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ACTIVATION ANALYSIS OF GEOLOGICAL MATERIAL USING RUTHENIUM AS A MULTIISOTOPIC COMPARATOR*

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The isotopes ^{97}Ru, ^{103}Ru and ^{105}Ru, produced by reactor irradiation of elemental ruthenium, were applied as triple comparators in the activation analysis of rock FU-41, a basanitoid from Fuerteventura, Canary Island. The concentrations of the following elements were determined: Sm, Sc, Fe, Co, Na, La, Hf, Eu, Th and Cr. The aim of this work was the experimental control of the error theory of the multiple comparator method as well as the experimental check of the accuracy.

Introduction

In earlier work[1,2] a relative multiple comparator method was proposed, making it possible to calculate the specific standard activities from the specific activities of at least two comparator isotopes irradiated together with the samples. An error theory was developed so as to obtain information about errors due to the pertinent variables.

This paper describes the application of ruthenium as a multiple comparator for reactor neutron activation analysis of a basanitoid from Fuerteventura, Canary Island. The concentrations of the elements Sm, Sc, Fe, Co, Na, La, Hf, Eu, Th and Cr were determined and compared with those obtained by classical activation analysis. This comparison made it possible to draw conclusions about the precision and the accuracy of the comparator method. This supplied additional information about the validity of the error theory of the comparator method.

Principles and errors of the multiple comparator method

In classical activation analysis use is made of the proportionality between the induced isotopic activities and the weights of sample and standard elements. Assuming identical parameters for standard and sample one can write:

$$\frac{A_x}{A_{st}} = \frac{w_x}{w_{st}} \qquad \text{or} \qquad A_{sp,x} = A_{sp,st} \tag{1}$$

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where A_x – activity induced in the sample;
A_{st} – activity induced in the standard;
w_x – weight of the sample;
w_{st} – weight of the standard;
$A_{sp,x}$ – specific activity of the sample;
$A_{sp,st}$ – specific activity of the standard.

Practical circumstances at times do not allow to work under identical conditions for samples and standards, e. g. when the place in the irradiation container is limited or the composition of the sample is unknown. These difficulties can be overcome by the use of a multiple comparator technique requiring the following steps:

(1) Experimental determination of a k_{ref} factor for each standard. These k_{ref} factors are defined as the ratio of the specific activity of a standard isotope to the specific activity of a comparator isotope in a reference irradiation position with a known thermal to epithermal reactor neutron flux ratio $(\Phi_{th}/\Phi_{epi})_{ref}$:

$$k_{ref} = \left(\frac{A_{sp,st}}{A_{sp,comp}}\right)_{ref} \tag{2}$$

(2) Experimental determination of $(\Phi_{th}/\Phi_{epi})_{anal}$, the thermal to epithermal neutron flux ratio in the analysis reactor position, which may be arbitrary chosen. This ratio can be calculated from the experimentally determined R value, defined as the ratio of the specific activities of two comparator isotopes (denoted as 1 and 2) after irradiation in the reference position, divided by the ratio of the specific activities of the same comparator isotopes after irradiation in the analysis position.

$$R = \frac{\left(\frac{A_{sp,1}}{A_{sp,2}}\right)_{ref}}{\left(\frac{A_{sp,1}}{A_{sp,2}}\right)_{anal}} = \frac{[f_{ref} + D_1][f_{anal} + D_2]}{[f_{ref} + D_2][f_{anal} + D_1]} \tag{3}$$

and

$$f_{anal} = \frac{R[f_{ref}D_1 + D_1D_2] - [f_{ref}D_2 + D_1D_2]}{[f_{ref} + D_1] - R[f_{ref} + D_2]} \tag{4}$$

where $f = \dfrac{\Phi_{th}}{\Phi_{epi}}$

$D = \dfrac{I_0}{\sigma_{th}}$, the ratio of the activation resonance integral at inifinite dilution to the thermal neutron activation cross-section.

(3) Conversion of the k_{ref} values to k_{anal} factors by the relation:

$$k_{anal} = k_{ref} \frac{[f_{anal} + D_{st}][f_{ref} + D_{comp}]}{[f_{anal} + D_{comp}][f_{ref} + D_{st}]} \tag{5}$$

(4) Calculation of the specific standard activities in the analysis reactor position $(A_{st,st})_{anal}$ from Eq. (6):

$$(A_{sp,st})_{anal} = k_{anal} (A_{sp,comp})_{anal} \tag{6}$$

The error factors Z_f, Z_k and Z, caused by the mathematical operations described above, can be defined as

$$Z_f = \frac{\left|\frac{d f_{anal}}{f_{anal}}\right|}{\left|\frac{dR}{R}\right|} \tag{7}$$

$$Z_k = \frac{\left|\frac{d k_{anal}}{k_{anal}}\right|}{\left|\frac{d f_{anal}}{f_{anal}}\right|} \tag{8}$$

and

$$Z = Z_f Z_k = \frac{\left|\frac{d k_{anal}}{k_{anal}}\right|}{\left|\frac{dR}{R}\right|} \tag{9}$$

From the mathematical treatment of the error factors the following conclusions can be drawn:

(1) Z_f is an error multiplication factor, as it is always larger than unity. It decreases when using two comparators with a large spread on their I_0/σ_{th} values and if their harmonic mean approximates to the value of the flux ratio in the analysis reactor position. Obviously Z_f is independent of the f_{ref} value.

(2) Z_k is an error reduction factor, as it is always smaller than unity. It decreases when the I_o/σ_{th} values for standard and comparator isotopes are similar and when their harmonic mean is very different from f_{anal}.

(3) The total error change factor is given by $Z = Z_f \cdot Z_k$.

The use of ruthenium as a multiisotopic comparator element

From the compilation of I_o/σ_{th} values[3,4] it appears that ruthenium can serve as the most suitable multiisotopic omparator element. Reactor neutron activation leads to the formation of three ruthenium radioisotopes which can be measured simultaneously on a Ge(Li) detector: ^{97}Ru, ^{103}Ru, and ^{105}Ru. Their nuclear data are summarized in Table 1. It is apparent that the spread on the I_o/σ_{th} values for the combination ^{103}Ru (I_o/σ_{th} = 3.3) – ^{97}Ru (I_o/σ_{th} = 23.1) is sufficiently large to give reliable results for most flux ratio determinations encountered in practical work. The other combinations ^{103}Ru - ^{105}Ru (I_o/σ_{th} = 13.0) and especially ^{105}Ru - ^{97}Ru will give acceptable results only when the flux ratio in the analysis reactor position is not much different from the harmonic mean of the respective I_o/σ_{th} values. With the exception of the last comparator set, it can be emphasized that the spread on the I_o/σ_{th} values is better than or comparable to that of the formerly used combination ^{60}Co (I_o/σ_{th} = = 2.03) - ^{198}Au (I_o/σ_{th} = 15.7).

As the absorption cross-section σ_a and the absorption resonance integral I_a for ruthenium are not higher than 2.6 b and 42 b respectively, it becomes possible to irradiate relatively large amounts of this comparator element without self-shielding effects. This is an additional advantage over Co and Au ($\sigma_{a_{Au}}$ = 98.8 b, $I_{a_{Au}}$ = 1,550; $\sigma_{a_{Co}}$ = 37 b, $I_{a_{Co}}$ = 75 b), which should be irradiated in a diluted form, e.g. Co - Al or Au - Al alloys.

The Ru isotopes give rise to satisfactory counting statistics on Ge(Li) detectors. As the most important γ-lines are between 200 and 750 keV (Fig. 1), no appreciable γ-attenuation occurs in the Ru samples when their weight is kept below 20 mg. This amount, irradiated in an integrated flux of 10^{15} n $\cdot$ cm^{-2}, supplies 10^2 counts per second in each of the 216, 497 and 724 keV peaks after 20 hr cooling, when placed 3 cm from a Ge(Li) detector with a 7.8% efficiency. The half-lives of the Ru isotopes allow a certain flexibility with respect to the irradiation and decay time. Indeed, the 4.44 hr ^{105}Ru isotope decays to the 35.5 hr ^{105}Rh daughter isotope, and thus the 319 keV line of the latter can be measured after an appropriate waiting period. For short decay times the 499 keV γ-line of ^{105}Ru disturbs the 497 keV γ-line of ^{103}Ru, as shown in Fig. 1.

This interfering 499 keV γ-ray is given in some references,[6,10] but is not mentioned elsewhere.[7,8]

Long irradiations at high fluxes do not cause an appreciable burn-up of the radioactive Ru isotopes as is the case with Au.

To enable γ-counting with a liquid source, Ru can be irradiated as the specpure, water-soluble compound $(NH_4)_2Ru(H_2O)Cl_5$.

Table 1
Nuclear Data for the Ru isotopes

Data \ Target nuclide	^{96}Ru	^{102}Ru	^{104}Ru
Reaction	^{96}Ru(n,γ)^{97}Ru	^{102}Ru(n,γ)^{103}Ru	^{104}Ru(n,γ)^{105}Ru ^{105}Ru $\xrightarrow{\beta^-}$ ^{105}Rh
Half-life[5]	2.89 d	39.8 d	4.44 h ^{105}Rh: 35.5 h
Abundance,[5] %	5.51	31.61	18.58
σ_{th}[5]	0.21	1.3	0.5
I_o[3]	4.8	4.3	6.5
I_o/σ_{th}[3]	23.1	3.3	13.0
Main γ-energies,[7] keV	216	497	724, 130 ^{105}Rh : 319

Activation analysis of rock FU 41

To control the accuracy and the precision of the multiple comparator method, the homogeneous rock FU 41, a basanitoid from Fuerteventura, Canary Island, was analysed non-destructively according to the above-described technique.

Procedure

Analysis reactor position

Three series (I, II, III) of samples (S) and comparators (C) were irradiated for a 7 hr period each in "analysis" channel 11 of the Thetis reactor of the Institute. Each irradiation capsule contained 5 samples and 4 comparators in the geometrical position, as shown in Fig. 2. The rock powders were irradiated as 1 g samples in

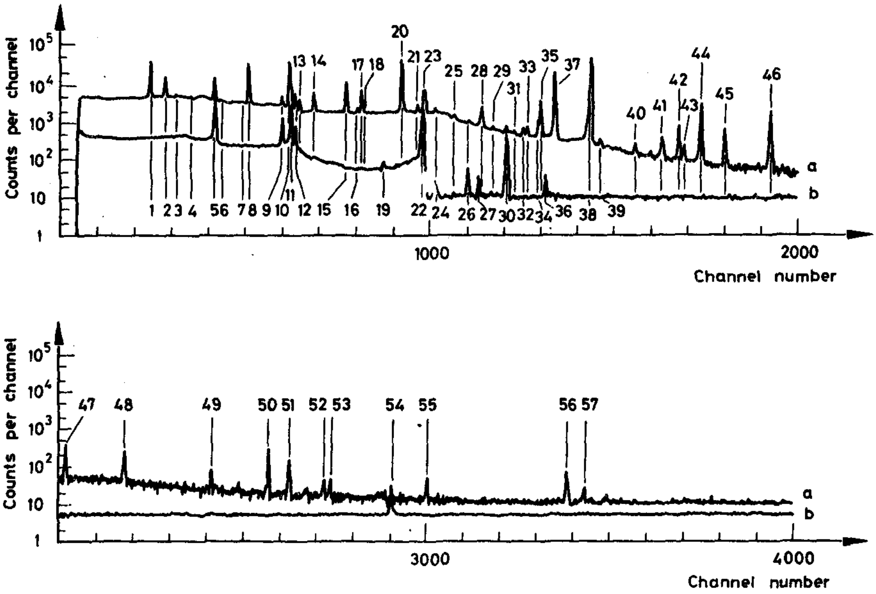

Fig. 1. Ge(Li) γ-ray spectrum of elemental ruthenium measured; (a) 4 hrs after irradiation and (b) 3 days after irradiation

Peak number	Energy, keV (reference)	Isotope	Peak number	Energy, keV (reference)	Isotope
1	129.7 (10)	^{105}Ru	29	591.3 (10)	^{105}Ru
2	149.2 (10)	^{105}Ru	30	610.406 (12)	^{103}Ru
3	163.6 (10)	^{105}Ru	31	621.0 (10)	^{105}Ru
4	183.6 (10)	^{105}Ru	32	625.0	
5	215.71 (11)	^{97}Ru	33	632.3 (10)	^{105}Ru
6	225.0 (10)	^{105}Ru	34	652.6 (10)	^{105}Ru
7	255.1 (10)	^{105}Ru	35	656.1 (10)	^{105}Ru
8	262.9 (10)	^{105}Ru	36	663 (6)	^{137}Cs
9	306.1 (10)	^{105}Rh	37	676.4 (10)	^{105}Ru
10	316.5 (10)	^{105}Ru	38	724.5 (10)	^{105}Ru
11	318.9 (10)	^{105}Rh	39	738.3 (10)	^{105}Ru

Peak number	Energy, keV (reference)	Isotope	Peak number	Energy, keV (reference)	Isotope
12	324.48 (11); 326.1 (10)	^{97}Ru; ^{105}Ru	40	785	
13	330.9 (10)	^{105}Ru	41	818.8 (6); 822.1 (10)	^{116m}In; ^{105}Ru
14	350.2 (10)	^{105}Ru	42	845.9 (10)	^{105}Ru
15	393.4 (10)	^{105}Ru	43	852.0 (10)	^{105}Ru
16	407.5 (10)	^{105}Ru	44	875.8 (10)	^{105}Ru
17	413.5 (10)	^{105}Ru	45	907.7 (10)	^{105}Ru
18	417.0 (6)	^{116m}In	46	969.4 (10)	^{105}Ru
19	443.77 (12)	^{103}Ru	47	1,017.2 (10)	^{105}Ru
20	469.4 (10)	^{105}Ru	48	1,097 (6)	^{116m}In
21	489.6 (10)	^{105}Ru	49	1,215.2 (10)	^{105}Ru
22	497.08 (12)	^{103}Ru	50	1,292 (6)	^{116m}In
23	499.2 (10)	^{105}Ru	51	1,321.3 (10)	^{105}Ru
24	513.7 (10)	^{105}Ru	52	1,368.4 (6)	^{24}Na
25	539.2 (10)	^{105}Ru	53	1,376.8 (10)	^{105}Ru
26	557.11 (12)	^{103}Ru	54	1,460.0 (6)	^{40}K
27	569.33 (11)	^{97}Ru	55	1,507.7 (6)	^{116m}In
28	575.3 (10)	^{105}Ru	56	1,697.4 (10)	^{105}Ru
			57	1,720.2 (10)	^{105}Ru

cylindrical polythene boxes (16 mm dia x 8 mm height). The ruthenium comparators were irradiated as specpure Ru sponge (5–10 mg), encapsulated in small cylindrical polythene boxes (8 mm dia x 9 mm height). The measurements of samples and comparators were performed on a Ge(Li) detector (resolution = 2.25 keV, efficiency = 7.8%) coupled to a 4,000-channel analyzer. The samples were measured one, two and four weeks after irradiation. The counting time was 1 hr, except in the latter case, where it was extended to 150 min. The γ-lines present in the spectra made it possible to determine 10 elements quantitatively: Sm, Sc, Fe, Co, Na, La, Hf, Eu, Th and Cr (Fig. 3). The specific activities of the comparator isotopes were derived from three measurements of the irradiated Ru sponge.

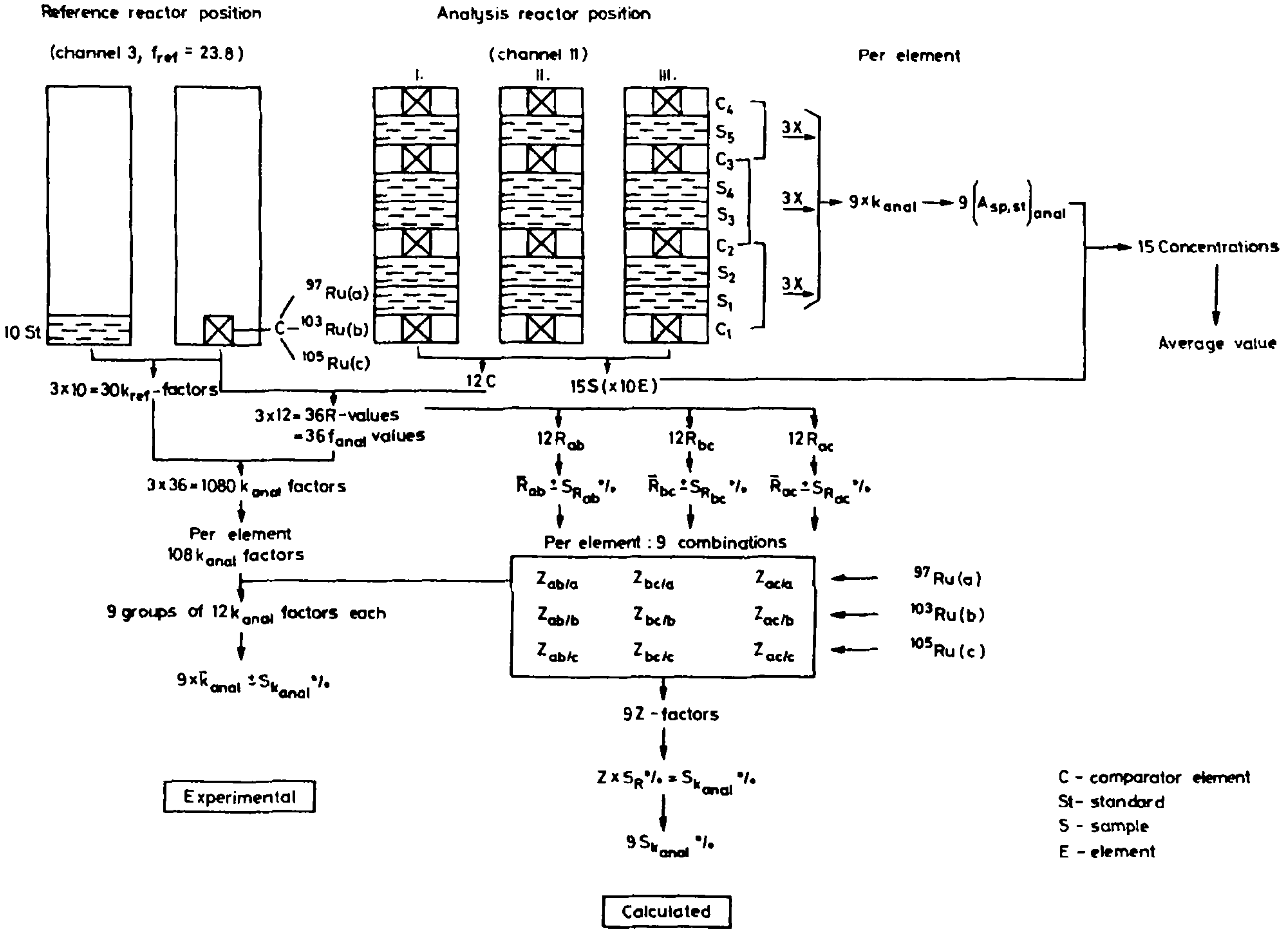

Fig. 2. Scheme of the procedure of analysis of rock FU-41 and of the error control of the multiple comparator method

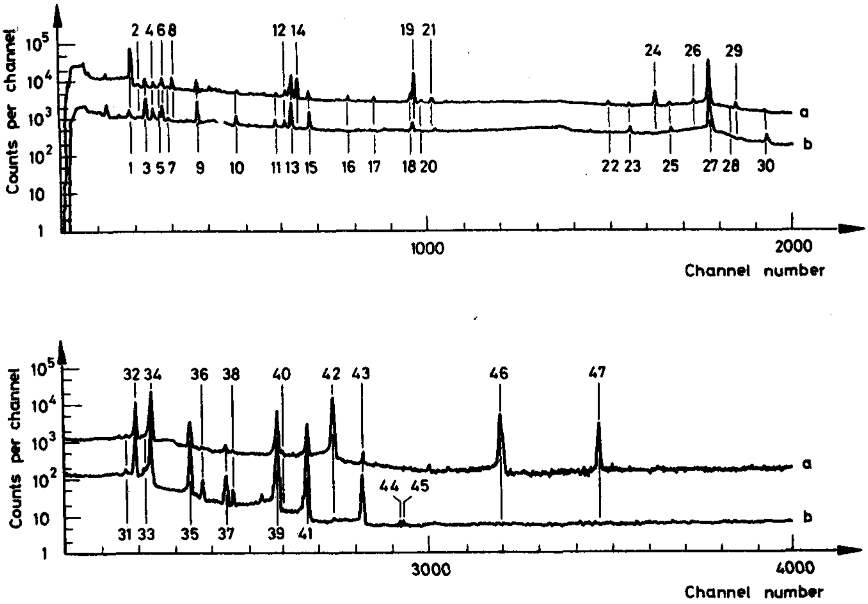

Fig. 3. Ge(Li) γ-spectrum of rock FU-41 measured; (a) one week after irradiation and (b) one month after irradiation

Peak number	Energy,[6] keV	Isotope	Peak number	Energy,[6] keV	Isotope
1	103. 2	^{153}Sm	25	834. 8	^{54}Mn
2	111. 0	^{233}Pa	26	867. 8	^{140}La
3	121. 8; 123. 1	^{152}Eu; ^{154}Eu	27	889. 3	^{46}Sc
4	133. 1	^{181}Hf	28	919. 6	^{140}La
5	142. 5	^{59}Fe	29	925. 2	^{140}La
6	145. 5	^{141}Ce	30	964. 4	^{152}Eu
7	152. 4	^{182}Ta	31	1, 086. 0	^{152}Eu
8	160. 0	^{46}Sc	32	1, 099. 3	^{59}Fe
9	192. 2	^{59}Fe	33	1, 112. 2	^{152}Eu
10	244. 7	^{152}Eu	34	1, 120. 5; 1, 121.2	^{46}Sc; ^{182}Ta
11	300. 1; 298. 6	^{233}Pa; ^{160}Tb	35	1, 173. 2	^{60}Co

Peak number	Energy,[6] keV	Isotope	Peak number	Energy,[6] keV	Isotope
12	311.9	^{233}Pa	36	1,189.0	^{182}Ta
13	320.1	^{51}Cr	37	1,221.3	^{182}Ta
14	328.8	^{140}La	38	1,230.9	^{182}Ta
15	346.0	^{181}Hf	39	1,291.5	^{59}Fe
16	396.1	^{175}Yb	40	1,297.1	^{47}Ca
17	432.5	^{140}La	41	1,332.5	^{60}Co
18	482.2	^{181}Hf	42	1,368.4	^{24}Na
19	487.0	^{140}La	43	1,408.1	^{152}Eu
20	496.3	^{131}Ba	44	1,458.3	^{152}Eu
21	511.0	β^+ annih.	45	1,460.0	^{40}K
22	751.8	^{140}La	46	1,596.6	^{140}La
23	779.1	^{152}Eu	47	1,732.1	^{24}Na D.E.
24	815.8	^{140}La			

Reference reactor position

The k_{ref} factors were determined for "reference" channel 3 of the Thetis reactor, with a flux ratio of $f_{ref} = 23.8$, as evaluated from the cadmium ratio of gold. The ruthenium comparator was irradiated and counted under similar conditions as described above for the analysis reactor position. The specific standard activities were obtained in two different ways, taking care that in every case the geometrical form was equal to that of the FU 41 rock samples. One series of results was obtained from an irradiation of appropriate amounts of specpure compounds, diluted with ultrapure Al_2O_3 up to the desired volume. A second series resulted from the irradiation of the standard rock BCR-1.[9] The results are shown in Table 2. The results are generally in good agreement.

Reproducibility. Experimental control of the error theory

From the specific activities of the standard and the comparator isotopes in the reference reactor position, k_{ref} values were calculated [Eq. (2)] as well as f_{anal} values [Eq. (4)], using the experimentally-determined R values [Eq. (3)]. With each

Table 2

Comparison of the specific activities of the self-prepared standards and BCR-1

Isotope	γ-Ray measured, keV	Specific activity of standards $\frac{c}{s \cdot mg\ S\ D}$		
		Pure elements	BCR-1	Average
^{153}Sm	103	$13.1 \cdot 10^7$	$12.5 \cdot 10^7$	$(12.7 \pm 0.3)\ 10^7$
^{46}Sc	889	$6.1 \cdot 10^7$	$6.3 \cdot 10^7$	$(6.2 \pm 0.05)\ 10^7$
^{59}Fe	1,099	$3.28 \cdot 10^3$	$3.10 \cdot 10^3$	$(3.15 \pm 0.04)\ 10^3$
^{60}Co	1,173+1,332	$9{,}34 \cdot 10^7$	$10.7 \cdot 10^7$	$(10{,}2 \pm 0.2)\ 10^7$
^{24}Na	1,368	$0{,}150 \cdot 10^7$	$0.141 \cdot 10^7$	$(0.146 \pm 0.003)\ 10^7$
^{140}La	1,595	$0.357 \cdot 10^7$	$0.357 \cdot 10^7$	$(0.357 \pm 0.010)\ 10^7$
^{181}Hf	482	$0.512 \cdot 10^7$	$0{,}489 \cdot 10^7$	$(0.496 \pm 0.010)\ 10^7$
^{152}Eu	1,407	$0.259 \cdot 10^9$	$0{,}260 \cdot 10^9$	$(0.260 \pm 0.007)\ 10^9$
^{233}Th $\xrightarrow{\beta^-}$ ^{233}Pa	312	$0.656 \cdot 10^7$	$0.623 \cdot 10^7$	$(0.633 \pm 0.011)\ 10^7$
^{51}Cr	320	$44.2 \cdot 10^4$	$44.5 \cdot 10^4$	$(44.3 \pm 0.5)\ 10^4$

of the f_{anal} values, the k_{ref} values were converted to k_{anal} values. As a Ru comparator consists of three radioisotopes, and taking into account that in each sample 10 elements were determined, it was possible to determine 30 k_{ref} values. As 12 comparators were irradiated in the analysis reactor position, each of them supplying three comparator sets, 36 R values and thus 36 f_{anal} values could be calculated. Thus, in all $30 \cdot 36 = 1{,}080$ k_{anal} values were computed.

Calculated standard deviations

The 36 R values were classified according to the comparator combinations. Considering the three containers (I, II, III), the 12 R values arising from one comparator set were accepted as belonging to the same population. This resulted in one average R value for each of the three comparator combinations. Thus, it was pos-

Table 3

Comparison of the calculated ($s_R\% \cdot z$) and the experimental standard deviations on a single determination of k_{anal}

($s_{R_{ab}} = 1.37\%$); ($s_{R_{bc}} = 1.65\%$); ($s_{R_{ac}} = 1.42\%$)

Comparator isotope		^{97}Ru(a) $\frac{I_o}{\sigma_{th}} = 23.1$		^{103}Ru(b) $\frac{I_o}{\sigma_{th}} = 3.3$		^{105}Ru(c) $\frac{I_o}{\sigma_{th}} = 13.0$	
Combination		$s_{k_{anal}}$, %		$s_{k_{anal}}$, %		$s_{k_{anal}}$, %	
		Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Sm $\frac{I_o}{\sigma_{th}} = 15.1$	a+b	0.428	0.425	0.956	0.956	0.135	0.129
	b+c	0.847	0.877	1.94	1.94	0.275	0.285
	a+c	1.087	1.082	2.47	2.50	0.347	0.353
Sc $\frac{I_o}{\sigma_{th}} = 0.5$	a+b	1.70	1.71	0.323	0.322	1.143	1.145
	b+c	3.45	3.47	0.644	0.643	2.307	2.316
	a+c	4.40	4.44	0.848	0.873	2.974	2.996
Fe $\frac{I_o}{\sigma_{th}} = 1.4$	a+b	1.59	1.60	0.212	0.196	1.034	1.03
	b+c	3.24	3.26	0.427	0.399	2.09	2.01
	a+c	4.12	4.13	0.559	0.584	2.69	2.71
Co $\frac{I_o}{\sigma_{th}} = 2.03$	a+b	1.52	1.53	0.140	0.136	0.960	0.965
	b+c	3.09	3.29	0.280	0.244	1.94	1.96
	a+c	3.93	3.43	0.367	0.385	2.50	2.27
Na $\frac{I_o}{\sigma_{th}} = 0.66$	a+b	1.68	1.73	0.302	0.296	1.123	1.132
	b+c	3.40	3.43	0.606	0.599	2.26	2.28
	a+c	4.36	4.55	0.795	0.860	2.93	3.14
La $\frac{I_o}{\sigma_{th}} = 1.28$	a+b	1.60	1.88	0.228	0.233	1.05	0.981
	b+c	3.25	3.28	0.455	0.455	2.108	2.124
	a+c	4.16	4.15	0.598	0.598	2.73	2.74
Hf $\frac{I_o}{\sigma_{th}} = 2.58$	a+b	1.46	1.46	0.078	0.098	0.898	0.902
	b+c	2.95	2.99	0.157	0.176	1.81	1.83
	a+c	3.76	3.77	0.204	0.214	2.33	2.35
Eu $\frac{I_o}{\sigma_{th}} = 0.67$	a+b	1.68	1.69	0.301	0.300	1.122	1.124
	b+c	3.40	3.44	0.603	0.602	2.26	2.28
	a+c	4.35	4.35	0.792	0.818	2.92	2.95
Pa $\frac{I_o}{\sigma_{th}} = 9.8$	a+b	0.787	0.791	0.591	0.600	0.230	0.231
	b+c	1.61	1.63	1.190	1.193	0.470	0.487
	a+c	2.03	2.02	0.154	0.155	0.595	0.594
Cr $\frac{I_o}{\sigma_{th}} = 0.49$	a+b	1.56	1.82	0.323	0.320	1.144	1.144
	b+c	3.45	3.53	0.647	0.648	2.307	2.318
	a+c	4.40	4.32	0.851	0.877	2.97	3.06

sible to calculate the three corresponding standard deviations on a single determination (s_R %). The total error change factors Z were calculated by combining each of the three R values (and thus each of the three comparator sets) with the three possible comparator isotopes used for the evaluation of the k_{anal} factors. This resulted in 9 Z factors per element. By multiplication of these Z factors by the corresponding s_R % values, the calculated standard deviations ($s_{k_{anal}}$ %) on a single determination of k_{anal} were obtained (Table 3).

Experimental standard deviations

The 1,080 k_{anal} factors for 10 elements can be subdivided into 108 values per element. As these factors were calculated from 9 combinations of comparator sets (for flux ratio determination) and comparator isotopes (for k_{anal} evaluation) it is apparent that each combination gives rise to 108/9 = 12 results of k_{anal}. The corresponding k_{anal} factors were averaged and the 9 experimental standard deviations ($s_{k_{anal}}$ %) on a single determination were calculated (Table 3).

Results and discussion

The results of the calculated and experimental standard deviations on a single determination of k_{anal} are shown in Table 3. Good agreement is found between both series. It is apparent that for a given element and a given comparator isotope, the combination ^{97}Ru - ^{103}Ru gives the best results, followed by the sets ^{103}Ru - ^{105}Ru and ^{97}Ru - ^{105}Ru. This is in agreement with the error theory, where it was stated that the error multiplication factor Z_f decreases with a large spread of the I_0/σ_{th} values for both comparator isotopes. Furthermore, it is obvious that for a given comparator combination and a given element the standard deviations are lower when the I_0/σ_{th} values for comparator and standard isotope are close together. This is again in agreement with the error theory. Finally, it should be emphasized that the multiple comparator method can be optimized by an appropriate choice for the combination of comparator and standard isotopes.

Accuracy. Comparison with classical activation analysis

As the rock FU 41 had already been analysed by classical activation analysis using the BCR-1 standard,[9] it was possible to compare both results.

For each irradiation container, the averaged k_{anal} values resulting from C_1 and C_2 were combined with the samples S_1 and S_2, C_2 and C_3 with S_3 and S_4, and C_3 and C_4 with S_5. This resulted in 9 k_{anal} factors and thus 9$[\bar{A}_{sp,st}]_{anal}$ values per element. By combination of these specific standard activities with the corresponding 15 samples, it was possible to calculate 15 results per element. The average values,

Table 4
Comparison of the analysis results obtained by the relative MCM and the classical standard method

Element	Concentration ppm	
	Relative MCM[a]	Classical standard method[9]
Sm	8.63 ± 0.09	7.95 ± 0.32
Sc	23.1 ± 0.2	21.8 ± 0.2
Fe	$9.82 \cdot 10^4 \pm 0.08 \cdot 10^4$	$9.35 \cdot 10^4 \pm 0.09 \cdot 10^4$
Co	52.8 ± 0.3	54 ± 1
Na	$2.45 \cdot 10^4 \pm 0.02 \cdot 10^4$	$2.42 \cdot 10^4 \pm 0.02 \cdot 10^4$
La	37.5 ± 0.3	35.5 ± 1.2
Hf	6.22 ± 0.05	6.0 ± 0.2
Eu	2.57 ± 0.03	2.64 ± 0.05
Th	3.41 ± 0.05	3.49 ± 0.43
Cr	336 ± 2	-

[a] Standard deviation on the mean (15 results).

together with the standard deviations, are listed in Table 4. The results of the classical activation analysis are also included. Obviously, both concentration series are in reasonable agreement, so that it can be concluded that the accuracy of the comparator method is satisfactory.

Conclusions

From the discussion about the reproducibility and the accuracy of the relative multiple comparator method, it can be concluded that this technique is a valuable alternative for classical activation analysis. It was proved that ruthenium can be used as a suitable triple comparator element. From comparison of theoretical and experimental standard deviations on the k_{anal} factors, the validity of the error theory was demonstrated. Consequently, it is possible for a given set of experimental conditions to calculate the errors that can be expected on the k_{anal} factors. This offers the possibility of improving the precision on the results by an appropriate choice of the comparator sets (for the flux ratio determination) and the combination of standard and comparator isotopes (for k_{anal} evaluation).

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