

## Preconcentration neutron activation analysis of lanthanides by cloud point extraction using PAN

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Methods for the simultaneous preconcentration of lanthanides by cloud point extraction and their determination using neutron activation analysis have been developed. The preconcentration method involves the use of a nonionic surfactant and a chelating agent. A fairly small volume of surfactant-rich phase was obtained under optimized experimental conditions, leading to detection limits between 0.3 and 3.0 ng·g<sup>-1</sup>. Critical parameters that influence extraction efficiency were solution pH and concentration of chelating agent, and to a lesser extent, ionic strength and temperature. Most of the chelates were quantitatively extracted (>90%) at high pH values. Selective separation can be achieved by varying some of the experimental conditions.

### Introduction

Lanthanides (*a.k.a.* rare earth elements, REE) are being increasingly used in many industries including glass and ceramic, metallurgy, nuclear, electronics, and more recently for the preparation of superconductor materials.<sup>1</sup> Combustion of fossil fuels also introduces large amounts of lanthanides in the atmosphere. These activities are continuously increasing the levels of lanthanides in the environment. Their determination has also become of analytical importance. Due to the low concentrations of lanthanides, even sensitive analytical techniques such as inductively-coupled plasma mass spectrometry (ICP-MS) and neutron activation analysis (NAA) may require a preconcentration step for interference-free measurements.

Classical spectrophotometric techniques are useful for the determination of the total amount of lanthanides. Simultaneous determination of several individual elements can be very difficult due to the non-availability of selective chromogenic reactants. Other widely-used techniques such as atomic absorption spectrometry (AAS) and atomic emission spectroscopy (AES) are of restricted use because these elements, besides presenting complex absorption and emission spectra, have a tendency to form refractory oxides as well as to undergo ionization.<sup>2</sup>

The determination of lanthanide ions in aquatic samples usually requires a preconcentration step since most of these elements are present in concentrations close to or below the detection limit of the analytical technique usually available. Preconcentration techniques currently used for lanthanides in water include coprecipitation,<sup>3</sup> ion-exchange,<sup>4</sup> liquid-liquid and solid-liquid extractions<sup>5</sup> and extraction chromatography,<sup>6</sup> absorption onto silica-immobilized 8-hydroxyquinoline or immobilized bacteria.<sup>7,8</sup> Chelating resins have been

one of the most popular preconcentration media for trace amounts of lanthanides in the last few years, however, an extra step is also required here to remove Mg<sup>2+</sup> and Ca<sup>2+</sup> ions. These procedures increase sample manipulation and possible contamination.<sup>9</sup> Micelle-based separation methods have grown in importance and applications in analytical chemistry. Among these methods, cloud point extraction (CPE) is an efficient extractive step for the enrichment of metals, including lanthanide ions, allowing their quantification at ng·g<sup>-1</sup> levels.<sup>10,11</sup>

Preconcentration of lanthanides using CPE has not yet been reported extensively in the literature. A few papers can be found on the use of CPE for the preconcentration of Er and Gd among the lanthanides. The CPE extraction of Er(III) with 2-(3,5-dichloro-2-pyridylazo)-5-dimethyl amino phenol as the chelating agent and PONPE-7.5 at 0.01wt.% has been reported by SILVA et al.<sup>11</sup> The detection limit of Er was reported as 24.8 ng·g<sup>-1</sup>. A similar CPE procedure was reported by OLSINA et al.<sup>12</sup> for the determination and monitoring Gd in urine samples, following the administration of Gd-based pharmaceuticals. Using a microscale CPE protocol, the total and free Gd(III) content can be determined. The limit of detection for Gd(III) was reported as 0.912 ng·g<sup>-1</sup>. The determination of total amount of lanthanides in ductile iron and micronutrient fertilizer was reported using a solid-liquid CPE with polyvinyl alcohol *p*-formylchlorophosphonazo.<sup>13</sup> More recently, surfactants have also been used to enhance the analytical response of lanthanides and their chelates,<sup>14–16</sup> but not as extraction media.

Most procedures used for preconcentration and/or determination of lanthanides usually report the results as the total content in the sample, since the separation and analysis of single elements can be very time-consuming and difficult.<sup>17</sup> The CPE procedure presented here offers

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the possibility of simultaneous determinations of the individual lanthanides.<sup>18</sup> A cloud point extraction (CPE) method has been developed in this work for the simultaneous extraction of 12 lanthanides, which were determined afterwards by NAA.

## Experimental

### *Reagents*

The surfactants polyoxyethylene nonylphenylether (PONPE) with 7.5 and 20 oxyethylene units used during the experimental work were of analytical grade and were purchased from Tokyo Kasei Industries. Puriss grade 1-(2-pyridylazo)-2-naphthol (PAN) was obtained from Fluka. Analytical grade citric acid, diammonium hydrogenphosphate, tris-(hydroxymethyl) aminomethane (Trizma base), and piperazine-N,N'-bis(2-ethanesulfonic acid) (PIPES) used for the preparation of buffer solutions were purchased from Sigma Chemicals. Glacial acetic acid ACS assured grade was bought from Caledon, and analytical grade potassium nitrate, nitric acid and ammonia solution (30%) from BDH. Ascorbic acid Analyzed Reagent was purchased from J.T. Baker Chemical Co.

All reagents were analyzed by instrumental neutron activation analysis (INAA) in order to determine possible elemental impurities. The water used in all work was deionized distilled water (DDW) obtained by passing distilled water through a mixed bed ion-exchange column (Barnstead 9-034-3 from Fisher Scientific Company). The multielement comparator standard solution was prepared from ultrapure elemental standard solutions for atomic absorption analysis (supplied by SPEX Chemicals).

### *Equipment*

A refrigerated bath model Haake F3 manufactured by Fisher Scientific was used for the cloud point measurements, and for keeping solution mixtures at the desired temperature before centrifugation. The precision of temperature measurements in terms of standard deviation was  $\pm 0.1$  °C. The pH measurements were done using Accumet pH meter (Model 820 manufactured by Fisher Scientific) with a precision of  $\pm 0.2$  pH units at 25 °C. Samples were centrifuged in a refrigerated superspeed centrifuge (Sorvall RC-5B from Du Pont Instruments) using a fixed-angle rotor type SS-34. The centrifuge tubes were made of polycarbonate (Nalgene Model #3138-0050). A freeze dryer Modulyo (Edwards) was used for drying the samples. The absorbance measurements were done in 1-cm quartz cells using a spectrophotometer (Hewlett Packard Model HP8452) fitted with a diode array detector. The irradiations were

performed at the Dalhousie University SLOWPOKE-2 Reactor (DUSR) with a nominal neutron flux of  $5 \cdot 10^{11} \text{ cm}^{-2} \cdot \text{s}^{-1}$  in the inner pneumatic sites. The irradiated samples were counted using a Canberra Ge(Li) detector. This detector had a resolution of 1.88 keV at the 1332 keV photopeak of <sup>60</sup>Co, a peak-to-Compton ratio of 35:1, and a relative efficiency of 9.5%. An Aptec multichannel analyzer (MCA) card built in a PC was used for the analysis of the photopeaks.

### *Preparation of a multielemental comparator standard*

A concentrated stock solution containing lanthanides was prepared at pH<3 in order to avoid adsorption problems. This solution was placed in a dark glass bottle with a Teflon cap. For testing the extraction procedure, a suitable amount of this stock solution was used. Aliquots of the comparator standard were irradiated regularly for internal quality assessment (IQA) purposes. The elemental concentration chosen was close to the expected metal concentrations in the water samples.

### *Determination of cloud point, phase ratio and percent of water in surfactant-rich phase*

The temperature at which the cloud point phenomenon occurs was determined by the method reported by CARVALHO et al.<sup>19</sup> The method is based on the visual observation of the separation of phases in the micellar solution. The initial solution was heated in the water bath at a specific temperature, which was well above its cloud point (turbid solution). Then the solution was cooled gradually with constant stirring and keeping the temperature stable at selected values. The cloud point was considered as the temperature at which the solution became clear. To verify the results, the opposite process was carried out by gradually heating the clear solution until turbidity appeared. The reported value was the average of these two determinations; in most cases, these two temperatures were within  $\pm 0.5$  °C. The phase diagram for PONPE-7.5 was obtained by determining the cloud point temperature of aqueous surfactant solutions at different concentrations, viz. between 0.05 and 32wt.%.

The percent of water in the surfactant-rich phase was also obtained using UV-spectrometry for the determination of the surfactant concentration in the surfactant-rich phase. A calibration graph was constructed using PONPE-7.5 solutions with concentrations between 0.005 and 0.035wt.%. After the CPE, suitable aliquots were taken from the surfactant-rich phase. A dilution of up to 10 ml was then done with DDW. Solutions prepared in this way were cooled prior to the measurement to avoid the possibility of clouding. The absorbance of the solutions was measured at 277 nm.

The volumes of the respective surfactant-rich and aqueous phases obtained after the separation of phases were determined using calibrated centrifuge tubes for calculating the preconcentration factor. Surfactant solutions (0.1%) containing typical amounts of the analytical reagents were extracted using the general CPE procedure, followed by the measurement of the respective phase volumes. The results reported here are the averages of three determinations.

#### *Cloud point extraction procedure*

The following reagents were added to a 50-ml centrifuge tube in the following order: 0.2 g of 20wt.% surfactant stock solution, 0.75 ml of buffer (containing  $\text{KNO}_3$   $0.05 \text{ mol}\cdot\text{l}^{-1}$  as an electrolyte), suitable amounts of PAN solution, 0.1 ml of the comparator standard solution, and DDW up to 40 ml. This mixture was stirred for 2 minutes in a shaker, then kept at  $40^\circ\text{C}$  for 10 minutes. The tube containing the sample and reagents was centrifuged at 10,000 rpm for 10 minutes in order to speed up the separation of phases. After centrifugation, phases were separated by pipetting the upper aqueous phase. The pH of the aqueous phase was measured after each extraction. The surfactant-rich phase was transferred to a 1.5-ml polyethylene vial. The centrifuge tube was rinsed with DDW ( $4\times 100 \mu\text{l}$ ) and the rinsings were added to the surfactant-rich phase. The degree of extraction (recovery) was calculated as the ratio of the amount of species extracted by the surfactant-rich phase to the amount initially added to the system. To ensure reproducibility of results, all experiments were done in triplicate. The dependence of the extraction efficiency on selected experimental conditions was studied. The parameters examined were solution pH, concentration of the chelating agent, and concentration of surfactant. The volumes of the concentrated samples obtained after CPE were reduced to 0.2 ml by evaporation.

Blank reagents and comparator standards were irradiated along with the samples in each set of measurements, and at least once a day to check for the possible presence of interfering nuclides in the  $\gamma$ -ray spectra. In order to determine the lanthanides with a minimum spectral interference from the overlapping  $\gamma$ -ray peaks and the minimum possible background, three different timing schemes were used (for irradiation, decay, measurement): 3 h, 1 h, 1 h (Dy, Er, Eu, La, Pr, Sm, Tb); 3 h, 24 h, 1 h (Ho, Gd); and 3 h, 5 d, 1 h (Lu, Tm, Yb). The radionuclides selected for NAA determination of lanthanides were the following:  $^{165}\text{Dy}$  (94.7 keV),  $^{171}\text{Er}$  (308.3 keV),  $^{152\text{m}}\text{Eu}$  (121.8 keV),  $^{159}\text{Gd}$  (363.6 keV),  $^{166}\text{Ho}$  (49.1 keV),  $^{140}\text{La}$  (487.0 keV),  $^{177}\text{Lu}$  (208.0 keV),  $^{142}\text{Pr}$  (1575.9 keV),  $^{153}\text{Sm}$  (103.2 keV),  $^{160}\text{Tb}$  (879.4 keV),  $^{170}\text{Tm}$  (84.3 keV),  $^{175}\text{Yb}$  (396.0 keV).<sup>20</sup>

## Results and discussion

### *Determination of cloud point, phase ratio and percent of water in surfactant-rich phase*

The phase diagram of the surfactant PONPE-7.5 obtained in this work coincides with that expected for a typical nonionic surfactant. The lowest cloud point value determined for PONPE-7.5 was  $21.5^\circ\text{C}$ , which corresponded to 0.1wt.%, and therefore, this concentration was used in the experimental procedure. A temperature of  $40^\circ\text{C}$ , well above the cloud point, was set as working temperature for the extraction. The volumes of the respective surfactant-rich and aqueous phases obtained after separation of phases were determined using graduated centrifuge tubes. The preconcentration factor was calculated as the volume ratio between the two phases after the separation of phases. The reported result  $0.6\pm 0.1$  ml was the average of 6 determinations.

It is known that the surfactant-rich phase usually contains a fair amount of water as a result of the separation of phases. The quantification of this amount can be very useful, since it may explain to some extent the behavior of solutes concentrated in this phase. A calibration curve of PONPE-7.5 in water was constructed and samples from the surfactant-rich phase were measured at 277 nm by UV-vis spectrometry. The results showed that about 81% by weight ( $\pm 1\%$  error) of the surfactant-rich phase is formed by water.

### *Optimization of the CPE procedure*

The parameters optimized were solution pH, and concentrations of the chelating agent and surfactant. This last factor was included to evaluate the possible influence of the capacity (effective volume) of the surfactant-rich phase on the efficiency of the extraction when a large number of elements is included.

### *Effect of pH*

For ionizable solutes, the charge of the solute can greatly influence its extent of binding to a micellar assembly. The ionic form of a molecule normally does not interact with and bind the micellar aggregate as strongly as does its neutral form. Thus, adjustment of the solution pH is of special importance when controlling experimental variables in CPE. Based on the reported pH values for the extraction of lanthanides with PAN,<sup>12,21</sup> the pH interval tested in the present work was between 5.5 and 9.5. Simultaneous extraction was achieved for 12 elements (namely, Dy, Er, Eu, Gd, Ho, La, Lu, Pr, Sm, Tb, Tm and Yb) at pH 8.5 as shown in Fig. 1. Quantitative recoveries were obtained for most of

the elements except Er, which suggests that the CPE procedure can be effectively used for the analysis of traces of lanthanides.

It is interesting to point out that Dy, La and Pr are not extracted at pH 7, while Eu, Gd, Ho, Tb, Tm and Yb are quantitatively extracted. This feature can be advantageously used as a separation technique between these two groups. This can be particularly useful in the case of La, since most geological and environmental samples contain large amounts of La that can induce interference for the initial equilibrium process and the subsequent irradiation and counting steps.

In this work, special attention was paid to select appropriate counting schemes and  $\gamma$ -ray energies for reliable measurement. However, the large total background obtained as a result of the combined activities of the different radionuclides present in the sample made the integration and definition of the peaks more difficult. This problem can appear when working with many elements of high sensitivity in NAA, such as some of the lanthanides, and is partially responsible for the high standard deviations that some elements show at particular values.

#### *Effect of concentration of PAN*

The study on the influence of the concentration of PAN on the CPE of lanthanides showed a quantitative recovery at  $1 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$  for most elements, except for Er whose recovery increased when less PAN was used. Nevertheless, it was possible to get fairly high recoveries at lower concentrations of PAN for Dy, Eu, Ho, Lu, Pr, Sm, Tb, Tm, and Yb (Table 1). Lanthanum showed a different behavior, producing a very low recovery at  $5 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$  of PAN, probably due to a lower stability constant in comparison with the rest of the lanthanides. This behavior, in combination with the low recovery at a pH lower than 7, can be useful to extract selectively other elements in the series in presence of large amounts of La. By adjusting the concentration of the chelating agent, spectral interferences can also be minimized and the total background can be decreased.

#### *Effect of concentration of surfactant*

The concentration of the surfactant does not seem to play an important role under the present conditions for the preconcentration of lanthanides by CPE. The recoveries obtained (Table 2) are very similar at the three concentrations investigated (0.05%, 0.1% and 0.2%). The slight decrease observed at a concentration of 0.2% is probably due to an increase in the surfactant-rich phase volume at this concentration.

#### *Uranium interference in determination of lanthanides*

It has been reported that spectral interferences from U-fission in NAA can cause analytical problems in the determination of some elements.<sup>22,23</sup> These spectral interferences occur when the product nuclides are identical to the activated nuclides being analyzed or when their characteristic  $\gamma$ -rays have energies very close to the analytical peaks of the activated nuclides. ILA et al.<sup>24</sup> reported a detailed study on U and U-fission interferences in multielement analysis of uraniumiferous rocks by NAA. The elements most affected by the spectral interferences were Ce, La, Nd, and Sm. Most fission product contributions, as well as the content of U, were evaluated by using the 277-keV  $\gamma$ -ray of  $^{239}\text{Np}$ , a decay-product of the fission of  $^{239}\text{U}$ . The authors recommended that, in routine analysis, the need to irradiate the U standard each time for the purpose of determining the fission interference can be avoided if the experimental conditions are normalized to some preset standard conditions.

Since no U was added to the multielement standards used in the CPE study described here, no spectral interference was considered in the analysis of the results. Nevertheless, the frequent presence of U in materials containing lanthanides suggests the necessity of correction factors to account for these interferences when applying the optimized CPE procedure to the analysis of samples.

About 10  $\mu\text{g}$  of U were extracted using the CPE procedure and the surfactant-rich phase was irradiated for 2 hours. The results using different decay times (same as described in the Experimental section) showed a major spectral interference of  $^{239}\text{Np}$  with the analytical peak characteristic of  $^{153}\text{Sm}$  (103.2 keV). If relatively large amounts of U are present in the sample, this interference may also affect the resolution of the 94.7 keV photopeak ( $^{165}\text{Dy}$ ). These interference effects can be corrected using correction factors, which will depend on the neutron flux as well as the counting geometry and the timing schemes used for the analysis.

#### *Internal quality assessment*

Schwartz control charts were constructed for the multielement standards of lanthanides used in this work. The majority of the experimental points were within the warning limits in all charts and the error was kept below 6%, with the exception of Dy (8%). The 94.7 keV photopeak of  $^{165}\text{Dy}$  is located in a high background region. This peak is also very close to the peaks produced by the X-rays from the Pb-shielding of the detector, which makes the integration procedure more difficult. However, the error associated with the counting statistics alone is usually considered to be around 10%.

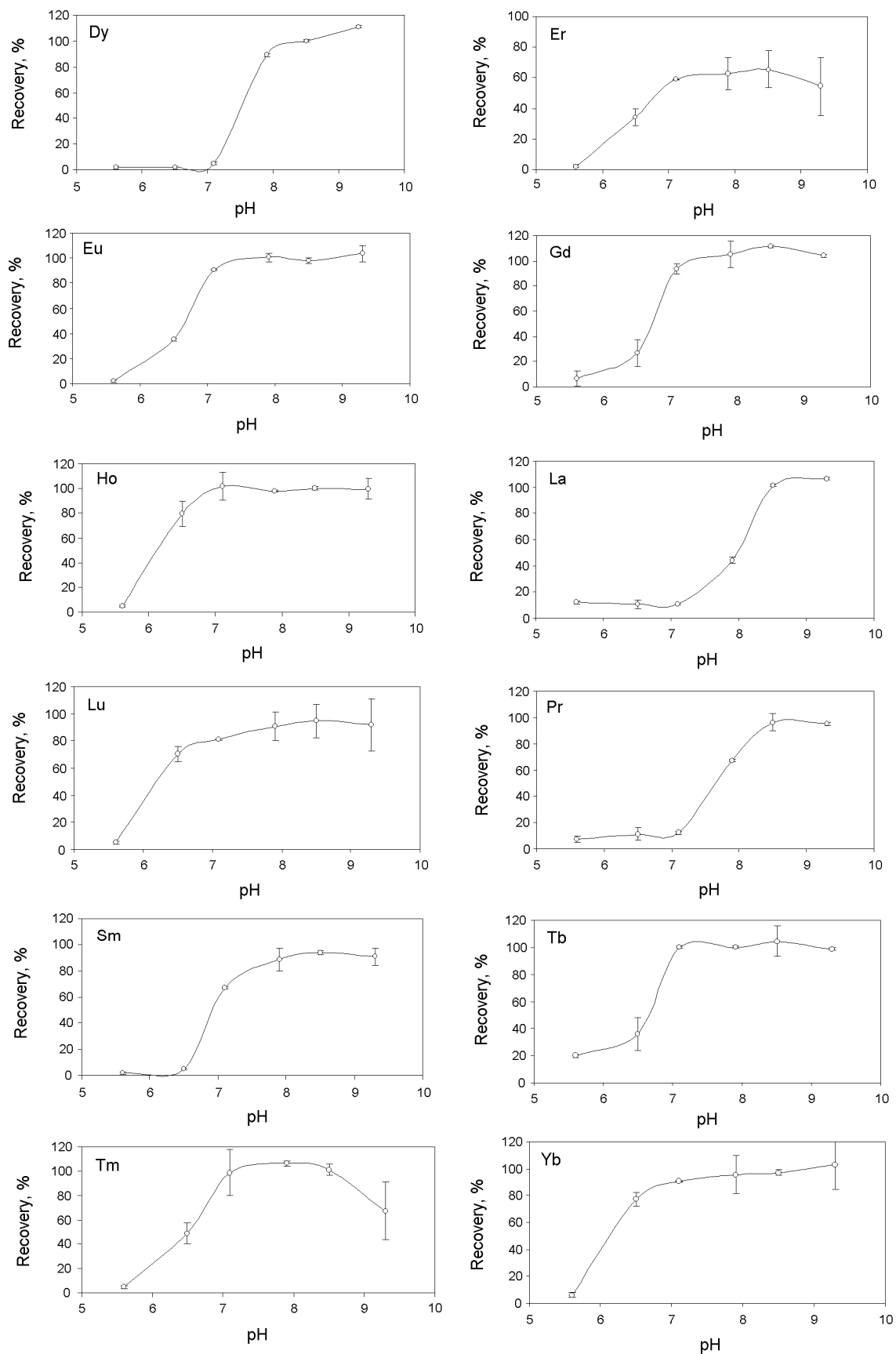


Fig. 1. Effect of pH on extraction recovery of lanthanides by CPE using PONPE-7.5 (0.1wt.%) and PAN ( $1 \cdot 10^{-4}M$ )

Table 1. Influence of the PAN concentration on CPE of lanthanides\*

Element	Recovery at selected PAN concentrations, %			
	$5 \cdot 10^{-5} \text{M}$	$7.5 \cdot 10^{-5} \text{M}$	$1 \cdot 10^{-4} \text{M}$	$2.5 \cdot 10^{-4} \text{M}$
Dy	98 ± 2	96 ± 2	100 ± 1	78 ± 1
Er	84 ± 13	74 ± 9	65 ± 12	41 ± 18
Eu	98 ± 2	107 ± 2	98 ± 2	76 ± 13
Gd	84 ± 1	90 ± 3	111 ± 1	87 ± 14
Ho	99 ± 7	101 ± 1	100 ± 2	86 ± 6
La	15 ± 4	29 ± 6	101 ± 1	89 ± 3
Lu	98 ± 1	97 ± 1	95 ± 1	71 ± 1
Pr	94 ± 13	108 ± 1	96 ± 6	82 ± 6
Sm	101 ± 1	95 ± 2	94 ± 2	69 ± 18
Tb	104 ± 7	104 ± 11	104 ± 12	93 ± 2
Tm	89 ± 12	86 ± 8	101 ± 4	64 ± 6
Yb	101 ± 4	101 ± 5	97 ± 2	72 ± 5

\* Results are the average of 3 determinations ( $\pm$  sign refers to the calculated standard deviation).

Table 2. Influence of the surfactant concentration on CPE of lanthanides\*

Element	Recovery (%) at selected surfactant concentrations, wt. %		
	0.05%	0.10%	0.20%
Dy	90 ± 5	100 ± 1	96 ± 1
Er	66 ± 8	65 ± 12	58 ± 10
Eu	98 ± 3	98 ± 2	89 ± 2
Gd	98 ± 5	111 ± 1	89 ± 5
Ho	96 ± 4	100 ± 2	87 ± 1
La	87 ± 7	101 ± 1	81 ± 9
Lu	89 ± 3	95 ± 1	86 ± 1
Pr	93 ± 9	96 ± 6	100 ± 3
Sm	88 ± 4	94 ± 2	88 ± 4
Tb	100 ± 7	104 ± 11	94 ± 3
Tm	97 ± 3	101 ± 4	83 ± 9
Yb	94 ± 5	97 ± 2	92 ± 3

\* Results are the average of 3 determinations ( $\pm$  sign refers to the calculated standard deviation).

Table 3. Sensitivity and detection limits of lanthanides\*

Element	Sensitivities, counts $\cdot \mu\text{g}^{-1}$	Detection limit, ng $\cdot \text{g}^{-1}$
Dy	$(2.6 \pm 0.2) \cdot 10^6$	$1.76 \pm 0.03$
Er	$44\,640 \pm 2\,060$	$1.72 \pm 0.03$
Eu	$(2.09 \pm 0.06) \cdot 10^7$	$3.07 \pm 0.02$
Gd	$1\,430 \pm 77$	$0.60 \pm 0.006$
Ho	$50\,490 \pm 956$	$0.87 \pm 0.004$
La	$23\,385 \pm 511$	$1.39 \pm 0.05$
Lu	$32\,570 \pm 500$	$0.57 \pm 0.007$
Pr	$1\,519 \pm 52$	$0.29 \pm 0.003$
Sm	$(8.4 \pm 0.5) \cdot 10^5$	$2.91 \pm 0.05$
Tb	$845 \pm 43$	$1.14 \pm 0.007$
Tm	$11\,080 \pm 499$	$0.98 \pm 0.005$
Yb	$4\,140 \pm 158$	$0.27 \pm 0.008$

\* Results are the average of 3 determinations ( $\pm$  sign refers to the calculated standard deviation).

### Sensitivity and detection limits

The sensitivities and the detection limits obtained are presented in Table 3. Most of the results are near to the  $1 \text{ ng} \cdot \text{g}^{-1}$  mark, which can be very useful for the determination of the lanthanides in environmental and biological samples. The standard deviations reported represent less than a  $\pm 3\%$  error.

### Conclusions

A simple one-step method for the simultaneous preconcentration of most of the lanthanides (Dy, Er, Eu, Gd, Ho, La, Lu, Pr, Sm, Tb, Tm and Yb) based on CPE has been developed. The method involves the extraction of the PAN/metal chelates in 0.1 wt. % micellar solutions of PONPE-7.5, and the use of different irradiation, decay and counting time schemes for NAA. The simultaneous extraction is quantitative at pH 8.5 using  $\text{KNO}_3$  (0.05M) as the electrolyte and  $1 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$  of PAN. An optimum temperature of  $40^\circ \text{C}$ , well above the cloud point of the micellar system, was found to be suitable for quantitative recovery. A preconcentration factor of 70 was obtained using this procedure under optimal conditions, which is in good agreement with the literature values reported for cloud point extractions. This factor can be useful for the analysis of environmental samples with low concentration of these metals. Selective separation can be achieved using the different behaviors of individual metal chelates at various pH values and PAN concentrations. Spectral interference from U-fission in the NAA procedure may affect the resolution of the 94.7 keV photopeak ( $^{165}\text{Dy}$ ), if relatively large amounts of U are present in the sample. The results of the internal quality control indicate that the method is operating under fairly good statistical control.

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