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SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS A COMPLEXING AGENT

XV. SEPARATION OF INTERFERENCES IN NEUTRON ACTIVATION ANALYSIS OF LANTHANIDES IN ROCKS

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A chemical procedure has been developed for the separation of U, Th, Fe, Sc, Na, Ta and Mo, which interfere in neutron activation analysis of the lanthanide elements in rocks. This methods in based on the extraction of interferents, before irradiation of the samples, using a solution of tetracycline in benzyl alcohol. The lanthanide elements remain in the aqueous phase and are coprecipitated with calcium oxalate or ferric hydroxide for irradiation and subsequent determination by gamma-ray spectrometry. Conditions for the separation of these interferences are examined determining the extraction curves. The chemical separation procedure was applied in the analysis of lanthanides in geological materials and the results showing the accuracy and the reproducibility of the method are presented. The sensitivity for all the lanthanides was determined.

Introduction

Neutron activation analysis is one of the most widely used techniques for the determination of lanthanides in geological materials,[1–4] providing useful information for geochemical and cosmochemical studies.

Both instrumental and destructive techniques may be applied in this analysis but in some cases, when the determination of all lanthanides is required and when the interference problem becomes serious, the destructive method has been used.

The main purpose of this work was to study the separation of lanthanides from the interfering elements U, Th, Fe, Sc, Na, Ta and Mo. Rocks containing large amounts of uranium in relation to the lanthanides show interferences due to the contribution from fission products of ^{235}U[5] as well as the photopeak interferences of ^{239}Np. The radioisotopes ^{40}La, ^{141}Ce, ^{143}Ce, ^{153}Sm and ^{147}Nd, which are commonly used in activation analysis of the corresponding elements, are also produced as fission products. ^{233}Pa produced from thorium, ^{182}Ta and ^{59}Fe emit gamma-rays with energies too close or with the same energy as those emitted by

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lanthanide radioisotopes. The interferences Sc, Na and Mo produce radioisotopes with high activities that mask the less intense ones produced by lanthanides.

The method presented in this paper consists in a solvent extraction of interferences using a tetracycline-benzyl alcohol solution. The lanthanides remaining in the aqueous phase are coprecipitated with calcium oxalate or ferric hydroxide for subsequent neutron activation analysis. When ferric hydroxide was used in the coprecipitation the element Ce was analyzed by measuring ^{143}Ce. The 142 keV gamma-ray energy of ^{59}Fe interferes with the 145 keV photopeak of ^{141}Ce.

The procedure has been used in the determination of lanthanide elements in three international geological standards GSP-1 and G-2 provided by the United States Geological Survey (USGS), GS–N from Centre des Recherches Petrographiques et Geochimiques (CRPG) and a volcanic rock from the region of Poços de Caldas, MG, Brazil, for evaluation of accuracy, reproducibility and sensitivity of the method.

Experimental

Reagents and apparatus

^{59}Fe, ^{46}Sc, ^{99}Mo, ^{182}Ta and lanthanide radioactive tracers used in the solvent extraction studies were obtained by irradiating a known amount of oxide, salt or metal of these elements in the IEA-R1 nuclear reactor. The irradiated compounds were dissolved using convenient reagents and then diluted with water. ^{234}Th radioactive tracer was obtained from uranyl nitrate solution by retention in alumina.[6]

Standard solution of lanthanides were prepared by dissolving appropriate amounts of Johnson Matthey "Specpure" oxides with nitric acid, with the exception of Ce. Cerium oxide was dissolved in concentrated sulfuric acid and some drops of hydrofluoric acid, evaporating to dryness and then dissolved in diluted nitric acid. All the oxides were previously heated for two hours at 800 °C and stored in a dessiccator before use.

The solution of 0.010M tetracycline in benzyl alcohol was prepared by dissolving tetracycline hydrochloride from Laborterapica Bristol-SP with benzyl alcohol previously saturated with distilled water.

The gamma-activities were measured in a NaI(T1) detector coupled to a single channel analyzer or in an Ortec Ge(Li) detector coupled to Hewlett-Packard (HP) 4096 channel analyzer connected to HP model 2100A minicomputer. The multichannel analyzer system has a resolution (FWHM) of 2.8 keV for the 1332.5 keV gamma-ray of ^{60}Co and it was calibrated with a standard source prior to use every day.

Dissolution of the rocks

Aliquots of about 100 mg of finely powdered rock samples were dissolved by multiacid digestion using 2 ml of each acid (40% HF, 65% HNO_3 and 70% $HClO_4$) in a Teflon cup. The Teflon cup was placed into a steel bomb and heated for about 6 h at about 110 °C. The cup was opened when cool and the resulting solution was evaporated to dryness on a heated sand bath to remove all F^- ions that interfere in the subsequent extraction system. The residue was taken up with 25 ml of 0.10M NH_4NO_3 and used as the aqueous phase of the extraction system.

Procedure for solvent extraction study of the elements

The procedure adopted for this study was the same one presented in previous papers.[7,8] The aqueous phase was prepared by adding a radioactive tracer of each element to the solution of 0.10M NH_4NO_3 used as supporting electrolyte. The pH of the aqueous phase of the extraction system was adjusted to the required value using diluted solutions of HNO_3 or NH_4OH. Aliquots of each phase were measured with NaI(Tl) detector to evaluate the distribution of the elements. To study the distribution of uranium, this element was determined by epithermal neutron activation method.[9] In order to examine the rock matrix effect in the separation, experiments were also carried out by adding the solution resulting from rock dissolution to the aqueous phase.

Group separation of the lanthanides and chemical yield determination

The interfering elements were eliminated by carrying out two extraction operations at pH 1.7. The aqueous solution resulting from the rock dissolution was transferred to a separatory funnel together with 25 ml of 0.010M tetracycline solution in benzyl alcohol. The pH of the aqueous phase was adjusted to 1.7±0.1 using dilute solutions of HNO_3 or NH_4OH. The funnel was shaken for 30 minutes at a temperature of 25 °C. The phases were separated by decantation. The organic phase was discarded. For a second extraction a new solution of 25 ml of 0.010M tetracycline solution was added to the aqueous phase in the same funnel. The aqueous phase was separated by decantation followed by centrifugation and 20 ml of this phase were taken up for coprecipitation either with ferric hydroxide (10 mg of Fe) or in calcium oxalate (10 mg of Ca). The precipitate was allowed to stand for a few hours and then it was separated from the liquid by centrifugation. The dried precipitate was transferred to a polyethylene capsule and irradiated for 8 h with thermal neutrons (flux of 10^{12} n · cm^{-2} · s^{-1}).

Multielemental standards were prepared by pipetting appropriate volumes of the individual lanthanide solutions into a polyethylene capsule and drying under an infrared lamp. Samples and standards were irradiated in the same vial ensuring the same irradiation geometry. The presence of lanthanide elements in the polyethylene capsule as well as in the blanks was previously examined and was found to be negligible.

After a decay period of about 40 h the irradiated sample and standards were counted with a Ge(Li) detector connected to a multichannel analyzer. The samples were measured during a period of three weeks in order to determine half-lives for certain lanthanides and to confirm identification. A program FALA[10] in Basic language was used to locate peak positions and energies and to calculate net areas. Table 1 lists the half-life and gamma-ray energies of each radioisotope selected for use.

Table 1
Nuclides and gamma-ray energies used for determination of lanthanides in this work

Nuclide	Half-life	Gamma-ray energy, keV
^{140}La	40.27 h	815.5; 1595.4
^{141}Ce	32.5 d	145.4
^{143}Ce	33.0 h	293.1
^{142}Pr	19.2 h	1575.5
^{147}Nd	11.06 d	91.4; 531.0
^{153}Sm	47.1 h	103.2
^{152}Eu	12.1 a	1408
^{160}Tb	73 d	298.6; 879.4
^{170}Tm	129 d	84.4
^{169}Yb	30.6 d	177.0; 197.8
^{177}Lu	6.75 d	208.4

The chemical yield of the procedure was evaluated by adding the lanthanide elements to the solution resulting from the rock dissolution.

Results and discussion

Extraction curves for the interferences and for lanthanides (represented by Eu) depicted in Fig. 1 show that the separation of Eu from U, Th, Sc, Fe and Mo is feasible, provided the extraction operation is carried out at a convenient pH. Eu was not extracted at pH 1.7, while the interferences Fe, U, Th, Sc and Mo were extracted into the organic phase. Ta was partially extracted and about 80% of this element was found adsorbed on the surface of the glass.

Previous experiments had shown that Na was not extracted by tetracycline/benzyl alcohol solution. Na is isolated from lanthanides in the coprecipitation step.

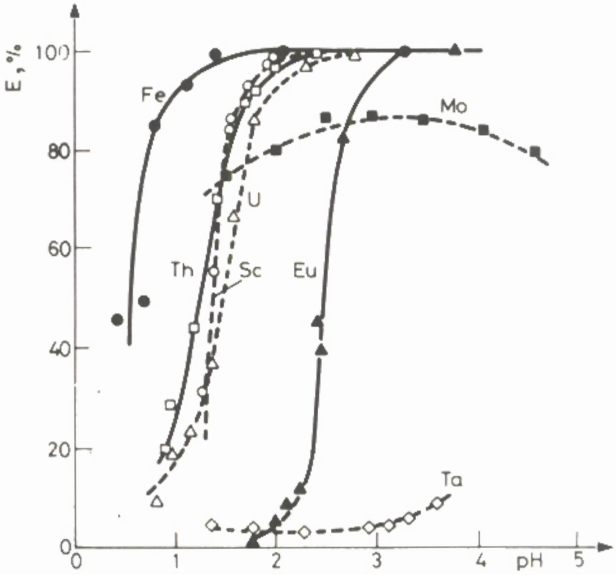

Fig. 1. Extraction curves of the elements as a function of pH

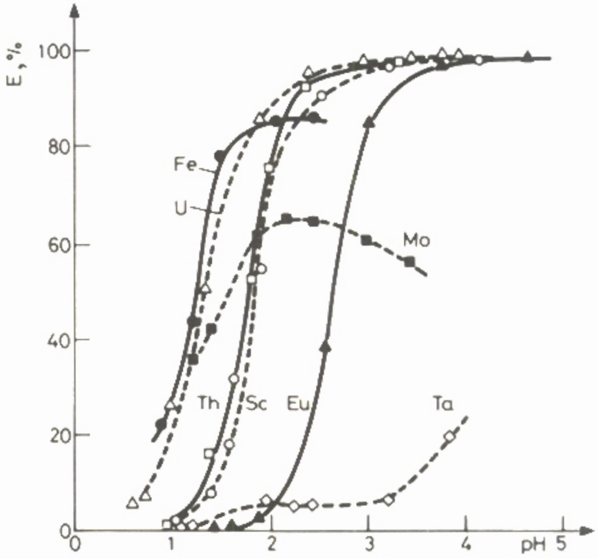

Fig. 2. Extraction curves of the elements as a function of pH in the presence of a solution containing the dissolved rock

Table 2
Percent extraction of elements and
separation factors (β) for interferences and europium

Element	Extraction, %	Separation factor (β)
Eu	0.49	–
Th	62.9	340
U	80.0	800
Mo	64.1	350
Fe	85.0	1100
Sc	50.0	200
Ta	3.9	8

[Tetracycline] = 0.010M; [Elements] = 10^{-5} – 10^{-3} M; pH 1.7; $\beta = D_I/D_{Eu}$ where D_I and D_{Eu} are distribution ratios of interferences and europium, respectively.

The matrix effect in the separation was also examined. Extraction experiments carried out by adding radioactive tracers to the dissolved rock matrix medium gave the results shown in Fig. 2. By comparing the extraction curves of this Fig. 2 with those presented in Fig. 1, it can be seen that the extraction curves are shifted towards higher pH values when the extraction is carried out in presence of dissolved rock solution.

In order to check the practical applicability of the extraction process, the separation factors at pH 1.7 were determined. Percent extraction of the elements and the separation factors given in Table 2 show that the interferences are not completely separated

Table 3
Results of concentrations of lanthanid

Element	GSP-1 Standard Rock		G-2 Standard Rock	
	This work	GLADNEY et al.[11]	This work[a]	GLADNEY et al.[11]
La	176 ±17	183 ±13	85 ± 5	86 ± 5
Ce	386 ±23	406 ±20	148 ±12	159 ±11
Pr	–	51 ± 8	–	19 ± 2
Nd	203 ±15	190 ±17	55 ± 3	53 ± 8
Sm	25.6 ± 2.5	26.8 ± 2.5	7.1 ± 0.4	7.2 ± 0.6
Eu	2.35 ± 0.25	2.36 ± 0.22	1.44 ± 0.09	1.41 ± 0.12
Tb	1.34 ± 0.14	1.36 ± 0.14	0.44 ± 0.04	0.48 ± 0.07
Tm	–	0.450 ± 0.120	–	0.170 ± 0.070
Yb	1.57 ± 0.15	1.7 ± 0.4	0.82 ± 0.11	0.78 ± 0.14
Lu	0.212 ± 0.037	0.220 ± 0.050	0.083 ± 0.017	0.113 ± 0.024

[a] *Results already presented in an earlier work.*[13]

[b] Chemical separation before irradiation.

from lanthanides after a single extraction operation and a two-step extraction procedure was required for an effective separation.

Chemical yields of the procedure were determined for all lanthanides with the exception of Dy and Pm. Our results showed that chemical yields of (85±3)% and (80±6)% may be achieved with $Fe(OH)_3$ and CaC_2O_4, respectively. All the lanthanide elements exhibited similar behaviour in the separation and they were not chemically fractionated.

In the present paper the solvent extraction technique has been applied to the analysis of lanthanides in the standard rocks (GSP-1, G-2, GS-N) and a volcanic rock from Poços de Caldas, São Paulo, Brazil. In each case samples were analyzed in triplicate or four replicas and their results are presented in Table 3 together with the literature values.[11,12] The volcanic rock was also analyzed by instrumental method after epithermal neutron activation. Comparing the results of the GSP-1, G-2 and GS-N standard rocks with the ones presented in References 11 and 12, it can be concluded that there is a good agreement for most lanthanides analyzed (relative error lower than 8%). A major discrepancy occurred in the case of Tb in the GS-N standard rock. No reason was found for this fact.

The relative standard deviations for several lanthanides were lower than 12%, which is generally considered as a good result in trace analysis. The reproducibility was not so good for Lu (16 to 26%) due to low concentration of this element (less than 1 ppm).

Six lanthanides (La, Ce, Nd, Eu, Tb and Tm) were determined in the volcanic rock without chemical pre-separation. The high concentration of U of (101±3) ppm present in this rock caused interferences as expected. The gamma-ray of 103 keV of

elements (ppm) in the rocks

GS-N Standard Rock		Volcanic Rock from Poços de Caldas	
This work	GOVINDARAJAU[12]	This work[b]	This work[c]
71 ± 5	*75**	152 ± 5	154±6
133 ±12	*140*	183 ±28	202
–	–	7.2 ± 1.9	–
54 ± 6	50	150 ± 7	192
7.8 ± 0.4	*8.2*	5.0 ± 0.7	–
1.7 ± 0.2	*1.7*	1.14 ± 0.08	1.31
0.68 ± 0.04	0.6	0.70 ± 0.04	0.67
–	–	0.341 ± 0.070	0.363
1.8 ± 0.2	*1.7*	2.54 ± 0.11	–
0.19 ± 0.03	0.2	0.930 ± 0.220	–

[c] Instrumental method of epithermal neutron activation.

*Numbers in italics are recommended values.

Table 4
Sensitivities for lanthanide elements; experimental conditions:
neutron flux = 10^{12} n · cm^{-2} · s^{-1}, irradiation time = 8 h, distance between Ge(Li) detector and sample = 3 cm, cooling time: 20 h – 30 d

Element	Radioisotope and gamma-ray energy used, keV	Determination limit, μg	
		a	b
La	^{140}La, 1596	0.003	0.7
Ce	^{141}Ce, 145	0.6	17
	^{143}Ce, 293	0.4	73
Pr	^{142}Pr, 1575	0.10	50
Nd	^{147}Nd, 531	4.0	104
Sm	^{153}Sm, 103	0.0006	0.2
Eu	^{152}Eu, 1407	0.09	1.3
Gd	^{153}Gd, 97	0.2	9.1
Tb	^{160}Tb, 879	0.1	1.4
Dy	^{165}Dy, 95	0.06	–
Ho	^{166}Ho, 80	0.003	1.0
Er	^{171}Er, 308	0.05	311
Tm	^{170}Tm, 84	0.1	3.1
Yb	^{169}Yb, 198	0.07	4.0
Lu	^{177}Lu, 208	0.003	1.2

[a] Lanthanides free of interferents and separated as a group.
[b] No pre-separation (sample: GSP-1).

^{153}Sm and 208 keV of ^{177}Lu could not be resolved due to interference of gamma-rays of 105 and 209 keV of ^{239}Np. Since the 198 and 179 keV photopeaks of Ta caused interferences in the 197 and 177 keV photopeaks of ^{169}Yb, Yb could not be determined without chemical pre-separation.

The sensitivities were evaluated according to CURRIE[14] in the case when the lanthanide elements were separated as a group and also when they were not separated from the rock matrix (instrumental analysis). Table 4 shows an increase of sensitivity for all lanthanides when they were separated prior to irradiation of the sample.

The chemical separation method presented is useful for reducing the major activity from the matrix and also for rock analysis containing very high uranium concentrations relative to the lanthanides. The chemical procedure is rather simple and permits the analysis of a great number of lanthanides when compared with the instrumental method of neutron activation analysis.

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