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SOME RADIOCHEMICAL SEPARATIONS EMPLOYED AT THE INSTITUTE OF NUCLEAR AND ENERGY RESEARCH – BRAZILIAN NUCLEAR ENERGY COMMISSION

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Several radiochemical separations have been employed at the Radiochemistry Division of the Institute of Nuclear and Energy Research – Brazilian Nuclear Energy Commission, for the analysis of a number of elements in different kinds of matrices. In the present paper some of these separations applied to the analysis of geological samples; geological and biological reference materials and Brazilian foodstuffs are described. The separation procedures utilized are mainly ion exchange, retention in inorganic exchangers like HAP, TDO and HMD and solvent extraction.

INTRODUCTION

Instrumental neutron activation analysis has been extensively applied to determine a great number of the elements of the periodic system in a wide variety of matrices.

Nevertheless, spectral interferences or strong matrix activities lead to the necessity of developing radiochemical separations to enhance limits of detection and accuracy in the analysis of several elements. This is the case in the analysis of noble metals like iridium in deep sea sediments, where strong activities of scandium and rare-earth elements do not allow a purely instrumental approach.

For the optimization of simultaneous analysis of rare-earth elements such as Nd and Gd, it is necessary also to develop a radiochemical separation in which interfering elements like Ta, Sc and Pa can be retained in an HAP column, in $HClO_4$ medium.

The determination of potentially toxic elements like Hg, Se, Sb and As in foodstuffs and in biological materials also poses a difficult problem for the analyst, if a purely instrumental approach is aimed at . The very low concentrations of these elements in biological materials and also spectral

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interferences such as are encountered between Hg and Se demand the employment of individual radiochemical separations of these elements.

In the present paper, some radiochemical separations employed at the Institute of Nuclear and Energy Research - Brazilian Nuclear Energy Commission are described, including results obtained for selected reference materials.

EXPERIMENTAL

Sample irradiation

The samples were irradiated at the IEA-R1 swimming-pool type research reactor of IPEN-CNEN/SP, from about 8 to 40 hours, under thermal neutrons fluxes that ranged from 10^{12} to $10^{13}.cm^{-2}.s^{-1}$.

Measurements and data evaluation

Several gamma-ray spectrometers were utilized for measurement of irradiated samples.

Solid state ORTEC and ENERTEC Ge(Li) or Ge detectors were coupled either to a multichannel analyser, e.g. ORTEC 7450A or to an ADCAM 918A multichannel buffer and associated electronics.

Data evaluation was performed by means of several softwares, such as FALA in BASIC language developed at IPEN, GELIGAM from ORTEC and VISPECT2 developed by D. Piccot from Saclay, France.

Analysis of alkaline rocks and of the USGS reference sample AGV-1[1]

A group separation scheme was developed for the radiochemical analysis of Fe, Na, K, Ba, Ta, Rb, Co, Cu, Zn, Ga, W, Sb, Hf, Sc, La, Ce, Nd, Sm, Eu, Tb, Ho, Yb, Lu, U, Th. A comparative study was made with data obtained for the same geological materials by INAA.

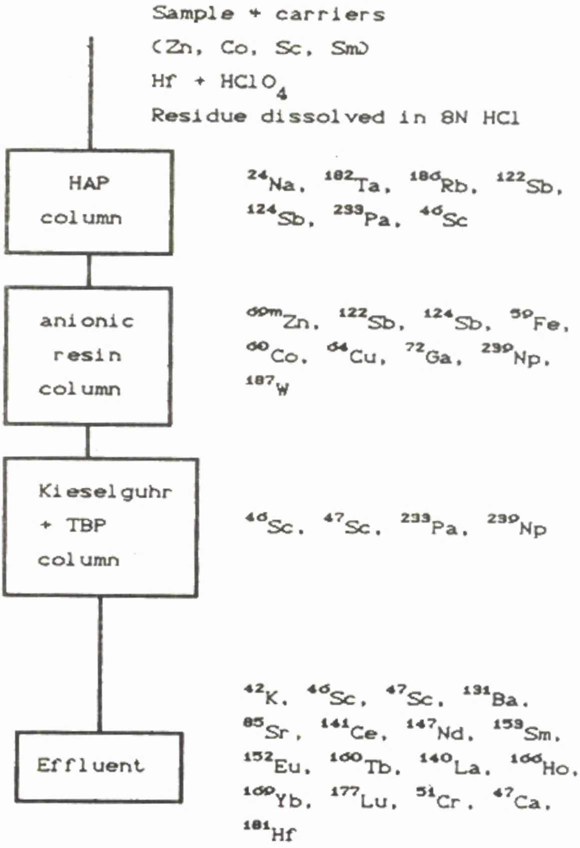

Figure 1
Radiochemical separation procedure scheme

Fig. 1 shows the radiochemical separation procedure employed. One advantage of this procedure is that all the influent and washing solutions were in 8 N HCl medium, which allowed a reduced analysis time, considering also that a system of coupled plastic columns was used, making the separation very convenient.

Analysis of iridium in sedimentary rocks and in the USGS reference material PCC-1[2]

In this work a radiochemical separation procedure was utilized for eliminating some interfering radionuclides, such as lanthanide elements and scandium, which prevented the determination of iridium at ppb levels in sedimentary rocks and in PCC-1 by INAA.

Sixteen samples of sedimentary borehole cores taken at several depths in the continental shelf of Rio de Janeiro, Brazil were analysed. These analyses were part of a study of noble metal contents in the Cretaceous/Tertiary interface in Brazil, related to the theory of meteoritic impact of ALVAREZ.[3]

The irradiated samples were dissolved in a mixture of HF, HNO_3 and $HClO_4$, in stainless steel bombs. The acids were evaporated to dryness and the residue obtained was taken up in 0.03 M HCl and H_2O_2 120 volumes and passed through a column of cationic resin Bio-Rad AG 50 W x 8 where the lanthanides, Sc, Na, Fe and Co were sorbed, and the eluate was counted.

The radiochemical separation yield as determined by tracer experiments was 76 ± 2 %.

Analysis of Nd and Gd in geological reference materials[4,5]

In general, about 8 rare-earth elements can be determined by INAA without much difficulty. In the specific case of the analysis of Nd and Gd, spectral interferences mainly of ^{182}Ta and ^{233}Pa in the low-energy part of the spectrum make the analysis more troublesome.

A radiochemical separation was developed to enhance the determination of these two elements, in which the lanthanides were first precipitated with NH_4OH, dissolved in 6 M $HClO_4$ and Ta, Sc and Pa were retained in an HAP column. Two further precipitations of the lanthanides were carried out, with NH_4OH followed by oxalate, thus eliminating other interfering activities.

Separation procedures using tetracycline as complexing agent[6]

Several radiochemical separations were carried out by using the antibiotic tetracycline (TC) as complexing agent. Individual extraction curves for the lanthanides, Zn, Sc, U, Th, Np and Pa were obtained. Separations of those elements from one another and of U from Se, Br, Sb, Ba, Ta and W were carried out. In some procedures, such as in the case of the pairs U-Np and Sc-Zn, the separation was achieved by carefully adjusting the pH of the aqueous phase.

In other cases, addition of masking agents, like EDTA and DTPA was necessary. Separations of Pa from Th and of U from Pa and Th were accomplished by simultaneously using NaF as masking agent for Pa and DTPA as masking agent for Th and Pa. In the separation of lanthanides from one another, it is necessary to use a multi-stage extraction procedure, since the stability constants for these elements are too close.

For the analysis of rare-earth elements in geological materials, the interfering elements were eliminated by carrying out two consecutive extractions at pH 1.7 before irradiation.[7] The solution of tetracycline had a concentration of 0.010 M benzyl alcohol.

The aqueous phase was separated by decantation followed by centrifugation and 20 ml of this phase was 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 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 $10^{12}.cm^{-2}.s^{-1}$).

Analysis of biological reference materials and Brazilian foodstuffs

For the determination of Hg and Se in biological reference materials and in Brazilian rice grains, a radiochemical procedure was employed in which both elements were distilled in HBr medium and precipitated respectively with thioacetamide and sodium metabisulfite.[8]

The elements As, Cr, Hg, Sb and Se were determined in biological reference materials by utilizing ion exchange, retention in inorganic exchangers and solvent extraction techniques for the radiochemical separations[9].

The irradiated samples were dissolved in a mixture of HNO_3 + H_2SO_4 or in HNO_3, by using teflon bombs in conventional ovens or in a microwave oven using PARR microwave dissolution bombs.

In one of the procedures, Hg and Sb were retained in a DOWEX 2x8 anionic resin, in 6 M HCl medium and As and Se were retained in a TDO column, in 3 M HCl[9].

In another procedure, Se was retained in a TDO column, in 1M HNO_3 medium. The effluent of the column was adjusted to pH 1 with concentrated NH_4OH and Hg was extracted with 0.005 M $Ni(DDC)_2$ in chloroform[9].

RESULTS AND DISCUSSION

Table 1 presents the results obtained for the USGS reference material AGV-1, by using the radiochemical procedure described in Fig. 1. Twenty-three elements were determined, and in general the results obtained were in very good agreement with the "consensus values" published by GLADNEY[10], specially for K, Ba, Co, Cu, Zn, Ga, La, Ce, Eu, Yb. Thus the separation proved to be fast and reliable.

As for iridium determination, it was possible to analyse this element at ppb level or less in 16 marine sediments of the "Campos" Basin - Rio de Janeiro, Brazil, as is shown in Table 2. For the analysis of the USGS standard rock PCC-1, the average of 14 determinations was of 5.37 ± 1.38 which agrees well with the GLADNEY's value[10] of 4.8 ± 1.9 ppb, considering the low concentration level of iridium.

Neodymium and gadolinium were determined in the USGS standard G-2 and in the Brazilian standards BB-1 and GB-1 by using the radiochemical procedure described above. The results are shown in Table 3.

The values for the three standards were in good agreement with literature values. In the case of GB-1 and BB-1, the results obtained are a contribution to the knowledge of the composition of these materials, since few other values are available.

Table 1

Results of the analysis of the USGS reference material AGV-1, obtained by radiochemical neutron activation[1]

Element	Average ± confidence limit	Gladney[10] consensus values
Fe (%)	4.82 ± 0.41 (6)	4.73 ± 0.13
Na (%)	3.52 ± 0.44 (6)	3.15 ± 0.09
K (%)	2.39 ± 0.25 (4)	2.41 ± 0.08
Ba	1196 ± 213 (4)	1221 ± 16
Ta	1.04 ± 0.64 (3)	0.92 ± 0.12
Co	15.2 ± 2.9 (4)	15.1 ± 1.2
Cu	60 ± 4 (5)	60 ± 6
Zn	88 ± 4 (6)	88 ± 2
Ga	19.9 ± 1.1 (5)	20 ± 3
W	0.46 ± 0.18 (5)	0.53 ± 0.09
Sb	4.1 ± 0.3 (6)	4.4 ± 0.4
Hf	5.3 (1)	5.1 ± 0.4
Sc	13.1 ± 2.2 (5)	12.1 ± 0.9
La	39 ± 3 (4)	38 ± 3
Ce	64 ± 5 (3)	66 ± 6
Nd	30 (1)	34 ± 5
Sm	5.6 ± 0.2 (4)	5.9 ± 0.5
Eu	1.67 ± 0.27 (4)	1.66 ± 0.11
Tb	0.56 ± 0.20 (2)	0.71 ± 0.10
Ho	0.59 ± 0.12 (2)	0.73 ± 0.08
Yb	1.70 ± 0.57 (4)	1.67 ± 0.17
Lu	0.31 ± 0.13 (4)	0.28 ± 0.03
U	2.0 ± 0.6 (3)	1.89 ± 0.25
Th	7.2 ± 2.1 (5)	6.5 ± 0.37

Results are given in ppm unless otherwise indicated.
In parenthesis are the number of determinations.

Many radiochemical separations developed by using tetracycline as a complexing agent are described by SAIKI et al[6]. In the case of analysis of geological samples, the separation was applied before irradiation and the USGS

Table 2

Results for the analysis of iridium in marine sediments of "Campos" Basin - Rio de Janeiro - Brazil[12]

Depth, m	Iridium contents, ng/g (mean ± standard deviation)	
2834.78	1.44 ± 0.63	(4)
2835.00	1.23 ± 0.56	(4)
2835.31	3.00 ± 1.75	(8)
2835.51	1.14 ± 0.32	(4)
2835.70	1.97 ± 1.03	(4)
2835.93	4.49 ± 0.68	(8)
2836.13	0.73 ± 0.19	(4)
2836.57	0.93 ± 0.17	(4)
2836.93	0.62 ± 0.10	(4)
2837.20	1.23 ± 0.23	(4)
2837.46	1.63 ± 0.67	(8)
2837.76	1.87 ± 0.06	(4)
2837.96	1.83 ± 0.29	(8)
2838.27	3.55 ± 1.37	(3)
2838.54	2.26 ± 0.09	(3)
2838.66	0.66 ± 0.28	(4)

In parenthesis are the number of determinations.

Table 3

Analysis of Nd and Gd in the geological standards G-2 (USGS), GB-1 and BB-1 (Federal University of Bahia, Brazil)[4,5] (ppm)

	Nd	Gd
G-2	55 ± 6	4.6 ± 0.3
GB-1	38 ± 6	3.9 ± 0.1
BB-1	32 ± 5	5.6 ± 0.6
GLADNEY et al[10] values for G-2	53 ± 8	4.1 ± 0.8
Literature[13] values for GB-1	39	3.9
Literature[13] values for BB-1	32.7	6.0

Table 4

Results of the analysis of rare-earth elements in geological reference materials by separating interfering elements with tetracycline[7] (ppm)

Elem.	GSP-1 Standard Rock		G-2 Standard Rock		GS-N Standard Rock	
	This work	GLADNEY et al.[10]	This work	GLADNEY et al.[10]	This work	GOVINDARAJU[11]
La	176±17	183±13	85±5	86±5	71±5	75
Ce	386±23	406±20	148±12	159±11	133±12	140
Nd	203±15	190±17	55±3	53±8	54±6	50
Sm	25.6±2.5	26.8±2.5	7.1±0.4	7.2±0.6	7.8±0.4	8.2
Eu	2.35±0.25	2.36±0.22	1.44±0.09	1.41±0.12	1.7±0.2	1.7
Tb	1.34±0.14	1.36±0.14	0.44±0.04	0.48±0.07	0.68±0.04	0.6
Yb	1.57±0.15	1.7±0.4	0.82±0.11	0.78±0.14	1.8±0.2	1.7
Lu	0.21±0.03	0.22±0.05	0.083±0.017	0.113±0.024	0.19±0.03	0.2

Table 5

Determination of Hg and Se in biological reference materials and in Brazilian rice grains using a radiochemical separation based on distillation and precipitation[8] (ng/g, dry weight)

Rice or Reference Material	Hg	Se	Certified values or best values	
			Hg	Se
Long Fine 1	7.65	< 24		
	11.54; 19.39	36.80; 44.38		
Long Fine 2	10.80; 15.23	< 24		
	14.70; 18.89	34.70; 18.67		
Yellow Long	< 1.2	< 24		
Japanese/Catete	2.19; 3.01	< 24		
Parboiled--Long Fine	5.20; 2.67	< 24		
Bovine Liver	5.4 ± 1.4	638 ± 75	4 ± 2	710 ± 70
BOWEN'S Kale	169 ± 19	123 ± 20	168 ± 25	133 ± 21

Table 6

Results of the determination of Hg, Se and Cr in biological reference materials using TDO inorganic exchanger and $Ni(DDC)_2$ solvent extraction[9]

Reference material	Concentration, This work (ppm)	Relative s.d., %	Relative error, %	Literature values[12]
Hay Powder IAEA-V-10	Hg: 0.015 ± 0.001	6.7	15.4	0.013 ± 0.004
Human Hair NIES-CRM-5	Hg: 3.81 ± 0.60	15.7	13.4	4.4 ± 0.4
	Se: 1.78 ± 0.06	3.4	27.1	1.4 ± 0.2
	Cr: 1.54 ± 0.04	2.6	10.0	1.4 ± 0.2
Mixed Human Diet IAEA-H9	Hg: 0.0055 ± 0.0004	7.3	14.6	0.0048 ± 0.0014
	Se: 0.14 ± 0.02	14.3	27.2	0.11 ± 0.01
	Cr: 0.10 ± 0.04	40.0	33.3	0.15 ± 0.04
Copepod IAEA-MA-A-1	Hg: 0.24 ± 0.02	8.3	14.3	0.28 ± 0.01
	Se: 2.85 ± 0.50	17.5	5.0	3.0 ± 0.2
Oyster Tissue NBS-SRM-1566	Hg: 0.049 ± 0.006	12.2	14.0	0.057 ± 0.015
	Se: 2.00 ± 0.01	0.5	4.8	2.1 ± 0.5
Mussel Tissue IAEA-MA-M-2	Hg: 0.87 ± 0.02	2.3	8.4	0.95 ± 0.10
	Se: 1.86 ± 0.04	2.2	18.1	2.27 ± 0.43
	Cr: 1.03 ± 0.03	2.9	20.0	1.25 ± 0.34
Fish Flesh IAEA-MA-A-2	Se: 1.47 ± 0.04	2.7	13.7	1.7 ± 0.3
	Cr: 1.11 ± 0.04	3.6	15.4	1.3 ± 0.1
Citrus Leaves NBS-SRM-1572	Cr: 0.82 ± 0.15	18.3	2.5	0.8 ± 0.2
Tomato Leaves NBS-SRM-1573	Cr: 4.4 ± 0.2	4.5	2.2	4.5 ± 0.5
Mixed Human Diet NBS-SRM-8431a	Cr: 0.116 ± 0.018	15.5	13.7	0.102 ± 0.006

reference materials GSP-1, G-2 and GSN were analysed as shown in Table 4. Good agreement was obtained with the values of GLADNEY et al[10] and GOVINDARAJU.[11]

Table 5 presents the results obtained for analysis of Hg and Se in biological reference materials SRM 1577a (Bovine Liver) and BOWEN's Kale and also in Brazilian rice grains. For the reference materials, the results agreed well with literature values and for rice the values found for Hg and Se were in the ppb range, below values set by Brazilian regulations.

Table 6 presents the results for Hg, Se and Cr in several biological reference materials using TDO inorganic exchangers and $Ni(DDC)_2$ solvent extraction. Here too, the agreement with literature values[12] was good.

CONCLUSIONS

The several radiochemical separation procedures presented in this paper proved to be reliable for the analysis of several elements mainly at trace levels in different kinds of matrices.

The procedures employed are in general relatively fast and reproducible.

Analyses were first carried out in reference materials before being applied to real samples.

In the case of analysis of toxic elements in biological materials, the use of radiochemical separations was mandatory, since INAA did not present the necessary sensitivity.

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