

The Sm-Nd Isotopic Method in the Geochronology Laboratory of the University of Brasília

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*Manuscript received November 3, 1998; accepted for publication on November 9, 1999;
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ABSTRACT

Nd isotopes represent one of the best tools to investigate the processes involved in the evolution of the continental crust and mantle. This is due mainly to the similar geochemical behaviour of Sm and Nd, both light rare earth elements, which inhibits their fractionation during most varied geological processes. In order to carry out crustal evolution studies in central Brazil, the Sm-Nd isotopic method was implanted at the Geochronology Laboratory of the University of Brasília. The Sm-Nd separation methodology is basically that described in Richard *et al.* (1976), with the addition of some improvements. In this study we describe in detail the methodology used in Brasília. Precision and accuracy were checked with the international standards such as JB-3, BCR-1, BHVO-1 and La Jolla, and the following results were found: JB-3 (Nd=15.74 ppm and Sm=4.28 ppm), BCR-1 ($^{143}\text{Nd}/^{144}\text{Nd}=0.512647\pm 8$, Nd=28.73 ppm and Sm=6.66 ppm), BHVO-1 (Nd=24.83 ppm and Sm=6.2 ppm) and La Jolla ($^{143}\text{Nd}/^{144}\text{Nd}=0.511835\pm 14$).

Key words: Sm-Nd method, isotope dilution, ion exchange chromatography, TIMS.

INTRODUCTION

The Sm-Nd geochronometer is based on the decay of ^{147}Sm to ^{143}Nd , with the emission of an α particle. The equation below describes the Sm-Nd isotopic evolution for any geological system:

$$^{143}\text{Nd} = ^{143}\text{Nd}_i + ^{147}\text{Sm}(e^{\lambda t} - 1)^{(1)}$$

Equation (1) can also be written as:

$$\frac{^{143}\text{Nd}}{^{144}\text{Nd}} = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_i + \frac{^{147}\text{Sm}}{^{144}\text{Nd}} (e^{\lambda t} - 1)$$

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The age t of the system can be calculated after the determination of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. Thermal Ionisation Mass Spectrometry (TIMS) is the most commonly used technique for the determination of isotopic ratios and also for the determination of REEs concentrations by isotope dilution. The isotopic analysis in the mass spectrometer is preceded by chemical treatment, involving the addition of a spike solution, dissolution of the sample and the chemical extraction of Sm and Nd by ion exchange. The extraction of Sm and Nd are accomplished in two stages. The first stage consists of the bulk separation of lanthanide fraction and in the second stage, the elements are separated from each other in order to avoid isobaric interference and also the presence of elements that make the ion beam unstable or that interfere with the ionisation efficiency of Sm and Nd.

This work reports an efficient method of micro-extraction used for Sm and Nd separation, based on the method employed by Richard *et al.* (1976).

METHODOLOGY

SUMMARY OF PREVIOUS CHEMICAL SEPARATION METHODS

Precise and accurate determination of isotopic ratios of metals cannot be achieved if they have not been efficiently separated from other interfering elements. If traces of elements of the matrix are present in the aliquot to be analyzed, isobaric interference can happen (Potts 1987). In the pioneer work of Ketelle & Boyd (1951), the difficulty to obtain efficient separation of each element of the REE group, was stressed.

The method most commonly applied in the separation of Sm and Nd for isotopic analyses of geological samples is described in Richard *et al.* (1976). It firstly uses an ion exchange column for the REE separation, followed by chromatography of reverse phase in order to separate Sm and Nd. This second column is packed with polytetrafluorethylene powder (PTFE), impregnated with DI-(2-ethylhexyl) phosphoric acid (HDEHP).

This method, however, is not capable of separating Ce and Pr, which are present in substantial amounts in the Nd fraction (White & Patchett 1984). The presence of Ce, for instance, can make the ion beam unstable if present in large amounts (Whitehouse 1989). Whitehouse (1989) describes a method capable of reducing the amount of Ce in the Nd fraction, oxidating from Ce^{3+} to Ce^{4+} with KBrO_3 and passing the solution through a HDEHP micro-column of approximately 1 cm. Another method that uses the classic ion exchange chromatography for the separation of the REEs was introduced by Eugster *et al.* (1970) and Dosso & Murthy (1980), where the fractions of Sm and Nd are separated in a secondary column packed with a cationic resin of the ion ammonium type. The elements are separated as organometallic complexes formed with the 2-hydroxi-isobutyric acid (α -HIBA). The method presents good resolution, and the fractions of Sm and Nd are practically free from other interfering elements. It is, however, a tedious and time-consuming method and the results do not present significant differences from those obtained by the previous method. Less

commonly used is the method that uses the anion exchange resin and acetic acid – nitric acid and methanol as eluent (Hooker *et al.* 1975, O’Nions *et al.* 1977). It is more efficient than the one that uses HDEHP, however it is necessary to work with the ^{142}Nd isotope which has ^{142}Ce , as an important isobaric interferent. A fast technique is the chromatography of high resolution Liquid Chromatography of High Resolution – HPLC (High Performance Liquid Chromatography), and Ionic Chromatography of High Resolution – HPIC (High Performance Ion Chromatography) which present high resolution and speed (Cassidy & Chauvel 1989).

SEPARATION TECHNIQUE USED IN BRASÍLIA

In Brasília we decided for the method using the HDEHP, with the use of the commercial LN-spec resin. This also consists of teflon powder impregnated with HDEHP, industrially prepared with a very small grain size (270 to 150 mesh). It presented very good efficiency for the separation of Ce and this element is almost totally absent in the Nd fractions (isobaric with ^{142}Ce). Another form of eliminating the interference of Ce is to avoid the use of ^{142}Nd isotope for fractionation and isotope dilution calculations.

Significant amounts of Pr were found in the Nd fraction, however this element does not represent an interferent when Nd isotopic measurements are done in the metallic form (Nd^+) instead of the oxide form, when small interference with Pr oxides, with masses 158 and 159 happen (Richard *et al.* 1976). In the same way, samples with high Ba concentrations, can also present an ineffective separation of Ba in the secondary column, which was proven to be the case in the experiments in this study. However this does not interfere either in the Nd measurement, because it is ionized before the Nd analysis start due to its lower ionisation temperature (Thirwall 1982). Most of the Ba can be removed during the process of chromatographic separation, eluting the solution with HNO_3 in a cationic resin, before the secondary elution for separation of Sm and Nd (Verma 1991), or still using the methodology presented by Stray & Dahlgren (1995), which combines classic chromatography of ionic change and HPIC for the separation and quantification of REEs in geological samples, based on the method of Le Roex & Watkins (1990).

The separation procedure used in the University of Brasília was efficient for the separation of Sm and Nd and, although time consuming, the procedure is simple and sufficiently effective. This is based, firstly, in the separation of the REE group, using a cation resin (primary column) followed by the extraction of Nd and Sm through a partition separation of phase-reverse (HDEHP), both using HCl as eluent.

EXTRACTION OF Sm AND Nd OF ROCK SAMPLES

Sample Digestion

50 to 100 mg of rock sample is mixed with the spike and the mixture is dissolved in teflon bombs covered with a steel jacket, using 1 mL of distilled conc. HNO_3 and 4 mL of concentrated and

distilled HF. Dissolution is followed by evaporation using a mounted evaporation system with infrared lamps and teflon capsules. The residue is taken again in HF:HNO₃ (4:1) mixture and back to the oven at ca. 190°C for 4 days. After complete dissolution, the sample was dried down and 2 mL of concentrated HNO₃ were added. The solution was dried down again, a new attack with 6 mL of distilled 6N HCl follows. The solution should be absolutely clear and homogeneous at this stage. Complete evaporation of the solution sample and addition of 2 mL of distilled 2.5N HCl follows. During the course of the study the evaporation procedure was modified. Samples are now evaporated on hot plates, inside clean air cabinets (class-100 air) placed in fume cupboards. This allows cleaner environment for the evaporation, and also allows the evaporation of a large number of samples at the same time.

As already observed in other studies (Getty *et al.* 1993, Rehkamper *et al.* 1996 and Sato 1998), we had successful attacks using Savilex® capsules. Some samples, however, such as garnet-rich rocks and some ultramaphic rocks were not entirely dissolved and needed to be transferred to bombs.

Separation of the REEs (Calibration of the Primary Column)

A quartz column (i.d. = 8 mm and height = 15 cm) was packed with ~ 2.2g (it evaporates for 60°C) or 12 cm of cation resin Bio-Rad AG 50W-X8 200-400 mesh in aqueous solution. The sample solution is eluted in the column using HCl (Fig. 1). The REE group is collected in the fraction between 1 and 15 mL of 6N HCl, after elution with 32 mL of 2.5N HCl. Together, with the REEs, Y and Ba are also collected (Richard *et al.* 1976). The column is regenerated with ca. 15 mL of 6N HCl and stored in diluted acid solution.

The 2.5N HCl was standardized by titrimetry, with NaCO₃ (anhydrous) as base and methyl orange as indicator.

Separation of Sm and Nd (Calibration of the Secondary Column)

The secondary columns are made of teflon (Savilex®) (i.d. = 5 mm and height = 10 cm) and packed with LN-Spec resin (liquid resin HDEHP-270-150 mesh powdered teflon coated with di-ethylexil phosphoric acid). Height of resin bed is 6.5 cm. The REE fractions were totally evaporated and re-dissolved in 200 µL of 0.18N HCl. This solution was loaded into the LN-Spec column. The Nd fraction was collected in 4 mL of 0.3N HCl after the initial 10 mL of 0.18N HCl (Fig. 2). After the extraction of Nd, 2 mL of 0.3N HCl were discarded and the Sm fraction was collected in 4 mL of 0.4N HCl, with a flow speed of ~ 1 mL/30 min. The regeneration of the resin was achieved with 6 mL of 6N HCl. The column was conditioned again with the purified 3 mL of H₂O (Nanopure) followed by 2×3 mL of 0.18N HCl.

CHROMATOGRAPHIC COLUMNS FOR MINERALS

Smaller columns, where set up for extracting Sm and Nd from low-REE materials.

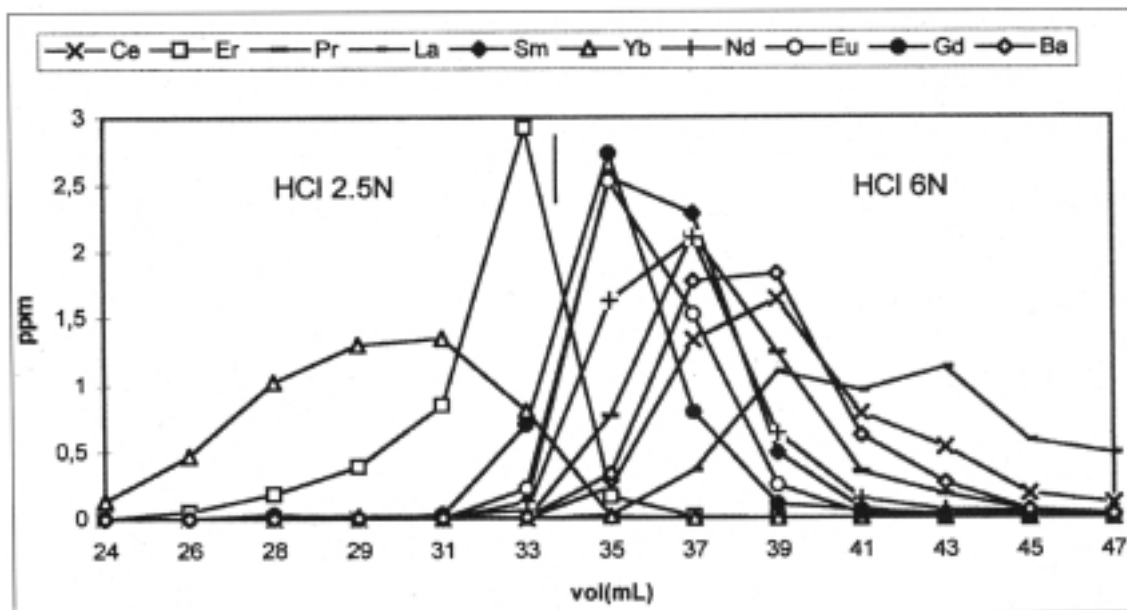


Fig. 1 – Separation of the REE group from the main elements of the rock.

As shown in Fig. 3a, the calibration showed the efficiency of the small columns for the separation of the REEs, using the Bio-Rad AG50W-X8 resin. The resolution of the secondary column (Fig. 3b) was also very good for separation of Sm-Nd, Ce-Nd, and Sm-Gd.

REE Separation (Primary Column)

The column was packed with cation resin to a height of 7 cm (column of i.d. = 5 mm and height of 10 cm). The flow speed was set at ca. 1 mL/10 min. 250 μ L of sample were added and washed with three times 250 μ L of 2.5N HCl. 7 mL of 2.5N HCl were discarded and the REE fraction comes out in 5 mL of 6N HCl. The column was regenerated with 15 mL of 6N HCl. Satisfactory results have also been obtained working with a larger aliquot of sample (500 μ L).

Sm-Nd Separation

The column was packed with the LN-spec resin to a height of 7 cm (\sim 100 mg) and 0.5 cm of anionic resin Bio-Rad 200-400 mesh was added on top. The flow speed was set at 1 mL/50 min. 100 μ L of sample in 0.18N HCl was added and washed three times with the same amount of 0.18N HCl. The elution was carried out (Fig. 3b) with 0.18N HCl. The first 6 mL were discarded and Nd was extracted in 3 mL of 0.3N HCl. Elution of 2 mL of 0.3N HCl, followed and Sm is extracted in 3 mL of 0.4N HCl. The column is regenerated with 5 mL of 6N HCl.

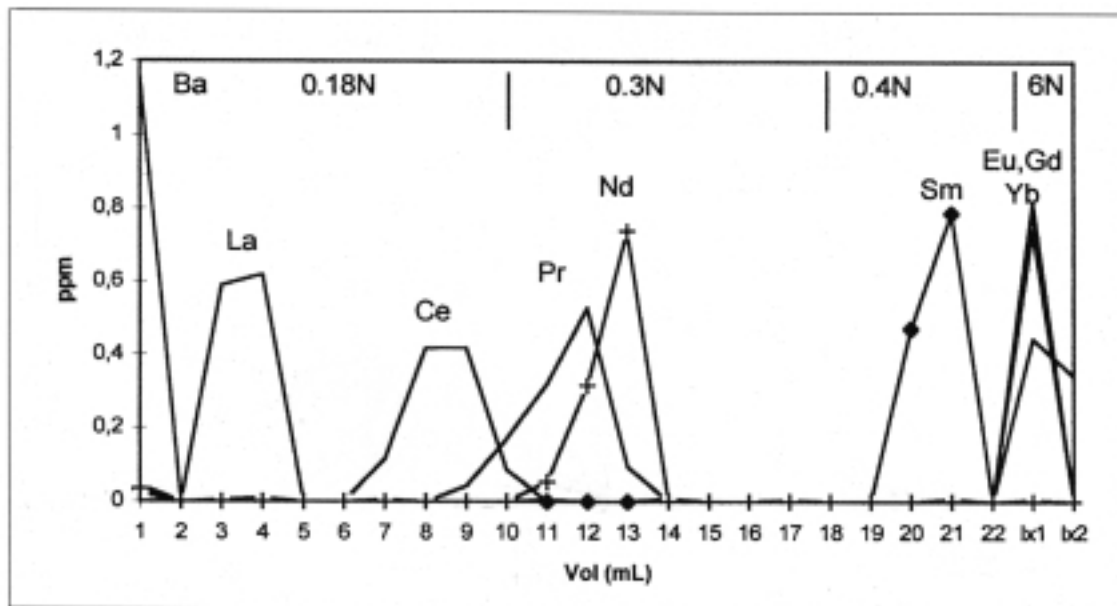


Fig. 2 – Sm and Nd separation. The calibration was made with LN-spec resin (HDEHP resin impregnated in teflon powder of 150-270 mesh). HCl was used as eluent in the calibration.

PRELIMINARY STUDIES

Partition Coefficient and Separation Factor

The selectivity (Table I) of the liquid HDEHP, using a fine grained (270-150 mesh) powdered teflon as support, showed better efficiency than using a coarse powder (60-40 mesh), due to the increase in the ion exchange capacity of the resin. In Fig. 4a, the ion exchange reverse behaviour of HDEHP resin is observed, where the light REEs are first eluted. For the separation of Ba-La-Ce-Pr-Nd, the best concentration of HCl to be used proved to be 0.18N. This has been already observed empirically during the calibration and later on with the determination of the partition coefficient (Fig. 4b). For the separation of Sm-Eu-Gd the best concentration of HCl proved to be between 0.35 and 0.4N (Fig. 4c and d). In this concentration, a large separation factor (ratio between the coefficients of distribution of these elements) is observed. The separation of Nd-Sm happens in concentrations $\leq 0.3N$ (Fig. 4e and f). The use of stronger acids will result in the elution of some of the Sm into the Nd fraction.

RESULTS AND DISCUSSION

ANALYTICAL PROCEDURE (MASS SPECTROMETRY)

The fraction collected in the secondary column is evaporated with 2 drops of 0.025N H_3PO_4 . The residue is dissolved in 1 μL of 5% distilled HNO_3 loaded onto a Re filament of double

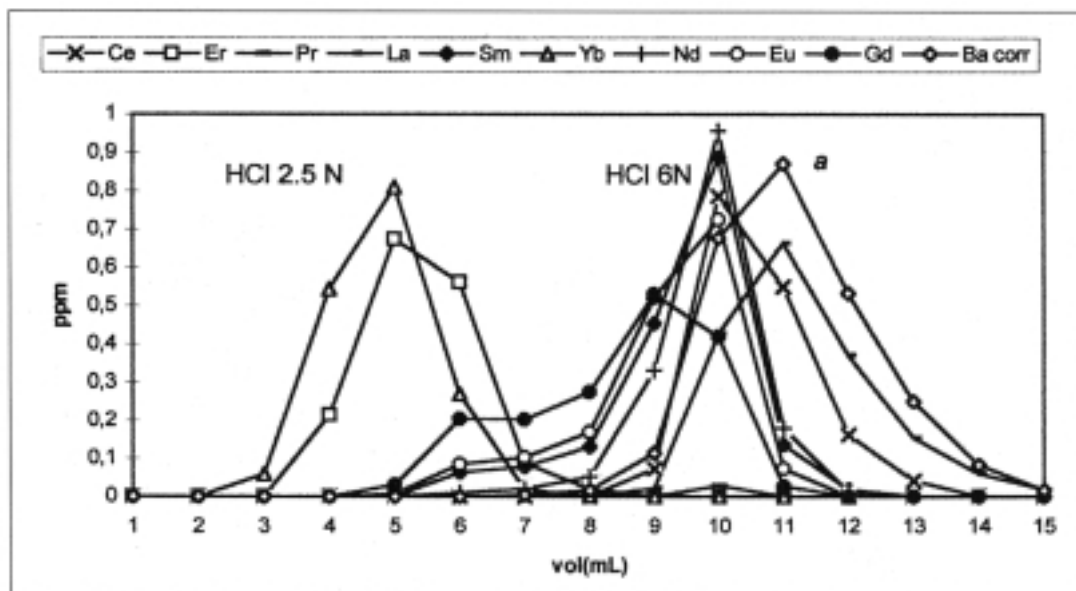


Fig. 3a – Columns calibration for minerals analysis: REEs elution, where was necessary the concentration correction from blank value obtained in ICP/AES for Ba element.

TABLE I
Chromatographic Columns Resolution

Results					
Separation	Separation Columns for Rock Analysis			Separation Columns for Minerals Analysis	
	Col. HDEHP 40-60 mesh	Col. HDEHP 150-270 mesh	Col. BioRad 8X 200-400 mesh	Col. HDEHP 150-270 mesh	Col. BioRad 8X 200-400 mesh
lanthanide					
La-Ce	–	1.42	–	1.2	–
Ce-Nd	–	1.0	–	1.3	–
Pr-Nd	–	–	–	0.7	–
Nd-Sm	1.5	2.4	–	4.0	–
Sm-Eu	–	–	–	2.0	–
Ca-Sr	–	–	1.1	–	0.6
Rb-Sr	–	–	2.2	–	–

filament assembly. The mass spectrometer used was a Finnigan MAT 262 with 7 collectors and the analyses have been accomplished in static mode. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio was normalised using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and the decay constant used was the value revised by Lugmair & Marti (1978) of $6.54 \times 10^{-12}/\text{y}$. The external precision (Table II) for $^{143}\text{Nd}/^{144}\text{Nd}$ ratios obtained for the

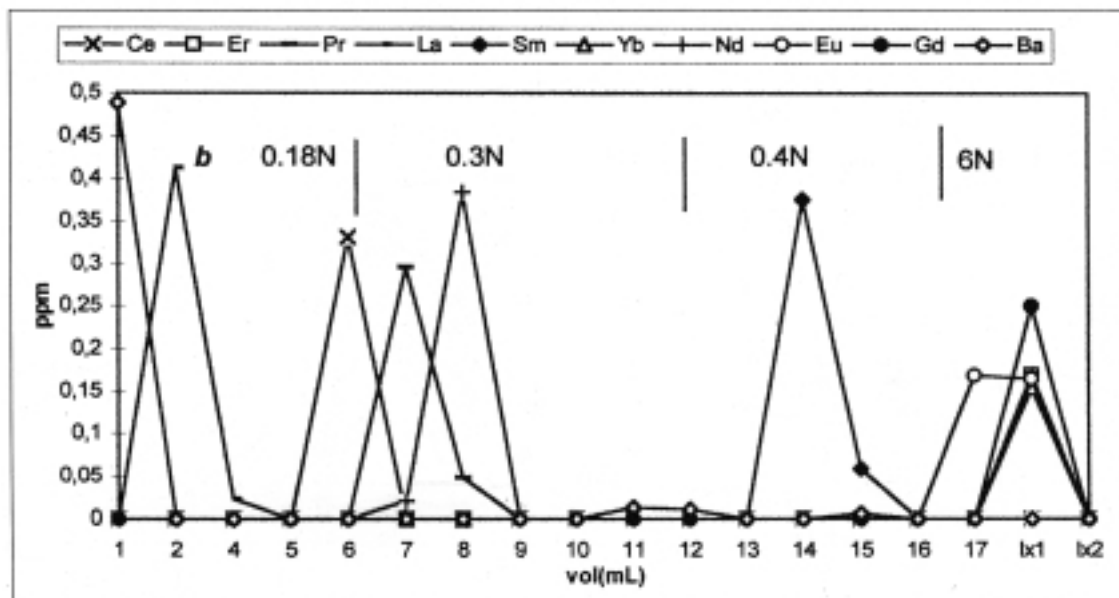


Fig. 3b – Columns calibration for minerals analysis: Sm and Nd separation.

different rock standards used varied between 0.0006-0.0016% and the analytical uncertainty for $^{147}\text{Sm}/^{144}\text{Nd}$ ratio was smaller than 0.19%.

TABLE II
Statistical treatment for the obtained data

Standard	SD%		$^{147}\text{Sm}/^{144}\text{Nd}$	
	$^{143}\text{Nd}/^{144}\text{Nd}$	Nd	Sm	(% error)
BCR-1	0.0007	0.3-0.4	0.7	0.11
BHVO-1	0.0016	0.2	0.03	0.009
JB3	0.0006	0.06	0.8	0.19

SD% = external precision.

*analytical error for the ratio $^{147}\text{Sm}/^{144}\text{Nd}$.

ANALYTIC CONTROL

International rock standards with very well-known Sm and Nd concentrations and Nd isotopic composition were analyzed. The analyses of these standards were necessary to test the reproducibility of the data and mainly to evaluate the reliability of the methodology in rocks of unknown composition. The standards used (Table III) were: BCR-1 (Basalt-USGS), JB3 (Basalt-GSJ), BHVO-1 (Basalt Hawaiian-USGS), JG2 (Granite-GSJ) and La Jolla.

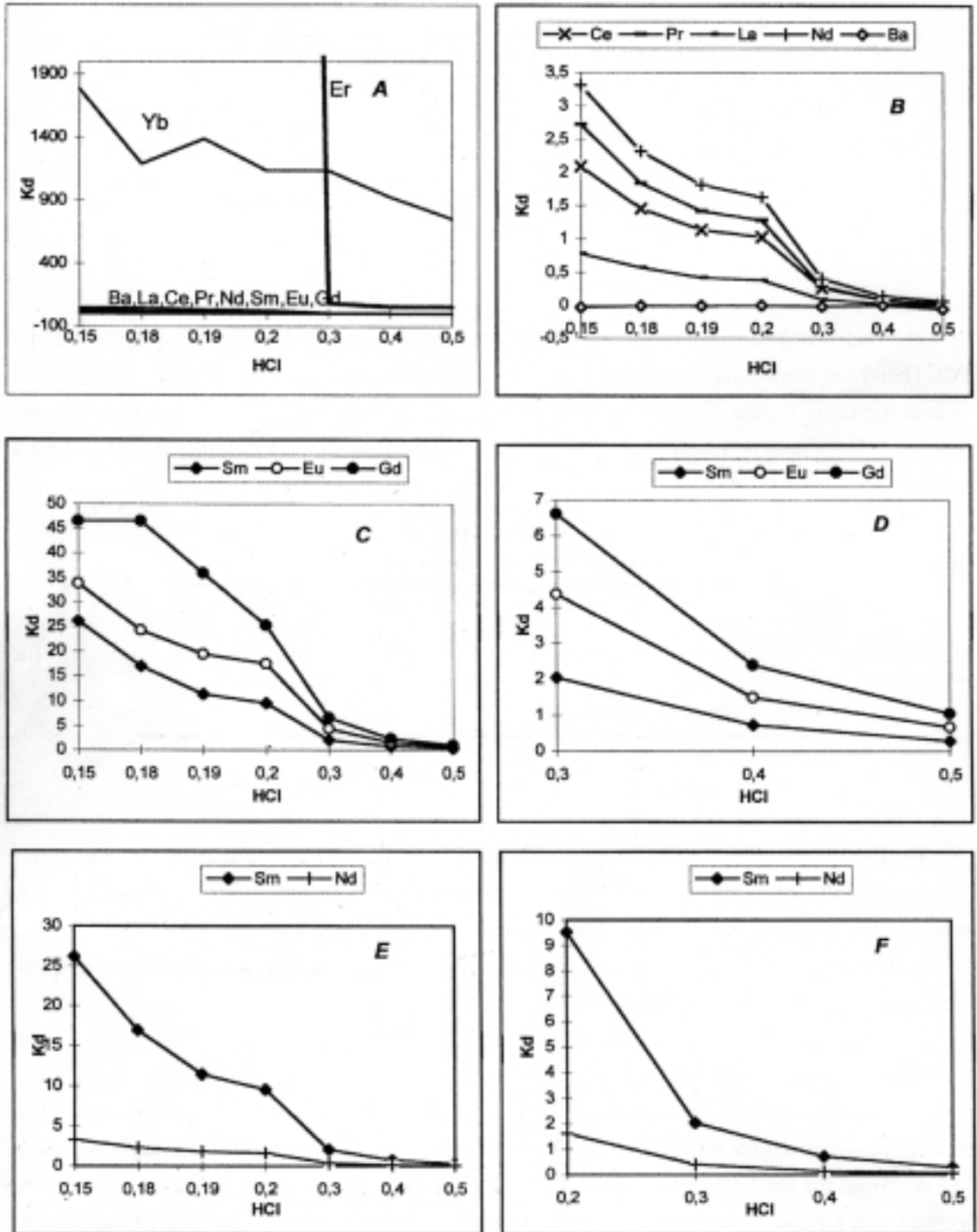


Fig. 4 – Determination of lanthanides partition coefficients.

TABLE III
Recommended values for the used standards (Govindaraju 1994)

Standards	La Jolla	BCR-1	BHVO-1	JB3	JG2
Nd (ppm)	–	28.8	25.2	15.4	25.8
Sm (ppm)	–	6.59	6.2	4.27	7.72
$^{143}\text{Nd}/^{144}\text{Nd}$	0.511860*	–	–	–	–

*normalised to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$.

The rock standard most frequently used for interlaboratorial comparison is the BCR-1 (Table IV). Therefore, some analyses of this standard were carried out during this study. They revealed an average value for the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512632 ± 2 (1σ , $n=5$). Concentration of Nd and Sm, were 28.73 ppm and 6.66 ppm respectively being in close agreement with the data obtained in other laboratories (Table V).

TABLE IV
Values for the analysed standards

Standards	La Jolla	BCR-1	BHVO-1	JB3	JG2
Nd (ppm)	–	28.73	24.83	15.74	25.16
Sm (ppm)	–	6.66	6.2	4.28	8.22
$^{143}\text{Nd}/^{144}\text{Nd}$	$0.511835 \pm 14^*$	–	–	–	–

*normalised to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$.

The BCR-1 standard, that has been used for so many years, is not available anymore. Therefore, we also used the BHVO-1 standard (Table IV). However, because BHVO-1 is only a recent rock standard, not much data from other laboratories are available in the literature.

Nevertheless, results for BCR-1, as well as for BHVO-1, presented good precision and accuracy, with the values being comparable to the recommended values.

The results for JB-3 and JG-2 were used in the preliminary evaluation of the method. The results obtained for standard JB-3 (a basalt) (Table IV) were satisfactory, presenting good precision, although the Sm and Nd concentrations were consistently 2% below the expected value. The concentrations results for JG-2 (Table IV) showed much greater scatter around the average, showing low precision for the final mean value. This value, however, is still statistically the same as the recommended value. One interpretation for the low precision of the data obtained for JG2 is that the standard is not as homogeneous (regarding the REE) as the other three rocks standards. This is only to be expect, because JG2 is a granite standard.

The data for the La Jolla standard in this study tended to be somewhat lower (Table IV) than the recommended value of 0.511860 (USGS). The average value of 0.511835 ± 14 (1σ) obtained

TABLE V
Interlaboratorial Comparison

Laboratories/ references	Equipment	BCR1 $^{143}\text{Nd}/^{144}\text{Nd}^*$	BCR1	
			Nd(ppm)	Sm(ppm)
This study (UnB)	MAT 262	0.512647(8)	28.73(13)	6.66(2)
IG-USP (Kawashita <i>et al.</i> 1991)	VG ISOMASS 354	0.512662(29)	28.52	6.53
PML-Japão (Makobo & Nakamura 1995)		0.512630(3)		
RSES-Austrália (Sun <i>et al.</i> 1995)	MAT 261	0.512653(5)		
(Gladney <i>et al.</i> 1983)			28.7	6.58
Kobe-Japão (Nakamura 1974)			28.8	6.72
Oxford (Hooker <i>et al.</i> 1975)			29.30	6.67
(Thirlwall 1991)		0.512643		
MAINZ (Ito <i>et al.</i> 1987)		0.512647		
(Wasserburg <i>et al.</i> 1981)		0.512647(20)		

*normalised to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$.

is, however, statistically the same as the recommended if 2σ uncertainties are considered.

The average value obtained for the La Jolla standard is comparable with the values obtained in other laboratories (Table V). Our mean value of 0.511835 ± 0.000014 is statistically the same as the expected value of 0.511850 (average of all laboratories).

Nd procedure blanks (Table VI) decreased from 385 pg in the beginning of this study to ca. 74 pg towards the end. Nowadays these blanks are commonly around 30 pg. Blanks tend to be smaller when dissolution is carried out in Savillex® capsules.

TABLE VI

Experimental blank data for Nd in the Geochronology Laboratory of the Brasília

Analyse	Nd(pg)
Total Blank 1 (Bomb)	385
Total Blank 2 (Bomb)	144
Total Blank 3 (Bomb)	74
Total Blank 1 (Savilex®)	50
Total Blank of Separation Columns	12-20

The Nd total blanks observed in Geochronology laboratory of the UnB is within the range of values obtained in other laboratories of the world (Table VII and Fig. 5). As shown in Table VI

the LN-Spec resin contribute little to the total blank indicating that the largest contribution for the blank is the memory effect in the dissolution vessels, as well as the reagents.

TABLE VII
Summary of obtained data for total blank in other geochronology laboratories

Laboratory/Reference	Blank Nd(pg)	Experimental Conditions
HARVARD/(Getty <i>et al.</i> 1993)	20	savilex/acid dissolution
SUNNY/(Hemming <i>et al.</i> 1995)	200	fusion with LiBO ₂
RSES/(Zhao & McCulloch 1995)	25-100	Bomb/acid dissolution
RSES/(Sun <i>et al.</i> 1995)	<50	Bomb/acid dissolution
RENNES/(Chavagnac & Jahn 1996)	180	Savilex and Bomb acid dissolution
(Mukasa <i>et al.</i> 1994)	40	teflon vial (PFA)
TUCSON/(Patchett & Ruiz 1987)	80	Bomb/acid dissolution
PML/(Maboko & Nakamura 1995)	10	Bomb/acid dissolution
RENNES/(Tourpin <i>et al.</i> 1991)	500	Bomb/acid dissolution
DENVER/(Li 1994)	50-100	Bomb/acid dissolution
UCLA/(DePaolo 1981)	1000 (without purification of HCl)	
	100	
WASHINGTON/(Sorensen & Wilson 1995)	51	Bomb/acid dissolution

ISOBARIC INTERFERENCE FOR Sm AND Nd

Samarium

$^{136}\text{CeO}^+$, $^{136}\text{BaO}^+$ (Table VIII) are isobaric interferents with $^{152}\text{Sm}^+$. These interferences can be suppressed by the average discharge due to the low ionization potential of these species, while the emission of the $^{152}\text{Gd}^+$ is inhibited by its high ionisation potential. In this study it was observed that the signal of BaO^+ is reduced to negligible proportions during the analysis of Sm and its main contribution, as $^{138}\text{BaO}^+$, will only interfere with masses 154 and 155 of Sm, not representing therefore any important interference. Gd was found in inexpressive amounts, as shown in Fig. 6. The amount of Gd is very small and $^{160}\text{Gd}^+$ does not appear in the mass scan. To avoid any possible interference of Gd with $^{152}\text{Sm}^+$, used for the concentration calculations, we carried out an evaluation of the amount of Sm collected in the chromatographic column (Figs. 6 and 7). Maximum contribution of the mass 155 and detection of the mass 160 is observed when Sm is collected in 4 mL of 0.5N HCl, indicating presence of Gd and/or the presence of oxide species as the $^{144}\text{NdO}^+$ or even $^{144}\text{SmO}^+$ (Fig. 7). In the 3 mL Sm fraction an insignificant amount of the mass 155 is present, which is probably due only to the contribution of the La oxide ($^{139}\text{La}^+$ present in the scan). It is

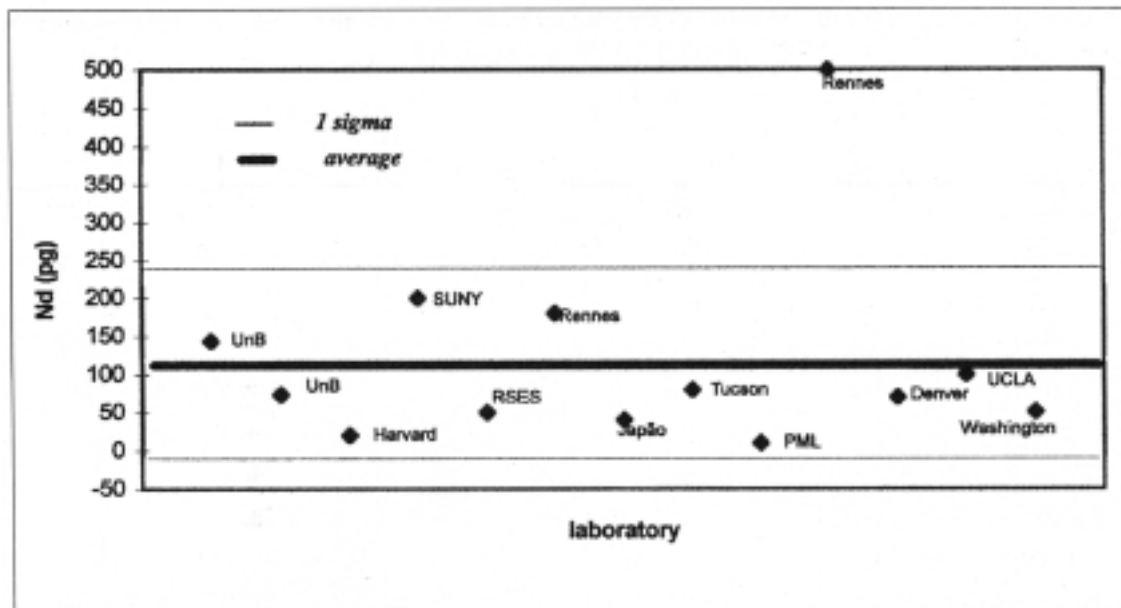


Fig. 5 – Interlaboratorial comparison of the experimental blanks.

observed that, even collecting the Sm fraction in of 4 mL of eluent, the contribution of the isotope 160 of Gd is insignificant, being smaller than 5 mV, what means a contribution smaller than 0.05 mV of $^{152}\text{Gd}^+$, being therefore, negligible.

TABLE VIII
Mass interferences in Sm isotopic determinations

N° of Mass	147	149	152
	$^{130}\text{Ba}^{17}\text{O}$	$^{132}\text{Ba}^{17}\text{O}$	$^{152}\text{Gd}^+$
			$^{136}\text{Ba}^{16}\text{O}$
			$^{136}\text{Ce}^{16}\text{O}$
			$^{135}\text{Ba}^{17}\text{O}$

Neodymium

The interference (Table IX) of BaO^+ is trivial. Most of Ba is vaporized before the Nd analysis. Additionally, the natural abundance of the interfering masses ($^{130}\text{Ba}^+$ and $^{134}\text{Ba}^+$) are low (0.11% and 2.42% respectively). Ce interferes (Table IX) with ^{142}Nd , however, due to the difficulty in separating Ce of Nd totally, it was preferred to use mass 146 as the reference isotope for the fractionation and isotopic dilution calculations. Previous studies have reported the presence of Ce as an important factor causing instability of the ion beam. In this study even when present in great

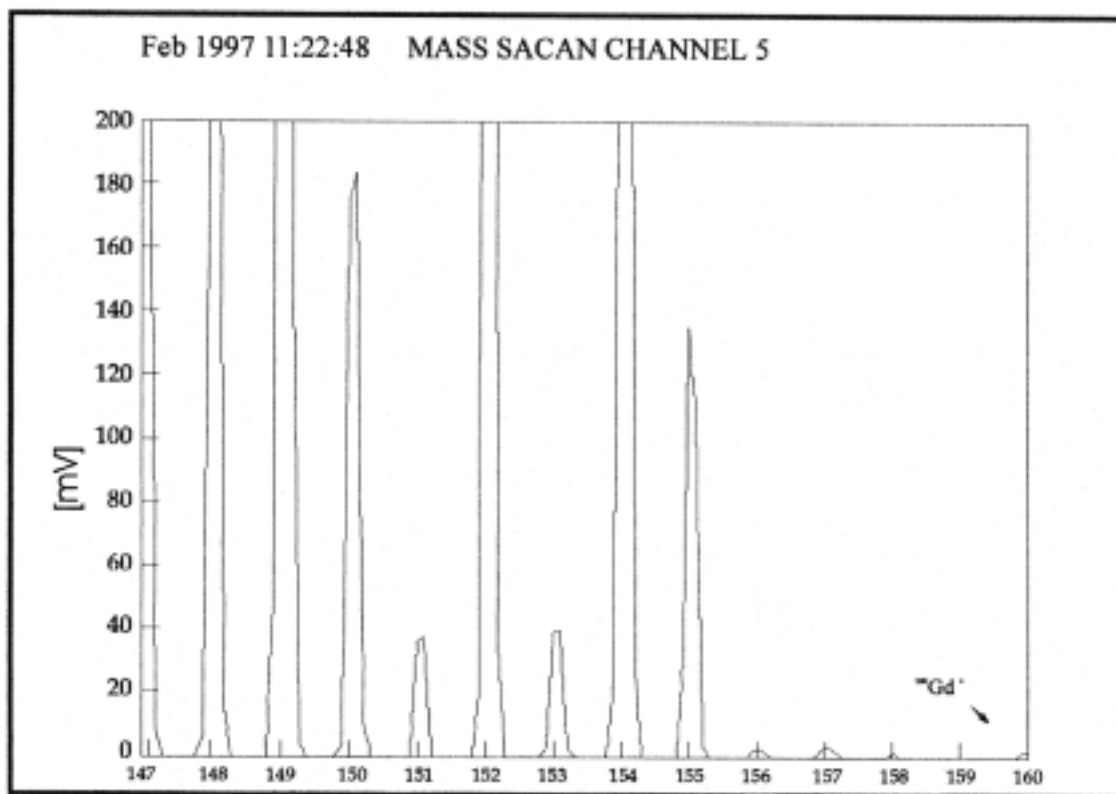


Fig. 6 – Interference of Gd on Sm. Increased scale, with 2.2 volts for ^{149}Sm .

amounts, little instability is observed in the beam. This is well displayed in Fig. 8 which shows that presence of Ce in the Nd fraction is incapable of generating beam instability.

TABLE IX
Mass interferences in Nd isotopic determinations

N° of Mass	142	143	144	146	150
	$^{142}\text{Ce}^+$		$^{144}\text{Sm}^+$	$^{130}\text{Ba}^{16}\text{O}$	$^{150}\text{Sm}^+$
					$^{134}\text{Ba}^{16}\text{O}$

Other isotope present during the analysis of Nd is $^{141}\text{Pr}^+$, but its presence does not represent isobaric interference in the metal form in spite of this. Its interference only happens when Nd is analyzed in the oxide form.

CONCLUSIONS

The improved chemical extraction used in this study following the preliminary determination of the partition coefficient of REEs in the HDEHP resin uses the best possible conditions for extraction of

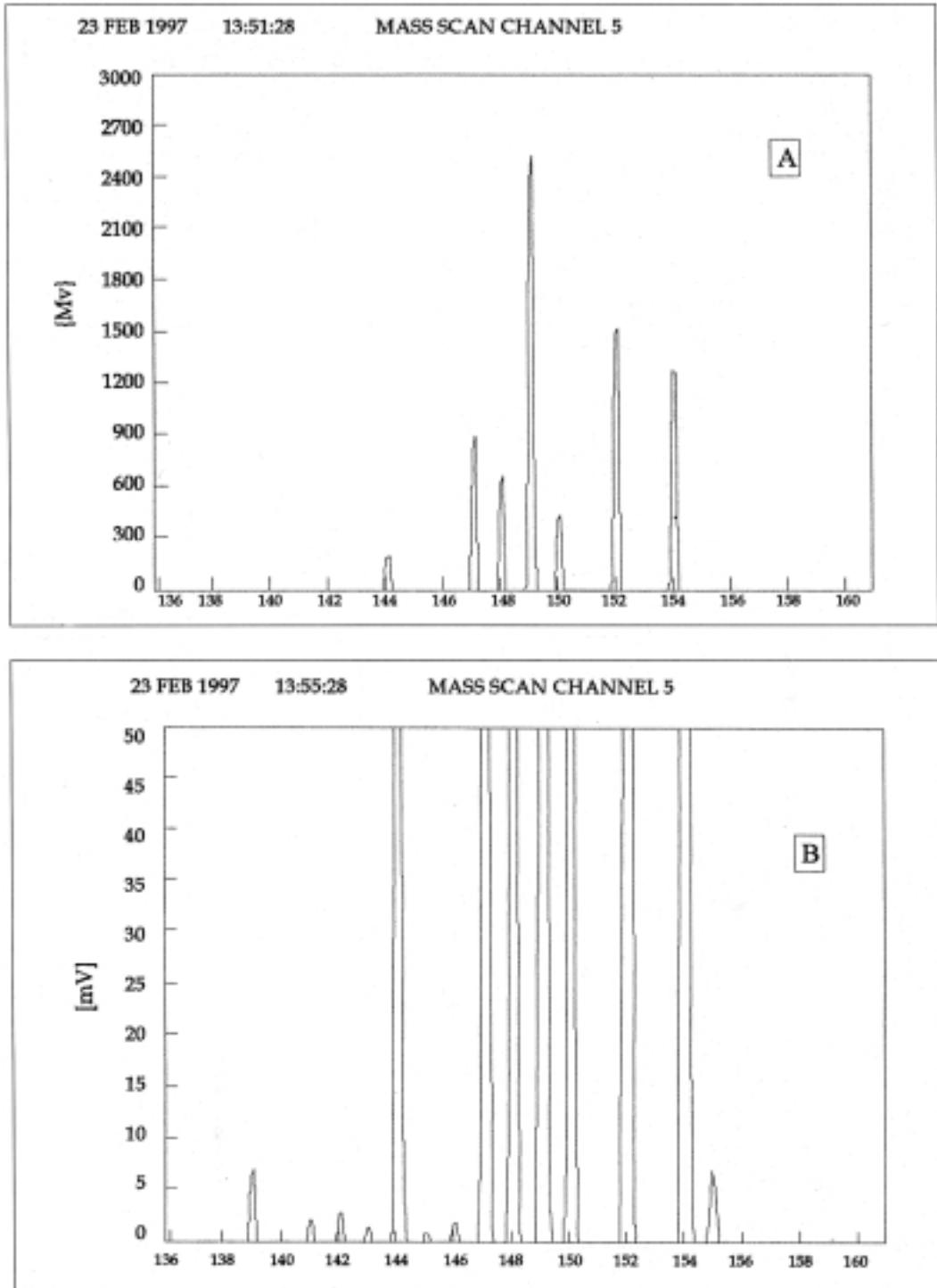


Fig. 7 – Mass interference for Sm. A – increased scale, B – with 2.6 volts for ^{149}Sm .

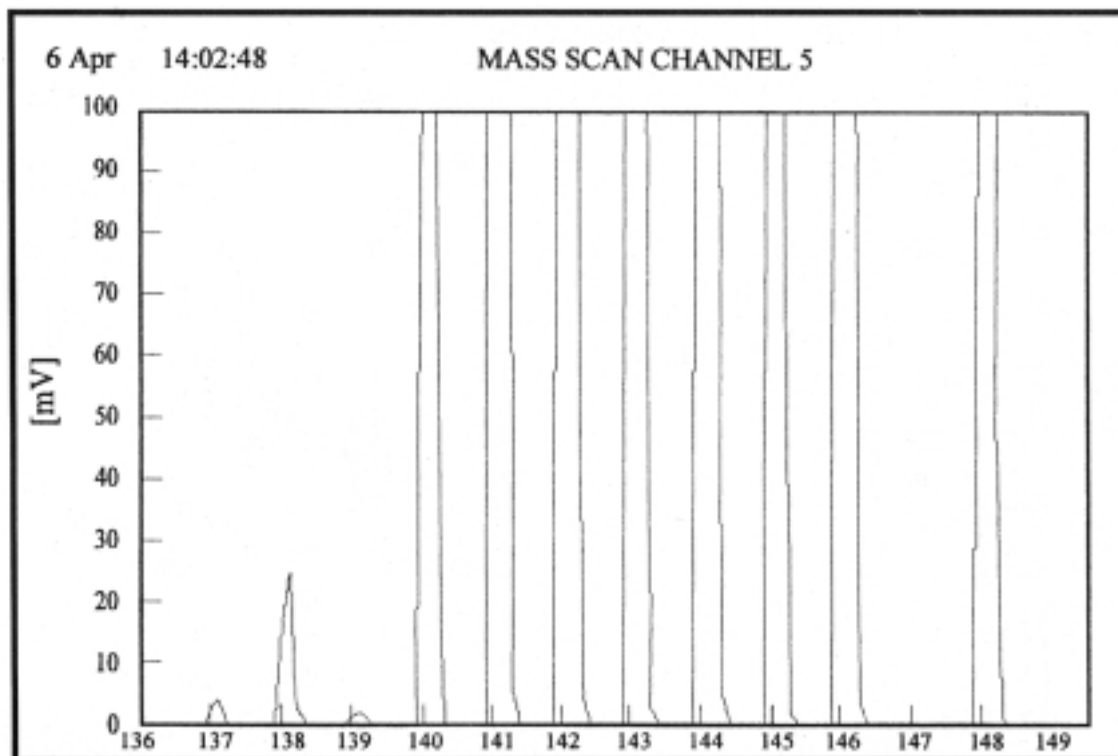


Fig. 8 – Mass interference for Nd. Increased scale, with 2.2 volts for ^{142}Nd .

Sm and Nd. The efficiency of the chemical separation appears in the spectrometric analysis where interferences with other elements are kept to a minimum.

In the mass spectrometry the presence of Ce and mainly Pr in the Nd fraction was observed. There is absolutely no isobaric interference between Sm and Nd using this procedure. In the Sm fraction there are detectable amounts of Eu, but this does not represent a problem, because its isotope do not interfere with the determination of the Sm isotopic ratios. The main isobaric interference of Sm, Gd, is not detected. Sm and Nd concentrations obtained for the JB3 and BCR-1 rock standards show good accuracy and precision, and isotopic ratio of $^{143}\text{Nd}/^{144}\text{Nd}$ for BCR-1 and La Jolla are comparable to the values obtained in other laboratories, demonstrating the reliability of the methodology used at the University of Brasília.

ACKNOWLEDGEMENTS

The authors thank CAPES and to CNPq, for the financial support. The geochemistry laboratory of the University of Brasília is also acknowledged for allowing the analyses of REEs by ICP/AES.

APPENDIX

Notation:

n: normal element

s: spike

i: individual any isotope

j: reference isotope (Nd-146; Sm-152)

u: primary isotope (Nd-150; Sm-149)

v: secondary isotope (Nd-144; Sm-147)

A: atomic mass

iA: atomic mass of an isotope

An: atomic mass of a normal element

As: atomic mass of a spike

W: mass in grams

P: n° of atoms

C: conc. in g/mL

F: atomic fraction

Condensed Notation:

R^S : ratio of the spike

R^N : ratio of the normal element

R^M : mix (spike + normal)

Δ : difference among atomic mass of $\Delta = uA - jA$; $\Delta = vA - jA$; $\Delta = iA - jA$

TABLE I

Isotopic ratios used for isotope dilution calculations in this study

Number	Isotopic ratio Nd	Isotopic ratio Sm
1	150/146	149/152
2	144/146	147/152
3	143/146	

1. CALCULATION OF THE ATOMIC FRACTION:

$$iF = \frac{i/j}{\sum_i \frac{i}{j}} \quad (1)$$

2. REPRESENTATION OF THE CALCULATION OF THE ATOMIC MASS:

$$A = \frac{\sum_i (i/j \times iA)}{\sum_i \frac{i}{j}} \quad (2)$$

3. CALCULATION OF THE CONCENTRATIONS:

no. of moles = mass of the element/A

mass of the element = C($\mu\text{g/g}$) \times W (mass in g)

$$\frac{C_n}{C_S} \times \frac{W_n}{W_S} \times \frac{A_S}{A_n} \times \frac{jF_n}{jF_S} = \frac{S_1 - T_1}{T_1 - N_1} \quad (3)$$

Using the equations (1) and (2) and simplifying the equation above and rearranging for Cn($\mu\text{g/g}$):

$$C_n = C_S \times \frac{W_S}{W_n} \times \frac{\sum_i \left(\frac{i}{j} n \times iA \right)}{\sum_i \left(\frac{i}{j} S \times iA \right)} \times \frac{S_1 - T_1}{T_1 - N_1} \quad (4)$$

Calculation of Nd Concentration

Using the equations mentioned, for a mixed spike of Sm and Nd enriched in ^{150}Nd (used in the laboratory of geochronology of UnB), we have:

$$\text{Nd}(\mu\text{g/g}) = \frac{Z_1 \times C_S \times P_S \times P.A.}{A \times P_a}$$

where:

C_S = concentration ^{150}Nd in the spike = 0.01691492 $\mu\text{mols/g}$

$P.A.$ = atomic mass of Nd (144.24 mol/g)

A = natural abundance of ^{150}Nd = 5.6251% (Russ *et al.* 1971 and Wasserburg *et al.* 1981)

$$Z_1 = \frac{R_S - R_M}{R_M - R_n}$$

where:

R_M = (146/150)m = measured in the spectrometer and corrected for mass fractionation.

R_S = (146/150) of the spike = 0.00464026 (calculated from Table II)

R_n = (146/150) natural = 3.05352835 (calculated from Table I – Wasserburg *et al.* 1981)

Calculation of Sm Concentration

For a mixed spike of Sm and Nd enriched in ^{149}Sm :

$$\text{Sm}(\mu\text{g/g}) = \frac{Z_2 \times C_S \times P_S \times P.A.}{A \times P_a}$$

where:

$R_M = (147/149)$ measured in the spectrometer and corrected for mass fractionation

$R_S = (147/149)$ in the spike = 0.0033163 (calculated from Table V)

$R_n = (147/149)$ natural = 1.088396 (calculated from Table IV – Wasserburg *et al.* 1981)

$C_S =$ concentration of the ^{149}Sm in the spike = 0.01334888 $\mu\text{mols/g}$

$P.A. = 150.35$ mol/g

$A =$ natural abundance of the $^{149}\text{Sm} = 13.8504\%$

4. CORRECTION FOR MASS FRACTIONATION

Thermal ionisation sources, involving the evaporation of the sample starting from a warm filament is subject to the effect of mass fractionation (Potts 1987).

The exact mathematical form of the fractionation law, that describes the instrumental mass fractionation by thermal ionisation is not very well known. The isotope chosen for the correction of the mass fractionation should have great mass difference and their ratio should be also relatively a close to the unit to minimize uncertainties. For Nd the best choice is $^{150}\text{Nd}/^{142}\text{Nd}$ and the second best is $^{146}\text{Nd}/^{142}\text{Nd}$ (Wasserburg *et al.* 1981). The factor of fractionation of the isotope of Nd for unit of atomic mass, it is defined as (Wasserburg *et al.* 1981):

$$\alpha_L(u, v) = \frac{[(R_{uv}^N/R_{uv}^M) - 1]}{m_{uv}} \quad (\text{Linear law}) \quad (5)$$

$$\alpha_P(u, v) = [R_{uv}^N/R_{uv}^M]^{1/m_{uv}} - 1 \quad (\text{Power law}) \quad (6)$$

$$\alpha_E(u, v) = \frac{\ln[R_{uv}^N/R_{uv}^M]}{m_j \ln[m_u/m_v]} \quad (\text{Exponential law}) \quad (7)$$

For cases where fractionation is small, these three different laws supply the same corrected values for the required accuracy. However, for cases in which the fractionation is important, each law will supply a different value for the corrected values depending on the choice of the isotope (u,v) used to calculate the correction.

For Nd and presumably also for Sm, the law of exponential fractionation seems to be better to correct the instrumental fractionation than the linear or power law. Therefore, the use of linear or power laws can introduce significant errors in the ratio $^{143}\text{Nd}/^{144}\text{Nd}$, and this only happens when running a highly fractional analysis. This effect can be minimised by the choice of a different pair of isotope for the normalisation. When $^{146}\text{Nd}/^{142}\text{Nd}$ is used the effect in $^{143}\text{Nd}/^{144}\text{Nd}$ is insignificant; however, for this normalisation, significant errors can be introduced in $^{150}\text{Nd}/^{144}\text{Nd}$. Also when we compare data from different laboratories that normalise in a different way, the use of the linear and power laws introduce small, but significant errors. If the data collected have a small fractionation ($-0.001 < \alpha < +0.001$), the choice of the fractionation law is not necessary.

The fractionation law was suggested in Russell *et al.* (1978) for the analysis of Ca and that

also used the Rayleigh fractionation law.

$$T_1 = M_1 \times (1 + f \times \Delta_1) \quad (8)$$

that corresponds to the equation of the Linear law. Solving for f (Boelrijk 1968):

$$f = \frac{N_2 \times S_1 - N_1 \times S_2 - M_2 \times (S_1 - N_1) + M_1 \times (S_2 - N_2)}{M_2 \times (S_1 - N_1) \times \Delta_2 - M_1 \times (S_2 - N_2) \times \Delta_1} \quad (9)$$

Nd isotope – Application in the UnB Laboratory

Reference: 146

Primary: 150

Secondary: 144

TABLE II
Ratio used for fractionation correction.

Ratios	No.
150/146	1
144/146	2
143/146	3

$$f = \frac{\{(\frac{144}{146})_n \times (\frac{150}{146})_S - (\frac{150}{146})_n \times (\frac{144}{146})_S - (\frac{144}{146})_M [(\frac{150}{146})_S - (\frac{150}{146})_n] + (\frac{150}{146})_M \times [(\frac{144}{146})_S - (\frac{144}{146})_n]\}}{\{(\frac{144}{146})_M \times [(\frac{150}{146})_S - (\frac{150}{146})_n] \times (144 - 146) - (\frac{150}{146})_M \times [(\frac{144}{146})_S - (\frac{144}{146})_n] \times (150 - 146)\}}$$

Linear law

$$T_3 = M_3 \times (1 + f \times \Delta_3)$$

$$T_2 = M_2 \times (1 + f \times \Delta_2)$$

where:

$$M_3 = 143/146$$

$$M_2 = 144/146$$

$$\Delta_3 = -3$$

$$\Delta_2 = -2$$

$$N_3 = T_3 + (T_3 - S_3) \times \frac{(T_1 - N_1)}{(S_1 - T_1)}$$

$$N_2 = T_2 + (T_2 - S_2) \times \frac{(T_1 - N_1)}{(S_1 - T_1)}$$

5. DETERMINATION OF THE RATIO $^{143}\text{Nd}/^{144}\text{Nd}$:

$$\frac{^{143}\text{Nd}}{^{144}\text{Nd}} = \frac{N_3}{N_2} = \frac{T_3 + (T_3 - S_3)}{T_2 + (T_2 - S_2)} \quad (10)$$

Isotope of Sm – Application in the Laboratory of UnB

Reference: 152

Primary: 149

Secondary: 147

TABLE III
Ratio used for the correction Sm fractionation

Ratios	No.
149/152	1
147/152	2

$$f = \frac{\{(\frac{147}{152})_n \times (\frac{149}{152})_S - (\frac{149}{152})_n \times (\frac{147}{152})_S - (\frac{147}{152})_M [(\frac{149}{152})_S - (\frac{149}{152})_n] + (\frac{149}{152})_M \times [(\frac{147}{150})_S - (\frac{147}{152})_n]\}}{\{(\frac{147}{152})_M \times [(\frac{149}{152})_S - (\frac{149}{152})_n] \times (147 - 152) - (\frac{149}{152})_M \times [(\frac{147}{152})_S - (\frac{147}{152})_n] \times (149 - 152)\}}$$

Linear law

$$T_1 = M_1 \times (1 + f \times \Delta_1)$$

$$T_2 = M_2 \times (1 + f \times \Delta_2)$$

where:

$$M_1 = 149/152 \text{ and } 1 = -3$$

$$M_2 = 147/152 \text{ and } 2 = -5$$

The ratio $(^{147}/^{149})_{\text{corrected}} = T_2/T_1$ (used for calculation of the concentration)6. DETERMINATION OF THE RATIO $^{147}\text{Sm}/^{144}\text{Nd}$:

$$\frac{^{147}\text{Sm}}{^{144}\text{Nd}} = \frac{\text{Sm}(\mu\text{g/g})}{\text{Nd}(\mu\text{g/g})} \times \frac{A_{\text{Nd}}}{A_{\text{Sm}}} \times \frac{^{147}\text{Sm}/\text{Sm}}{^{144}\text{Nd}/\text{Nd}} \quad (11)$$

Using the equation (2):

$$A_{\text{Nd}} = 144.23987$$

$$A_{\text{Sm}} = 150.35402$$

Using the values of the tables I, IV and VII:

$$^{144}\text{Nd}/\text{Nd} = 1/(3.690111 - 143/144)$$

$$143/144 = 0.512 \text{ or calculated individually for each sample.}$$

$$^{147}\text{Sm}/\text{Sm} = 0.5651235/3.7488669 = 0.150745$$

7. TABLES OF USED DATA

The used data for isotopic dilution calculations and Mass Fractionation, are shown in Tables I to VII.

8. CALCULATION OF THE AMOUNT OF SPIKE TO BE MIXED WITH THE SAMPLE

A correctly spiked mixture should have the $^{150}\text{Nd}/^{146}\text{Nd}$ ratio close to 1:

Spike

Enriched in $^{150}\text{Nd} = 0.01691492$ moles/g

$^{150}\text{Nd} = [^{150}\text{Nd}_{\text{spike}}] \mu\text{moles atomic} \times A_{150}$ (mass of the isotope 150 of Nd)

using data on Table VII:

$$^{150}\text{Nd} = 0.01691492 \times 149.9209 = 2.5359 \mu\text{g/mL}$$

Sample

TABLE I

Isotopic Ratios for natural Nd used for Isotope Dilution Calculations.

Ratio	Composition*	Composition**
142/146	1.581703	1.581712
143/146	0.709269	0.710131
144/146	1.385291	1.385245
145/146	0.48266	0.482642
146/146	1	1
148/146	0.334648	0.334639
150/146	0.32749	0.327479
Total	5.821061	5.821852

*Oxford

**Wasserburg *et al.* 1981.

% ^{146}Nd natural (Table III) = 17.1767

$[^{146}\text{Nd}]\mu\text{g}/\text{mL} = [\text{Nd}]\mu\text{g}/\text{mL} \times 17.1767/145.913126$

Factor of Proportion (f) = $[^{150}\text{Ndspike}]\mu\text{g}/\text{mL}/[^{146}\text{Ndamostra}]\mu\text{g}/\text{mL}$ (16)

The amount of spike P_s (mg) is:

$$Pa = f \times Ps$$

$$Pa = (21.5420/[\text{Nd}]) \times Ps \quad (17)$$

where, Pa = weight of the sample (mg) and Ps = weight of the spike (mg).

TABLE II

Isotopic Ratios for Nd in mixed Spike, calibrated against with the Blankwash-Tech and BCR-1 rock standards

Ratio	*Composition	Error(\pm)
150/144	196.278416	0.01443186
142/144	0.833347772	$1.9776.10^{-5}$
143/144	0.49491642	$8.5537.10^{-6}$
146/144	0.91078328	$3.0677.10^{-5}$
148/144	0.73598967	$3.5142.10^{-5}$
145/144	0.43648743	$1.1085.10^{-5}$

*Spike previously calibrated in the laboratory of Montreal.

TABLE III

Isotopic Abundance for Nd (%)

Isotopic	**Spike	Natural*
142	0.415241	27.1686
143	0.24667	12.1977
144	0.498281	23.7940
145	0.217493	8.2902
146	0.453826	17.1767
148	0.366730	5.7480
150	97.801821	5.6250
Total	99.999999	100.0001

*Wasserburg *et al.* 1981

**Montreal.

TABLE IV

Isotopic Ratio for natural Sm used in the Isotopic Dilution

Ratio	Composition*	Composition**
144/152	0.1164211	0.1164212
147/152	0.5651235	0.5651235
148/152	0.4230413	0.4230413
149/152	0.519226	0.5192261
150/152	0.2768503	0.2768391
152/152	1	1
154/152	0.8482157	0.8482157
Total	3.7488779	3.7488669

*Oxford.

**Wasserburg *et al.* 1981.

TABLE V

Isotopic Ratio for natural Nd in mixed Spike, calibrated using Blankwash-tech and BCR-1 rock standards.

Ratio	*Composition	Error(±)
149/152	145.301196	0.00765741
147/152	0.4818679	3.65.10-5
150/152	0.81790385	3.5771.10-5
148/152	0.76123316	5.3087.10-5
144/152	0.04911417	2.0569.10-5
154/152	0.48525055	1.633.10-5

*Montreal.

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TABLE VI
Isotopic Abundance for Sm (%)

Isotope	**Spike	Normal*
144	0.032985	3.1055
147	0.323626	15.0745
148	0.51125	11.2845
149	97.585324	13.8502
150	0.54931	7.3846
152	0.671607	26.6747
154	0.325898	22.6259
Total	100.032985	99.9999

*Wasserburg *et al.* 1981.

*Montreal.

TABLE VII
Atomic mass (Wapstra & Bos 1977)

Isotope	Nd	Isotope	Sm
142	141.907731	144	143.912009
143	142.909823	147	146.914907
144	143.910096	148	147.914832
145	144.912582	149	148.917193
146	145.913126	150	149.917285
148	147.916901	152	151.919741
150	149.920900	154	153.922218

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