

AUTOMATIC INTERPRETATION OF GAMMA-RAY DATA OBTAINED IN NON-DESTRUCTIVE ACTIVATION ANALYSIS

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The procedure in use at our institute for the extraction of the desired element concentrations in a sample from the peak data obtained by a spectrum analysis program, is described in detail. The method is based on the use of zinc as a single comparator and takes into consideration primary activation products as well as their daughter isotopes. After assigning isotopes to spectrum peaks on the basis of γ -ray energies, the list of possible isotopes is reduced to a list of present isotopes with their concentrations using criteria based on half life, specificity and intensity of γ -rays. For elements not observed, detection limits are estimated. The procedure has been used extensively during the last two years and has shown to produce reliable results.

Introduction

A few methods, for instance that of ADAMS and DAMS,¹ have been published for the interpretation of data, in terms of concentration, obtained with γ -spectrum analysis computer programs. Work carried out at our own institute on this subject has lead to a paper,² describing the preliminary program for this purpose. Since then, our method has been improved in a number of ways and now it takes into account also:

- genetical relations between isotopes,
- different routes for production of the same isotope,
- different isotopes produced from the same element.

Moreover, detection limits are estimated for elements for which no evidence about their presence is found in the spectrum.

As with every interpretation technique, the accuracy of the results depends strongly on the reliability of the physical data of the isotopes taken into account. Since literature values are sometimes conflicting and in many cases inaccurate, we felt it necessary to use experimentally determined values for all necessary quantities (see below), with the exception of the isotope half-lives. The determined values have been published in the form of a catalog of gamma-ray and isotope data.³

The method is based on the use of zinc as a single comparator which will be discussed in the next section. It is followed by a detailed description of the actual

interpretation technique. It forms the second part of our routine activation analysis program ⁵ and is preceded by the mathematical analysis of the spectrum. It could also easily be coupled to other analysis programs.

Single comparator method

This technique has been introduced by GIRARDI, ⁴ to overcome the problems associated with the use of many separate standards, or a compound standard of acceptable homogeneity and stability. It makes use of a single element as standard for which we have selected zinc. In separate measurements a normalized ratio between comparator activity and the activity induced in each element of interest is determined, which can be used later to calculate the concentration of the element in the sample.

Zinc can be obtained in good purity and can be easily handled in the form of discs or sticks. Moreover, two isotopes are produced upon irradiation with thermal neutrons: ^{69m}Zn (T = 13.9 h) and ⁶⁵Zn (T = 244 d), so that a good comparator activity is available at any time after the irradiation.

A disadvantage of the single comparator method is that the ratio of the activities induced in standard and sample depends on the neutron spectrum at the irradiation position. This problem can be overcome by using a dual or triple comparator technique, ^{6,7} but as a result, the analysis procedure becomes more complicated.

So far we are using the single comparator while all irradiations are carried out in the same position in the reactor core, in which the neutron spectrum is approximately constant in time. Moreover, calibration measurements are repeated regularly.

The program can handle three modes of production of an isotope:

(1) Direct production.

The concentration of an element in the sample can be calculated from:

$$C_x = \frac{\psi_x}{I_x} \cdot \frac{D_s}{D_x} \cdot \frac{P_x}{P_s} \cdot \frac{G_s}{G_y} = \frac{P_x}{I_x} \cdot \psi_x \cdot S_1 \quad (1)$$

where:

$$D = \frac{1 - \exp(-\lambda T)}{\lambda T \exp(\lambda t)} \cdot \frac{\exp(\lambda t_m/2) - \exp(-\lambda t_m/2)}{\lambda t_m}$$

$$\psi_x = \frac{M_x \theta_s \hat{\sigma}_s \lambda_s \gamma_s}{M_s \theta_x \hat{\sigma}_x \lambda_x \Sigma \gamma_x}, \quad I_x = \frac{\gamma_x}{\Sigma \gamma_x}, \quad P_x = \frac{A_x}{\epsilon_x}$$

- x, y, s - subscripts, denoting element, sample, and standard,
 C - concentration,
 p - measured peak intensity,
 A - measured activity of a certain gamma ray,
 I - fractional intensity of the gamma ray,
 ε - counting efficiency for the gamma ray,
 γ - abundance of the gamma ray,
 G - weight,
 D - decay term, correcting for decay during counting,
 irradiation and waiting,
 T - irradiation time,
 t - waiting time after irradiation,
 t_m - duration of measurement,
 θ - abundance of parent isotope,
 λ - decay constant,
 σ̂ - effective cross section,
 M - atomic weight of stable parent isotope.

(2) Indirect production (as a result of radioactive decay).

The concentration is now calculated from:

$$C_x = \frac{\psi_x}{I_x} \frac{p_x}{p_s} \frac{G_s}{G_y} \frac{\lambda_d - \lambda_p}{\lambda_p} \frac{D_s}{D_p - D_d} = \frac{p_x}{I_x} \psi_x S_2 \quad (2)$$

where p, d - subscripts, denoting primary and secondary reaction product.

(3) Production by both direct and indirect reactions.

If ψ_1 represents the ψ -value for direct production, and ψ_2 for indirect production, the concentration can be calculated from:

$$C_x = \frac{p_x}{I_x} \frac{1}{\frac{1}{S_1 \psi_1} + \frac{1}{S_2 \psi_2}} \quad (3)$$

where S_1 and S_2 have the values defined for production mode 1 and 2 respectively.

It should be noted that an isotope can be produced in these ways from different elements, as for instance in the case of fission products.

The S_1 - and S_2 -values both contain the factor p_s/D_s , the comparator activity corrected for efficiency and for decay during irradiation, measurement and

weighting period. As already mentioned above, when zinc is used as comparator element, two isotopes are available for the determination of the comparator activity: ^{65}Zn (main γ -ray at 1115.5 keV, $T = 244$ d), and $^{69\text{m}}\text{Zn}$ (γ -ray at 438.8 keV, $T = 13.9$ h). It can easily be derived from Eq. 1, that the zinc activities for these two peaks are related through:

$$\frac{P_{438.8}}{D_{69\text{m}}\text{Zn}} = \frac{P_{1115.5}}{D_{65}\text{Zn}} \cdot \frac{I_{438.8}}{\psi_{69\text{m}}\text{Zn}}$$

Therefore, if both peaks are available, the program calculates the weighted average of the corrected activities of both peaks, weighing the activities with the reciprocal variance of the peak intensity, according to:

$$\frac{P_s}{D_s} = \frac{\frac{3 P_{1115.5}}{\Delta p^2_{1115.5} D_{65}\text{Zn}} + \frac{W_{69} P_{438.8}}{\Delta p^2_{438.8} D_{69\text{m}}\text{Zn}} \frac{\psi_{69\text{m}}\text{Zn}}{I_{438.8}}}{\frac{3}{\Delta p^2_{1115.5}} + \frac{W_{69}}{\Delta p^2_{438.8}}}$$

An extra weighting factor W_{69} is introduced to reduce the influence of the unknown uncertainty in the half life of the short-lived $^{69\text{m}}\text{Zn}$. The value of this weighting factor as function of the waiting time is given in Table 1 (W_{65} is always equal to 3).

The associated error in p_s/D_s is calculated from:

$$\text{error}^2 = \frac{3}{\frac{3}{\Delta p^2_{1115.5}} + \frac{W_{69}}{\Delta p^2_{438.8}}}$$

As the ψ -values depend on the neutron spectrum, it is necessary to determine them experimentally for the irradiation facilities used. The method requires also accurate energy and intensity data of the gamma rays. As literature information turned out to be insufficiently reliable, we have determined these quantities at the same time. ³

Table 1
 W_{69} as a function of waiting time

Waiting time, hrs	W_{69}
0 - 40	3
40 - 80	2
80 - 120	1
> 120	0

Qualitative and quantitative interpretation

For the interpretation process, the following quantities of each isotope have to be available:

- the name of the isotope,
- the decay constant (in s^{-1}),
- the intensity threshold value (see below),
- the number of γ -rays emitted by the isotope,
- the γ -ray (energy and intensity) to be used for the estimation of the detection limit,

for each mode of production:

- the atomic number of the parent element,
- the primary isotope in the case of indirect production,
- the ψ -value,

for each γ -ray:

- the energy
- the fractional intensity.

These isotope data, with the exception of the γ -ray energies and intensities, are stored in the order of increasing atomic number and of increasing atomic weight (for each Z).

The γ -ray data are stored separately in the order of increasing energy. In our activation analysis system, this information is presently available for 194 isotopes with 1518 γ -rays.

The interpretation process begins with the estimation of a detection limit for each element. This detection limit is based on one γ -ray, separately specified for this purpose for each isotope (see above). The list of determined peak energies is first scanned to check the presence of a peak with equal (within 1.2 keV) energy in the spectrum, in which case the detection limit will be calculated on the corresponding peak intensity.

If such a peak is not observed, the program makes use of some information about the spectrum, retained after the spectrum analysis part of the program, to estimate the minimum detectable peak, namely:

- a calibration curve of peak position as a function of γ -ray energy,
- the same for peak width versus position,
- background estimates of 64 chosen half-overlapping regions of the spectrum, obtained by averaging the five lowest channel contents within the region.

The theoretical position of the peak is calculated from the position/energy calibration curve. The peak intensity will now be based on the background estimates. The program assumes a not observed peak to have a maximum height of five times the square root of the appropriate background estimate, with a minimum of 50 counts, and calculates the corresponding peak intensity using the width/position relationship, and the efficiency curve for the applied measuring geometry. The element concentration corresponding to this peak intensity is calculated from the appropriate Eqs (1), (2) or (3).

If too many half lives of the isotope have passed since the irradiation ($\lambda t < 9$), or the calculated value exceeds 100 percent, the value is set equal to 100 per cent. If a detection limit, based on another isotope produced by the same element was already calculated, the new value replaces this value only if it is lower.

In the next stage a preliminary interpretation of the observed peaks is carried out, in which an isotope is assigned to a peak if the cataloged energy of one of its γ -rays differs less than ± 1.2 keV from the spectrum value. Although such a relatively large energy window is not necessary with respect to the accuracy of the energy calculation, it enables the program to account for small contributions of unresolved, underlying peaks.

For each assignment, the involved isotope and the fractional intensity of the specific gamma ray* are saved in the so-called interpretation list. When this has been carried out for all peaks, the other gamma ray data are no longer necessary.

The program begins now with the elimination of isotope assignments from this interpretation list. The first criterion to discriminate between relevant and irrelevant assignments, is the sum of the fractional intensities of the gamma rays of an isotope, present in the spectrum. For each isotope we have assessed a threshold value, being the sum of the fractional intensities of those prominent peaks which under all circumstances should be observed if the isotope is present. If the measured sum stays below this threshold value, all entries of the isotope in the interpretation list are deleted.

*The background activity in the counting room is treated as if it originates from a single isotope with infinite half life. Since this activity is geometry independent, it is necessary to correct the cataloged intensities of the background γ -rays, with the relative efficiency curve for the applied measuring geometry. There is no intensity threshold for this "background isotope".

A second criterion is found in the time elapsed since the irradiation. If, for a directly produced isotope, more than approximately 13 half lives ($\lambda t = 9$) have passed, the isotope is also deleted from this list. For indirectly produced isotopes a different criterion taking into consideration both the half life of the primary and of the secondary reaction product is used:

if

$$t_w > 13 T_{\text{prim.}} + 13 T_{\text{second.}}$$

the isotope is deleted.

If an isotope passes both criteria, the S_1 -, or S_2 -values are calculated.

At this point preliminary results are printed to serve as a reference. For each peak the measured energy, intensity, and intensity error estimate are printed, as well as the assigned isotopes and corresponding element concentrations, calculated on the assumption that the entire peak is due to that isotope alone.

It will be clear that the various concentration data found on the basis of every single gamma ray, will in general not correspond. Therefore, in the next stage, a more sophisticated treatment of the data is necessary. In this process the program makes use of so-called standard gamma rays. Such a gamma ray is selected if the energy is characteristic for an isotope, while its intensity is relatively high. They are not necessarily the most intensive ones. Some isotopes have more than one standard gamma ray, others have no gamma rays which are sufficiently unique. The procedure is repeated a number of times and is referred to as the interpretation loop. It works as follows: all peaks to which only one isotope is assigned are considered. If there are standard gamma rays among these single assignments, the corresponding ratio of observed peak intensity and corresponding cataloged gamma ray intensity is calculated. If more than one standard peak is available for a certain isotope, the weighted average of these ratios is calculated. As weighting factors, the reciprocal variances of the peak intensities are used:

$$R = \frac{\sum_{j=1}^n \frac{1}{\sigma_j^2} \frac{P_j}{I_j}}{\sum_{j=1}^n \frac{1}{\sigma_j^2}} \quad \Delta R^2 = \frac{1}{\sum_{j=1}^n \frac{1}{\sigma_j^2}}$$

where R - average ratio of peak intensity to cataloged γ -ray intensity,

σ_j - error estimate of the peak intensity,

P_j - peak intensity (= A_j / ϵ_j),

I_j - cataloged fractional intensity of the γ -ray,

n - number of standard γ -rays available.

The now determined ratio applies naturally also to other γ -rays of the isotope. This makes it possible to calculate its contribution of the various γ -rays of the isotope to the various peaks in the spectrum. There are three possibilities:

- (1) The contribution of the isotope is negligible (less than one per cent). The isotope assignment to this peak is deleted from the interpretation list.
- (2) The contribution is within limits of error equal to or greater than the peak intensity. Then other isotope assignments to this peak, if any, can be deleted.
- (3) The contribution is between 1 and 100 per cent. No action is taken by the program.

When isotope assignments could be deleted in one of the ways mentioned under 1 and 2, the sum of the fractional intensities of the gamma rays of some of the remaining isotopes may have decreased below the threshold value. This leads to the deletion of that isotope. As a result of the various simplifications in the interpretation list, the number of peaks with only one isotope assignment and which correspond to a standard gamma ray, may have increased. In that case more isotopes can be determined or an isotope can be determined on the basis of more peaks.

Therefore, the loop should be repeated and this continues until the results of two subsequent passes through the loop are identical. When this happens, a limit is reached for the number of isotopes which can be determined without any manipulation of the original peak data (interpretation class 1). Substitution of R for p_X/I_X in the appropriate Eqs (1), (2) or (3) yields the concentrations of the corresponding elements. Furthermore, the ΔR -values are given as error estimates for the given concentrations. The sum of the fractional intensities (normalized to 100%), and the number of γ -rays of the isotope found in the spectrum compared to the total number of cataloged γ -rays are given as a check of the interpretation.

The now determined isotopes are eliminated from the interpretation list by subtraction of their calculated contributions from the intensities of all peaks to which they are assigned according to:

$$p'_k = p_t - R I_k$$

$$\Delta p_k^2 = \Delta p_k^2 + I_k^2 \Delta R^2$$

If the remaining peak intensity is less than 10 per cent of the original value, the peak will no longer be used in the interpretation process.

The search for standard peaks in single assignments is now carried out again according to the procedure described above. The contributions of the determined isotopes are again subtracted and the entire process is repeated until no more standard peaks can be isolated. This yields a list of isotopes and corresponding element concentrations for interpretation class 2.

Table 2
Analysis of USGS geological standard G-2

Element	Concentration, ppm			
	IRI (4 an.)	FLANAGAN ⁸	FILBY ⁹	GORDON ¹⁰
Ba	$(1.73 \pm 0.14) \cdot 10^3$	$1.95 \cdot 10^3$	$1.54 \cdot 10^3$	$1.80 \cdot 10^3$
Ce	$(1.90 \pm 0.05) \cdot 10^2$	$1.66 \cdot 10^2$	$1.30 \cdot 10^2$	$1.44 \cdot 10^2$
Co	4.43 ± 0.13	4.9	5.0	4.3
Cr	8.7 ± 1.0	9.0	7.2	4.6
Cs	1.43 ± 0.09	1.5	1.5	1.4
Eu	1.15 ± 0.03	1.5	1.5	1.37
Fe	$(1.76 \pm 0.03) \cdot 10^4$	$1.93 \cdot 10^4$	$1.65 \cdot 10^4$	$1.72 \cdot 10^4$
Hf	8.5 ± 0.5	7.5	8.6	7.8
K	$(3.93 \pm 0.15) \cdot 10^4$	$3.7 \cdot 10^4$	-	$4.0 \cdot 10^4$
La	$(9.9 \pm 0.2) \cdot 10^1$	$1.12 \cdot 10^2$	-	$8.1 \cdot 10^1$
Na	$(2.90 \pm 0.05) \cdot 10^4$	$3.1 \cdot 10^4$	$3.0 \cdot 10^4$	$2.95 \cdot 10^4$
Rb	$(1.59 \pm 0.09) \cdot 10^2$	$2.34 \cdot 10^2$	$1.40 \cdot 10^2$	$1.29 \cdot 10^2$
Sc	3.28 ± 0.10	3.9	4.0	3.5
Sr	$(4.3 \pm 0.5) \cdot 10^2$	$4.6 \cdot 10^2$	$4.2 \cdot 10^2$	-
Ta	$(8.3 \pm 0.4) \cdot 10^{-1}$	$9.1 \cdot 10^{-1}$	$8 \cdot 10^{-1}$	1.0
Tb	$(4.2 \pm 0.8) \cdot 10^{-1}$	$5.2 \cdot 10^{-1}$	$6 \cdot 10^{-1}$	$5.2 \cdot 10^{-1}$
Th	$(2.42 \pm 0.05) \cdot 10^1$	$2.52 \cdot 10^1$	$2.65 \cdot 10^1$	$2.59 \cdot 10^1$
U	2.09 ± 0.24	1.99	1.93	-
Yb	$(5.6 \pm 2.5) \cdot 10^{-1}$	1.0	1.3	$8 \cdot 10^{-1}$
Zn	$(8.5 \pm 0.5) \cdot 10^1$	$7.5 \cdot 10^1$	$8.4 \cdot 10^1$	-
Zr	$(3.1 \pm 0.6) \cdot 10^2$	$3.2 \cdot 10^2$	$2.62 \cdot 10^2$	$2.50 \cdot 10^2$

The results for interpretation class 3 are obtained in the same way as described for class 1. However, also singly assigned non-standard γ -rays are taken into account. This is also true for the 4th pass, proceeding in the same manner as described for interpretation class 2, i. e. after subtraction of class 3 isotopes.

The only available information which may yield further progress in the interpretation at this stage, is contained in the estimated detection limits. The R-value corresponding to the detection limit can be calculated for each isotope left on the interpretation list, and compared with the (p/I)-values for the peaks to which it is assigned. If the estimated contribution of the isotope to such a peak is less than 0.1%, the isotope assignment to the peak is deleted. This may lead to

Table 3
Analysis of IAEA simulated airfilter Air-3

Element	IRI (5 an.)	Concentration, $\mu\text{g}/\text{filter}$	
		True value ¹¹	Mean and standard deviation of results of intercomp. ¹¹
Fe	$(1.72 \pm 0.07) \cdot 10^2$	$1.94 \cdot 10^2$	$(1.91 \pm 0.41) \cdot 10^2$
Zn	$(6.38 \pm 0.22) \cdot 10^1$	$7.4 \cdot 10^1$	$(7.07 \pm 0.97) \cdot 10^1$
Mn	4.28 ± 0.14	4.2	4.63 ± 1.29
Cr	1.70 ± 0.08	1.85	2.13 ± 0.54
As	1.61 ± 0.04	2.04	1.75 ± 0.49
Cd	2.71 ± 0.07	3.06	3.21 ± 0.77
Ni	5.0 ± 0.6	5.3	6.67 ± 1.41
Cu	2.78 ± 0.09	3.04	3.19 ± 0.81
Hg	$(6.1 \pm 1.7) \cdot 10^{-2}$ *	$2.4 \cdot 10^{-1}$	$(2.6 \pm 1.2) \cdot 10^{-1}$
Se	$(6.8 \pm 0.7) \cdot 10^{-1}$	$8.5 \cdot 10^{-1}$	$(7.7 \pm 1.6) \cdot 10^{-1}$
Ba	$(1.18 \pm 0.08) \cdot 10^{-1}$	$1.38 \cdot 10^1$	$(1.30 \pm 0.26) \cdot 10^1$

*Manually corrected for interference from ^{75}Se .

the determination of other elements, using the main interpretation loop (interpretation class 5).**

When reviewing the various principles applied one realises that up till now no use was made of the internal check of concentrations of different isotopes produced from the same element.

In principle it is possible to apply such a check at various stages of the interpretation process. However, it involves activity ratios which are time-dependent because of the different half lives of the isotopes, which may be insufficiently accurate after a substantial waiting time. Therefore, it was decided not to use these interrelations as part of the interpretation loop. Instead the check is done after the completion of the interpretation procedure. If more than one isotope due

**A typical example where the described routine yields a solution is in analysing the ^{51}Cr peak (320.1 keV), which may be mixed with the 319.2 keV peak of ^{105}Rh , produced from the decay of ^{105}Ru . The detection limit of the Ru can be deduced from one of the other Ru-isotopes and shows in many cases that the ^{105}Rh -contribution to the 320.1 keV peak is negligible.

to the element is observed, the weighted average of the corresponding concentrations is calculated. At the same time isotopes which can be produced from more than one element (for instance certain fission products), are corrected for the contribution of one of the elements. In such a way freedom is given to the analyst to replace the final element concentration by the single value for one of the isotopes if there are reasons (long waiting time, experimental and other errors) to suspect the other value(s).

Application

The procedure described in this paper is used on routine basis in the instrumental neutron activation analysis of mainly geological and environmental samples. The applicability to these types of materials is demonstrated with the results obtained from the analysis of USGS geological standard G-2 (Table 2) and of IAEA intercomparison airfilter Air-3 (Table 3).

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