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Application of Hypermet-PC in PGAA

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Hypermet-PC has been developed in the mid-nineties at the Institute of Isotopes and Surface Chemistry based on a successful FORTRAN code from the seventies. With additional calibration routines and other helping features it has proved to be a very useful tool in quantitative analysis performed either with NAA or with PGAA. The sophisticated built-in peak-shape function allows the fitting of asymmetric peaks from large-volume germanium detectors over a very wide energy range needed for PGAA. The experience collected when evaluating several thousands gamma-spectra acquired for routine analysis and spectroscopic research, is summarized in the paper.

Introduction

The original Hypermet code was developed at the Naval Research Laboratory, Washington, D.C., in the early seventies for automatic evaluation of multichannel gamma-ray spectra.[1] The first version was written in FORTRAN and ran on a mainframe computer. Because of the level of computing at that time, the code was written so that it required minimum input from the user: the spectrum and only a very few adjustable parameters. The greatest advantage of the algorithm, which still is maintained, has been the peak-shape function specifically designed for use with the Ge(Li) detectors starting to proliferate that time. Later a commercial version called ND Hypermet 1.1 running under VAX VMS was introduced by Nuclear Data and later marketed by Canberra Industries.

The source code of the original Hypermet was kindly provided by the authors to the Central Research Institute for Physics (KFKI, Budapest), where it was first installed on a mainframe computer and later on IBM compatible personal computers. Colleagues working in the field of gamma-ray spectrometry here had ample experiences to test and apply the program. But with the changes in computational techniques, the need gradually arose to rewrite the code for use as an interactive platform on a personal computer.

In parallel with the installation of the new PGAA facility at the Budapest Research Reactor,[2] it was decided to make a major software revision, thus the many-year long Hypermet-PC project is started. The main goal was to produce a fast, user-friendly and interactive graphical software for the evaluation of gamma-spectra on DOS-based IBM-PC compatible machines. New calibration routines and other helping tools were also planned, while preserving the superior peak fitting feature of the original program. The essential needs of scientists working in the fields of neutron activation analysis (NAA) and prompt gamma activation analysis (PGAA) were kept in mind. The project was going on from 1993 to 1999 in the Department of Nuclear Research under the leadership of G. L. MOLNÁR and A. SIMONITS, and the programming work was done by B. FAZEKAS† and J. ÖSTÖR. The project was continued by J. ÖSTÖR and B. FAZEKAS, after leaving the academic field, with the intellectual guidance of A. SIMONITS, in order to rewrite the program under Windows operating system and to adjust it to the up-to-date needs of the users.[3]

The first version of Hypermet-PC, written in Turbo C++, was not much more than an interactive upgrade of the original FORTRAN code. The program handled several spectrum storage formats, e.g., Canberra S100, AccuSpec, SAMPO90, Ortec ACE etc., displayed the channel contents in a tabular format, and did the automatic peak fitting using the original non-linear least-squares optimization algorithm.[4,5]. It also contained some basic calibration routines. In an upgraded version a complete quality assurance package and the handling of dual spectra used for loss free counting were included.[6,7] Using the improved calibration routines, efficiency and non-linearity functions constructed from orthogonal polynomials could be fitted to data points from several different measurements.[8] This feature made it possible to derive accurate counting efficiencies and non-linearity functions fitted to several hundred data points. The relative uncertainty of the efficiency curve determined this way was as low as 0.4% at mid energies, and an 8th order polynomial proved to be adequate to cover the whole energy range from 50 keV to 11 MeV.[9] The quality assurance package also contains a differential non-linearity test for ADC-s, and the peak-width test for checking the stability of the spectrometer energy resolution.

The fitting module for this upgraded version allows inserting or deleting peaks manually, thus modifying interactively the results of the Hypermet peak-search algorithm which is based on statistical criteria. A nuclide identification routine was also appended to the software. Using a predefined dataset of decay and prompt gamma-

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peaks it also provides an output list of masses calculated from the peak area and the neutron flux.[10] Based on this list, a quantitative analysis can be performed.

The last modification made in Hypermet-PC was the inclusion of calibration of some peak-shape parameters, and manual peak-summing. Thanks to the modified calculation of the peak position, even in the case of asymmetric peaks the same peak positions can be obtained using either the centroid determination by peak-count summing, or from fitting using special peak-shape functions.[11] In an international comparison Hypermet proved to be the software with the highest resolving power, and several other features also were placed well.[12] Hypermet is still being used in our laboratory for PGAA, and – as far as we know – in several others mainly for the purpose of NAA. The accurate calibration routines and the sophisticated peak-shape functions make Hypermet-PC a unique tool in the field of PGAA. Several thousands of PGAA spectra, each having several hundreds of peaks covering the energy range up to 12 MeV, have been evaluated using this versatile program. Though some features seem out-of-date now, it still suffices for our work in routine analysis, as well as in spectroscopic research requiring high stability and accuracy. In this paper our experiences, collected while using Hypermet-PC in the evaluation of wide-energy-range prompt-gamma spectra are summarized.

Requirements and solutions

The needs of prompt gamma spectroscopy push the applied electronics and the evaluation software to their limits. In spite of the large number of peaks typically appearing in most prompt gamma-ray spectra, the spectrometer must yield reproducible peak positions for an unambiguous qualitative analysis. The other mensuration requirements of quantitative analysis are also severe; the net peak area should depend linearly on the quantity of the element of interest in a wide dynamic range, and in any matrix resulting in different spectral interferences. There is no spectrometer system which can meet all these demands, but the quality of the spectroscopy can be improved by using a reliable evaluation software. Hypermet-PC has been developed to meet these extraordinary requirements.

Nonlinearity

The non-linearity of most ADC-s is in the order of 0.1%, which may result in a discrepancy of 1–2 channels from the ideal linear calibration. In the case of a 16k ADC using a coarse gain of 0.7 keV/channel to reach 11–12 MeV at the high-energy end of the spectra, this nonlinearity results in a systematic error up to 1 keV in peak position determinations, which makes reproducible peak identification impossible. The most important part of the prompt gamma-spectrum is the low energy region (<1 MeV) and the high energy region (typically above 5 MeV). In the low energy range the density of characteristic peaks is so large that the uncertainty of the peak energy determination should not be greater than 0.1 keV. In the high energy region where the peaks are not so numerous, 0.5–1 keV accuracy is good enough.

To produce peak positions with an accuracy of less than 0.1 keV in the low energy range and of about 0.5 keV in the high energy range, one needs to correct for the system nonlinearity. One common and simple solution, provided with most MCA cards, is the fitting of a second order polynomial to the centroids of three reference peaks in the spectrum. A more sophisticated solution is the utilization of a multi-parameter nonlinearity function.

Nonlinearity is an intrinsic feature of the spectrometer system; being not sensitive to minor and slow changes in gain and DC levels.[13] The routine procedure in PGAA applied in Budapest is the following:

Nonlinearity functions of an 8th order polynomial are determined[8] regularly at the beginning of every semester using the lines of a ^{152}Eu-source[14] and that of the ^{35}Cl(n,γ)^{36}Cl reaction.[15] A typical nonlinearity function can be seen in Fig. 1. The same nonlinearity is used throughout the semester for all spectra acquired with similar coarse gain and shaping time constant settings. If significant changes occur in the setup, individual nonlinearity files are usually produced. After determining the non-linearity function, a simple linear energy calibration using a low- and a high-energy line is performed for each spectrum. In our experience, peak positions can be determined reproducibly in this way within a 2–3 sigma limit, i.e., the estimated peak positions scatter throughout the region with 2–3 times of their estimated uncertainty. Table 1 shows a few peak positions selected from all parts of the energy scale as measured in the past six years in different samples to demonstrate the reproducibility of the algorithm described above. The reference values have been determined relative to chlorine lines.[15] The systematic errors (where the discrepancy is greater than 3 times the uncertainty) are most likely due to the imperfect correction of the nonlinearity, which may vary in time, or depend on the count-rate etc., significantly. However, this accuracy is already adequate for quantitative analysis.

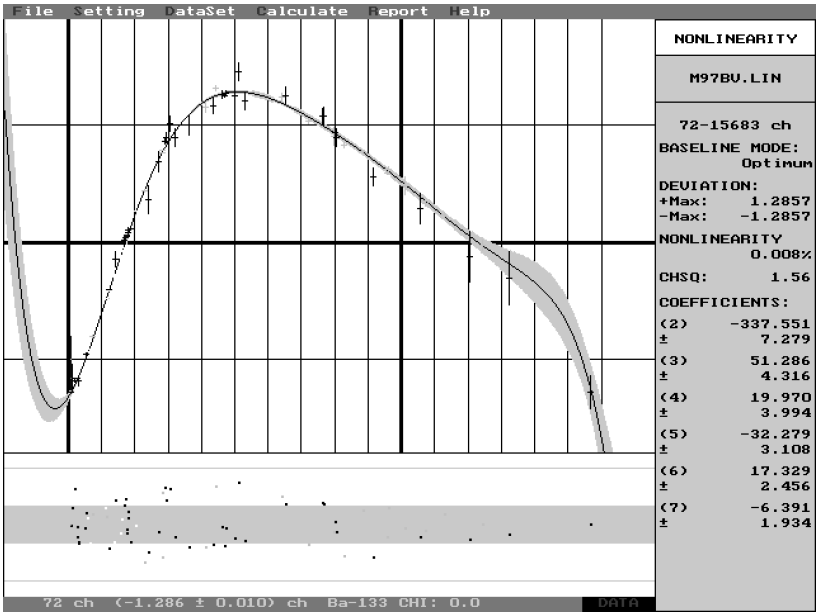

Fig. 1. Nonlinearity vs. channel number for a 15% relative efficiency HPGe detector measured at the Budapest PGAA facility in 1997

Peak area

For reliable quantitative analysis it is also important to determine peak areas reproducibly. The same peak may appear in different spectral environments, depending on the matrix, but the peak area is expected to be independent from the neighboring peaks. The uncertainty of the fit obviously depends on the counting statistics.

For large volume HPGe detectors, the peak shapes cannot be described with a Gaussian alone. The semi-empirical model function built into Hypermet has proved to be valid over the wide energy range of PGAA spectra. The peak shape function implemented in Hypermet consists of two terms: a Gaussian and an exponentially modified Gaussian (EMG), the so-called skew term, which accounts for the tailing on the low-energy side. The background is divided into two parts, a peak-dependent component and the baseline. The baseline can be described with a maximum second order polynomial, while the peak-dependent background consists of two terms: the tail-term and the step function. The first one is another EMG function, but it is expected to extend further in the low-energy direction. The step is an erf function whose inflection point is at the centroid of the Gaussian. The expressions can be found in detail, e.g., in Reference 11. All terms are based on physical effects,[1] and do not necessarily appear in every peak.

Low-count peaks can be described well enough with only a Gaussian. The width of the Gaussian is determined in a constrained fit, i.e., the initial value of it is derived from the usual square-root function: $\sqrt{(a+bE)}$, where a and b are determined from the width calibration normally performed in parallel with the energy calibration. A ±20% tolerance in width is allowed in the final fit.

The built-in threshold, above which skew-, tail- and step terms are fitted, is 500 counts. In the case of the 25% HPGe detector used for PGAA in Budapest, the skew term is considerable over the whole energy range. The original concept, where the height is fixed to the amplitude of the Gaussian and the slope to the width of the Gaussian, seems to be valid in narrower energy ranges only. It works well with spectra of radioactive sources and in NAA, but fails in PGAA. In the latest version of Hypermet-PC the height of the skew may be fixed to the peak area and its slope, i.e., the exponential tail is constant. This means the parameters of the skew term have an energy dependence similar to the peak width. This process proved to be valid for the whole energy range used in PGAA. The scaling values for the height and the slope of the skew term were determined in a trial-and-error procedure for our detector when this approach was first introduced.

The tail appears only at low energies (typically at a few hundred keVs), and for strong peaks (more than 10,000 counts). Otherwise its contribution is negligible. Due to the collimators in front of the detector, a considerable inverse step appears under the full-energy peaks. In our case, its height is approximately equal to –1/1000 of the peak area and slowly increases below 500 keV to –1/500. For escape peaks a reverse step appears, but these peaks are not used for analysis.

Table 1. Variation of peak positions during the past six years as determined with Hypermet-PC in different samples

Date	Sample	Al 1778.85(3)		Al 7723.8(3)		Fe 352.332 (16)		Fe 7631.05(9)		H 2223.259(19)	
		Energy, keV	*Z*-score	Energy, keV	*Z*-score	Energy, keV	*Z*-score	Energy, keV	*Z*-score	Energy, keV	*Z*-score
06/98	Cement	1778.82(5)	–1.0	7723.76(22)	0.3	352.28(4)	–0.7	7631.01(21)	–0.4	2223.11(10)	–0.7
06/99	Clinker	1779.02(8)	2.0	7724.06(16)	0.9	352.33(5)	0.0	7631.09(13)	0.3	2223.39(8)	1.6
07/00	Basalt	1779.02(5)	3.1	7724.17(23)	1.1	352.353(9)	1.1	7631.25(23)	0.8	2223.34(06)	1.3
03/01	Background	1778.85(4)	0.0	7724.4(3)	1.6	n/a		7631.30(21)	1.1	2223.19(5)	–1.2
01/02	Galenite	1778.8(9)	–0.1	n/a		352.301(7)	–0.4	7631.08(18)	0.2	2223.29(11)	0.3
11/02	Al + Mg metal	1778.85(3)	0.0	7723.8(3)	0.0	352.29(7)	–0.6	7631.2(3)	0.5	2223.16(4)	–1.3
02/03	Geological standard	1778.93(5)	1.4	7723.84(21)	0.2	352.36(3)	–0.1	7631.01(20)	–0.2	2223.27(6)	0.2
01/04	Glass	1778.96(6)	1.7	7723.8(4)	–0.1	n/a		n/a		2223.08(15)	1.4

Table 2. Mass values and their uncertainties for chlorine in different samples as determined with Hypermet-PC

Sample:	[Co(bipy)3](Clo4)3			Cement			PVC			Chert		
Date:	06/1997			12/2001			11/2001			01/2003		
Mass:	0.5 g			6 g			0.2 g			4.6 g		
Cl content:	12.80%			80 ppm			56%			7 ppm		
Energy, keV	Mass, g	Unc., %	*Z*-score	Mass, g	Unc., %	*Z*-score	Mass, g	Unc., %	*Z*-score	Mass, g	Unc., %	*Z*-score
1164.83	0.094	1.3	1.3				0.00994	1.1	–0.5	0.00173	3.7	0.2
517.077	0.096	1.7	2.2	0.000226	8.0	–0.6	0.01027	1.1	2.6			
6110.71	0.085	2.6	–2.9	0.000216	7.7	–1.1	0.00934	2.8	–2.3	0.00181	9.3	0.5
1951.15	0.093	1.4	0.4				0.00974	1.2	–2.1	0.00167	9.8	–0.3
788.37	0.104	1.9	0.3	0.000263	8.5	0.2	0.01091	1.2	0.2	0.00198	11.0	0.3
1959.36	0.092	1.7	0.0	0.000245	13.5	0.2	0.00979	1.3	–1.6	0.00171	14.9	–0.1
786.182	0.105	1.9	0.3	0.000299	9.6	0.5	0.00955	1.2	–0.1	0.00161	11.0	–0.1
7413.92	0.086	3.1	–2.0							0.00152	9.7	–1.2
7790.28	0.087	3.6	–1.4				0.00918	2.4	–3.4	0.00143	11.5	–1.5
6619.58	0.084	3.1	–2.8				0.00924	2.0	–3.9	0.00175	25.0	0.1
5715.16	0.087	3.3	–1.7				0.00968	2.1	–1.4	0.00144	23.2	–0.7
2863.76	0.094	2.7	0.6	0.000275	16.8	1.0	0.00993	1.6	–0.4	0.00231	16.9	2.0
6627.87	0.083	4.4	–2.3				0.00933	2.3	–2.9			
4979.75	0.089	4.5	–0.9				0.00984	2.1	–0.7			
1601.06	0.093	3.2	0.3				0.00976	1.5	–1.6			
3061.76	0.092	3.2	0.0				0.01019	2.0	1.0			
8578.58	0.090	4.5	–0.6	0.000295	22.7	1.1	0.00934	3.2	–2.0	0.00137	19.5	–1.1
6977.75	0.087	5.6	–1.1				0.00931	2.9	–2.3			
1162.56	0.071	9.1	–2.5				0.00990	5.0	–0.2			
1131.18	0.092	3.5	–0.2				0.01002	1.7	0.2	0.0028	20.0	3.3
5517.13	0.087	7.0	–0.8				0.00969	3.2	–1.0			
2676.11	0.089	5.4	–0.7				0.01012	2.4	0.6			
5902.75	0.078	7.7	–2.0				0.00872	4.7	–2.7			
1327.36	0.098	4.5	1.3				0.00990	2.0	–0.5			
4944.35	0.083	7.4	–1.4				0.00968	3.1	–1.0			
Mean:	**0.0927**	**2.2%**		**0.000237**	**5.8%**		**0.0100**	**3.4%**		**0.00172**	**4.2%**	
External error:		**3.7%**			**8.7%**			**3.7%**			**7.0%**	
χ^2:			**2.3**			**0.6**			**3.3**			**1.6**

The above constraints work well with about 90% of the peaks. It usually fails in regions mixed with X-ray peaks or complicated overlaps, and also in the case of extremely large peaks. X-ray peaks are not used for analysis. In case of overlaps, splitting up the region and manual modification of fitting criteria usually helps. In case of large peaks, which may be distorted due to pile-up effects, a ±20–30% tolerance is also allowed for the slope, or finally for the amplitude of the skew term. The acceptability of the fit is determined using the χ^2-value. With the present computers the automatic evaluation of the usual prompt gamma-spectra takes less than a minute, and an experienced analyst can scrutinise and occasionally correct the fits in a few minutes. The procedure discussed above ensures reproducible peak areas needed for reliable quantitative analysis.

Table 2 shows mass values for chlorine in different samples measured at different dates. The masses were determined using peak areas and detector efficiencies determined with Hypermet-PC,[9] as well as gamma-ray production cross sections tabulated in a spectrum atlas and data library.[16] The relative uncertainties and the *Z*-scores from weighted means are also given. The mean values for the uncertainties, i.e., the internal errors are calculated, too, for the statistical evaluation of the data. External errors are usually somewhat higher than the internal errors, but χ^2 values indicate relatively good fits. Mass values scatter within the 2σ limit (i.e., χ^2 is smaller than 4). A discrepancy of greater than 3σ, usually indicates systematic errors from unresolved peak interferences. In the case of samples, where chlorine is present only in trace amounts, fewer lines proved to be greater than the detection limit. Lines with greater discrepancies are mostly omitted on the basis of their uncertainties and *Z*-scores which make the dataset more consistent, i.e., the internal and the external errors become closer to each other, and the χ^2 value approaches unity. From this example it can be seen, that the peak fitting algorithm built in Hypermet-PC provides reproducible peak areas, and reliable analytical data in a wide concentration range.

Conclusions

Hypermet-PC running under MS DOS has proved to be an ideal tool for the evaluation of prompt gamma-spectra. With its quality assurance routines, the detector system can be calibrated easily and accurately. Using the nonlinearity correction, peak positions can de obtained after a 2-point energy calibration with an accuracy that meets the strict requirements of qualitative analysis. An accurate peak-efficiency curve can easily be derived from several measurements on radioactive and (n,γ)-sources covering the whole energy range. Applying it to the peak areas, they can be transformed into accurate emission rates, and finally, into masses of the components. The development of Hypermet-PC has been discontinued in our department. A new version of the Hypermet algorithm has been built into a new product (HyperLab) and has been tested in the field of NAA.[3] The improved visualization and the convenient database containing all measured data seems to be a good helping tool for NAA laboratories, handling large number of samples. However, it has never been tested in prompt gamma activation analysis.

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