

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231188335>

Low flux multielement instrumental neutron activation analysis in archaeometry

ARTICLE *in* ANALYTICAL CHEMISTRY · SEPTEMBER 1976

Impact Factor: 5.64 · DOI: 10.1021/ac50005a009

CITATIONS

44

READS

18

1 AUTHOR:



Ronald G.V. Hancock

McMaster University

262 PUBLICATIONS 2,212 CITATIONS

SEE PROFILE

Low Flux Multielement Instrumental Neutron Activation Analysis in Archaeometry

R. G. V. Hancock

Department of Chemical Engineering and Applied Chemistry, and SLOWPOKE Reactor Facility, University of Toronto, Toronto, Ontario, Canada M5S 1A4

A routine instrumental method has been developed for the analysis of 35 elements in potsherds by means of neutron activation analysis at fluxes of $\leq 2.5 \times 10^{11}$ n/cm² s. Using a SLOWPOKE reactor, each sample was bombarded 3 times with increasing neutron doses, and the resultant γ -ray emissions were analyzed following suitable decay periods. The accuracy and precision of measurement was estimated by analyzing a "standard" pottery and 2 Standard Reference Materials. For these samples, agreement with published results was within ± 5 –10% for the majority of elements, and analytical precisions were comparable. Only 3 out of 35 elements were in serious disagreement with published results for the standard pottery.

Over the past five years, considerable advances have been made in the field of archaeometry. A relatively small number of research groups has been employing either x-ray fluorescence (XRF) (1, 2) or instrumental neutron activation analysis (INAA) (3–5) for multielement analysis of ancient potsherds. As instrumentation has improved, there has been an increase in the number of elements analyzed.

Currently, 16–20 elements are being measured by INAA (3, 4) in order to establish the provenance of potsherds. The elements which have been determined are those which produce reasonably long-lived radioisotopes ($T_{1/2} > 2$ h). This restriction was necessary because of a physical separation of the laboratory from the nuclear reactor employed in activation and/or because of the limiting of access to relatively high neutron fluxes in conventional reactors. *

It is not impossible to use conventional reactors to determine elements producing short-lived radioisotopes in ceramic

materials (6), but the extra work required to produce satisfactory results appears to make the task impracticable on a routine basis.

Low flux reactors, such as the SLOWPOKE (Safe Low Power Critical Experiment) reactor at the University of Toronto (7), allow access to relatively low neutron fluxes (10^{11} – 10^{12} n/cm² s) and can be most profitably employed for the analysis of short-lived isotope-producing elements in pottery.

The flux limitations of such a reactor are obvious, but are not sufficient to eliminate their use for the analysis of elements which produce long-lived isotopes. As an example, at the SLOWPOKE reactor, cobalt in potsherds (averages 5–30 ppm) may be determined either by the production of ^{60m}Co (10.5m half-life) or by the production of ⁶⁰Co (5.26 years half-life).

Since the number of elements previously studied has been restricted by analytical technique rather than geological or ceramic considerations, a program was instituted to develop a more comprehensive multielement analytical scheme which could be routinely applied to the analysis of potsherds.

Because of the stable nature of the neutron flux in the SLOWPOKE reactor system (8), multielement standards are not normally employed in the routine analysis of samples.

The present work described an INAA procedure in which 35 elements are quantized for each potsherd. Included are elements indicative of the provenance and the method of production of the ceramics.

EXPERIMENTAL

Samples and Standards. Two Standard Reference Materials, Coal (SRM 1632) and Fly Ash (SRM 1633), from the U.S. National Bureau of Standards, Washington, D.C., were analyzed as were samples of

Table I. Nuclear Data and Procedures Employed in Ceramics Analyses

Element symbol	Isotope measured	Half-life	γ -ray used, keV	Irradiation ^a	Decay time
Na	²⁴ Na	15.0 h	1369	B	16–30 h
Mg	²⁷ Mg	9.45 m	1014	A	15–25 m
Al	²⁸ Al	2.31 m	1779	A	15–25 m
Cl	³⁸ Cl	37.3 m	2167	A	15–25 m
K	⁴² K	12.5 h	1525	B	16–30 h
Ca	⁴⁹ Ca	8.8 m	3083	A	15–25 m
Sc	⁴⁶ Sc	83.9 d	889	C	10–20 d
Ti	⁵¹ Ti	5.8 m	320	A	15–25 m
V	⁵² V	3.75 m	1434	A	15–25 m
Cr	⁵¹ Cr	27.8 d	320	C	10–20 d
Mn	⁵⁶ Mn	2.56 h	1811	A	15–25 m
Fe	⁵⁹ Fe	45.6 d	1099	C	10–20 d
Co	⁶⁰ Co	5.26 y	1173	C	10–20 d
Ni	⁵⁸ Co	71.2 d	811	C	10–20 d
Cu	⁶⁴ Cu	12.8 h	511	B	16–30 h
Zn	⁶⁵ Zn	245 d	1115	C	10–20 d
Ga	⁷² Ga	14.3 h	833	B	16–30 h
As	⁷⁶ As	26.4 h	559	C	5–6 d
Br	⁸² Br	35.5 h	554	C	5–6 d
Rb	⁸⁶ Rb	18.7 d	1077	C	10–20 d
Sr	^{87m} Sr	170 m	388	A	15–25 m
Sb	¹²² Sb	67.1 h	564	C	5–6 d
Cs	¹³⁴ Cs	749 d	796	C	10–20 d
Ba	¹³⁹ Ba	83 m	166	A	15–25 m
La	¹⁴⁰ La	40.2 h	487	C	5–6 d
Ce	¹⁴¹ Ce	32.5 d	145	C	10–20 d
Sm	¹⁵³ Sm	46.8 h	103	C	5–6 d
Eu	^{152m} Eu	9.35 h	122	B	16–30 h
Dy	¹⁶⁵ Dy	140 m	94	A	15–25 m
Yb	¹⁶⁹ Yb	32.0 d	177	C	10–20 d
Lu	¹⁷⁷ Lu	6.74 d	208	C	10–20 d
Hf	¹⁸¹ Hf	42.5 d	482	C	10–20 d
Ta	¹⁸² Ta	115 d	1221	C	10–20 d
Th	²³³ Pa	27.0 d	312	C	10–20 d
U	²³⁹ U	23.54 m	75	A	15–25 m

^a A = 1 m at 10^{11} n/cm² s. B = 6 m at 2.5×10^{11} n/cm² s. C = 16 h at 2.5×10^{11} n/cm² s.

Standard Pottery prepared by Perlman and Asaro (6) at Berkeley, Calif. These samples were analyzed as unknowns.

Standards were prepared in duplicate from metals or stable salts. Dilute standard solutions were employed where necessary.

Irradiations. Samples were irradiated in the low flux SLOWPOKE-1 nuclear reactor at the University of Toronto (7). A maximum of two sample vials could be placed in each irradiation capsule. All irradiations were made in sample site No. 1, which has the highest neutron flux. The sample site is located horizontally in the beryllium side reflector in the mid-plane of the core. This horizontal location results in a significant neutron flux differential along the length of the irradiation capsule. The flux difference between a sample in the outermost vial and one in the innermost vial was determined to be approximately 17%. The two sample vial positions within the same irradiation capsule were therefore treated as separate irradiation positions. Accordingly, the standard materials were irradiated in both sample vial positions, and independent calculations leading to the determination of elemental concentrations were made.

Since the neutron flux in the SLOWPOKE reactor can be controlled to within $\pm 2\%$ over long periods, despite fuel burnup, it was feasible to irradiate the standards and samples separately. This allowed for convenient preparation of standards, with many elements being irradiated singly to determine the specific activity of each major γ -ray emitted. For elements producing short-lived isotopes, repeated determinations were made to obtain average values. Elements producing isotopes with half-lives longer than several weeks were irradiated once and counted several times over a reasonable time period so that averages could be calculated. In both cases, the specific activities were corrected for decay after irradiation.

The samples were irradiated for three different periods of time at various neutron fluxes to allow for convenient instrumental γ -ray spectrometric analysis of a number of isotopes with greatly different half-lives.

(a) Individual 200-mg samples in small polythene vials were irradiated for 1 min at a neutron flux of 1×10^{11} n/cm² s. The irradiated samples were counted once, for a period of 5 min, after a decay time of 21 min to allow the ²⁸Al to decay to a reasonable level. Al, Ba, Ca, Cl, Dy, Mg, Mn, Sr, Ti, V, and U concentrations were determined from the results. The isotopes found, together with their half-lives and γ -ray energies employed, are listed in Table I. Cobalt concentrations were not determined using ⁶⁰Co because the precision of measurement was found to be better using ⁶⁰Co after a long irradiation in SLOWPOKE.

(b) After 3 days, individual samples were irradiated for 6 min at a neutron flux of 2.5×10^{11} n/cm² s. In this case, the samples were allowed to decay for at least 16 h so that the short-lived isotopes listed above would be either dead or greatly reduced in intensity. Cu, Eu, Ga, K, and Na concentrations were determined from these irradiations (See Table I).

(c) Batches of 10 samples were then sealed in small, clean, hand-made polythene bags and were placed in groups of five at each end of the irradiation capsule. They were then irradiated for 16 h at 2.5×10^{11} n/cm² s.

After a cooling period of 5–6 days, the samples were transferred back to 1-ml poly-vials and were counted serially for 500 s. From this counting, the concentrations of Au, As, Br, La, Sb, Sm, and Yb were determined. After a total cooling period of ≥ 12 days each sample was counted in turn for 100 min. The elements determined by counting the remaining long-lived isotopes at this last stage include Ce, Co, Cr, Cs, Fe, Hf, Lu, Ni, Rb, Sc, Ta, Th, Yb, and Zn. (See Table I for all isotopes, half-lives, and γ -rays used.)

Gd, Nd, Tb, and Tm were also identified as being present in hard-to-detect amounts, but since a representative set of rare earth elements had been readily determined, the concentrations of these elements were not determined.

Activity Measurements. Measurements of γ -ray activities were made with a Canberra Ge(Li) detector coupled through a 452 Ortec spectroscopy amplifier to an 8100 series, 4096 channel Canberra analyzer. The detector has a nominal relative counting efficiency of 6.7% and a FWHM resolution of 1.9 keV for the 1332 keV γ -ray of ⁶⁰Co. It is mounted horizontally in a model 7600 cryostat.

Samples were counted adjacent to the vertical face of the detector. To account for possible irregular distributions of the small quantities of standard material in the vials, each measurement was duplicated after the vial had been rotated through 180° about the vertical axis.

The effects of isotopes produced in the sample vial itself were found to be negligible in the work done with the standards. However, since some low-concentration components of the standard materials were common to the irradiation vials, the irradiated powders were transferred to fresh vials before counting.

Gamma-ray peak intensities were evaluated by automatic analyzer integration of suitable manually selected spectral regions of interest at and near each peak. The teletype output integrals were then processed using a programmable Wang 350 calculator to determine elemental concentrations.

RESULTS AND DISCUSSION

A total of 35 elements have been satisfactorily analyzed in potsherds by INAA using the SLOWPOKE reactor.

Except for nickel, where the (n,p) reaction ⁵⁸Ni(n,p)⁵⁸Co was used, all elements were determined using thermal neutron capture (n, γ) reactions. Zinc-65 and ⁶⁴Cu are the only isotopes which suffer gross spectral interference. Because of the relative amounts of zinc and scandium, the 1115-keV γ -ray peak of ⁶⁵Zn must be corrected for interference from the 1120-keV peak of ⁴⁶Sc. Similarly the 511-keV γ -ray of ⁶⁴Cu must be corrected for the effect of the 511-keV γ -ray from ²⁴Na.

Nuclear interferences from (n,p) and (n, α) reactions were found to be trivial in the analyzed material ($<0.5\%$) for all isotopes except for ²⁷Mg which, because of its low concentration relative to aluminum, is significantly affected by the ²⁷Al (n,p) ²⁷Mg reaction.

More than 300 potsherds have been analyzed by the described method. Results from the analysis of 5 samples each of NBS-SRM 1632-coal, NBS-SRM 1633 Fly Ash, and Perlman's "standard" pottery are displayed in Table II. In the table, the errors shown are group standard deviations based on replicate analyses. A comparison is made between the el-

Table II. INAA of NBS Standard Coal and Fly Ash, and Perlman's Standard Pottery

Element, ppm unless noted	NBS-SRM 1632 Coal		NBS-SRM 1633 Fly Ash		"Standard" Pottery	
	Found	Literature	Found	Literature	Found	Literature
Na	360 ± 20	414 ± 20 ^b	3410 ± 80	3200 ± 400 ^b	2740 ± 60	2580 ± 40
Mg (%)	0.19 ± 0.04	0.20 ± 0.05 ^b	1.9 ± 0.3	1.8 ± 0.4 ^b	1.32 ± 0.16	5 ± 2
Al (%)	1.51 ± 0.08	1.85 ± 0.13 ^b	10.8 ± 0.2	12.7 ± 0.5 ^b	13.6 ± 0.4	15.3 ± 0.2
Cl	920 ± 30	890 ± 125 ^b	<100	42 ± 10 ^b	<150	<130
K (%)	0.27 ± 0.03	0.28 ± 0.03 ^b	1.87 ± 0.05	1.61 ± 0.15 ^b	1.40 ± 0.05	1.35 ± 0.04
Ca (%)	0.37 ± 0.04	0.43 ± 0.05 ^b	4.07 ± 0.11	4.7 ± 0.6 ^b	0.2 ± 0.1	<0.02
Sc	3.88 ± 0.15	3.7 ± 0.3 ^b	25.5 ± 1.2	27 ± 1 ^b	18.1 ± 0.1	20.6 ± 0.3
Ti	920 ± 50	1110 ± 100 ^b	6850 ± 240	7400 ± 300 ^b	8440 ± 740	7820 ± 340
V	32.3 ± 1.5	35 ± 3 ^a	216 ± 7	214 ± 8 ^a	150 ± 10	N.D.
Cr	21.5 ± 1.0	20.2 ± 0.5 ^a	137 ± 7	131 ± 2 ^a	111 ± 2	115 ± 40
Mn	41 ± 2	40 ± 3 ^a	496 ± 12	493 ± 7 ^a	37.6 ± 1.9	40.9 ± 0.5
Fe (%)	0.92 ± 0.03	0.87 ± 0.03 ^a	7.28 ± 0.33	6.2 ± 0.3 ^b	0.91 ± 0.02	1.02 ± 0.01
Co	6.57 ± 0.47	5.7 ± 0.4 ^b	45.5 ± 2.6	41.5 ± 1.2 ^b	16.5 ± 0.8	14.1 ± 0.2
Ni	18 ± 5	15 ± 1 ^a	N.D.	98 ± 3 ^a	460 ± 60	279 ± 20
Cu	18.1 ± 0.8	18 ± 2 ^a	130 ± 10	128 ± 5 ^a	55 ± 14	59 ± 5
Zn	37 ± 10	37 ± 4 ^a	250 ± 10	210 ± 20 ^a	43 ± 7	59 ± 8
Ga	9 ± 2	9.3 ± 2.3 ^c	76 ± 16	70 ± 5 ^c	65 ± 5	44 ± 5
As	6.5 ± 0.3	5.9 ± 0.6 ^a	65.3 ± 2.2	61 ± 6 ^a	32.7 ± 0.6	30.8 ± 2.2
Br	16.6 ± 0.6	19.3 ± 1.9 ^b	6.5 ± 0.4	12 ± 4 ^b	2.4 ± 0.5	2.3 ± 0.9
Rb	23 ± 3	21 ± 2 ^b	140 ± 10	125 ± 10 ^b	70 ± 3	70 ± 6
Sr	120 ± 20	161 ± 16 ^b	1090 ± 90	1700 ± 300 ^b	<160	145 ± 20
Sb	3.8 ± 0.4	3.9 ± 1.3 ^b	6.28 ± 0.19	6.9 ± 0.6 ^b	1.76 ± 0.16	1.71 ± 0.05
Cs	1.8 ± 0.1	1.4 ± 0.1 ^b	9.84 ± 0.35	8.6 ± 1.1 ^b	9.60 ± 0.60	8.31 ± 0.55
Ba	320 ± 20	352 ± 30 ^b	2660 ± 100	2700 ± 200 ^b	610 ± 150	712 ± 32
La	9.76 ± 0.45	10.7 ± 1.2 ^b	81.6 ± 1.7	82 ± 2 ^b	45.0 ± 1.2	44.9 ± 0.5
Ce	21.5 ± 1.7	19.5 ± 1.0 ^b	136 ± 9	146 ± 15 ^b	79.6 ± 2.3	80.3 ± 3.9
Sm	1.55 ± 0.07	1.7 ± 0.2 ^b	12.0 ± 0.4	12.4 ± 0.9 ^b	6.44 ± 0.14	5.87 ± 0.12
Eu	0.34 ± 0.01	0.33 ± 0.04 ^b	3.10 ± 0.10	2.5 ± 0.4 ^b	1.26 ± 0.05	1.29 ± 0.03
Dy	0.57 ± 0.04	0.49 ± 0.08 ^c	4.28 ± 0.40	4.80 ± 0.32 ^c	4.43 ± 0.20	4.79 ± 0.19
Yb	1.0 ± 0.2	0.7 ± 0.1 ^b	7.47 ± 0.13	7 ± 3 ^b	3.34 ± 0.15	2.80 ± 0.36
Lu	0.14 ± 0.02	0.14 ± 0.01 ^b	0.73 ± 0.06	1.0 ± 0.1 ^b	0.424 ± 0.017	0.402 ± 0.036
Hf	1.10 ± 0.07	0.96 ± 0.05 ^b	9.1 ± 0.6	7.9 ± 0.4 ^b	6.55 ± 0.50	6.23 ± 0.44
Ta	0.25 ± 0.03	0.24 ± 0.04 ^b	2.48 ± 0.13	1.8 ± 0.3 ^b	1.6 ± 0.3	1.55 ± 0.04
Th	3.2 ± 0.5	3.2 ± 0.2 ^b	23.7 ± 1.3	24.8 ± 2.2 ^b	12.7 ± 0.3	13.96 ± 0.39
U	1.6 ± 0.2	1.4 ± 0.1 ^a	12.3 ± 0.6	11.6 ± 0.2 ^a	6.5 ± 0.8	4.82 ± 0.44

^a NBS Certificates of Analysis, SRM 1632 and 1633. The certificate quotes 2 standard deviations. All other numbers show 1 standard deviation. ^b Ref. 9. ^c Ref. 10.

emental concentration found using the SLOWPOKE reactor and either NBS certified values or recent literature values (9). For the determination of gallium and dysprosium in coal and fly ash, values have been compared with results obtained by Ontario Hydro personnel (10). Other published work (11) appears to be in general agreement with these values.

It may be seen that most elemental concentrations are in reasonable agreement (within ±5–10%) with both the NBS certified values, with those of Ondov et al. (9), and with those of Perlman and Asaro (6).

As can be seen from the relative sizes of errors shown in Table II, the problem of a significant intersample dispersion of antimony values observed by Ondov et al. (9) was not observed in the present work.

The only serious discrepancies in agreement appear to be for nickel, gallium, and uranium in the standard pottery. This, however, means that out of 35 elements determined, 32 may be readily used for direct comparison of archaeometric data produced at Berkeley and Toronto.

Finally, given that the non-NBS values are relatively accurate, it is clear that the described multielement analysis scheme, using a low flux SLOWPOKE nuclear reactor, may profitably be applied to provenance studies in archaeometry. In fact, an overabundance of analytical data is produced with relative ease, so that the problem becomes one of choosing suitable diagnostic elements with which to determine the provenance of potsherds.

ACKNOWLEDGMENT

The substantial encouragement of L. Levine, West Asian Department, Royal Ontario Museum, and U. M. Franklin, Department of Metallurgy and Materials Science, is appreciated.

LITERATURE CITED

- (1) M. Picon, M. Vichy and E. Meille, *Archaeometry*, **13** (2), 191 (1971).
- (2) A. B. Poole and L. R. Finch, *Archaeometry*, **14** (1), 79 (1972).
- (3) F. Widemann, M. Picon, F. Asaro, H. V. Michel, and I. Perlman, *Archaeometry*, **17** (1), 45 (1975).
- (4) R. Abascal-M., G. Harbottle, and E. V. Sayre, *Adv. Chem. Ser.*, **138**, 81 (1974).
- (5) G. Banterla, A. Stenico, M. Terrani, and S. Villani, *Archaeometry*, **15** (2), 209 (1973).
- (6) I. Perlman and F. Asaro, "Science and Archaeology," R. H. Brill, Ed., M.I.T., Cambridge, Mass., 1971.
- (7) R. E. Kay, J. W. Hilborn, P. D. Stevens-Guille, and R. E. Jervis, *Int. J. Appl. Radiat. Isot.*, **24**, 509 (1973).
- (8) R. G. V. Hancock, 58th Chemical Conference, Toronto, Canada, Paper No. 41 (1975).
- (9) J. M. Ondov, W. H. Zoller, I. Olmez, N. K. Aras, G. E. Gordon, L. A. Rancitelli, K. H. Abel, R. H. Filby, K. R. Shah, and R. C. Ragaini, *Anal. Chem.*, **47**, 1102 (1975).
- (10) A. Guest, Ontario Hydro Research Division, Toronto, Ontario, personal communication, 1975.
- (11) A. Chattopadhyay and R. E. Jervis, *Anal. Chem.*, **46**, 1630 (1974).

RECEIVED for review February 24, 1976. Accepted May 17, 1976. This research was supported by an Atomic Energy Control Board SLOWPOKE-1 reactor operating grant.