

Determination of lanthanides in Kola nitrophosphate solution by cation-exchange ion chromatography

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Abstract

Lanthanides and yttrium are present in Kola phosphate rock. Digestion of this rock with concentrated nitric acid in the Odda process of fertilizer production leads to the dissolution of these metals in the resulting nitrophosphate solution. This nitrophosphate solution is considered as a complex analytical matrix. In this paper, we present an analytical method with a total analysis time of 18 min for the direct determination of lanthanides and yttrium in the above nitrophosphate solution, based on cation-exchange ion chromatography. The analytical columns involved in this method are silica-based cation exchanges. Elution was carried out with a concentration gradient of HIBA (α -hydroxyisobutyric acid) at a pH range between 3.8 and 4.2, coupled with post-column spectrophotometric detection with PAR or ARSENAZO III at 530 and 658 nm respectively. These silica columns can also offer the direct analysis of lanthanides in organic solutions taken from experimental research samples, investigating the extraction of these metals from the nitrophosphate solution by liquid–liquid extraction.

1. Introduction

Norsk Hydro has been involved in fertilizer production since 1905. The fertilizer production plant located at Hydro Porsgrunn, Norway, utilizes the Odda process of fertilizer production, which involves the digestion of phosphate rock with concentrated nitric acid to produce a nitrophosphate solution [1].

This nitrophosphate solution is cooled down to -5°C to crystallize calcium nitrate, which is removed by filtration. The mother liquor resulting from this crystallization will undergo further treatment in the fertilizer production process chain. Table 1 shows the complete analytical data of a mother liquor solution obtained from the digestion of Kola phosphate rock.

The digestion of Kola phosphate rock, which

is relatively rich in lanthanides, produces a mother liquor solution containing these metals. In contrast to the wet process of fertilizer production, in which sulphuric acid is used to achieve the digestion, a large percentage of the lanthanide salts precipitate with the gypsum [2].

Several articles have been published investigating the recovery of lanthanides and yttrium from this nitrophosphate solution [3]. Some investigations were abandoned because of the lack of an analytical procedure for these metals [4]. Norsk Hydro Research Centre, Porsgrunn, has undertaken a feasibility study on the recovery of these metals from the mother liquor solution in the Odda process of fertilizer production. The success of this study depended, to a large extent, on the accuracy of the analytical data produced from a large number of samples.

Lanthanides play an important role in many current technological industries. These include

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Table 1
Typical composition of a Kola mother liquor solution

Ion	Range of concentration
P	10.17–9.27%
Ca	3.26–3.09%
F	0.31–0.28%
Total N	11.16–11.40%
N-NO ₃ ⁻	6.13–6.34%
N-NH ₄ ⁺	5.03–5.06%
Na	2105–1600 mg/l
Mg	510–430 mg/l
Al	3668–3400 mg/l
Ti	580–840 mg/l
V	83–79 mg/l
Mn	191–190 mg/l
Fe	2175–2000 mg/l
Cu	37–38 mg/l
Zn	26–28 mg/l
Sr	5133–5100 mg/l
Ba	151–130 mg/l
Y	212–240 mg/l
La	1238–1200 mg/l
Ce	2350–2375 mg/l
Pr	220–230 mg/l
Nd	950–965 mg/l
Sm	125–121 mg/l
Eu	35–36 mg/l
Gd	90–94 mg/l
Tb	9–11 mg/l
Dy	45–60 mg/l
Ho	8–9 mg/l
Er	16–24 mg/l
Tm	2–2.3 mg/l
Yb	8–11 mg/l
Lu	1–1.3 mg/l
Th	12–11 mg/l
U	4–4.2 mg/l

the nuclear, metallurgy, electronic, ceramic and laser industries. They are also important catalysts in the petroleum industry and as fluorescent labels for biological molecules. Determination of lanthanides in geological materials is also important, especially for petrogenetic studies [5].

The ideal method for the determination of lanthanides would combine the advantages of high specificity and sensitivity, high precision and accuracy, complete element cover and low cost. A variety of instrumental methods have been used, including neutron activation analysis [6], mass spectrometry [7], X-ray fluorescence spec-

trometry [8], atomic absorption spectrometry [9] and inductively coupled plasma (ICP) with atomic emission spectrometry [10] (ICP-AES) or with mass spectrometry [11] (ICP-MS). Absorption methods with spectrophotometric reagents, on the other hand, are simple, reliable and low-cost methods for routine analysis. A large number of spectrophotometric reagents have been proposed to increase the sensitivity for the determination of either individual lanthanide ions or total lanthanide content [12].

An ion chromatograph coupled with a post-column detection technique can take advantage of this enhanced sensitivity of the lanthanide ion with spectrophotometric reagents. Post-column detection of metal ions today represents an important analytical mechanism [13].

2. Experimental

2.1. Instrumentation

A Dionex 4000i (Dionex, Sunnyvale, CA, USA) eluent pump system with 50 μ l injection volume, a Gilson Model 221 autosampler (Gilson, France) and a Spectra-Physics UV150 detector (Spectra-Physics, Santa Clara, CA, USA) were used. Data handling was performed with a multichrom system (VG Instruments, UK).

The analytical columns used were silica based with strong cation-exchange functionality: Nucleosil ET 250/8/4 SA10 (Macherey-Nagel, Düren, Germany) and Supelcosil LC-SCX (Supelco, USA).

The post-column reagent was introduced (0.7 ml/min) via a low-volume T-mixer with a helium-pressurized delivery system. The length of the reaction coil between the mixing tee and the detector was 10 cm.

2.2. Reagents

Eluent, standards and sample solutions were prepared with pretreated water via ion exchange and double distillation, then passed through a Milli-Q water purification system (Millipore,

Waters Chromatography Division, Oslo, Norway).

The pH of 0.4 M α -hydroxyisobutyric acid (HIBA) (Fluka) was adjusted with lithium hydroxide (Fluka). Elution was achieved with a concentration gradient of HIBA, 0.04 to 0.08 M in 5 min, then increasing to 0.3 M in 15 min at an eluent flow-rate of 1 ml/min.

The eluted metal ions were detected after post-column reaction with 4-(2-pyridylazo)resorcinol (PAR) (0.2 mM, 1 M glacial acetic acid 100% and 3 M NH_3) [14] at 530 nm or with Arsenazo III [2,2'-(1,8-dihydroxy-3,6-disulphonaphthylene-2,7-bisazo)bisbenzenearsonic acid] (0.1 mM, and 0.5 M glacial acetic acid 100%) [15] at 658 nm.

Standard solutions (1000 $\mu\text{g/ml}$) of the lanthanides were obtained from Teknolab (Drøbak, Norway).

2.3. Sample preparation

Aqueous samples were diluted with water or very dilute acid (0.05 M HNO_3) to prevent rare earth phosphates precipitation, and filtered through a 0.45- μm filter before injection. The mother liquor solution was diluted 1:100 and the extracted mother liquor raffinate was diluted 1:50.

Organic samples were diluted with methanol or acetonitrile and filtered through a 0.45- μm filter before injection. The organic samples were diluted 1:100.

3. Results and discussion

Several articles have been published dealing with the analysis of lanthanides in different analytical solutions. Although the chemistry of the chromatography can vary, the detection method is identical in all of them.

The analysis of lanthanides using an organic resin cation-exchange column and an organic anion-exchange column has been reported [14]. Elution was achieved by concentration gradient of α -hydroxyisobutyric acid or oxalic and diglycolic acids respectively.

A recent method for the separation and determination of the lanthanides, based on ion interaction chromatography, has been reported [15]. The most recent version of this approach uses gradient elution with sodium octanesulphonate as an ion interacting reagent. This provides virtual ion-exchange sites by adsorption on a non-polar (C_{18}) stationary phase with α -hydroxyisobutyric acid as the complexing eluting component.

The direct analysis of the nitrophosphate solution obtained from the Odda process of fertilizer production on an organic exchange column (Dionex IonPac CS3) produced unsatisfactory chromatograms, consisting of overlapping and tailing peaks. Dionex IonPac CS3 columns are packed with an agglomerated particles, which have a pellicular structure. The poor separation efficiency may be due to the relatively large particle size of the stationary phase and the degree of organic polymer cross-linking. A more likely hypothesis for the poor efficiency is that the column was overloaded, as can easily happen with low-capacity Dionex columns.

Application of the ion interaction technique to the analysis of lanthanides in this nitrophosphate matrix has also produced negative results. This was because of the low solubility of rare earths phosphate in the eluent, which contains 10% (v/v) organic modifier, either methanol or acetonitrile [15]. Ion interaction chromatographic separation of lanthanides which does not involve organic modifier was not attempted in this study [16,17].

The negative results obtained using the above techniques prompted the investigation into another stationary phase material or a more suitable mobile phase.

In this work, silica-based cation-exchange columns produced much sharper peaks with good peak separation and excellent calibration curves. Table 2 illustrates some examples of the calibration and coefficient values obtained with PAR detection.

These lanthanides examples are listed because they are representative of the heavy lanthanides (Lu), middle lanthanides (Eu) and light lanthanides (Pr and La). Other lanthanides produced

Table 2
Calibration and coefficient values

Metal	Linear range ($\mu\text{g/ml}$)	Area ($\mu\text{V s}$)	Coefficient
Lu	1.0	249040.640	0.99991
	2.0	512355.750	
	5.0	1290546.015	
Eu	2.0	895150.624	0.99894
	5.0	2358007.030	
	10.0	4470265.620	
Pr	5.0	1219345.465	0.99561
	10.0	2774559.370	
	20.0	5010205.620	
La	5.0	567226.875	0.99782
	10.0	1291062.340	
	20.0	2422444.200	

similarly good calibration and coefficient of determination values.

The detection limit of each lanthanide depended on the detection reagent and the nature of the particular lanthanide involved (Table 3).

Fig. 1 shows the difference in sensitivity for the lanthanides with two post-column reagents. Analysis of the mother liquor solution was performed with Arsenazo III detection, as this reagent is more selective for lanthanides. PAR detection was used in organic samples since the organic layer of the extraction system contains many fewer interfering ions because of the selectivity of the organic extractant mixed in an aliphatic hydrocarbon diluent.

Detection limits were calculated on a 50 μl injection loop volume.

The most important advantage gained of applying this method to a nitrophosphate fertilizer solution is that the analytical media can be applied directly for analysis. To demonstrate the reproducibility of this chromatographic method, the relative standard deviation of multiple (ten) injections was calculated and found to be ± 0.7 – 3.0% for samples (organic and aqueous) detected with PAR and ± 0.6 – 2.5% for samples (organic and aqueous) detected with Arsenazo III. These repeatability experiments were conducted on

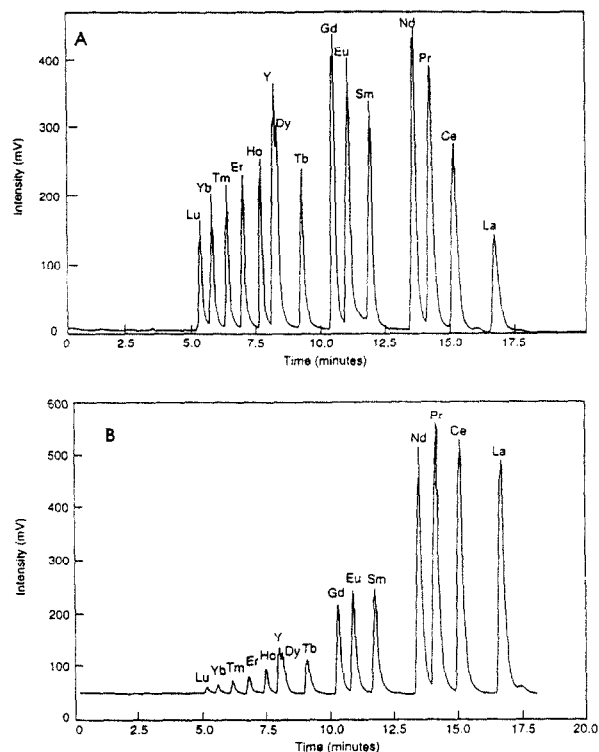


Fig. 1. Standard solution analysis: Lu, Yb, Tm, Er, Ho, Y, Dy, Tb 5 $\mu\text{g/ml}$; Gd, Eu, Sm, 10 $\mu\text{g/ml}$; Nd, Pr, Ce, La, 20 $\mu\text{g/ml}$. Injection loop: 50 μl . Supelcosil LC-SCX column 250/4.6 mm. Elution with HIBA pH 4.2 (0.04 M to 0.08 M in 5 min, then to 0.3 M in 15 min). Eluent flow-rate: 1 ml/min. Post-column reagent flow-rate: 0.7 ml/min. (A) PAR detection; (B) Arsenazo III detection.

samples whose concentration was more than ten times the detection limit.

To demonstrate the accuracy of this method in an aqueous medium a comparison was made

Table 3
Detection limits of lanthanides

Metal	Detection limit PAR ($\mu\text{g/l}$)	Detection limit Arsenazo III ($\mu\text{g/l}$)
Lu, Yb, Tm, Er, Ho, Dy, Tb and Y	100	1000
Gd, Eu, Sm	500	500
Nd, Pr, Ce, La	1000	100

between the analytical data obtained by this method and data taken from the ICP-MS technique analysis [18] of an identical mother liquor sample. Table 4 demonstrates the comparison.

The accuracy of this method in an organic matrix has not been evaluated because of the limited availability of independent analytical instrumentation to perform such an analysis. However, calculation of the distribution coefficient of each lanthanide, which can be obtained from the ratio of each lanthanide concentration (g/l) in the organic phase to the same lanthanide concentration in the aqueous phase (g/l), produced values similar to those reported in literature [19].

Increasing the eluent HIBA concentration or pH resulted in decreased retention times. In aqueous solution, lanthanides are present as trivalent cations. Since the ionic properties of the lanthanides are similar, they cannot be separated easily by cation exchange as trivalent cations. However, the selectivity of the ions can be increased with the use of appropriate chelating agents such as HIBA. Because the chelating agents are negatively charged, the result is a net decrease in the charge of the metal as the complex, with the largest decrease for the strongest complex.

Table 4
Lanthanides analytical data of a typical mother liquor solution

Lanthanide	ICP-MS ($\mu\text{g/ml}$)	IC ($\mu\text{g/ml}$)
Lu	0.64	0.50
Yb	6.90	7.10
Tm	1.50	1.40
Er	16.00	16.50
Ho	6.70	6.50
Y	190.00	185.00
Dy	43.00	45.00
Tb	11.00	10.00
Gd	110.00	110.00
Eu	31.00	34.00
Sm	110.00	109.00
Nd	850.00	856.00
Pr	220.00	219.00
Ce	2100.00	2150.00
La	1400.00	1385.00

The smallest ions, the last lanthanides in the series, form the strongest complexes and are least positively charged. Therefore, when the lanthanides are separated by cation exchange with HIBA in the eluent, the elution order is Lu→La [14].

An example of the application of this method directly to a mother liquor solution (see Table I for composition) taken from a fertilizer production line is shown in Fig. 2. The sample was diluted with water (1:100) and injected directly. Fig. 2 shows some interference near the samarium peak and an unknown peak near the lanthanum peak with PAR detection. Fig. 2 also shows overlapping between yttrium and dysprosium peaks.

This unknown peak near lanthanum and the overlapping peak with samarium can be eliminated from the analytical chromatograms by applying post-column detection with Arsenazo III. The resolution of the yttrium–dysprosium peak can be performed by reducing the eluent pH from 4.2 to 3.9. Fig. 3 demonstrates the resulting chromatogram by the application of these two conditions. It is important to emphasize here that the yttrium–dysprosium peak can be also resolved by PAR detection, provided that eluent pH is maintained at 3.9.

Fig. 4 shows the analysis of an organic sample diluted with methanol (1:100), with PAR detection, which was taken from experimental re-

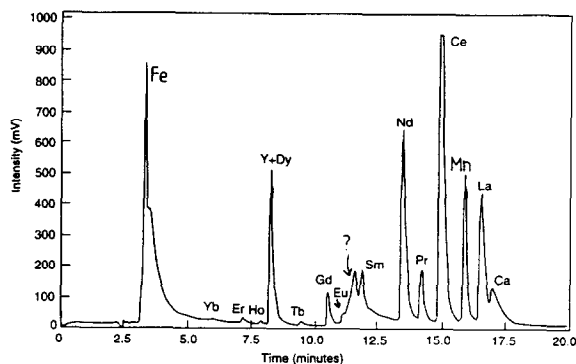


Fig. 2. Analysis of a nitrophosphate mother liquor solution by PAR detection. Sample dilution 1:100 with 0.05 M HNO_3 . Similar chromatographic conditions to Fig. 1.

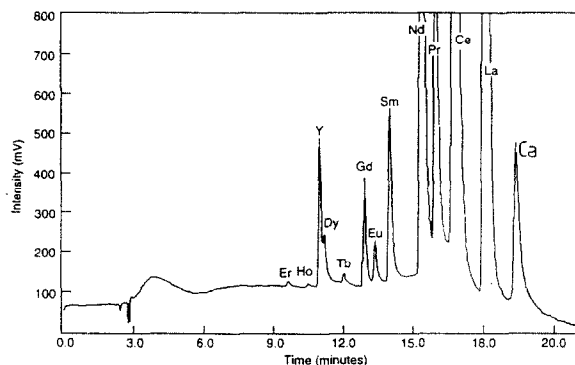


Fig. 3. Analysis of a nitrophosphate mother liquor solution by Arsenazo III detection. Sample dilution 1:100 with 0.05 M HNO₃. Similar chromatographic condition to Fig. 1, but eluent pH 3.9.

search tests, investigating the feasibility of lanthanides extraction from this nitrophosphate solution. A variety of organic extractants in various diluents were involved in this study. Arsenazo III can also be utilized to detect lanthanides in organic matrix.

These organic analyses were important in determining the extraction coefficient of each lanthanide under a particular set of conditions. This ability of a silica-based cation-exchange column to directly analyse organic solution is essential, since an organic-based cation exchange column is sensitive to non-polar organic solvents.

The stability of these silica-based cation-ex-

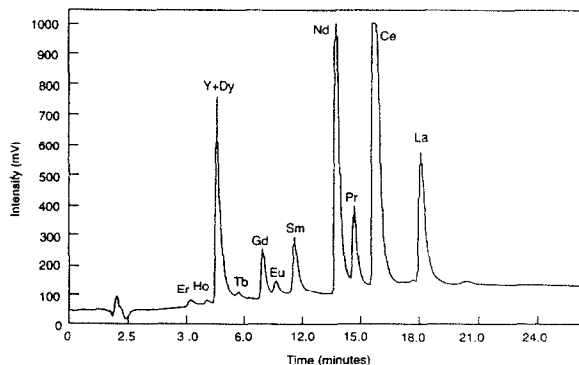


Fig. 4. Direct analysis of an organic solution by PAR detection. Sample dilution 1:50 with methanol. Injection loop 50 μ l. Nucleosil SA10, 250/4.6 mm. Elution with HIBA pH 4.2 (0.04 M to 0.3 M in 15 min). Eluent flow-rate: 1 ml/min. Post-column reagent flow-rate: 0.7 ml/min.

change columns was monitored. The analysis of over 250 samples both organic and aqueous on one column did not affect the peak efficiency of the column (identical peak retention time, height and half-length width). The most important factor affecting the lifetime of these columns is the eluent pH. The eluent pH would have to be between 3 and 7 to ensure maximum lifetime [20].

4. Summary

The nitrophosphate solution obtained from the digestion of phosphate rock with concentrated nitric acid in the Odda process of fertilizer production is a complex analytical matrix. The direct analysis of this solution by cation-exchange chromatography or ion interaction chromatography utilizing organic modifiers reported in the chemical literature has produced unsatisfactory results.

We used a silica-based cation-exchange column to perform the analytical separation. Elution was achieved by a concentration gradient of HIBA (0.04 M to 0.08 M in 5 min, then to 0.3 M in 15 min) at pH 3.8–4.2, and post-column detection with PAR or Arsenazo III, followed by spectrophotometric visible detection at 530 nm and 658 nm, respectively.

Mother liquor solutions and extraction raffinate solutions were analysed using Arsenazo III detection, since it is more selective for the lanthanides than PAR. Analysis of organic solution was performed by PAR, since organic phase matrix has fewer metal impurities because of the selectivity of the organic extractant employed.

5. References

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