Chapter Y

Instrumental neutron activation by abbreviated count

By James R. Budahn and Gregory A. Wandless

U.S. Geological Survey Open File Report 02-223-Y

Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey

Contents

Tables

Instrumental neutron activation analysis by abbreviated count

By James R. Budahn and Gregory A. Wandless

Code: R021 Accepted: provisional 1996

: T15 Revised: 2/7/02

Principle

Instrumental neutron activation analysis (INAA) selectively measures radioactive nuclide activity produced by nuclear reactions on naturally occurring isotopes. The activity of the indicator radionuclide produced during irradiation is directly proportional to the amount of the element in the sample. The analytical determination is made by comparing the induced activity in the sample with well-characterized standards activated under identical conditions of neutron flux. The activities of the samples and standards are measured using gamma-ray spectroscopy. Gamma-ray radiation emitted by a radionuclide is converted to an electrical signal by a semiconductor detector. The electrical signal is analyzed by a multichannel analyzer. Semiconductor detectors, such as high-purity and lithium-drifted germanium detectors, are used to exploit their high resolution. Spectra produced are analyzed by software which locates peaks, identifies peaks, and calculates the area of each peak. Refer to Gordon and others (1968), Baedecker and McKown (1987), and Laul (1979) for more detailed descriptions of the principles of INAA.

Interferences

Neutron activation analysis is matrix dependent. Uranium concentrations higher than 100 ppm increase the detection limits for select rare earth elements and Zr from the generation of fission products. Detection limits are also affected by samples containing high abundances of certain elements, such as the rare earth elements and ore-type samples. Ore-type samples that contain elevated abundances of what are normally trace elements, require special counting and computer analysis for accurate determinations. On the opposite extreme, samples with very low abundances of most trace elements (for example, metamorphic marbles, limestones and quartzites also require special handling and analysis. A detailed discussion of other known interferences can be found in Baedecker and McKown (1987).

Scope

Not all of the elements shown in table 1 can be determined in all matrixes. Samples having unusual matrixes will require adjustments to the counting protocol. A minimum of 1 month is required for completion of the analysis. The technique is “non-destructive” and if a limited amount of sample is available it may, with some safety/health restrictions, be analyzed by other methods. Reporting limits are matrix dependent and may be higher for routine analyses. A lower limit on the concentration of an element is calculated by estimating the minimum detectable peak area above the observed background using the peak detection criteria used in the peak fitting algorithm. The minimum detectable peak is determined by 3 sigma, where sigma is the standard deviation of the count rate (reeves and Brooks, 1978). Reporting limits are matrix dependent and may be higher for routine analysis.

Table 1.—Reporting limits for element determinations by INAA abbreviated count.

Element	*Lower limit (ppm)*	*Element*	*Lower limit (ppm)*
Ca	1,000	Ce, Co, Cr, Cs, Ho, Sb,	0.1
K	100	Sm, Th, U, Yb, W	
Ba, Fe, Ni, Sr, Zr	10	Eu, Hf, La, Lu, Sc,	0.01
As, Na, Nd, Rb, Zn	1	Ta, Tb	

Apparatus

- Germanium-Lithium drifted [Ge (Li)], High-Purity Germanium (HPGe) , and low-energy Intrinsic Planar Germanium (LEP) detectors
- Associated electronics for detector signal processing, i.e. amplifier, high-voltage power supply, analog-to-digital converter
- A multi-channel analyzer (Alpha-255 Genie-ESP), with a minimum of 2048 channels

Reagents

None

Safety precautions

Samples returning from irradiation in the nuclear reactor are radioactive. Handling precautions are used to minimize exposure to gamma radiation. All personnel are monitored with radiation badges and dosimeters as regulated by the Nuclear Regulatory Commission.

Procedure

1. For each irradiation at least one USGS or NIST reference sample is used as a QC monitor. A synthetic composite quartz standard (CQS) or spiked Horse Mountain Obsidian (HMS) is used as a multi-element standard and is run in triplicate.
2. Samples received for analysis are normally ground to -100 mesh and require no further treatment. Samples, standards, and QC monitor(s) are weighed (0.3 - 1.0 g) into appropriate containers and irradiated for 6.5 to 8 hours in a uniform neutron flux (2.4×10^{12} $ns^{-1}cm^{-2}$).
3. The detector/data acquisition system is energy calibrated prior to sample counting by a source of known gamma-ray energies.
4. Data acquisition is performed by a multichannel analyzer adjusted for 0.1 keV/channel for low energy detectors and 0.5 keV/channel for high energy detectors (Table 2).
5. Spectra are acquired for samples, standards, and QC monitor(s) on the same detector, at the same counting geometry for short half-life nuclides 6 to 9 days after completion of the irradiation on a HPGe or Ge(Li) and a LEP detector, and for intermediate and long half-life nuclides after 23 days on a HGe or Ge(Li) and a LEP detector. This schedule may be altered as needed for ore-type samples or samples containing high concentrations of interference elements.
6. Spectra for two or three CQS or HMS standards are collected near the beginning, at the end and sometimes in the middle of each count sequence. The irradiation set is concentration calibrated by averaging the specific activity for each radionuclide. Standard outlier tests are used to reject any anomalous results.

7. Data reduction is performed using the computer program, SPECTRA, Baedecker (1976), Baedecker and Grossman (1989) and Baedecker and Grossman (1994) or by the commercial program SAMPO (Routti, 1969) to determine photo-peak areas. These data are processed with in-house data reduction programs to determine concentration values.
8. The precision, σ, is determined by counting statistics. Data for QC monitors are compared with expected results. Results that deviate from expected by more than 3 σ, determined by counting statistics, are checked for experimental error. Long term accuracy is determined by control charts.

Table 2.—Energy calibration of instrument.

Detector	Low Energy	High Energy
Multichannel analyzer	2048 channels	4096 channels
	0.1 keV/channel	0.5 keV/channel
Gamma-ray source	^{57}Co, ^{241}Am, ^{182}Ta, ^{214}Pb, ^{226}Ra	^{60}Co, ^{237}Am, ^{88}Y, ^{137}Ba, ^{214}Pb

Calculation

Elemental concentration are determined by calculating comparitor factors for standards (MCF) and for samples (SCF). The equations for those calculations are shown below. For more details of the calculations, refer to Baedecker (1977), Baedecker and Grossman (1989), and Baedecker and Grossman (1994).

$$MCF = \frac{(peak\ area) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(standard\ weight) \cdot t_l \cdot (1 - e^{-\lambda t_c})}$$

$$SCF = \frac{(peak\ area) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(sample\ weight) \cdot t_l \cdot (1 - e^{-\lambda t_c})}$$

$$CONCENTRATION = \frac{SCF}{Average\ MCF}$$

where

λ = the decay constant for the indicator radionuclide
t_d = the elapsed time between the start of the first count in the sample set and the start of the count being processed
t_l = live time duration of the count
t_c = clock time duration of the count

Assignment of Uncertainty

Table 1 lists the analytical results for selected reference materials by the INAA abbreviated count protocol.

Table 3.—Analytical performance summary for elements by INAA abbreviated count

[Preferred values (*pv*) in **BOLD** are recommended values from Govindaraju (1994), USGS Certificate of Analysis or International proficiency test for analytical geochemistry laboratories reports; other values are informational values]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Denver, CO laboratory data

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Antimony, Sb (ppm)							
OU-4	microdiorite	3	0.23	0.01	**0.30**	2	77
BCR-2	basalt	3	0.33	0.01		3	
AGV-2	andesite	2	0.43	0.02	0.60	6	72
OU-6	slate	3	0.55	0.01	**0.55**	2	100
BCR-1	basalt	2	0.66	0.01	0.62	2	106
AGV-1	andesite	2	3.90	0.15	**4.3**	4	91
Arsenic, As (ppm)							
AGV-2	andesite	2	0.75	0.21		28	
BCR-1	basalt	2	0.84	0.05	**0.65**	6	129
AGV-1	andesite	2	0.85	0.01	0.85	1	100
BCR-2	basalt	3	0.88	0.11		13	
OU-4	microdiorite	3	1.20	0.10		8	
OU-6	slate	3	14.2	0.14	**13.0**	1	109
Barium, Ba (ppm)							
OU-4	microdiorite	3	342	6	**361**	2	95
OU-6	slate	3	506	3	**477**	1	106
BCR-1	basalt	2	669	17	**681**	2	98
BCR-2	basalt	3	717	64	**683**	9	105
AGV-2	andesite	2	1100	50	**1140**	5	96
AGV-1	andesite	2	1155	15	**1226**	1	94
Calcium, as CaO (wt percent)							
OU-6	slate	3	1.12	0.06	**0.74**	5	151
OU-4	microdiorite	3	4.59	0.18	**4.48**	6	102
AGV-1	andesite	2	4.84	0.38	**4.94**	9	98
AGV-2	andesite	2	5.15	0.25	**5.20**	5	99
BCR-1	basalt	2	6.82	0.15	**6.95**	2	98
BCR-2	basalt	3	7.51	0.18	**7.12**	3	105
Cerium, Ce (ppm)							
BCR-2	basalt	3	52.7	1.82	**53.0**	3	99
BCR-1	basalt	2	53.2	0.65	**53.7**	1	99
OU-4	microdiorite	3	54.9	0.69	**55.7**	1	99
AGV-2	andesite	2	68.6	1.00	**68.0**	1	101
AGV-1	andesite	2	69.5	0.20	**67.0**	0	104
OU-6	slate	3	82.9	0.29	**74.4**	0	111

Table 3.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Cesium, Cs (ppm)							
BCR-1	basalt	2	0.93	0.03	**0.96**	2	97
AGV-2	andesite	2	1.11	0.03	1.16	3	96
BCR-2	basalt	3	1.13	0.02	1.10	2	103
AGV-1	andesite	2	1.26	0.09	**1.28**	7	98
OU-4	microdiorite	3	1.96	0.04	**2.07**	2	95
OU-6	slate	3	8.49	0.04	**8.02**	0	106
Chromium, Cr (ppm)							
AGV-1	andesite	2	9.5	0.2	**10.1**	2	94
BCR-1	basalt	2	11.7	0.8	16	7	73
AGV-2	andesite	2	15.9	0.6	**17**	4	94
BCR-2	basalt	3	16.1	1.4	**18**	9	89
OU-4	microdiorite	3	52.1	1.1	**54.7**	2	95
OU-6	slate	3	71.7	0.5	**70.9**	1	101
Cobalt, Co (ppm)							
OU-4	microdiorite	3	13.0	0.1	**13.5**	1	96
AGV-1	andesite	2	15.3	0.3	**15.3**	2	100
AGV-2	andesite	2	15.6	0.5	**16.0**	3	98
OU-6	slate	3	30.1	0.1	**29.1**	0	103
BCR-1	basalt	2	38.7	0.2	**37.0**	1	105
BCR-2	basalt	3	38.9	1.4	**37.0**	8	105
Europium, Eu (ppm)							
OU-6	slate	3	1.43	0.01	**1.36**	1	105
AGV-2	andesite	2	1.50	0.04	1.54	3	97
AGV-1	andesite	2	1.57	0.02	**1.64**	1	96
OU-4	microdiorite	3	1.61	0.01	**1.64**	1	98
BCR-1	basalt	2	1.93	0.03	**1.95**	2	99
BCR-2	basalt	3	1.99	0.01	**2.00**	1	100
Hafnium, Hf (ppm)							
BCR-2	basalt	3	4.76	0.06	4.8	1	99
BCR-1	basalt	2	4.87	0.16	**4.95**	3	98
OU-6	slate	3	4.87	0.02	**4.70**	1	104
AGV-2	andesite	2	4.90	0.02	5.1	0	96
AGV-1	andesite	2	5.01	0.06	**5.1**	1	98
OU-4	microdiorite	3	5.20	0.08		1	
Holmium, Ho (ppm)							
AGV-2	andesite	2	0.66	0.01	0.71	2	93
AGV-1	andesite	2	0.72	0.01	**0.67**	2	107
OU-6	slate	3	1.11	0.03	**1.01**	2	110
BCR-1	basalt	2	1.24	0.01	**1.26**	1	98
BCR-2	basalt	3	1.25	0.03	1.33	2	94
OU-4	microdiorite	3	1.51	0.14	**1.63**	8	93

Table 3.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Iron, as FeO (wt percent)							
OU-4	microdiorite	3	5.21	0.07	**5.24**	1	99
AGV-2	andesite	2	5.99	0.04	**6.11**	1	98
AGV-1	andesite	2	6.13	0.04	**6.08**	1	101
OU-6	slate	3	8.34	0.06	**8.11**	1	103
BCR-1	basalt	2	12.27	0.02	**12.07**	1	102
BCR-2	basalt	3	12.54	0.36	**12.41**	3	101
Lanthanum, La (ppm)							
OU-4	microdiorite	3	23.8	0.9	**25.0**	4	95
BCR-2	basalt	3	24.5	0.3	**25.0**	1	98
BCR-1	basalt	2	25.4	0.6	**24.9**	2	102
OU-6	slate	3	34.2	0.2	**33.0**	1	104
AGV-2	andesite	2	37.6	0.1	**38.0**	0	99
AGV-1	andesite	2	38.1	0.6	**38.0**	2	100
Lutetium, Lu (ppm)							
AGV-2	andesite	2	0.24	0.00	0.25	0	96
AGV-1	andesite	2	0.25	0.01	**0.27**	2	93
OU-6	slate	3	0.50	0.005	**0.45**	1	111
BCR-2	basalt	3	0.52	0.005	0.51	1	102
BCR-1	basalt	2	0.54	0.01	**0.51**	1	106
OU-4	microdiorite	3	0.69	0.01	**0.71**	1	97
Neodymium, Nd (ppm)							
OU-4	microdiorite	3	27.7	1.4	**27.9**	5	99
BCR-1	basalt	2	30.0	1.0	**28.8**	3	104
BCR-2	basalt	3	30.0	0.6	**28.0**	2	107
AGV-2	andesite	2	30.9	1.3	**30.0**	4	103
AGV-1	andesite	2	32.6	0.4	**33.0**	1	99
OU-6	slate	3	33.8	0.2	**29.0**	1	117
Nickel, Ni (ppm)							
BCR-2	basalt	3	10.3	1.1		11	
BCR-1	basalt	2	14.5	2.3	13	16	112
AGV-1	andesite	2	18.6	3.1	16	18	104
AGV-2	andesite	2	20.4	2.7	**19**	13	107
OU-4	microdiorite	3	27.8	4.5	**21.0**	16	132
OU-6	slate	3	45.7	1.4	**39.8**	3	115
Potassium, as K_2O (wt percent)							
BCR-2	basalt	3	1.67	0.12	**1.79**	7	93
BCR-1	basalt	2	1.69	0.04	**1.69**	2	100
OU-4	microdiorite	3	2.47	0.07	**2.70**	3	91
AGV-1	andesite	2	2.72	0.11	**2.91**	4	93
AGV-2	andesite	2	2.93	0.05	**2.88**	2	102
OU-6	slate	3	2.99	0.05	**3.05**	2	98

Table 3.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Rubidium, Rb (ppm)							
BCR-1	basalt	2	47.0	4.3	**47.2**	9	100
BCR-2	basalt	3	49.6	1.6	**48.0**	3	103
AGV-1	andesite	2	67.0	1.5	**67.3**	2	100
AGV-2	andesite	2	67.3	4.3	**68.6**	6	98
OU-4	microdiorite	3	95.2	0.6	**98.5**	1	97
OU-6	slate	3	126.0	0.8	**120.2**	1	105
Samarium, Sm (ppm)							
AGV-2	andesite	2	5.88	0.01	**5.70**	0	103
AGV-1	andesite	2	5.89	0.03	**5.90**	1	100
OU-6	slate	3	6.56	0.06	**5.92**	1	111
BCR-2	basalt	3	6.64	0.02	**6.70**	0	99
BCR-1	basalt	2	6.67	0.05	**6.59**	1	101
OU-4	microdiorite	3	7.25	0.07	**6.94**	1	104
Scandium, Sc (ppm)							
AGV-1	andesite	2	12.2	0.00	**12.2**	0	100
AGV-2	andesite	2	12.7	0.10	**13.0**	1	98
OU-4	microdiorite	3	19.8	0.26	**19.1**	2	104
OU-6	slate	3	25.1	0.05	**22.1**	0	114
BCR-1	basalt	2	34.4	0.10	**32.6**	0	106
BCR-2	basalt	3	34.4	0.61	**33.0**	2	104
Sodium, as Na_20 (wt percent)							
OU-6	slate	3	1.81	0.01	**1.78**	1	102
BCR-2	basalt	3	3.18	0.12	**3.16**	4	101
BCR-1	basalt	2	3.36	0.05	**3.27**	1	103
OU-4	microdiorite	3	3.60	0.02	**3.61**	1	100
AGV-2	andesite	2	4.18	0.01	**4.19**	1	100
AGV-1	andesite	2	4.31	0.01	**4.26**	1	101
Strontium, Sr (ppm)							
OU-4	microdiorite	3	110	3	**100**	2	110
OU-6	slate	3	150	2	**131**	2	110
BCR-1	basalt	2	336	13	**330**	4	102
BCR-2	basalt	3	356	11	**346**	3	103
AGV-2	andesite	2	642	16	**658**	2	98
AGV-1	andesite	2	649	22	**662**	3	98
Tantalum, Ta (ppm)							
BCR-1	basalt	2	0.83	0.01	**0.81**	1	102
BCR-2	basalt	3	0.83	0.01		1	
AGV-2	andesite	2	0.88	0.01	0.89	1	99
AGV-1	andesite	2	0.92	0.01	**0.90**	1	102
OU-4	microdiorite	3	0.99	0.03	**1.00**	3	99
OU-6	slate	3	1.09	0.01	**1.06**	1	103

Table 3.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Terbium, Tb (ppm)							
AGV-2	andesite	2	0.61	0.03	0.64	5	95
AGV-1	andesite	2	0.64	0.03	**0.70**	5	91
OU-6	slate	3	0.90	0.01	**0.85**	1	106
BCR-2	basalt	3	1.05	0.02	1.07	2	98
BCR-1	basalt	2	1.07	0.07	**1.05**	6	102
OU-4	microdiorite	3	1.17	0.04	**1.25**	3	94
Thorium, Th (ppm)							
BCR-2	basalt	3	5.92	0.13	**6.20**	2	95
BCR-1	basalt	2	6.03	0.08	**5.98**	1	101
AGV-2	andesite	2	6.03	0.21	**6.10**	3	99
AGV-1	andesite	2	6.40	0.27	**6.50**	4	98
OU-4	microdiorite	3	7.88	0.07	**8.42**	1	94
OU-6	slate	3	12.00	0.08	**11.51**	1	104
Tungsten, W (ppm)							
AGV-2	andesite	2	0.70	0.13		19	
BCR-2	basalt	3	0.73	0.54		74	
AGV-1	andesite	2	0.76	0.32	0.55	42	138
BCR-1	basalt	2	1.02	0.51	**0.44**	51	232
OU-4	microdiorite	3	1.19	0.09		8	
OU-6	slate	3	1.40	0.21		15	
Uranium, U (ppm)							
BCR-1	basalt	2	1.77	0.03	**1.75**	2	101
BCR-2	basalt	3	1.79	0.03	**1.69**	2	106
AGV-2	andesite	2	1.88	0.03	**1.88**	2	100
AGV-1	andesite	2	1.97	0.14	**1.92**	7	103
OU-4	microdiorite	3	2.14	0.07	**2.19**	3	98
OU-6	slate	3	2.17	0.03	**1.96**	1	111
Ytterbium, Yb (ppm)							
AGV-1	andesite	2	1.66	0.04	**1.72**	3	97
AGV-2	andesite	2	1.67	0.09	**1.60**	5	104
OU-6	slate	3	3.39	0.06	**3.00**	2	113
BCR-1	basalt	2	3.59	0.02	**3.38**	1	106
BCR-2	basalt	3	3.64	0.05	**3.50**	1	104
OU-4	microdiorite	3	4.52	0.03	**4.70**	1	96
Zinc, Zn (ppm)							
AGV-1	andesite	2	90	5	**88**	4	102
AGV-2	andesite	2	95	2	**86**	2	111
OU-6	slate	3	109	1	**111**	1	98
OU-4	microdiorite	3	110	1	**69.5**	1	157
BCR-2	basalt	3	132	6	**127**	5	104
BCR-1	basalt	2	136	6	**129.5**	4	105

Table 3.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Zirconium, Zr (ppm)							
BCR-2	basalt	3	192	24	**188**	12	102
BCR-1	basalt	2	195	1	**190**	1	103
OU-6	slate	3	210	33	**174**	15	121
AGV-1	andesite	2	224	20	**227**	9	99
AGV-2	andesite	2	225	16	**230**	7	98
OU-4	microdiorite	3	239	3	**195**	1	123

Table 3.–Continued—No Duplicate data available at this time

Table 3.–Continued—No method blank data available at this time

Bibliography

Baedecker, P.A., 1976, SPECTRA: Computer reduction of gamma-ray spectroscopic data for neutron activation analysis, *in* Taylor, R.E., ed., Advances in Obsidian Glass Studies: Park Ridge, New Jersey, Noyes Press, p. 334-349.

Baedecker, P.A., and McKown, D.M., 1987, Instrumental neutron activation analysis of geochemical samples, *in* Baedecker, P.A., ed., Methods for Geochemical Analysis: U.S. Geological Survey Bulletin 1770, p. H1-H14.

Baedecker, P.A., and Grossman, J.N., 1989, The computer analysis of high resolution gamma-ray spectra from instrumental activation analysis experiments: U.S. Geological Survey Open-File Report 89-454.

Baedecker, P.A., and Grossman, J.N., 1994, the SPECTRA program library: A PC based system for gamma-ray spectra analysis and INAA data reduction: U.S. Geological Survey Open-File Report 94-168.

Gordon, G.E., Randle, K., Goles, G.G., Corliss, J.B., Besson, M.H., and Oxley, S.S., 1968, Instrumental activation analysis of standard rocks with high-resolution X-Ray detectors: Geochimica et Cosmochimica Acta, v. 32, p. 369-396.

Govindaraju, K., ed., 1994, 1994 Compilation of working values and sample descriptions for 383 geostandards: Geostandards Newsletter v. 18, Special Issue, p. 1-158.

Laul, J.C., 1979, Neutron activation analysis of geological materials: Atomic Energy Review, v. 17, p. 93-114.

Potts, P.J., Tindle, A.G., and Webb, P.C., 1992, Geochemical reference material compositions: CRC Press Inc., Boca Raton, Fla., p. 42-45.

Routti, J.T., 1969, SAMPO, A fortran program for computer analysis of gamma spectra from Ge(Li) detectors, and for other spectra with peaks. Lawrence Radiation Laboratory, 34 pp., UCRL-19452, UC-34 Physics, TID-4500 (55th edition).