

FURTHER STUDIES IN THE ADVANCE PREDICTION
OF GAMMA-RAY SPECTRA
AND DETECTION LIMITS IN INSTRUMENTAL NEUTRON
ACTIVATION ANALYSIS

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This computational procedure, described earlier for NaI(Tl) gamma-ray spectrometry, has now been set up for Ge(Li) spectrometry measurements, has been extended further in various details, has been partially computerized, and has been tested experimentally on both biological and geochemical types of samples—with good results. The procedure enables one to compute, in advance of any activations, the approximate Ge(Li) pulse-height spectrum of a sample for any selected flux and irradiation, decay, and counting times — and to compute the lower limits of instrumental NAA detection of any trace elements of interest — if the principal composition of the matrix is known. Various other useful parameters are also readily calculated.

Introduction

The activation analyst is often asked variations of the question, “How low a concentration of element X can you detect in a sample matrix Y by thermal-neutron activation analysis (NAA)?” Numerous “interference-free” NAA sensitivity tables are available in the literature,¹ for various irradiation and detection conditions, so one can readily employ such information to answer such a question — providing that the induced activity of interest can be measured in the absence of other induced activities. In complicated matrices, this usually means that post-irradiation radiochemical separations are necessary in order to attain the interference-free lower limit of detection.

If one wishes to employ a purely-instrumental procedure (INAA), no single table of limits of detection is possible, since the nature and levels of other induced activities vary tremendously with the matrix that is to be analyzed. Earlier,² a

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computational procedure was described that enables one – with only a knowledge of the approximate levels of major and minor elements in a matrix – to calculate (for any desired conditions) the approximate NaI(Tl) pulse-height spectrum of a sample, and the approximate lower limits of INAA detection for any trace elements of interest in that matrix. (If no information at all is available regarding the matrix elemental composition, one or two simple exploratory INAA measurements can supply the needed information).

The above calculational procedure has now been extended considerably in a number of respects, has been worked out for a rather typical Ge(Li) detector (a 38 cm³ coaxial detector), and now takes into account not only all significant photopeaks from (n, γ) products, all Compton levels, and all Compton edges – but also escape peaks from high-energy gamma rays and contributions to the 511 keV peak from high-energy gamma rays. At present, the procedure does not allow for a number of other variables that are usually (though not always) negligible or only of secondary importance: such possible variables as bremsstrahlung, backscatter peaks, fast-neutron products, daughter activities (except in a few common cases), ⁴¹Ar, recoil-proton induced activities, double neutron-capture products, sum peaks, thermal-neutron self shielding, activation by epithermal and resonance neutrons, or sample attenuation of gamma rays. If it is felt to be worthwhile, some of these additional variables can later be introduced into the procedure. At present, the procedure has been partly computerized. After further testing, then incorporating any modifications (if any) that are felt to be necessary, it will be completely computerized and made available to anyone interested. Only then, of course, will it become a rapid and highly useful procedure.

The calculational procedure

The first step in the development of the procedure was to prepare a set of tables for each gamma-emitting (n, γ) product of each element – one table per radionuclide. From present “best” values of atomic weights, isotopic abundances, and thermal-neutron (n, γ) cross-sections, a saturation specific activity, at a thermal-neutron flux of 10^{13} n · cm⁻² · sec⁻¹ was calculated for each induced activity, expressed in (dps) o/g element. Then, using literature decay schemes, and experimentally-measured γ -ray detection efficiency vs. γ -ray energy and photofraction vs. γ -ray energy curves (both for the 38 cm³ Ge(Li) detector at a sample-to-detector face distance of 2 cm), the total counting rate, photopeak counting rate, and Compton counting rate due to each gamma ray was calculated for each radionuclide (each value in cps per gram of the element, at the end of a saturation irradiation at

10^{13} flux). Next, from the calculated Compton edge of each gamma ray, and assuming a flat Compton region, the contribution of each gamma ray to the Compton level was calculated, in cps/keV/gram element, still for saturation at 10^{13} flux. Also entered into each table was the FWHM value, in keV, of each photopeak, read from an experimentally-measured energy resolution curve for the 38 cm^3 Ge(Li) detector. Table 1 shows an illustrative table for one (n, γ) product, ^{56}Mn , showing the inclusion of each of its three gamma rays. This is the only (n, γ) product of Mn, so only one table is needed for the element. For elements that form more than one (n, γ) product (e.g., Cu, Br, Zn, etc.), each radionuclide requires one table.

Also included in each radionuclide table, as shown in Table 1, are the photopeak cps/g values for the first and second escape peaks of each high-energy gamma ray, and their respective energies. The 511 keV photopeak counting rate caused by pair-production interactions in the detector shield are also included for each high-energy gamma ray. These are obtained by use of a series of experimentally-measured curves, versus γ -ray energy, for this detector. In the example of ^{56}Mn , of course, only the 1811 and 2113 keV gamma rays produce escape peaks and generate 511 keV gamma rays.

As illustrated in Table 1, each radionuclide table also includes calculated values of the saturation factor (S) and the decay factor (D) for times of irradiation (for S) or of decay (for D) of 0.1, 0.3, 1, 3, 10, 30, 100, 300, 1000, 3000, 10 000, and 30 000 minutes. Essentially the full range of practically used values of irradiation and decay times, in steps of approximately 3-fold, are thus included – for 0.1 minute (6 seconds) to 30 000 minutes (500 hours, or 20.8 days).

The procedure employed in using these tables to predict the γ -ray Ge(Li) pulse-height spectrum of any kind of sample whose approximate main composition is known, following activation with thermal neutrons for any selected period of time, and decay for any selected period of time, is as follows. The first input is a list of the elements known to be present in the sample, with the approximate level of each, expressed in grams of element per gram of sample. Next, the desired thermal-neutron flux, irradiation time, decay time, counting time, and counting geometry are each specified. Then, each relevant radionuclide table is processed, in turn, to provide the net photopeak counts (including escape peaks, in the case of high-energy gamma rays), the contribution to the Compton level (in counts/keV), and the contribution to the 511 keV peak (in the case of high-energy gamma rays) from each gamma ray of each (n, γ) product of each element – per gram of sample irradiated and counted under the conditions selected. For simplicity, the counting rate of each activity is assumed to be constant during the counting period. For sample-to-detector face distances other than 2 cm, the table counting-rate values

Table 1
An illustrative data bank table for one (n, γ) product, ^{56}Mn

Element: Mn
Atomic weight: 54.94
Target: ^{55}Mn
% Abundance: 100
(n, γ) cross-section: 13.3 b

Radionuclide: ^{56}Mn
Half-life: 2.576 hrs
Saturation activity: $1.46 \cdot 10^{12}$ dps/g
Thermal-neutron flux: $1.00 \cdot 10^{13}$ n \cdot cm $^{-2}$ \cdot s $^{-1}$

E_γ , keV	Intensity, %	γ , dps/g	ϵ , %	γ , cps/g	PF
847	99	$1.44 \cdot 10^{12}$	4.84	$6.98 \cdot 10^{10}$	0.0960
1811	29	$4.23 \cdot 10^{11}$	3.86	$1.63 \cdot 10^{10}$	0.0465
2113	15	$2.19 \cdot 10^{11}$	3.68	$8.05 \cdot 10^9$ $9.42 \cdot 10^{10}$	0.0405

PP, cps/g	Compton, cps/g	CE, keV	Compton, cps/keV \cdot g	FWHM, keV
$6.70 \cdot 10^9$	$6.31 \cdot 10^{10}$	651	$9.70 \cdot 10^7$	2.3
$7.58 \cdot 10^8$	$1.55 \cdot 10^{10}$	1587	$9.77 \cdot 10^6$	3.2
$3.26 \cdot 10^8$	$7.72 \cdot 10^9$	1885	$4.10 \cdot 10^6$	3.4

Secondary peaks:

	1st EP		2nd EP		511 keV
	E, keV	PP, cps/g	E, keV	PP, cps/g	PP, cps/g
From 1811 keV γ	1300	$2.79 \cdot 10^7$	789	$6.12 \cdot 10^7$	$1.07 \cdot 10^7$
From 2113 keV γ	1602	$2.39 \cdot 10^7$	1091	$5.25 \cdot 10^7$	$7.80 \cdot 10^6$

t_i or t_d , min	S	D	t_i or t_d , min	S	D
0.1	$4.48 \cdot 10^{-4}$	1.000	100	0.361	0.639
0.3	$1.34 \cdot 10^{-3}$	0.999	300	0.740	0.260
1	$4.48 \cdot 10^{-3}$	0.996	1 000	0.989	$1.13 \cdot 10^{-2}$
3	$1.34 \cdot 10^{-2}$	0.987	3 000	1.000	$1.43 \cdot 10^{-6}$
10	$4.39 \cdot 10^{-2}$	0.956	10 000	1.000	$3.33 \cdot 10^{-20}$
30	0.126	0.874	30 000	1.000	$3.68 \cdot 10^{-59}$

are all multiplied by the counting-geometry correction factor obtained from the equation

$$F = 25/(d + 3.0)^2$$

in which d is the selected distance, in cm.

Next, the total counting rate of the one-gram activated sample, at the start of the counting period, is obtained by summing all of the radionuclide/gamma-ray counting rates. The maximum allowable sample size (up to one gram) is then calculated from the upper limit that has been set for the total counting rate so that the spectrum will not be appreciably distorted. For the present system, this usually means an analyzer deadtime of not more than 10%, which in a typical spectrum means setting the maximum initial counting rate at about 5000 cps. With the (usually) smaller sample weight now defined, each of the previously-calculated counting rates is then scaled down proportionally in the calculations.

The next step in the procedure is to reject each radionuclide whose total counts are less than 0.01% of that of the largest activity present, thus expediting the subsequent calculations. For the remaining activities, which are (or the smaller ones may be) significant, the next step is to calculate the levels (in counts/keV) of each of the Compton levels in the pulse-height spectrum of this smaller sample – using all of the Compton-edge values and summing the contributions of each gamma ray to the various Compton levels. Next, the standard deviation of the counts in each photopeak is computed. In this calculation, the base of the peak, in keV, is taken to be 3 times the FWHM for that energy, and the Compton base line is calculated for a range of 1.5 times the FWHM on each side of the base of the peak. All contributions to the 511 keV peak are summed. Any photopeaks for which the calculated relative standard deviation is less than $\pm 10\%$ are considered to be peaks that will be definitely observable; those in the range of ± 10 to 30% , observable but small; those in the range of ± 30 – 100% either barely observable or not detectable; and those with relative standard deviations greater than $\pm 100\%$ not detectable.

To calculate the lower limit of instrumental NAA detection, under the selected conditions, for any of the trace elements of interest known to be present, but that do not show up in the preceding calculation as significantly detectable peaks, the procedure calculates the amount (and then ppm concentration) of the element that would need to be present to give a number of net photopeak counts equal to 3 times its standard deviation, taking into account the Compton level in that region of the spectrum. This calculated lower limit of detection is one whose relative standard deviation would be $\pm 35\%$, i.e., definitely detectable, but close to the lower limit of definite detection. A similar calculation is made for the lower limit of instrumental detection for each of any other trace elements of interest that are

not known to be present in the matrix at all, i.e., elements not included in the original sample matrix known approximate composition input. The corresponding radionuclide data tables for these elements are used in these calculations.

Once fully computerized, all of the above calculations can be carried out rapidly with even a moderate-sized computer, since all of the mathematical operations required are extremely simple. A sizeable memory storage is needed, in order to store all of the information contained in the library of radionuclide data tables. In the current computerized system, which as yet does not include some of the more recent refinements and additions to the procedure, provision is also made for a computer plot of the predicted pulse-height spectrum – showing all peaks, Compton levels, and Compton edges. Photopeaks are shown as triangles, with a $3 \times$ FWHM base. The present computer program works very well, and only needs to be modified in minor respects, to include the most recent changes in the data tables.

The program can also indicate the optimum conditions for the instrumental NAA detection of any element of interest, that is, to provide a minimum relative standard deviation (i.e., maximum precision) for a readily detected element known to be present, or the lowest possible limit of detection – within the framework of available fluxes, irradiation times, decay times, and counting times – for any element not even known to be present at all in the sample. To perform this optimization calculation, the procedure first calculates the relative standard deviation of each peak of each (n, γ) product radionuclide of that element, in the sample matrix, for a roughly optimum set of conditions. These roughly optimum conditions are: (1) maximum available flux, (2) closest counting geometry, and (3) irradiation, decay, and counting times each equal approximately to the half-life of the radionuclide – with reasonable upper limits, however, for long-lived activities. For example, one may wish to limit the irradiation time, for practical reasons, to not more than 300 minutes (5 hours), the decay time to not more than 30 000 minutes (500 hours, or 20.8 days), and the counting time to not more than 100 minutes – in the case of a very long-lived induced activity. The calculation is then repeated for adjacent values of t_i , t_d , and t_c , and the combination that results in the lowest relative standard deviation, or the smallest lower limit of detection, is taken as the optimum set of conditions. In these calculations, only the stepwise set of possible irradiation and/or decay times (i.e., 0.1, 0.3, 1, 3, 10, . . . minutes) used in each of the radionuclide data tables is used. Unless otherwise selected, the counting time is considered to be equal to the irradiation time, up to some pre-selected maximum counting time, e.g., 100 minutes.

The procedure is also of use for NAA involving either pre-irradiation or post-irradiation chemical separations. For example, if (as is often the case) the dominant induced activity is ^{24}Na , one may wish to employ a post-irradiation removal of

sodium via hydrated antimony pentoxide. In such a case, the procedure would calculate everything as before, but sodium would not be included in the calculation.

An example of use of the procedure

The calculational procedure has been applied to a number of common matrices of interest and more such calculations are in progress. Some of these have also been checked by subsequent experimental results. In particular, a number of widely used intercomparison reference materials or NBS Standard Reference Materials have been or are being tested. The example cited below is that of the IAEA H-4 Animal Muscle reference material. It's approximate elemental composition is shown in Table 2. In this case, much more is known, at least approximately, about its trace-element composition than is really necessary for the calculations. As can be seen, the only activatable elements present at levels above 0.1% (1000 ppm) are Cl, K, Mg, Na, P, and S. As will be shown, the activities generated by the first four of these constitute some 91% of the Ge(Li) total counting rate, under the example conditions, and hence by themselves largely determine the Compton-level shape and magnitude of the resultant pulse-height spectrum. The known elements

Table 2
Current "best" values for the elemental composition of the IAEA animal muscle H-4 reference material.³ All values in $\mu\text{g/g}$ dry weight

Element	ppm	Element	ppm	Element	ppm
Ag	0.3	F	(2)	S	9600
Al	9.5	Fe	49	Sb	0.005
As	0.006	Hg	0.014	Sc	0.0008
Ba	(0.02)	I	0.011	Se	0.28
Be	(0.001)	K	15 600	Si	(100)
Br	4.1	La	0.004	Sn	0.009
Ca	186	Mg	1040	Sr	(0.1)
Cd	0.09	Mn	0.52	Tl	(0.02)
Ce	0.02	Mo	0.068	U	0.003
Cl	1950	Na	2080	V	0.004
Co	0.009	Ni	1.0	W	0.005
Cr	0.1	P	9050	Zn	86
Cs	0.13	Pb	0.25		
Cu	3.9	Rb	18		

Remaining 96.0%: H, C, N, O.

add up to 4.0% by weight of the mass of the Animal Muscle powder, the remaining 96.0% consisting of major-constituent elements that are not detected in the usual instrumental thermal-neutron activation analysis method: H, C, N and O.

The conditions selected for the advance calculations of the Animal Muscle material were: irradiation of one gram of the material in a thermal-neutron flux of $2.5 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ for 3 minutes, followed by counting for 3 minutes after a decay period of 3 minutes, at a sample-to-detector face distance of 1 cm. The program first calculated the activities resulting from some 81 (n, γ) product radio-nuclides for these conditions. Of these 81 induced activities, only the following were calculated to be significant contributors to the Ge(Li) total counting rate (i.e., were ones generating more than 0.01% as much activity as the largest activity, ^{38}Cl): ^{24}Na , ^{27}Mg , ^{28}Al , ^{37}S , ^{38}Cl , ^{42}K , ^{49}Ca , ^{52}V , ^{56}Mn , ^{64}Cu , ^{66}Cu , $^{69\text{m}}\text{Zn}$, ^{80}Br , ^{82}Br , ^{88}Rb , and ^{108}Ag . It was decided that the analyzer deadtime should be limited to about 2%, which then dictated a sample size of 20 mg.

The values of Compton and photopeak counts (including escape peaks and the 511 keV peak) for a 20 mg sample were then calculated, and the predicted pulse-height spectrum was calculated. Also, the standard deviation of each photopeak was calculated. The only statistically-significant peaks were found to be those of ^{24}Na (1368, 2754 keV, and the two escape peaks of the 2754 keV γ), ^{27}Mg (844, 1014 keV), ^{28}Al (1779), ^{37}S (3102), ^{38}Cl (1642 and its second escape peak; 2167 and its first and second escape peaks), ^{42}K (1525), and ^{49}Ca (3083).

A 19 mg sample of the Animal Muscle material was then activated and counted under these conditions. The predicted values and the experimental values are compared in Table 3. It should be noted that agreement between the two only to within a factor of even 2 or 3 would not be surprising, and would still be quite sufficient for the purposes for which the results of the calculations are used. As can be seen from Table 3, however, the agreement between calculated and experimental values is much better than that. All of the calculated photopeak-count values agree with the measured values to within a factor of at least 2 and most are much closer – the average ratio of measured value to calculated value for the 15 peaks shown in Table 3 is 1.06 ± 0.36 . Similarly, for the nine Compton levels (all except the very low level at the highest energy in Table 3), the agreement in each case between calculated and observed is within a factor of 1.8 or better; for these nine Compton levels, the average ratio of observed value to calculated value is 0.93 ± 0.23 .

Only one other peak appeared in the measured pulse-height spectrum besides the 15 peaks listed in Table 3. This was the 511 keV peak, which was not listed because of its composite nature. In its case, the calculated counts were 201 ± 41 and the measured counts were 310 ± 37 . The calculations indicated that 70% of

Table 3
Comparison of predicted and experimental Ge(Li) pulse-height spectra
for IAEA animal muscle H-4

Conditions: 19 mg sample, $\Phi_{th} = 2.5 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$, $t_i = t_d = t_c = 3$ minutes each,
counting geometry = 1 cm

E_γ , keV	Predicted, counts/keV	Observed at midpoint, counts/keV
Compton regions		
0- 648	120	102
648-1153	106	58
1153-1306	71	58
1306-1421	67	59
1421-1556	40	36
1556-1938	35	30
1938-2520	12	12
2520-2847	2.6	2.9
2847-2866	1.3	1.8
2866-3831	0.1	1.1
Photopeaks		
620 ($^{38}\text{Cl EP} + ^{80}\text{Br}$)	191 \pm 57	97 \pm 34
844 (^{27}Mg)	718 \pm 53	697 \pm 42
1014 (^{27}Mg)	187 \pm 50	196 \pm 37
1145 ($^{38}\text{Cl EP}$)	319 \pm 44	363 \pm 40
1368 (^{24}Na)	2120 \pm 77	2285 \pm 60
1525 (^{42}K)	297 \pm 56	380 \pm 34
1642 (^{38}Cl)	1908 \pm 67	1536 \pm 48
1656 ($^{38}\text{Cl EP}$)	147 \pm 28	82 \pm 22
1732 ($^{24}\text{Na EP}$)	427 \pm 33	411 \pm 32
1779 (^{28}Al)	300 \pm 56	501 \pm 34
2167 (^{38}Cl)	1812 \pm 54	1509 \pm 45
2243 ($^{24}\text{Na EP}$)	202 \pm 21	210 \pm 22
2754 (^{24}Na)	1070 \pm 33	978 \pm 34
3083 (^{49}Ca)	13 \pm 4	16 \pm 6
3102 (^{37}S)	11 \pm 3	21 \pm 6
Total counts:	175 000	156 000
Deadtime, %:	1.8	~2

the 511 keV counts were the result of interactions of high-energy gamma rays in the shield (largely from ^{24}Na and ^{38}Cl gamma rays), and 30% were due to positron emission in the sample (largely from ^{80}Br). All of the peaks listed in Table 3 were single peaks, except the 620 keV escape peak of ^{38}Cl , which also includes counts from the 617 keV gamma ray of ^{80}Br .

In the Animal Muscle example, it is also of interest to calculate the lower limit of INAA detection, under the stated conditions, for some of the trace elements known to be present, but at levels too low to be detected. For example, it was predicted that V (0.004 ppm present), Cu (3.9 ppm), Zn (86 ppm), Rb (18 ppm), and Ag (0.3 ppm) would not be detected – and experimentally indeed they were not. It was then calculated that, to be barely detectable, the V concentration would need to be 0.17 ppm (43 times larger than the concentration present), the Cu concentration 24 ppm (6.1 times larger), the Zn concentration 1600 ppm (19 times larger), the Rb concentration 670 ppm (37 times larger), and the Ag concentration 2.5 ppm (8.3 times larger).

Such calculated minimum detectable levels have not yet been checked experimentally – by spikings with known additional amounts of the elements – for the Animal Muscle material, but they have been for some other matrices. For example, the same types of calculations were made for a geological type of sample, using approximately known levels of some 15 elements as input. So far as was known, only a trace of tungsten was present in the material. For a one-hour irradiation at a flux of $1.0 \cdot 10^{12}$, followed by a 48-hour decay period and a 10-minute counting period, it was calculated that the lower limit of INAA detection of tungsten (via the 686 keV gamma ray of 23.9-hour ^{187}W) in this material should be about 48 ppm. A sample was then activated and counted under these conditions, along with samples spiked with 10 ppm W, 25 ppm W, 50 ppm W, and 550 ppm W. In agreement with the predictions, no 686 keV peak was detectable in the spectra of the unspiked sample or those spiked with only 10 ppm or 25 ppm W. However, a small 686 keV peak, with a relative standard deviation of $\pm 37\%$, appeared in the spectrum of the sample spiked with 50 ppm W (to be compared with the 48 ppm W predicted lower limit of detection). The sample spiked with 550 ppm W showed a very large peak at 686 keV, with a relative standard deviation of only $\pm 4.6\%$, as well as similarly large ^{187}W peaks at 134 keV ($\pm 5.3\%$) and 479 keV ($\pm 4.5\%$).

Summary and conclusions

A system of predicting the main features of the gamma-ray pulse-height spectra of samples activated with thermal neutrons, from only approximately known levels of the major and minor elements present in them, has been developed further. It

now includes Ge(Li) detection, and includes escape peaks and contributions to the 511 keV peak from high-energy gamma rays interacting with the detector shield. It has been shown experimentally, for both biological and geological matrices, to predict Compton levels, photopeaks (including escape peaks), and lower limits of detection quite well. For selected irradiation and decay conditions, it indicates the maximum sample size to be used, to limit the analyzer deadtime to any selected maximum value. For induced activities that emit two or more gamma rays, it indicates which one gives the best INAA precision, or the lowest limit of detection. By reiteration, it provides values for the optimum combination of irradiation time, decay time, and counting time for any specified activity. It can also be applied to cases in which either pre-irradiation or post-irradiation simple or group separations are employed. The procedure has been successfully computerized (including a computer plot of the pulse-height spectrum), but is currently being recomputerized – to incorporate the more recent additions to the calculational procedures and the input library. When in final form, copies will be made available to any interested scientists who request them. The program can be modified to conform to Ge(Li) detectors other than the 38 cm³ one for which it is currently specifically designed.

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