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ACTIVATION ANALYSIS OF ALKALINE ROCKS. A COMPARISON BETWEEN DESTRUCTIVE AND NON-DESTRUCTIVE METHODS

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The United States Geological Survey reference sample AGV-1 andesite, and three alkaline rocks from the apatite mine of Jacupiranga, Brasil, were analyzed by thermal neutron activation analysis using destructive and non-destructive methods, and high resolution Ge(Li) gamma-ray detectors. One of the rocks, a carbonatite, was also analyzed by instrumental activation analysis with epithermal neutrons. A greater number of elements can be determined using the radiochemical separation, but the precision and accuracy attained by INAA and RNAA were of the same order for most of the elements analyzed. Epithermal activation was more advantageous for tantalum, terbium and holmium. Comparison of the analytical results for USGS reference sample (AGV-1) with the data published by others gave good agreement. Statistical tests used for comparison of the results of destructive and non-destructive methods, as well as other results are presented.

Introduction

The great possibilities of neutron activation analysis for the determination of trace elements in geological materials such as rocks, soils and ores, have been pointed out by many authors.[1,2,3] Some of them, like GORDON et al.[4] resort to the exclusively instrumental approach (instrumental neutron activation analysis, INAA) with Ge(Li) detectors, determining from 20 to 30 elements. Others, like KEAYS et al.[5] perform a radiochemical group separation (radiochemical neutron activation analysis, RNAA) prior to counting. LAUL and RANCITELLI[6] apply, in sequence, instrumental and group radiochemical separation techniques. Epithermal neutron activation (ENAA) can lead to better results for the analysis of some elements with high resonance integrals. In this case the high interfering activities

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generated by some elements commonly occurring in rocks, like sodium and manganese, are eliminated to a large extent. BRUNFELT and STEINNES[7] demonstrated the advantage of epithermal activation for the determination of Rb, Sr, Sb, Cs, Ba, Tb, Hf, Ta, Th and U in some geological materials. SCHELHORN et al.[8] made a comparative study of the INAA and RNAA techniques for biological materials and determined the detection limits for each technique.

Due to the geochemical importance of the knowledge of trace element concentration in the alkaline rocks of apatite mines in the state of São Paulo, Brasil, comparative instrumental and radiochemical group separations techniques with the mentioned material were carried out.

Among the many schemes for radiochemical group separations described in the literature, the one developed by MORRISON et al.[9] for trace determinations in geological samples was found to be very interesting due to its simplicity and efficiency. The scheme applies basically the processes of retention in an inorganic selective ion retention medium followed by ion exchange and solvent extraction. An adaptation of the MORRISON process was made for the present work and the elements were separated in four groups by means of a system of coupled columns. The solvent extraction with TBP was substituted by extraction chromatography, impregnating silanized kieselguhr with TBP.

In order to test the performance of the methods the USGS standard rock AGV-1 was first analyzed and then three rocks, which came from the mine of Jacupiranga, São Paulo, were studied. One of them was an ijolite (Hj 4A), the other one a piroxenite (Hj/7), and the third a carbonatite (Hj 130/1). The USGS rock BCR-1 was used as standard. This rock has been analyzed by many authors such as BRUNFELT and STEINNES.[2] The values published by FLANAGAN[10] for the elemental concentrations in the USGS standard rocks were used for the calculations. In the case of epithermal activations only the carbonatite (Hj 130/1) was analyzed.

In order to evaluate the performance of the destructive and non-destructive methods, a statistical analysis[11] of the data was made. The parameters of the distribution of each group of results were calculated: mean, standard deviation, relative standard deviation and also the confidence limits of the mean. The existence of anomalous results was checked through a test of r maximum and r minimum.[11]

For the study of the precision of both methods, RNAA and INAA, an F-test for the comparison of variances was applied. By means of Student's t-test, which permits the checking of the hypothesis of equality of the true value μ (only for the standard rocks) and $\bar{x}$ (mean of a series of results) it was possible to verify the accuracy of the methods.

By means of another t-test we can verify if there is a statistically significant difference in the results of analysis carried out by two different methods. In this case, it is necessary to make sure that the variances of the two systems of observations do not differ significantly.

The destructive and non-destructive methods of thermal neutron activation analysis were also classified, according to the criterion of McFARREN et al.[12] and ECKSCHLAGER.[13] in "Excellent", "Acceptable" or "Unacceptable".

Experimental

Treatment of the rocks

The USGS standard rocks, AGV-1 and BCR-1 were received as very fine powders and were submitted to no further treatment.

The alkaline rocks of Jacupiranga came in chips of approximately 0.5 cm.

These chips were crushed to smaller fragments in a porcelain mortar until a reasonable size for grinding in a mechanical agate mortar was obtained.

After grinding the rocks, the treatment was continued in a manual agate mortar until all the powder passed through a 150 mesh sieve. This final treatment was considered necessary to assure a reasonable homogeneity of the material.

Contact with metallic parts was avoided, since the problem of contamination of the samples by foreign elements can be very serious at this level of granulometry. It was observed that the grinding of the rocks in a mechanical tungsten carbide mill, instead of the manual agate mortar, resulted in severe contamination by tungsten, a strong activity of ^{187}W (T = 24.0 hrs) being observed upon irradiation of the samples thus processed. For this reason the use of the tungsten carbide mill was abandoned.

Standard

The USGS rock BCR-1, basalt, was chosen as standard for all the samples to be analyzed.

Irradiation

Samples and standards were irradiated together in aluminium tubes, at a neutron flux of approximately $5 \cdot 10^{12}$ n $\cdot$ cm^{-2} $\cdot$ sec^{-1} for a period of 8 hrs.

For the INAA about 50 mg of the standard rock and 100 mg of the samples were weighed in high purity plastic containers. Generally two samples and one standard were irradiated in each aluminium tube, the standard being placed between the samples. The distance between samples and standard was such that it was not necessary to make corrections for neutron flux gradient. For the irradiation with epithermal neutrons, the samples and standard were placed inside a 1 mm thick cylindrical cadmium tube of 10 mm external diameter and 20 mm height. In this case the rock powders were weighed inside common polyethylene envelopes. Blanks of the envelopes were also irradiated together with samples and standards. The cadmium ratio for gold at the site of irradiation was equal to 4.5.

In the case of RNAA the samples were irradiated inside aluminium foil envelopes. In this way, the transference to the beakers for dissolution was much easier. Two samples and one standard were also irradiated together in the same tube.

Counting equipment

The detection equipment used for counting was an ORTEC Ge(Li) detector of 30 cm^3 volume. The resolution of the detector was of 4.1 keV in the FWHM for the 1332.5 keV peak of ^{60}Co and 2.9 keV in the FWHM for the 661.6 keV of ^{137}Cs. The Ge(Li) detector was coupled to a Hewlett-Packard 4096 channel analyzer connected to a Hewlett-Packard model 2100A minicomputer.

In the case of analysis with epithermal neutrons, a new ORTEC detector was used (resolution of 2.8 keV for the 1332.5 keV peak of ^{60}Co).

Treatment of data

A program, FALA,[14] in BASIC language was used to locate peak positions and energies and to calculate net areas. Coincidence losses correction was provided by the program using WYTTENBACH's[15] method. The identification of radioisotopes was carried out by consulting the table of ADAMS and DAMS[16] and the ZADDAC catalogue.[17] In case of doubt, when a radioisotope presented only one peak, half-life determinations were made.

Statistical tests

After calculation of the parameters for the various groups of results, that is arithmetic mean ($\bar{x}$), standard deviation of a single result (s_x) relative standard deviation ($s_x/\bar{x}$), relative error ($\bar{x} - \mu/\mu$) (μ is the "true value") standard deviation of the mean ($s_{\bar{x}}$) and the confidence limits of the mean, statistical tests were applied in order that a non-subjective comparison of the methods of analysis could be made. The statistical tests were as follows.[11]

Verification of the hypothesis of homogeneity of results and rejection of suspicious results

If one or two of the results obtained seem to be suspicious, for instance the maximum and the minimum values of a set of results, we must consider the distribution of the maximum deviation. We then calculate

$$r_{max} = \frac{x_{max} - \bar{x}}{s_x \sqrt{\frac{n-1}{n}}} \quad \text{or} \quad r_{min} = \frac{\bar{x} - x_{min}}{s_x \sqrt{\frac{n-1}{n}}}$$

x_{max} and x_{min} are the maximum and minimum values for the experimental results, respectively.

If the calculated values of r_{max} or r_{min} are larger than the corresponding tabulated values[11] for the level of significance selected, such a measurement can be rejected as rough. If the contrary occurs, we must consider the set of results as homogeneous.

Comparison of variances by means of the F-test

In experimental work it often becomes necessary to verify the hypothesis regarding the equality of the population variances σ_1^2 and σ_2^2 if the sample variances s_1^2 and s_2^2 are known. This problem is solved with the help of the F-distribution.

Let us consider the case when it cannot be stated beforehand, from the set of experiments, that one of the variances is larger than the other. We can then consider three possibilities: $\sigma_1^2 < \sigma_2^2$, $\sigma_1^2 > \sigma_2^2$ and $\sigma_1^2 = \sigma_2^2$. In this case it is necessary to use two-sided confidence limits, which can be represented by the inequality:

$$\frac{\text{Larger variance}}{\text{Smaller variance}} > F_{p/2}(f_M, f_m)$$

f_M and f_m are the degrees of freedom for the larger and smaller variance values, respectively. The hypothesis $\sigma_1^2 = \sigma_2^2$ will be rejected when the ratio of the larger variance to the smaller variance will exceed the tabulated values of $F_{p/2}(f_M, f_m)$.

Comparison of two means with the help of STUDENT's t-criterion

Suppose that a sample was analyzed by two different methods and the results obtained were:

$$x_1 \; x_2 \; \ldots \; x_{n_1}$$

$$y_1 \; y_2 \; \ldots \; y_{n_2}$$

We wish to determine if there is a statistically significant difference in the results of analysis carried out by these two methods. This problem can be solved with the help of the t-criterion, if the observations follow a normal distribution and the variances of the two systems or methods do not differ significantly from each other (F-test). When these conditions are fulfilled, the weighted mean of the two variances

$$\overline{s^2} = \frac{(n_1 - 1)\, s_x^2 + (n_2 - 1)\, s_y^2}{n_1 + n_2 - 2}$$

and

$$t = \frac{\bar{x} - \bar{y}}{\sqrt{\overline{x^2}}} \quad \frac{n_1 \;\; n_2}{n_1 + n_2}$$

are calculated for verification of the null hypothesis $\mu_x - \mu_y = 0$

The number of degrees of freedom is $f = n_1 + n_2 - 2$. If the value found for t exceeds, in absolute magnitude, the tabulated value for the 1% level of significance, the null hypothesis is rejected, i.e. the means are considered as different.

Comparison of the mean obtained ($\bar{x}$) and the true value (μ)

By means of the STUDENT's t test we can also decide if the divergence between a value that can be considered as the "true value" (μ) of the quantity being measured and the experimentally obtained mean ($\bar{x}$) is statistically significant. In other words, we can verify if the divergence between $\bar{x}$ and μ is accidental (so it can be neglected) or systematic (statistically significant). The value of t is calculated by:

$$t = \frac{\bar{x} - \mu}{s_x / \sqrt{n}}$$

If the calculated value of t is smaller than the tabulated one, for the level of significance chosen, we can consider the divergence between μ and $\bar{x}$ as non-significant.

Confidence limits

The confidence limits of the mean are defined by: $\bar{x} \pm ts_{\bar{x}}$, where t is the tabulated value[11] for a given level of significance, p, and $n - 1$ degrees of freedom. For instance, if p is chosen as 0.05, we can expect, with a probability of 95%, that the sample mean will deviate from the population mean within the limits $\pm ts_{\bar{x}}$.

Non-destructive analysis

The non-destructive analysis were carried out by irradiations for 8 hrs followed by counting at several cooling times. These times were usually a few days to one week, two weeks and one month, approximately, for the thermal neutron analysis. The following radioisotopes were detected in these countings: ^{166}Ho, ^{153}Sm, ^{47}Sc, ^{140}La, ^{24}Na, ^{42}K, ^{122}Sb, ^{177}Lu, ^{181}Hf, ^{141}Ce, ^{160}Tb, ^{233}Pa, ^{51}Cr, ^{175}Yb, ^{131}Ba, ^{46}Sc, ^{59}Fe, ^{147}Nd, ^{182}Ta, ^{152}Eu, ^{60}Co.

The counting time was generally 50 min.

Analysis with chemical separation

Dissolution of the rocks

After irradiation and a cooling time of about 40 hrs, the samples and standard were transferred from the aluminium envelopes to teflon beakers.

Group carriers made up of the following elements were then added: Zn (1 mg), Co (50 μg), Sc (250 μg) and Sm (1 mg). Dissolution was performed with a mixture of 38% HF and 70% $HClO_4$. To a mass of sample of about 100 mg, 4 ml of hydrofluoric acid and 20 drops of perchloric acid were initially added. The mixture was heated in a sandbath and more hydrofluoric acid was added for complete dissolution of the samples. The solution was evaporated to dryness and the residue taken up in 8N hydrochloric acid with gentle heating. A clear solution was obtained for all the rocks subjected to this treatment.

Radiochemical group separation scheme

In Fig. 1 is presented the radiochemical group separation scheme, which is based on the work of MORRISON et al.[9] Four groups were separated.

The following changes were introduced:

(a) Arsenic and bromine results were not requested for the alkaline rocks from the apatite mine and, for this reason, the trapping of volatiles in MORRISON's process was omitted.

(b) The batch and column operation with hydrated antimony pentoxide (HAP) for the retention of sodium was substituted by a single column operation.

(c) The elution of the elements Fe, Co, Cu, Ga and Np, from the anionic resin column, with 0.5N HCl was suppressed and all the elements retained in the column were counted in the same group.

(d) The solvent extraction of Hf, Zr, Sc and Pa with TBP was substituted by extraction chromatography, impregnating the TBP into a silanized kieselguhr column.

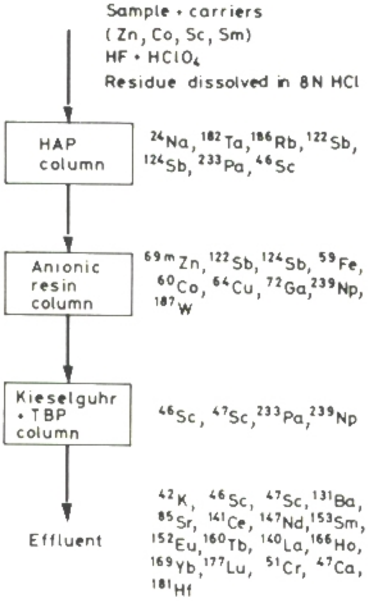

Fig. 1. Radiochemical Group Separation Scheme

Preparation of the columns

Hydrated antimony pentoxide (HAP) column. The HAP was sieved and divided into three fractions. The fraction between 60 and 100 mesh was used to make the columns. Several decantations were necessary to eliminate the finer particles. Clogging of the columns would occur if the HAP was not decanted. This treated HAP was dried at 100 °C for about one hour before use.

Anionic resin column. The anionic resin Amberlite CG-400, Type II, 200 mesh, in the chloride form, was washed with water, to remove the fines, and conditioned with 8N HCl.

Column of kieselguhr impregnated with TBP. Silanized kieselguhr (Merck), of granulometry 0.2–0.3 mm (45–70 mesh ASTM), was mixed with TBP dissolved in diethyl ether. The TBP had been previously washed with 5% Na_2CO_3 according to PEPPARD.[18] After evaporation of the ether, the dried kieselguhr was placed in small portions into the columns, each portion being gently pressed with a glass rod. Conditioning with 8N HCl followed this procedure. The relation of TBP volume to the kieselguhr mass was 1 : 1.

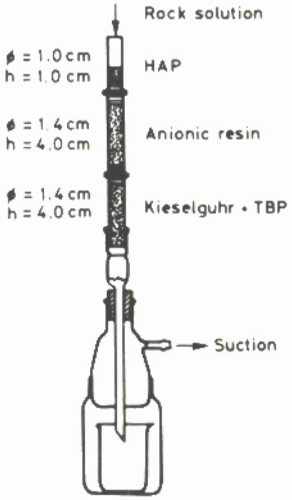

Fig. 2. System of Coupled Columns for Radiochemical Separation

System of coupled columns

Evaporation of the column effluents after each step of the separation process is time consuming. Since in the radiochemical separation process, all the influent solutions must have the same HCl concentration (8N) as the washing solutions, it is not difficult to make the coupling of the three columns. In Fig. 2 such a system is presented.

The solutions (10 ml) were placed in a separatory funnel so that more solution could be slowly added to the first column. Suction was adjusted in order to allow a flow rate of 1 ml/min in the effluent. After the sample solution had passed through the system of three columns, the columns were washed with 30 ml of 8N HCl. The whole process of separation and washing was carried out in about 45 min.

Counting

After group separation, the system of columns was dismounted and the column fillings were transferred to the counting flasks with the aid of a 8N HCl solution. The flasks used for counting were "penicillin" type containers of 2.8 cm external diameter. The material inside the flasks was well mixed and centrifuged to assure a good counting geometry. In the case of counting of the effluent, glass containers of 4.1 cm external diameter were used. The effluent was counted in the collecting flask itself so that losses upon transfer were avoided.

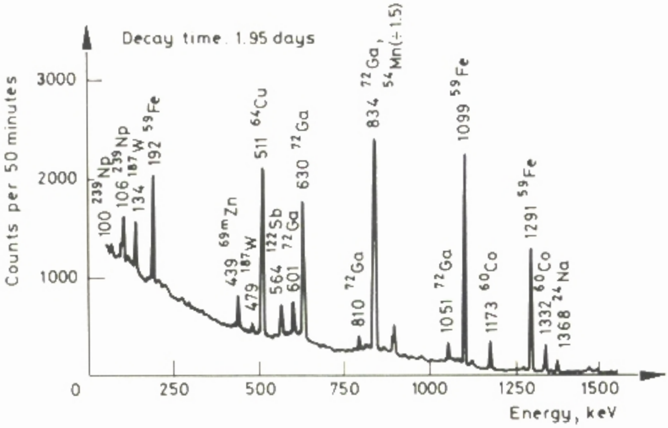

Fig. 3. Destructive Analysis: Gamma-Ray Spectrum of the Anionic Resin Column-Rock BCR-1

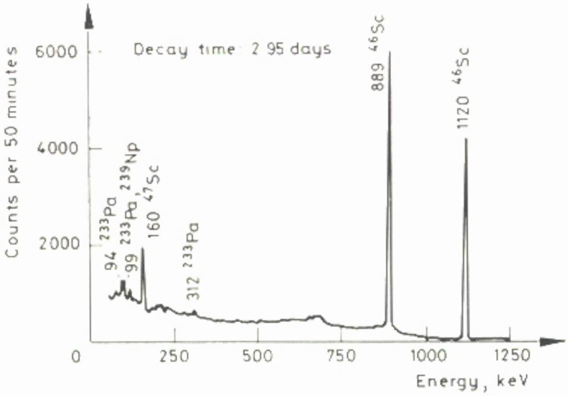

Fig. 4. Destructive Analysis: Gamma-Ray Spectrum of the Kieselguhr Column-Rock BCR-1

Spectra

In Figs 3, 4 and 5 are shown spectra of the second, third and fourth groups of the separation scheme: anionic resin column, kieselguhr impregnated with TBP and effluent, respectively.

In the spectrum corresponding to the anionic resin, most of the radioisotopes which could not be detected in the non-destructive analysis are present: ^{187}W, ^{239}Np, ^{69m}Zn, ^{64}Cu, ^{72}Ga. The spectrum of the kieselguhr column is dominated by the 889 and 1120 keV peaks of ^{46}Sc and only ^{239}Np and ^{233}Pa could also be detected besides ^{46}Sc.

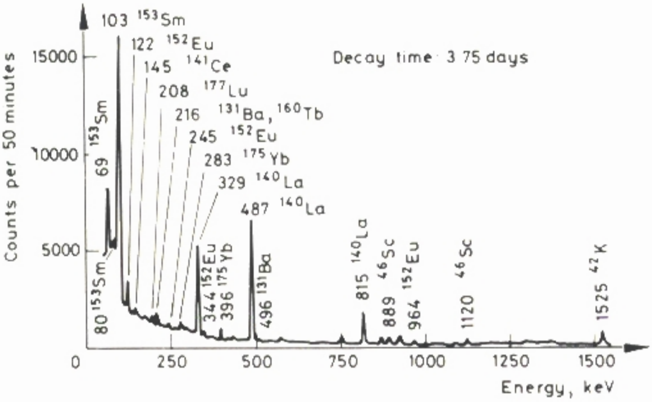

Fig. 5. Destructive Analysis: Gamma-Ray Spectrum of the Effluent-Rock BCR-1

The presence of ^{181}Hf and ^{97}Zr was expected in this column, too, since they both are extracted by TBP. Nevertheless, in the extraction chromatographic column they were not detected. ^{97}Zr was not detected in any group, due to its low activity, but Hf was determined with good results in the effluent. GHERSINI[19] has already observed that at high acid concentrations the stationary and mobile phases of the extraction chromatographic process give rise to hardly predictable volume changes and correlation between liquid-liquid and chromatographic data is often unfeasible.

In the effluent (Fig. 5) are the rare earths, barium and sometimes chromium and potassium. Scandium was also detected several times in the effluent, probably due to leaking of the TBP impregnated into the kieselguhr column, caused by the high pressure necessary to force the solution through the system of three columns.

Results and discussion

In Tables 1, 2, 3, 4 and 5 the results of INAA and RNAA are presented. In Table 6 are presented the results for ENAA of rock Hj 130/1. In Table 1 FLANAGAN's[10] results for the standard rock AGV-1 are also presented as well as some of the data obtained by GORDON[4] for this same rock in his classical work of instrumental activation analysis with high resolution gamma-ray detectors.

Although the present study was more specifically concerned with trace element determinations, some major and minor elements were also analyzed, since the data for the calculations were available as in the case of iron, calcium, sodium and potassium.

Table 1

Results of the analysis of the standard

Element	INAA		RNAA	
	No. of analyses	Confidence limit	No. of analyses	Confidence limit
Fe	7	4.81% ± 0.20	6	4.82% ± 0.41
Ca	7	3.00% ± 0.28	(a)	(a)
Na	5	3.26% ± 0.31	6	3.52% ± 0.44
K	(a)	(a)	4	2.39% ± 0.25
Ba	7	1307 ± 66	4	1196 ± 213
Ta	5	0.99 ± 0.08	3	1.04 ± 0.64
Rb	(a)	(a)	1	87
Co	7	16.6 ± 1.1	4	15.2 ± 2.9
Cu	(a)	(a)	5	60 ± 4
Zn	(a)	(a)	6	88 ± 4
Ga	(a)	(a)	5	19.9 ± 1.1
W	(a)	(a)	5	0.46 ± 0.18
Sb	(a)	(a)	6	4.1 ± 0.3
Hf	7	5.4 ± 0.6	1	5.3
Sc	7	12.4 ± 0.55	5	13.1 ± 2.2
Cr	4	14 ± 4	(a)	(a)
La	7	40 ± 2	4	39 ± 3
Ce	7	97 ± 14	3	64 ± 5
Nd	(a)	(a)	1	30
Sm	6	5.8 ± 0.3	4	5.6 ± 0.2
Eu	7	1.76 ± 0.16	4	1.67 ± 0.27
Tb	6	0.56 ± 0.18	2	0.56 ± 0.20
Ho	1	1.5	2	0.59 ± 0.12
Yb	7	1.74 ± 0.25	4	1.70 ± 0.57
Lu	8	0.28 ± 0.02	4	0.31 ± 0.13
U	(a)	(a)	3	2.0 ± 0.6
Th	8	6.5 ± 0.4	5	7.2 ± 2.1

Results are given in ppm unless otherwise indicated.
(a) Analysis not made.
(b) Not reported.

rock AGV-1 by INAA and RNAA

FLANAGAN's results[10]	GORDON's results[4]	Relative standard deviation, %		Relative error, %	
		INAA	RNAA	INAA	RNAA
4.74%	4.3 ± 0.2	4.4	8.1	1.5	1.6
3.50%	(b)	10.2	(a)	14.3	(a)
3.16%	3.15% ± 0.15	7.7	12.0	3.2	11.5
2.40%	2.2% ± 0.4	(a)	6.6	(a)	0.54
1208	1180 ±100	5.5	11.2	8.2	0.99
0.9	1.0 ± 0.2	6.8	24.8	10.0	15.2
67	61 ± 10	(a)	(a)	(a)	29.8
14.1	14.7 ± 0.5	7.7	12.1	17.7	7.6
59.7	(b)	(a)	6.0	(a)	0.86
84	(b)	(a)	10.7	(a)	5.2
20.5	(b)	(a)	3.1	(a)	2.9
0.55	(b)	(a)	31.0	(a)	16.2
4.5	5.2 ± 1.0	(a)	6.2	(a)	8.2
5.2	5.4 ± 0.2	12.3	(a)	3.8	1.9
13.4	11.7 ± 0.4	4.8	13.5	7.5	2.3
12.2	8.6 ± 1.5	18.6	(a)	14.7	(a)
35	33 ± 3	5.9	5.0	14.3	10.2
63	57 ± 3	15.8	3.1	54.0	1.3
39	(b)	(a)	(a)	(a)	21.7
5.9	5.4 ± 0.5	4.7	2.2	1.7	5.8
1.7	1.55 ± 0.06	10.1	10.0	3.5	1.8
0.70	0.77 ± 0.04	31.2	3.9	20.0	19.8
6.6	(b)	(a)	2.3	150.0	2.2
1.7	1.6 ± 0.3	16.5	20.9	2.3	0.18
0.28	0.37 ± 0.06	9.9	26.6	1.4	10.5
1.88	(b)	(a)	12.9	(a)	5.8
6.41	7.0 ± 0.5	7.5	24.1	1.4	11.7

Table 2
Statistical tests applied for the comparison of INAA and RNAA
(U.S.G.S. Reference Sample AGV-1)

Element determined	F-test comparison of variances	t-test comparison of means	Comparison of μ and $\bar{x}$		Classification*	
			INAA	RNAA	INAA	RNAA
Fe	–	–	–	–	E	E
Ca	(a)	(a)	+	(a)	A	(a)
Na	–	–	–	–	E	A
K	(a)	(a)	(a)	–	(a)	E
Ba	–	+	+	–	E	A
Ta	+	(a)	+	–	E	U
Co	–	–	+	–	A	A
Cu	(a)	(a)	(a)	–	(a)	E
Zn	(a)	(a)	(a)	+	(a)	A
Ga	(a)	(a)	(a)	–	(a)	E
W	(a)	(a)	(a)	–	(a)	U
Sb	(a)	(a)	(a)	+	(a)	E
Hf	(a)	(a)	–	(a)	A	(a)
Sc	+	(a)	+	–	E	A
Cr	(a)	(a)	–	(a)	A	(a)
La	–	–	+	+	A	E
Ce	+	(a)	+	–	U	E
Sm	–	–	–	+	E	E
Eu	–	–	–	–	E	E
Tb	–	–	–	–	U	E
Ho	(a)	(a)	(a)	–	(a)	E
Yb	–	–	–	–	A	A
Lu	+	(a)	–	–	E	U
U	(a)	(a)	(a)	–	(a)	A
Th	+	(a)	–	–	E	U

(a) Analysis not made.
\+ Variances or means significantly different.
– Variances or means not significantly different.
* McFARREN et al.[12] :– ECKSCHLAGER[13] criterion-E: Excellent; A: Acceptable; U: Unacceptable.

Considering the results presented in the Tables and the statistical tests applied, it is possible to draw the following conclusions, about the methods of analysis used.

Thermal neutron activation analysis (INAA and RNAA)

Comparison of means. In general, there is a good agreement between the means obtained by the two methods (destructive and non-destructive) for all the rocks analyzed. This agreement was checked by using the t test applied for the comparison of means, when possible, that is, when there was no statistically significant difference between the variances. When the application of this test was not possible, the comparison was made considering the calculated confidence limits.

The main differences between the two methods occurred for the elements cerium (in all rocks), holmium (AGV-1), chromium (Hj 4A and Hj 7), antimony (Hj 7 and Hj 130/1), terbium (Hj 4A and Hj 130/1), ytterbium (Hj 130/1), neodymium (Hj 130/1), barium (AGV-1), sodium (Hj 4A) and potassium (Hj 4A). Such a discrepancy is readily explained in the case of cerium by the interference of the 142 keV peak of ^{59}Fe in the 145 keV peak of ^{141}Ce in the case of INAA. When radiochemical separation is performed, this interference is eliminated and better results are obtained for cerium. This can be observed in Table 1 if we compare the results for the two methods, with the values presented by FLANAGAN[10] and GORDON.[4] The best result for cerium comes from the radiochemical analysis.

In the radiochemical determination of antimony, there were some problems related to the unreproducible chemical behaviour of this element during the group separation process. Antimony is partly retained in the HAP column, probably by isotope exchange, and it is difficult to make the necessary corrections due to the high activity of ^{24}Na in this column, which interferes with the counting of ^{122}Sb. The peaks of ^{124}Sb are also detected in this column after the decay of sodium but their activity is very low. For the elements holmium, chromium, terbium, ytterbium, in all rocks, we can relate the high errors to bad counting statistics since the concentrations of these elements, and consequently the corresponding activities, were rather low. Especially in the case of chromium, the main problem was the low concentration of this element in the rock BCR-1 used as standard.

In the case of barium and sodium, the differences encountered between the means obtained by INAA and RNAA were not expected. For potassium in rock Hj 4A, only one result was obtained by INAA and the activity of the 1525 keV of ^{42}K at the time of counting was very low, which would lead us to consider as better the result achieved by RNAA.

Precision. In the case of the elements analyzed by both methods, and for which it was possible to make a comparison, the reproducibility, represented by the

Table 3
Results of the analysis of ijolite (Hj 4A) and statistical tests for the comparison of INAA and RNAA

Element determined	INAA		RNAA		Relative standard deviation, %		F-test comparison of variances	t-test comparison of means
	No. of analyses	Confidence limit	No. of analyses	Confidence limit	INAA	RNAA		
Fe	8	7.22% ± 0.42	7	7.50% ± 0.28	6.8	4.0	–	–
Ca	6	8.69% ± 0.60	(a)	(a)	6.6	(a)	(a)	(a)
Na	4	3.55% ± 0.19	6	3.86% ± 0.16	3.4	3.9	–	+
K	1	1.87%	8	2.36% ± 0.14	(a)	7.3	(a)	(a)
Ta	(a)	(a)	2	0.81 ± 0.94	(a)	10.1	(a)	(a)
Rb	(a)	(a)	4	46 ± 6	(a)	8.0	(a)	(a)
Co	5	47 ± 4	7	47 ± 4	9.9	8.4	–	–
Cu	(a)	(a)	7	19.0 ± 1.7	(a)	9.9	(a)	(a)
Zn	(a)	(a)	6	51 ± 6	(a)	11.0	(a)	(a)
Ga	(a)	(a)	7	13.9 ± 0.7	(a)	5.7	(a)	(a)
W	(a)	(a)	7	0.80 ± 0.16	(a)	21.8	(a)	(a)
Sb	2	2.0 ± 5.9	7	1.9 ± 0.5	32.8	29.0	–	–

Hf	5	3.0 ± 0.4	6	3.1 ± 0.5	11.5	14.5	–	–
Sc	8	36.4 ± 1.4	8	36.9 ± 1.6	4.6	5.0	–	–
Cr	4	107 ± 24	8	185 ± 21	14.1	13.6	–	+
La	8	14.0 ± 1.3	7	14.8 ± 0.7	10.9	4.8	+	(b)
Ce	8	29.4 ± 1.9	7	35.1 ± 1.2	7.9	3.7	–	+
Nd	1	23	6	18 ± 6	(a)	24.9	(a)	(a)
Sm	7	3.68 ± 0.07	8	3.80 ± 0.21	2.0	6.7	+	(b)
Eu	8	1.16 ± 0.12	7	1.07 ± 0.03	12.3	3.1	+	(b)
Tb	2	0.20 ± 0.14	4	0.43 ± 0.20	77.3	29.4	–	–
Ho	(a)	(a)	8	0.27 ± 0.06	(a)	29.2	(a)	(b)
Yb	3	0.79 ± 0.21	8	0.72 ± 0.06	10.7	10.4	–	–
Lu	5	0.12 ± 0.02	8	0.12 ± 0.03	14.5	26.3	–	–

Results are given in ppm unless otherwise indicated.

(a) Analysis not made.

(b) Comparison not possible (t-test not applicable due to different variances).

\+ Variances or means significantly different.

– Variances or means not significantly different.

Table 4
Results of the analysis of the piroxenite (Hj 7) and statistical tests applied for the comparison of INAA and RNAA

Element determined	INAA		RNAA		Relative standard deviation, %		F-test comparison of variances	t-test comparison of means
	No. of analyses	Confidence limit	No. of analyses	Confidence limit	INAA	RNAA		
Fe	8	11.32% ± 0.33	8	11.42% ± 0.45	4.0	4.7	–	–
Ca	7	10.32% ± 0.43	(a)	(a)	4.8	(a)	(a)	(a)
Na	6	0.233% ± 0.007	8	0.222% ± 0.0012	2.9	4.0	–	–
K	(a)	(a)	2	55 ± 12	(a)	2.3	(a)	(a)
Ta	(a)	(a)	7	0.53 ± 0.18	(a)	37.1	(a)	(a)
Co	8	72 ± 4	8	69 ± 3	6.7	5.7	–	–
Cu	(a)	(a)	8	11.4 ± 0.7	(a)	7.5	(a)	(a)
Zn	(a)	(a)	6	53 ± 9	(a)	16.9	(a)	(a)
Ga	(a)	(a)	8	13.3 ± 0.7	(a)	6.7	(a)	(a)
Sb	2	1.58 ± 8.26	8	1.10 ± 0.20	58.2	22	+	(b)

Hf	7	4.1 ± 0.3	6	4.3 ± 0.3	8.2	5.8	–	–
Sc	7	78 ± 2	8	83 ± 5	2.2	6.6	+	(b)
Cr	5	511 ± 53	8	455 ± 74	8.3	19.3	–	+
La	6	7.9 ± 0.5	8	7.6 ± 0.2	6.2	3.9	–	–
Ce	1	7.5	8	20.3 ± 1.0	(a)	5.7	(a)	(a)
Nd	(a)	(a)	6	17.5 ± 1.1	(a)	6.2	(a)	(a)
Sm	8	3.07 ± 0.09	8	3.08 ± 0.05	3.3	2.0	–	–
Eu	8	1.09 ± 0.14	8	1.06 ± 0.08	15.4	9.1	+	(b)
Tb	(a)	(a)	4	0.30 ± 0.07	(a)	14.0	(a)	(a)
Ho	(a)	(a)	6	0.20 ± 0.06	(a)	26.4	(a)	(a)
Yb	1	0.38	7	0.44 ± 0.04	(a)	8.8	(a)	(a)
Lu	5	0.10 ± 0.04	7	0.080 ± 0.010	29.0	13.3	+	(b)

Results are given in ppm unless otherwise indicated.
(a) Analysis not made.
(b) Comparison not possible (t-test not applicable due to different variances).
\+ Variances or means significantly different.
– Variances or means not significantly different.

Table 5
Results of the analysis of carbonatite (Hj 130/1) and statistical tests applied for the comparison of INAA and RNAA

Element determined	INAA		RNAA		Relative standard deviation, %		F-test comparison of variances	t-test comparison of means
	No. of analyses	Confidence limit	No. of analyses	Confidence limit	INAA	RNAA		
Fe	8	2.22% ± 0.15	6	2.11% ± 0.09	7.9	4.0	–	–
Ca	4	25.7% ± 1.6	(a)	(a)	4.0	(a)	(a)	(a)
Na	5	0.0233 ± 0.0011	4	0.023% ± 0.0023	3.9	6.4	–	–
K	1	0.098%	5	0.085% ± 0.009	(a)	8.4	(a)	(a)
Ba	4	963 ±214	6	961 ± 62	14.0	6.9	–	–
Ta	(a)	(a)	3	1.4 ± 0.8	(a)	22.5	(a)	(a)
Co	7	15 ± 1	7	16.2 ± 0.6	8.2	4.3	–	–
Cu	(a)	(a)	6	9.2 ± 2.8	(a)	29.1	(a)	(a)
Zn	(a)	(a)	3	16.2 ± 0.8	(a)	1.9	(a)	(a)
Sb	4	3.9 ± 2.5	7	1.6 ± 0.5	39.9	31.4	+	(b)

Sc	8	14.1 ± 0.8	8	14.8 ± 1.5	6.4	11.9	–	–
Cr	3	11.0 ± 3.9	(a)	(a)	14.2	(a)	(a)	(a)
La	8	134 ± 8	6	137 ± 7	7.5	5.1	–	–
Ce	8	370 ± 18	6	268 ± 7	5.8	2.4	+	(b)
Nd	1	93	6	156 ± 14	(a)	8.8	(a)	(a)
Sm	8	21.8 ± 1.4	6	22.9 ± 0.9	7.4	3.9	–	–
Eu	8	5.8 ± 0.4	6	5.2 ± 0.5	8.7	8.6	–	–
Tb	5	1.0 ± 0.3	6	1.8 ± 0.2	27.7	9.7	–	+
Ho	(a)	(a)	6	1.3 ± 0.1	(a)	8.2	(a)	(a)
Yb	8	1.70 ± 0.17	7	2.20 ± 0.22	12.0	11.0	–	+
Lu	8	0.24 ± 0.02	6	0.27 ± 0.04	11.7	12.4	–	–
Th	3	0.87 ± 0.42	(a)	(a)	19.6	(a)	(a)	(a)

Results are given in ppm unless indicated.
(a) Analysis not made.
(b) Comparison not possible (t-test not applicable due to different variances).
\+ Variances or means significantly different.
– Variances or means not significantly different.

standard deviations or by the variances, were generally not significantly different. This was demonstrated by the application of the F-test for the comparison of variances.

A higher precision was obtained with the non-destructive method for the following elements: tantalum (AGV-1), scandium (AGV-1 and Hj 7), samarium (Hj 4A), lutetium (AGV-1) and thorium (AGV-1). The lower precision for scandium and thorium in the case of RNAA, can be explained in terms of the necessity of summing up the activities encountered in more than one column. For tantalum, a much lower activity was obtained in the HAP column as compared with the activity of this element counted in the non-attacked rock due to less favourable counting geometry. The destructive procedure showed a better reproducibility for the elements lanthanum (Hj 4A), cerium (AGV-1, Hj 130/1), europium (Hj 4A, Hj 7) lutetium (Hj 7) and antimony (Hj 7, Hj 130/1). For cerium, as already pointed out, the elimination of the interference of iron by chemical group separation leads to much better results for this element. For the case of antimony and lanthanum, the problem in the non-destructive analysis was the low activity of the radioisotopes ^{140}La and ^{122}Sb, since it was necessary to wait for the decay of the majority of ^{24}Na before the counting of ^{140}La and ^{122}Sb. The precision of RNAA for antimony was also not very good, due to unreproducible chemical behaviour, but still better than that of INAA. For europium and lutetium there is no apparent reason why one or the other method should be better.

The relative standard deviations for most elements in all rocks, were lower than 10%, which is generally considered as a good result in trace analysis.

The cases where the reproducibility was not so good were mainly the following: elements whose radioisotopes used for the analysis suffer significative interferences in thei peaks. Such was the case of interference of ^{59}Fe and ^{141}Ce peaks in the instrumental analysis; elements that, in the radiochemical separation process, are distributed among the groups, making it necessary to sum the activities present in each group with a consequent increase in the total error, as in the case of scandium and thorium; elements that, due to their low thermal neutron absorption cross-sections, give low activities for Ge(Li) counting, such as zinc, barium and neodymium; elements that occur in very low concentrations in the rocks. Among these are terbium, lutetium, holmium, ytterbium, tungsten and hafnium.

Accuracy. The study of accuracy was made by comparison of the results obtained by INAA and by RNAA with the results published by FLANAGAN[10] for the rock AGV-1. Student's t-test was used for such a comparison. The test was applied for all the elements analyzed, even though FLANAGAN's "recommended values" were not available for all of them.

In the case of some of the elements for which FLANAGAN's recommended values[10] are available, there was a statistical significant difference between the mean obtained ($\bar{x}$) and the "true value" (μ) for zinc in the radiochemical method, and barium and tantalum in the non-destructive procedure. The determination of zinc was unfavourable due to bad counting statistics of the 439 keV peak of ^{69m}Zn since the cross-section for the formation of ^{69m}Zn with thermal neutrons is very low. In the destructive analysis, the value of d (difference between μ and $\bar{x}$) was higher for tantalum than in the non-destructive process, but since the spread between the results obtained was broad, a statistically significant divergence between the mean and the real value could not be established.

For the determination of barium, the mean obtained was much higher than the value of FLANAGAN in the non-destructive determination, while in the destructive one a good agreement was obtained.

Let us consider now the elements for which FLANAGAN's recommended values are not available in rock AGV-1 and for which the t-test showed a significant difference between the result found and the tabulated (although not recommended) value.

Calcium

Calcium was determined non-destructively only and the result obtained using the 160 keV peak of ^{47}Sc (3.00% ± 0.28%) was lower than the value of FLANAGAN (3.50%). BRUNFELT and STEINNES[2] also found low results for calcium in BCR-1, by measuring the 160 keV peak and using pure calcium standards.

Cobalt

The main difference found was in the non-destructive determination. But both results, that is, destructive (15.2 ppm) and non-destructive (16.6 ppm), were higher than the value of FLANAGAN (14.1 ppm). It must be considered that the value for cobalt in the rock BCR-1, taken as standard, is only an "order of magnitude". If the result reported by BRUNFELT and STEINNES[2] for cobalt in BCR-1 were used as reference, lower values would be obtained, that is, 14,4 ppm for the radiochemical and 15.4 ppm for the instrumental method.

Antimony

This element was determined only after chemical group separation in the rock AGV-1, and the calculated mean (4.1 ppm) was somewhat lower than the reference value (4.5 ppm). This fact can be attributed to the non-reproducible chemical behaviour shown by antimony, which was retained in varying proportions in the HAP column, besides being found in the anionic resin column too.

Corrections were applied for the amount adsorbed by the HAP, but they could be made by only after practically all of the ^{24}Na had decayed. Under these conditions the activities corresponding to the peaks of ^{122}Sb and ^{124}Sb were very small, and the errors due to bad counting statistics were high.

Scandium

A low mean value (12.4 ppm) was obtained for scandium, compared with FLANAGAN's value (13.4 ppm), in the instrumental method. The value of FLANAGAN for this element in BCR-1 (33 ppm) is also an "order of magnitude". Recourse to the result of BRUNFELT and STEINNES (30.7 ppm) would lead to a still lower mean for scandium.

Lanthanum

Both methods gave high results for lanthanum in AGV-1 (INAA, 40 ppm; RNAA 39 ppm) compared with the 35 ppm value of FLANAGAN, which is a mean of the results obtained by several authors. The mean published by BRUNFELT and STEINNES[2] for BCR-1 is equal to 23.7 ppm, which would lead to lower results (36 and 35 ppm for the non-destructive and destructive methods, respectively). GORDON[4] obtained a mean of 33 ± 3 ppm for lanthanum.

Cerium

The mean obtained radiochemically for cerium (64 ± 5 ppm) agreed very well with the result of FLANAGAN[10] (63 ppm). It must be remarked that the value for cerium in BCR-1, on which the determination was based, was a "recommended value". The result obtained non-destructively was 97 ± 14 ppm because of interference of ^{59}Fe.

Samarium

A low mean (5.6 ± 0.2 ppm) was obtained with the destructive method as compared with the instrumental procedure (5.8 ± 0.3 ppm) and with FLANAGAN's[10] result (5.9 ppm). No apparent reason was found for this fact.

It can be concluded that the use, as standards, of the values published by FLANAGAN[10] for the elements in rock BCR-1 lead, in general, to good results. When only "order of magnitude" values are available in FLANAGAN's work,[10] results published by other authors, like BRUNFELT and STEINNES,[2] can be used.

Total error. The statistical test for the evaluation of the total error of analytical methods, developed by McFARREN[12] and modified by ECKSCHLAGER,[13] classify the methods as "Excellent", "Acceptable" or "Unacceptable", with total errors up to 25% (Excellent), larger than 25% but smaller than 50% (Acceptable) and larger than 50% (Unacceptable). McFARREN's[12] "total error" is defined as

$$\text{Total error} = 100\,\frac{d + 2s}{\mu}$$

where μ – true value;

d – absolute value of the mean error $= |\mu - \bar{x}|$;

s – standard deviation.

In the present work, it was found that both the purely instrumental and the radiochemical methods could be classified in the "Excellent" or "Acceptable" category for most of the elements determined, as shown by Table 2. This study of error was done only for rock AGV-1, since for the apatite mine rocks there were no values of reference to be taken for the calculation of the mean error, $d = \mu - \bar{x}$.

The elements for which either the RNAA or INAA method gave "Unacceptable" results were those that suffer serious interferences, like cerium (INAA), or those that give rise to very low activities, like terbium, tantalum, tungsten, lutetium and thorium, due to very low proportion in the samples. In the case of thorium, there is also the problem of distribution of its descendant, protactinium-233, in more than one column, which increases the error due to summing up of activities.

Considering the elements that could be determined by both methods, we come to the conclusion that there is no marked superiority of one method to the other, as far as the total error criterion is concerned.

Advantage of the radiochemical method. The main advantage of the radiochemical method was that, in the case of the present work, a larger number of elements could be determined. This was especially true for those elements that give rise to radioisotopes of half-lives close to the half-life of ^{24}Na (15.0 hrs), like copper, gallium, tungsten and zinc, since ^{24}Na is a rather high "interfering element" in the INAA method. Besides this, the group separation implies lowering the counting background of each group, so that some very small peaks, like the 1077 keV peak of ^{86}Rb could be detected, after the decay of ^{24}Na, and which could not be detected in the INAA.

Comparison with the results obtained by GORDON. If we compare, in Table 1, the results obtained by GORDON et al.[4] for the instrumental analysis of the rock AGV-1, with the ones obtained in the present work, we come to the conclusion that there is a fairly good agreement for most of the elements analyzed, considerin the confidence limits established for each element. Greater divergences were found for the elements, lanthanum, cerium, terbium and chromium.

It can also be observed that, for most of the elements, the means of the results obtained in the present work, either by the instrumental or the destructive method were closer to the values reported by FLANAGAN[10] than the means presented by GORDON et al.[4] Only in the cases sodium, lanthanum, terbium and cobalt did the contrary occur.

It can be concluded that the USGS rocks can be used successfully as standards for the activation analysis of trace elements in geological samples.

Epithermal neutron activation analysis of carbonatite

It can be seen from Table 6, that a smaller number of elements were determine by epithermal activation of the carbonatite. This is due to the fact that the resona integrals for most of the elements under consideration are low.

For three elements, tantalum, terbium and holmium, ENAA was more advantageous than INAA or RNAA in the case of the carbonatite rock. This can be easily confirmed by the results in Table 6, that is, 1.99 ± 0.09 ppm for tantalum, 1.45±0 ppm for terbium and 1.02 ± 0.03 ppm for holmium; the confidence limits calculate

Table 6
Epithermal neutron activation analysis of the carbonatite (Hj 130/1).
Results and statistical tests applied for the comparison with INAA

Element determined	No. of analyses	Confidence limits, ppm	Relative standard deviation, %	ENAA vs. INAA	
				F-test	t-test
Ba	8	1036 ± 76	7.9	–	–
Ta	8	1.99 ± 0.09	5.0	+	(a)
Sc	8	12.1 ± 0.4	3.8	–	+
La	8	138 ± 18	16.0	+	(a)
Ce	2	227 ± 288	14.1	–	+
Sm	8	22.4 ± 0.98	5.2	–	–
Eu	7	5.1 ± 0.8	17.1	–	–
Tb	7	1.45 ± 0.05	4.1	+	(a)
Ho	7	1.02 ± 0.03	3.0	+	(a)

(a) Comparison not possible (t-test not applicable due to different variances).
\+ Variances or means significantly different.
– Variances or means not significantly different.

for ENAA were narrower and the relative standard deviations much smaller than in thermal neutron activation. Two of these elements, holmium and tantalum, could not be determined by INAA. Some results could be obtained by RNAA, but they were of inferior quality.

In the case of samarium, cerium, barium and scandium, the reproducibilities obtained by the two instrumental methods (ENAA and INAA) were of the same order, as demonstrated by the application of the F-test. Nevertheless, only for samarium and barium was the hypothesis of equality of the means considered as valid, through a t-test. The comparison of RNAA with ENAA leads to very similar conclusions.

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