

ANCILLARY PROGRAMS OF A NUCLEAR SPECTROMETRIC PROGRAM PACKAGE CLOSELY RELATED TO EXPERIMENTAL ANALYSIS

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Received May 2, 1984

Summary

The operation of two ancillary computer programs is presented. The programs are applied as parts of an evaluating program system for gamma-ray spectrometry. The programs perform advance prediction of intensities of gamma-lines of expectable isotopes in samples to be measured and assessment of limits of detection in measured spectra, respectively, thus adding a lot to the efficiency of the total program package as well as to that of routine analytical work. Since these programs do not need further large data libraries their appropriate versions can be readily included into a hardware environment with even low memory capacity. Some representative results are presented.

Introduction

Complex program systems for processing gamma-spectrometric data obtained by semiconductor detectors are widely used in applied nuclear analytical laboratories. In recent years some of these program systems have become available as commercial products (e.g. ref. [1]). Nonetheless, according to the results of some international intercomparisons, the actual implications of these programs proved quite different in terms of their accuracy and effectiveness (see e.g. [2]). This experience can be explained by two main reasons:

- the actual hardware environment (including not only the computer and its direct devices but the total measuring and data acquisition setup as well) can require significant modifications;
- the “finé tuning” of the programs makes up a basic factor of the total effectiveness and this task is mainly left to the actual operating staff.

Owing to these reasons, especially in case of small computers, it still can be advisable to construct an independent program package applying useful hints of some acknowledged programs. The general tasks (and parts) of a complex program can be classified the way below:

- a) Control programs for the irradiation-, measuring- and spectral data acquisition systems.

- b) Determination and control of necessary calibration data of the measuring system (gamma-energy vs. channel no., resolution (f. w. h. m.) vs. gamma-energy; efficiency vs. gamma-energy, etc.).
- c) Determination of "draft" data of peaks: area (intensity) and position (energy) with the aid of fast digital methods.
- d) Resolution of multiplets and optional modification of singlet data by fitting optimized peak-shape functions.
- e) Identification of nuclides: qualitative analysis.
- f) Calculation of radioactive and/or inactive concentrations: quantitative analysis. In case of activation analysis (thermal and fast NAA, GAA, cyclic activation, etc.) options should be included to provide for the absolute, multistandard, monostandard (single-comparison) and other versions of calibration.
- g) Ancillary programs, e.g.:
 - corrections for possible losses (pile-up, deadtime, burnup, etc.),
 - determination of detection limits,
 - programs for planning of analyses (advance prediction).

Some features of the program package applied in our laboratory were presented in different papers [3, 4]; a general overview will be published soon as a thesis. In this paper we introduce two of the routinely used ancillary programs.

Advance prediction program (AP)

Input requirements

- a) The energy calibration function: gamma-energy vs. channel no. (see eq. (1) below):

$$E_{\gamma} = a_1 \cdot CH + a_2 \quad (1)$$

where E_{γ} : energy of gamma-line, CH: channel no. of peak position, a_1 , a_2 : calibration constants.

- b) Resolution calibration function: full width at half maximum (f. w. h. m.) values of the peaks (in energy units) vs. gamma-energy. If the AP program encounters annihilation or escape peaks, special factors are applied to determine the width of these peaks. The function is shown as equation (2):

$$F = b_1 \cdot E_{\gamma} + b_2 \quad (2)$$

where F : f. w. h. m. calculated by interpolation combined with fitting of a Gaussian; b_1 , b_2 : calibration constants. According to our experience, the annihilation peak (511 keV) occurs as 1.25 times broader than the corresponding value calculated from eq. (2), the respective factor for single and double escape peaks is 1.8.

c) Efficiency calibration function: absolute efficiency calculated for full energy peaks vs. gamma-energy (eq. (3)):

$$\ln \epsilon = c_1 \cdot (\ln E_\gamma)^2 + c_2 \cdot \ln E_\gamma + c_3 \quad (3)$$

where ϵ : absolute efficiency, c_1, c_2, c_3 : calibration constants. Eq. (3) is applied to energy ranges below and over an "inflection" energy value of 240 keV with two different arrays of the constants. Furthermore this relation is determined for four different cases of source-detector geometry.

The errors in values calculated according to eqs (1-3) can be assessed as follows: the error in gamma-energies is ≤ 0.6 keV as determined experimentally with an approximate 0.8 keV/channel gain; the uncertainties in f. w. h. m. and efficiency values are 7% and 12% on average, respectively. The great latter value is mainly due to the error in activities of calibration standards.

d) Estimated elemental composition.

The samples analyzed in our laboratory are mainly of biological or environmental origin, their major constituents are light elements hardly sensitive to thermal neutron activation. However, matrix effects can be encountered due to the presence of Na, K and Cl as minor components. In addition to the generally known quantities of these elements, different trace element contents can be input to reveal sensitivity levels, possible coincidences and therefore need for radiochemical separations.

e) Data of neutron activation.

Thermal neutron activation can be performed in the Training Reactor of our university and in the Research Reactor of the Isotope Institute. (Approximate neutron flux in irradiation channels: up to $2 \cdot 10^{11}$ n/cm² s and $2 \cdot 10^{12}$ n/cm² s, respectively.) Epithermal flux is neglected in advance prediction, its influence being right below the overall uncertainty limit, which is set mainly by the errors in efficiency and in nuclear data of the elements analyzed (see section f) below).

The duration of irradiation can be varied up to 6 hours generally, the minimum cooling time is about 30 minutes and 2 hours respectively, in case of the two reactors applicable.

f) Nuclear data library.

The data library was compiled from several nuclear data tables (refs. [5, 6, 7]). Two different library files were created: the first library contains data on isotopes formed by thermal (n, γ) reactions as well as the nuclear background of the measuring chamber; the other one is made up of heavy nuclei liable to spontaneous fission and of their possible fission products, the background is included again of course. At present the AP program applies only data of thermal activation. Library entries of this file are arranged according to increasing gamma-energy. An entry contains the following data:

— Energy in keV, rounded to one-tenth accuracy;

- Formula and atomic mass number of the respective isotope;
 - Gamma abundance relative to one decay;
 - Half-life in seconds;
 - Product of thermal neutron cross-section and isotopic abundance of the target nuclide in barns;
 - Optional pointer to the ancillary file containing parent-daughter relation data (isotope identification codes and respective branching ratios).
- The last three items are not applicable for background lines.

Operation of the AP program

After initialization the program chooses the possible isotopes which correspond to the element given as input. If the isotope fails to pass one of these tests below (see eqs (4) and (5)), its gamma-lines are omitted from the working file of the current library:

$$t_D = k_1 \cdot t_H \quad (4)$$

$$t_I = k_2 \cdot t_H \quad (5)$$

where t_D is the decay (cooling) time of the sample, t_I is the time of irradiation, t_H is the half-life, k_1 and k_2 are experimental constants. Their values are 20 and $5 \cdot 10^{-3}$ respectively, in case of matrix elements, and 10 and 10^{-2} in case of trace elements.

Following these tests, gamma-lines of descendants are added to the working library, if these nuclei are formed in reasonable amounts. Then the intensities of the predicted gamma-lines are calculated (see eqs. below) as well as the intensity/mass ratios. Presence of the latter data makes the results easy to convert to other concentration values of the same elemental composition.

$$I = A \cdot \epsilon \cdot \gamma \quad (6)$$

where I : intensity in cps, A : activity in Bq, γ : gamma abundance per decay.

$$A = m/N_A \cdot (f \cdot \sigma_0) \cdot \Phi \cdot [1 - \exp(-\lambda t_I)] \cdot [\exp(-\lambda t_D)] \quad (7)$$

where m : mass of inactive element in g, N_A : Avogadro-number, f : isotopic abundance of the target nuclide, σ_0 : thermal neutron cross-section (in cm^2), Φ : thermal neutron flux in neutrons/ cm^2 s, λ : decay constant in s^{-1} . The well-known equations above should be appropriately modified when applied to gamma-lines of descendants. Full-energy peaks of the background are represented directly by their known intensities.

One may be disapproved of all the gamma-lines being detectable in the composite spectrum. To overcome this ambiguity the expected spectrum can be constructed. This operation is indispensable for calculating the errors in

expected intensities. (One must be aware that the errors cannot be related proportionally to mass units like the intensities.) The full-energy peaks are represented by Gaussians:

$$y = y_0 \cdot \exp(-(x - x_0)^2 / 2w^2) \quad (8)$$

where y : counts, x : channel number, x_0 : peak position in channels, w : peak width parameter in channels, calculated from the f. w. h. m. and energy calibration functions, y_0 : maximum peak height in counts.

$$y_0 = \frac{I \cdot t_M}{w \cdot (2\pi)^{1/2}} \quad (9)$$

where t_M : measuring time in seconds (input parameter).

The Compton-plateaus and Compton-edges are represented by parabolic and logarithmic functions for each full energy peak. These data are calculated making use of a calibrated (input) parameter assessing the peak-to-Compton ratio (generally set to 20). The spectral regions are connected smoothly to each other since the subsequent regions are forced to have the same slope at the joining point. The low energy side of the Compton plateaus are drawn only above 160 keV, below this value the bremsstrahlung region is not related to individual peaks instead it is represented by a common logarithmic function joining smoothly to the summed counts of the Compton-plateaus.

Annihilation and escape peaks are included applying peak widths different from that of full-energy peaks (see section 1 for resolution calibration). The peak height of escape peaks are related to the corresponding full-energy peaks using measured experimental factors.

To achieve a more realistic picture of the spectrum, the counts are modified by a randomization procedure in order to reflect the expected statistical fluctuations. In accord with our intention that the AP program does not have to give a proper image of the spectrum, we did not include "secondary" spectral features such as asymmetry of the full-energy peaks, backscatter peaks, pile-up, true coincidences, correction for decay during measurement, etc.

Outputs and results

The AP program outputs the calculated intensities of gamma-lines which are anticipated to be present in the spectrum together with the estimated errors and (optionally) the specific intensity values. In addition, the predicted spectrum can be output to a plotter via the multichannel analyzer. The effectiveness of the program is illustrated by an example: Table 1 shows an output list of the gamma-spectrum of an activated fictitious biological matrix.

Table 1

Predicted intensities of the gamma-spectrum of a fictitious "Bowen's kale" sample

Input parameters: total mass: 100 mg

Run 1.: irradiation time: 4 hours

decay time: 2 hours

thermal neutron flux: $2 \cdot 10^{12}$ n/cm² s

Run 2.: irradiation time: 4 hours

decay time: 24 hours

thermal neutron flux: $2 \cdot 10^{12}$ n/cm² s

95% of the ²⁴Na activity is considered to have been removed by chemical separation prior to measurement

Element	Concentration* (ppm dry wt.)	Isotope	E (keV)	Run 1.		Run 2.	
				Intensity (cps)	Error (%)	Intensity (cps)	Error (%)
Br	24.3	⁸² Br	554.2	9.05	43.5	5.91	41.5
			776.5	7.81	45.0	5.08	39.0
Cl	3330	³⁸ Cl	1642.0	57.4	26.5	—	—
			2166.8	62.4	25.0	—	—
Cu	4.81	⁶⁴ Cu	511.0	6.96	56.5	2.10	48.0
Mn	14.9	⁵⁶ Mn	846.8	338.5	22.0	0.92	55.0
Mo	2.33	⁹⁹ Mo	140.5	—	—	0.17	63.5
Na	2594	²⁴ Na	1368.6	1526	17.5	27.6	21.0
			2754.1	1115	15.0	20.2	19.5
Zn	31.88	^{69m} Zn	438.7	—	—	0.24	58.5

*: According to ref. [12]

Determination of limits of detection (LOD program)

Detection limits (LOD's) are calculated generally according to the formulation of Currie [8] and Rogers [9]. The programmed versions of this method can slightly differ from one another on account of modifications based on experience with the actual measuring system (see refs. [10, 11] e.g.). We applied a somewhat different way of thinking in our LOD program in that we made a distinction between "baseline" and "peak" regions (see details below) of the spectrum to be treated.

Input requirements

Most input data (calibration functions, constants, library files) are the same as those of the AP program, in addition to the measured spectra of course. Optionally the spectra can be converted to different measuring times, because the sensitivity to a certain element strongly depends on the actual number of counts.

Operation of the LOD program

Two general modes of operation are possible: if a list of elements is specified as input, LOD values are calculated for the energies of the major gamma-lines of these isotopes only. If no entries are given, LOD is calculated for the total spectrum using an energy window equal to the actual f. w. h. m. In the latter case it can be given in activity units only of course. As indicated above, the minimum detectable peak areas are determined in two different ways.

$$N_{\min} = j_1 \cdot (j_2 \cdot F \cdot \bar{y})^{1/2} \quad (\text{usually } j_1 = j_2 = 2) \quad (10)$$

$$N_{\min} = N_t - N_0 = j_3 \cdot N_0 \quad (\text{usually } j_3 = 0.33) \quad (11a)$$

$$\sigma_{\text{rel. min}} = \frac{[(1 + j_3) \cdot N_0]^{1/2}}{j_3 \cdot N_0} = j_4 \quad (\text{usually } j_4 = 0.5) \quad (11b)$$

where N_{\min} : minimum detectable peak area in counts, F : f. w. h. m., \bar{y} : average number of counts in a $2F$ channels wide window, $\sigma_{\text{rel. min}}$: relative error in N_{\min} , N_t : total peak area, N_0 : peak area found in the spectrum in the region of interest.

Eq. (10) refers to a case when no peaks are present in the region of interest. This equation is the same as suggested by Rogers [9]. Eqs (11a) and (11b) refer to the case when a peak is present in the region of interest. Provided that the overlap of the present and the fictitious peak would be too strong to be resolved successfully (it is the "worst" case of course) detectability of the two gamma-lines as individuals depends on the ratio of the area of the sum peak to that of the "original" (undisturbed) peak. The "new" (fictitious) peak area has to meet the condition that its relative error be less than a preset percent. If the peak fails to pass this test, the window width (that is the area of the "original" peak) will be scaled up. Value of the j_1 constant is fixed on account of statistical rules representing the 90% confidence level, the values of the other constants were determined experimentally.

Outputs and results

If the minimum detectable peak areas are calculated the LOD values can be given in terms of activity and/or mass units according to the user's intention. These calculations are performed using the calibration data of the measuring system and the data libraries in the same way as it was presented with the AP program.

The effectiveness of the LOD program is illustrated by the results of the recent evaluation of the IAEA intercomparison material "AG-B-1" (Seaweed sample). (See Table 2.) LOD values are given for the anticipated components

Table 2

Limits of detection for the IAEA intercomparison sample
"AG-B-1"

measuring time: 99 000s

Nuclide	E (keV)	LOD values	
		intensity (cps)	specific activity (mBq/g sample)
¹³⁴ Cs	604.7	0.016	305
	795.8	0.010	299
⁵⁸ Co	810.8	0.009	339
⁵⁴ Mn	834.8	0.009	254
⁶⁵ Zn	1115.4	0.008	592
²⁴⁰ Pu	104.2	0.015	8.95 · 10 ⁵
²⁴¹ Am	59.5	0.019	981

that could not be detected by instrumental analysis. The input spectrum of the AG-B-1 sample contained the nuclear background in addition to the detected peaks of ⁶⁰Co and ¹³⁷Cs found to be present.

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