Preconcentration and elimination of matrix effects in XRF determinations of rare earth elements by preparing a thin film through chemofiltration

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Trace rare earth elements (REE) can be enriched by collecting them on a filter after they have formed their complexes with 2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo) bisbenzenearsonic acid (Arsenazo III) through a process called chemofiltration. The filter, which constitutes a thin film, is passed directly to the X-ray fluorescence (XRF) spectrometer, eliminating, in this manner, the interelemental effects produced in XRF determinations. High preconcentration factors and low detection limits are obtained: 18.3 ng mL^{-1} for Sm, 17.5 ng mL^{-1} for Eu and 34 ng mL^{-1} for Gd. The method was applied to the determination of these elements in NIST standard reference glasses with very good precision.

Introduction

Preconcentration methods applied before the determination of the trace inorganic elements in different samples enhance the potential of instrumental analysis using organic reagents. In trace analysis not only the low concentration of the analytes in the matrix, but the possible matrix interferences, must be considered. These difficulties can be overcome by preconcentrating the trace metal and, in this form, obtaining the enrichment of the trace elements and separation of them from the matrix.

The rapid advance in instrumental techniques has led researchers to develop new methodologies of preconcentration. Many methods of preconcentration and separation have been reported, which involve precipitation,[1] ionic exchange,[2] immobilization of reagents,[3] chelating resins,[4,5] etc. When measuring by XRF, the interelemental (matrix) effects produced can be eliminated if the sample is presented to the XRF spectrometer as a thin film. This work was devoted to developing one methodology for the two purposes.

The presence of trace quantities of REE in high purity metals, semiconductors and glasses has an important influence on the electrical, magnetic, mechanical, nuclear and optical properties.[6] Some standard fluoride glasses are now the basis of industrial optical fibers for a variety of applications, ranging from infrared technologies to fiber lasers and medicine. An increasing interest is devoted to active fibers, which could be used for new laser lines and for optical amplification. In both cases REE play a major role and their specific spectroscopic properties determine to a large extent the characteristics of the final device.[7] Apart from practical applications, the study of REE in fluoride glasses may help to understand the mechanism of glass formation. While lanthanides are not reported to be glass progenitors in fluoride systems, some recent results suggest that Y and some REE could be vitrifiers in so far as YF_3 is the major component. REE cations appear rather as intermediates between glass progenitors such as Zr^+ or Al^{3+} and modifying cations such as Na^+ or Ba^{++}. One of the ways

to convert infrared light to the visible range is with sensitised luminescence and stage-wise pumping of the higher levels of trivalent rare earth ions in fluoride crystals and glasses.[8]

This paper describes a new preconcentration method for trace REE realized through a procedure called chemofiltration, which is based to a certain extent upon the earlier developed principle of concentration of elements by coprecipitation with organic coprecipitants from a diluted solution. But all the drawbacks produced can be overcome by membrane filtration.

The principle of this procedure implies that the complex formation of the determined elements is carried out with selective organic reagents in solution followed by sorption of this complex onto the membrane in the course of filtration. Highly selective preconcentration can be attain by optimising the working conditions and selecting the proper complexing agent.

The method presented here proposes the use of 2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo) bisbenzenearsonic acid (Arsenazo III) as the complexing agent. Arsenazo III has been used in the spectrophotometric determination of Bi, REE, Fe, Pb^{2+}, UO_2^{2+}, etc.,[9] but its use as a complexing agent has not been reported in chemofiltration processes.

One of the most important advantages of this method is the possibility of obtaining large preconcentration factors and, as a consequence, low detection limits in XRF determinations, taking into account that the concentrated complex is distributed only on the membrane surface and it is feasible to pass large volumes of samples (1 L or more) through the filter.

Experimental

Reagents and apparatus

Rare earth element standard solutions 1000 mg L^{-1} 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^{-1} HCl and diluting to 100 mL with water. The oxides (99.99% purity) were purchased from

Aldrich Co (Milwaukee, WI, USA). A 1.28×10^{-3} mol L^{-1} solution of Arsenazo III was prepared by dissolving 100 mg of the reagent in water up to 100 mL. Diluted solutions were prepared by adding water to the concentrated solutions. Arsenazo III ($C_{22}H_{18}AsN_2O_{10}S_2$), 95% purity, was purchased from Aldrich Co. Buffer solutions of pH 4 and pH 9 were prepared with potassium hydrogenphthalate (5×10^{-2} mol L^{-1}), and sodium tetraborate (1×10^{-2} mol L^{-1}) respectively, for calibrating the pH-meter electrode. Membrane polyamide filter papers of 0.2 μm pore size were from Whatman. All other chemicals used were of analytical-reagent grade and doubly distilled water was used throughout.

A Philips PW1400 X-ray fluorescence spectrometer (Almelo, The Netherlands) was used for Sm, Eu and Gd Lα line measurements. The measurement parameters were: $2\theta = 66.23$ for Sm Lα, $2\theta = 67.57$ for Eu Lα and $2\theta = 61.10$ for Gd Lα; Rh tube, 50 kV, 50 mA; LiF (200) crystal; 75–25% window width; counting time for peak and background 100 s; and gas proportional-scintillation counter in tandem arrangement. A Gilford response UV-VIS 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, Bedford, MA, USA). The pH of the solutions was 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 Arsenazo III–metal formation

Influence of pH. In order to establish the best pH of the complex formation, solutions containing 10 mg L^{-1} Gd and 1.28×10^{-3} mol L^{-1} in Arsenazo III were adjusted to different pH values with NaOH (0.01 mol L^{-1}) or HCl (0.01 mol L^{-1}) and measured spectrometrically at 654 nm. The process was repeated with Sm and Eu.

Determination of optimum Arsenazo III/metal rate. Solutions with different Arsenazo III/metal (REE) rates were adjusted to pH 2.6 with sodium hydroxide (0.01 mol L^{-1}). The complex concentrations were determined spectrometrically at 654 nm.

Studies of the variables that affect chemofiltration

Influence of pH on the chemofiltration. Portions of 50 mL of solution containing the complex Arsenazo III–Gd (3 mol L^{-1}– 1 mol L^{-1}) were adjusted to different pH values with sodium hydroxide or hydrochloric acid. The solutions were filtered on the polyamide membrane and the Lα lines of the analyte were measured by XRF spectrometry. The same procedure was carried out with Sm and Eu.

Influence of the shaking time on the membrane retention. Portions of 50 ml of solutions of Arsenazo III (1.28×10^{-3} mol L^{-1}) and Gd, Sm or Eu (10 mg L^{-1}) at pH 2.25 were shaken during different periods of time (2, 5, 10, 15, 20, *etc.,* min). The complex was then filtered through a polyamide membrane and the amount of complex retained on the membrane was determined using XRF spectrometry by measuring the metal (Gd, Sm, Eu) Lα line intensity.

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

Determination of the maximum capacity of retention of the membrane. Solutions containing different concentrations of the complex Arsenazo III–Gd at pH 2.25 were passed through

the membrane in order to determine the quantity of complex which saturates it. The metal Lα line was measured by XRF in the chemofiltrate on the membrane. The same experiments were realized with Sm and Eu.

Percentage recovery. This study was realized by determining, at 654 nm and at pH 2.6, the quantity of the complex ArsenazoIII–REE in the filtrate not retained by the membrane.

Enrichment factor. This parameter was calculated by measuring with a Köfer thickness meter, with ± 1 μm precision, the final thickness of a film prepared by chemofiltration of a solution containing 4 mg L^{-1} of Gd on the surface of the polyamide membrane on which it was distributed. The percentage of recovery was also considered.

Preconcentration and determination of Sm, Eu and Gd iun different samples

Sample treatment. A disc of NIST SRM 613 was broken into small pieces and fragments were placed in an agate micro-mill. The glass was reduced to a fine powder and 0.3 g of this powder were weighed and put into a PTFE vessel. The sample was digested with 2 mL of HNO$_3$ and heated in a sand bath to obtain a paste. Then, 2 mL HNO$_3$–HCl (1 : 3) were added and the digest was heated again until all nitrous vapours were eliminated. 12 mL HNO$_3$–HCl (1 : 3) and 24 mL of HF were added in portions of 2 and 4 mL, respectively, and the sample was softly heated. Lastly, 0.5 mL of HClO$_4$ were incorporated and the solution was evaporated until white vapours of HClO$_4$ appeared. The sample was redissolved in 10% HCl and made up to 25 mL in a volumetric flask, for subsequent REE preconcentration and determination.

A series of appropriate standards solutions of Sm, Eu or Gd, containing 1.28 mol L^{-1} Arsenazo III at pH 2, were shaken for 10 min and chemofiltered at a flow rate of 10 ml min^{-1} with a polyamide membrane. The XRF measurement parameters were as given under Reagents and apparatus.

Results and discussion

During the chemofiltration process there exists an interaction between the complex (REE–Arsenazo III) and the polyamide membrane. So, it was necessary to establish first the optimum conditions for the complex formation. The effects of the hydrogen concentration on the formation of the complex Arsenazo III–Gd showed that the highest concentration of the complex was obtained at pH 2.6. Similar results were obtained for Eu and Sm. For this reason, in all subsequent studies the pH was adjusted to 2.6 as the optimum pH value.

By varying the concentration of metal to organic reagent rate, the maximum absorbance corresponding to the optimum relation for the Gd–Arsenazo III complex formation was obtained with a 1 to 3 concentration ratio. These results were useful for determining the minimum organic reagent concentration necessary for the following experiments.

Once the optimum variables for the complex formation were established it was necessary to study the best conditions for the chemofiltration process.

Savvin *et al.*[10,11] suggest that the retention mechanism of the metal ion and the organic reagent complex on the polyamide membrane filters is based not only on electrostatic forces, but also on non-hydrophobic interactions between the polymer matrix and the molecules of organic reagent.

The influence of acidity on the retention of the complex of REE ions from the aqueous solutions on the polyamide membrane was examined by the batch method. At low pH values, the REE complexes were not retained on the membrane, they began to be retained at higher pH values
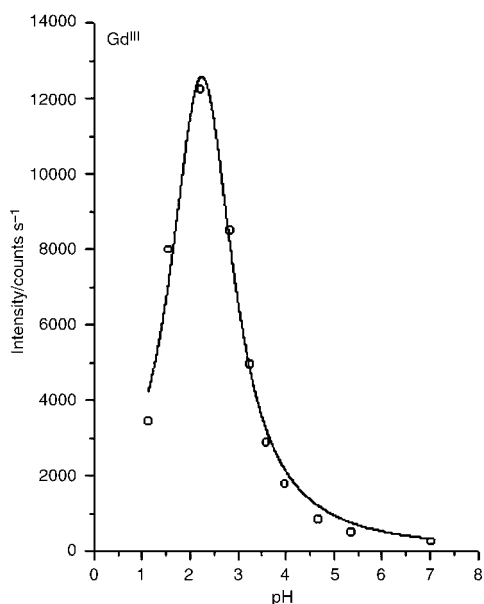
Fig. 1 Retention of Gd–Arsenazo III complex on a polyamide membrane as a function of pH.

and were quantitatively retained in a pH range between 2.25 and 2.3 (Fig. 1).

The influence of the shaking time on the chemofiltration was evaluated after mixing the Gd and the Arsenazo III solutions, shaking during different times and filtering through the polyamide filter. Between 8 and 10 min were needed for reaching the maximum complex retention on the membrane. The same results were obtained for Sm and Eu complexes (Fig. 2).

By modifying the flow rate it was demonstrated that when the flow rate of filtration was approximately 10 ml min^{-1} the quantity (measured by XRF) of REE retained on the membrane reached its maximum concentration. So this flow rate value was adopted for all experiments.

In order to analyse large volumes of sample it was necessary to determine the amount of complex that saturates the membrane. In Fig. 3, the XRF intensity of Gd Lα as a function of the Gd concentration filtered as the Arsenazo III complex on the membrane is shown. For very low amounts of
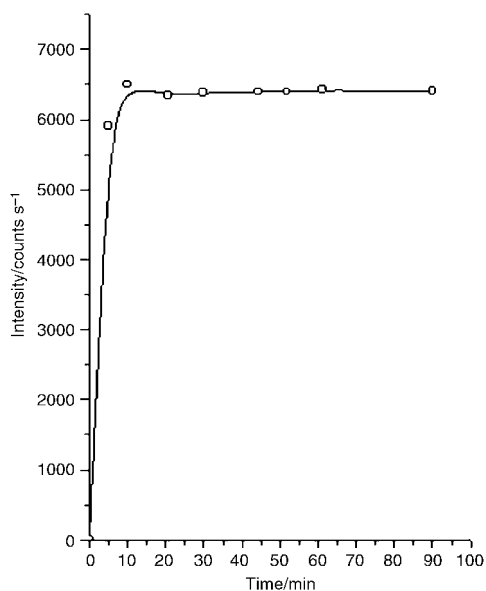

Fig. 2 Effect of shaking time on the retention of the complex Sm–Arsenazo III.
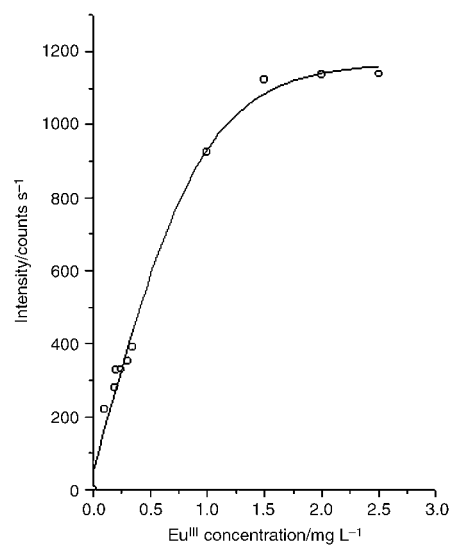

Fig. 3 Saturation curve for Eu–Arsenazo III complex.

the complex, the concentration is proportional to the Gd Lα intensity. The plot is linear up to 1.5 mg L^{-1} of Gd and becomes constant at higher Gd concentrations. It was observed that, when reaching this constant value, the filtrate showed the complex colour, which indicated that the membrane was saturated. It is convenient to work with a Gd concentration below 1.5 mg L^{-1} because it was demonstrated that below this value the membrane was not saturated and could retain the REE. Using these conditions, it was confirmed that we were working with a thin film. This is very important for XRF determinations because in a thin film the XRF intensity of the analyte is proportional to its concentration and the absorption–enhancement effects produced in XRF measurements are negligible. Neither primary nor analyte X-rays lines are significantly absorbed in the extremely thin layer. The percentage of the Arsenazo III–REE complex not retained by the polyamide membrane was determined spectrometrically in the filtrate. The percentage retained was in all cases 85%.

The enrichment factor is defined as:[12] $F = (Q_T/Q_M)/(Q_T^0/Q_M^0)$ 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 quantities of the matrix before and after the enrichment. The enrichment factor was calculated by considering: the film obtained from the chemofiltration of 100 ml of the REE solution (1.5 mg L^{-1}); the final thickness of 4 μm; the surface deposited on the membrane of 1.767 cm^2; and the percentage of recovery for Sm, Eu and Gd. The preconcentration factor obtained was 1.1×10^5, which is highly satisfactory for trace analysis by XRF.

The detection limits obtained by using this preconcentration method were: 18.3, 17.5 and 34 ng mL^{-1} for Sm(III), Eu(III) and Gd(III), respectively.

The REE X-ray intensity measured in standards containing the same quantity of each REE and different composition of the matrix, and preconcentrated by this method, was the same in each case. The reason of this is that the other elements present in the sample do not interfere in the determination because either they do not react with Arsenazo III or, if they

Table 1 Linear regression parameters for the calibration curves of Sm, Eu and Gd preconcentrated with Arsenazo III, where: $y = A + Bx$ and s = standard deviation

Element preconcentrated	A	B	RSD	s
Sm	24.531	258.89	0.991	15.006
Eu	21.057	394.95	0.977	30.522
Gd	41.477	954.90	0.994	38.622

Table 2 Analysis of Sm, Eu and Gd in NIST SRM 613 Glass

Sample $n=6$		Content/mg kg^{-1}		Quantity found/mg kg^{-1}	E (%)
Trace Elements in a	Sm	39[a]	38.5[b]	42.39±1.06	8.0
Glass Matrix N° 613	Eu	36[a]	35.51[b]	36.35±2.05	0.97
Certif. by NIST	Gd	39[a]	38.09[b]	37.36±1.98	4.2

[a]Reported by NIST. [b]Reported by Geostandards.[13]

do, the absorption–enhancement effects are eliminated in a thin film. The linear regressions for the calibration curves are shown in Table 1.

The method was applied to the determination of Sm, Eu and Gd in NIST SRM 613 Glass samples. NIST only certifies up to eight elements in this glass and gives an estimate of the others, but Pearce *et al.*[13] compiled the concentration data from approximately sixty published works for fifty-eight trace elements contents in this certified material. There is good agreement between the compiled averages and the NIST data for REE (Sm, Eu and Gd). The results obtained by us are shown in Table 2. Our results are also in good agreement with the data given by NIST and the averaged compiled data of Pearce *et al.*[13]

Conclusions

It has been shown that the direct measurement of the XRF analyte lines on a thin film obtained on the polyamide filter allows the matrix interferences (interelemental effects) to be suppressed. The high enrichment factors obtained encouraged us to propose this preconcentration methodology as a worthy tool in trace analysis, not only in XRF determination. It gives lower detection limits and permits the determination of trace elements with high precision.

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