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ON-LINE SAMPLE PRETREATMENT AND DETERMINATION OF LANTHANIDES IN COMPLEX MATRICES BY CHELATION ION CHROMATOGRAPHY

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ABSTRACT

The rapid determination of lanthanides in complex matrices has been developed by an on-line sample pretreatment of chelation ion chromatography. In the present system, selective chelating resin and sulfonated cation exchanger concentrated lanthanides while eliminating bulk quantities of alkali, alkaline earth and transition metals from sample matrices. The concentrated lanthanides which were separated on a mixed-bed ion exchange column were eluted by a concentration gradient of

oxalic acid (Ox) and diglycolic acid (DGA), coupled with post-column spectrophotometric detection with 4-(2-pyridylazo) resorcinol (PAR) at 520 nm. The overall analysis time after sample digestion was less than 55 min. The method detection limits (signal-to-noise ratio 3:1) from heavy lanthanides to light lanthanides were in the range of 0.6 -5.5 ng mL⁻¹ and the R.S.Ds were within 1.8%-5.5%. This method was applied to soil, ore, nodular cast iron, plant, grain, and rare-earth fertilizer samples. The results of those real sample analyses were satisfactory.

INTRODUCTION

Lanthanides played important roles in many current technological fields. They could improve the performance of iron and the yield of crops.^{1,2} They were also important catalysts in the petroleum industry and as fluorescent labels for biological molecules.³ The increasing utilization of lanthanides has enhanced the need for rapid and sensitive methods for their determination.⁴

Numerous analytical techniques have been employed in the determination of trace lanthanides. Ion chromatography was one of the most effective and simple methods which were capable of separating individual lanthanides.⁵ But, the high concentration of certain metals such as alkali, alkaline earth, iron, aluminum, and other transition metals usually interfered with the separation and determination of trace lanthanides in the complex matrices. Heberling et al.⁶ has successfully separated and determined the transition and lanthanide metals in synthetic solution by utilizing a conventional, mixed-bed ion exchange column and selective complexing eluent. However, this method could only be used in the samples which had same magnitude level of the lanthanides and interferences.⁷ It could not be used to the real complex samples.

Some off-line techniques have been used to eliminate matrix, to produce a lanthanides fraction free of alkali, alkaline earth, and transition metals.^{8,9} Due to high selectivities of iminodiacetate-based resins towards transition metals, and property of the complexes to be kinetically labile, they had been widely used for enrichment of trace lanthanides from the complex matrices.¹⁰⁻¹³ They have been used to graphite furnace atomic absorption spectrophotometry,¹⁴ inductively coupled plasma mass spectrophotometry,¹⁵ X-ray fluorescence spectrophotometry and neutron activation analysis.¹⁶⁻¹⁸ But the off-line sample handling steps were too tedious and the reproducibility of the method relied heavily on the operator skill.

In order to eliminate the remaining interferences of complex matrices, chelation ion chromatography was the new technique which combined the on-line analyte concentration and matrix elimination.¹⁹⁻²³ Unlike conventional ion-exchange concentration methods, which were typically not selective for ions of the same valency,¹⁰ chelation concentration was a selective concentration method. It could concentrate all the lanthanides while eliminating the high concentrations of alkali, alkaline earth metals, iron, aluminum, and other transition metals prior to ion chromatography separation. This paper described the method development and application of chelation ion chromatography for determination of lanthanides in soil, plant, grain, nodular cast iron, ore, and rare-earth fertilizer samples. The detection limit was greatly improved and the total analysis time was greatly shortened to less than 55 min after sample digestion.

EXPERIMENTAL

Instrumentation

Chromatographic analyses were performed on a metal-free Dionex DX-300 ion chromatography (Dionex Corp., Sunnyvale, CA, U.S.A), equipped with two advanced gradient pumps (AGP), a MetPac CC-1 chelation column (50 mm × 4 mm, I.D. packed with a styrene-based macroporous 12% cross-linked iminodiacetate-functionalized chelating resin, the particle was 20 μm and the capacity of resin was about 0.9 mequiv.), a TMC-1 concentrator column (25 mm × 3 mm, I.D. containing fully sulfonated PS-DVB cation-exchange resin with high capacity 2.2 mequiv.), an IonPac CG5 Guard column, and an IonPac CS5 analytical column (250 mm × 4.6 mm, I.D., 13 μm bead diameter polystyrene divinylbenzene functionalized with both quaternary ammonium and sulfonate functional groups), a 3.66 mL injection loop and a Dionex variable wavelength detector with a post-column reactor. The MetPac CC-1 and TMC-1 columns were used for sample pretreatment. The lanthanides separation was performed on the IonPac CS5 column.

All measurements were made at room temperature and all samples were filtered through a 0.45-μm filter prior to injection. Data collection and operation of all components in the system were controlled by Dionex AI-450 chromatographic software interfaced via an ACI-2 advanced computer interface to an AST Power Premium 3/33 computer.

Reagents and Standards

Ammonia solution, glacial acetic acid, hydrochloric acid, nitric acid, ammonium acetate, ethanol, lithium chloride, and lithium hydroxide monohydrate were of analytical-reagent grade reagents (Peking Chemical Works, Peking, China), perchloric acid, hydrofluoric acid, oxalic acid dehydrate, and 4-(2-pyridylazo) resorcinol (PAR) were of guaranteed-reagent grade reagents (Peking Chemical Works, Peking, China), pyridine-2,6-dicarboxylic acid (PDCA) was of chromatographic grade reagent (Aldrich, U.S.A), diglycolic acid (DGA) was of chromatographic grade reagent (Fluka).

Working standard solutions were prepared daily by standards ($1000 \mu\text{g mL}^{-1}$) which were obtained from National Research Centre for Certified Reference (China). Solutions were prepared with pretreated water, which was purified with a ML-Q system ($>18\text{M}\Omega$, Millipore, Waters chromatography division, Oslo, Norway).

Eluents and Post-Column Reagent Solution

All reagents were prepared with the $18\text{M}\Omega$ de-ionized water. Eluents: E_1 : 4.0 M HCl- 65% EtOH; E_2 : 2.0 M NH_4OAc , PH 5.5; E_3 : 1.0 M HNO_3 , 0.1 M Ox; E_4 : 0.1 M NH_4NO_3 , PH 3.4; E_5 : $18\text{M}\Omega$ DI water; E_6 : 0.1 M Ox, 0.19 M LiOH; E_7 : 0.1 M DGA, 0.19 M LiOH; E_8 : 0.006 M PDCA, 0.01 M LiOH and 0.05 M LiCl; "carrier" acid: 0.1M HNO_3 .

Post-column reagent: 0.8 mM PAR, 1.0 M glacial acetic acid and 3.0 M ammonia solution. The eluted lanthanides were detected after post-column reaction with PAR at 520 nm. The flow-rate was 0.7 mL min^{-1} .

Samples and Sample Preparation

Samples used in this study were Baotou ore and Baotou east ore (Beijing General Research Institute of Mining & Metallurgy), GBW 07401, nodular cast iron (National Research Centre for Certified Reference, China), soil, the leaf and grain of corn (Research Center for Eco-Environmental Sciences of Academia Sinica), "changle" rare-earth fertilizer 1 and 2 (Chinese Science and Technology University), among which GBW 07401 was certified reference soil sample. Lanthanides in GBW 07401 were well-distributed, stable, and had accurate content. It was used to evaluate the accuracy of method.

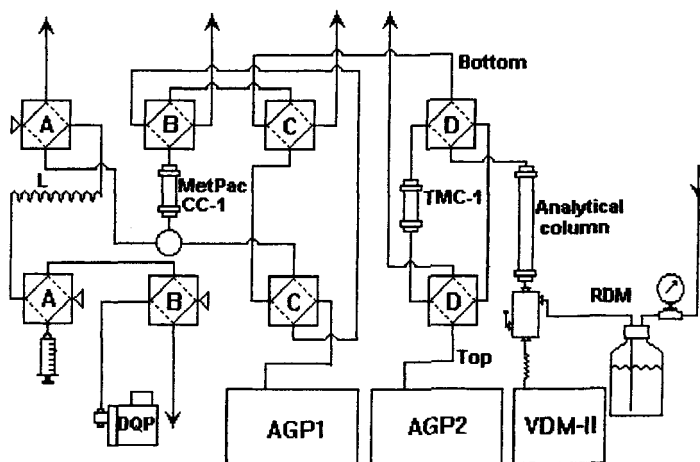


Figure 1. Schematic of the chelation ion chromatography system.

The first seven samples: 250 mg of powdered sample was weighted respectively. The sample was added into a closed polytetrafluoroethylene (PTFE) beaker and wetted with a small amount of water, 5 mL of concentrated nitric acid was added and heated nearly to dryness. Then 20 mL of 50% (w/w) hydrofluoric acid was added and heated to dryness. Furthermore, 5 mL of 60% (w/w) perchloric acid was added to the residue and heated until white fumes of perchloric acid appeared. After allowing to cool, 2 mL of concentrated nitric acid was added and evaporated to dryness again. Finally, the residue was dissolved to 25 mL with 0.1 M HNO_3 .

The two rare-earth fertilizer samples were diluted directly by 0.1 M HNO_3 respectively. Before injection, each solution needed to be further diluted to a proper concentration within its linear range and filtered through a 0.45- μm filter.

Experimental Procedure

The detailed schematic of the chelation ion chromatography system was shown in Figure 1. Valve A&B were controlled by V5 of AGP1, valve C was controlled by V6 of AGP1, valve D was controlled by V5 of AGP2.

Table 1

Chelation Concentration and Matrix Elimination Operating Conditions for Analysis of the Lanthanides (AGP-1 Program)

Time (min)	E ₁ (%)	E ₂ (%)	E ₃ (%)	E ₄ (%)	Valve A [#] Valve B [#]	Valve C [#]	Flow Rate (mL min ⁻¹)	Simple Pump
0.0	0	100	0	0	off	on	1.0	on
2.0	0	100	0	0	off	on	2.0	off
4.0	0	100	0	0	off	on	2.0	off
4.1	0	0	0	100	off	on	2.0	off
5.0	0	0	0	100	off	on	2.0	off
5.1	100	0	0	0	on	on	1.5	off
9.5	100	0	0	0	on	on	1.5	off
9.6	0	0	100	0	off	off	1.0	off
13.5	0	0	100	0	off	off	1.0	off
13.6	0	0	0	100	off	off	2.0	off
17.0*	0	0	0	100	off	off	1.0	off
17.1	0	0	100	0	on	off	2.0	off
18.5	0	0	100	0	on	off	2.0	off
18.6	0	100	0	0	on	off	3.0	off
21.0	0	100	0	0	on	off	0.0	off
55.0	0	100	0	0	off	off	2.0	off
60.0	0	100	0	0	on	off	0.0	off

* Begin sample analysis

off: real line connected. on: dotted line connected

Sample pump flow rate: 2.0 mL min⁻¹

The AGP1 pretreatment program shown in Table 1 was entered into the method file in AI-450 operating software and subsequently down loaded onto the AGP1. The AGP2 concentration gradient program listed in Table 2 was entered through the AGP2 front panel. These elution containers were pressurized with N₂ to 5 psi. When the operation started, sample was flushed by acid carrier to the mixing tee where it was buffered with ammonium acetate solution and entered the MetPac CC-1 column. All anions and monovalent cations could not be retained. Following, the alkaline earth metals were selectively removed by acetate buffer solution. Then, the other metals were transferred to the TMC-1 column by HCl-EtOH solution, and there rinsed by O_x-HNO₃ solution further. The lanthanides were quantitatively retained while iron, aluminum and other transition metals were eluted to the waste. Finally,

Table 2

**Gradient Separation Program for Analysis of the Lanthanides
(AGP-2 Program)**

Time (min)	E ₅ (%)	E ₆ (%)	E ₇ (%)	E ₈ (%)	Valve D [#]	Flow Rate (mL min ⁻¹)
0.0	0	0	0	100	off	1.0
17.0*	0	0	0	100	on	1.0
18.0	0	0	0	100	on	1.0
18.1	100	0	0	0	on	1.0
21.0	100	0	0	0	on	1.0
21.1	40	60	0	0	on	1.0
26.0	30	70	0	0	on	1.0
35.0	59	25	16	0	on	1.0
45.0	54	25	21	0	on	1.0
50.0	54	20	26	0	on	1.0

* Begin sample analysis

off: real line connected, on: dotted line connected

after the AGP1 delivered ammonium nitrate to convert the TMC-1 column from hydrogen form to ammonium form, the AGP2 delivered PDCA to elute lanthanides from TMC-1 column to CS5 column. Following separation, the lanthanides were detected photometrically using PAR postcolumn reagent at 520 nm.

RESULTS AND DISCUSSION

Matrix Elimination and Concentration

The first matrix elimination step was performed on a MetPac CC-1 column to remove alkali and alkaline earth metals from sample matrix. The MetPac CC-1 column contained macroporous iminodiacetate chelating resin which had a very high affinity for transition and lanthanide metals compared to the alkali and alkaline earth metals. The higher valency of the metal ion, the stronger bound the metal ion was to the resin. Before the sample stream passed through the MetPac CC-1 column, the sample previously loaded into the sample loop was flushed by acid carrier and buffered on-line with 2.0 M

ammonium acetate eluent in the PH range of 5 to 6. All anions and monovalent cations were not retained. By using the ammonium acetate eluent further, alkaline earth metals could be selectively eluted, while most of the transition and all lanthanide metals remained quantitatively bound to the resin. 10 mg of Ca could be eluted completely within 5 mL eluent. The other alkaline earth metals had the same results. Changes of the flow-rate from 1 to 3 mL min⁻¹ did not influence the recoveries of the retained metals. Then, the remaining ammonium acetate was removed by ammonium nitrate, or else the high concentration of ammonium acetate would crystallize in the MetPac CC-1 column.

The selective elimination process proceeded further to remove the bulk quantities of iron, aluminum and other transition metals on high capacity TMC-1 concentrator column. The concentrator column contained fully sulfonated cation exchange resin which had high affinity for multivalent cations. The selective matrix removal was based upon the stable metal chloride complexes in a mixture of 4.0 M hydrochloric acid - 65% ethanol eluent. The mixture not only promoted the formation of relatively stable metal chloride complexes, it also decreased the distribution coefficient of the metal complexes on the cation exchange resin.¹⁹ It was the effect of high concentration of ethanol that was a reduction of water molecules around the metals, a decrease in the forces binding the coordinated hydrated shell, and a decrease in the size of the outer hydration cloud. As a result, the transition metal chloride complexes formed in the mixture were more stable than in the aqueous system.

On the other hand, the lanthanides formed less stable metal chloride complexes. Thus, the relatively stable metal chloride complexes of transition metals were selectively removed from the TMC-1 column while lanthanides were quantitatively retained and concentrated. 10 mg of transition metals could be eluted within 6 mL eluent. But there were still partial iron and aluminum on the column. Some of them were from the matrix that could not be eluted completely and the others were introduced by the eluents, so, they were eluted further by 1.0 M Ox⁻- 0.1 M HNO₃ eluent, which existed as Fe(Ox)₃³⁻ and Al(Ox)₃³⁻. The acidity of this eluent was very important, or else, the lanthanides would be eluted as La(Ox)₃³⁻. Before the lanthanides were eluted to the CS5 column, the TMC-1 column must be converted from hydrogen form to ammonium form, otherwise the remaining matrices would interfere with the separation of the lanthanides. Sometimes, they could overlap with the peak of La. Table 1 showed the optimization of chelation concentration and matrix elimination operating conditions.

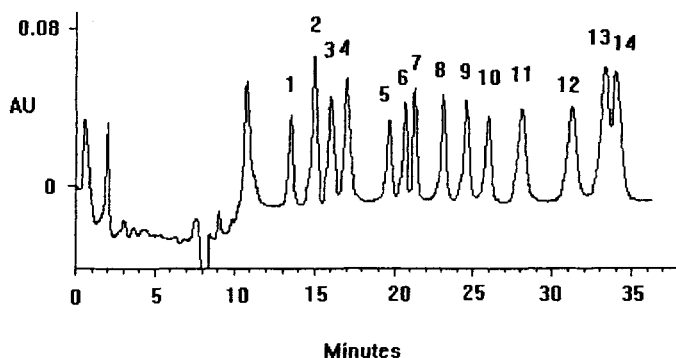


Figure 2. Chromatogram of lanthanides in synthetic solution. Chromatographic conditions as in Table 1 and 2, Post-column reagent : 8×10^{-4} M PAR, 3 M NH_3 , 1 M HOAc, Flow-rate: 0.7 mL min^{-1} , Detection $\lambda = 520 \text{ nm}$. Peaks: 1= La (240 ng mL^{-1}), 2 = Ce (200 ng mL^{-1}), 3 = Pr (96 ng mL^{-1}), 4 = Nd (96 ng mL^{-1}), 5 = Sm (32 ng mL^{-1}), 6 = Eu (32 ng mL^{-1}), 7 = Gd (32 ng mL^{-1}), 8 = Tb (32 ng mL^{-1}), 9 = Dy (32 ng mL^{-1}), 10 = Ho (40 ng mL^{-1}), 11 = Er (32 ng mL^{-1}), 12 = Tm (53.3 ng mL^{-1}), 13 = Yb (64 ng mL^{-1}), 14 = Lu (80 ng mL^{-1}), Al (3.0 mg mL^{-1}), Fe (3.0 mg mL^{-1}), Ca (6.0 mg mL^{-1}), Mg (6.0 mg mL^{-1}), Cu, Ni, Zn, Co, Mn ($200 \mu\text{g mL}^{-1}$) respectively.

Chromatographic Separation

The separation of lanthanides was accomplished by anion exchange of lanthanide-chelator complexes on the mixed-bed IonPac CS5 analysis column. In this separation, PDCA eluent removed iron and aluminum from the analysis column introduced by Ox and DGA eluents. The metal contaminants commonly found in these eluents, such as iron and aluminum, existed as $\text{Fe}(\text{Ox})_3^{3-}$ and $\text{Al}(\text{Ox})_3^{3-}$ were bound strongly by the anion exchange sites of the resin. On the other hand, when the TMC-1 column was placed in-line with the analysis column, PDCA eluted the concentrated lanthanides and trace transition metals from the TMC-1 column as Metal-PDCA complexes to the IonPac CS5 column. The lanthanides formed stable trivalent anionic complexes. The transition metals formed stable divalent anionic complexes which were eluted before La. But, the remaining PDCA on CS5 column would affect the separation and detection of lanthanides. Thus, it must be removed by DI water first. Then the lanthanides were separated by using the gradient Ox and DGA eluents. The separation was based on the stability of the lanthanide-chelator complexes, the smallest ions formed the strongest complexes and were least negatively charged. Therefore, when the lanthanides was separated by anion exchange with Ox and DGA eluents, the eluent order was from La to Lu.

Before starting the analysis, the gradient separation required column equilibration after analysis with the PDCA eluent for 17 min. The analytical system equilibrated while the sample pretreatment steps were being performed. A series of concentration gradient separating conditions had been tested. From those experiments, an optimum condition was chosen as shown in Table 2. A typical chromatogram of synthetic solution was illustrated in Figure 2. The individual lanthanides peaks were well separated. Although there were bulk quantities of alkali metals, alkaline earth metals, aluminum, iron, and other transition metals in the solution, they could not affect the separation and determination of lanthanides.

Accuracy and Detection Limit

In this work, an optimized program shown in Table 1 and 2 was selected. It produced much sharper peaks with good peak separation and excellent calibration curves. It was clear from Figure 2 that the method sensitivity was different among the individual lanthanides. The absorbance of light-lanthanides was less than the middle and heavy-lanthanides. Table 3 illustrated the linear range, correlation coefficients, relative standard deviations (R.S.D.), and detection limits.

It was shown that all lanthanides had good linearities whose correlation coefficients were greater than 0.998. The R.S.D. based on >10X detection limits concentration was found to be in the range of 1.8%- 5.5% and the detection limits (signal-to-noise ratio 3:1) of this method were lower than ever.

Analysis of Standard Reference Soil Sample

As a validation of the analytical technique, a standard reference soil sample GBW 07401 was analysed. Table 4 showed the comparison. They were the averages of three totally independent analyses involving sample digestion and chelation ion chromatography procedures. They were obtained based on the system calibration with our standards. It was found that the IC values were in good agreement with the certified values. Most of them had good recoveries. But some elements such as Eu and Tm had bigger deviations. This was because their concentrations in their solutions were close to their detection limits. The concentration of Lu was very low and covered by Yb peak, so it could not be determined. If they had enough concentrations, they would also have good accuracies.

Table 3

The Linear Range, Correlation Coefficients, R.S.D., and Detection Limits of Lanthanides

Lanthanide	Concentration Range (ng mL ⁻¹)	Correlation Coefficient (r) ¹	R.S.D. (%) ²	Detection Limit ³ (ng mL ⁻¹)
La	15-480	0.9990	5.5	6.7
Ce	12.5-400	0.9992	4.1	2.7
Pr	6-192	0.9999	5.3	1.7
Nd	6-192	0.9998	4.8	1.3
Sm	2-64	0.9997	4.1	0.7
Eu	2-64	0.9999	3.8	0.7
Gd	2-64	0.9998	4.9	0.6
Tb	2-64	0.9999	1.8	0.7
Dy	2-64	0.9999	4.2	0.6
Ho	2-64	0.9998	4.6	0.7
Er	2.5-80	0.9998	2.1	0.9
Tm	3.34-106.7	0.9998	4.7	1.3
Yb	4-128	0.9996	4.4	1.5
Lu	5-160	0.9988	4.9	1.9

¹ diluted 1:1, 1:2, 1:4, 1:8, 1:16, 1:32

² concentration > 10X detection limits (n=7)

³ signal-to-noise ratio 3:1

From Table 4 it can be seen which sample was spiked. The spiked recoveries of all lanthanides were acceptable. Because of the appreciable overlap between the Ho and Y peaks, it was difficult to obtain the separated values.

Figure 3 showed the chromatogram of GBW07401. Table 5 showed the main matrix composition in GBW 07401. It could be seen that most of the interference had been eliminated during the sample pretreatment. They did not affect the separation and determination any more. System blanks were well below the detection limits for all the lanthanides, and there was no indication of any memory effect when a blank was run immediately after a sample with high lanthanides concentration.

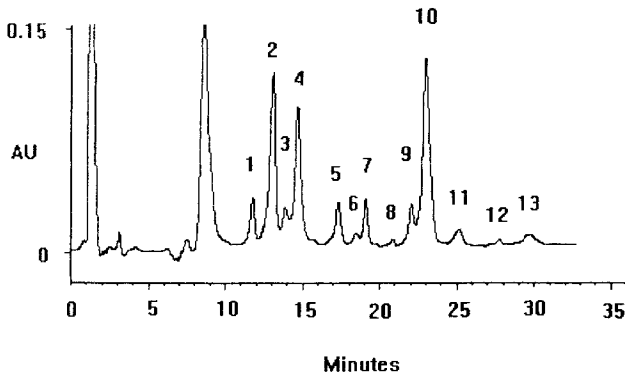


Figure 3. Chromatogram of lanthanides in GBW 07401. Similar chromatographic conditions to Fig 2.

Table 4

Lanthanide Analytical Results of GBW 07401 Soil Sample

Lanthanide	IC (μgg^{-1})	Certified (μgg^{-1})	Recovery (%)	Spiked (μgg^{-1})	Found (μgg^{-1})	Recovery (%)
La	36.0	34	105.9	19.2	54.8	97.9
Ce	64.7	70	92.4	16.0	80.3	97.5
Pr	7.0	7.5	93.3	7.68	14.6	99.0
Nd	29.2	28.0	104.3	7.68	36.4	93.8
Sm	5.25	5.2	101	2.56	7.8	99.6
Eu	1.21	1.0	121	2.56	3.86	103.5
Gd	4.64	4.6	100.9	2.56	7.24	101.6
Tb	0.69	0.75	92	2.56	3.36	104.3
Dy	4.44	4.6	96.5	2.56	7.12	104.7
Ho+Y	27.8	0.87+25	/	2.56	30.2	93.7
Er	2.87	2.6	110.4	3.2	6.12	104.4
Tm	0.50	0.42	119.0	4.4	5.0	102.3
Yb	2.32	2.66	87.2	5.12	7.68	104.7
Lu	N.D.	0.41	/	6.4	7.0	109.4

N.D.: not detected

Table 5

The Main Matrix Composition in GBW 07401

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	MnO	ZnO	ZrO	Na ₂ O	K ₂ O
Content (%)	62.6	14.18	5.19	1.81	1.72	0.2	0.1	0.03	1.66	2.55

Table 6

Lanthanides Analytical Results of Nodular Cast Iron, Baotou Ore, Baotou East Ore, Soil, the Leaf and Grain of Corn Samples

Lanthanide (mg g ⁻¹)	Nod Cast Iron		Baotou Ore		Baotou East Ore		Soil		Leaf		Grain	
	IC	ICP-MS	IC	ICP-MS	IC	ICP-MS	IC	ICP-MS	IC	ICP-MS	IC	ICP-MS
La	4.59	4.50	4.52	4.72	5.33	5.55	20.4	32.8	18.2	18.51	N.D.	7.7
Ce	9.90	10.82	11.09	12.31	10.53	10.57	65.4	68.3	10.09	10.04	N.D.	192
Pr	0.89	0.79	2.23	2.05	1.39	1.27	7.2	7.3	3.92	3.45	N.D.	21
Nd	2.25	2.45	8.51	9.38	4.37	4.59	25.6	29.2	5.65	5.19	N.D.	88
Sm	0.187	0.192	0.83	0.92	0.41	0.42	5.2	5.4	0.57	0.51	N.D.	17
Eu	0.022	0.018	0.133	0.129	0.074	0.082	1.0	1.02	N.D.	0.045	N.D.	23
Gd	0.125	0.139	0.187	0.188	0.123	0.131	4.4	4.78	0.40	0.38	N.D.	12
Tb	N.D.	0.016	0.030	0.031	0.017	0.021	0.58	0.77	N.D.	0.045	N.D.	2.8
Dy	0.051	0.054	0.045	0.043	0.047	0.051	4.1	4.0	N.D.	0.013	N.D.	4.3
Ho	0.010	0.0088	0.018	0.016	0.006	0.0056	4.6	3.99	N.D.	0.0026	N.D.	1.9
Er	0.033	0.029	0.038	0.044	0.025	0.027	2.0	2.02	N.D.	0.022	N.D.	7.6
Tm	N.D.	0.005	N.D.	0.0014	N.D.	0.0005	0.59	0.32	N.D.	0.0007	N.D.	0.73
Yb	N.D.	0.027	N.D.	0.0057	N.D.	0.0018	2.4	1.9	N.D.	0.0015	N.D.	0.52
Lu	N.D.	0.009	N.D.	0.00075	N.D.	0.0009	N.D.	0.30	N.D.	0.0011	N.D.	0.27

N.D.: Not detected

These results indicated that the present chelation ion chromatography system was useful for the determination of lanthanides in samples with complex matrices. One of the most important advantage gained of applying this method was that the analytical media could be injected directly for analysis after sample digestion.

Analysis of Samples

Samples used in this study were nodular case iron, Baotou ore, Baotou east ore, soil, the leaf and grain of corn, whose lanthanides had previously been

Table 7

Lanthanide Analytical Results of Rare-Earth Fertilizer 1 and 2 and Grains of Corn Samples

Lanthanide	Fertilizer 1				Fertilizer 2				Grain			
	IC	Spiked ($\mu\text{g g}^{-1}$)	Found	Recov. (%)	IC	Spiked ($\mu\text{g g}^{-1}$)	Found	Recov. (%)	IC	Spiked ($\mu\text{g g}^{-1}$)	Found	Recov. (%)
La	125	82.4	208.5	103.5	126	49.4	178	104.7	N.D.	9.6	9.25	96.4
Ce	38.6	68.7	104	95.3	41.2	41.4	81.6	98.4	N.D.	8.0	7.85	98.1
Pr	17.3	33	52	105.1	18.8	19.8	39.5	105	N.D.	3.84	4.09	106.5
Nd	41.2	33.0	74.3	100.4	47.9	19.8	67.6	100.1	N.D.	3.84	4.01	104.3
Sm	2.67	11.0	13.2	95.5	2.83	6.58	9.74	105	N.D.	1.28	1.31	102
Eu	0.37	11.0	11.2	98.4	0.32	6.58	7.1	102.9	N.D.	1.28	1.37	107
Gd	0.59	11.0	10.4	98	0.67	6.58	7.34	101.3	N.D.	1.28	1.27	99.1
Tb	N.D.	11.0	10.5	95.9	N.D.	6.58	6.34	96.2	N.D.	1.28	1.26	98.4
Dy	N.D.	11.0	10.9	99	N.D.	6.58	6.62	100.6	N.D.	1.28	1.36	106
Ho	N.D.	11.0	10.9	99	N.D.	6.58	6.38	97.1	N.D.	1.28	1.25	97.7
Er	N.D.	13.7	14.3	104	N.D.	8.23	8.33	101.2	N.D.	1.6	1.57	98.4
Tm	N.D.	18.9	18.5	97.9	N.D.	11.3	11.0	97	N.D.	2.2	2.3	104.5
Yb	N.D.	22.0	22.8	103.9	N.D.	13.2	12.9	97.6	N.D.	2.56	2.80	109
Lu	N.D.	27.5	28.7	104.4	N.D.	6.5	16.4	99.5	N.D.	3.2	3.15	98.5

N.D.: Not detected

determined by ICP-MS. and rare-earth fertilizer 1 and 2 whose lanthanides had not previously been determined. The chelation ion chromatography datum were presented in Table 6 and Table 7. It was seen from Table 6 that IC values also had a good agreement with the ICP-MS values. Thus, chelation ion chromatography had the similar accuracy with ICP-MS. It became one of the most effective method for separating and determining lanthanides.

The lanthanides concentration in grains of corn were too low to be determined. But its spiked recoveries were rather well. The lanthanides, in rare-earth fertilizer which were not determined by ICP-MS previously, had good spiked recoveries as shown in Table 7.

The properties of lanthanides were very similar. But, there were strong light lanthanides enrichment in samples (e.g. ore, nodular cast iron). All the lanthanides could not be determined in a single run. In order to maintain the lanthanides concentration in the analyte solution within the linear calibration range and above the detection limit of the technique, it was necessary to analyse in different concentrations for the same sample. But, some lanthanides in samples (c.g. grain, nodular cast iron, rare-earth fertilizer) were too low to be

determined. If the solutions were too thick, the concentration of the interference would be too high to be eliminated completely through the sample pretreatment and the high concentrated lanthanides would cover the low concentrated lanthanides. This needed to be studied further in our next work.

CONCLUSIONS

The on-line chelation IC technique performed accurate and precise analyses of lanthanides in complex matrices in a relatively short time and at low cost. The reagent and sample consumption were also relatively low compared to the off-line techniques. The instrument was extremely easy to operate and was not difficult to maintain. The sample preconcentration and matrix elimination covered a wide range of sample matrix concentration. It was an extremely versatile technique and the determination of lanthanide was easily adaptable to a wide variety of analytical problems in geological, agricultural and metallurgical fields.

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