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Instrumental Neutron Activation Analysis
Limits of Detection in the Presence of Interferences

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RÉSUMÉ

Many tables of neutron activation analysis (NAA) limits of detection, in the
absence of interferences, for various irradiation and counting conditions, may
be found in the literature. This paper presents a method for estimating, in
advance, the instrumental NAA limits of detection for any elements of interest
in any given matrix, including ones generating high interference levels. The
rationale of the method is presented, and the procedure for applying it is
illustrated.

INTRODUCTION

The literature of neutron activation analysis (NAA), contains many tables
of sensitivities (limits of detection) for the various elements, for various
conditions of thermal-neutron flux (ϕ), irradiation time (t_i) , counting time,
etc. However, all of these tabulated limits of detection are for situations in
which the levels of interfering activities are negligible, or become so by decay
or via suitable radiochemical separations with carriers and hold-back carriers
before counting. The study reported here is an attempt to extend the useful-
ness of estimated limits of detection to instrumental NAA of matrices that
exhibit significant to even very large levels of interfering activities.

There are three main types of possible interferences in instrumental
NAA work: (1) interferences resulting from formation of the same radio-
nuclide, from fast-neutron (n, p) or (n, α) reactions on an element one or two
units higher in Z than the element of interest, that is formed by (n, γ) thermal-
neutron reaction by the element of interest, (2) interferences resulting from the
formation of one or more other radionuclides that emit gamma rays of energies
sufficiently close to the γ-ray energy of the activity of interest that the total-
absorption peaks ("photopeaks") overlap significantly, and (3) interferences
resulting from high Compton levels in the pulse-height spectra, caused by

interactions of gamma rays of higher energy than the peak of interest, upon which the peak of interest is superimposed. There are reasonably good means for treating the first kind of interferences, i.e., that of activations with and without cadmium. The second type of interference is less frequently encountered now, because of the far better energy resolutions provided by Ge(Li) detectors than are provided by older, poorer-resolution NaI (Tl) detectors--and over-lapping peaks can be resolved mathematically rather easily with a modest computer program.

This study is addressed to the problem of the third type of interference--that caused by high Compton levels, from other activities of higher gamm-ray energies, upon which a peak of interest must be detected. As will be shown, a rather straightforward procedure allows one to estimate reasonably well the limit of instrumental NAA detection of any element of interest, for any given set of irradiation and counting conditions, for any given matrix.

THE METHOD

The method developed assumes that either the major constituents (major from the standpoint of the levels of gamma-emitting radionuclides it will produce) of the matrix are known, or that they have been established by means of a simple and rapid exploratory activation and gamma-ray spectrometry measurement.

For the method to be of ready and practical use, one must first prepare a table of calculated gamma-ray disintegration rates and counting rates, per gram of element, of each (n, γ) product of significance for every element--for the one or more standard sets of irradiation and counting conditions used in his laboratory. For example, in this study, to date, such a table has been prepared for many elements for the typical case of 1-hour irradiations in a thermal-neutron flux of 10^{13} n/cm^2-sec, zero decay, and counting 2 cm above a conventional 3-inch x 3-inch solid NaI(Tl) detector (coupled to a multi-channel pulse-height analyzer). In the calculations, literature values of chemical atomic weights, isotopic abundances, and isotopic thermal-neutron (n, γ) cross sections; decay schemes (from the "Table of Isotopes, Sixth. Edition"[1]); and NaI (Tl) detection efficiencies and photofractions (from Heath's "Scintillation Spectrometry Gamma-Ray Spectrum Catalogue"[2]) are used. Thus, for example (taking a simple case), the first part of the table entry for potassium is as follows:

Potassium   (AW = 39.102)

$\underline{12.36 \text{ h} {}^{42}\text{K}}$

$(a_{41}=6.91\%, \sigma \approx 1.5\text{b})$

$(\text{dps})_0/\text{gK} = 1.60 \times 10^{10}$ at saturation

$(\text{dps})_0/\text{gK} = 8.73 \times 10^8$ for t_i = hr

$\underline{1524 \text{ keV} \gamma (18\%)}$
(for t_i = 1 hr)
($\epsilon = 0.107$)
(PF = 0.321)

$(\gamma \text{dps})_0/\text{gK} = 1.57 \times 10^8$

$(\gamma \text{cps})_0/\text{gK} = 1.68 \times 10^7$
$(\gamma \text{pp cps})_0/\text{gK} = 0.54 \times 10^7$
$(\gamma \text{Compton cps})_0/\text{gK} = 1.30 \times 10^7$

$\underline{310 \text{ keV} \gamma (0.2\%)}$
(for t_i = 1 hr)
($\epsilon = 0.190$)
(PF = 0.832)

$(\gamma \text{dps})_0/\text{gK} = 1.75 \times 10^6$

$(\gamma \text{cps})_0/\text{gK} = 3.32 \times 10^5$
$(\gamma \text{pp cps})_0/\text{gK} = 2.76 \times 10^5$
$(\gamma \text{Compton cps})_0/\text{gK} = 0.56 \times 10^5$

(Most of the calculations are carried out to 3 significant figures, even though some of the input data are known to only 1 or 2 significant figures). Potassium-42 is the only radionuclide of significance formed by potassium by (n, γ) reaction (${}^{40}\text{K}$ is naturally radioactive, and is also formed from ${}^{39}\text{K}$ by (n, γ) reaction, but its activity level is negligible, due to its very long half life, 1.26×10^9 years).

The second part of the table entry for potassium is as follows:

$\underline{1524 \text{ keV} \gamma}$

(t_i = 1 hr)

FWHM of photopeak = 83.8 keV
keV range of Compton region = 0 to 1305 keV
$(\text{cps})_0/\text{gK/keV}$ in Compton region = 9.96×10^3

$\underline{310 \text{ keV} \gamma}$

(t_i = 1 hr)

FWHM of photopeak = 31.6 keV
keV range of Compton region = 0 to 170 keV
$(\text{cps})_0/\text{gK/keV}$ in Compton region = 3.29×10^2

As an example of the application of the method, a simple illustrative case is shown below. Suppose that one wishes to determine the approximate instrumental NAA limit of detection (under the irradiation and counting conditions specified earlier) for iodine in an otherwise pure potassium matrix. The pertinent information for potassium has already been given above. The portion of the corresponding information for iodine needed for the limit-of-detection calculation is shown below (by (n, γ) reaction, iodine forms only 24.99-minute ${}^{128}\text{I}$, and the principal gamma ray of ${}^{128}\text{I}$ is that at 441 keV):

$(\gamma pp\ cps)_o/g\ I = 3.92 \times 10^9$ at 441 ke V

FWHM of photopeak = 39.7 ke V

Next, the total counting rate of the major matrix activity must be considered. Per gram of K this would be 1.68×10^7 cps (from the 1524 ke V γ of ^{42}K) plus 0.03×10^7 cps (from the 310 keV γ of ^{42}K), or 1.71×10^7 cps. If the maximum total counting rate is set at 10^5 cps, to avoid excessive dead-time loss and overloading of the electronics, the maximum sample size is then seen to be 5.85 milligrams of K.

The 441 ke V photopeak of ^{128}I must be detected on top of the Compton continuum of ^{42}K. In the region of the central portion of the 441 ke V photopeak of ^{128}I, that is, the region included in the FWHM of the peak (which is 76% of the net peak area), the ^{42}K Compton counting rate is seen to be

$$0.00585\ g\ \times\ \frac{1.68 \times 10^7}{1.71 \times 10^7}\ \times\ 9.96 \times 10^3\ \frac{cps}{keV - g}\ \times\ 39.7\ ke\ V,$$

or 2.27×10^3 cps. In a 10-minute counting period, the ^{42}K would produce 1.36×10^6 Compton counts in this region. The standard deviation of this number of counts is $\pm\ 1.17 \times 10^3$ counts.

A conservative limit of detection for iodine may then be computed as that amount that, under these conditions, would give enough ^{128}I 441 ke V photopeak counts, in the region covered by the FWHM of the peak, to amount to 6σ of the ^{42}K Compton baseline counts in this region. This amounts to 7.01×10^3 counts. Since one gram of iodine would produce 1.56×10^{12} counts, in 10 minutes, in this region, the approximate instrumental limit of detection for iodine in a potassium matrix is seen to be $7.01 \times 10^3 / 1.56 \times 10^{12}$, or 4.49×10^{-9} g, i.e., $4.49 \times 10^{-3} \mu g$. In terms of concentration, this corresponds to $4.49 \times 10^{-3}\ \mu g\ I/0.00585\ gK$, or 0.768 ppm iodine. Thus, the approximate instrumental NAA limit of detection for iodine in potassium, under the specified conditions, should be about 0.8 ppm (whereas in the absence of any interferences, it is about 4×10^{-4} ppm, in a 1-gram sample[3]).

DISCUSSION

The method developed would obviously be extremely time-consuming to apply to more complicated matrices, if calculations had to be performed manually. However, once computerized, it can operate very rapidly. At present, all of the basic elemental data are being calculated, and a computerized system is being developed. When completed, all of the detailed information will be published in report form, and the computer program will also be made available. Stepwise, also, the system will be programmed to allow one to vary all of the major controllable variables: flux, irradiation time, decay time, sample size, etc. Also, a parallel set of data will be obtained for a typical Ge(Li) detector, such as the 36 cm^3 coaxial detector used in the author's laboratory.

REFERENCES

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3. V. P. Guinn, Neutron Activation Analysis chapter in Physical Methods of Chemistry. Volume 1. Part IIID, edited by A. Weissberger and B. W. Rossiter. John Wiley and Sons, New York, 1972 (pp. 447-500).