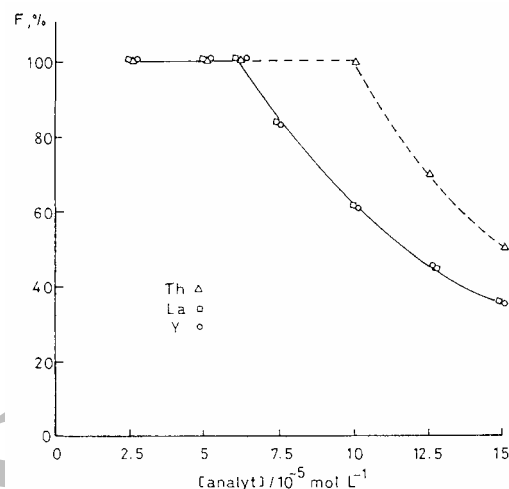
Influence of ECR Concentration

ECR forms 1:2 complexes with Th(IV) [35], La(III) [36] and Y(III) [37]. To investigate the role of ECR concentration on the floatability of Th, 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} of Th, La and Y each in a separate set of floatation cells. To each set, different concentrations of ECR were added after adjusting the pH to 7. The process of flotation-separation was carried out and the data obtained are shown in Fig. 3. The data show that the floatability of Th, La and Y gradually increased with increasing molar concentration of ECR, reaching the maximum separation percentage (*i.e.*, ~100%) at a molar ratio of 1:3 (metal: ECR) for Th, and of 1:5 for La and Y. The addition of excess ECR over the molar ratios had no adverse effect on the separation efficiency, thus facilitating the work in real samples with unknown analyte

82

Fig. 3. Influence of ECR concentration on the floatability of 5×10^{-5} mol l^{-1} of Th, La and Y at pH 7 in the presence of 2×10^{-4} mol l^{-1} HOL.

Fig. 4. Floatability of different concentrations of Th, La and Y at pH 7 using 2×10^{-4} mol l^{-1} HOL in the presence of 4×10^{-3} mol l^{-1} ECR.

concentrations.

Influence of the Analyte Concentration

The floatability of different concentrations of Th, La and Y at pH 7 in the presence of a fixed concentration of ECR (3×10^{-4} mol l^{-1}) using 2×10^{-4} mol l^{-1} HOL was studied. Figure 4 shows that the floatabilities of La and Y reach their maximum value of 100% at concentrations $\leq 6 \times 10^{-3}$ mol l^{-1} of La and Y whereas the floatability of Th reaches its maximum at a concentration $\leq 1 \times 10^{-4}$ mol l^{-1}. At higher concentrations of the analytes, the decrease in the floatability of Th, La and Y could be attributed to the insufficient quantity of ECR required for complete complexation of the analytes.

Influence of Temperature

The flotation efficiency of 5×10^{-5} mol l^{-1} of Th, La and Y, under the previous optimized conditions of pH, ECR and HOL concentration, was studied at different temperatures. This was done by adding the recommended quantities of ECR and HOL quickly to the analytes solutions. The mixtures were introduced into flotation cells jacketed with 1 cm of fiberglass insulation. The flotation procedure was then followed. The results obtained indicated that the floatability of Th, 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

The induction time, τ, is the time necessary for the incorporation of traces of the investigated microelements in the collector precipitate. The experiment showed that, under the prevailing conditions, ECR could quantitatively collect Th, La and Y during 1-5 min. However, in practice, an induction time of 5 min was sufficient to perform the investigation.

Influence of Sample Volume

Series of experiments were conducted to float different concentrations of Th, La and Y from different aqueous volumes using suitable large flotation cells under the recommended conditions (ECR = 4×10^{-3} mol l^{-1}, HOL = 2×10^{-4} mol l^{-1}, induction time = 5 min). The obtained results, shown in Fig. 5, 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 μg ml^{-1}.
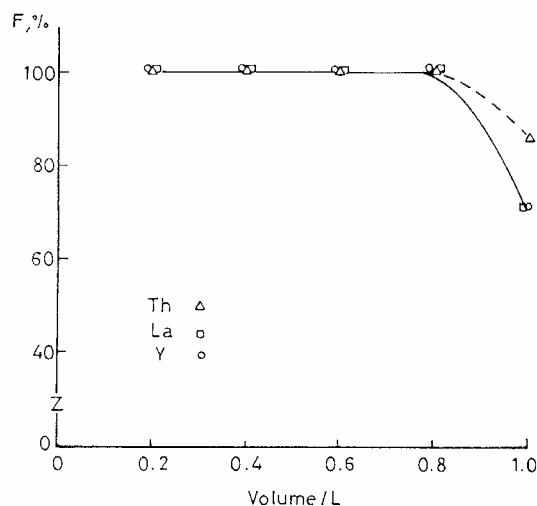
Fig. 5. Influence of sample volume on the floatability of Th, La and Y.

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 Th, 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 µg ml^{-1} of Th, La and Y, the scum layer was stripped with 4 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 µg ml^{-1} of Th, La and Y was separated

by the recommended procedure; the scum layer was stripped with 4 ml of 3% HCl. The amounts of Th, La and Y in the aqueous phase after stripping the organic (scum) layer were determined spectrophotometrically, as mentioned before. The recovery percentage (R%) was calculated. For the preconcentration of 0.5 µg ml^{-1} Th, 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 3% HCl for stripping 0.05 µg ml^{-1} of Th, La and Y yielded a recovery of ~100%. Accordingly, 4 ml of 3% HCl was used for stripping.

Interfering Effects of Various Species

The interfering effects of various ions on the spectrophotometric determination of Th, La and Y in aqueous solutions have been studied elsewhere [9-16]. The flotation of the metal-ECR 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 5.0×10^{-5} mol l^{-1} of Th, La and Y and ions, commonly found in water and ore samples were analyzed for Th, La and Y as described under the analytical procedure. Results are shown in Table 1. It was found that as little as 5.0×10^{-5} mol l^{-1} of Th, 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 remaining investigated foreign species interfere to a variable extent. This effect could be completely eliminated by increasing the

Table 1. Influences of Foreign Species on the Separation and Determination of 5×10^{-5} mol l^{-1} of Th, La and Y at Different ECR Concentrations. Conditions: pH = 7, HOL = 2×10^{-4} mol l^{-1}

Foreign species	Concentration (ppm)	Separation (%)					
		Th		La		Y	
		a	b	a	b	a	b
Ca, Mg, Cd, Li, Sr, Pb, Ag, Ba, Zn, Si, Hg, UO$_2$	1000	100	100	100	100	100	100
Hf, Zr	100	60	100	60	100	60	100
V	20	65	100	79	100	79	100
Pt, Pd, Au	50	85	100	90	100	90	100
Mo, W, As	50	76	100	95	100	95	100
Al, Fe	100	85	100	87	100	87	100
Co, Cu, Ni, Mn, Cr, Sc	50	89	100	90	100	90	100

a. [ECR] = 2×10^{-4} mol l^{-1}. b. [ECR] = 2×10^{-3} mol l^{-1}.

amount of ECR (up to 2×10^{-3} mol l^{-1}) to cover the requirements for complexation of the foreign species.

To study the effect of ionic strength, sodium, potassium, calcium and magnesium as chlorides, nitrates, sulfates, perchlorates and iodides were added during the flotation separation of the analytes at the recommended conditions. It was found that these salts, even up to 0.1 mol 10^{-1} concentration levels had no effect on the flotation efficiency of Th, La and Y.

Flotation Mechanism

In studies concerning separation via flotation, the role of the surfactant is of utmost importance [21-24,29]. The nature of interaction between oleic acid surfactant and the complex formed must be studied to approach the actual mechanism of flotation. The flotation mechanism may be either physical or chemical. The physical mechanism proceeds through a physical force *viz.* van der Waals 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-ECR–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 van der Waal forces, 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 Th, La and

Y. 2) The floated chelates have the same color as those obtained in aqueous solution. 3) The IR spectra revealed that there is no obvious difference between the IR spectrum of La-ECR complex (taken as an example) isolated in aqueous and that isolated in HOL solution, reflecting that no coordination or hydrogen bonding was formed between the metal-ECR complex and HOL. In such cases, 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 Th, La and Y was most probably due to physical interaction between the HOL surfactant and the metal-ECR complex.

Applications

Simultaneous determination of Th, La and Y in ores. Under the optimal experimental conditions (ECR = 4.0×10^{-3} mol l^{-1}, HOL = 2.0×10^{-4} mol l^{-1}, induction time = 5 min) described in the analytical procedure, Th, La and Y could be simultaneously floated to the scum layer. Th is spectrophotometrically determined at 540 nm using 1 ml of 0.05 % thorin with satisfactory results (Table 2).

La and Y, on the other hand, were spectrophotometrically determined at 650 nm using 1 ml of the 0.05% arsenazo(III) and 2 ml of the formate buffer and their concentrations were determined using the MSC standard calibration. Calibration with MSC, imitating the matrix of the investigated samples, is a well-known approach in many analytical techniques [9,30-32]. Table 2 presents the results of ores after

Table 2. Determination of Th, La and Y in Ore Samples. Conditions: n = 3, pH = 7, ECR = 2×10^{-4} mol l^{-1}, HOL = 2×10^{-4} mol l^{-1}

Ore sample [composition]	Analyte	Concentration (ppm)		Recovery (%)
		Certified	Found	
202 83 MALI NIM-G (Granite), (ppm)	Th	51	50.8	99.6
[Eu(0.35), F(4200), Ga(27), Gd(14),	La	109	108.6	99.6
Hf(12), Li(12), Lu(2), Mo(3), Nb(53),	Y	143	142.4	99.6
Nd(22), Tb(3), U(15),V(2), Yb(14.2),				
Zn(50), Zr(300)]				
203 83 MALINIM-L (Lujavrite), (ppm)	Th	66	66.1	100.2
[Eu(1.2), F(4400), Ga(54), Hf(190),	La	250	249.5	99.8
Li(48), Lu(0.4), Mo(4),Nb(960),Nd(22),	Y	22	21.8	99.2
Tb(0.7),U(14),V(81),Yb(3, Zn(400)]				

All measured RSD values range from 1-5%.

Table 3. Recovery of 0.5 and 1×10^{-5} mol l^{-1} of Th, La and Y Added to Some Natural Water Samples. Conditions: n = 3, pH = 7, ECR $= 2 \times 10^{-4}$ mol l^{-1}, HOL $= 2 \times 10^{-4}$ mol l^{-1}

Water sample	Recovery (%)		
	Th	La	Y
DDW	100±0.2	100±0.4	100±0.3
	100±0.3	100±0.2	100±0.4
Domestic water	100±0.4	100±0.3	100±0.5
	100±0.2	100±0.5	100±0.3
Nile water (Mansoura city)	100±0.5	100±0.2	100±0.4
	100±0.2	100±0.2	100±0.1
Nile water (Talkha city)	100±0.4	100±0.1	100±0.2
	100±0.2	100±0.3	100±0.4

calibration of the spectrophotometer with MSC and after flotation separation procedure. Each experimental value is the mean of three determinations and is characterized by the respective standard deviation.

Application to natural water samples. The developed procedure for the determination of Th, La and Y, using a flotation methodology and spectrophotometry, was applied to several natural water samples. The recoveries of spiked known additions to different water samples lay within the range 99.5-100.5% (Table 3).

REFERENCES

[1]   Y. Chen, Z. Li, Z. Zhu, J. Pan, Analyst 124 (1999) 1839.

[2]   S. Vijayan, A.J. Melnky, R.D. Singh, K. Nuttall, Min. Eng. 41 (1989) 13.

[3]   P. Moller, P. Cerwy, F. Saupe, Lanthanides, Tantalum and Niobium, Springer Verlag, Berlin, 1989.

[4]   P. Henderson, Rare Earth Geochemistry, Elsevier, Amsterdam, 1984.

[5]   Fthirlwall, Chem. Geol. 35 (1982) 155.

[6]   J.W. Jackobs, R. L. Koritev, D.D. Balchard, L.A. Haskin, J. Radioanal. Chem. 40 (1977) 93.

[7]   A.R. Date, AL. Gary, Spectrochim. Acta Part B 40 (1985) 115.

[8]   J.G. Crock, F.E, Lichte, Anal. Chem. 54 (1982) 1329.

[9]   A. S. Amin and T. Y.Mohammad, Talanta 54 (2001) 611.

[10]   S. B. Savvin, Talanta 8 (1961) 679.

[11]   J.M. Pan, C.G. Hsu, H. He, Michrochem. J. 35 (1987) 218.

[12]   M.H. Khan, S.M. Hasany, M.A. Khan, A. Ali, Radioanal. Nucl. Chem. 188 (1994) 341.

[13]   J. Erich, Z. Chem. 7 (1967) 31.

[14]   K.N. Munshi, S.C. Srivastava, A. K. Dey, J. Indian Chem. Soc. 45 (1968) 817.

[15]   K. Hiiro, D.S. Russell, S.S. Berman, Anal. Chim. Acta 37 (1967) 209.

[16]   P.K. Spitsyn, V.S. Shvaren, Zh. Anal. Khim. 25 (1970) 1503; 26 (1971) 1313.

[17]   K. Terada, Anal. Sci. 7 (1991) 187.

[18]   M. Torre, L. Marina, Crit. Rev. Anal. Chem. 24 (1994) 327.

[19]   K. Cundeva, T. Stafilov, G. Parlovska, Spectro. Chim. Acta B 55 (2000) 1081.

[20]   T. Stafilov, G. Parlovska, K. Cundeva, Michrochem. J. 60 (1998) 32.

[21]   M.A. Kabil, M.A. Akl, A.M. Abdallah, D.S. Ismael, Anal. Sci. 6 (2000) 113.

[22]   M.E. Khalifa, M.A. Akl, S.E. Ghazy, Chem. Pharm. Bull. (Jpn.) 46 (2001) 664.

[23]   M.A. Kabil, M.A. Akl, M.E. Khalifa, Anal. Sci.(Jpn.) 15 (1999) 433.

[24]   M.A. Akl, M.E. Khalifa, S.E. Ghazy, M.M. Hassanein, Anal. Sci.(Jpn.) 11 (2002) 234.

[25]   Z. Marczenko, H. Kalowska, Chem. Anal. 25 (1980) 555.

[26]   Z. Marceznko, H. Kolowska, Mikrochim. Acta 2 (1979) 507.

[27]   Y. Xy, X. Chen, Z. Hu, Anal. Lett. 20 (1987)1001.

[28]   M. Jarosz, Analyst 11 (1986) 681.

[29]   M.A. Akl, M.A. Kabil, A.M. Abdallah, D.S. Ismael, Sep. Sci. Technol. 36 (2001) 2747.

[30]   X. Cao, Zhao, M. Yin, J. Li, Analyst 123 (1998) 1115.

[31]   P.K. Srivastava, A. Premadas, JAAS 14 (1999) 1087.

[32]   R. Djingova, J. Ivanova, Talanta 57 (2002) 821.

[33]   Z. Marczenko: Separation and Spectrophotometric Determination of Elements, Ellis Horwood Limited John Wiley & Sons, New York, 1986.

[34] C.E. Meloan, Chemical Separations, Principles, Techniques and Experiments, John Wiley & Sons. Inc., New York, 1999.

[35] Y. Shigo, Bunsekikagaku 22 (1973) 1489.

[36] J.F.C. Boodth and W. Saffiom, An. Acad. Cienc. 51 (1979) 97.

[37] K.N. Munshi, S.C. Srivastava, A.K. Dey, Indin Chem. Soc. 45 (1986) 817.