TECHNICAL NOTE

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Enrichment method for trace amounts of rare earth elements using chemofiltration and XRF determination

Abstract A preconcentration method for subsequent determination of rare earth elements (REE) by X-ray fluorescence (XRF) spectrometry was developed. The method is based on using (o-[3,6-disulfo-2-hydroxy-1-naphthylazo]-benzenearsonic acid) (Thorin) as a complexing agent which is retained on a polyamide membrane by a chemofiltration process. The pH dependence of the chemofiltration of these metal ions on the membrane and other variables, such as flow-rate, contact time, kinetic of complex formation, etc. were determined. The membrane containing the chemofiltrate formed a thin film, which eliminated the interelemental effects when measured by XRF. The detection limits were 23, 23 and 49 ng/mL for Sm(III), Eu(III) and Gd(III), respectively. High enrichment factors were obtained. The method was successfully applied to the preconcentration of Sm(III), Eu(III) and Gd(III) from different samples.

Introduction

In trace analysis, preliminary analytical procedures, such as preconcentration or selective separation of the analyte prior to its determination, are frequently necessary in order to minimize or eliminate the interferences caused by the matrix.

During the last years a great number of preconcentration and separation techniques have been reported. However, the need for rapid and selective methods of preconcentration has led to the development of new methodologies. They involve preconcentration methods like precipitation [1], ion exchange [2], immobilizing reagents [3], chelating resins [4, 5], etc. The interelemental effects pro-

duced by the matrix in X-ray fluorescence (XRF) spectrometry can be eliminated if the sample is presented as a thin film.

The determination of lanthanides in geological samples is one of the most difficult and complicated analytical tasks, especially at trace levels, because of their similar chemical behavior. On the other hand, the knowledge of the fundamental laws governing the distribution and redistribution of elements during metamorphic processes enables geochemists to predict the probability of the occurrence of economically interesting minerals in a particular geological environment. Special interest is attached to the mineralization process occurring during the alteration of the rock by hydrothermal action. In petrology, the distribution of trace elements gives an idea about the genesis of the ore. The rare earth elements (REE) due to their similarity serve as a particularly suitable group of indicator elements. The determination of REE in other materials is also of interest. The presence of trace quantities of REE in high purity metals, semiconductors and glasses has an important influence on their electrical, magnetic, mechanical, nuclear and optical properties [6].

The method suggested here is based to a certain extent upon the earlier developed principle of element concentration by coprecipitation with organic coprecipitants from diluted solutions. In most cases the concentrated residue must be transferred into a soluted state. This procedure cannot provide high concentration coefficients. These drawbacks can be overcome by membrane chemofiltration.

The main principle of the preconcentration method presented here is the formation of a complex of the element to be analyzed with a selective organic reagent in a solution which is in further interaction with the membrane during the course of filtration and the formation of a thin film with the solid deposited on the membrane. This allows high selectivity when using selective organic reagents and considering the optimal experimental conditions.

In our work, we chose Thorin as a complexing agent for the REE. Although Thorin reacts with the REE, in this work only Sm, Eu and Gd were chosen, since they represent the transition between light (Sm) and heavy (Gd)

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REE. Eu shows a behavior different from the general trend that characterizes the rest of the REE. This is known as Eu anomaly and can be positive or negative depending on the concentration relation $<>1$. Thorin has been used as the immobilizing reagent in chelating resins [7], but its use has not yet been reported as complexing agent in chemofiltration processes.

The main advantage of this preconcentration method is that the concentrated complex is distributed only on the membrane surface and it is possible to use great volume of samples (1 L or more), resulting in large enrichment factors.

Experimental

Reagents and apparatus

Rare earth elements standard solutions (1000 mg/L) were prepared by dissolving 115 mg of Sm_2O_3, 115 mg of Eu_2O_3 and 116 mg of Gd_2O_3 in 0.1 mol/L HCl and diluting to 100 mL with water. The oxides of 99.99% purity were purchased from Aldrich Co.

Thorin ($C_{16}H_{13}AsN_2O_{10}S_2$) was purchased from Hopkin and Williams, 95% purity. The 5×10^{-3} mol/L solution of Thorin was prepared by dissolving 266 mg of the reagent in water up to 100 mL. Diluted solutions were prepared by adding water to the concentrated solutions. Buffer solutions of pH 4 and pH 9 were prepared with 5×10^{-2} mol/L potassium biphthalate and 1×10^{-2} mol/L sodium tetraborate, respectively, for calibrating the pH-meter electrode. All other chemicals used were of analytical grade, and doubly distilled water was used throughout. Membrane polyamide filter papers were Whatman of 0.2 μm pore size.

A Philips PW1400 X-ray Fluorescence Spectrometer was used for Sm, Eu and Gd L_α lines measurement. The measurement parameters were $2\theta = 66.23$ for Sm L_α, $2\theta = 67.57$ for Eu L_α and $2\theta = 61.10$ for Gd L_α; Rh tube, 50 kV, 50 mA, LiF(200) crystal, 75–25% window width, counting time for peak and background 100 s, and a gas proportional-scintillation counter in tandem arrangement was used for the analysis. A Gilford response UV-Visible Spectrometer was used with glass cells of 10 mm path length.

The ICP-AES measurements were performed with a sequential inductively coupled plasma spectrometer (Baird ICP 2070). The pH of the solutions were measured by an Orion 701-A pH-meter with an Ag/AgCl electrode. The filtrations were performed in a special filtration apparatus with a vacuum pump.

Studies of the complex Thorin-metal formation

Effect of pH. In order to establish the optimum pH for the complex formation, different pH values were applied in the sample solutions containing 10 mg/L Gd(III) and 1.75×10^{-5} mol/L Thorin. The pH values were adjusted with 0.01 mol/L NaOH or 0.01 mol/L HCl. The spectrophotometric absorbance was measured at 540 nm. The same procedure was carried out for Sm(III) and Eu(III).

Determination of optimum Thorin/metal rate. Solutions containing different Thorin/metal (REE) ratios were adjusted at pH 6 with 0.01 mol/L sodium hydroxide. The complex concentration was determined spectrophotometrically at 540 nm.

Studies of the variables affecting chemofiltration

Influence of pH on chemofiltration. Portions of 50 mL of solution containing the complex Thorin-Gd(III) (5 mol/L : 1 mol/L) were adjusted to different pH values with sodium hydroxide or hydrochloric acid. The solutions were filtered through a polyamide

membrane and the L_α lines of the analyte were measured by XRF spectrometry. All intensities measured were corrected for background intensity. The same procedure was carried out for Sm(III) and Eu(III).

Influence of the shaking time on the membrane retention. 50 mL portions of solutions with 8.65×10^{-5} mol/L Thorin and 10 mg/L metal were shaken at pH 4.8 during different periods of time (5, 10, 15, 20, etc. min). The complex was filtered through a polyamide membrane and the amount of complex retained on the membrane was determined measuring the metal (Gd(III), Sm(III), Eu(III)) L_α line intensity by XRF spectrometry.

Flow rate of complex filtration. In this experiment the complex formed was filtered through a polyamide membrane using different flow rates. The amount of complex retained on the membrane was determined measuring the metal (Gd, Sm, Eu) L_α line intensity by XRF spectrometry.

Determination of the maximum capacity of retention of the membrane. Solutions containing different concentrations of the complex Thorin-Gd(III) at pH 4.8 were passed through the membrane to determine the saturation quantity of complex. The metal L_α line was measured in the chemofiltrate on the membrane by XRF. The same procedure was carried out for Sm(III) and Eu(III). The background intensity was measured at the REE L_α 2θ angle on a blank sample. This blank is prepared by chemofiltration of a solution containing only Thorin on the membrane.

Percentage recovery. The quantity of the complex Thorin-REE in the filtrate not retained by the membrane was measured spectrophotometrically at 540 nm and pH 6.

Enrichment factor. 50 mL portions of solutions containing 4 mg/L of each REE and 8.65×10^{-5} mol/L Thorin were chemofiltrated through a polyamide membrane. The thickness of the thin film obtained was measured with a thickness meter (Köfer) with 0.1 μm precision. The enrichment factor was calculated considering the percentage of recovery

Determination of Sm, Eu and Gd in synthetic and reference samples

A series of appropriate standard solutions of Sm, Eu and Gd were preconcentrated by chemofiltration through a polyamide membrane and their X-ray fluorescence lines were measured. The background intensity was measured at the REEs L_α 2θ angle on a blank sample.

Sample treatment. In Teflon vessel 1 g of the reference sample G-2 from USGS was moistened with water and 2 mL of HNO_3 (c). Then, 2 mL of $HClO_4$ (c) and 20 mL of HF (c) in portions of 3 mL each were added. This mixture was heated in a sand bath up to dryness. In case the residue was resistant to decomposition, the addition of $HClO_4$ and HF was repeated. Finally, the residue was dissolved in HCl (c) to give a final concentration of 2 mol/L. The solution was diluted up to 50 mL.

The separation of the matrix elements was carried out by ion exchange according to the procedure of Crock et al. [8]. The ion exchange apparatus consisted of a 30×1 cm glass column, packed with a 20 cm long bed of 200–400 mesh Dowex 2×8 cation exchange resin. This resin was washed with 8 mol/L HNO_3 in order to eliminate iron, until the washing liquid analyzed by ICP-AES revealed no signal of Fe.

The resin was consecutively activated with 50 mL of 1 mol/L HCl, then with 25 mL of 2 mol/L HCl and loaded with 50 mL of sample solution already dissolved in 1 mol/L HCl. The elution was carried out with 50 mL of 2 mol/L HCl, followed by 50 mL of 2 mol/L HNO_3 with a flow rate of 1 mL/min, discarding both eluates. Then the resin was eluted with 75 mL of 7.5 mol/L HNO_3. This eluate was collected, evaporated to dryness and made up to a final volume of 10 mL for subsequent determination of REE.

Table 1 Experimental conditions and results of the experiments for complex formation

| Experiment	REE examined	Variable parameter	Experimental conditions	Detection	Results
					Maximum absorbance
Influence of pH on the Thorin-metal complex formation	Sm, Eu, Gd	pH values: 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12	Solution of 1.75×10^{-5} mol/L of Thorin and 10 mg/L of REE (Sm, Gd, Eu) pH adjustment with 0.01 mol/L HCl or 0.01 mol/L NaOH	UV-VIS 540 nm	Sm pH 6 Eu pH 6 Gd pH 6
					Thorin-metal rate
Determination of optimum Thorin-metal rate	Sm, Eu, Gd	Thorin-metal rate: 2:1, 3:1, 4:1, 5:1, 6:1, 8:1	Solution of 1 mol/L of REE (Sm, Eu, Gd) and solution containing 1; 2; 3; 4; 5; 6 and 8 mol/L of Thorin, pH 6	UV-VIS 540 nm	Sm 5:1, Eu 5:1, Gd 5:1
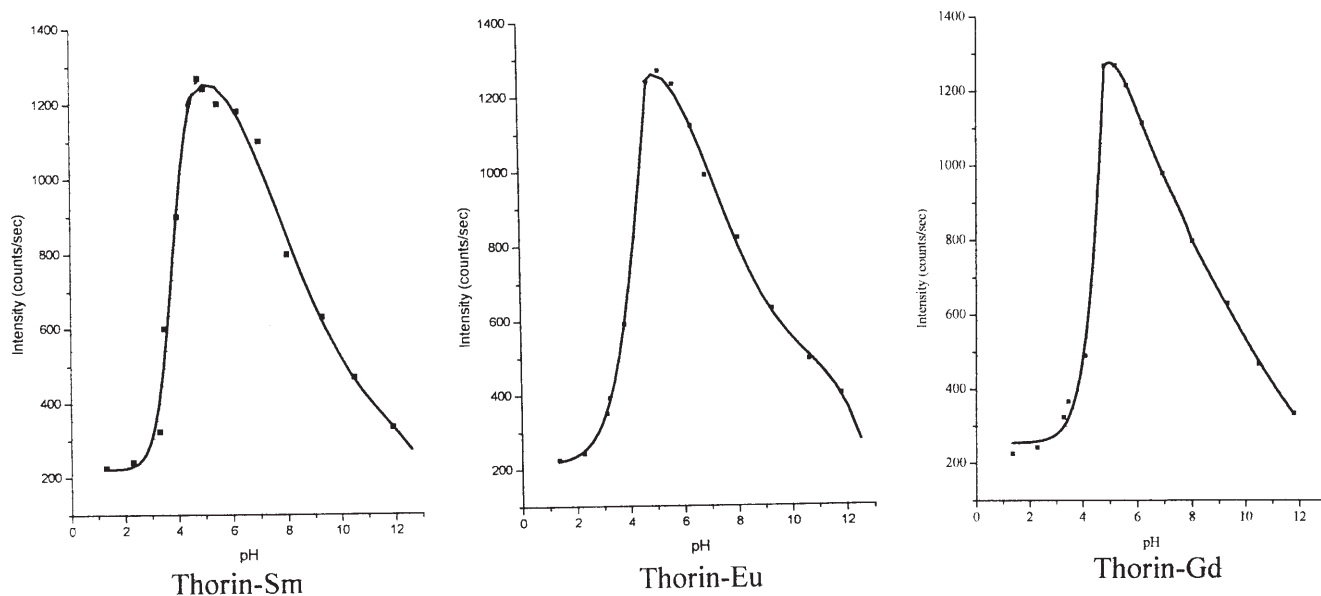
Fig. 1 Retention of REE-Thorin complex on polyamide membrane as a function of pH. XRF intensity measurements: Sm L$_\alpha$ 2θ = 66.23, Eu L$_\alpha$ 2θ = 67.57 and Gd L$_\alpha$ 2θ = 61.10. REEs concentration: 1 mol/L, Thorin concentration: 5 mol/L

The synthetic samples were prepared according to the composition of the reference samples GS-N and AGV-1 of United States of Geochemical Standards (USGS).

Results and discussion

As the preconcentration method presented is based on the formation of a complex which will interact with the membrane during the chemofiltration, it was necessary to establish first the optimum conditions for the complex formation of rare earth ions-Thorin.

The spectral curve of the complex Gd-Thorin shows a maximal molar absorptivity at 540 nm. The effect of pH value on the complex formation was then studied measuring the absorbance at 540 nm for different pH values. The results showed that the highest absorbance of the complex was obtained at pH 6 for all REE studied. Thus, the subsequent experiments were carried out at this pH value.

It was also necessary to establish the best metal – Thorin concentration ratio. This was determined by varying the metal to organic reagent ratio. In all cases the maximum absorbance was obtained for the ratio metal:Thorin 1 to 5. These data were useful to determine the minimum organic reagent concentrations necessary for the following experiments.

The results of the experiments for complex formation are summarized in Table 1.

The retention of the complex of REE ions on the polyamide membrane from the aqueous solutions at various acidity values was examined by the batch method. The REE concentrations were determined measuring their L$_\alpha$ lines by XRF spectrometry. At pH values lower than 2, the REE complexes were not retained on the membrane, at about pH 2 the retention started and was quantitative in a pH range between 4.8 and 5. The result of the influence of pH on the chemofiltration of REE-Thorin complexes is shown in Fig. 1. This behavior can be explained by the form in which the reagent is retained on the membrane. Savvin et al. [9, 10] suggest that the retention mechanism of the metal ions and the organic reagent complex on the polyamide membrane filter is based not only on electrostatic forces but also on non-hydrophobic interactions be-
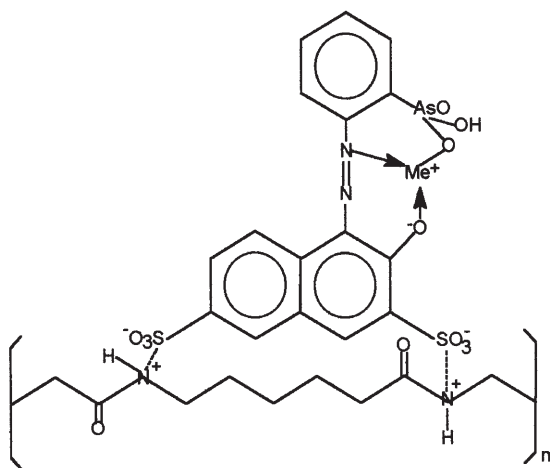
Fig. 2 Interaction between the complex Me-Thorin and the polyamide membrane after the chemofiltration process

tween the polymer matrix and the molecules of organic reagent.

The interaction between the complex Me-Thorin and the membrane proposed is shown in Fig. 2.

The influence of the shaking time on the chemofiltration was evaluated after mixing the REE and the Thorin solutions, shaking during 2, 3, 4, 5, 10, 15, 20, etc. min and filtrating through a polyamide filter. Between 8 and 10 min were needed for reaching the maximum complex retention on the membrane for the three REE studied.

The retention of the Gd-Thorin complex modifying the flow rate demonstrated that when the flow rate of filtration was aproximately 1 mL/min, the quantity (measured by XRF) of REE retained on the membrane reached its maximum concentration. This flow rate was adopted for the following experiments.

In the case of preconcentration of large volumes of sample, it was necessary to determine the amount of complex, which saturates the membrane. The plot in Fig. 3 shows the XRF intensity of Gd L_α, as function of the concentration of Gd filtered as Thorin complex on the membrane. As can be seen for very low complex amounts, the concentration is proportional to the analyte line intensity. The plot is linear up to 4 mg/L and becomes constant at higher concentration values. The results were the same for all rare earths investigated. We could observe that when reaching this constant value the filtrate showed the color of the complex, which indicates that the membrane was saturated and could not retain more complex. It was convenient to work with REE concentrations below 4 mg/L. Below this value the membrane is not saturated and could retain quantitatively the REE. Under these conditions we could also confirm that we were working with a thin film. This item is very important for XRF determinations because in a thin film the XRF intensity of the analyte is proportional to its concentration, and absorption-enhancement effects produced in XRF are negligible. Neither primary nor analyte X-ray lines are significantly absorbed in the thin layer. The percentage of REE-Thorin complex not re-
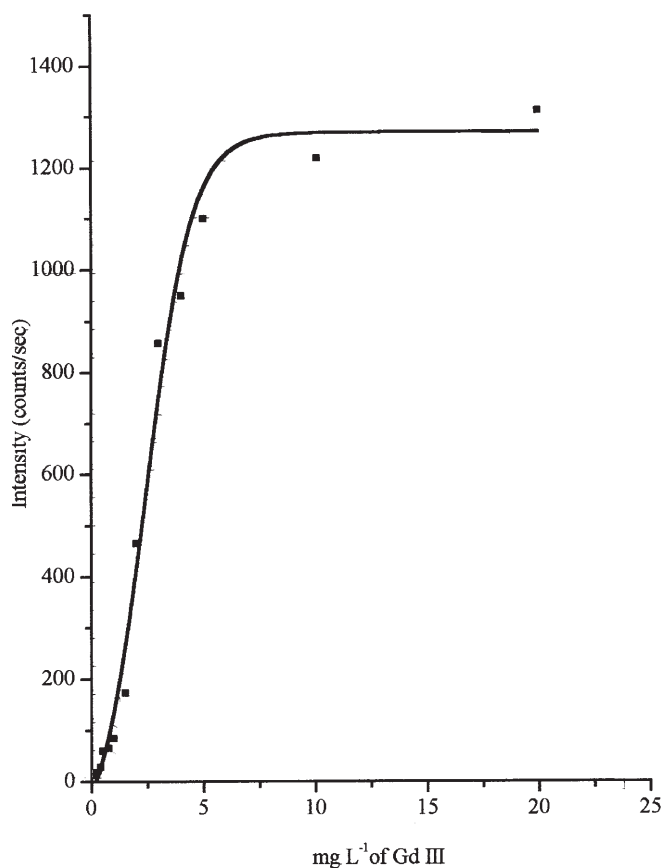

Fig. 3 Saturation curve for Gd-Thorin complex on a polyamide membrane. XRF intensity measurements: Gd L_α $2\theta = 61, 10$. $n = 6$. Correlation coefficient: 0.99227 (for calibration curve)

tained by the polyamide membrane was determined spectrophotometrically in the filtrate and was in all cases of 76%.

The enrichment factor is defined according to [11] as: $F = (Q_T/Q_M)/(Q_T^0/Q_M^0)$ where Q_T^0 and Q_T are the analyte quantities before and after the preconcentration, and Q_M^0 and Q_M are the amounts of the matrix before and after the enrichment.

Considering that the film obtained by chemofiltration of 100 mL solution of 4 mg/L REE had a final thickness of 4 μm, that the ion surface deposit on the membrane is 1.767 cm^2, and the percentage of recovery of (practically) 100% for Sm(III), Eu(III) and Gd(III), the enrichment factor calculated was 110000. This value led us to claim that this preconcentration method is a very worthy tool because its application prior to the determination of trace metal can remarkably enhance the XRF sensitivity. The detection limits were: 23, 23 and 49 ng/mL for Sm (III), Eu(III) and Gd (III), respectively.

The method was applied to the determination of Sm, Eu and Gd in real and synthetic samples which had a similar composition as the reference samples AGV-1 and GS-N of the USGS. The spectral interferences between the measured elements (analytes) and the other REE present in the certified samples analyzed by the developed methodology, were corrected by the method proposed by

Table 2 Determination of Sm, Eu and Gd in synthetic and reference samples

Sample	Contents in mg/L			Quantity found mg /L			E %[b]			Correction factors		
	Sm	Eu	Gd	Sm	Eu	Gd	Sm	Eu	Gd	Sm	Eu	Gd
G-2												
Certif. by USGS	5	1.5	7.3	4.68	1.48	7.6	6.4	1.33	4.11	0.362	0.488	0.264
Sample A[a]	7.7	1.7	5.2	7.8	1.4	5.0	1.29	6.68	3.84			
Sample B[a]	5.9	1.7	5.5	4.97	1.56	5.08	15.7	8.23	7.63			

[a] Sample A and B have the same composition as the reference samples AGV-1 and GS-N of the United States of Geochemical Standards (USGS)

[b] E % = $100 \times |V_r - V_e|/V_r$ where V_r: certified concentration value. V_e: experimental value

Gasquez et al. [12]. This method uses a factor obtained relating to the intensity of the interference line in the 2θ angle corresponding to the analyte line and the intensity of a line of the interference element that can be measured on the specimen and without any type of interferences. This relation was obtained measuring the intensities in samples containing only the element of interest by dissolution of its oxide. For each specimen, the intensity of the interferent line can be calculated from the measured intensity – free from interferences – of the second line of the interferent element. The correction factors for the three REE XRF intensities are shown in Table 2.

The other elements present in the sample do not interfere with the determination because either they do not react with Thorin or, if they do, in the thin film the absorption-enhancement effects are eliminated. The results obtained in the analysis of these samples are shown in Table 2.

Conclusions

The development of this new preconcentration method for REEs and its application to the determination by XRF analysis appear to be a promising alternative for highly selective separation, preconcentration and determination of trace metals ions. The direct measurement of the XRF analyte lines on a thin film formed on the polyamide filter allows the matrix interferences (interelemental effects) to be suppressed. In addition, the high enrichment factors obtained with this preconcentration method allows the detection of very low REE concentrations. This is of great importance for trace elements analysis by XRF.

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