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INAA of geological materials using a combination of epithermal activation and Compton suppression: Prediction of possibilities

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Nuclear data relevant to the determination of elements in geological materials by instrumental neutron activation analysis using a combination of epithermal neutron activation and Compton suppression counting are presented. The feasibility of this combination is discussed considering data for desired as well as interfering nuclides. Among elements determined after short irradiation, the conditions for Sr, Zr, I, Cs, Eu and U should be improved. After long epithermal irradiation and appropriate decay, Compton suppression should lead to improvement in determination of As, Rb, Sr, Mo, Sn, Sb, Ba, Gd, Ho, Tm, W, Au, Th, and U. In the case of Ga, Se, Ag, In, Cs, Tb, Yb, Hf, Ta, and W, the use of Compton suppression in connection with epithermal activation is not recommended because the radionuclides concerned decay with coincident γ-rays. In general, the use of Compton suppression should improve the determination of trace elements in geological materials by epithermal neutron activation analysis, but more work is needed to better quantify these improvements.

Introduction

Instrumental neutron activation analysis (INAA) has played an important role over the years for the determination of trace elements in geological materials. A main limitation of this technique is the Compton continuum of high-energy gamma-emitters such as ^{24}Na, ^{27}Al, ^{46}Sc, ^{56}Mn, ^{59}Fe, ^{60}Co, and ^{140}La in the induced spectrum, often hiding peaks used for the determination of other elements. Activation analysis with epithermal neutrons (ENAA), screening the thermal neutrons with a cadmium or a boron filter, facilitates relative enhancement of activities from nuclides produced from a stable isotope with a high resonance activation integral compared to its thermal neutron activation cross section. In this way, the determination of a number of elements in geological samples including As, Rb, Sr, Mo, Sb, Tb, Hf, Ta, Au, Th, and U is significantly improved because the major interferences are strongly reduced. A somewhat similar means of improvement in INAA is the use of Compton suppression, reducing contributions from nuclides decaying with coincident gamma-rays relative to other gamma-emitters. This approach is currently used in several areas of application, partly in combination with ENAA, but has to the knowledge of the author not been systematically tested in analysis of geological samples. In this presentation the possibilities offered by a combination of the two techniques are predicted and discussed based on the author's own experience in ENAA and recent literature on the use of Compton suppression in INAA.

Background of the present work

BRUNFELT and STEINNES[1] were the first to use ENAA for the determination of trace elements in geological samples. Further developments of this approach were discussed in a follow-up paper.[2] Extension of the technique to the low-energy range was demonstrated by BAEDECKER et al.[3] The general background of the use of ENAA in geochemistry was discussed in a separate paper.[4] This technique was also shown to be potentially very useful for trace element determinations in related materials such as coal and coal fly ash[5] and has over the years become an integral part of INAA.

Use of the Compton suppression (CS) technique in γ-spectrometric measurements related to INAA was suggested by COOPER and BROWNELL[6] already in 1967, but this approach did not come into general use before the 1990s. LANDSBERGER and PESHEV[7] published a comprehensive review on CS, describing the features of the technique and its application in activation analysis. The main feature of the CS technique is a significant reduction of the Compton continuum from high-energy γ-rays, which often disturbs seriously the measurement of lower-energy γ-rays. An additional feature of this technique is that contributions in the spectrum from radionuclides decaying with two or more γ-rays emitted in coincidence will be reduced, particularly if the sample is placed near the detector. Several nuclides induced by neutron activation in excessive amounts in many sample types decay with two or more coincident γ-rays.

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Application of a CS facility may thus appreciably reduce the interference of such radionuclides in the determination of other elements if the radionuclide used for that particular determination decays with non-coincident γ-rays.

The combination of the CS technique with epithermal activation has been found successful in some cases, such as in analysis of aerosol filters,[8] natural waters,[9] and biological reference materials.[10] It seems, however, that the feasibility of employing this combination for the analysis of geological material has not yet been discussed in the literature. In the present paper, therefore, the potential of this combination is critically examined.

Presentation of the relevant data

In the following tables, nuclear data relevant for evaluation of the feasibility of combining epithermal activation and CS techniques in INAA are presented. The data are separated in two tables dealing with short-lived and long-lived products of (n,γ) reactions, respectively. Table 1 shows data for the discussion of elements determined by means of nuclides with half-lives less than 15 hours, whereas longer-lived reaction products are treated in Table 2. The reason for this subdivision is that ^{24}Na, with a half-life of 15.0 hours, represents a major interference in INAA of geological material both with respect to short-lived and longer-lived radionuclides.

Table 1. Selected nuclear data for relevant short-lived nuclides ($T_{1/2}$<15 h)

Element	Radionuclide	Half-life	I_0/σ_0*	Gamma-energy, keV	Coincident %
Na	^{24}Na	15.0 h	0.59	1368	100
				2754	100
Mg	^{27}Mg	9.5 min	0.68	842	2
				1013	0
Al	^{28}Al	2.3 min	0.74	1780	0
S	^{37}S	5.1 min	1.1	3090	0
Cl	^{38}Cl	37.3 min	0.69	1600	100
				2170	100
K	^{42}K	12.4 h	0.97	1524	0
Ca	^{49}Ca	8.8 min	-	3100	0
Ti	^{51}Ti	5.8 min	0.66	928	1
V	^{52}V	3.8 min	0.55	1434	1
Mn	^{56}Mn	2.58 h	1.05	847	48
				1811	98
Ni	^{65}Ni	2.56 h	0.64	1115	40
				1481	0
Cu	^{64}Cu	12.8 h	1.10	511	100
	^{66}Cu	5.1 min	1.01	1039	3
Zn	^{69m}Zn	13.8 h	2.9	439	0
Ga	^{72}Ga	14.1 h	6.6	835	90
Sr	^{87m}Sr	2.83 h	5.7	388	0
Zr	^{97}Zr	17.0 h	231	747	7
	^{97}Nb	72 min		665	0
Mo	^{101}Mo	14.6 min	18.8	2080	0
	^{101}Tc	14.0 min		307	10
In	^{116}In	54.0 min	16.3	417	100
				1097	100
				1293	100
I	^{128}I	25.0 min	23.7	441	15
Cs	^{134m}Cs	2.90 h	13.2**	127	0
Ba	^{139}Ba	82.9 min	0.89	1430	0
Sm	^{155}Sm	22.4 min	6	104	0
Eu	^{152}Eu	9.3 h	3.9**	122	100
				963	0
Dy	^{165}Dy	139.2 min	<0.5**	94	0
Er	^{171}Er	7.5 h	5.3**	124	100
				308	100
U	^{239}U	23.5 min	100	75	0

* Data from MOENS et al.[11]
** Data from STEINNES.[4]

Table 2. Selected nuclear data for relevant long-lived nuclides ($T_{1/2}$>15 h)

Element	Radionuclide	Half-life	I_0/σ_0*	Gamma-energy, keV	Coincident %
Na	^{24}Na	15.0 h	0.59	1368	100
				2754	100
Ca	^{47}Ca	4.53 d	1.28**	1300	0
	^{47}Sc	3.43 d		160	0
Sc	^{46}Sc	83.9 d	0.44	889	100
				1121	100
Cr	^{51}Cr	27.8 d	0.49	320	0
Fe	^{59}Fe	44.6 d	1.3	1095	0
				1292	5
Co	^{60}Co	5.26 y	1.99	1173	100
				1332	100
Zn	^{65}Zn	244 d	1.91	1115	0
Ga	^{72}Ga	14.1 h	6.62	630	100
				835	100
As	^{76}As	26.5 h	13.6	559	20
Se	^{75}Se	120.4 d	10.0	122	100
				136	100
				265	100
				280	100
				401	87
Br	^{82}Br	35.3 h	18.5	554	100
				777	100
				1044	100
				1475	61
Rb	^{86}Rb	18.7 d	11.3	1078	0
Sr	^{85}Sr	64.9 d	13.3**	514	0
Zr	^{95}Zr	64.0 d	4.61	724	0
				756	0
	^{95}Nb	35.2 d		765	0
Mo	^{99}Mo	66.0 h	53.1	181	33
				740	100
	^{99m}Tc	6.0 h		143	0
Ag	^{110m}Ag	250 d	15.4	657	100
				764	100
				884	100
				937	100
				1387	100
Cd	^{115}Cd	53.5 h	78**	530	2
	^{115m}In	4.50 h		335	0
In	^{114m}In	50.0 d	131**	192	0
Sn	^{113}Sn	115 d	30	393	2
	^{117m}Sn	14.0 d	82	158	100
Sb	^{122}Sb	2.80 d	33.9	564	5
	^{124}Sb	60.3 d	30.2	603	78
				1692	100
Cs	^{134}Cs	2.05 y	12.4	605	100
				796	100
Ba	^{131}Ba	11.5 d	25**	123	100
				216	15
				373	35
				493	100
La	^{140}La	40.2 h	1.32	326	100
				487	100
				815	100
				1596	73
Ce	^{141}Ce	32.5 d	0.82	145	0
Nd	^{147}Nd	11.1 d	2.3**	91	6
				531	0
Sm	^{153}Sm	46.8 h	14.4	103	40
Eu	^{152}Eu	12.4 y	1.15**	122	100
				965	100

Table 2. Continued

Element	Radionuclide	Half-life	I_0/σ_0*	Gamma-energy, keV	Coincident %
				1087	0
	^{154}Eu	8.5 y	4.21	1408	100
				123	100
				724	100
				1278	100
Gd	^{159}Gd	18.0 h	24**	363	0
Tb	^{160}Tb	72.1 d	17.0	87	100
				298	100
				879	100
				966	50
				1178	100
Ho	^{166}Ho	26.9 h	10.3	81	0
Tm	^{170}Tm	128.6 d	13.5**	84	0
Yb	^{169}Yb	30.7 d	4.6**	63	100
				94	100
	^{175}Yb	4.2 d	0.46	283	100
				396	0
Lu	^{177}Lu	6.7 d	<0.5**	113	50
				208	100
Hf	^{181}Hf	42.4 d	2.62	133	100
				482	100
Ta	^{182}Ta	115.0 d	33.5	100	100
				179	100
				222	100
				264	100
				1189	100
W	^{187}W	23.9 h	13.2	134	100
				478	100
				686	0
Ir	^{192}Ir	74.2 d	3.8**	308	84
				316	100
				468	100
Au	^{198}Au	2.70 d	15.7	412	0
Hg	^{197}Hg	64.1 h	0.49	77	0
	^{203}Hg	46.9 d	0.98	279	0
Th	^{233}Pa	27.0 d	11.5	300	100
				312	0
				416	0
U	^{239}Np	2.35 d	100	106	100
				228	100
				278	0#

Provided that the coincident 7.9 keV γ-ray is not detected by the coincidence shield.
* Data from MOENS et al.[11]
** Data from STEINNES.[4]

Discussion

The feasibility of epithermal activation is illustrated in the tables by means of the ratio I_0/σ_0 (resonance activation integral/thermal neutron activation cross section) of the stable nuclide subject to neutron activation, using values from MOENS et al.[11] In some cases where values were not found in MOENS et al.,[11] older data from STEINNES[4] were used. The radionuclides and corresponding γ-rays most frequently used for the determination of each element by INAA are listed and the fraction of the disintegrations where each γ-ray is emitted in coincidence with one or more other γ-rays is estimated from the compilation by LEDERER and SHIRLEY.[12]

After epithermal activation the gross activity of the sample is in most cases substantially reduced and the irradiated sample may be counted much closer to the detector without problems associated with high dead time. Given that the counting efficiency for ENAA can be increased such as the total sample counting rate is equal to that of the sample irradiated with the whole reactor spectrum, then the relative activity enhancement of a desired radionuclide (d) over an interfering radionuclide (D) may be expressed as follows:

$$F = (I_0/\sigma_0)_d/(I_0/\sigma_0)_D$$

The advantage observed just by introducing a CS system instead of a regular germanium detector is not readily quantified because it depends on the characteristics of the CS system as well as the position of the sample relative to the main detector. According to LANDSBERGER and WU,[10] the CS system can usually reduce the background by a factor of 5 to 10. BACCHI et al.[13] found suppression factors of around 5 for ^{137}Cs in their system, varying somewhat with distance from the detector. If the radionuclide d disintegrates with a non-coincident γ-ray whereas the interfering γ-rays from D are coincident, further advantage should be achieved by CS counting. LANDSBERGER et al.[14] state that radio-nuclides having two or more gamma-rays in strong coincidence with each other, are severely suppressed in a CS system, but they give no figures to quantify this suppression. Obviously the suppression of coincident γ-rays depends on the detector configuration and presumably even more on the distance between sample and detector. On the other hand placing the sample near the detector makes the system sensitive to dead-time losses even at moderate counting rates, due to random coincidences.

Thus, it seems difficult at the present stage to quantify the added advantage of CS measurements in ENAA of geological material. Considering the properties of the main interfering radionuclides, however, it is possible to predict in general terms what cases are favorable and which are not, based on the data in Tables 1 and 2. The main interfering radionuclides in short-lived INAA of geological materials are in most cases 2.3 min ^{28}Al, 2.58 h ^{56}Mn, and 15.0 h ^{24}Na. As far as ^{24}Na is concerned, the 1368 keV and 2754 keV γ-rays are coincident and could be considerably reduced by CS. In the case of ^{56}Mn, the 1811 keV γ-ray could be similarly reduced and the 847 keV γ-ray also partly, whereas the 1780 keV γ-ray of ^{28}Al is mono-energetic. Thus the advantage of introducing CS in ENAA based on short irradiations would be mainly for product nuclides with half-lives of 10–15 minutes or more.

Longer-lived nuclides usually constituting the main components of neutron-activated silicate rock samples are 40.2 h ^{140}La, 44.6 d ^{59}Fe, 83.9 d ^{46}Sc, and 5.26 y ^{60}Co. With the exception of ^{59}Fe these nuclides emit coincident γ-rays and, therefore, should be considerably reduced by CS measurements. Hence, there are many cases of ENAA based on long-lived radionuclides where CS measurement should improve the detection limit significantly due to reduction of interference from major components in the γ-ray spectra.

Given these facts and considering the I_0/σ_0 and γγ-coincidence data in Tables 1 and 2 for elements previously indicated to be good cases for ENAA, the determination of the following elements should be markedly improved by CS measurement:

Short-lived:

Sr (^{87m}Sr), Zr (^{97}Zr/^{97}Nb), I, Cs (^{134m}Cs), Eu (9.3 h ^{152}Eu, 963 keV), U (^{239}U).

Long-lived:

As, Rb, Sr (^{85}Sr), Mo (^{99m}Tc), In (^{114m}In), Sn (^{113}Sn), Sb (^{122}Sb), Ba (^{131}Ba, 216 keV), Gd, Ho, Tm, W (^{187}W, 686 keV), Au, Th, U (^{239}Np).

For other elements conveniently determined after epithermal activation (Ga, Se, Ag, In, Cs, Tb, Yb, Hf, Ta, W) the use of CS is not recommended. All considered, however, the use of Compton suppression spectrometry should generally improve the determination of trace elements in geological materials by epithermal neutron activation analysis.

Conclusions

In previous times the determination of trace elements in geological materials was one of the main application areas of neutron activation analysis, as, e.g., illustrated by the extensive use in analysis of samples from the Apollo lunar missions. More recently, NAA has lost its strong position in this area, and novel developments appear to be necessary in order to defend its position for the future.[15] As shown in this paper there are good reasons to believe that the combination of epithermal activation and Compton suppression γ-spectrometry represents such a development. It is now up to scientists possessing Compton suppression detection systems to quantify the advantages that may be obtained.

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