Journal of Radioanalytical Chemistry, Vol. 72, No. 1–2 (1982) 195–207

EPITHERMAL NEUTRON ACTIVATION ANALYSIS OF SHORT-LIVED NUCLIDES IN GEOLOGICAL MATERIAL

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(Received July 7, 1981)

The cadmium ratios of 52 short-lived nuclides have been measured. Epithermal neutron irradiation reduces the activities of ^{20}F, ^{27}Mg, ^{28}Al, ^{38}Cl, ^{49}Ca, ^{46m}Sc, ^{51}Ti, ^{56}Mn and ^{66}Cu by factors of 20–30. The calculated improvements in detection limits for Ga, Br, Rb, Y, Mo, Rh, Pd, Ag, In, Sn, Sb, I, Ba, Nd, Sm, Gd, Dy, Er, Yb, Hf, W, Re, Pt, Au, Th and U are in the range 1–6. Hafnium was measured in USGS rocks : AGV–1 (4.9 $\mu g\, g^{-1}$), G–2 (7.5 $\mu g\, g^{-1}$) and GSP–1 (14.7 $\mu g\, g^{-1}$) and IAEA standards: SOIL–5 (6.3 $\mu g\, g^{-1}$) and SL–1 (4.6 $\mu g\, g^{-1}$). CCRMP reference concentrates PTC and PTM were analysed for rhodium (1.1 and 0.75 $\mu g\, g^{-1}$, respectively) and silver (69 and 5.8 $\mu g\, g^{-1}$, respectively).

Introduction

Epithermal neutron activation has become an established technique for the trace element analysis of geological samples[1]. Thermal neutron filters of cadmium[1,2], boron[3] and cadmium plus boron[4] have been used to reduce the interfering activity from long-lived nuclides such as ^{24}Na, ^{46}Sc, ^{51}Cr, ^{60}Co and ^{64}Cu. The gamma ray spectra of geological samples after a 1 min irradiation in a thermal neutron flux are dominated by ^{28}Al, ^{46m}Sc, ^{51}Ti, ^{52}V, ^{56}Mn, ^{60m}Co and ^{66}Cu. Although thermal neutron filters have been used to enhance the activation of some short-lived nuclides[5], the technique is seldom applied to nuclides with half-lives of less than a few minutes due to the problems associated with reactivity effects during transfer of the sample into and out of the reactor core.

A fast pneumatic transfer system has been installed in the University of London reactor with irradiation sites for both thermal neutron activation and epithermal neutron irradiations under cadmium. This facility was used to study the feasibility of applying epithermal neutron activation to short-lived nuclides in the analysis of geological samples. Cadmium ratios were measured for nuclides of elements of interest with chemical standards. The gamma-ray spectra of different rock types were analysed qualitatively after irradiation for 1 min in both thermal and epithermal neutron fluxes. Finally the technique was applied to the quantitative analysis of reference rock standards for hafnium, rhodium and silver.

Experimental

Irradiation

All the irradiations were made in the fast pneumatic transfer system shown in Fig. 1. The samples, packed in polythene capsules (30 x 10 mm, 1 ml capacity) were introduced sequentially into the reactor

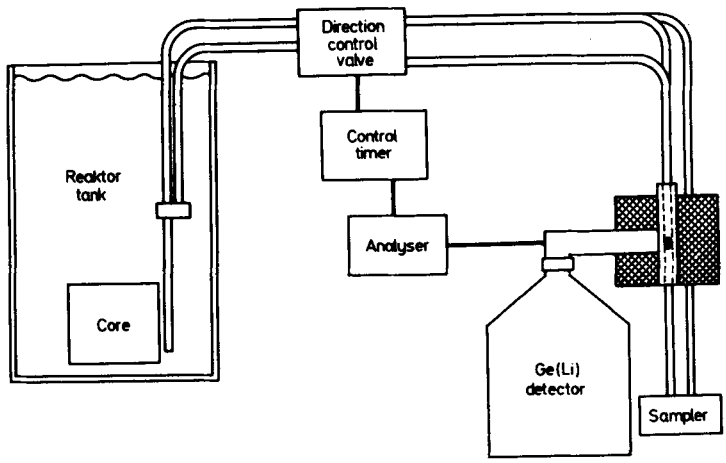

Fig. 1. Schematic diagram of the irradiation facility

core from the sampler and out to the counting position, propelled by pressurised nitrogen gas, under timer control. There were two irradiation sites : the 'thermal' neutron tube (ϕ_{th} = 1.3 x 10^{12}n $cm^{-2}s^{-1}$, ϕ_{epi} = 6.1 x 10^{10}n $cm^{-2}s^{-1}$, $R_{Cd_{Au}}$ = 2.3) and the 'epithermal' neutron tube with a 1 mm thick cadmium lining (ϕ_{th} = 4.9 x 10^{10}n $cm^{-2}s^{-1}$, ϕ_{epi} = 4.1 x 10^{10}n $cm^{-2}s^{-1}$).

Gamma-ray spectrometry

The samples were measured at a position 12 mm from the end cap of a lithium-drifted germanium detector (Princeton Gamma-Tech, FWHM : 1.69 at 1.33 MeV, Peak/Compton ratio : 27.7 at 1.33 MeV, efficiency : 4.9%), close to the irradiation site and enclosed in lead shielding. The gamma-ray spectra were measured with a Laben 8000, 4096 channel analyser and evaluated by the total peak area method with dead-time and random summing corrections.

Elemental standards

Standards were made by evaporation of 0.1 ml aliquots of standard solution onto filter paper in polythene irradiation capsules. The solutions were prepared from 'Specpure' compounds or standard 10 mg ml^{-1} solutions (Johnson Matthey Chemicals Ltd.) of suitable concentration to give the two sets of single element standards listed below:

(i) 10 mg of Mg, Cl, Ca, Ga, Ge, Mo, Sn
1 mg of F, Ti, Br, Rb, Y, Ba, Nd, Sm, Gd, Er, Yb, Th
100 µg of Al, Mn, Cu, Pd, Sb, I, W, Re, Ir, Pt, Au
10 µg of V, Co, Rh, Ag, Eu, U
1 µg of Sc, Se, In, Dy, Hf

(ii) 100 mg of Mg, Cl, Ca

10 mg of F, Ti, Ga, Ge, Mo, Sn

1 mg of Al, Mn, Cu, Br, Rb, Y, Ba, Nd, Sm, Gd, Er, Yb, Th

100 µg of V, Co, Pd, Sb, I, W, Re, Ir, Pt, Au

10 µg of Sc, Se, Rh, Ag, Eu, U

1 µg of In, Dy, Hf

Cadmium ratio determination

All the standards were irradiated for 1 min and counted for 1 min after a 1s delay. Standards (i) were irradiated in the thermal neutron tube and standards (ii) in the epithermal neutron tube. The cadmium ratios for the nuclides were calculated from the ratio of the specific activity induced in standards irradiated in the thermal neutron flux to the activity induced in the epithermal neutron flux. Because the cadmium-lined tube cannot be removed from the reactor core, no equivalent thermal neutron activation could be made in the same position. Therefore the activation by thermal neutrons was made in the adjacent tube, with an epithermal neutron flux higher by a factor of 1.5. No correction was made to the cadmium ratios for this difference.

Geological samples

USGS reference andesite, AGV-1, CCRMP noble-metals bearing nickel-copper matte, PTM, and a sample of magnetite from the Bushveld Complex, S. Africa, were irradiated in powdered form (50-100 mg) for 1 min in both thermal and epithermal neutron fluxes and counted for 1 min after a 1s delay to evaluate the gamma-ray spectra qualitatively. USGS reference

rocks : andesite, AGV-1, granite, G-2 and grandiorite, GSP-1, and IAEA standards : soil, SOIL-5, and lake sediment, SL-1, were analysed for hafnium with an epithermal neutron irradiation (30s irradiation, 1s decay, 30s count). CCRMP noble-metals bearing sulphide concentrate, PTC, and nickel-copper matte, PTM, were analysed for rhodium and silver (1 min irradiation, 1s decay, 1 min count).

Results

Cadmium ratios

Table 1 lists the cadmium ratios of the nuclides together with the appropriate nuclear data. The cadmium ratios for the interfering nuclides ^{27}Mg, ^{28}Al, ^{38}Cl, ^{49}Ca, ^{46m}Sc, ^{51}Ti, ^{52}V, ^{56}Mn and ^{66}Cu, which cause problems in the analysis of short-lived nuclides in geological material, are in the range 20-30. The trace elements of interest have cadmium ratios of 1.4 - 12. Table 1 also includes the improvement factor[6] which is a measure of the expected improvement in detection limit for the trace element irradiated in an epithermal neutron flux. These factors have been calculated with ^{28}Al as the interfering nuclide and in most cases there is an improvement in the detection limit of 1-6. The sensitivity values listed in Table 1 have been calculated from measured specific activities for elements irradiated for 1 min in an epithermal neutron flux and counted for 1 min after a 1s delay. These values are corrected for detector efficiency to give gammas $\mu g^{-1} s^{-1}$ for ease of comparison with calculated values compiled in a recent review[13]. Detection limits of better than 10^{-7}g were calculated for ^{46m}Sc, ^{104}Rh, ^{104m}Rh, ^{110}Ag, ^{116m}In, ^{165m}Dy, ^{179m}Hf and ^{239}U under ideal conditions. Nuclides with detection limits between 10^{-5} and

Table 1
Nuclear properties, cadmium ratios, improvement factors and sensitivities for short-lived nuclides

Element	Nuclear Reaction	σ_o (barn)[7]	I_o (barn)[7-11]	Half-life[12]	γ-ray energy (keV)[12]	R_{Cd}[a]	Improvement factor[b]	Sensitivity (gammas $\mu g^{-1} s^{-1}$)[c]
F	$^{19}F(n,\gamma)^{20}F$	9.5E-3	1.8E-2	11.0s	1632.6	34	0.17	1.6
Mg	$^{26}Mg(n,\gamma)^{27}Mg$	3.8E-2	2.5E-2	9.46m	834.8	25	0.23	1.4E-1
Al	$^{27}Al(n,\gamma)^{28}Al$	2.3E-1	1.7E-1	2.24m	1778.7	32	-	3.9E1
Cl	$^{37}Cl(n,\gamma)^{38}Cl$	4.2E-1	3.1E-1	37.3m	2167.6	33	0.17	4.8E-1
Ca	$^{48}Ca(n,\gamma)^{49}Ca$	1.1	9.0E-1	8.72m	3084.4	29	0.20	2.4E-2
Sc	$^{45}Sc(n,\gamma)^{46m}Sc$	9.6		18.7s	142.5	37	0.15	7.0E2
Ti	$^{50}Ti(n,\gamma)^{51}Ti$	1.8E-1	1.2E-1	5.80m	319.7	30	0.19	4.5E-1
V	$^{51}V(n,\gamma)^{52}V$	4.9	2.7	3.76m	1434.1	38	0.15	2.5E2
Mn	$^{55}Mn(n,\gamma)^{56}Mn$	1.3E1	1.4E1	2.58h	846.8	21	0.27	3.0E1
Co	$^{59}Co(n,\gamma)^{60m}Co$	2.0E1	4.0E1	10.5m	58.6	12	0.47	2.4E1
Cu	$^{65}Cu(n,\gamma)^{66}Cu$	2.2	2.4	5.10m	1039.2	21	0.27	2.2
Ga	$^{69}Ga(n,\gamma)^{70}Ga$	1.7	1.6E1	21.1m	175.5	2.2	2.6	1.3E-1
Ge	$^{74}Ge(n,\gamma)^{75m}Ge$	1.4E1		48s	139.7	9.2	0.62	5.2
Se	$^{76}Se(n,\gamma)^{77m}Se$	2.1E1		17.4s	161.9	28	0.20	7.4E1
Br	$^{79}Br(n,n')^{79m}Br$			4.9s	207.3	1.3	4.4	2.4E1
	$^{79}Br(n,\gamma)^{80}Br$	8.5	9.2E1	17.6m	616.9	3.5	1.6	1.5E2
Rb	$^{85}Rb(n,\gamma)^{86m}Rb$	5.0E-2	1.2	1.02m	556.1	2.9	2.0	2.2E1
Y	$^{89}Y(n,n')^{89m}Y$			16.1s	909.1	1.3	6.7	1.1E2
Mo	$^{100}Mo(n,\gamma)^{101}Mo$	2.0E-1	3.8	14.6m	191.9	2.4	2.4	5.0E-1
Rh	$^{103}Rh(n,\gamma)^{104}Rh$	1.4E2	1.1E3	42.3s	555.7	4.9	1.2	2.0E3
	$^{103}Rh(n,\gamma)^{104m}Rh$	1.1E1	8.9E1	4.34m	51.4	4.5	1.3	5.2E2

Table 1 (cont.)

Element	Nuclear Reaction	σ_o (barn)[7]	I_o (barn)[7-11]	Half-life[12]	γ-ray energy (keV)[12]	R_{Cd}[a]	Improvement factor[b]	Sensitivity (gammas $\mu g^{-1} s^{-1}$)[c]
Pd	$^{106}Pd(n,\gamma)^{107m}Pd$	1.3E-2		21.3s	214	2.1	2.7	2.6
	$^{108}Pd(n,\gamma)^{109m}Pd$	2.0E-1	2.3	4.69m	188.9	2.1	2.7	1.6E1
Ag	$^{109}Ag(n,\gamma)^{110}Ag$	8.9E1	1.1E3	24.4s	657.8	2.9	2.0	2.5E3
In	$^{115}In(n,\gamma)^{116m}In$	6.5E1	2.1E3	54.1m	1293.5	2.4	2.4	2.1E4
Sn	$^{122}Sn(n,\gamma)^{123m}Sn$	1.0E-3	8.3E-1	40.1m	159.7	3.2	1.8	4.3E-2
	$^{124}Sn(n,\gamma)^{125m}Sn$	1.3E-1	8.7	9.5m	332.0	1.5	3.8	3.9
Sb	$^{121}Sb(n,\gamma)^{122m}Sb$	5.5E-2		4.2m	61.5	1.8	3.2	2.4E1
	$^{123}Sb(n,\gamma)^{124m}Sb$	3.5E-2		93s	602.7	2.1	2.7	9.7
I	$^{127}I(n,\gamma)^{128}I$	6.2	1.5E2	25.0m	442.9	2.6	2.2	9.8E1
Ba	$^{136}Ba(n,\gamma)^{137m}Ba$	1.0E-2	7.5E-1	2.55m	661.6	1.4	4.1	7.5
	$^{138}Ba(n,\gamma)^{139}Ba$	3.5E-1	2.0E-1	82.9m	165.8	25	0.23	1.9E-2
Nd	$^{148}Nd(n,\gamma)^{149}Nd$	2.5	1.9E1	1.73h	211.3	5.6	1.1	1.7E-1
	$^{150}Nd(n,\gamma)^{151}Nd$	1.2	1.4E1	12.4m	138.8	2.8	2.0	5.0E-1
Sm	$^{154}Sm(n,\gamma)^{155}Sm$	5.5	3.0E1	22.4m	104.3	5.6	1.1	1.1E1
Eu	$^{151}Eu(n,\gamma)^{152m}Eu$	3.3E3	2.8E3	9.3h	121.8	26	0.22	6.9
Gd	$^{160}Gd(n,\gamma)^{161}Gd$	7.7E-1	7.0	3.7m	360.9	3.5	1.6	8.8
Dy	$^{164}Dy(n,\gamma)^{165m}Dy$	1.7E3		1.26m	108.2	5.5	1.0	1.3E3
Er	$^{166}Er(n,\gamma)^{167m}Er$	1.5E1		2.28s	207.8	1.0	5.7	1.8E1
	$^{170}Er(n,\gamma)^{171}Er$	5.7	2.0E1	7.52h	308.2	5.8	1.0	1.6E-1
Yb	$^{176}Yb(n,\gamma)^{177m}Yb$			6.4s	104.0	2.9	2.0	3.9

Table 1 (cont.)

Element	Nuclear Reaction	σ_o (barn)[7]	I_o (barn)[7-11]	Half-life[12]	γ-ray energy (keV)[12]	R_{Cd}[a]	Improvement factor[b]	Sensitivity (gammas $\mu g^{-1} s^{-1}$)[c]
Hf	$^{178}Hf(n,\gamma)^{179m}Hf$	5.3E1		18.7s	217	2.5	2.3	7.4E3
W	$^{182}W(n,\gamma)^{183m}W$			5.3s	105	1.9	3.0	1.2E1
	$^{184}W(n,\gamma)^{185m}W$	2.0E-3		1.66m	131.7	4.2	1.4	7.0E-1
Re	$^{187}Re(n,\gamma)^{188}Re$	1.6	3.0E2	16.9h	155.0	7.3	0.78	4.8
	$^{187}Re(n,\gamma)^{188m}Re$	7.3E1	8.8	18.7m	105.9	7.3	0.78	3.5
Ir	$^{191}Ir(n,\gamma)^{192m}Ir$	3.0E2	1.1E3	1.45m	58.0	9.2	0.62	1.3E1
Pt	$^{198}Pt(n,\gamma)^{199}Pt$	3.7	5.6E1	30.8m	542.8	2.6	2.2	5.4
	$^{198}Pt(n,\gamma)^{199m}Pt$	2.7E-2		14s	391.9	3.0	1.9	4.2
Au	$^{197}Au(n,n')^{197m}Au$			7.2s	279.3	1.4	4.1	6.4E1
Th	$^{232}Th(n,\gamma)^{233}Th$	7.4	8.5E1	22.3m	86.5	3.3	1.7	5.4
U	$^{238}U(n,\gamma)^{239}U$	2.7	2.8E2	23.5m	74.7	1.5	3.8	4.9E2

a $R_{Cd_{Au}} = 3.4$ 'Thermal' neutron irradiation : $\phi_{th} = 1.3 \times 10^{12} ncm^{-2}s^{-1}$, $\phi_{epi} = 6.1 \times 10^{10} ncm^{-2}s^{-1}$, $R_{Cd_{Au}} = 2.3$

'Epithermal' neutron irradiation : $\phi_{th} = 4.9 \times 10^{10} ncm^{-2}s^{-1}$, $\phi_{epi} = 4.1 \times 10^{10} ncm^{-2}s^{-1}$

b Improvement in detection limit ($= \sqrt{R_{Cd_d}}/R_{Cd_D}$, where d is the interfering nuclide and D is the nuclide of interest[6]), calculated for interfering nuclide ^{28}Al

c Gamma-ray emission rate during a 1 min count after a 1 min irradiation $\phi_{epi} = 4.1 \times 10^{10} ncm^{-2}s^{-1}$,

$\phi_{th} = 4.9 \times 10^{10} ncm^{-2}s^{-1}$.

10^{-6}g were : ^{28}Al, ^{52}V, ^{56}Mn, ^{60m}Co, ^{75m}Ge, ^{77m}Se, ^{79m}Br, ^{80}Br, ^{86m}Rb, ^{89m}Y, ^{109m}Pd, ^{122m}Sb, ^{124m}Sb, ^{128}I, ^{137m}Ba, ^{155}Sm, ^{152m}Eu, ^{161}Gd, ^{167m}Er, ^{183m}W, ^{192m}Ir, ^{199}Pt, ^{197m}Au and ^{233}Th. The remaining nuclides had detection limits above 10^{-5}g.

Geological samples

The gamma-ray spectra of geological samples activated in both thermal and epithermal neutron fluxes are shown in Figs. 2-4. The ^{28}Al peaks that dominate the spectrum of AGV-1 in Fig. 2 are mainly produced by the ^{27}Al(n,γ)^{28}Al reaction. The activity is sufficiently reduced by epithermal neutron irradiation to enhance the gamma-ray line of ^{179m}Hf at 217 keV. In Fig. 3 the interfering activities of ^{28}Al, ^{46m}Sc, ^{51}Ti, ^{52}V and ^{56}Mn are prominent in the spectrum produced by thermal neutron activation and ^{179m}Hf is enhanced by the epithermal neutron irradiation. The spectrum of PTM in Fig. 4 is dominated by ^{60m}Co, ^{66}Cu and ^{77m}Se, all of which are reduced by epithermal neutron activation, enhancing both ^{110}Ag

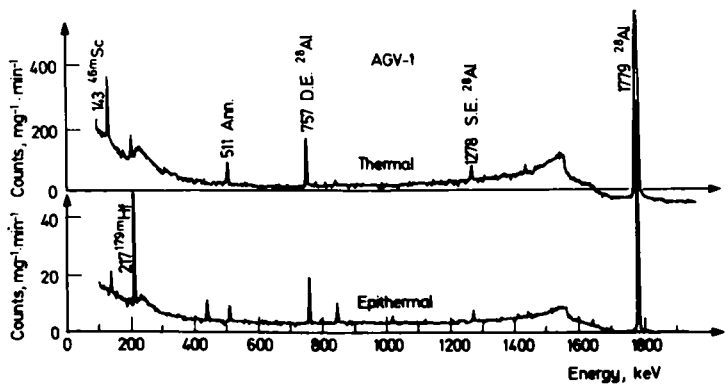

Fig. 2. Gamma-ray spectra of AGV–1, irradiated in thermal and epithermal neutron fluxes (1 min irradiation, 1s decay, 1 min count)

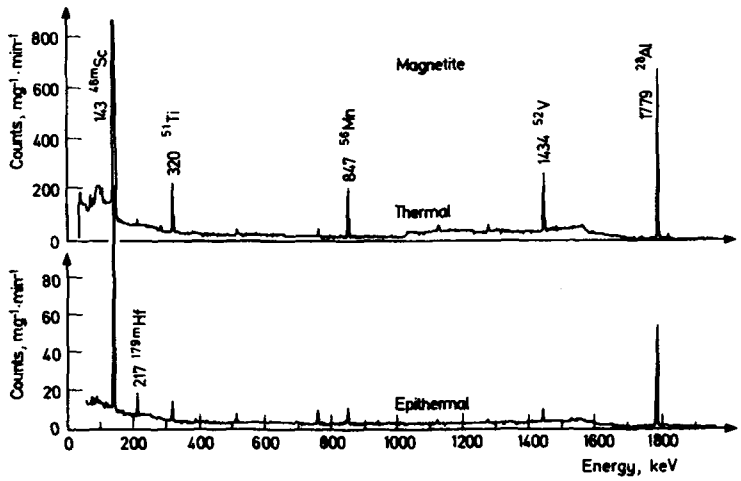

Fig. 3. Gamma-ray spectra of magnetite, irradiated in thermal and epithermal neutron fluxes (1 min irradiation, 1s decay, 1 min count)

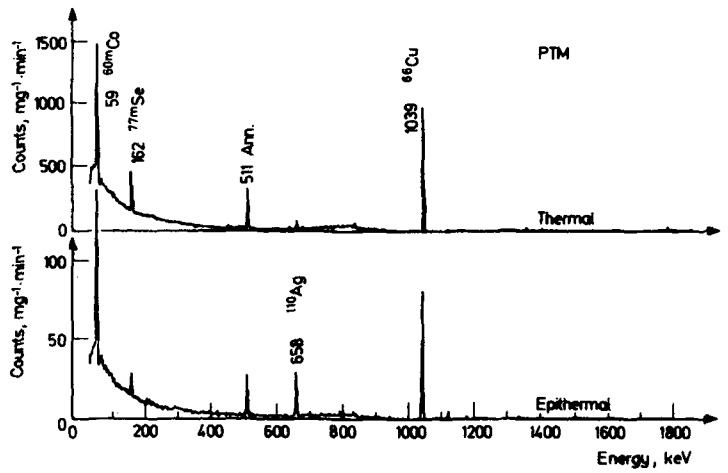

Fig. 4. Gamma-ray spectra of PTM, irradiated in thermal and epithermal neutron fluxes (1 min irradiation, 1 s decay, 1 min count)

which is seen clearly in Fig. 4, and ^{104}Rh, a small peak at 556 keV close to the detection limit in this sample.

The analyses of reference rock standards for hafnium are given in Table 2. The results are in good agreement with the reference values.

Table 2
Determination of hafnium in reference material

Sample	Hafnium (μg g^{-1})	
	This work	Reference value[14-16]
AGV-1	4.9 ± 0.5	5.2
G-2	7.5 ± 0.4	7.5
GSP-1	14.7 ± 0.8	13
SL-1	4.2 ± 0.6	4.5 ± 1.4
SOIL-5	6.2 ± 1.0	6.3 ± 0.3

Table 3
Determination of rhodium and silver in reference material

Sample	Rhodium (μg g^{-1})		Silver (μg g^{-1})
PTM	This work	0.75 ± 0.28	5.8 ± 0.5
	Reference value[17]	0.62 ± 0.07	5.8 ± 0.3
PTC	This work	1.1 ± 0.3	69 ± 5
	Reference value[18]	0.9 ± 0.3	66 ± 7

The detection limit for hafnium in silicate rocks is estimated to be 10^{-8}g or 0.1 μg g^{-1}. The analyses of CCRMP reference concentrates for rhodium and silver are listed in Table 3. Although the results agree with the reference values, there is a wide variation due to sample heterogeneity.

The detection limits for both rhodium and silver in copper-rich samples were estimated to be 5×10^{-8}g or 0.5 μg g^{-1}.

Discussion

Epithermal neutron activation under cadmium will theoretically improve the detection of many short-lived nuclides in different rock types. The method has been applied successfully to the determination of hafnium, silver and rhodium, and although applications are limited several elements such as Sc, Co and Se may be determined simultaneously. The method could be extended to the determination of other trace elements, for example, Ge, Br, Rb, Y, Pd, In, Sb, I, Ba, Sm, Gd, Dy, Er, W, Ir, Pt, Au, Th and U which all have detection limits of better than 10^{-5}g under ideal conditions.

In addition to reducing the interfering matrix activity an advantage of the method is that larger sample sizes may be irradiated to further improve detection limits. The use of a boron or boron plus cadmium filter would probably also enhance detection of the trace element, as already demonstrated for long-lived nuclides in geological material.

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