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Software for nuclear spectrometry

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Wagramer Strasse 5
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A-1400 Vienna, Austria

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FOREWORD

With the objective of discussing the new requirements for nuclear analytical software an Advisory Group Meeting (AGM) on Software for Nuclear Spectrometry took place in December 1994 in Vienna, Austria. The AGM was devoted to the specific field of software for gamma ray spectrometry. Nevertheless, many of the issues discussed and the recommendations made are of general relevance to any software on nuclear spectrometry.

This TECDOC reports on the technical discussions and presentations that took place at this particular meeting. But at the same time it reflects the needs and 'present status' of nuclear analytical software in general. Although some time has passed since the AGM, most conclusions and recommendations are still valid.

This TECDOC will be useful to those involved in gamma ray spectrum analysis at different levels and in different types of institute (laboratories, computer centres, quality control offices, etc.). It will be of special relevance to persons developing nuclear spectrum analysis software, in particular gamma ray spectrum analysis software.

The IAEA is grateful to V. Osorio for his help in compiling and editing the manuscript. S. Fazinic of the Division of Physical and Chemical Sciences was the IAEA officer responsible for this publication.

EDITORIAL NOTE

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1. INTRODUCTION

With the advances of personal computer, PC-based software packages started to play a key-role in the control, acquisition and validation of the data in any nuclear experiment. Because of the range of applications of nuclear spectrometry, various spectrum analysis software packages are among the most used software in any nuclear laboratory. However, with the advent of new (and more powerful) computer hardware, operating systems and programming languages, further development in the field of nuclear spectrum analysis software is predicted. Also with the evolution of new nuclear instruments and spectrometers, further requirements of nuclear analytical software are foreseen.

The Advisory Group Meeting (AGM) on Software for Nuclear Spectrometry was dedicated to review the present status of software for nuclear spectrometry and to advise on future activities in this field. Because similar AGM and consultant's meetings had been held in the past; together with an attempt to get more streamlined, this AGM was devoted to the specific field of software for gamma ray spectrometry. Nevertheless, many of the issues discussed and the recommendations made are of general concern for any software on nuclear spectrometry.

After this AGM, an intercomparison of gamma ray spectrum analysis software (IAEA-TECDOC-1011) was organized in December 1995. Twelve PC-based programs for gamma ray spectrum analysis were tested. It was found that all programs yielded peak areas without bias, relative to each other. However, most of the programs could analyze a spectrum containing only singlets in reasonable statistical control with respect to peak areas. Peak positions generally were reported with too small or absent uncertainties. Statistical control was found to be lacking in the analysis of doublet peak areas. These deficiencies have still not been solved correctly in most programs.

The report is organized by sections. The 'Summary' below gives conclusions and recommendations adopted at the AGM. These conclusions and recommendations resulted from the discussions held during and after presentations of the scientific and technical papers. These papers are reported here in their integral form in the following Sections. The list of acronyms used in the report is given at the end.

1.1. SUMMARY

The following pages in this Section summarize the discussions held at the AGM. The summary is organized and presented under major topical discussion subjects.

1.1.1. Gamma ray software needs related to experiments

The discussions here were focused on the needs and requirements to the existing gamma ray analysis software from the point of view of an experimentalist. Details could be found in Section 2.

Only main topics and recommendations are listed in this summary. They were identified as:

(1) The spectrum analysis should be performed on an unmodified measured spectrum. The analysis programme may have the option to display smooth spectra and spectra obtained by "channel-by-channel" instrument background subtraction. These modified data should not be used for analysis.

(2) If repeated measurements on the same sample are made, the individual results may be averaged with due account of statistics. Whenever it is relevant, decay corrections have to be applied. Suspicious measurements should be deleted from the summed spectra.

(3) *Software flexibility.* The software should offer to the end-users as much flexibility as possible in the analysis procedures. For example, there should be several possibilities to select a region of interest for a peak analysis, e.g., manually, reading it from a file, or derived from programmed rules within the software. Several methods for peak analysis should be available as, for example, simple summing or various fitting functions may either be selected by the user or chosen automatically by the software. If a fitting function is chosen, the option to select which parameters are free and which are fixed should be implemented in the code.

(4) *User defined peak analysis library.* A strong requirement is a library-driven (or nuclide-driven) analysis. The user must be able to define in advance the radionuclides or gamma ray energies of interest so that the programme concentrates on the analysis of these particular elements or peaks.

(5) *Baseline must be handled properly.* If baseline is subtracted, determined peak's baseline count rates must be subtracted from corresponding peaks in the sample spectrum. Uncertainty propagation must include the contribution from the baseline.

(6) *Results of the codes. All intermediate and final results* should be listed in tables and/or files and visualized as data plots. Plots of peak shape, energy, and efficiency calibrations must be available. Experimental data, fitted functions, and residuals must also be available and presented graphically to the user.

(7) *Data file information.* The following information is considered useful to be included into the file containing the measured spectrum, as an example of attempts to provide more information on the analysis:

- Data or description characterizing the sample and gamma ray measurement.
- Calibration Standard Certificate data (source identification, radionuclide, half-life, activity and its uncertainty, reference date).
- Input data used for energy and efficiency calibration.
- Correction factors for coincidence summing and self-attenuation.
- List of data containing results of quality assurance measurements, such as detector resolution and efficiency vs. time.
- Used data library name.

(8) *Uncertainties* for all input quantities (calibration data, emission probabilities, etc.) and derived quantities (peak areas, energies, efficiencies, sample activities) must be given. Propagation of uncertainties must be done correctly. Correlation factors should be considered as far as possible.

(9) *Limits of activity* for user-selected radionuclides must be calculated when statistically significant full-energy peaks are not present.

(10) *Correction factors.* Due attention must be paid to corrections for true coincidence summing (in case of close measuring geometry) and gamma ray attenuation (in measurements with thick samples). The program should provide the option of either calculating the corrections or allowing the user to enter corrections manually.

(11) *Reports on result.* The program should be able to provide a complete or abbreviated report either at the completion of the analysis and at intermediate steps during the

analysis. Whenever it is possible a "user-defined" reports should be implemented in the codes.

(12) *Software documentation.* The program documentation must contain, as a minimum, the following information:

(13) Description and references to all algorithms used.

(14) All fitting functions available, including a description of weighting factors.

(15) Method used to determine uncertainties.

(16) Method used to determine lower limit of detection.

(17) Reference for radionuclide library data if the IAEA's recommended library is not used.

(18) All internationally accepted standards (technical terms and specifications) relevant to the analysis of gamma ray spectra should be used in the program menus, reports, on-line help and user's manuals.

1.1.2. Gamma ray spectrum analysis

The discussion concentrated on the spectrum analysis aspects of gamma ray spectrometry, techniques and methods, i.e. obtaining net peak areas and other peak parameters from the measured pulse height spectra. It should be emphasized that although spectrum analysis is an important part of gamma ray spectrometry, it should be considered in connection with all other parts of the gamma spectrometry software.

The discussion was divided into two major parts:

(1) Present status and future prospects of gamma ray spectrum analysis software,

(2) New emerging technologies.

1.1.2.1. Techniques & methods

During the discussion on the status of gamma ray spectrum analysis software attention was paid to the following topics:

- algorithms,
- implementation,
- platforms.

Considering the "classical" spectrum analysis algorithms (peak search, baseline subtraction, peak integration, multiplet fitting) it was concluded ***that these methods have reached a high degree of maturity*** and that ***it is quite unlikely that spectacular new developments will emerge in the near future***. On the other hand, it is realized that the way these algorithms are implemented in today's spectrum evaluation software still reflects to a large extent the memory and processing power of the computers of one or two generations ago. With current computer resources (particularly for personal computers) it must be possible to make new implementation of these basic algorithms so that the overall performance of the software is improved.

There is still room and need for improvements in the spectrum analysis software. Up to now most of the software development efforts were directed towards improving the user interface, e.g. by porting the existing software to a windows-based environment. Moreover, these new "user friendly" windows-based implementations of the spectrum analysis software might create the false impression that people can work with it in a correct way. It should be clearly understood that no matter how sophisticated the algorithms are, each of them has its limitations because of the statistical nature of the data we are dealing with. These limitations and the pitfalls that are associated with them are to some extent specific for the implementation (of the program).

Based on this the following recommendations could be made:

(1) *Methods and algorithms description.* Producers of spectrum analysis software should, as a minimum requirement, state clearly which algorithm they are using to perform a certain task and give sufficient literature references about the method. Ideally, the producer should include a detailed description of the algorithm and its implementation into the documentation of the program.

(2) *The limitations* and possible pitfalls of the implemented algorithms should be clearly stated and the program should warn the user when he is operating the program beyond these limits.

(3) *Consistency of the calculations.* One of the most important aspect of spectrum analysis programs is the consistency of the results, e.g. the concept "peak area" is only defined by the method that is used to obtain the value of that quantity, the peak area obtained from summing the channels after baseline subtraction is different from the peak area obtained by fitting. In practice this is often not a problem since the difference is mostly small and several methods rely on peak ratios rather than on absolute measurement. The program should inform the user about any decision taken and the user should be able to exercise complete control over the program letting the execution according to the users decision.

(4) *Quality control.* Consistency in results can only be guaranteed by implementing quality assurance at all levels of the spectrometric method, including at the level of the spectrum evaluation. **Organizations of intercomparison runs are very useful in this respect.**

(5) *Training.* It was also felt important that organized training on the use of specific gamma ray analysis programs could be very helpful. This is probably the only way that one can guaranty the correct use of the software in a particular situation.

(6) *Basic Training.* Next to training on specific analysis programs it would be of value to include lectures that explain the function of these algorithms at a basic level in training courses. The basic understanding of the algorithms must be seen as the foundation for the advanced training on the use of a specific gamma ray analysis program. Without this fundamental knowledge, the specific knowledge would be superficial and does not really improve the level of the laboratories involved.

(7) It is realized that computers' hard and software are in full evolution. MS Windows® is becoming the "*de facto*" standard operating system. In the near future 32 and even 64-bit platforms will be considered as *standard* in well equipped laboratories. Nevertheless, it is believed that spectrum analysis software running on a standard DOS will remain important, and future support and further development of DOS based software, both for MCA emulation and spectrum analysis, should not be abandoned. While, at the same time, further development on the bases of newly emerging OS will dominate.

(8) *IAEA's software.* The software built under the auspices of the IAEA, particularly GANAAS, is considered particularly useful for training in various IAEA programmes.

New developments can also be tested using this software. A good example of the usefulness of software developed under the auspices of the IAEA is the creation of generally accepted format for interchange of spectral data (see further). This "IAEA format" was originally used in the Agencies QXAS and GANAAS software and today adopted by many commercial gamma-spectrometry software packages.

(9) IAEA-supported software is now available to the scientific community via the Internet®. In this way people are able to contribute to the further development by commenting on the software and contribute to its improvement.

1.1.2.2. New emerging technologies

Since a number of years the scientific community is experimenting with advanced software systems for problem solving. These systems require high performance computers and try to build in some knowledge or intelligence into the software. These developments should be followed up, *but at the current state it is not considered sufficiently developed to promote the extensive use of these systems.*

One area in this field might require further research. It is observed that often gamma ray spectra are not acquired under optimum conditions. This is related to many small problems that can occur with the experimental set-up. Solving these problems requires a large amount of experience that can only be acquired by a person after an extensive practice. Laboratories often lack the possibility to build up this knowledge e.g. due to staff mobility. It could be useful to initiate or to stimulate research to build up a knowledge base (a set of rules, also called a rule base) for this purpose. The rule base could then be implemented in a software system (expert system). Such a rule base is interesting for training purposes and the system is considered useful for diagnostic of the experimental set up as well.

Research is currently going on in some areas of spectroscopy (e.g. XRF) to use simulation methods for quantitative analysis. At this stage these methods are not considered appropriate for gamma ray spectrometry or neutron activation analysis. However, for training purposes these systems could be extremely useful. Public domain software for gamma spectrometry is available and after possible adaptation this software might be used in training.

1.1.3. New developments and needs in gamma ray analysis software

Based on the experience with existing programs and considering the potential enhancements, a number of proposals for the improvement and additions in gamma ray spectrometry codes have been made.

Here, the major needs from the viewpoint of the software development and new requirements are presented. This advisory group agrees that from the software point of view:

(1) Programs should provide internal control sections, which help to detect and possibly correct user's mistakes in the programme handling or data evaluation (operational nonsense). This point is related to experts systems mentioned above.

(2) Programs should provide possibilities to either open or lock the access to internal details.

(3) The length and type of the printouts (or file results) must be selectable

(4) Spectrum analysis should be possible using different methods of area determination (fitting, integration, peak-height comparison, etc.) and different methods of running control (fully automatic, user controlled, interactive, library oriented, etc.).

(5) Flexibility in conducting global overview or nuclide/line-specific analyses

(6) Iterative analyses should allow considering, in the next step, the additional information gained in the previous step.

(7) Programs should provide access to all internal procedures and enable the user to turn them on or off. However, one should also be able to run analyses without any possibility of user input (batch mode).

(8) Programs should give the most reliable, correct, precise results with associated uncertainties. This might also involve the need to use different algorithms to find a specific solution. This feature, however, needs **proper description in the user information** (manual and on-line help facility). Precautions have to be provided that different algorithms are then connected to their respective calibration data sets; and uncertainties are consistently defined.

(9) Programs should provide means for self-diagnosis and control. This statement refers to spectrum related quality control features or also to experiment-related features where the program may connect back to the running experiment and suggest modifications.

(10) Programs may possibly provide open entries (macro-languages) where the user can supply his own algorithm or procedure.

(11) Programs should provide entries for additional "a priori" information about spectra, sample, etc. This additional information would be considered later in the analysis of the spectra. It is clear that this kind of feature needs a very extensive database with a complex structure to hold the data and decision trees.

(12) Programs should provide facilities to transport results into other environments for further treatment.

(13) Programs should be able to learn symbolic decision processes, i.e. non-numerical but rather logical decisions which are based on calculated results, "a priori" information and other relevant sources.

(14) Programs should provide facilities that help the user to qualify the calculated results and which tag questionable data.

(15) Programs should provide routines for the automatic (easily used, operator independent) energy-, efficiency- and shape calibration procedures.

(16) It should be possible to adapt codes to the language spoken or understood by the user.

1.1.3.1. Software quality assurance

Detailed aspects of quality assurance for nuclear spectrometry are reported in Section 5.

After some discussion, it was agreed to limit the subject to the *essential* characteristics of the software, while excluding facilities that could be included in separate systems:

corrections for self-absorption, decay, coincidences etc., as well as calibrations and library facilities.

The discussion session was focused on the needs and requirements for a set of spectra for intercomparison and quality assurance purposes.

It was stated that the essential features of programs for gamma-spectrum analysis, which are common to all uses, are:

- Detection of peaks: identification of singlets/doublets
- Evaluation of peak areas: definition and uncertainty
- Peak position and its uncertainty.

In this contest it was agreed that no separate test spectrum was needed to test the ability of the program to detect peaks, but that test spectra for peak area evaluation should contain peaks at/or below the expected limit of detection. It was also stated that the same test spectra would test the ability of the program to determine correct peak positions.

The results of the subsequent discussions concerning the specifications for these test spectra are summarized below and represent a broad consensus among the participants in the meeting, both external advisers and IAEA staff.

- The test spectra should be an improved and updated edition of the test spectra issued by the IAEA in 1976 and still available according to the IAEA AQCS Programme[1].

- The number of channels should preferably be 16 K, but since some programs can only handle 8 K, all-important features should be included in the first half of the spectrum.

- The spectra should be accurately known mixtures of actually measured spectra, recorded by counting actual radioactive sources for different periods of time. Test spectra would be obtained by super-imposing such simpler spectra on each other in accurately known increment.

- Each spectrum should be counted under identical conditions at least 6 times, so that 6 sets of identical test spectra are supplied with different counting statistics.

- In addition, a comparator spectrum is supplied, which contains singlet peaks with good counting statistics, the majority of which would also be present in the test spectra.

- The test spectra should contain most, but not all peaks found in the comparator spectra, riding on a Compton continuum that continues into a Bremsstrahlung spectrum at the lower channel numbers.

- In the first 8K channels the test spectra should contain at least 20 singlets, covering a peak-to-baseline range of at least two orders of magnitude. In addition it should contain at least 20 doublets and 1-2 triplets, separated by 0.5 to 3 FWHM and with peak-height ratios of the lower to higher energy ranging from 1:10 to 10:1. One of the components of the multiplets should be present in the comparator spectrum.

- The FWHM of peaks in the test spectra should vary with the channel number exactly as they do in the original experimental spectra and must be preserved during the subsequent manipulations. The lowest FWHM should be about 2 channels, which means that the highest could probably not be higher than 15 channels.

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[1] *Analytical Quality Control Services Programme, 1994/1995. IAEA, Vienna, Austria.*

- The test spectra would contain at least one peak with an odd shape, namely the 511 keV annihilation peak. In addition the spectra should contain a pulsar peak in a high channel number and with a FWHM smaller than that of a photo peak. Both these should be identified by the programme and treated in a special way. Generally speaking, peculiar peaks should be detected by the analysis codes and tagged properly.
- A slight deformation of the peaks attributed to pile-up in the test spectra, relative to the comparator spectra, should be aimed at. A maximum of 10% peak broadening would be the limit of deformation.
- The results of the analysis of these spectra should be reported for each of the 6 test spectra as follows:
  - Peaks that are present in both test and comparator spectrum must be reported as the ratio and its standard deviation.
  - Peaks that are not present in the comparator spectrum should be reported relative to the largest peak in the test spectrum as a ratio and its standard deviation.
  - Peaks that are found to deviate from the expected shape should be indicated as suspect.
  - Peaks in multiplets should be reported as ratios to the peak in the same multiplet that is present in the comparator spectrum.

It was recommended to make every effort to "make" each set of test spectra different from all others. Alternatively, a batch of 25–50 different sets could be made simultaneously and distributed randomly to the users.

1.1.3.2. Nuclear data libraries

It was strongly recommended to use international available and recommended[2] nuclear data libraries. Scientists were encouraged to get into the IAEA updated network[3].

The AGM was on the opinion that specialized nuclear data library are needed on the following fields:

- Calibration
- Environmental radioactivity measurements
- Neutron activation analysis (naa) library: thermal, epithermal and fast NAA
- Charged particles
- NPP libraries
- Primary coolant
- Exhaust control for NPP
- Nuclear medicine
- Fission products
- Prompt gamma
- Natural radionuclide library.

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[2] *For recommended Nuclear Data Libraries refer to the "Index of Nuclear Data Libraries". IAEA-NDS-7, Rev. 94/11.*

[3] *C.L Dunford and T.W. Burrows "Online Nuclear Data Service". IAEA-NDS-150 (1994).*

"Nuclear Structure and Decay Data Network". Nuclear Data Newsletter. No 20, November 1994. IAEA.

It was a general consensus of the AGM that there is a great need of "recommended" *uncertainties*, particularly for:

- Half-life
- Emission probabilities and
- Emission energies.

1.1.3.3. Gamma spectrometry software for particular purposes

Some very specific and particular measurements are declining in interest for commercial companies due to their relatively rare application in nuclear institutions. However, they **are still extremely important** nuclear analytical tools and methods. In many cases, these techniques have been supported/installed under the auspices of the IAEA's Technical Co-operation programme.

In particular, gamma ray software analysis for some specific areas were assessed during this AGM as presented bellow:

- *Moessbauer*
- *Air monitoring*. A general-purpose gamma spectrometry programme that takes into account the particulars of air monitoring is in need. In this line, corrections that takes into consideration the decreasing air throughput during the sampling, decay of activity, etc. have to be implemented in this type of analytical codes.
- *Applications based on NaI detectors*. As for example: Nuclear Medicine and environment measurements.
- Charged particle induced gamma emission (*PIGE*) measurements.
- *Loss-free counting system*. Software for dual-memory acquisition and correction algorithms for dead time and pile-up losses are needed.
- Rapid Instrumental Neutron Activation Analysis (*INAA*): software for analysis of decay curves.
- *In-situ gamma spectrometry*. Developments on corrections for efficiency calibration, extended surface and depth analyses are in need.

In the field of **Safeguards** the following technical issues were assessed:

- It has been found that codes developed for specific safeguards purposes are of the better performance than those of general gamma ray spectrum analysis.
- The software for these purposes should be able to treat spectra collected from different types of detectors: NaI(Tl), Ge and CdTl.
- Software to be used during field measurements must have alarm systems (early warning) for detection of strong activities and should advise inspectors on their experimental setup.
- Low level counting dedicated software would get in the future relevant importance for monitoring and detection of non-declared ongoing nuclear programmes. Some aspects in this field, like a dedicated nuclear data library and a detailed study of the background, would need further developments.

1.1 3 4. Data file structure

This advisory group meeting came to the agreement to support the IAEA data file structure as a simple, clear and comprehensive data file mode and possible way of exchange of information between nuclear analytical software packages. Following is an example of the IAEA data file format:

Example of the IAEA spectrum data file structure:

```
$MEAS_TIM
 50400  50469
$DATE_MEA
10-30-2060  17 11 13
$MCA_CAL
3
-1 272245e+000 3 992803e-001 -1 089764e-006
$DATA
    0   8191
    0     0     0     0     0     0     0     0     0     0
  506  1939  2404  2391  2327  2263  2369  2370  2244  2289
 2250  2290  2249  2271  2239  2263  2203  2156  2102  2185
 2107  2075  2112  2047  2052  2044  1987  2053  2004  1946
 1953  1953  1942  1934  1897  1979  1942  1945  1993  1993

$SHAPE_GAM
2 720268e-001 1 841427e-003 -4 671822e+000
1 800231e-004 1 200000e+000 4 000000e-001
$ENER_FIT
2 719160e+000 2 495980e-001 -2 153720e-008
$RES_CAL
3 006840e-001 1 841430e-003 0 000000e+000
$ENER_DATA
   11
  480 46   122 06
  654 85   165 85
 1097 49   276 40
 1203 46   302 85
 1416 47   356 01
 1527 92   383 85
 2641 49   661 64
 3335 84   834 81
 3589 12   898 04
 4461 16  1115 45
 7350 29  1836 13
$DATA_ID
 SHIELDED GEOMETRY, 10 cm
 PGT, 18%
$GANAAS$CALSPE
C \GANAAS\SPECT\EXAMPLE SPE
$OPERATE_GAM
 1 5   5  2 5   2 0   6 0   30
$RES_DATA
   11
  480 46   122 06
  654 84   165 85
 1097 48   276 40
 1203 42   302 85
 1416 47   356 01
 1527 92   383 85
```

The IAEA data file is intended to be a plain ASCII file structured in blocks. Block names are in relation to the data presented. In the IAEA spectral data format, data is stored in so-called BLOCK STRUCTURED ASCII files (BSA-files). A BSA-file is an ASCII file, and therefore, it can be viewed with any text editor. A BSA-file is divided into blocks. As can be seen from the given example, each block is identified by a string that starts with a dollar sign ($) and ends with a colon(:), thus, $BLOCK_NAME:. Programs may add or modify blocks by coping all other blocks and than append the new or modified block. The advantage of this is that the programs which operate on BSA-files do not need to have knowledge about all the blocks. Moreover, the file can contain much more information than relevant for a particular program.

It will be useful to define **in a detailed and unique way** the key words and the structure of the adopted data file with a minimum amount of data blocks that each file should contain. The document containing this information and a dictionary of unique key words to be used will be useful to the interested nuclear institutions, software programmers and commercial companies.

In order to make first steps on the side of exchange of information, this AGM strongly advised commercial companies and software programmers to adopt the IAEA data file structure as the format for data exchange.

This AGM recommended an international adopted data file structure to be used in nuclear spectrometry for traceability reasons, as much as possible *valuable* information has to be included in the output file and it should be stored in *one unique file.*

2. REQUIREMENTS ON GAMMA RAY SPECTRUM ANALYSIS PROGRAMS[4]

2.1. SUMMARY

Many programs intended for the evaluation of gamma ray spectra have been written. Most of them cover the basic needs but there are several options a user might want to have which are not incorporated. This paper attempts to list all general and some special requirements on such programs. Recommendations on details of the physical and technical methods to match the requirements and the citation of any existing program are avoided.

2.2. INTRODUCTION

Gamma ray spectrometry is applied in many fields of basic and applied research. Although there is a variety of gamma ray detectors that could be used for spectrometry, high-purity germanium semiconductor detectors nowadays play the dominant role. Silicon semiconductor detectors are used in the low-energy range, mainly for X ray spectrometry in analytical techniques like XRF and PIXE. NaI(Tl) detectors decreased in importance after the advent of semiconductor detectors in the 1960s but - because of their relatively low price and their availability in large sizes - they are still used in routine and low-level measurements when the spectral resolution is of minor importance. In this paper only gamma ray spectrometry with germanium detectors is considered.

The usual objective of gamma ray spectrometry is to determine the energy and number of gamma rays emitted by a source. These quantities are obtained from the recorded pulse height spectrum, which is continuous even for monoenergetic gamma rays and exhibits peaks

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[4] *Prepared by K. Debertin, Physikalisch-Technische Bundesansalt, Germany.*

corresponding to the gamma ray energies. These "full-energy" or "total absorption" peaks provide the information needed and have to be analysed; the rest of the spectrum is "background", unwanted but unavoidable. For quantitative measurements, the system must be calibrated for energy and efficiency with appropriate standard sources. In many applications the measured energies and emission rates are used to identify the radionuclides present in the source and to determine the activity of the individual components.

The analysis of the pulse height spectra is almost everywhere performed with the aid of commercial or sometimes self-made computer programs implemented in a personal or other computer. The automation of the analysis can go so far that after some initialization and calibration procedures, the program reads the measured spectrum and delivers as the final output a list of radionuclides with their activities including the uncertainties, without any further action or intervention by the operator. In many cases, however, it will be necessary or advisable to take a look at the spectra in order to discover anomalies, to decide which peaks are to be analysed, how broad the windows around the peaks should be, whether multiple lines need a special treatment, or how the background should be chosen. It may also be that corrections not covered by the program have to be applied to the "final" data. For these reasons, a program must be interactive between all its individual steps.

In the following, necessary and optional requirements on a gamma ray analysis program are given which should be fulfilled in order to make it flexible and suitable for the most important application fields of gamma ray spectrometry. On programs for special applications like X ray fluorescence analysis or in-situ gamma ray spectrometry further requirements exist. The aspects considered are peak search, peak fitting, deconvolution of multiple peaks, choice of analysis range, background subtraction, energy and efficiency calibration, uncertainties, detection limits, dead-time and pile-up losses, coincidence summing effects, self-attenuation corrections, data libraries, activity determination, quality assurance and program documentation. No recommendations are given on "best" algorithms or fitting functions.

2.3. PEAK SEARCH

After a pulse height spectrum has been recorded, the peaks of interest must be identified. If the user knows "his" peaks these may be marked on the graphics display by hand and analysed by the program. Alternatively, the user may ask the program to analyse peaks in regions predetermined in a data file. In other cases he may wish to run an automatic peak search subroutine in order to get a list of all peaks in the spectrum.

Several principles for automatic peak search and location are applied [1]. Whichever algorithm is used, the program must make it possible to vary the sensitivity parameters, allowing the user to let the program find more or fewer peaks. As the routine is pushed to find more of the small but real peaks, it will naturally find more "peaks" that are statistical fluctuations or background structures rather than real peaks. The program manual must describe the mathematical base of the program, the meaning of the sensitivity parameters and their effect on the number of peaks identified.

It would be of help to the user if a test spectrum with small and large peaks on a high and low background was supplied for training purposes to be used to get a feel for the effect of the sensitivity parameters. Some years ago the IEC [2] and the IAEA [3] started to create such test spectra and criteria for the quality of peak search routines but neither project was completed.

A list of all peaks found should contain an approximate value of the peak location (in channels and energy if an energy calibration has been performed) and amplitude or area. These data need not be accurate, as they are only intended to give the user an idea of the relative position and height of the peaks. The routine should be able to identify multiple peaks, at least if they are visible, and those with anomalously low or large widths due to artifacts or unresolved double peaks. Such peaks should be tagged in the edited list, the tags being changeable at the user's discretion. The peaks found by the routine must be markable on the display, and it must be possible for the user to erase or add marks on the display or entries in the data file for the following analysis.

2.4. PEAK ANALYSIS

Peak analysis means the determination of the position of the peak centroid and the number of counts in the peak region. The analysis may include the derivation of peak shape parameters, among which the full-width-at-half-maximum (FWHM), w, is the most important.

The program must allow the user to choose the peak regions used for the analysis either by setting individual windows (ROI - regions of interest) over the peaks on the display, or by an automatic procedure where the ROI is defined as a multiple f of the FWHM, e.g. $\pm 1.5\ w$. The user might choose for himself or take the value predetermined by the program. In the case of multiple peaks the region should extend from $-f{\cdot}w$ below the lowest-energy peak and $+f{\cdot}w$ above the highest-energy peak. If neighboring regions overlap, the program should warn the user, who may then decide whether these peaks should be analyzed individually or as a group.

The simplest procedure to obtain the peak area is to sum all counts in the ROI and subtract the background defined either by the endpoints of the ROI or by regions below and above the ROI. This option should be available because it is a fast and sufficiently accurate procedure for some applications. Usually, it does not work, if a deconvolution of multiple peaks is needed. In favorable cases however, the contribution of one or more components can be derived from other information in the spectrum, so that this component can be subtracted from the total sum.

In addition to the simple summing procedure a peak-fitting algorithm, which is in most cases the only choice for determining the components in a multiple peak, must be available. The fitting function for a single peak usually has as basic terms a Gaussian function and a background function to which other functions taking into account the asymmetrical shape of the peaks are added. For a multiple peak, the fitting function is the sum of the individual peak-related functions and one background function.

At a minimum the fit parameters comprise the centroid(s), area(s), FWHM and background function parameters. Further parameters are introduced by the asymmetry terms. In routine measurements not all parameters will be free in the fitting process. In particular the asymmetry parameters and the FWHM may have been determined in calibration runs as a function of energy and are kept fixed. In some applications the user may wish to keep fixed even the position of a peak, for example, in the deconvolution of a multiple peak with weak components of known energy or in low-level activity measurements where a hardly discernible peak is to be analyzed to obtain a detection limit. In general, for all parameters the program should therefore allow the decision to keep them free or fixed.

For the fitting of the background, i.e. of the distribution of all events in the peak region that are not due to gamma rays of the energy in question, a choice between first- and second-order polynomials should be possible. The typical increase in counts below a peak compared to the counts above it, i.e. the step in the continuous distribution in the region around the ROI, should not be taken as part of the background. The step height is related to the peak height and should be covered by an additional term in the peak-fitting function.

In the program description it must be clearly stated which terms of the fitting function are used and how the peak area is calculated from the fitting parameters. The asymmetry functions, in particular the step function mentioned, frequently extend to regions far from the peak and their full inclusion in the area calculation may not be reasonable. If the Gaussian function is the dominating component, the area parameter of this function should be taken for the area calculation.

In the analysis of multiple peaks the program should allow the number of components to be chosen by the user. The FWHM and the asymmetry parameters may be the same for all components. The background may be represented by one function as in the case of single peaks.

In the final list of results, which should be stored in a file, the entry for one peak must comprise all fitted and fixed parameters, i.e. the centroid, the area, the FWHM, the parameters of the asymmetry function(s) and of the background function. If the parameters were fitted, uncertainties must be given. Additionally, the reduced chi-square value must be stated. If this value is larger than two, the entry should be tagged. In multiple peak analyses the results for the components must be clearly arranged in a group.

2.5. CALIBRATION FEATURES

The program must provide routines for the energy and full-energy peak efficiency calibration of the spectrometer system and for the determination of the peak shape parameters as a function of energy. After the analysis of a spectrum taken for these purposes the relevant data must be stored in a file. It must be possible to enter data from different measurements into this file.

In the case of an energy calibration the user marks the selected peaks in each of the measured spectra and enters the corresponding energies, which may, but need not be, taken from the data library of the program. The program must provide a first- and second-order polynomial, optionally also other functions, to fit the calibration data. The parameters of the fit and the residuals for all calibration energies should be given in a table, the residuals including the measurement uncertainties also in a plot. The energy calibration parameters must be stored for use in the actual measurements.

The procedure for the determination of the peak shape parameters as a function of energy is similar. In addition to first- and second-order polynomials as fitting functions, for the FWHM a function of the type $\sqrt{(a_1 + a_2 E)}$ should be available. A plot of the parameters versus energy including the fitting function should be possible.

For the efficiency calibration, which should have been preceded by an energy calibration, the user must supply the information on the calibration source. Typically, this at least comprises the radionuclides i and their activities $A_i(t_0)$ at a reference date t_0. Using the internal clock the program is expected to calculate the activity $A(t)$ at the measuring time t. The calibration sources available to the user and the relevant data including the uncertainties of the activities should be listed in an extra file for any later use. In addition, the half-life and the gamma ray emission probability $p(E_{ij})$ of the gamma rays j of energy E_{ij} are needed to calculate the efficiency $\varepsilon = N/(p\,AT)$, where N is the peak area and T the measuring time.

These data may have been entered by the user into the calibration source file, or they are taken from the data library. The individual ε values are collected in an efficiency data file.

No recommendations on the fitting function for the efficiency data are given except that it shall be continuous and should be smooth. A linear fit in a log-log representation, which in most cases is not sufficient, should be possible for orientation purposes. Tables and plots of the efficiency data and the residuals should be provided. The efficiency calibration parameters must be stored for use in the actual measurements.

In addition to the possibility of determining the full-energy peak efficiency as a function of energy there should be the option of calculating and storing radionuclide-specific efficiencies $\varepsilon_{RN} = N/(A\ T)$ which are dependent on the energy of the gamma rays considered.

Attention must also be given to the background spectrum. In general, any peaks in the background must be subtracted from actual peaks at the same energy. For that purpose a background file must be available where the energies and peak count rates including the uncertainties are stored. This file should allow several entries at different times, which can be averaged.

2.6. EVALUATION OF A SAMPLE SPECTRUM

For the evaluation of a pulse height spectrum obtained from a measurement of the sample to be studied, the user must either have already performed the necessary calibrations or must use this spectrum also for calibration purposes. In the first case the necessary files with the calibration parameter entries have to be called up. In the second, these files have to be created. When using a peak search routine, prior to applying it a determination of the FWHM at least in the low- and high-energy range of the spectrum may be necessary to allow suitable peak search sensitivity parameters to be chosen.

Before starting the peak analyses the user must have the opportunity to look at the list of energies of peaks found by the search routine. Peaks may then be erased or added and it must be decided which peak parameters will be kept fixed in the fitting procedure. After the fitting, for those peaks coinciding with background peaks the latter must be subtracted and a file with energies, peak areas and/or gamma ray emission rates $N/(\varepsilon\ T)$ and other fitting parameters must be produced. If there are peaks outside the efficiency calibration intervals, an extrapolated efficiency may be taken but a warning mark must appear in the file.

The energies and emission rates may be used to identify radionuclides and to determine their activity. If the user is interested in specific radionuclides, these may be entered, and the program then calculates the activity using the energies and emission probabilities from the data library. Alternatively, the user may want a complete radionuclide analysis. In that case the program must allocate to each energy the possible radionuclide(s) and calculate the activity. Peaks that cannot be allocated to a radionuclide should be tagged.

If a radionuclide emits gamma rays with more than one energy, the activity is to be calculated for all energies. If there is an energy at which no peak was identified, the analysis should be repeated in the corresponding ROI. If there is an overlap with other peaks of the spectrum, a multiple peak analysis must be performed.

The final file with the identified radionuclides must contain, ordered according to radionuclide, all energies (also those for which no peak was found), the corresponding activities, the relative standard uncertainties of the peak area and a tag indicating whether the peak is a component of a multiple peak. In addition, for each radionuclide the weighted mean of the activity values should be calculated. As weights the inverse of the sum of the squared relative standard uncertainties of peak area, efficiency and emission probability should be taken.

The program may run into trouble if two (or more) radionuclides emit gamma rays of the same energy. In that case the program must check whether the peaks with appropriate relative areas corresponding to the other energies of those radionuclides are present. If this is not successful, it must confront the user with the question which radionuclide is to be chosen.

If a measurement is repeated several times under identical conditions, it may be necessary either to evaluate the spectra separately, determine the peak parameters and then form a mean, or to sum the individual spectra. Both of these options must be available. In the latter case, in particular for measurements over a long period, the spectrum may have shifted. In that case the individual spectra should be condensed or stretched so that the positions of the peaks coincide.

If the aim of a measurement is the determination of specific activities or activity concentrations the division by mass or volume, which should have been entered in some measurement identification file, should be possible.

An export of the data in all files mentioned up to now must be foreseen in order to allow the user to produce graphs and tables according to his special needs.

2.7. DATA LIBRARY

For the purpose of radionuclide analyses a data library with entries for natural radionuclides and those artificial ones that occur in the nuclear fuel cycle and in the major application fields of radioactivity must be available. The data should be grouped according to fields of application so that the user can select a sub-group according to his needs. The user might also wish to set up his own set of radionuclides or vary and supplement the existing groups.

For each radionuclide the half-life, the main gamma ray energies and emission probabilities and their uncertainties must be given. If a nuclide has a short-lived daughter, separate data sets for the daughter, the parent and the parent/daughter equilibrium should be given and correspondingly marked. The special case of the natural decay chains should be considered.

The data source must be quoted. If IAEA-recommended data exist, they should be given preference. Otherwise, data from generally acknowledged files should be taken.

The data format must allow for the entry of additional data. These may be, for example, correction factors for coincidence summing effects or self-attenuation. For an individual gamma ray of a radionuclide, these factors depend on the measuring geometry and sample type. Since the user might have many such geometry or sample types, it must be possible to enter these data for all of them. A minimum of ten additional entries per gamma ray should be possible. Alternatively, the additional data may be in other files or be calculated in subroutines (see below), but then a connection to the library must exist.

2.8. CORRECTIONS

The most important corrections in gamma ray spectrometry are:

- dead-time and pile-up corrections,

- coincidence summing corrections,
- corrections for differences in the attenuation properties of calibration source and actual measuring sample,
- corrections for differences in the measuring geometries used for calibration and actual measurement,
- corrections for decay during the measurement, and
- corrections for parent/daughter relationships.

The gamma ray spectrometry system may include options for the correction of dead time and pile-up losses, so that the analysis program need not be concerned with any further corrections. In many cases the live time correction of the multichannel analyser is sufficient. At high-count rates, however, some means for pile-up corrections should be available. As a matter of fact, for various reasons the pile-up rejection circuits are not so widely used. Instead, use is made of the pulsar method [1] in which pulses from a pulse generator are fed into the test input of the preamplifier. The analysis of the resulting pulsar peak in the spectrum must take into account that this peak is usually narrower than the gamma ray peaks and has no low-energy tail. So the user must be given the opportunity to mark the pulsar peak prior to the spectrum evaluation and to enter the true number of generator pulses. The program should then calculate the ratio of true and observed generator pulses and apply this correction factor to all peak areas.

The determination of coincidence summing corrections is more difficult. This correction is different for each gamma ray and depends on the measuring geometry and details of the decay scheme. If the user is doing the determination of the corrections himself experimentally or with some other program, it must be possible to enter these correction factors into the data library. A better solution would be for the gamma ray spectrum evaluation program to come with a subroutine for the calculation of these factors. In that case the data library must be appreciably extended and the file with the full-energy peak efficiencies must be supplemented by the total efficiencies. For extended samples still more effort, for example Monte Carlo calculations, is necessary.

The actual measurement samples frequently differ from the calibration sources with respect to density and/or chemical composition, so a correction for the differences in the self-attenuation is necessary. As in the preceding case of coincidence summing corrections, either the user performs the calculation of the correction factor himself or the program provides a suitable subroutine. It may not be necessary to activate this calculation procedure for each measurement, as it may be sufficient to store the data for a set of energies in a file and to derive the factors for intermediate energies from an interpolation. This file should be large enough to allow entries for at least ten sample types or densities.

Differences in the measuring geometry are hard to handle. Some programs allow, for example, a calculation of the efficiency for arbitrary geometries from point-source calibrations. As input, such calculations need, among other data, details of the detector construction and the detector dimensions. But the nominal data given by the detector manufacturer may not be sufficiently accurate, and such efficiency calculations may lead to intolerably inaccurate values. If a program makes use of such subroutines, the results should be marked with a warning symbol.

For radionuclides with half-lives short in comparison with the measuring time, a correction should be made for the decay during the measurement. The program should be able to handle parent/daughter relationships. Sometimes gamma rays of the daughter nuclide are used to determine the activity of the parent nuclide. In the case of radioactive equilibrium the daughter activity has to be multiplied by a factor (frequently near unity), under non-equilibrium conditions the time-dependent relation between daughter and parent activity must be considered.

2.9. UNCERTAINTIES AND DETECTION LIMITS

All uncertainties, whether calculated by the program or given in the data library or the various data files mentioned, should be quoted in terms of standard deviations. The usual rules for the propagation of uncertainties must be applied. If means are formed, they should be weighted means. The full covariance matrix resulting from the fits should be available for use if needed, for example when an efficiency is calculated from a function whose parameters were obtained from a fit to measured efficiency data.

Uncertainties must be given for all fitted parameters in the peak analysis, for the half-lives and emission probabilities in the data library, for any measured or calculated efficiency values and the activities. Uncertainties for the energies in the library and for the correction factors, if calculated by the program, are optional. A special option must be available to calculate detection limits for defined gamma rays of a given radionuclide. The algorithm for this calculation must be quoted. If the ISO standard presently being prepared [4] is published, its recommendations should be followed.

2.10. QUALITY ASSURANCE

Most programs available nowadays are not sufficiently well documented. Considering the increasing importance of quality assurance and the demonstration of traceability of activity measurements to national standards, it is of vital importance for the user to be able to describe how an activity or any other quantity was derived from the measurements. An official auditor will not be content with the statement that the program XYZ is used for the analysis unless the documentation on that program contains the details of the analysis procedure. If a publication of the program exists, a copy should be added to the documentation. The program supplier need not make available the source program, but all mathematical formulas, functions and algorithms used for calculations and fitting procedures must be clearly and explicitly given. The source of the data in the library must be quoted.

Means should be provided to store and display data taken for quality assurance purposes. The user should be guided by the program to initiate special runs for quality assurance purposes. As a minimum, files should be installed for the results of repeated measurements of background (integral and peak count rate) and of energy and efficiency calibrations. Plots showing the corresponding time dependence should be possible. Even warnings might be provided, if the predetermined checking period has passed.

REFERENCES TO SECTION 2

[1] DEBERTIN, K. AND HELMER, R.G., Gamma- and X-ray Spectrometry with Semiconductor Detectors, North Holland, Amsterdam (1988).

[2] Definition of Quality Criteria for Computer Programs Used in High Resolution Gamma-Ray Spectrometry - Determination and Analysis of Full Energy Peaks, Rep. IEC TC 45(Sec)273, International Electrotechnical Committee, Geneva (1988).

[3] DOLNICAR, J., Consultants Meeting on Evaluation of Gamma Spectra and the Preparation of Programme for IAEA Training Courses on Gamma-Ray Spectroscopy, Vienna, 1988 (internal report).

[4] Determination of the Lower Limits of Detection and Decision for Ionizing Radiation Measurements - Part 1: Fundamentals and Applications to Counting Measurements without the Influence of Sample Treatment, Rep. ISO/DIS 11929-1 (TC 85), International Standards Organization, Geneva (1994).

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3. SOME DEFICIENCIES AND SOLUTIONS IN GAMMA RAY SPECTROMETRY[5]

3.1. SUMMARY

A number of problems in high-resolution gamma ray spectrometry as well as some deficiencies of existing computer programs for the quantitative evaluation of spectra are discussed and some practical solutions are proposed.

3.2. INTRODUCTION

In discussing a high-resolution gamma ray spectrum we usually make several implicit assumptions. For example:

(1) The signals coming from the linear analog electronics connected to the detector are converted into digital numbers where the value of the number is linearly proportional to the height of the analog signal.

(2) These numbers are used by a multichannel analyser to address elements in an array of memory words and to perform an "increment-by-one" sequence in the addressed word. The array of memory words is called a spectrum and the individual memory words are called the spectrum channels. There is an almost linear correlation between the channel number where an event is counted and the registered photon energy.

(3) In the graphical representation of a spectrum as shown in Figure 1, the abscissa is divided into bins of energy intervals (the channels) which are of equal width in terms of energy and which are defined in integer increments. All events whose energy falls into the interval from the start to the end of a bin will be defined as the count rate in that channel. The ordinate lists the number of counts per channel, i.e. the count rate accumulated during the measuring time. The display of a spectrum should be either a dot display, where the dots are positioned at the centres of the channels or, preferably, a histogram display where a horizontal bar marks over the total width of the bin the number of counts in the channel. The horizontal bars in adjacent channels are connected by vertical lines at the channel boundaries.

This section will address typical mistakes which may occur in the measuring of the spectra and which are sometimes overlooked as well as selected topics concerned with the analysis of spectra.

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[5] *Prepared by W Westmeier, Gesellschaft f. Kernspektrometrie, Germany*

3.3. ERRORS IN SPECTRUM MEASUREMENT

3.3.1. Pole-zero settings

The improper setting of the P/Z correction circuitry in the linear amplifier may lead to severe peak shape distortion, which may even show up as satellite peaks on either the low- or the high-energy side of the main peaks. In these cases, the peaks are analyzed as having shoulder or satellite companions which fill the excess number of counts in improper locations, and the residua found after peak analysis will indicate several additional peaks in the flank of the main peak. One can in principle invent and fit peak shapes which take into account such poor P/Z settings, i.e. peak shape functions which include low- or high-energy tailing contributions to the respective analytical shape. However, these procedures disable the program to detect and analyse real shoulder peaks, which might be found close to major components, as these then will also be taken as "P/Z satellites". It is therefore highly recommended that spectra be measured with properly set P/Z circuitry in the spectroscopy amplifier. Operator control of the P/Z setting with an oscilloscope has been proven to be the best suited most reliable and most economical procedure.

3.3.2. Measurements at high count rates

In measurements at very high count rates one will often find the problem that random pileup processes become dominant and the shape of the peaks is significantly distorted. There are amplifiers on the market, which can correct (disable) for pileup events, but in our experience, these electronic methods may lead to other effects which complicate the quantitative analysis of the spectrum such as an incorrectly defined lifetime correction. It is therefore recommended that count rates should be kept so low (<10 kcps) that there is no significant random pileup encountered. This can be achieved by a larger distance between the sample and the detector, by the choice of a shorter shaping time in the spectroscopy amplifier, or sometimes even through modifications in the experimental set-up. One can, for example, reduce significantly the number of random pileup events encountered in a measurement with an n-type semiconductor detector by placing a 0.3 mm thick cadmium cap over the detector. This absorbs essentially all low-energy gamma- and X rays and reduces the count rate significantly. In addition, it is a very effective means of avoiding the X ray/gamma ray true coincidences that make quantitative analyses with these detectors very difficult. If one cannot avoid measuring spectra at very high count rates, one should either use electronic correction circuitry which allows the consideration and correction of distorted events ("Loss-Free Counting") or, even much better, one may use extremely fast signal processing technology which is now available. The latter unit is called "Analog-to-Digital Signal Processor" (ADSP) and it works in principle as follows: A very fast 12-bit sampling ADC directly converts the preamplifier output signal every 50 ns. The digitized signal shape goes on-line into an array of signal processors which analyze, correct (e.g. for ballistic deficit) and permanently calculate the events. The digitally corrected result of the integration (= the channel number) is directly fed into the multichannel-analyzer (MCA). The advantages of the ADSP unit lie in the abandoning of disturbing and "slow" analog electronics, in the extremely high count rate throughput, in the intrinsic corrections for distorted signal shapes, in the very effective pileup suppression (400 ns pulse pair resolution), and the specification that there is essentially no ADC deadtime. The spectrum broadening is reported to be less than 10% change in FWHM for the 1332.5 keV line of ^{60}Co at 1.5 µs shaping time, 300 kcps input rate and 30% throughput. The spectrum shift under these conditions is less than 100 ppm.

3.3.3. Odd–even effects

It is surely a rare event but nevertheless still seen that the contents of counts per channel show a significant odd-even effect (Figure 1).

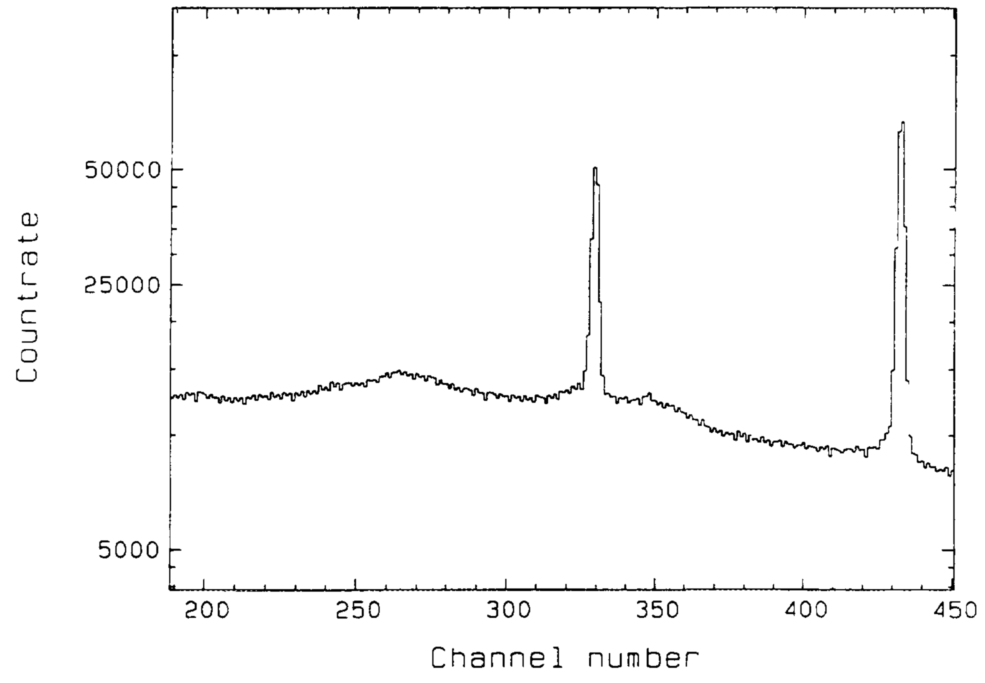

FIG. 1. Example of a spectrum with a pronounced odd-even effects in every second channel.

This feature, in which channels in binary increments show excessive or missing count rates as compared to the other channels, is caused either by a very poor differential linearity in the ADC or very rarely through binary transfer errors between the ADC and the MCA. In the more frequent case of odd-even effects through a poor differential linearity, all events measured by the detector do appear in the spectrum, however, some of them are in a systematically placed in the wrong channel number. Thus, the area of any peak analysed will be almost correct, but the residuals and correspondingly the uncertainties of the calculated results will be unacceptable. Normally these odd-even effects are easily detected as regular patterns upon visual inspection of peak-free areas of the spectrum.

3.4. COMPUTER-AIDED SPECTRUM EVALUATION

In the first years after the boom of personal computers in 1981, the number of computer codes for the analysis of gamma ray spectra grew tremendously and one could find essentially one gamma-spectrum code per laboratory. This situation was unsatisfactory and puzzling because one could not find a widely accepted program that might serve as reference for intercomparison purposes. The situation has been significantly corrected in the last years through the effort of international organizations or other authorities to find acceptable criteria which may serve for intercomparison purposes and which may qualify and rank the codes, so that at present, there are less than 40 codes on the market which are in an open competition for user's interest. Some of these codes, however, are highly specialized for certain applications and should not be counted as general purpose gamma ray codes. This situation when only few, well tested codes are available seems more favourable, but there is a big "caveat" for users: Modern gamma spectrum analysis codes are very complex programmes in which very many procedures and tasks are implemented through machine-oriented programming tools. These computational procedures allow the very fast execution of very complex calculations or decisions, but they also allow the very fast propagation of complete nonsense. Thus, one still has to find methods and procedures that help to control these highly complicated programs. One has to make sure that the listed results are in fact in agreement with the results to be expected and that the uncertainties assigned to the calculated results are in conformity with the accepted rules and definitions.

There are several problem areas in which computational, algorithmic or logical errors may occur and where the results output by programs may need to be looked at very carefully. Some of the more common of these are described below.

3.4.1. Gamma ray/X ray mix

Whenever a gamma ray spectrum covers the energy range below ca. 80 keV one will also find the X ray peaks from activities assayed as well as fluorescence induced X rays from the detector construction and surrounding material. In most cases one simply ignores the X ray peaks in the spectrum because these cannot be correctly analysed with a gamma ray analysis program. The peak shape of X rays is by principle different from the shape of gamma ray peaks; it is a Voigt function, i.e. a function with a significantly widened peak base, and this peak-shape is normally not considered by gamma ray analysis codes. As a consequence one will never find correct results when one analyses overlapping peaks in the X ray regime above ca. 30 keV with a gamma ray code. One can, however, easily analyse a gamma ray singlet peak, which has no considerable overlap with other X ray peaks. At energies below ca. 30 keV the Lorentzian contribution to the Voigt function is essentially negligible and one will get acceptable results when a multiplet of gamma ray and X ray peaks is simultaneously analysed. In these cases one has only to take into account that, due to the very close positioning and overlay of several X ray peaks from nearby subshell transitions, the shape of X ray peaks may be significantly different from the gamma ray peaks, i.e. the program must allow for different shape parameters of the individual overlapping peaks in one region.

3.4.2. Backgrounds in gamma ray spectra

There is often quite a bit of confusion when the term "background" is used in gamma ray spectrometry because there are different sources of counts which do not belong to the net full-energy peak area, which are denoted as background. Generally one should discriminate between the "external" and the "internal" background:

The external background is determined by those events, which are measured when no sample is placed in front of the detector. These include contributions from terrestrial and natural sources of radioactivity, cosmic radiation, induced X rays from construction materials etc. The external background is a spectrum with some continuum distribution and discrete full-energy peaks sitting on top. It should be very well determined for each measurement set-up. The external background spectrum, out of which the peak contributions are to be analysed, should be measured for a considerably longer time than any sample spectrum. All peaks in the external background spectrum must be quantified in terms of counts per unit time together with their corresponding uncertainties. In every sample spectrum one can then later subtract the contribution of the external background to the measured peak-areas with proper consideration of the statistically correct uncertainties. Any other method of pro-rata subtraction of an external background spectrum from a sample spectrum will lead to a resulting net spectrum with distorted statistics.

The internal background constitutes of those events other than full-energy peak counts, which are produced by the sample in front of the detector. Among these are the results of photon interactions with the detector material (Compton, ballistic deficit, and escape events, etc.) or with the surrounding material (backscattering, fluorescent excitation) and all related secondary events. Again, the internal background consists of a spectrum with some continuum distribution and discrete full-energy peaks. The internal background spectrum cannot be assayed and processed ahead and considered later in the analysis of the sample spectrum. Rather, one has to separate out the continuum part, analyse all peaks in the sample spectrum and define (quantify) the contributions from the internal background.

There are yet other events which are often denoted as "background" and which must be quantified and subtracted from the gross count-rate in order to find the net full-energy peak counts. These are the events underlying the full-energy peak, which come from Compton events of other peaks at higher energy, from full-energy counts suffering from ballistic deficit, or from other secondary interactions. In order to avoid confusion it is recommended that the distribution of these events under the full-energy peak should be denoted as ***baseline*** [6]. It has been noted long ago [3] that the shape of the baseline under full-energy peaks follows a step-function. In fact the baseline constitutes of two components, namely a smooth, almost linear Compton contribution from events at higher energies plus a step-function contribution which is caused by the events in the full-energy peak itself.

An algorithm has been published [15, 16] which allows to calculate the baseline distribution under singlet and multiplet peaks without prior knowledge of either the number of components in a multiplet or the shape of the peaks. The algorithm even enables one to calculate the correct shape of the baseline under escape peaks where the continuum distribution on the high-energy side of the peak sits at a considerably higher level than at the low-energy side (Figure 2). This "step-up" feature comes from the fact that three events are coincidentally involved in the pair production process. The primary photon energy minus 1022 keV (twice the electron mass) is found as kinetic energy of the electron and positron, respectively, and there are two 511-keV photons from the annihilation of the positron, which was originally created in the pair production process. Thus, because the kinetic energy of particles is always measured as a full-energy event (the double escape peak), there is an additional probability that all or part of the energy of another photon will be registered in coincidence and the summing event is measured in a higher channel number. The additional probability of such an event to occur gives rise to an elevated continuum distribution at the high-energy side of escape peaks. It should be noted that due to the above-described mechanism one will find the characteristic Compton distribution and one Compton edge for a 511-keV event above the double escape peak (Compton 1) and above the single escape peak (Compton 2), as well as the usual Compton distribution and Compton edge below the full-energy peak (Compton 3). In Figure 3 one can distinguish the characteristic features measured from high energy photons, where the Compton edge above the single escape peak is buried in this example under another small peak.

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[6] *The term "baseline" was proposed by K. Heydorn from Risø (Denmark).*

3.4.3. Length of spectra

With the availability of cheap computer memory and mass storage devices it has become fashion that spectra are measured with an ever-increasing number of channels. Whereas the first MCA units in the seventies had only 256 channels for a spectrum one can now find ADC and MCA units which allow to digitize and store spectra with up to 64k channels. The enhanced resolution in terms of keV per channel, however, does not automatically give better possibilities to resolve closely positioned peaks. In fact, it is very often a significant disadvantage when spectra are measured with an excessive number of channels. There is no generally applicable recipe, which allows one to define the optimized spectrum length, but there are several constraints that should be considered:

It is clear that the resolution of the detector is the most important variable, which defines the spectrum length. Most of the common non-linear least-squares algorithms used for the fitting of peaks are mathematically stable and yield reliable results when the full-widths-at-half-maximum (FWHMs) of peaks are in the range of 3 to 6 channels. This finding comes from the fact that most algorithms make point-fits, i.e. for the minimized function (Y_{exp}-Y_{calc}), the calculated function value Y_{calc} and the experimental number of counts in a channel Y_{exp} are both taken to be situated in the centre of a channel. This algorithm yields correct results as long as the FWHM of peaks is larger than ca. 3 channels because the shape of the peak function within the energy bin is then very well approximated by a straight line and the Centre-of-gravity of the function lies in the centre of the channel. If, however, the FWHM of peaks is significantly smaller than 3 channels, the curvature of the function within the energy bin must be considered and one may no longer apply a point-fit procedure. In a systematic survey we have shown that using an integrating fit which considers the curvature of the function within each channel, one can achieve a reliable and stable fit of peaks where the FWHM is as small as 0.9 channels. However, as most commercial spectrum analysis codes do not provide this integrating fit feature, it is recommended that the rule-of-thumb "the FWHM of peaks to analyse should be 3 channels or above" be applied. Nevertheless, one should try to keep the number of channels in the spectrum as small as possible!! Thus if one wants to measure peaks at 120 keV and above, and the detector resolution at 120 keV is 1.2 keV FWHM, then the spectrum should be measured with a resolution of 1200 eV / 3 channels = 400 eV/channel and the spectrum length is determined by the maximum energy assayed. As almost all essential gamma rays from nuclear decay are found at energies below 1500 keV it is normally sufficient to measure spectra with 4k channels (4096 channels) in length. The measurement of nuclear reaction gamma spectra with energies usually up to 10 MeV or above will require spectrum lengths of 8k or even 16k channels. The main reason for this recommendation of a spectrum as short as possible is the enhanced statistical significance of the data. When the same number of counts are distributed over 8k channels rather than 4k channels, then the statistical accuracy of the count rate in each channel is SQRT (8k/4k)=1.4 times worse and the fit algorithm will encounter less strict driving forces through the weights of the count rates in the channels. Therefore any analysis code will have problems in spectra which are measured over too many channels to find and quantify either small peaks sitting on a high background or less significant shoulder peaks. Furthermore, there are the advantages of the saving of deadtime in Wilkinson ADCs, of space on the storage disk, and of time for the analysis of the spectrum.

3.4.4. Backscattering bumps

It can be seen from Figure 4 that all energies of photons that initial energies over ca. 500 keV and which are scattered under an angle of ca. 180 degrees (backscattering) lie around about the same energy. This clustering of the backscattering energies, irrespectively of the initial energy of the photon, is the reason for the bumpy structure found around 220 keV, most prominently in spectra measured with shielded detectors. If the initial energies of the photons decrease considerably below 511 keV, the backscattered photons will of course be found at even lower energies, but the energy gap between the initial and the backscattered photons will become smaller and the backscattering bumps come closer to the full-energy peak. Thus, the backscattering bumps from the 79.8 and 81.0 keV peaks of ^{133}Ba are still well separated from the peaks whereas those of the 59.5 keV peak of ^{241}Am already merge with the full energy peak (Figure 5). Any analysis procedure will therefore have to consider this merging at lower energies and the sums of backscattering and full-energy peaks must be analyzed as sitting on one unique baseline.

3.4.5. The resolution (FWHM) function

When photons interact with the detector material most of the deposited energy goes into thermal vibrations of the crystal lattice. Only a small, constant fraction of the deposited energy is used to promote electrons from their ground states into the conduction band. The fraction used for this promotion process is defined by the Fano factor. This lifting of electrons into the conduction band is a statistical process, i.e. the number of electrons made available when an amount of energy (E) is deposited in the detector will have an average value N(E) with a variance of the order SQRT[N(E)]. In addition to this intrinsic variance of the signal one will then have further broadening through the noise of the linear electronics and the resulting resolution function should theoretically be described by a function of the form

$$\mathrm{FWHM(E) = A + B * SQRT(E)} \tag{1a}$$

where FWHM is the full width at half maximum (in keV) of a full-energy peak from photons with an average energy E (in keV), and A and B are polynomial coefficients to be adjusted for each individual detector. In a spectrum, however, the experimentally available quantities are channel numbers and the number of counts per channel and thus the experimentally determined resolution function should be written as

$$\mathrm{FWHM(channel) = A + B * SQRT(channel)} \tag{1b}$$

When one determines the resolution functions of Ge(Li) and HPGe detectors one will find, that there is rarely ever this theoretically expected linear dependence of FWHM with SQRT(channel), but that at high energies the FWHM is often significantly larger than expected. The reason for this enhanced FWHM lies in secondary effects such as charge density, impurity losses, recombination etc. which are more prominent when many electrons are promoted into the conduction band. A practical proposal for the spectrometrist therefore is that one should use a second order polynomial as a function of channel number

$$\mathrm{FWHM(channel) = A + B * channel + C * channel^2} \tag{2}$$

where A, B, and C are polynomial coefficients to be adjusted. This functional description has proven to fit all resolution functions well which the author has measured from a large variety of different p- and n-type germanium detectors. In most cases the coefficient C has a very small negative value.

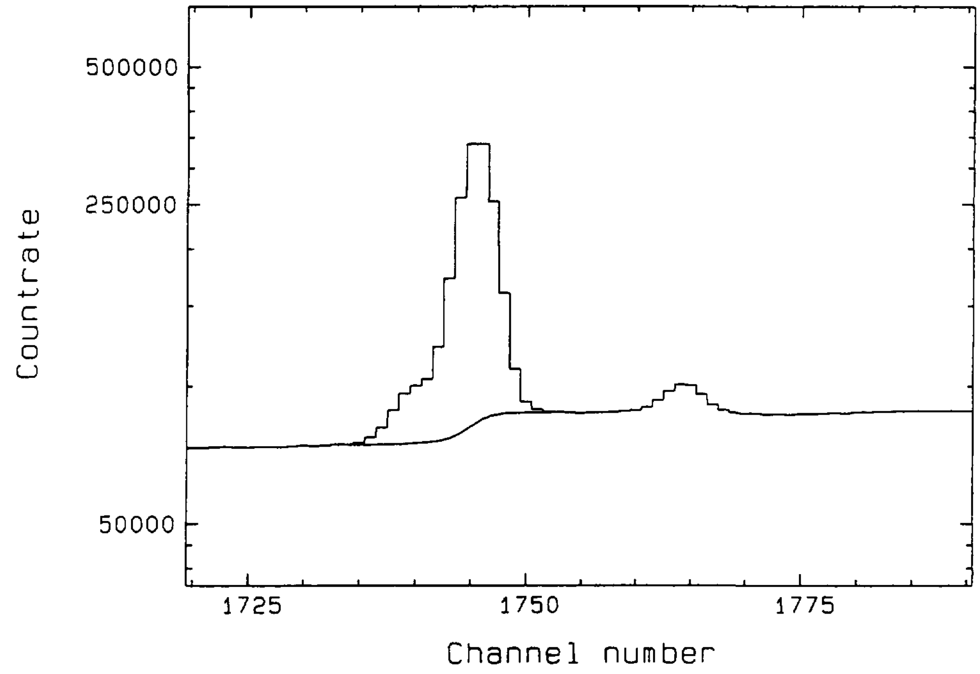

FIG. 2. Baseline distribution under an escape peak, which has a low-energy shoulder peak.

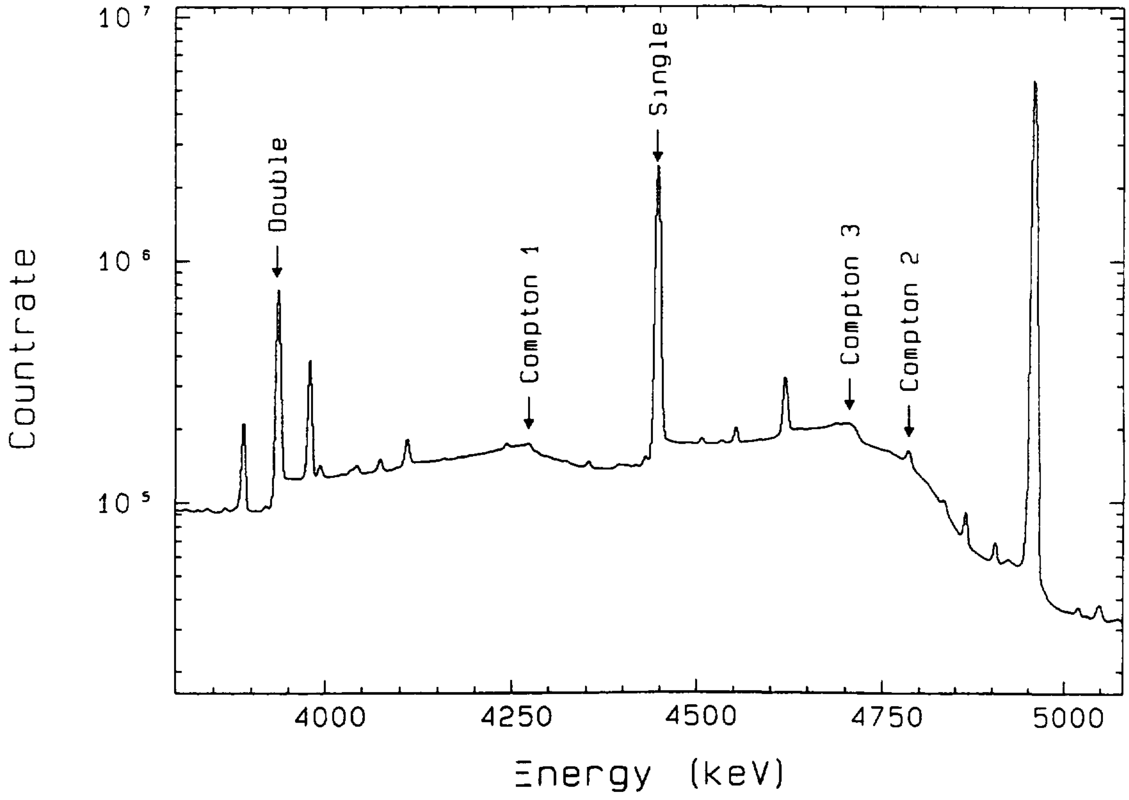

FIG. 3. A high-energy main peak and its escape peaks together with the Compton edges.

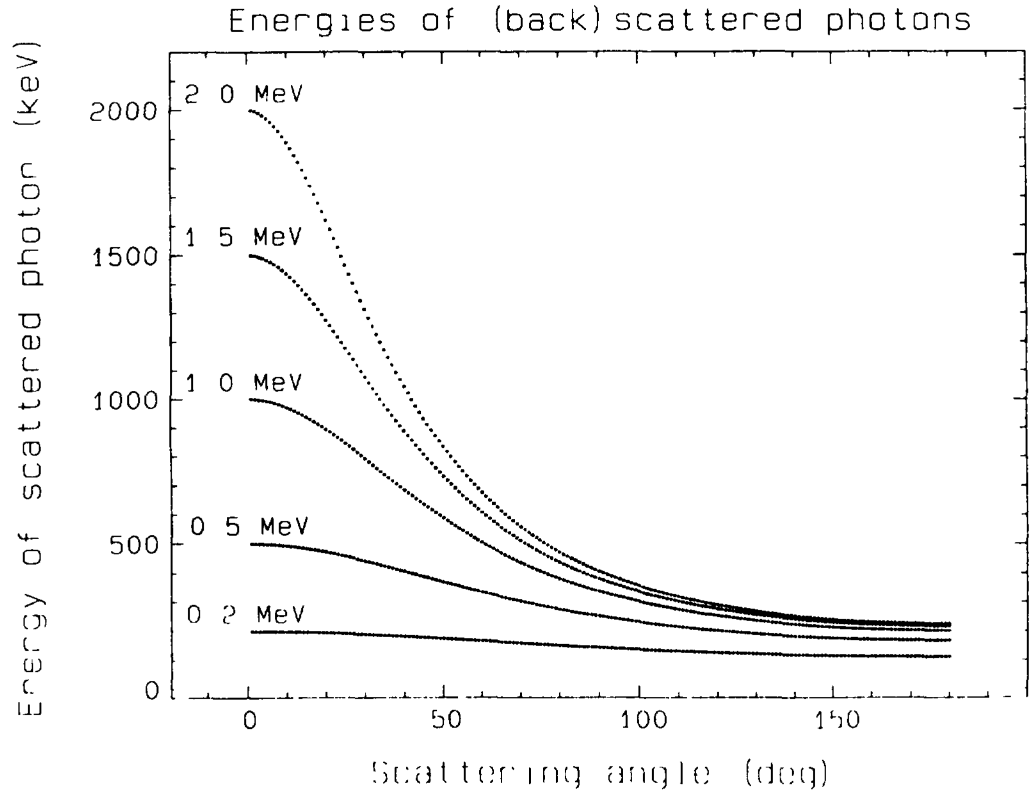

FIG. 4. Energy distributions as a function of scattering angle for photons of different primary energies.

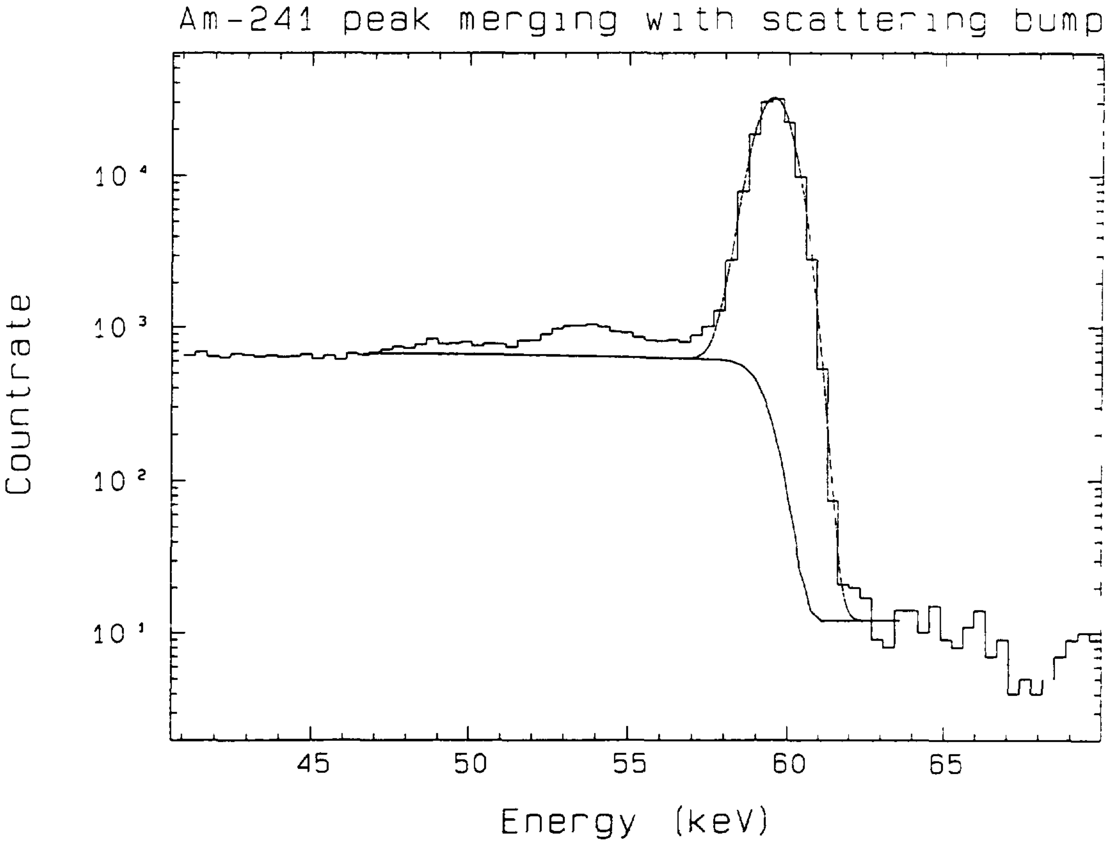

FIG. 5. The backscattering bump merges with the main peak at around 60 keV.

3.4.6. True coincidence summing

Whenever a decay process through negatron-, positron-, alpha decay or fission occurs, the electron shells of the daughter nucleus will be significantly distorted and X rays are emitted. In addition, the decay may leave the daughter in a short-lived excited state which then decays by the emission of a gamma ray or a cascade of gamma rays. Most of both these photon emission processes proceed on a time scale, which is too short to be discriminated by a semiconductor detector. Thus, if several photons originating from the same single decay process enter the detector the sum of the deposited energies will be measured. This is called a "true coincidence" and complicates quantitative analyses. Assuming that the emission of the photons reveals no angular correlation, i.e. gamma rays and X rays are emitted isotropically without any angular relation between one and the other, the probability that a second event is registered in coincidence with the first one is defined by the total efficiency for the second event. The total efficiency (as opposed to the full-energy peak efficiency) is the probability, that any that amount of energy of a photon is deposited in the detector. It considers all processes of energy deposition such as full-energy peak, Compton events, backscattering etc. The total efficiency is normally very much higher than the full-energy peak efficiency (for ^{137}Cs it may be 5 times larger) and as a consequence true coincidence summing may be very disturbing when the sample sits in close geometry and the efficiency is large. Every event assayed in coincidence with a full-energy event will "remove" the count from the full-energy peak and place it somewhere else (called "summing out"). When the coincident count is also a full-energy event the signal will be counted as a sum-peak event which may be another full-energy peak from the decay cascade (called "summing in"). At any rate, true coincidences remove counts from their proper locations in the spectrum. It will then be difficult to calculate activities because the full-energy peak efficiency function is no longer valid. One can calculate and correct for true coincidence effects [e.g. 2], but these calculations are very tedious because they need quite a bit of sophisticated experimental and tabular data input. The calculations need two sets of input data:

- One has to supply the total efficiency as a function of the primary photon energy. This data set must be measured once for each geometry in which samples are to be assayed. In order to determine the total efficiency function one should have a set of nuclides, which emit photons of only one single energy. The energies of the nuclides should cover the range from below 20 keV up to the highest energies to be found in the real samples. This set of nuclides is very difficult to find in most laboratories, which have no intense neutron source available.

- One has to supply the complete decay scheme for each nuclide where true coincidence corrections are to be applied.

  In some typical cases such as ^{60}Co, the amount of true coincidence losses from the full-energy peak efficiency function may be known and the correction applied accordingly. For most nuclides, however, the full-blown calculation of true coincidence correction factors is necessary, or these corrections should be avoided altogether. There are some practical solutions of how to deal with true coincidences in gamma ray spectra:

- The easiest way to avoid coincidence losses is to measure spectra at a large distance between the detector and source, so that the efficiency is small and true coincidences are negligible.

- In many applications it may not be necessary to quantify all lines from all nuclides contained in the sample. All lines or nuclides for which true coincidence losses to the count rates are known to be significant may be ignored.
- A "private" nuclides library may be created in which the apparent abundance of the gamma ray transitions for the nuclides are stored, i.e. the abundance as measured in a specific geometry by a specific detector. These "apparent" abundance have to be determined experimentally with each user's equipment and the user has to have different libraries for each specific setup. This is equivalent to needing different efficiency functions for each specific setup.

The latter method is definitely very tedious and time consuming but in many routine applications it has proven to be a very reliable and straightforward way to cope with the problem of true coincidence losses. Due to the fact that coincident X rays are encountered with almost every nuclear decay process it is especially important to apply coincidence loss corrections when n-type germanium detectors are used which measure these X rays with high efficiency. In fact, a practical recommendation is to avoid using n-type detectors for quantitative nuclide analyses.

3.4.7. Full-energy peak efficiency

There are several approaches to describing the full-energy efficiency as a function of the photon energy. In the most primitive approximation a linear function in a double logarithmic display (log(efficiency) vs. log(energy)) is used above ca. 200 keV and the absorption losses at lower energy are ignored. More sophisticated approximations use several polynomials which each describe a fraction of the efficiency function and which match smoothly at certain transition points. In most modern programs, however, the complete full-energy efficiency function is described by one unique function that is either a high-power polynomial [5] or the intrinsic function for p-type detectors [7]. For all n-type detectors as well as for those p-type units where one encounters a "dip" in the efficiency function around 600 keV, the polynomial representation seems to be the best suited description. When one uses the polynomial description one has to make sure that the whole energy range to be assayed in the sample spectra is also covered by as many as possible efficiency data calibration points. A high number of calibration points is essential because high-power polynomials will at any rate "bend" to match the data points but the functional trend in between the points may be rather arbitrary. Using 8 well defined data points and a fifth power polynomial we have found discrepancies between the fitted polynomial and the correct shape of the function of up to 8 percent of the correct value [7]. If one can supply very many data points over the whole energy range any such large deviation from the correct curve in regions between the points will be avoided. Furthermore, one may never apply a fitted efficiency function outside the range of energies which is confirmed through data points (extrapolation is forbidden!!).

It is a general rule that the efficiency function must be determined for each individual set-up in which samples shall later be assayed. The term "set-up" in this context means:

- One specific detector,
- One specific relative position between the source and the detector, (Strictly speaking, this refers also to the position of a source around the detector endcap. One may find a different efficiency when one measures a point source at the same relative height but 5 cm right or 5 cm left of the cap.)

- One specific sample geometry, (i.e. the shape and consistency of the actual sample which contains the activity. For example, if one uses always the same Marinelli beaker but its filling height is different in various measurements, or it is filled once with a fluid and in the next measurement with lumpy stone granules, then the sample geometry is not the same.)
- One specific sample composition.

If any of the first three of the above four conditions is changed one has to measure a new full-energy peak efficiency function. Modifications in the sample matrix composition will require additional corrections for self-absorption (see below) which could also be handled with a new efficiency function. It takes quite some effort to arrive at efficiency data points, which are as well defined as in the example function from Figure 6. A large number of well-calibrated expensive sources - some of which are very short lived - is needed to fill the energy range from below 50 keV up to almost 2000 keV. The sources themselves must be produced having exactly the same geometric distribution of the activity and they must be placed at exactly the same position. In many cases it is possible to produce one liquid mixed nuclide source from calibrated activity solutions, part of which is then poured into the desired geometry. The calibration spectrum should be counted for a sufficient amount of live time that all peaks to be analysed for the efficiency function have an area of at least 100 000 counts. The spectrum should be analysed with a real spectrum analysis program (most procedures implemented in the MCA emulation programmes are not suited because they apply too many approximations) and the peak areas must be corrected for true coincidence summing. If one considers the many complications and the amount of work involved to arrive at a good efficiency function, one might be tempted to scale that function linearly in order to correct for a different distance between the sample and the detector. Such linear scaling of efficiency functions (e.g. by $1/r^2$), however, must be avoided, as the efficiency functions measured at different distances do **not** run parallel. The *slopes* of the rising and the falling branches of efficiency functions will change when the source is placed at different distances. The amount of this change of slope is dependent on the type of the detector as well as the size and shape of the crystal. We have not yet been able to quantify the distance-scaling of efficiency functions in a systematic way.

3.4.8. Self-absorption corrections

Whenever a source of gamma rays has a finite thickness the gammas will interact with the matrix of the source and be partly absorbed. There may be additional absorption between the emission and registration of the photon such as interactions in the container, in the air between source and detector, in the detector endcap, and in the dead layer on the detector. The effects of absorption are most prominent when the source is thick, like in a Marinelli beaker, and when it consists of material with high atomic numbers. There are many attempts to calculate or approximate corrections for photon absorption effects [e.g. 1, 2, 4, 9, 11, 13, 14] some of which yield quite consistent and acceptable results. However, it seems to be the simplest, most precise and best method to determine experimentally several self-absorption corrected efficiency functions for each typical source geometry [10] and to use the best suited one. As an example several normalized efficiency functions are shown in Figure 7 which were measured in a Marinelli-beaker geometry from calibration nuclides mixed into sources of different matrix compositions.

The matrix densities of the sources were in the range of $0.42\ \mathrm{g/cm^3} \leq \rho \leq 1.60\ \mathrm{g/cm^3}$ and the atomic numbers Z of the matrix elements were in the range of $1 \leq Z \leq 26$. The functions in the figure are the ratios of the efficiency functions measured in a specific matrix divided by the efficiency function measured in a polymerized ethylene (brandname: Lupolen). From the varying shapes of the functions and even the crossing of different functions it is clear that any density- or Z-dependent scaling of a reference efficiency function will not yield a reliable method of simultaneous absorption correction. One can, however, use the appropriate efficiency function out of a set of measured data in order to correct for the absorption in an actual sample. The function to be used is easily found through an absorption measurement at two significantly different energies [12, 10]. The efficiency function from that sample matrix is then to be used, in which the ratio of the attenuation coefficients for the two energies is nearest to the ratio found in the actual sample.

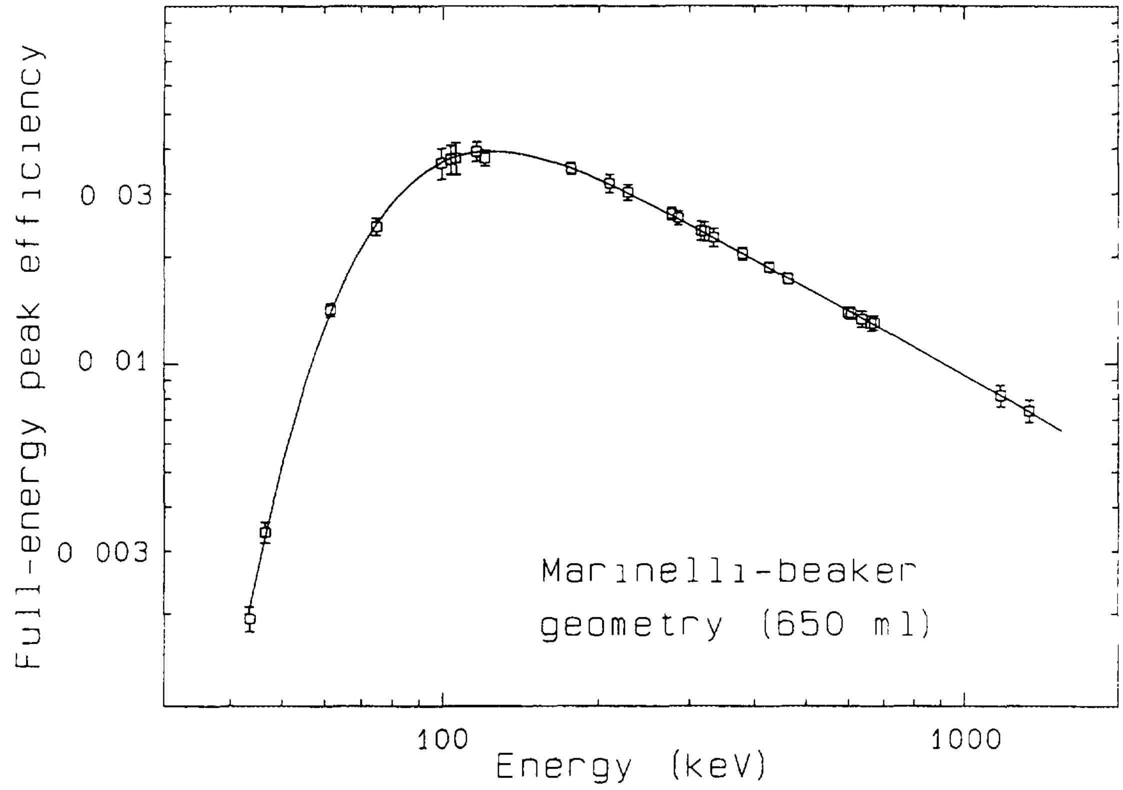

FIG. 6. Full-energy peak efficiency function for a 650 ml Marinelli-beaker geometry.

3.4.9. Uncertainty calculation

It is well known that the minimum 1-STD statistical uncertainty of a large number of counts (N) is approximated by SQRT(N). This simple formula may be applied if all counts originate from the same process and they are generated and treated in the same way. However, it does not apply when the area uncertainty for a peak in a gamma ray spectrum is to be defined since

- the peaks in a spectrum always sit on top of a baseline distribution, there may be one or several other peaks whose area overlaps with the one peak under inspection, and
- the definition of a region-of-interest (ROI) to be analysed is arbitrary.

These additional constraints are to be considered in the analysis of the spectrum and their contributions to the overall uncertainties of the peak areas must be reflected in the area of uncertainty. Therefore one may not define the area uncertainty as x-times SQRT(area) where x is a convenient multiplier. The uncertainty must consider the deviations in each channel of the fitted from the measured counts, the contributions of the baseline counts, the partition of count rates to different peak areas, and also the possibility of missing or extra peaks in the analysis of a ROI. Unfortunately the sum of all these and possibly other sources of error leads to total uncertainties which are much larger than users wish them to be. In most programs for the analysis of gamma ray spectra, there is no such very detailed estimate of uncertainties but rather, a few simplifying assumptions are made. These are:

- the border channels of a ROI are correctly defined,
- all peaks in a ROI are consistently determined, there are no missing nor extra peaks,
- the peak shape used in the fitting process is physically correct,
- the functional description of the baseline is physically correct,
- all peaks in one ROI have identical peak shape parameters.

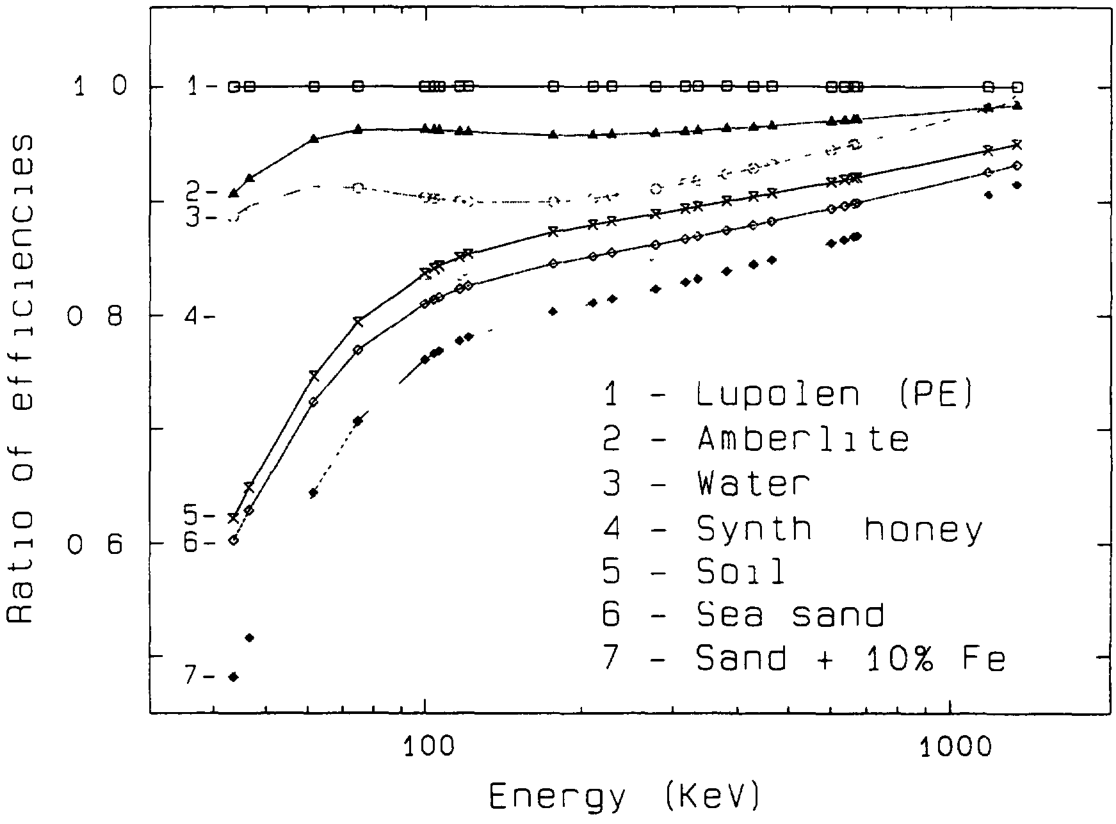

FIG. 7. Ratios of self-absorption corrected efficiency functions measured in the same geometry but using different matrix materials. The lines are to guide the eye.

Provided that these assumptions are justified and that the least-squares fitting process has really found the minimum deviation in the multiparameter space, then the area of each peak can be calculated as the integral over the peak function from $-\infty$ to $+\infty$. In many cases this integral can be solved in a closed form and the area is written as a function

$$\text{AREA} = f(a,b,c,...) \qquad (3)$$

where a, b, c, ... are functional parameters whose numerical values are either known or approximated in the fitting process. The 1-STD uncertainty of the area then is calculated as

$$\Delta AREA^2 = (\delta f/\delta a)^2 \bullet \Delta a^2 + (\delta f/\delta b)^2 \bullet \Delta b^2 + ... \quad (4)$$

where Δa, Δb, ... are the 1-STD uncertainties of the parameters. These are taken from the estimated covariance matrix [C] of the standard uncertainties in the fitted parameters α: $[C]=[\alpha]^{-1}$ (if a nonlinear matrix algorithm is applied) or from the properly weighted residua (if a nonlinear, non-matrix algorithm is used). Again, these methods to define the uncertainties of fitted parameters are only justified if the resulting uncertainties in repeat analyses are normally distributed. In spectrometric analyses this will normally be the case if the above five assumptions are justified, i.e. if the analysis was "*correctly*" made.

The final result from most spectrometric analyses is the quantitative definition of activities from nuclides in the sample. This quantification requires calibration operations that are based on fitted experimental data and therefore also have uncertainties, such as the efficiency calibration or the self-absorption corrections. The uncertainties coming from these calibration procedures must be considered according to the statistical law of uncertainty propagation (equation 4) when the total uncertainty is calculated. Uncertainty contributions from these calibration procedures can be very large, as shown in Figure 8 where the example of the well-determined efficiency function from Figure 6 is employed. Figure 8 shows that the ratios between the experimental data points and the fitted function, i.e. the solid line at unity marks the fitted function. The enveloping functions above and below the data points are the limits of the 1-STD uncertainty of the fitted function as calculated from equation 4. Although this efficiency function is very well determined through data points and it is well fitted, there are very large contributions up to 10% to the overall uncertainty, especially at low energies. These contributions must be considered when peak areas are corrected for efficiency and activities are calculated. Thus, in the above example a nuclide which is assayed through a low-energy line alone (such as e.g. ^{210}Pb via the 46.5 keV line) cannot be determined to better than ±10 percent.

3.4.10. Spectrum formats

Most modern multichannel analyzers allow the storing of measured spectra on permanent mass storage devices such as the hard disk, floppy disk or tape. This very useful feature, however, suffers from the fact that there is no agreed standard of how these spectra should be formatted. It is a bad habit that every supplier of spectrometric hardware has his own spectrum format, which is by principle incompatible with every other format. As an additional complication one may find several different, internally incompatible formats in different hardware from the same supplier, and as an extra surprise, one supplier even had a total of three different formats used in the same hardware. The differences are found in the length, contents and structure of header and trailer blocks as well as in the representation of the spectral data. The latter point is especially annoying because there is good emulation software, which allows the storing of data with 32 bits per channel or a poor system that provides only 20 bits for each channel. On 20 bits, however, one can only store data with a maximum of 1 048 575 counts in one channel, which is definitely not sufficient for any spectrometric purpose. Counting only the more abundant MCAs, there are more than 20 different spectrum formats on the market, which are completely incompatible with each other. This situation is most unsatisfactory, and users ought to make frequent complaints in order to pressure producers to agree on one standardized spectrum format.

As a starting point the author would propose that an ASCII header and spectrum format be used which resembles the structure employed in the current QXAS file format of the IAEA programs. The format is set up in a keyword-controlled structure with a limited number of pre-defined keywords and any number of user-defined keywords. Thus, there is no limitation for each hardware supplier to implement his own ideas and options. As an example, a keyword controlled spectrum format might look like the following:

```
$channels$8192
$realtime$1007
$livetime$1000
$deadtime%$0.4
$startgrab$21 aug 94 16:30:04
$endgrab$7 oct 94  09:04:51
$startcount$12 oct 94  08:01:09
$mass-g$17.941
$begin_data$
0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 9
14 36 102 367 1009 2047 2081 2107
...
...
$end_data$
```

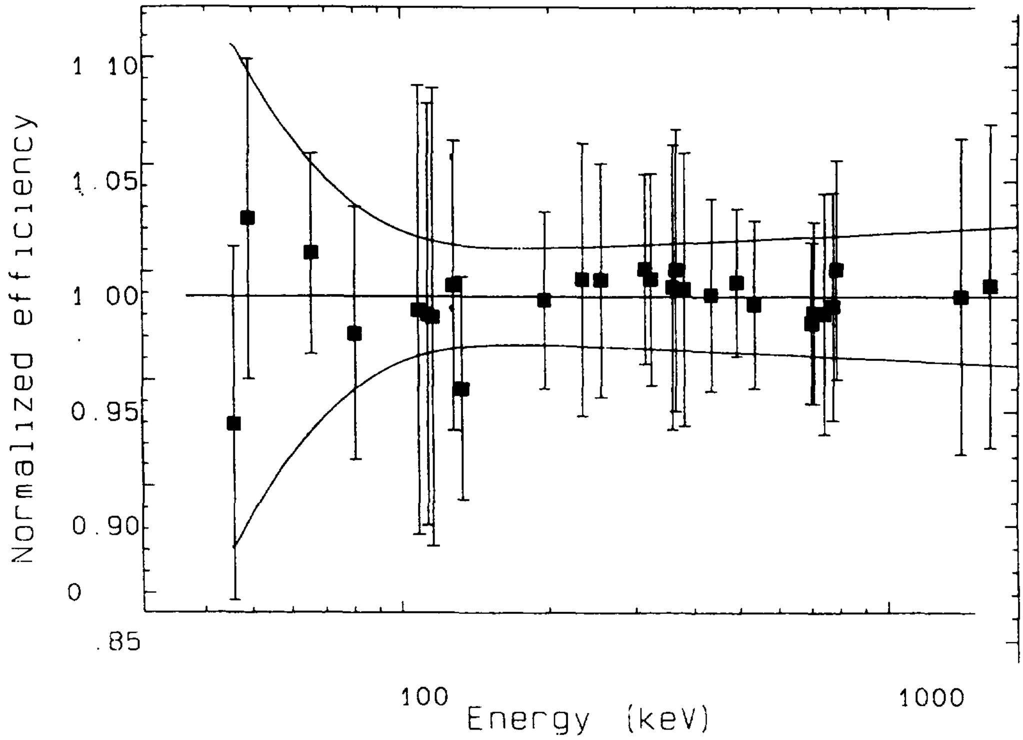

FIG. 8. Efficiency data points from the function from Figure 6, normalized to the fitted function. The enveloping lines show the 1-STD uncertainty band of the fit.

In the above example the keywords are enclosed in "$" signs for easy decoding. A similar proposal of a keyword-controlled ASCII spectrum format has been made before [8] and it could also be pursued. It is an unnecessary waste of user's time and programmer's brain to have to handle so many complicated, poorly documented and inaccessible spectrum formats. The argument that ASCII formats are too space consuming and expensive for practical purposes is no longer valid, because in today's computers the price of mass storage space is below 30 cents for 1 MB of storage capacity and it will drop further.

3.5. CONCLUSIONS

The techniques of measurement and evaluation of high-resolution gamma ray spectra have been developed and refined since over 20 years and are generally good and reliable now However, there are still several problems, inconsistencies and simplifications that require solutions and improvement. In the present paper I have pointed out and proposed solutions for the most frequently occurring hardware problems as well as some of the areas in which existing software may need modification. Of these problems, there are two important topics for which there are not yet practical, easy-to-use solutions. They relate to the quantification of activities in samples and involve the true coincidence summing and the self-absorption corrections. Ways to approximate these two correction functions have been discussed, but it would certainly be desirable that basic solutions for these problems be found.

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4. EXPERT SYSTEM BASED RADIONUCLIDE IDENTIFICATION[7]

4.1. SUMMARY

An expert system coupled with the gamma spectrum analysis system SAMPO has been developed for automating the qualitative identification of radionuclides as well as for determining the quantitative parameters of the spectrum components. The program is written in C-language and runs in various environments ranging from PCs to UNIX workstations. The expert system utilizes a complete gamma library with over 2600 nuclides and 80 000 lines, and a rule base of about fifty criteria including energies, relative peak intensities, genesis modes, half lives, parent-daughter relationships, etc. The rule base is furthermore extensible by the user.

This is not an original contribution but a somewhat updated version of papers and reports previously published elsewhere [1, 2, 3].

4.2. INTRODUCTION

A complete analysis of a gamma spectrum is a demanding task even for modern gamma ray spectrum analysis programs. It requires that all the peaks above a given threshold are found and their intensities and energies correctly defined. Correctly here necessarily requires also that the error estimates be in statistical control. After the *quantitative analysis* the peaks must be associated with correct radionuclides so that their intensities are all attributable to identified nuclides within the uncertainties of the statistics and measuring procedures.

We must emphasize that, in our opinion, there does not exist a computer code, which can do a complete analysis of a general gamma spectrum without strong user intervention. In some special cases, however, this may be possible. If the analyst is only interested in some specific nuclides or transitions, the analysis can be automated.

Several highly effective computer programs for the gamma spectrum analysis are also available, including programs of the SAMPO family [4]. With the latest SAMPO versions it is possible to do a complete quantitative analysis of even very complex gamma spectra. Due to automatic residual analysis of the fits even overlapping multiplets can be correctly analyzed without user intervention. The most complex cases, however, require interactive use of the code where the analyst visually verifies the fitting results.

In many cases this kind of quantitative analysis does not go quite far enough. Although it gives very accurate information about the gamma peaks present in the sample, it does not tell anything about the radionuclides that produce these peaks. This information is often crucial when doing real world measurements, whose goal is to find out about the composition and history of the sample. Many reasons for such measurements exist. One may want to find out where a specific sample originates from, i.e., is its activity of natural origin or does it come from a nuclear reactor or radioactive fallout of some kind. Procedures that try to identify the composition of the sample and to make deductions based on this information are known as the *qualitative analysis*.

To this date quantitative analysis has been the more automated discipline of the two. This can be easily understood considering the difference in nature of the two analysis phases. Quantitative methods are mathematically fairly exact and well defined, which makes it more

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[7] *Prepared by P.A. Aarnio, J.J. Ala-Heikkil, T.T. Hakulinen and M.T. Nikkinen, Helsinki University of Technology, Finland.*

natural to try to automate them using a computer. Qualitative analysis, on the other hand, requires many heuristic deductions in addition to exact mathematical methods. Computers have been notoriously ineffective in any problem requiring heuristics, and therefore, the qualitative analysis is even today mostly carried out by human experts who possess the required knowledge.

With the development of faster computers and suitable computing techniques for processing of heuristic knowledge, a system for the qualitative analysis has become feasible. The problem at hand can be attacked by using an *expert system*, which is a specialized program for reasoning. Expertise of a human expert has been programmed into the expert system. The system aims to reproduce the chain of reasoning of the expert in such a way that the same inputs produce similar outputs in both cases.

A considerable amount of testing is necessary for determination of the efficiency and quality of an expert system. The system must be verified against real world cases. Any deviations from the expected results indicate that the heuristics need to be reviewed. It is also essential that the tests are made as comprehensive as possible to cover a wide range of the projected applications. Our current research interest is in the integration of the quantitative and qualitative analysis phases in a user oriented environment where complete analysis of any spectra is feasible. That is, even if the user is only interested in a few transitions he will end up doing the complete analysis because it will be so simple. The final aim is to be able to do the complete analysis without user intervention.

In this paper we concentrate on the qualitative analysis of gamma ray spectra. That is, we present *SHAMAN*, an expert system for the identification of radionuclides in the measured gamma ray spectrum. *SHAMAN* is an expert system designed specifically for carrying out the qualitative radionuclide identification and quantitative activity determination on a measured spectrum. High level logic is implemented as abstract rules and mathematical algorithms as separate functions. *SHAMAN* is written in ANSI C [5] for maximum portability. It has been ported to BSD, AIX, Linux, Windows, OS/2 and DOS.

4.3. EXPERT SYSTEM CONCEPTS

An expert system is a computer program, where the flow of execution is governed by the problem specific data rather than a preprogrammed algorithm [6]. The system consists of *rules* that hold knowledge about the conditions that the data must fulfill as well as the actions taken in such a case. An *inference engine* continually monitors rules for validity as the data in the system changes and appropriately *fires* valid rules at the suitable instance thereby causing the data to be modified.

SHAMAN rules are simple if-then constructs, which are stored in the system as a list accessible to the inference engine. Rule's *antecedent* holds logical clauses that depend on the data in the system. Any C-language construct that returns zero value for false and non-zero otherwise can be used. Rule's *consequent* holds the actions to be executed when the rule is fired. These actions modify data and may cause further rules to become valid. Rules are grouped according to their application domain, which allows control over orthogonal blocks of knowledge in the system. It is thus possible to exclude rules concerning, for example, genesis modes of nuclides. Each rule has an associated numerical priority value, which is used to determine the relative precedence of rules.

Data items are contained in special tagged structures, which exhibit selected features of object oriented frame systems, e.g., *inheritance* and automatic creation of certain standard *handlers*. Instances of data structures have additional data fields for the data type tag and the last modification time. This information is necessary for the inference engine.

Rules and data objects are written in the system using a special rule language, which can be machine-translated to standard C-code using a separate rule compiler. This allows proper type checking for the objects and enforces internal consistency of the knowledge base whenever rules and objects are modified.

The inference engine is conceptually fairly straightforward implementing only *forward chaining* as its inference strategy. Inference operates in a loop. After a rule has been fired it is checked for each rule in the system whether its rule group is enabled and whether the data the rule depends on has been modified since the last check. If these criteria hold, rule's antecedent is checked. If the antecedent *matches*, i.e., evaluates true, the rule is placed in the *agenda*, which is a list holding rules scheduled for firing in the relative order of their priority. If there are yet unfired rules in the agenda, whose antecedent no longer matches, they are removed from the agenda. It is also possible to define the rule *edge-sensitive*, which means that the rule stays in the agenda even if the antecedent becomes false. When all rules have been checked, the first enabled rule in the agenda is fired and the rule entry removed from the agenda. The inference loop continues in the above manner as long as there are enabled rules in the agenda, after which the solution has hopefully been reached.

4.4. MEASURED SPECTRUM

Spectra to be identified are measured using germanium detectors and the quantitative analysis is carried out using SAMPO-90 gamma ray spectrum analysis program [7, 8]. After this the analysed data are converted to a special format required by *SHAMAN*.

The quantitative analysis proceeds roughly as follows: The measured spectrum is analysed using SAMPO-90. Calibrations for energy, efficiency, and peak shape are assumed to have been correctly determined earlier. The analysis is assumed complete, i.e., all peaks, whose statistical significance exceeds the value of peak search significance, are actually found in the spectrum and correctly analysed. This analysis yields a peak table where peak centroids, areas, intensities, and respective statistical errors are calculated. In addition, SAMPO-90 outputs the energy ranges that were used in peak fitting and area determination including information about the actual functions fitted to the peaks and the background.

These data are further processed to form a special format input file for *SHAMAN*, because some of the data provided by SAMPO-90 are unnecessary, whereas some essential information is missing. The following information is necessary for the identification:

(a) All found peaks in the spectrum, their energies and intensities with respective errors. The identification process is considerably simplified if it can be assumed that all detectable peaks in the spectrum have been found. In *SHAMAN* detection and determination limits are calculated according to Currie [9].

(b) The background as a function of energy. It is formed for each channel in the spectrum by summing channels around the centroid. The summing interval is the peak width multiplied by a confidence factor. Background is required for the detection limit calculations of the candidate nuclides.

(c) Measured energy ranges. Gamma lines of the candidate nuclides, which fall outside of the measured range, are excluded from analysis. Piecewise energy ranges are possible.

(d) Sample mass, which is required for calculating the limiting activities of candidate nuclides.

(e) Irradiation, cooling and counting times. If the end of irradiation is unknown, a conservative estimate is the time, when the sample was received for measurement.

(f) The origin and the physical state of the sample. This information allows one to make deductions about the possible genesis modes of the sample.

(g) Energy, efficiency and shape calibration. Calibrations are obtained from SAMPO-90, but the actual efficiency calibration is different for candidates that are classified as background nuclides and must therefore be carried out in *SHAMAN*.

(h) Information about the measurement environment. The efficiencies of background nuclides in lower energies are generally affected by matrix effects, which depend on the materials present in the measurement room. If the spectral background has not been subtracted in the measurement time, an approximate correction can be applied.

4.5. RADIONUCLIDE LIBRARY

The radionuclide library used by *SHAMAN* is compiled from the databases ENSDF and NUDAT retrieved from NNDC [10]. It contains 2616 nuclides with about 80 000 lines. The data base was converted into a more concise form to save space and to speed up file operations. Some additional data were taken from other publications [11, 12, 13, 14]. In particular, all parent-daughter relationships and respective branching ratios were completed, which is essential for correct activity calculations. The following data of all the nuclides are used by *SHAMAN*: mass and element numbers, half life, mass and element numbers and the respective branching ratios of immediate daughters, mass and element numbers of immediate parents, genesis modes and various discrete status information. For each gamma ray line the following data are used: energy and absolute intensity of the transition with corresponding errors and some status information.

The library is organized as a random access binary file, which is indexed according to mass and element numbers as well as gamma line energies. An index file is a sorted binary file, which can be searched sequentially to locate a pointer to the main data file. The library is basically static, which means that only casual updates are necessary based on new compilations of nuclide data in the future. This makes it possible to keep the library structure fixed, thereby simplifying library management.

SHAMAN includes a library manager for easy access to the library. It carries out all requests for candidates. Search can be performed according to mass number, element number, and the energy of a gamma transition or any combination thereof. Additional discrimination criteria can be given for individual gamma ray lines based on their status information to rule out, e.g., all X ray lines or lines.

4.6. IDENTIFICATION RULES AND METHODS

4.6.1. Selection of preliminary candidates

The identification process begins by reading in the preprocessed spectrum. Thereafter candidate nuclides are read from the library and checked against several conditions in order to be accepted into final solution.

According to the first rule all nuclides having a gamma transition close enough to a peak in the spectrum are read in. Peaks are processed sequentially starting from the highest energy peak, because the density of gamma transitions per unit energy decreases roughly exponentially as a function of energy. Since the number of candidates is low and the resolution good at high energies, less candidates remain to be handled for low energy peaks. The energy tolerance used is the peak width multiplied by an adjustable confidence factor.

No candidates are accepted on the basis of the annihilation peak only. Annihilation peak is present for positron emitters and high-energy gamma ray emitters due to pair production. In both cases other lines must be visible too, because otherwise it would be impossible to discriminate between several candidates. A special dummy nuclide is associated to the annihilation peak to account for the possible unexplained portion of intensity due to external annihilation radiation. Thus, the annihilation peak will always be fully explained and the peak shares of other nuclides will not be distorted in the activity calculation.

Upon reading candidates into the system, several calculations are done:

(a) The distance to the nearest peak and the significance compared to the background are calculated for all lines. The significance value is corrected for matrix effects.

(b) The *primary line* is determined. It is the most significant line in the measured energy range.

(c) All parent nuclides of the candidate are read in by tracking the decay chain upwards. In general, if decay chains can be assumed to be in equilibrium, the *effective half life* of the nuclide is defined as the half life of the longest lived precursor in the chain. This is especially true for background nuclides that belong to natural decay chains. For newly irradiated samples decay chains are often not in equilibrium, which renders this kind of calculation invalid.

(d) The *pure nuclide activity* is calculated. It is defined as the activity that the candidate nuclide would have immediately after the irradiation, if the sample consisted entirely of that isotope. The *effective pure nuclide activity* is calculated using effective half life instead. Pure nuclide activity is meaningless for background nuclides.

(e) If the candidate has gamma lines that are not found in the spectrum, the *threshold line* is determined. It is the most significant unfound line in the measured energy range.

(f) The *threshold activity* is calculated. It is defined as the minimum detectable activity of the candidate based on the threshold line, i.e., it is the maximum activity that the candidate nuclide in the sample can have for the threshold line to remain unseen in the spectrum.

After all the above quantities have been calculated, pruning rules in the knowledge base become effective. Rules are assigned priorities so that the most efficient pruning rules are handled first. Five possible states exist for a candidate. The candidate is ***possible***, when it is considered a part of the solution, ***impossible***, when there are strong reasons for discarding the candidate, ***improbable***, when the candidate is believed to be absent but there are doubts, ***insignificant***, when the candidate strictly speaking is present in the sample but its effect for some reason is negligible, and ***unfitting***, when the candidate is part of an interfering set of nuclides, and activity calculation indicates that this candidate is extraneous. Impossible candidates are never looked into again but improbable, insignificant or unfitting nuclides may be reconsidered if a satisfactory solution cannot otherwise be reached.

4.6.2. Early pruning

Early pruning rules operate on candidate nuclides before the activity calculation has taken place. They are used to strip the amount of candidates to the minimum to yield as small initial interference matrices as possible, which considerably eases activity calculation.

- If the primary line of the candidate is not found in the spectrum, the candidate is judged impossible. This is the most efficient rule being typically responsible for 80% of all discarded candidates.
- If neither the candidate nuclide nor any of its parent nuclides have suitable genesis modes, the candidate is judged impossible. The knowledge about valid genesis modes comes from the user in some form and is based on the origin of the sample and the particular measurement setup.
- If the physical state of the sample is other than gaseous and the sample is in an open space, all noble gas candidate nuclides are judged improbable. Since noble gases are inert and form very few compounds, they will soon fly away from a porous sample.
- If there is a candidate, whose gamma line branching ratios match closely (within a given tolerance) to the intensities of the respective spectrum peaks, all other candidates, whose most significant lines are associated to these peaks are judged improbable. The more found gamma lines the nuclide has, the more reliable this judgment is. In particular, this rule cannot be used if the candidate has only one found gamma ray line.
- If the candidate nuclide is an isomer, whose longer-lived parent has not been found, the candidate is judged improbable. It is assumed that an isomeric nuclide cannot be present in detectable quantities except as a decay product.
- If no candidates are associated to a peak, it is checked, whether it is an escape peak. If there is a stronger peak at 511 keV or 1022 keV higher energy, the unassociated peak is marked as escape peak and not included in the activity calculation. Strictly speaking, estimates for the relative escape peak efficiencies should be calculated to be sure [15, 16], but this would require knowledge of some additional detector characteristics.
- If no candidates have been associated to a peak, and it does not seem to be an escape peak, discarded candidates that have earlier been associated to this peak are reconsidered. Reconsidered candidates cannot be discarded again on the same grounds. Candidates marked as impossible are never reconsidered.
- If the user has especially told *SHAMAN* not to accept the candidate for any reason, it is discarded. The judgments as well as the reasoning are given by the user. This will offer the user a way to affect the inference process.

4.6.3. Activity calculation

When initial candidates have been read in for all spectrum peaks and there is no more pruning to be done, activity calculation is performed. In general, most candidate nuclides are associated to several spectrum peaks as well as most peaks to many candidates. This means that a best estimate approximation is required. The standard method is to fit candidate nuclides to the spectrum in the least squares sense.

Although the problem is mathematically straightforward, situations exist that are difficult for many algorithms to handle. The first of these cases appears, when the coefficient matrix is singular, i.e., the matrix contains some degenerate vectors. The other case occurs, when the matrix is underdetermined, i.e., there are less linearly independent equations than free variables. In activity calculations of gamma spectra both of these cases appear frequently.

To reach a mathematically optimal solution in all cases, a sophisticated algorithm is required. Standard methods are Gauss-Jordan elimination, QR-factorisation and singular value decomposition SVD [17, 18]. Although all these methods in principle work in cases, where clearly singular matrices have been eliminated, rounding errors typical for numerical calculations may cause the solution to be unstable or even push a regular matrix to singular. To prevent this, one has to analyse the matrix in advance taking appropriate actions whenever ill-conditioned cases are encountered. This is precisely what SVD-algorithm allows one to do. The algorithm produces a set of *singular values* of the initial coefficient matrix, which are used to take into account nearly singular cases. The only drawback of SVD is its longer execution time compared to the other methods.

The SVD-algorithm produces also a covariance matrix, whose diagonal elements are the variances of calculated activities, as well as a vector containing peak residuals characterizing the unexplained portions of the peaks. Negative residuals indicate over-explained peaks.

In addition to the solution provided by SVD, *SHAMAN* uses also information about the particular interference setup: which candidate nuclides belong to which interference group, how the submatrices are determined and whether they are columns degenerate.

4.7. ACTIVITY BASED RULES

After the activity calculation is complete, several new pruning rules become active. Most of these rules are only effective on the particular interference setup, which is subject to change after each recalculation of activities.

- If the calculated activity is greater than threshold activity, the candidate is judged unfitting. In other words this means that the calculated activity is so great that the threshold line should be seen in the spectrum.
- If the decay corrected pure nuclide activity of the sample is smaller than the smallest detectable activity, the candidate is judged impossible. This rule is quite effective in eliminating candidates with short half-lives, and given the correct values of sample mass, decay time and effective half-life, it is also extremely reliable. However, for background nuclides the mere concept of pure nuclide activity is meaningless and this rule therefore useless.
- If the decay corrected value for the candidate nuclide mass in the sample based on the calculated activity exceeds the sample mass, the candidate is judged impossible. The relative concentration of individual nuclides is typically small, which makes this rule very reliable.
- If the calculated activity of the nuclide is negative, the candidate is judged unfitting. A negative activity value indicates that other interfering candidates are able to (more than adequately) explain all the peaks in question. It is possible that by discarding some other nuclide the results would be better, but as a first approximation this is most likely the false candidate.
- If the error of the calculated activity is large, the candidate is judged unfitting. The error value is produced by the fitting algorithm and depends on the interference setup. By default *SHAMAN* uses a 50% threshold.

- If the same peaks are associated to both a parent nuclide and its daughter, which is a shorter lived isomeric state of the parent; the daughter nuclide is judged insignificant. This rule actually discards a nuclide that is present in the sample. This is necessary, however, so that the activity of the parent could be correctly determined.
- If the same peaks are associated to both a parent nuclide and its non-isomeric longer lived daughter, the parent nuclide is judged insignificant. This rule is based on the assumption, that all short lived parents have decayed into their respective daughters, which is true if the decay chain is in equilibrium.
- If a peak is poorly associated, i.e., its relative intensity residual is great, and it does not seem to be an escape peak, discarded candidates that have earlier been associated to this peak are reconsidered. By default SHAMAN uses an 80% threshold.

4.8. USER INTERFACE AND REPORT GENERATION

The user interface of *SHAMAN* is command line oriented. When the system is started, the user is placed to command interpreter prompt, where it is possible to view and set system parameters and run inference. Even as identification proceeds, it is possible to suspend inference to view system status etc. *SHAMAN* has also a simple macro facility to help automate repetitive tasks.

SHAMAN outputs currently two distinct reports about the inference results. These reports are quite detailed and aimed for an expert, who wishes to easily evaluate the validity of the result. Most of the numerical data and reasoning that SHAMAN produces are presented in some form in these reports.

Spectrum Identification Report presents information about the spectrum peaks: nuclides associated to each peak, explanation percentages, various status information and lists of nuclides that have once been associated to each peak.

Nuclide Identification Report presents detailed information about each accepted candidate: half lives, genesis modes, parent-daughter relationships and calculated activity values. For each gamma line the report contains its energy, intensity, distance from the nearest spectrum peak, peak share if the line is associated to a peak, the statistical significance and various status information. Information is also presented about the inference process: the statistical parameters used, lists of all discarded nuclides, background nuclides and reconsidered nuclides with appropriate reasoning.

For complete information about the identification process it is also possible to have *SHAMAN* log all its actions to file. This enables the user to follow the course of inference in great detail.

4.9. TEST SPECTRA

In order to evaluate the performance of *SHAMAN* a set of test spectra was created. The spectra were chosen with the general-purpose nature of *SHAMAN* in mind, i.e., they include spectra from several fields of applications of gamma spectroscopy. From a practical point of view, it is well motivated to keep the contents of the library constant during the development of the system. In this way the effects of modifications can easily be detected by comparing the new results to the previous ones.

The varying complexity of the test spectra required consideration of several aspects:

- The complexity of the nuclide identification depends primarily on the number of peaks in a spectrum. The number of peaks found in a gamma spectrum is typically 10 ...100, but in a very complicated spectrum even a few hundred peaks may be found.
- The complexity of the nuclide identification depends also on the quality of the peaks. Small peaks usually have bigger relative intensity errors than larger peaks. More candidate nuclides can be assigned to low energy peaks than to high-energy peaks. The X ray, escape and sum peaks are often difficult to distinguish from normal photopeaks during the analysis. Only if a peak can not be explained with the photopeaks of the candidate nuclides can it be recognized to be an X ray, escape or sum peak.
- The complexity of the nuclide identification depends also on the time parameters of the measurements. The shorter the cooling time the more short-lived nuclides must be regarded as possible candidates. Some conclusions can also be drawn from the length of the irradiation time, if the irradiation conditions are known accurately enough.

The selected 51 spectra are of varying complexity. Half of the spectra are real measured ones, whereas half of them have been synthesized in order to achieve a more versatile test set. The number of peaks in the spectra varies from 10 to 130 (except for the very complicated Chernobyl fallout spectrum with 275 peaks) and the number of present nuclides varies from 1 to 52. The measured spectra include some X ray, escape and sum peaks, but the synthesized spectra do not. The irradiation and cooling times vary from zero to one year.

The measured spectra in the library can be categorized as follows:

- Ten spectra of different combinations of 8 standard sources ^{22}Na, ^{54}Mn, ^{57}Co, ^{60}Co, ^{137}Cs, ^{133}Ba, ^{152}Eu, ^{241}Am).
- Two spectra with different measuring times of a weak natural uranium source.
- Two spectra with different measuring times of an irradiated uranium oxide sample.
- One spectrum of an irradiated indium sample.
- Four background spectra measured in the same laboratory with different measuring times.
- Six spectra of environmental, NAA and reactor samples measured with different detectors and in different geometries.
- One spectrum of a wipe sample of the Chernobyl fallout.

The synthesized spectra have been done with a non-commercial subroutine package of SAMPO-90. The synthesis model includes a tailed Gaussian photopeak and a Compton continuum, but no X ray, escape, sum or backscatter peaks. The Compton continuum has been modeled using the peak-to-Compton ratio as the only parameter. The spectra of the different gamma energies are summed together and statistics are added to the summed spectrum.

The versatility of the spectrum library can easily be enhanced by including synthesized spectra. Another advantage is that the nuclides present and their activities are known in advance, whereas measured spectra must be carefully analysed manually. However, there are some disadvantages with synthesized spectra. First, the spectra are only as good as the model. If the model is crude, so are the synthesized spectra. Second, the spectra are correct only as long as the input data are correct. In our case, the same gamma library was used in the synthesis and analysis and thus if the spectra are not exactly correct, at least they are consistently biased. Third, the modelling of decay chains requires a complete decay database and a carefully implemented decay calculation. In our spectrum synthesis model, the decay chains have been totally neglected for simplicity, but this is not a serious defect as the activities of the daughter nuclides have been calculated by hand and given as input to the synthesis program.

The synthesized spectra in the library can be categorized as follows:

- Four spectra of totally artificial nuclide combinations.
- Four spectra with typical radionuclide inventories of the coolant and the gaseous waste of a nuclear power plant.
- Four spectra with some radionuclides generated by charged particle reactions (in an accelerator).
- Seven NAA-spectra with totally artificial element combinations.
- Six NAA-spectra with realistic element combinations found in literature.

The test spectrum library is comprehensive enough for an evaluation of the expert system *SHAMAN* or any other nuclide identification system. Eventual new interesting test cases can still be added to the library, but there should be no need to discard any of the current spectra.

4.10. PERFORMANCE

The evaluation of the expert system *SHAMAN* has been done on an IBM RS/6000 workstation, but the results do not essentially depend on the computer environment. The eventual differences can be explained with rounding errors associated to different floating-point representations in different computers.

The general requirements for an acceptable identification can be listed as follows:

(a) *Good qualitative and quantitative identification of the nuclides.* Every nuclide present should be identified and no extra nuclides should be included. In fact, it is not very serious to have a few spurious nuclides in the solution as long as none of the nuclides really present are missing. It frequently happens that the decision between some nuclides can not be made with the rule base available to the expert system. Good quantitative identification means correct determination of the nuclide activities and other numerical parameters.

(b) *Good qualitative and quantitative explanation of the peaks.* Every peak should be explained as a photopeak, X ray peak, escape peak or sum peak of the present nuclides. Every photopeak should also be quantitatively explained within the intensity error limits.

(c) *Working rule set.* The rules should form a set with which an acceptable solution can be achieved and they should not be oversensitive to variations in the identification parameters. A working rule set is actually presupposed by the two previous requirements.

(d) *Speed.* The speed requirements vary from one application to another, but it is clear that given the same task, the expert system should be faster than a skilled human analyst. This is also a strong function of available computing resources, a factor that is constantly improved by advancing technology.

The test runs were made with an older version of *SHAMAN* dated from January 1992, after which several corrections and new features have been implemented. Therefore, the results given herein do not necessarily apply directly to the current development version, but rather serve to give a general understanding of the performance of the system. A new evaluation of the performance will be done in the near future when the next frozen version of *SHAMAN* is available.

Both the measured and synthesized test spectra were analysed with analysis program SAMPO-90. The peak finding and fitting was performed interactively to ensure that all multiplets and deformed peaks were included in the analysis results. The analysis results were converted using a special utility program into a format suitable for *SHAMAN*.

In the evaluation, each spectrum was identified using the full nuclide library. Also, the identification parameters of *SHAMAN* were kept constant, except for three spectra where drift in the gain required a larger energy tolerance. The use of some rules was also controlled by the user. These included the genesis modes with charged particle and photon reactions, which were defined unacceptable in NAA spectra. This kind of data is usually available to the analyst, but since it cannot be deduced from the spectrum itself, its manual introduction to the expert system is well justified. All the modifications above can be achieved using the scripting facility of the system, so an automated testing procedure can be created. With the exception of the items above *SHAMAN* identified the spectra with minimum of user intervention.

The results of the evaluation show that *SHAMAN* performs generally very well even for relatively difficult spectra. Over 90% of the nuclides present in the test spectra are identified by *SHAMAN*, and most of the unidentified nuclides have been discarded either because the activity calculation has turned against them or because some of their prominent gamma peaks are missing from the spectrum, i.e., they are near their detection limit. Also, almost all peaks are correctly explained, with the exception of some X ray, escape or sum peaks, whose identification is currently not on a very sophisticated level.

There are, however, extra nuclides in the identification results, which shows that *SHAMAN* is overconservative when discarding nuclides. An average spectrum in the library has 12 nuclides and 54 peaks. Of them *SHAMAN* correctly identifies 11 nuclides, but there will also be 6 spurious nuclides included in the result. The problem with spurious accepts is especially difficult for strongly interfering nuclides, since it is generally quite difficult to decide which nuclide, if any, should be dropped to improve the solution. This problem can be partially solved by developing the processing of the interference groups. As a whole, however, the current rule base operates well.

Recently a coincidence correction scheme has been implemented in *SHAMAN* which corrects for true cascade decay coincidences at close measuring geometries [3]. It calculates both the loss and increase of the apparent intensities of the cascade lines. It also calculates the intensities of the coincidence sum peaks, which are not part of the decay scheme of the nuclide in question.

The effect of coincidence corrections can be best illustrated with some representative examples by comparing the explanation of peaks with and without coincidence correction. Three example nuclides with strong coincidence summing effects from a spectrum measured at a close geometry are shown in Table III. The explained peak shares should ideally be 100%. With coincidence correction they seem to be well in agreement with each other, with the exception of three clearly over-explained peaks: 1.5424 MeV of ^{110m}Ag, 1.32551 MeV of ^{124}Sb and 1.4005 MeV of ^{134}Cs. These are peaks with strong summing-in effects, as can be seen by comparing the intensities in columns 3 and 5 in Table III. These peaks have not been explained at all or they have been clearly under-explained without coincidence correction, so that even their explanation has improved with coincidence correction. Thus, the introduction of coincidence correction in *SHAMAN* will lead to better results when identifying spectra measured in close geometries.

The quantitative results have received less attention in these tests, because the activity calculation has been tested earlier and has been found to be quite reliable. The execution speed was not a major concern either, especially because it depends heavily on the hardware, the operating system and the particular spectrum. The running time of SHAMAN varies from 1 to 20 minutes in a typical Unix workstation.

TABLE 1. IDENTIFICATION RESULTS OF THE MEASURED TEST SPECTRA

Spectrum label	Present nuclides	Unidentified nuclides	Spurious nuclides	Number of peaks	Description
Meas0	10	0	5	45	8 standard sources
Meas1	6	1	5	56	3 standard sources
Meas2	6	0	0	16	3 standard sources
Meas3	5	2	5	33	4 standard sources
Meas4	7	1	1	17	4 standard sources
Meas5	9	0	2	20	4 standard sources
Meas6	6	1	5	37	4 standard sources
Meas7	6	0	1	14	5 standard sources
Meas8	7	1	1	10	5 standard sources
Meas9	7	0	1	17	6 standard sources
Meas10	14	0	3	49	Natural uranium
Meas11	18	0	8	114	Natural uranium
Meas12	21	2	2	56	Irradiated uranium
Meas13	23	4	3	94	Irradiated uranium
Meas14	2	0	3	22	Irradiated uranium
Backgd0	19	2	14	126	Room background
Backgd1	14	1	10	74	Room background
Backgd2	9	1	3	30	Room background
Backgd3	8	0	1	15	Room background
Stuk1	10	0	2	46	Environmental sample
Stuk2	16	1	10	50	Environmental sample
Stuk3	23	1	14	112	Environmental sample
Stuk4	33	2	17	87	NAA sample
Stuk5	25	3	11	74	NAA sample
Stuk6	6	2	7	46	Gaseous reactor waste
Chernobyl	52	8	63	275	Chernobyl fallout
Average	**13.9**	**1.3**	**7.6**	**59**	

TABLE 2 IDENTIFICATION RESULTS OF THE SYNTHESIZED TEST SPECTRA

Spectrum label	Present nuclides	Unidentified nuclides	Spurious nuclides	Number of peaks	Description
Synt40	1	0	5	66	^{70}Lu source
Synt41	4	0	0	17	Artificial sample
Synt42	4	0	0	18	Artificial sample
Synt43	2	0	0	16	Artificial sample
Synt44	9	0	1	39	Gaseous reactor waste
Synt45	7	2	3	30	Gaseous reactor waste
Synt46	19	1	9	108	Reactor coolant
Synt47	13	1	1	41	Reactor coolant
Synt48	7	0	4	48	Accelerator nuclides
Synt49	7	1	11	114	Accelerator nuclides
Synt50	7	0	12	43	Accelerator nuclides
Synt51	6	0	15	99	Accelerator nuclides
Synt60	12	6	11	38	Artificial NAA sample
Synt61	9	1	6	28	Artificial NAA sample
Synt62	12	2	8	46	Artificial NAA sample
Synt63	9	0	9	16	Artificial NAA sample
Synt64	11	4	14	34	Artificial NAA sample
Synt65	21	0	7	98	Artificial NAA sample
Synt66	11	0	4	89	Artificial NAA sample
Synt67	7	0	0	17	Realistic NAA sample
Synt68	10	0	2	24	Realistic NAA sample
Synt69	8	0	1	37	Realistic NAA sample
Synt70	15	0	3	43	Realistic NAA sample
Synt71	10	1	2	40	Realistic NAA sample
Synt72	14	1	4	52	Realistic NAA sample
Average	**9.4**	**0.8**	**5.3**	**48**	

TABLE 3 EXPLANATION OF PEAKS OF THREE SAMPLE NUCLIDES IN SPECTRUM STUKI WITHOUT AND WITH COINCIDENCE CORRECTION IDEALLY THE EXPLAINED PEAK SHARES WOULD BE 100% THE DATA HAVE BEEN TAKEN DIRECTLY FROM THE SHAMAN REPORT FILES

Nuclide	E (MeV)	I (%)	Peak share (%)	I (%)	Peak share (%)
		(without coinc. corr.)		(with coinc. corr.)	
^{110m}Ag	0.446811	3.750	105.131	1.9510	86.795
	0.62036	2.806	124.780	1.4429	101.821
	0.657762	94.600	96.846	58.8866	95.664
	0.677623	10.350	113.368	5.2983	92.093
	0.687015	6.440	100.870	3.6439	90.569
	0.706682	16.440	101.794	8.8146	86.609
	0.744277	4.730	99.130	2.6643	88.607
	0.763944	22.290	103.266	13.6509	100.357
	0.818031	7.340	116.410	3.7198	93.617
	0.884685	72.700	101.492	44.6764	98.973
	0 937493	34.360	95.914	21.5004	95.239
	1 3843	24.280	88.385	16.4682	95.130
	1.47579	3.995	85.983	2.9009	99.077
	1.50504	13.040	85.793	8.6291	90.090
	1.5424	0.000	0.000	4.1143	156.303
	1.5623	1.029	39.509	1.2635	76.981
^{124}Sb	0.60273	97.800	96.325	83.5675	106.629
	0.645855	7.380	109.249	5.2122	99.021
	0.70932	1.350	110.996	0.8465	89.321
	0.713781	2.270	110.444	1.4904	93.060
	0.722786	10.760	103.556	7.6064	93.947
	0.968201	1.888	102.941	1.2396	86.737
	1.04513	1.840	99.899	1.1538	80.391
	1 32551	1.620	74.161	2.2358	131.352
	1.36816	2.620	98.008	1.7202	82.581
	1 43656	1.230	91.333	1.0903	103.897
	1.69098	47.300	91.465	37.5700	93.234
^{134}Cs	0.47535	1.460	95.614	0.9591	64.928
	0.563227	8.380	111.323	5.2990	72.764
	0.569315	15.430	113.179	9.7957	74.271
	0.604699	97.600	104.372	74.4136	82.257
	0.795845	85.400	101.923	64.9025	80.069
	0.801932	8.730	113.106	5.7351	76.806
	1.03857	1.000	98.165	0.8863	89.935
	1.16794	1.800	84.186	2.0485	99.034
	1.36515	3.040	70.668	3.8606	92.767
	1.4005	0.000	0.000	6.4794	157.596

4.11. DISCUSSION

The aim of expert system *SHAMAN* is to solve the problem of radionuclide identification in gamma spectrum analysis, which is rather difficult when using a full radionuclide library with 50 000...80 000 gamma lines. The system has been verified using a well-defined set of test spectra, and the performance has been found to be generally very good, but naturally with some room for improvement. It must be kept in mind that when evaluating performance for a radionuclide identification system, there are several factors that need consideration. The actual requirements for the accuracy and speed of identification depend strongly on the application at hand. For an early warning monitoring system high speed is preferred over pinpoint accuracy whereas the best identification results might be required in another application. An identification system such as *SHAMAN* should preferably be able to satisfy both of these somewhat contradicting requirements.

The test suite described in this paper is an excellent metric by which the performance of an identification system can be measured. After the results from the test suite have become available, the development effort of *SHAMAN* has concentrated on making the identification results more consistent and in a better agreement with the expected results. This development still continues.

The existing set of rules in the expert system is a good basis for a number of site-specific rule sets, which can be used to make more advanced deductions about the particular problem. This requires a facility by which the user can easily define his own rules in the system. The current procedure of recompiling the rule base is efficient but somewhat awkward in this respect. Specialized rule sets can also be created for different application domains, like environmental measurements or nuclear reactor monitoring systems. It should be noted that all the above results have been obtained by using *SHAMAN* as a `black box'. We are currently developing a graphical user interface that facilitates an easy user intervention and intuitive display of the results obtained. This will allow the user to easily verify the correctness of the results and guide *SHAMAN* to recalculate some results, if necessary. Currently the user intervention is mostly needed in discarding spurious nuclides. These extra nuclides are mainly due to the conservative rule base and reconsidering mechanism of *SHAMAN*.

When integrating the quantitative and qualitative analysis phases a direct feedback from identification results and activities to the peak energy and area determination becomes possible. Currently *SHAMAN* assumes that all the peaks above a given threshold are correctly analysed. If the results, however, suggest that it is not the case, the user has to do a separate analysis update and then run *SHAMAN* again. When the integration has been completed we wish to have a seamless system from gamma spectrum measurement and analysis to full identification and activity determination.

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5. QUALITY ASSESSMENT OF SOFTWARE FOR GAMMA RAY SPECTRUM ANALYSIS[10]

5.1. SUMMARY

Computer programs play an important role in the analysis of gamma ray spectra. However, computer results should be in statistical control. In this line, tests carried at Risø National Laboratory and some guidelines on QA/QC are hereafter presented.

5.2. INTRODUCTION

Although the aim of nuclear activation analysis is to determine the amount of a stable isotope in a sample, rather than the amount of a radioactive isotope, there is no substantial difference between the two types of measurement with respect to the processing of gamma ray

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[10] *Prepared by K Heydorn, Risø National Laboratory, Denmark*

spectra. In both cases we want to compare spectra of the unknown sample with those of samples having known activity or an activated sample having known composition. [1]

The result of such a comparison should have an accurately known precision and a negligible bias - in other words results should be in complete statistical control and corrected for all known systematic errors.

5.3. ANALYSIS OF PRECISION

Statistical control means that there is full agreement between the actual variability among results y_i and the estimated standard deviations σ_i of the individual results. This is tested by the *Analysis of Precision* of replicate results

$$T = \sum_{1}^{n} \frac{(y_i - \hat{\mu})^2}{\hat{\sigma}_i^2} \tag{1}$$

where $\hat{\mu}$ is the weighted mean of n independent results. When results are in statistical control the statistic T is closely approximated by a chi-square distribution with n - 1 degrees of freedom.

Such a test was carried out on a computer program for γ ray spectrometry developed at Risø National Laboratory by analyzing spectra obtained by 9 replicate counting of a ^{152}Eu source. [2] With 25 γ rays in each spectrum we found a value of T = 224.4 for 200 degrees of freedom, which confirms that statistical control was maintained.

A test for the absence of bias, however, requires the analysis of γ-spectra with accurately known composition. Such spectra were produced by the International Atomic Energy Agency in 1976, and we studied 4 different programs for photo-peak evaluation on the basis of 6 replicate spectra each with 22 peaks. [3] Results are shown in Table 1.

Clearly, program 4 can be rejected on the basis of this test, but acceptance of the other 3 programs depends on the agreement with the entire chi-square distribution. This is tested by comparing the results obtained with the cumulative distribution of T by means of the Kolmogoroff-Smirnov test, as shown in Fig. 1.

TABLE 1. TEST OF OVERALL PRECISION OF PHOTOPEAK INTEGRATION PROGRAMS

Program	T	Degrees of freedom	$P(\chi^2 \geq T)$
1	101.82	110	0.70
2	88.81	105	0.87
3	89.22	110	0.93
4	455.37	110	$<10^{-100}$

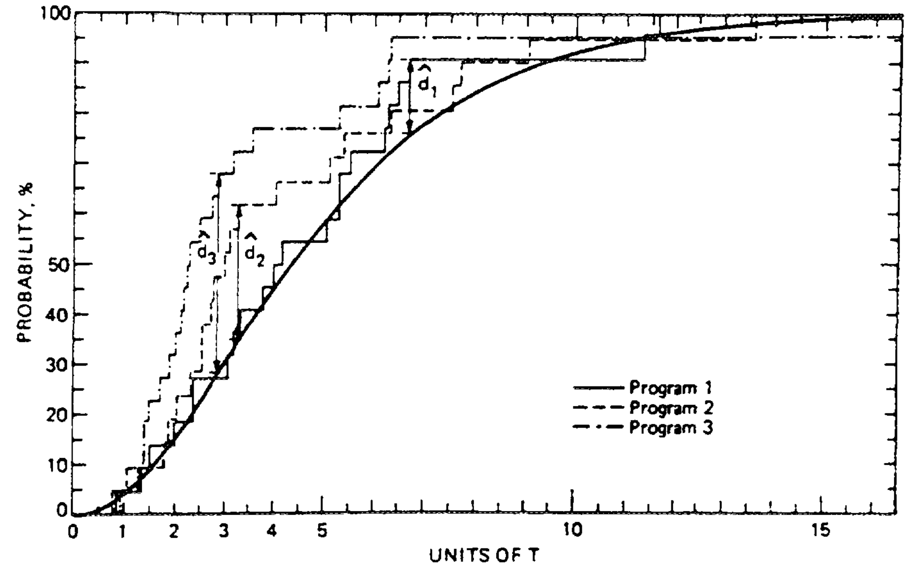

FIG. 1. Cumulative distribution of values of T for three different programs compared with the chi-square distribution for 5 degrees of freedom [3].

The outcome of this test is shown in Table 2 together with the probabilities of exceeding the observed deviation from the true distribution. Clearly, results for program 3 are not random samples from a chi-square distribution, and consequently the method is not in statistical control.

The remaining two programs can now be tested for their agreement with the true results μ_j by the statistic

$$X = \sum_{i}^{m} \frac{(\hat{\mu}_j - \mu_j)^2}{\hat{\sigma}_j^2} \qquad (2)$$

where $\hat{\mu}_j$ is the weighted mean of results for photo peak j and $\hat{\sigma}_j^2$ is the squared standard error of the mean. Results shown in Table 3 ascertain the trueness of results for these methods, when tested by the relevant chi-square distribution.

These two programs can now be used for testing the variability of results obtained by instrumental methods of neutron activation analysis [4] and [5].

TABLE 2. KOLMOGOROFF-SMIRNOV TEST OF CUMULATIVE DISTRIBUTIONS

Program	$\hat{d}$	m	P(d=0)
1	0.154	22	>0.10
2	0.276	21	>0.05
3	0.405	22	<0.01

TABLE 3. TEST FOR ACCURACY OF WEIGHTED MEAN VALUES

Program	X	Degrees of freedom	$P(\chi^2 \geq X)$
1	16.68	20	0.67
2	17.94	19	0.53

5.4. TRACEABILITY

Although traceability has been documented to the IAEA spectra the narrow peaks and the small number of channels might jeopardize the accuracy under practical conditions of measurement. Therefore a special investigation was made of the influence of peak width on the reliability of results [6].

A ^{152}Eu reference source was counted 29 times in succession, while the gain was changed from 0.4 to 0.1 keV/channel in small increments. From these spectra we obtained results for 14 different photopeaks with Full Width at Half Maximum (FWHM) ranging from 2.5 to 15 channels. The statistic T was calculated for replicates of each γ ray, and results are shown in Table 4.

TABLE 4. VERIFICATION OF THE PRECISION OF NORMALISED RESULTS FROM A REFERENCE PEAK EVALUATION PROGRAM FOR REPLICATE COUNTINGS AT FWHM RANGING FROM 2.8 TO 15 CHANNELS

γ-energy keV	Total peak area counts	Number of replicates	Statistic T
245	43440 ± 72	29	23.23
344	103578 ± 95	29	45.95
368	3166 ± 38	29	26.29
411	7281 ± 34	29	22.02
444	9244 ± 39	29	27.40
689	1673 ± 30	29	23.07
779	21074 ± 52	27	30.55
867	6150 ± 44	23	25.25
964	19102 ± 49	19	29.64
1112	15362 ± 48	17	25.66
1213	1505 ± 25	14	10.58
1299	1629 ± 19	13	8.53
1408	19319 ± 45	13	16.01
All energies		300	314.18

With the possible exception of the peak at 344 keV, all peaks are in excellent statistical control with T = 268.2 at 259 degrees of freedom, corresponding to $P(X^2 > T) = 0.34$. Results for the 344 keV peak were subjected to correlation analysis with respect to FWHM and showed no significant correlation in the FWHM range of 3 to 13 channels. Thus, no systematic errors were found to be associated with changes in peak width, and in this way we may accept traceability for the program based on the IAEA spectra in spite of the narrow peaks.

Other programs were tested in the same way, but were found to get out of statistical control for FWHM above 11, as shown in Fig. 2.

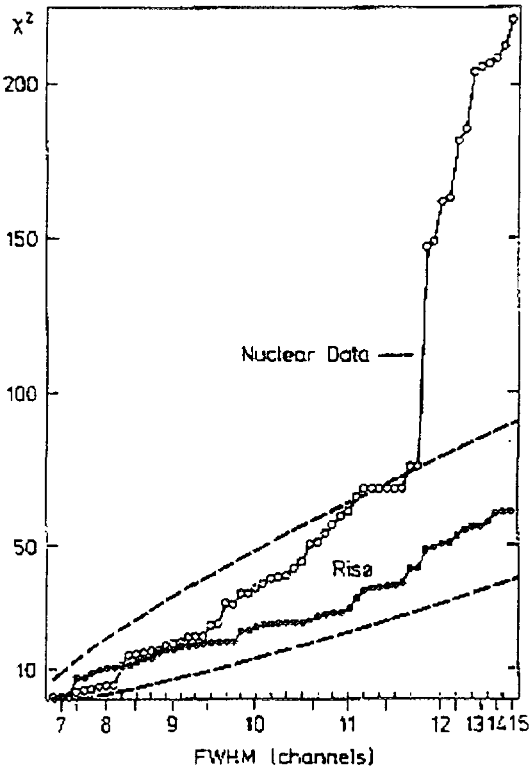

FIG. 2. Cumulative distribution of χ^2-values in the order of increasing FWHM for 61 duplicate peak area results obtained by the Nuclear Data Peak Search Program, shown together with results obtained by the Risø Peak Evaluation Program. The dotted lines indicate 1% and 99% levels of significance [6].

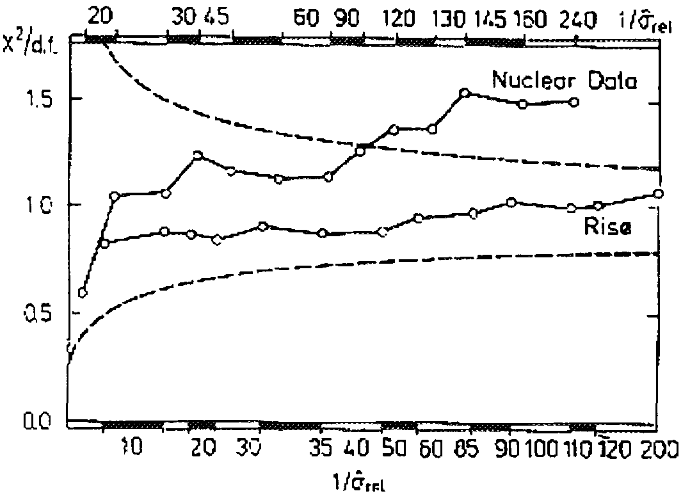

FIG 3. Chi-square over degrees of freedom as a function of relative precision based on results from 13 photopeak areas obtained by the Risø Peak Evaluation Program (lower scale), shown together with corresponding results from the Nuclear Data Peak Search Program (upper scale). Horizontal scales indicate values of reciprocal relative standard deviations, calculated by the respective programs. The dotted lines indicate 1% and 99% levels of significance [6].

5.5. LIMITS OF PRECISION

The loss of statistical control observed with the 344 keV line could also be associated with the high precision of 0.5 % that the peak area has. This was also tested for other programs, and Fig. 3 shows results for the same program as in Fig.2 with the reduced chi-square as a function of relative precision. Below approximately 1% relative precision the ND program is no longer in statistical control. Other programs have the same property, as shown in Fig. 4.

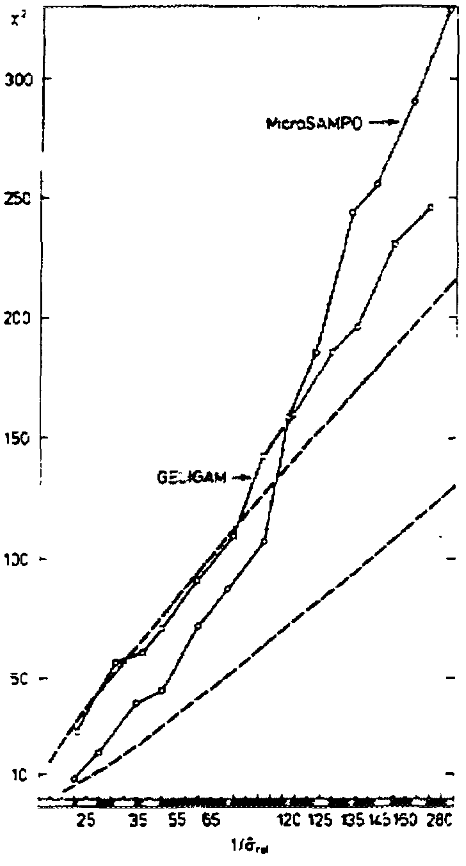

FIG. 4. Cumulative distribution of χ^2-values in the order of increasing precision based on results from 13 photopeak areas obtained by the MicroSAMPO program, shown together with corresponding results from the Ortec Geligam program. The horizontal scale indicates values of reciprocal, relative standard deviation instead of degrees of freedom, and the dotted lines indicate 1% and 99% levels of significance

Increasing peak-width may also result in a systematic change of reported peak area, as shown in Fig. 5.

5.6. RESOLUTION OF DOUBLETS

Overlapping peaks need to be resolved before any statistical control can be ascertained, and most programs have problems with correctly separating those peaks, which are less than one FWHM from each other. This is illustrated in Fig. 6, which shows the error resulting from non-linear fitting of Gaussian peaks to two photopeaks of equal peak area, obtained by a digital offset of two spectra from 1 to 10 channels.

Small peak separations with resulting deformation of the peak shape results in a positive error of up to 50%, while a negative error of more than 10% was observed, even when a satisfactory separation appears to be achieved. Only with a separation in excess of 1.5 FWHM were satisfactory results obtained.

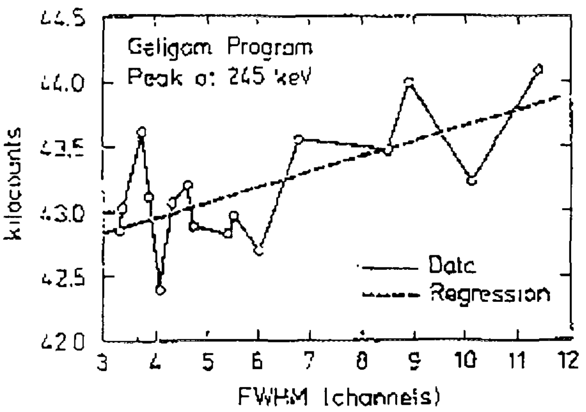

FIG 5. Area of 245 keV photopeak calculated by the Ortec Geligam Program as a function of FWHM [6]. The straight regression line indicates the significant positive correlation observed.

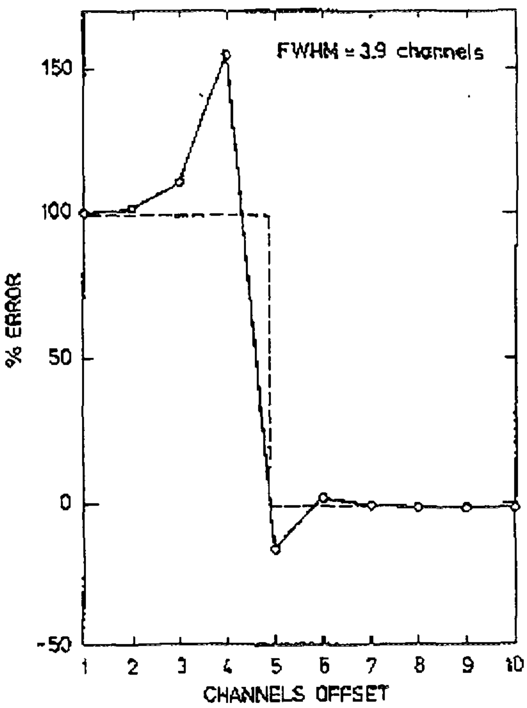

FIG 6. Calculation of peak area of a particular photopeak superimposed on another photopeak with the same area separated by 1 to 10 channels from the photopeak evaluated by means of a typical program using Gaussian fitting. The dotted line shows the correct result corresponding to either completely resolved or completely unresolved photopeaks [7].

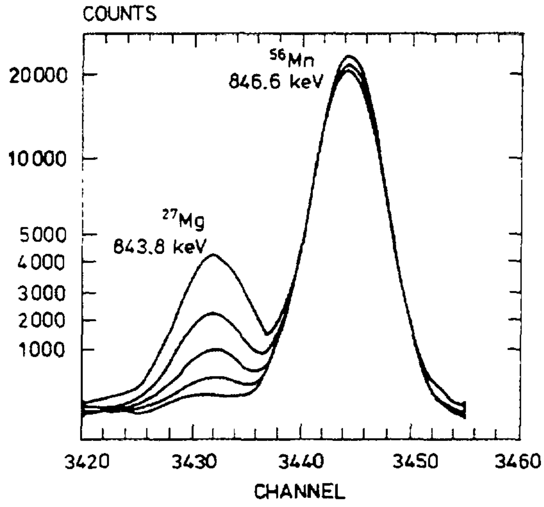

FIG 7. The 843.8 keV and 846.6 keV ^{27}*Mg/*^{56}*Mn doublet recorded at five successive decay times (9, 21, 32, 43, 54 minutes) [8]*

This is, however, not sufficient for satisfactory resolution of peaks of widely different size, and therefore a special study was carried out [8] for the doublet ^{56}Mn/^{27}Mg with a separation of 2.8 keV, corresponding to more than 3 FWHM (see Fig.7).

A BCR reference material with an approximate ratio of 50 between Mg and Mn was irradiated for 1 min at a neutron flux density of 4 x 10^{13}n/cm^{2}s and counted 8 times in succession for 10 minutes. The peak area ratio for ^{56}Mn gamma rays 847 and 1811 keV were determined and found to be indistinguishable from that in pure ^{56}Mn for intensity ratios for 844 to 847 keV up to 0.04. This is clearly seen in Table 5, where the T-test reaches significance and thereby detects interference at a ratio of slightly above 0.04.

TABLE 5: DETECTION OF DOUBLETS BY THE METHOD OF OPTIMUM PEAK BOUNDARY SELECTION

Intensity Ratio	Peak Area Ratio		Analysis of Precision		
(844/847 keV)	(847/1811 keV)	$\hat{\sigma}$	T	d.f	P($\chi^2 \geq$T)
calculated *	measured				
0.20	9.653	0.111	242.2	8	
0.10	8.863	0.102	68.5	7	$<10^{-10}$
0.04	8.221	0.085	11.4	6	0.076
0.02	8.156	0.089	6.75	5	0.24
0.008	7.947	0.084	3.98	4	0.41
0.004	7.877	0.086	3.58	3	0.31
0.002	8.059	0.094	0.40	2	0.82
0.001	8.017	0.091	0.40	1	0.53
Zero	8.099	0.093			

* Approximate intensity ratios at successive decay times calculated for a mixture of 2.5 mg Mg and 50 µg Mn irradiated for 1 minute in a flux of neutrons.

Table 6 shows the corresponding test for the 844 keV from ^{27}Mg, where peak areas are found to be not significantly different from zero up to the same intensity ratio of 0.04, when a peak is detected by the Analysis of Precision. Similar tests were also made for two commercially available programs, and results are shown in Table 8. These results are not in statistical control, and both of them are strongly correlated with the decay time even after correction for decay.

TABLE 6. PEAK AREA EVALUATION BY THE METHOD OF OPTIMUM PEAK BOUNDARY SELECTION

Decay time	Intensity Ratio	Residual	Analysis of Precision		
minutes	(844/847 keV)	$\hat{\sigma}$	T	d.f.	$P(\chi^2 \geq T)$
9	0.20	27721±1592			
21	0.10	14313±1581	80.9	6	$<10^{-10}$
32	0.04	3430±1423	11.4	5	0.04
43	0.02	2186±1420	5.88	4	0.21
54	0.008	-1180±1341	2.49	3	0.48
65	0.004	-2197±1346	2.32	2	0.31
76	0.002	541±1335	0.11	1	0.74
87	0.001	-57±1254			

When the results for the 844 keV peak are corrected for decay and dead time, they are in satisfactory statistical control, as shown in Table 7.

TABLE 7. PEAK AREAS BY THE METHOD OF OPTIMUM PEAK BOUNDARY SELECTION CORRECTED FOR DEAD TIME AND DECAY

Decay time	843.8 keV	Analysis of Precision		
minutes	counts	T	d.f	$P(\chi^2 \geq T)$
9	72352 ±4155			
21	81870 ±9043	4.05	2	0.13
32	42258 ±17531			

TABLE 8. PEAK AREA EVALUATION BY UNRESTRICTED RESOLUTION OF DOUBLETS

Decay time minutes	Peak areas corrected for dead time and decay of ^{27}Mg	
	Nuclear Data	SAMPO-80
9	79311 ± 724	71683 ± 693
21	82287 ± 940	69209 ± 877
32	86693 ±1335	63295 ±1230
43	96322 ±2211	54301 ±1931

When doublet resolution is carried out with known positions of the two peaks, the non-linear fitting is replaced by a much simpler solution of a set of simultaneous equations. These gives far better results for both commercial programs tested, and one of them remains in statistical control through the range of peak ratios from 0.4 to 0.001.

TABLE 9. PEAK AREA EVALUATION BY RESOLUTION OF DOUBLETS INTO PEAKS WITH KNOWN POSITIONS: MODIFIED SAMPO80

Decay time minutes	843.8 keV Peak Area*	Analysis of Precision		
		T	d.f.	$P(\chi^2 \geq T)$
9	76854 ± 728			
21	79322 ± 974	4.12	1	
32	78389 ± 1370	4.31	2	0.12
43	78313 ± 2177	4.35	3	0.23
54	77336 ± 3705	4.37	4	0.36
65	88866 ± 7593	6.47	5	0.26
76	128185 ± 15135	17.5	6	0.008
87	159030 ± 20871	32.6	7	$< 10^{-4}$

TABLE 10. PEAK AREA EVALUATION BY RESOLUTION OF DOUBLETS INTO PEAKS WITH KNOWN POSITIONS: GELIGAM

Decay time minutes	843.8 keV Peak Area*	Analysis of Precision T	d.f.	$P(\chi^2 \geq T)$
9	77906 ± 1460			
21	80261 ± 3130	0.46	1	0.50
32	81038 ± 6563	0.63	2	0.73
43	87660 ± 14200	1.05	3	0.79
54	101090 ± 30529	1.59	4	0.81
65	142971 ± 69627	2.45	5	0.78
76	147954 ± 149433	2.67	6	0.85
87	348053 ± 331346	3.33	7	0.85

* Peak area corrected for dead time and decay

It can therefore be concluded that the resolution of multiplets cannot be expected to give results in statistical control, unless the identity of the components is known in advance.

The choice of components in suspected multiplets should not be left to the computer program and its associated library, because it may lead to completely erroneous results. [7] This is illustrated in Table 11, which lists the radionuclides used for fitting by a program, when the spectrum is a pure ^{152}Eu without any other nuclides present.

TABLE 11. UNSUPERVISED RESOLUTION OF DOUBLETS IN A PURE ^{152}Eu γ-SPECTRUM

^{152}Eu γ-energy (keV)	Doublet reported	
	γ-energy (keV)	Radionuclide
121.8	121.1	^{75}Se
	123.73	^{131}Ba
295.9	298.5	^{160}Tb
344.3	345.9	^{181}Hf
488.7	487.0	^{140}La
	488.9	^{47}Ca
564.0	563.2	^{134}Cs
656.5	657.0	^{76}As
778.9	776.5	^{82}Br
964.1	966.2	^{160}Tb
1112.1	1115.5	^{65}Zn

Unsupervised resolution of multiplets can thus never be trusted.

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6. PROCESSING OF COMPLEX GAMMA RAY SPECTRA[11]

6.1. SUMMARY

In this paper a general review on analysis of gamma ray spectra is reported. At the same time, practical recommendations on the improvements for general-purpose gamma ray spectrum analysis software as well as for particular applications, are given. The present work at the BARC in this field is presented.

6.2. INTRODUCTION

Gamma ray spectrometry is the science (and sometimes art) dealing with the use of gamma spectrometer and subsequent analysis of the data obtained from it. A combination of a detector and subsequent electronic system (including multichannel pulse height analyser) is commonly referred to as a gamma spectrometer. The output of this system i.e. a pulse height spectrum provides information about the energy of incident photons which is deposited (partial or full) in the detector. This spectrum represents the incident energy spectrum of the photons in all respects except for the following two aspects. Firstly, the line broadening effects caused mainly due to inherent statistical spreading in the number of charged-carriers produced [1], convert spectral lines into peaks. Secondly many gamma photons may not impart their full energy to the absorbing medium, in which case, the pulse height will represent only part of the energy. In spite of these limitations the availability of high-

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[11] *Prepared by M C Abani, Bhabha Atomic Research Centre, India*

resolution detectors (especially HPGE) makes gamma ray spectrometric analysis a very important tool in the field of experimental physics. In the field of radiation safety also this technique is commonly used.

To benefit from the high resolution of the presently available detectors, gamma ray spectra should be digitized using a MCA with large number of channels preferably 4096 or 8192. Because of the extremely good resolution of a HPGE detector, the spectrum obtained with this system has a large number of peaks. Various techniques and methods have been developed to analyse this complex spectrum.

6.2.1. Response function

In many applications of radiation detectors, the object is to measure the energy distribution of the incident radiation. These efforts are in general classified as radiation spectroscopy. An important property of a detector in radiation spectroscopy can be examined by its response to monoenergetic photon sources. Because of different types of interactions taking place in the detector even for a monoenergetic photon source, one gets a differential pulse height distribution. This distribution is called the response function of the detector for the energy used in this determination.

6.2.2. Methods for the analysis of NaI(Tl) spectra

Before the advent of Ge(Li) and HPGe detectors, NaI(Tl) detector was used for gamma spectrometry work. Due to poor quality resolution of NaI(Tl), very few peaks are observed in its spectrum. Several methods were developed to analyse these spectra [2, 3, 4]. Most of the methods need generations of response functions of the detector for each component of the spectrum.

In any gamma spectrum the low energy peaks will have a considerable contribution from the Compton interaction of higher energy photons. In the most commonly used method of analysis i.e. the method of least squares, entire spectrum is analysed at a stretch. In this case it is not possible to analyse one peak at a time. For this type of analysis one needs response function of the detector for each energy (or a group of energies for a given isotope) present in the sample. In a simpler approach, i.e. using spectrum stripping method, one peak is analysed at a time. But in this case the errors will go on increasing as the number of peaks increases. Though simpler, it also needs response functions of the detector for various energies of interest.

6.2.3. Analysis of HPGe spectra

Because of its poor resolution, NaI(Tl) detector is seldom used in the laboratory nowadays. HPGe detector has now replaced NaI(Tl) in most of the applications. It has extremely good resolution compared to that of NaI(Tl). We now discuss below the methods used for the analysis of HPGe spectra.

6.2.4. Analysis of Ge(Li) and HPGe spectra

Despite the superb energy resolution of Ge(Li) and HPGe detectors compared to that of NaI(Tl) detector, analysis of their spectra is necessary [5]. Analysis of the spectrum entails firstly the assignment of energy to the peaks of the spectrum and secondly determination of the area under each peak.

Programs developed for the analysis of NaI(Tl) spectra could not be used directly to analyse data obtained using Ge(Li) or HPGe detectors. With the large number of data points in the HPGe spectrum and its capability to resolve the complex peaks (which increases the number of peaks, in a spectrum significantly) and also somewhat non-Gaussian shape of the peaks (specially tailing on the low energy side) and increased prominence of escape peaks (due to poor efficiency of the detector), the approach for analysis of these spectra have to be complete different.

In analysing the data obtained using a NaI(Tl) detector, great emphasis is on the calculation of response functions. In case of HPGe Spectra, such response functions are not readily available; and even if they are available, it will be difficult to handle them mathematically. This is because of the fact that these detectors have much better resolution and thereby their spectra have large number of peaks. Similarly stripping method cannot be applied in this case because when one goes on subtracting one component after other, statistical errors go on accumulating.

The high resolution of semiconductor detectors suggests another approach. Due to the high resolution, the peak overrides the Compton and therefore it is possible to get information about energy and intensity from a peak after subtracting the Compton contribution due to higher energies present. This method has two advantages.

(1) Since no response function is required, it can be applied to different detector systems and experimental conditions.

(2) Errors and uncertainties of one part of the, spectrum do not propagate to the other and therefore errors don't. get accumulated.

Unlike the assignment of energy to a peak, which is straightforward, the determination of the area under a peak is not simple. It is because of the fact that the area under a peak includes contributions from other high-energy gammas that are present in the sample. For calculation of correct area this contribution has to be subtracted from the peak area. Normally photo peak is chosen for this analysis because its energy is generally characteristic of the isotope and in this on a better sample to background counts ratio is obtained. However, while selecting a photo peak there are many factors which will influence its choice. The various criteria used are as follows:

(1) It is essential to select a peak, which does not overlap with the peaks of other radionuclides.

(2) It is desirable to select peaks exhibiting a high total counting efficiency. This encompasses two factors
    - Gamma abundance
    - Gamma energy (low-energy photons will have a higher intrinsic efficiency, resulting in a higher peak to Compton ratio).

(3) But low energy peaks show high Compton interference from high-energy peaks, while in high-energy peaks this interference is less prominent. Thus a judicious choice has to be made.

(4) Low energy peaks are less influenced by gain shift.

(5) High-energy peaks give better resolution by definition.

It is important to note that the above criteria can be used only as a guideline. The actual selection will depend upon the particular spectrum.

After selecting the photopeak position, one has to find the total number of channels within the photopeak, which are to be used for the peak area calculation. The thumb rule is to take equal number of channels on both sides of the peak so that gain shift of one channel will not affect the result to a great extent. Because of the nearly Gaussian (normal) shape of the peak, the counts lost due to the gain shift of one channel will be approximately equal to the counts gained.

The methods that have been developed for determination of the area can be classified into two groups, (i) methods that treat the data in the peak (i.e. counts per channel) directly and (ii) the methods that fit a known function to the peak region.

An easy method of analysis of a gamma ray spectrum is to sum the counts in the full energy peak (photopeak) region. Methods that treat the data directly give the area under the peak by adding the counts from all the channels in the region of the peak and subtracting a "base background". The methods differ in the way they define the "base" and the number of channels that define the peak. Some methods use a straight line to define the base while others use a low degree polynomial. It is easy to use this method. The use of this method has been nicely explained by Covell [6]. However, this approach is not commonly used for the analysis of HPGe spectra.

6.2.5. Analytical approximation of gamma ray spectra

The most commonly used methods nowadays are those which fit an analytical function to a peak. This function is used for the calculation of quantities of interest such as the Centroid (position) of the peak, the area (intensity) under the peak, counts in the peak channel and full width at half maximum (FWHM), etc.

The shape of the peak depends upon the physical process-taking place in the detection of gamma ray and varies from one detector to the other. It will depend both on the size and quality of the material of the detector.

Various analytical functions, which define the peak shape and background, are available in the literature. Helmer and Lee [7] have given a good account of these functions. In most of the cases, fitting is performed by non-linear least squares method. In order to achieve a fast and high precision analysis a minimum number of parameters should be analysed to define the peak. Some analytical representations commonly used are discussed below.

6.2.6. Physical aspects

The exact calculation of the response of a detector to photons is very difficult because of the complex physical and statistical phenomena involved in the gamma ray interaction process. The calculation requires a precise knowledge of the property and structure of the detector, which are not well understood in most cases. For this reason and also because the shape of a peak can be sensitive to small variations in the experimental parameters such as, counting rate and degree of collimation, one has to determine directly an analytical representation for the photopeak. However, to define an analytical representation one has to take into account the physical mechanisms involved in detection of gamma rays.

The first contribution to the photopeak in a semiconductor detector is due to the statistical fluctuations in sharing the absorbed energy between ionization and heating the crystal network. This gives rise to a Gaussian distribution with a small width.

The average energy (ε) required to create a pair of electron hole in a cooled germanium detector is 2.91 eV. The variance, σ^2, of the produced electron holes is given by

$$\sigma^2 = \frac{F.E}{\varepsilon} \tag{1}$$

where E is the incident energy of the photon and F is the Fano factor. F is about 0.13 for germanium. The contribution from statistics to the full width at half maximum (FWHM) is given by

$$\text{FWHM} = 2.355\left(\text{E}\varepsilon\text{F}\right)^{1/2} \tag{2}$$

The difference between the calculated FWHM given by eq.(2) and the measurement depends on factors such as the quality of the detector and the associated electronics. The physical properties of the material and the impurities in the detector affect the charge collection and the electronic background. Incomplete compensation of the impurities and partial collection of the charges deteriorates the energy resolution and cause a distortion in low energy side of the peak. In low energies, the contribution of the preamplifier to the background is high. At higher energies, the instability of the amplifier and the analyser affects the width of the photopeak. The continuum under the peak is due to Compton effect from gamma rays of higher energies and the normal background.

Following the considerations given in the preceding section, the analytical representation of the photopeak should have a principal Gaussian form. However, a deviation from this Gaussian form can be included in the analytical description if required.

6.3. WORK DONE AT OUR LABORATORY (BARC, INDIA)

Some work in developing the spectrum analysis methods has been done in our laboratory. It is described below briefly.

Most of the codes for the analysis of Ge(Li) or HPGe detectors were originally written for the mainframe computers. They need large memory and are computationally intensive because they mostly use iterative methods. In our laboratory we have developed a program which needs much less memory space and is non-iterative [9]. Details of the program are given below. It can be easily implemented on PC's.

Basic formulation for this package is from reference [8], which has been extended to analyse complex spectra and made interactive. The program works on the following lines:

(1) **Smoothing of data**: Data is smoothed to remove random fluctuations. The convolution coefficients of Savintzky and Colay [10] have been used for this purpose.

(2) **Method for peak location**: For finding the peak locations, correlation technique is applied on the smoothed data. The algorithm used here is due to Robertson et al [11] and can be viewed as a sliding digital filter. In this type of data, the width of the correlation function is chosen in such a way that whenever slope of the spectrum is constant or slowly varying within the limits of statistical fluctuations, the value of correlation co-efficient tends to zero. It helps in rejecting Compton edges and backscatter peaks, which are slowly varying functions. After calculating the correlated spectrum, a test is applied to find out the statistically significant peaks.

(3) **Peak limits and background subtraction**: After finding the peak positions, the program analyses each peak in a sequential order. The first part of the analysis is to find out the limits for each peak i.e. the first and the last channel of the peak, commonly called the "region of interest" (ROI). Various algorithms are available to find the ROI.

Finding ROI is important because one will have to subtract the background from this region (i.e. contribution of high-energy photons in this region), and then calculate the area under the peak. Helmer and Lee [7] have given compilation of these methods. In the literature various methods have been described for the background subtraction; however, the most commonly used functions are:

- linear
- Polynomial (low degree) and
- Step like fit (Gunnink's method) [12].

Since our program is interactive in nature, it gives the user an option to choose any one of types of background functions given above.

After background subtraction, Gaussian fitting is performed on the peak (in the ROI) using linear least squares criteria. For this purpose, the Gaussian function is linearized and the two parameters **m** and **b** which define the peak are calculated, **m** and **b** are slope and intercept of the straight line $Y= mX+b$. Detailed formulation is given in reference [9]. Using this formulation value of σ and peak position are calculated. Once σ is known, area under the peak can be calculated as follows:

FWHM = 2.355 x σ

Area = 1.064 x FWHM x Peak count

where peak count is the number of counts in the peak channel.

For the purpose of comparison, the peak area is also found by simple summing of the counts (after subtracting the background) in the peak region. The program also calculates the coefficient of fit and the percentage error in the calculated peak area counts. A typical output after fitting a singlet is shown in Fig 1.

(4) **Fitting of doublets:** In the second part of the program, doublets are fitted. By looking at the results, user can decide where doublets are expected. When a doublet is fitted as a single peak, the full width at half maximum [FWHM] will be very large and value of coefficient of fit also will be much higher than expected in that ROI.

In the first part of the program, user is asked a question whether or not to make a table of FWHM. If the answer is 'YES', a table is created which will contain the channel numbers and their corresponding values of FWHMs. This table is saved in a file. FWHM data file should be created using standard sources containing well-resolved singlets and also this data should have a good counting statistics.

For fitting the doublets, the program needs the channel limits where a doublet is expected. Once this limit is specified, the program assumes that FWHM for both the peaks in the doublet is same. This is a reasonable assumption as both the peak positions would always be close to one another.

The formulation used for finding the exact peak positions in the doublet and area under the peak are taken from Mukoyama [13]. He defines a doublet as the sum of two Gaussian functions. Fig. 2 gives a typical output obtained after fitting a doublet.

```
 FITTING PEAK AT CHANNEL NO.  426

 LEFT   418       285.09          RIGHT   433        215.09

CHANNEL          DATA     SMOOTH DATA  BACKGROUND   COUNT-BG   CONV FUNCTION

  415           295.00      294.57
  416           296.00      292.66
  417           280.00      279.66
  418           279.00      285.09      285.09        1.00          0.00
  419           329.00      322.49      280.42       42.07          0.00
  420           395.00      399.54      275.75      123.79          0.00
  421           518.00      522.37      271.09      251.29          0.00
  422           686.00      665.43      266.42      399.01          0.00
  423           836.00      869.86      261.75      608.10          0.00
  424          1145.00     1133.60      257.09      876.51        584.67
  425          1395.00     1397.20      252.42     1140.78       1372.39
  426          1501.00     1491.31      247.75     1243.56       1579.20
  427          1399.00     1387.77      243.09     1144.69       1375.39
  428          1138.00     1157.54      238.42      919.12        772.29
  429           898.00      888.49      233.75      654.74         96.77
  430           631.00      631.26      229.09      402.17          0.00
  431           403.00      406.09      224.42      181.67          0.00
  432           265.00      267.57      219.75       47.82          0.00
  433           215.00      215.09      215.09        1.00          0.20
  434           209.00      204.80
  435           205.00      206.77
  436           210.00      205.03

AREA FOR PEAK NO.  6

                          12036.69     4001.37     8037.31

RR =  0.997     FWHM =  6.037

PEAK  POSTION =  426.073

        AREA CALCULATED      7989.88

        % ERROR IN COUNTS  ±  1.576
```

FIG 1. Computer output for a singlet calculation.

```
            Fig. 2. : Computer Output of a Doublet.


CHANNEL LIMITS ARE  1838     1859
FWHM =            4.771605    NC =             1848

FIRST PEAK CHANNEL & PEAK COUNTS =             1846.28        3300.851
AREA OF FIRST PEAK =  16758.38

SECOND PEAK CHANNEL & PEAK COUNTS =            1852.362       9985.98
AREA OF SECOND PEAK =  50698.7
```

FIG. 2. Computer output of a doublet.

6.3.1. Digital signal processing methods for analysis of complex spectra

Most of the peak-fitting programs use least squares fitting functions. An alternate to this approach is using methods of digital signal processing. Inouye [14] has proposed a signal processing method using a Fourier integral transform. In our laboratory we have used the modified discrete Fourier transform to analyse the doublets. In this analysis the raw spectra are processed in steps that include smoothing, finding peak limits to get spectral envelopes, background subtraction, identification of the components of the doublets, area evaluation under the envelopes and their division to get areas of the components of doublets. For background subtraction, Gunnink's method [12] has been used. This complete method is described in detail in ref. [15].

6.3.2. Use of SAMPO

Our laboratory extensively uses SAMPO [16, 17] program for analysis of complex spectra obtained by using HPGE detectors. We have got the mainframe version of SAMPO available with us for nearly two decades. A few years back this program was modified and made compatible for use with microcomputers. This program is extensively used for the analysis of various types of samples such as fission products, neutron activation products, environmental samples, marine samples, food samples, etc. Another area of health physics where they are extensively used is whole body counting and bioassay analysis. An interesting example where this methods has been used is described below

6.3.3. Estimation of Pu/Am ratio

Persons working in a reprocessing facility are likely to inhale dust containing insoluble plutonium. Pu will remain in longs for a long time after inhalation. The main decay component of Pu is alpha., and it cannot travel more than a few microns in tissue. Thus, it is not possible to detect the Pu in lung by alpha counting methods. Pu also emits a few gamma rays but their yield is very low. In addition to these radiations, Pu decay gives uranium L-X rays by internal conversion. Other isotopes of Pu are also present in the sample to a small extent. ^{241}Pu decays by beta emission to ^{241}Am. With a half life of 14.5 years. Thus with the passage of time, the quantity of ^{241}Am will go on increasing. ^{241}Am decays by alpha emission and also gives neptunium L-X rays. Since Am is always associated with Pu, it can be used as a tracer in the estimation of Pu [18]. Normally nasal swipe or excreta of a subject is analysed to estimate the Pu burden in the body. The energies of L-X rays of uranium are 16.43 keV and 17.22 keV and that of neptunium 16.85 keV and 17.75 keV. Since these X rays are very closely spaced, one has to use a detector having high resolution for the analysis of the sample. Normally, HPGe or Si(Li) detectors are used for this purpose. It is observed that even HPGe detector is not able to clearly resolve these closely spaced X ray energies. Thus one has to take recourse to peak fitting methods. We have used the SAMPO program for this purpose. The program is able to resolve all these peaks and gives fairly accurate results. Using data from this fit, it is possible to calculate the Pu/Am ratio in a sample.

6.3.4. Aerial gamma spectrometric survey

Around all the nuclear plants, routine radiological survey is carried out to asses the impact of the normal operations of the plant on the surrounding environment. These surveys are carried by a variety of fixed and mobile monitoring systems on a routine basis. However in case of a major reactor accident or release of a large airborne activity due to any other reason, a very wide area (spanning into few square kilometres) may get contaminated. In such a situation the prime objective will be to promptly assess the levels of the ground contamination, so that quick counter measures can be taken for mitigating the radiological consequences.

The aerial survey of a contaminated area offers many advantages over the ground-based survey, because it is quick, flexible and leads to minimum exposure of monitoring personnel. The main advantage will be that it can cover a wide area in a short time and also it is possible to survey the areas that are not easily accessible to ground survey teams. An easier way to estimate the ground contamination is to do aerial survey using a dose rate meter. Dose rate measured at an altitude of approx. 100 meters may give erroneous results about the level of contamination on the ground. As the attenuation coefficient (μ) is energy dependent, the dose rate recorded by the survey meter (which is at a reasonable height from the ground level) will depend on the energy of the isotope. Also for applying control measures on vegetation, food, etc. It is essential to identify the radionuclide contaminating the ground apart from finding out the level of contamination. Thus aerial gamma spectrometric survey is the only viable alternative for quick assessment of contamination over a wide area.

Because of the high efficiency and ease of handling under field conditions, normally NaI(Tl) is used as a detector in aerial surveys. It is connected to a 256 channel MCA and a Laptop PC-386 for quick analysis of data. During the survey a spectrum is acquired every one or two seconds and stored in the PC memory in a sequential order for further analysis.

The main aim of an aerial survey exercise is to estimate the minimum detectable level (MDL) of ground contamination and the optimization of flight parameters like speed, altitude, etc. Since in normal times it is not possible to have uniform ground contamination over a wide area- this situation is simulated by deploying on the ground- sources of known strength in a uniform gird pattern. Radioactive isotopes of short half life are normally preferred for such exercises. This type of exercise is conducted in two parts. In the first part the entire area is surveyed as it is, to generate the base line data. Base line data becomes the reference value for comparison in case of accident situations. In the second part of the survey, as explained above, sources are deployed in a grid pattern. The distance between sources is optimized such that from a far off distance, they give the impression of an uniform ground contamination. Normally ^{192}I, ^{137}Cs and ^{60}Co sources are used for this survey. Since the data generated is voluminous and the number of isotopes is only few, stripping method is normally used for analysis of the data.

Two such exercises have been successfully conducted in our country. The main aim of these exercises was to generate the calibration factors for the detector system and estimate the correlation factors at various heights corresponding to different levels of ground contamination. Although this data can be generated theoretically, an experimental validation is essential before the system can be used in an actual emergency situation. Within the limits of experimental uncertainty, the experimental results matched very well with the theoretical data. The exercise described above is an important practical application of gamma spectrometry in an emergency situation.

6.4. PRESENT STATUS IN INDIA

In conclusion I would say that our research centre is extensively using the technique of gamma spectrometry in the field of nuclear physics, radiation safety and emergency preparedness. Presently we are mostly using Si(Li) and HPGe detectors but still there are situations where NaI(Tl) is preferred due to ease of handling. Most of the analysis is done using IBM PCs. Efforts are made continuously to develop software for the purpose of peak finding, peak area calculation and fitting of doublets & multiplets, etc.

For exchange of information in the field of gamma spectrometry and to make scientists aware about the state of the art both in the fields of detectors as well as spectrum analysis, we regularly conduct gamma spectrometry workshops. Intercomparison between various methods of spectrum analysis used by different units of Department of Atomic Energy (Government of India) is done periodically.

6.5. CONCLUSIONS

From the discussions above, it can be concluded that for accurate analysis of spectra obtained using NaI(Tl), generation of response matrix of all the radionuclides present in a sample is essential. Sometimes it may not be possible to generate response matrix of all the radionuclides because standards for all these may not be available. In such a case the analysis will not be accurate. In case of spectra obtained from semiconductor detectors no such limitation exists i.e. one does not need all the standards for the analysis. It is a great advantage.

Also due the easy availability of microcomputers and computer-based analysers, the task of data reduction and qualitative and quantitative analysis of gamma spectra has become much easier.

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7. EVALUATION OF ACTAN CODE IN GAMMA RAY SPECTRA PROCESSING[12]

7.1. SUMMARY

The program ActAn is a research grade Gamma Spectroscopy and Neutron Activation Analysis software package recently developed. Spectrum analysis includes peak search, peak fitting, nuclide identification and activity calculation. Using experimental peak shape functions makes possible to resolve complex multiplets with strong overlapping peaks at peak separation up to 1.5 FWHM. The ActAn code was used to analyze the IAEA G-1 Intercomparison Spectra as one measure of the code performance. Peak search and area calculation algorithms for singlets and deconvolution procedures for multiplets were tested. The results show that singlet peak area determination is in statistical control. Small peak search and multiplet deconvolution capabilities of the code are excellent.

7.2. INTRODUCTION

In the past, gamma ray analysis codes such as GAMANAL [1] and SAMPO [2] required the use of large mainframe computers to perform data analysis and spectral identification. The recent development of the IBM PC™, PC-XT™ and PC-AT™ classes of personal computers has resulted in a dramatic increase and availability of microcomputers. Moreover, with the introduction of the whole data acquisition system directly into the personal computer, we have powerful data acquisition and processing capabilities. It could be used in the field to provide immediate results, as well as in the stable environment of the base laboratory. Besides, from the economical point of view, these new systems are available even for laboratories in developing countries.

In co-ordination with the IAEA Physics Section the ActAn computer code was developed. It is a research grade Gamma Spectroscopy and Neutron Activation Analysis program designed to work on a standard personal computer. It is intended for the analyst who requires the maximum flexibility in the analysis of complex gamma pulse height spectra. A menu-base user interface and other interactive options have been designed to make the program more *user friendly*. This paper will discuss the evaluation of the gamma ray analysis part of the ActAn code.

7.3. METHODS

Gamma spectrum analysis includes peak search and area determination. A number of computer programs for analysis of germanium detector gamma spectra have been reported. A good review is given in Refs.3 and 4. None of the programs seemed to satisfy all the

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[12] *Prepared by R. Capote, R.Perez, L. F. Desdin, P. Sarria (Center of Applied Studies for Nuclear Development) and V. Osorio (IAEA); The authors are very indebted to E.Lopez for several suggestions and fruitful discussions.*

requirements of a completely automatic and reliable peak search and multiplet deconvolution in an efficient, easy to use program. In the development of the ActAn program many techniques and algorithms were considered from Refs. 1,2,5,6,7 and 8. We have adopted those which worked best over the wide variety of spectra tested, and have modified or devised new techniques where necessary for reliability, accuracy, speed and efficiency.

7.3.1. Peak search method

The ActAn peak search routine is based on a combination of zero-area square-wave and rectangular filters as proposed by Philips and Marlow [5]. However, additional tests had to be included to discriminate against Compton edges and other non-peak structures. Peak and resulted convoluted spectrum are shown in Fig.1.

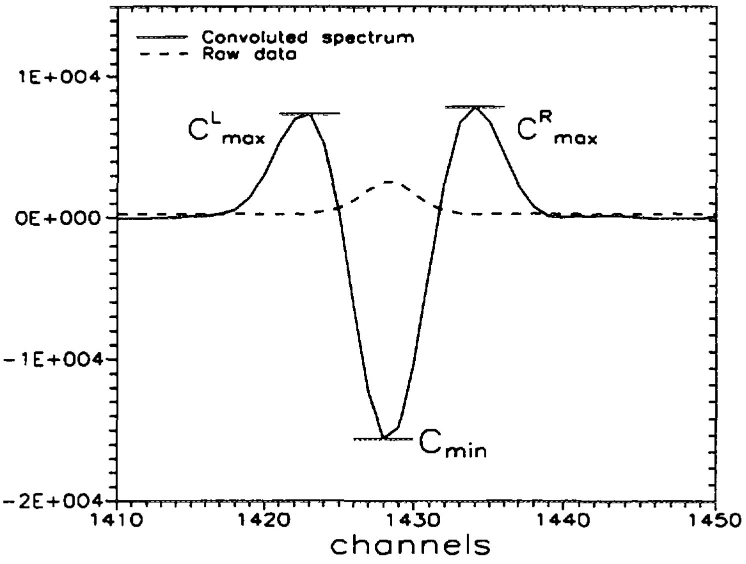

FIG. 1. Convolution function used in the ActAn code for peak search.

We define two quantities, namely K_1 and K_2:

$$K_1 = \frac{\left(C^L_{\max} + C^R_{\max} - C_{\min}\right)}{\sqrt{\left(S^L_{\max} + S^R_{\max} + S_{\min}\right)}} \qquad K_2 = \frac{2*\left|C^L_{\max} - C^R_{\max}\right|}{-C_{\min}} \qquad (1)$$

In the above formula C and S are convoluted spectrum and corresponding statistical variance for each channel (see Fig.1 for explanation of the symbols in equation (1)). A non-peak structure is rejected if the quantity K_1 is less than five. If K_1 is less than 30, then the possible peak is accepted as *small*, otherwise the possible peak is investigated to discriminate against Compton edges. The quantity K_2 serves as the measure of the asymmetry of the peak. Whenever K_2 is greater than 0.8 this peak is taken as a possible Compton edge. Final judgement is done according to the following criteria: if $\left(i_{peak} - i_{\max}^{L}\right) \geq 1.905 * FWHM(i_{peak})$ or $\left(i_{\max}^{R} - i_{peak}\right) \geq 1.905 * FWHM(i_{peak})$ then a possible peak is rejected. These criteria were defined according to 2-year experience in processing quite different gamma ray spectra resulting from neutron activation.

In this way all the peaks in the spectrum can be found. To test the search routine of the ActAn code we used the IAEA G1 Reference Spectrum S200. Results are reported in the following section. Special importance for the statistical quality of the results has the selection of fitting intervals. The ActAn code uses an "*a priori*" choice of the integration limits of the photopeak according to the experimental peak shape previously stored. The final channel of the peak region *iend* is taken if no other peak is present in 1.5*FWHM channels of the last peak, otherwise the limit is recalculated taking this new peak as the final in the region. In this way limits for all singlets and multiplets in the spectrum can be determined.

7.3.2. Peak shape function

The typical semiconductor gamma ray spectra are normally analysed on the assumption that peak shapes are represented by some modified gaussian function including both low and high-energy tailings. In the vicinity of the peak, the spectrum is described

$$y_i = B_i + \sum_{j=1}^{NP} h_j p\left(\sigma_j, i - O_j\right) \tag{2}$$

where y_i is the number of counts in channel *i*, B_i is the baseline or background function at *i*, NP is the number of peaks in this region, *p(...)* is the peak shape function, σ_j and O_j are the standard deviation and position of the j^th^ peak, and h_j is the height of the j^th^ peak. The Poisson error is generally much smaller than B_i and h_j, and was not considered. A number of analytical peak shape functions have been recently reviewed by Debertin and Helmer [3]. Special feature of the ActAn code is the adoption of an experimental peak shape function to calculate the peak shape via interpolation in an empirical peak shape table, as was proposed by Ritter and Currie [9]. In this way very time consuming calculation of trascendentals is avoided. The table is derived from a series of standard peaks recorded with the gamma spectrometer using known isotope sources with a few statistically good well-separated singlets. The ActAn code uses direct parabolic interpolation among the peak shape table entries to fit experimental peaks. This method is very fast. Experimental peak shape fitting uses scaling of the peak shape table as proposed by Stockman [10].

7.3.3. Background evaluation

In addition to peak description, background should be assessed in the simplest instance by linear interpolation between peak limits or by a number of mathematically derived functions. The ActAn code employs the peak stripping method as described by Ralston and Wilcox [11] to calculate the local background under an isolated peak or multiplet. The method is based on the removal of rapidly varying structures in the spectrum by replacing the channel content y_i with the average $\bar{y}_i$ over an interval *(2N+1)* about i whenever $(y_i - \bar{y}_i) > \alpha\sqrt{\bar{y}_i}$, where $\bar{y}_i = \frac{1}{(2N+1)}\sum_{j=i-N}^{j=i+N} y_j$.

The resulting secondary spectrum is treated in the same way with a smaller value for α. The procedure is carried out 10 times, α taking the values 9.2,8.2,...,0.2. As pointed out in Refs.11 and 12 the success of the technique depends upon the choice of the number of smoothing points N. We have taken the interval (2N+1) equal to 0.7 FWHM at the peak region. As was shown in Ref.12 in the Ralston-Wilcox type methods, we have to be aware of possible long-range influences on the calculated background. This will most likely occur when the peaks are superimposed on Compton edges or when they are situated in a very crowded portion of the spectrum. In this special case, we use the empirical method developed by Westmeier[13], where an explicit function calculates the interpolated background values under the peak grouping. This function was modified to take into account the slope of the background. The modified function has the following form:

$$B_i = B_H(i) + \left[B_L(i) - B_H(i)\right]\frac{\sum_{j=i}^{iend}\left(y_j - B_j^{(0)}\right)}{\sum_{j=ibeg}^{iend}\left(y_j - B_j^{(0)}\right)} \tag{3}$$

where:	B_i	computed background at channel *I,*
	ibeg	the first channel of the peak region,
	iend	the last channel of the peak region,
	$B_i^{(o)} =$	previously computed background by the iterative peak stripping method,
	$B_H(i) =$	average background level of the high energy side of the peak, calculated as the weighted average of the previously computed background and the straight line fitted to five channels after *iend* channel,
	$B_L(i) =$	average background level of the low energy side of the peak, calculated as the weighted average of the previously computed background and the straight line fitted to five channels before *ibeg* channel.

This empirical function is similar to the one proposed by Gunnick [1, 7] and employed in the GAMANAL program. It produces smoothed steps in the background that occur at positions of greatest intensity. In the ActAn code this empirical function is employed, whenever background levels at beginning and at the end of the peak region are different by more than 20%. Typical step background under multiplet superimposed on the Compton edge is shown in Fig.2.

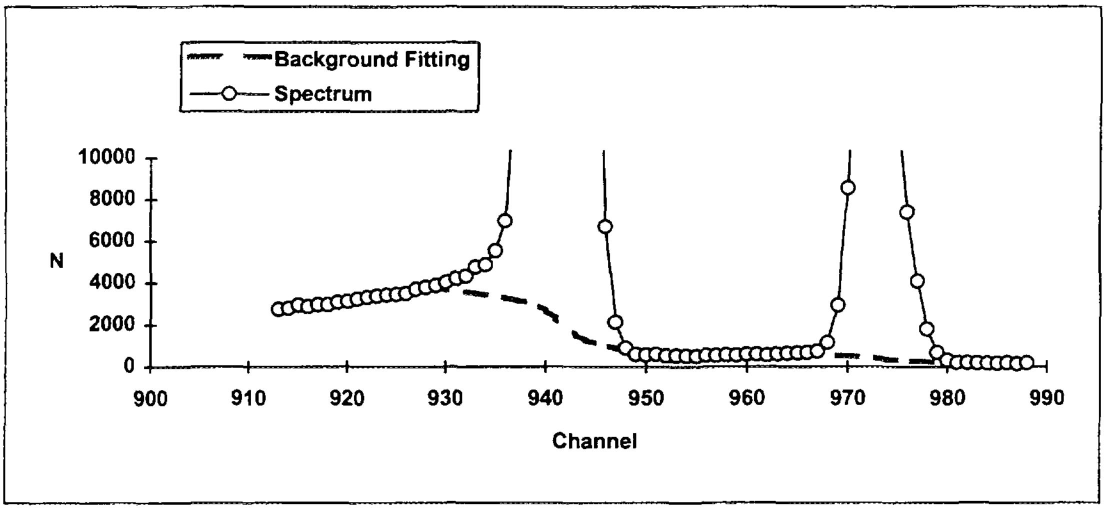

FIG. 2. Step background used in the special case of peak superimposed on a Compton edge or other non-linear background.

7.3.4. Peak area evaluation

Once background is evaluated, we should finally calculate the net area under peak regions. The ActAn code differentiates two cases: a) singlets, b)multiplets.

In the first case the net peak area is calculated using the Total Peak Area (TPA) method, employing the gross counts in the spectrum and subtracting the calculated background under the peak. In TPA integration the summation was stopped when a point in the peak wings was smaller than the calculated base line.

In the second case, the net area of the peaks in the multiplet is calculated by fitting, according to the experimental peak shape previously stored. Open multiplets are deconvoluted by linear method of fitting [14]. In this case only peak heights are free parameters and can be obtained solving a system of linear equations. The resulting linear system is solved efficiently by the Gauss-Seidel iterative method with 3 iterations. The implementation is straightforward and it can be done using fast integer arithmetic [10]. Closed multiplets, the most complex case, are processed, by non-linear least squared fitting, where peak heights and peak positions are free parameters. The experimental peak shape functions are calculated by numerical parabolic interpolation and scaling, from the stored peak shape table, as done in the linear case.

After deconvolution the peak centroid positions are refined. For each peak the central 5 channels are stripped of the components of all other interfering peaks. A parabola is fitted to these five channels, and the turning point of the parabola is taken as the new estimate of the peak centroid.

In all cases search of residual is done. The residuals spectrum R_i is calculated via

$$R_i = y_i - B_i - \sum_{j=1}^{N_p} h_j p(\sigma_j, i - O_j) \qquad (4)$$

for all channels $\imath$ such that $i \in [ibeg,iend]$ and fitted spectrum $\sum_{j=1}^{N_p} h_j p(\sigma_j, \imath - O_j)$ is greater than background $B_\imath$. The three channels where residuals get maximum value are selected. A new peak at channel k is accepted if:

(1) $R_k \geq \sqrt{y_k}$,

(2) $R_k \geq \sqrt{y_k}$,

(3) $|k - O_j > 0.25 * FWHM(k)$ for all j,

(4) $(Y_k - B_k)\ R_k < max\_ratio$,

where *max_ratio* is typically 5 to 15. Only one peak can be added per residual search, deconvolution of the peak group terminates when residual searches fail to identify a new peak.

7.4. VALIDATION

No single program for gamma spectra evaluation is likely to be superior under all experimental conditions, and no method of photopeak integration has been found to be the best in every respect. In the published documentation of computer programs, quality assurance should be based on internationally recognized standard reference spectra. Such reference spectra are distributed as the G-1 test spectra set by the IAEA as a part of its analytical quality control services [15]. The set consists of nine separate gamma ray spectra: a reference spectrum (S100), a peak detection test (S200), one spectrum to test multiplet determination and resolution (S400) and six replicated spectra (S300-S305) with 22 photopeaks differing only with respect to the counting statistic. The S100 reference spectrum was used to make the energy and peak-shape calibrations. Peak areas determined in the reference spectrum were used as a benchmark to determine how well ActAn performed in each of the three following tests:

(1) Detection of single peaks nears the limit of detectability. The ActAn code was able to detect 18 of the 22 expected peaks using the primary sensitivity parameter equal to three (3-sigma level). It is interesting to remark that no false peaks with relative errors less than 90% was detected, even in the region of a large simulated Compton edge. A summary of the results is shown in the Table 1. For detected peaks expected and calculated ratios to the corresponding S100 reference spectrum areas are shown. Between parenthesis the calculated error is given. The data is almost self-explanatory. The quality factor for peak detection, as defined in Ref.15 is 0.82. Therefore, the code performance in detection of small peaks can be evaluated as excellent.

(2) Peak positions and areas of easily detectable single peaks. The general features of the replicate spectra for this test are the same as for the *Peak Detectability* test. The six spectra supplied differ each to other only in the counting statistic. They allow employing the methodology of Heydorn [16] for quality assurance of singlet peak area

integration method. The test parameter T is calculated from a set of six areas A_{im} for each mth detected peak with its associated standard deviation $\sigma_{i\,m}$ according to

$$T=\sum_{m=1}^{22}\sum_{i=1}^{6}\frac{\left(A_{im}-\bar{A}_{m}\right)^{2}}{\sigma_{im}^{2}} \tag{5}$$

TABLE 1. SUMMARY OF RESULTS FOR THE PEAK FIND TEST (S200 SPECTRUM)

No	Peak calc.	Centroid expected	Net Peak Area	Actual Ratio	Expected Ratio
1	214.1	214	1145 ± 421	104 ± 38	78.65
2	284.3	285	655 ± 418	184 ± 117	133.54
3	520.8	521	2942 ± 459	53 ± 8	58.89
4	632.2	632	1085 ± 429	159 ± 63	146.53
5	767.2	767	2086 ± 426	91 ± 18	83.88
6	827.6	827	1322 ± 346	144 ± 37	138.23
7	927.1	927	1715 ± 524	122 ± 37	109.64
8	967.4	967	1458 ± 463	152 ± 48	142.86
9	1107.5	1107	800 ± 74	289 ± 26	283.58
10	1187.7	1188	539 ± 75	267 ± 36	263.16
11	1309.7	1309	193 ± 71	1341 ± 493	1014.49
12	1398.8	1398	283 ± 65	925 ± 214	963.86
13	1467.7	1467	219 ± 62	1196 ± 337	1005.59
14	1566.3	1566	527 ± 69	242 ± 31	263.16
15	1741.8	1742	41 ± 39	4318 ± 4080	1014.49
16	1834.6	1834	167 ± 59	1876 ± 661	2222.22
17	1898.1	1899	146 ± 51	1585 ± 557	2618.18
18	1960.7	1961	507 ± 75	627 ± 92	616.82

From the properties of the chi-square distribution it can be shown that T follows a chi-square distribution with (6-1)*22=110 degrees of freedom. The obtained value of T for precision test is equal to 101.3. The cumulative probability of exceeding this value of T is equal to 0.70. With a total of more than 100 degrees of freedom, this test is quite sensitive to discrepancies between the estimated and the observed variability of photopeak areas, as calculated by the TPA method for singlets evaluation in the ActAn code. A summary of averaged net peak area results for the six replicated spectra is shown in Table 2.

Nonetheless the modest underestimation of the precision for some types of photopeaks and/or background may still be compensated by overestimating others, therefore we decide to test the ActAn code to ensure statistical control at the level of the individual peaks. This is carried out by testing whether the 22 individual terms in equation (5), corresponding to 22 photopeaks, are random samples from a chi-square distribution with 5 degrees of freedom. The observed cumulative distribution of our data is presented in the Fig. 3. For continuous populations, such as the present chi-square distribution, the Kolmogoroff-Smirnov test makes more complete use of the available data and is not affected by arbitrary choices of classes for comparison. This procedure is based on the deviations between the cumulative observed frequencies of T and the cumulative chi-square distribution curve for five degrees of freedom. With maximum deviation equal to 0.086, we can say that ActAn code results for singlet photopeak area evaluation are in statistical control for all tested peak-to-base ratios. It is evident, that calculated net peak area does not depend on the background under peak.

TABLE 2. SUMMARY OF RESULTS FOR PEAK AREA CALCULATION AND STATISTICAL QUALITY TEST (S300-S305 SPECTRA).

No.	Centroid	Mean Area	Mean Ratio	Expected Ratio
1	130.2	23675 ± 554	5.5 ± 0.1	5.3
2	207.1	4742 ± 451	25.0 ± 2.2	24.1
3	306.3	18228 ± 489	6.6 ± 0.2	6.3
4	361.3	5090 ± 453	24.6 ± 2.2	23.3
5	563.1	18015 ± 497	8.7 ± 0.2	8.5
6	655.5	5029 ± 480	34.0 ± 3.3	34.2
7	774.9	22039 ± 510	8.6 ± 0.2	8.5
8	818.0	4586 ± 450	40.5 ± 4.1	40.5
9	863.7	25866 ± 529	7.7 ± 0.2	7.6
10	924.6	5237 ± 461	39.5 ± 3.5	39.0
11	1011.6	19342 ± 548	11.4 ± 0.3	11.8
12	1095.5	1077 ± 99	211.7 ± 20.0	211.1
13	1195.8	6132 ± 124	23.4 ± 0.5	23.3
14	1300.2	920 ± 87	277.3 ± 26.2	271.0
15	1430.3	10236 ± 137	25.6 ± 0.3	25.4
16	1484.4	999 ± 87	261.3 ± 23.0	257.1
17	1522.1	7061 ± 126	39.8 ± 0.7	39.0
18	1574.2	5338 ± 114	23.8 ± 0.5	23.3
19	1734.7	675 ± 82	259.9 ± 32.0	271.0
20	1823.5	895 ± 79	338.0 ± 31.0	337.3
21	1904.3	5903 ± 113	39.2 ± 0.8	39.0
22	1947.1	5704 ± 114	55.7 ± 1.1	55.5

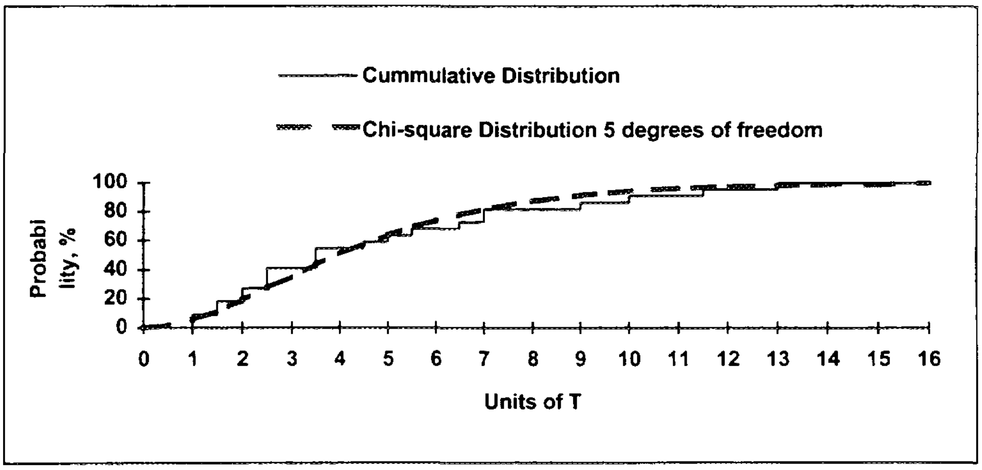

FIG. 3. Cumulative distribution of values of T for the ActAn results compared with the chi-square distribution for 5 degrees of freedom.

Programs in statistical control give results with reliable standard deviations; thus deviations from the true values can be tested for significance. The test of accuracy verifies the absence of significant deviations between the true ratios A_{std} given by the IAEA and the ratio $\overline{A}_m$ of the weighted mean of the six replicates of each photopeak to the comparator:

$$X = \sum_{m=1}^{22} \frac{\left(\bar{A}_m - A_{std}\right)^2}{\sigma_m^2} \qquad \frac{1}{\sigma_m^2} = \sum_{i=1}^{6} \frac{1}{\sigma_{im}^2} \tag{6}$$

The weighted sum X of the squares of the deviations from the true values follows a chi-square distribution with 22 degrees of freedom. The obtained value of X for accuracy test is equal to 10.2 of 22 degrees of freedom, therefore the ActAn code yields unbiased estimates of the true ratios.

(3) Peak position and areas of overlapping double peaks. This is a test of the code's ability to detect and resolve a multiplet structure.

The peaks range from fully resolved equally partitioned open doublets, to very difficult closed multiplets, where the components are separated by only one-two channels. The ActAn code was able to deconvolute all the multiplets. The results of deconvolution are shown in Table 4. It is useful to say that all closed multiplets were found by residual checking after net peak area evaluation of the corresponding peaks as singlets. For detected peaks expected and calculated ratios to the corresponding S100 reference spectrum areas are shown. Between parenthesis the calculated error is given.

TABLE 4. SUMMARY OF RESULTS FOR THE PEAK SPLITTING TEST (S400 SPECTRUM)

No .	Centroid calculated	Centroid expected	Area Error	Actual Ratio	Expected Ratio	Multiplet Classification
1	986.9	987	19853 ± 290	11.16 ± 0.17	35.2	VERY DIFF.
2	987.8	988	49158 ± 334	4.51 ± 0.03	3.52	VERY DIFF.
3	1032.4	1033	20751 ± 282	10.68 ± 0.15	9.16	VERY DIFF.
4	1033.6	1034	75843 ± 364	2.92 ± 0.02	3.05	VERY DIFF.
5	1077.3	1077	63199 ± 329	3.66 ± 0.02	3.08	VERY DIFF.
6	1078.4	1078	86023 ± 361	2.69 ± 0.01	3.08	VERY DIFF.
7	1118.1	1118	2988 ± 223	77.32 ± 5.77	55.47	VERY DIFF.
8	1121.4	1121	42533 ± 298	5.43 ± 0.04	5.55	VERY DIFF.
9	1404.4	1404	11838 ± 264	22.12 ± 0.50	21.85	DIFF.
10	1407.4	1407	36252 ± 308	7.22 ± 0.06	7.28	DIFF.
11	1452.4	1452	33967 ± 296	7.71 ± 0.07	7.77	DIFF.
12	1455.4	1455	33921 ± 295	7.72 ± 0.07	7.77	DIFF.
13	1789.7	1789	3713 ± 163	84.38 ± 3.70	81.39	MIDDLE
14	1795.7	1795	38525 ± 247	8.13 ± 0.05	8.14	MIDDLE
15	1846.6	1846	16547 ± 200	18.93 ± 0.23	18.31	MIDDLE
16	1852.6	1852	51611 ± 274	6.07 ± 0.03	6.10	MIDDLE
17	1928.0	1928	38438 ± 250	8.27 ± 0.06	8.26	EASY
18	1934.0	1934	38446 ± 250	8.27 ± 0.06	8.26	EASY

Net peak area evaluation for the components of the closed multiplets was done by non-linear least squared fitting with FWHM taken from the calibration. The code deconvolution capabilities can be evaluated as excellent. In Figs.4 and 5 accurate open and closed multiplet deconvolution are shown as example, together with the calculated residuals.

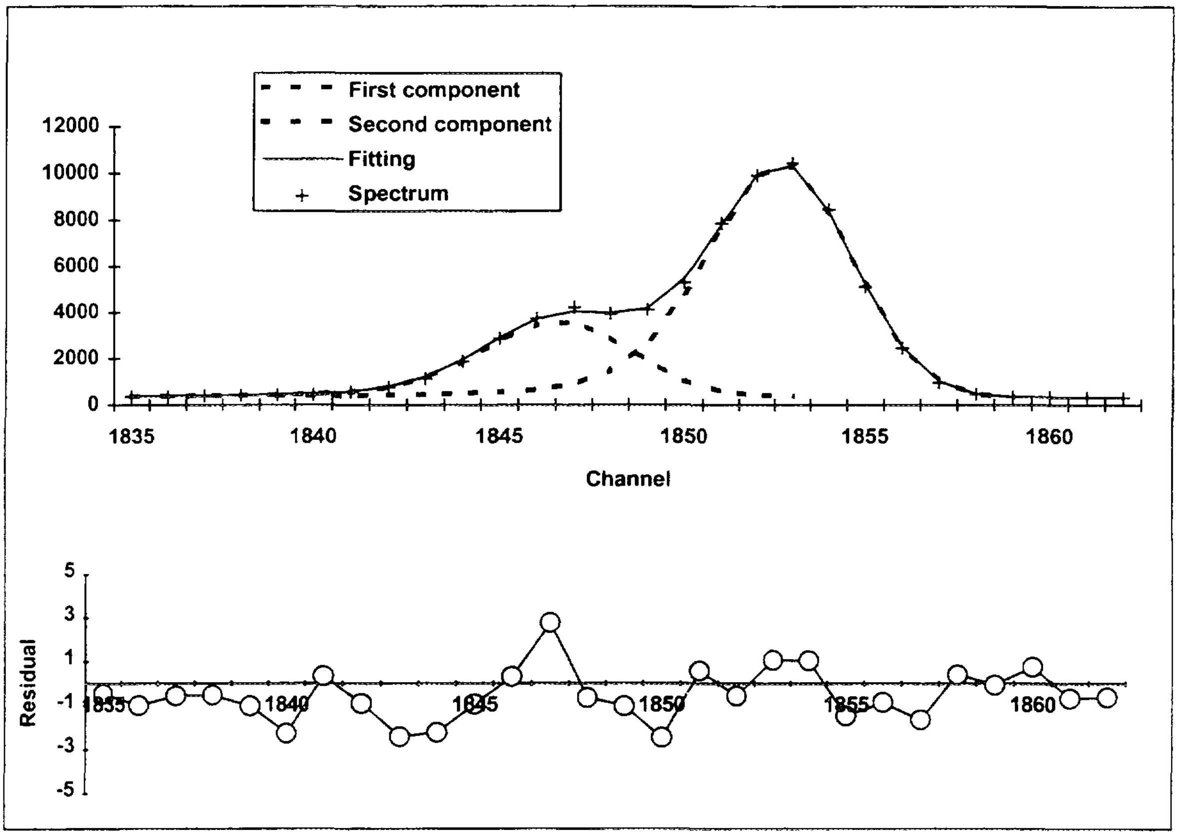

FIG. 4a: 1846 - 1852 open multiplet in S400 spectrum.

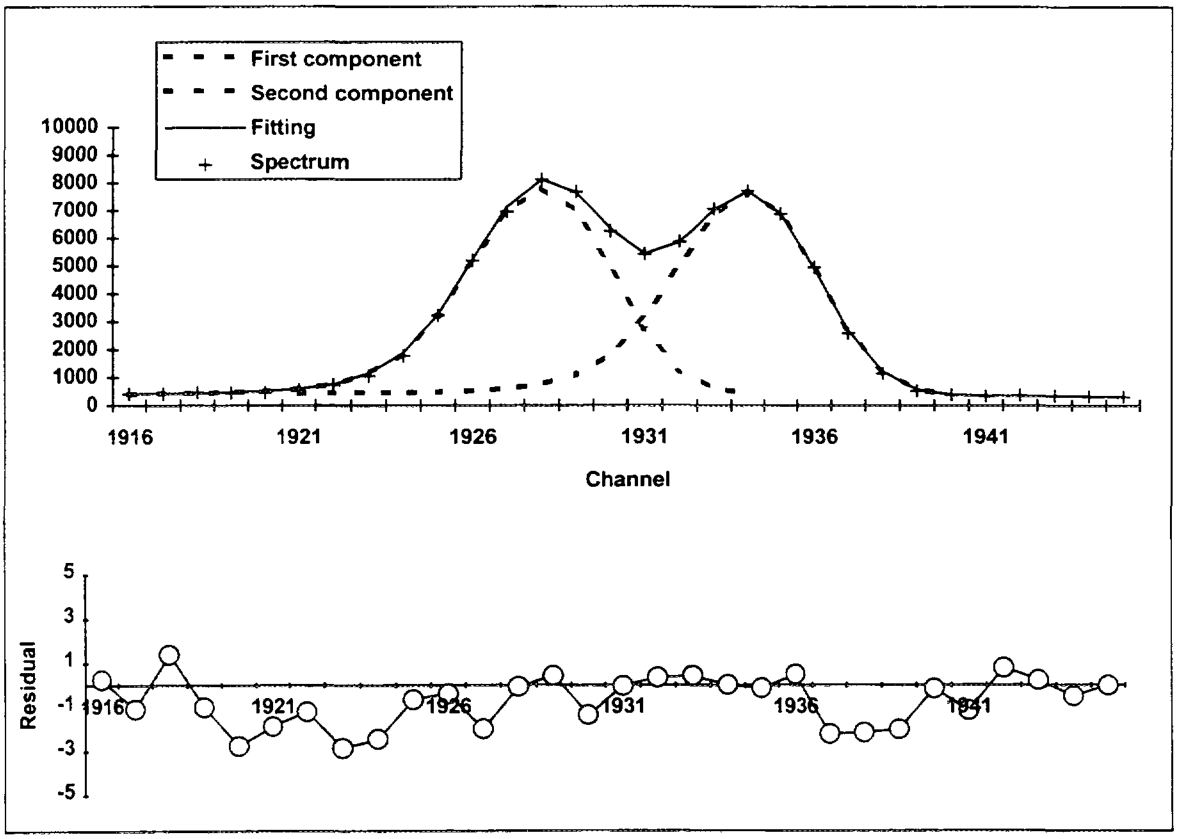

FIG. 4b. 1927 - 1933 open multiplet in S400 spectrum.

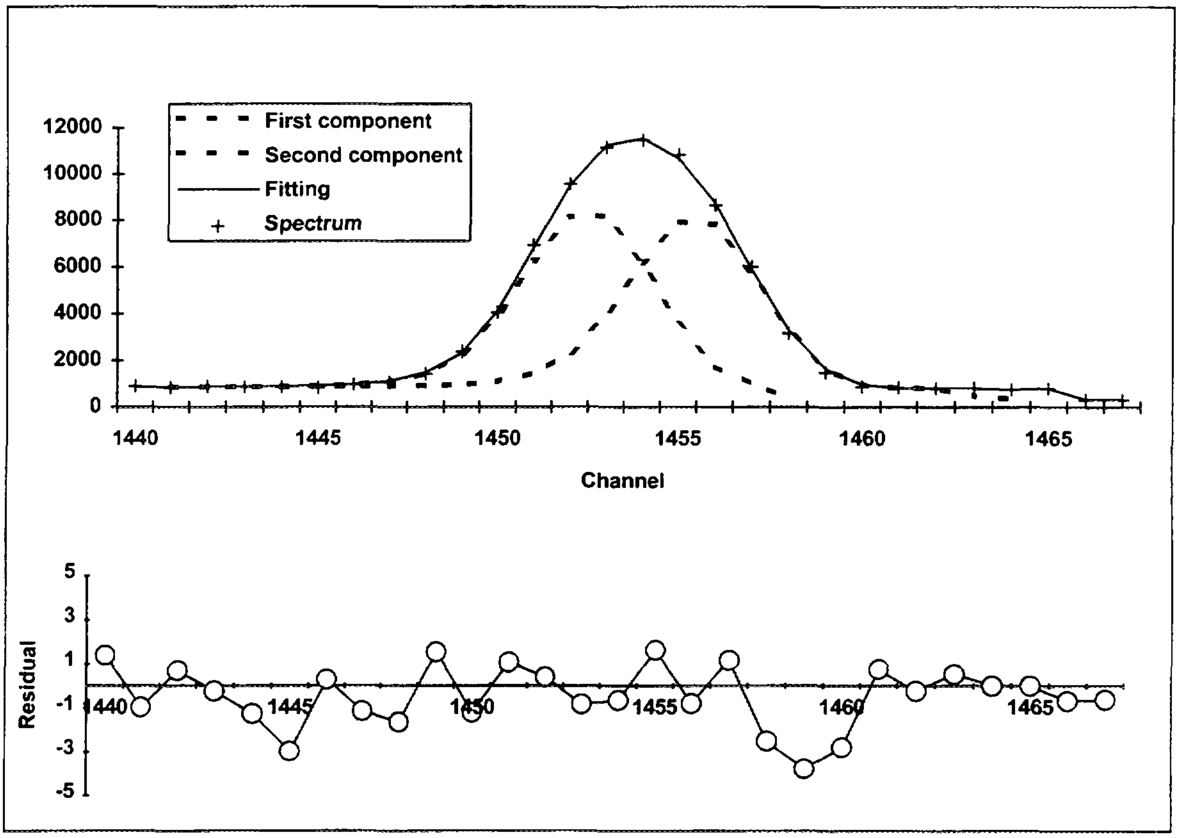

FIG. 5a. 1453 - 1456 closed multiplet in S400 spectrum.

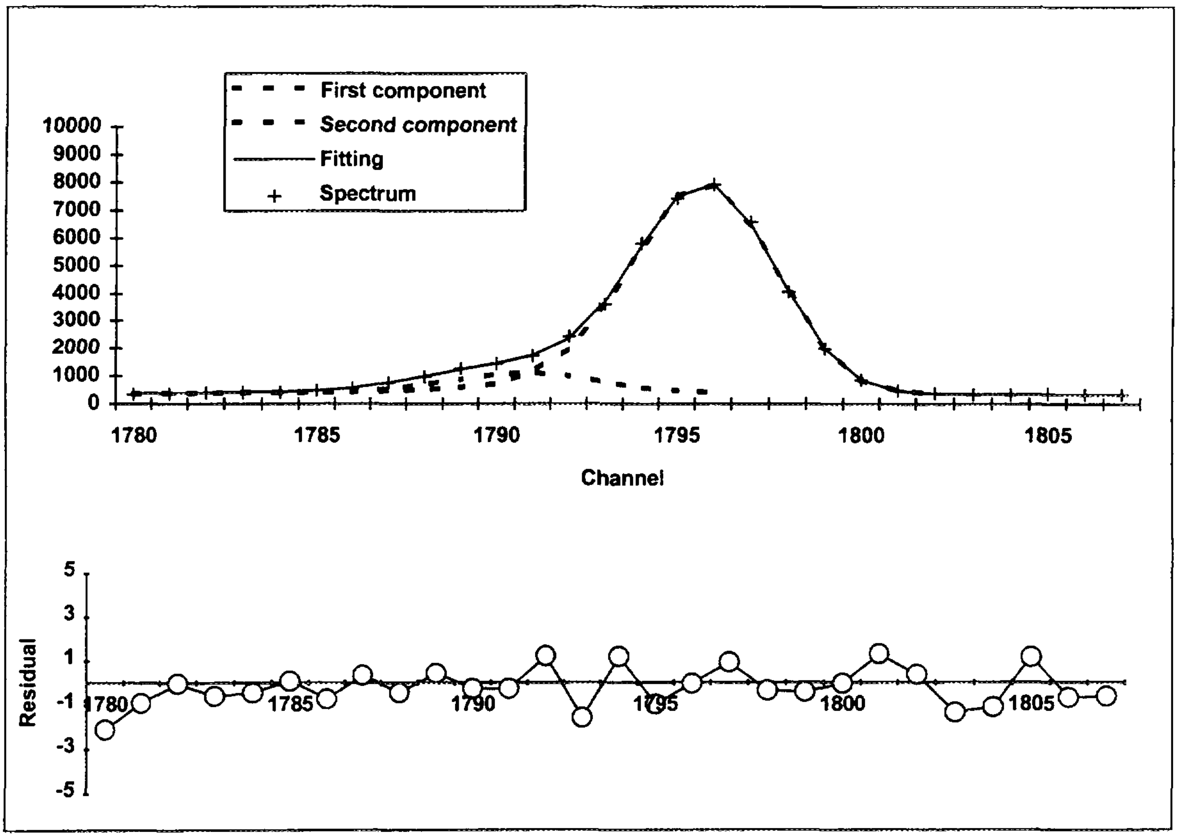

FIG. 5b. 1789 - 1795 closed multiplet in S400 spectrum.

The control of precision of the multiplet deconvolution results of the ActAn code deserves a separate publication.

7.5 CONCLUSIONS

Recently developed ActAn code was tested. We learned a lot about specific performance characteristics of the ActAn code by using it to analyze the IAEA G-1 spectra The intrinsic peak finding ability was very good. Special mention deserves the strong discrimination achieved against false peaks, Compton edges and other non-peak structures. The ActAn code allows deconvoluting strong overlapping multiplets up to 1.5 FWHM peak separation.

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8. ADVANCE FEATURES IN THE SPAN AND SPAN/XRF GAMMA RAY AND X RAY SPECTRUM ANALYSIS SOFTWARE[12]

8.1. SUMMARY

This paper describes the advanced techniques, integral peak background, experimental peak shape and complex peak shape, which have been used successfully in the software packages SPAN and SPAN/XRF to process gamma ray and X ray spectra from HPGe and Si(Li) detector. Main features of SPAN and SPAN/XRF are also described. The software runs on PC and has convenient graphical capabilities and a powerful user interface.

8.2. INTRODUCTION

With the advance of high resolution HPGe, Ge(Li) and Si(Li) detectors, γ ray and X ray spectrometry has made great progress and has been widely used in many fields of pure and applied science, e.g. neutron activation analysis and X ray fluorescence analysis. The processing of γ ray and X ray spectrum data includes peak searching, background subtracting, multiplet resolving, and nuclide or element identification. To me, the key (important technique) is multiplet resolving, i.e., to get an accurate analytical result of photopeaks in multiplet for X ray and γ ray spectrum.

Now-a-days most authors in their software for nuclear spectrometry use analytical functions hereafter called peak shape functions, to fit and resolve multiplets [1, 2]. Many peak shape functions has been applied [11, 12, 13, 14], which consist of a main Gaussian function and some additive components. The Gaussian function is the simplest peak shape function, which deals with only three parameters:

$$F_i = \frac{S}{\sqrt{2\pi} * \sigma} * \exp\left(- \frac{(i - i_0)^2}{2\sigma^2} \right) \tag{1}$$

where: i_0 is the center of the peak,

σ is the peak width,

S is peak area.

The additive components are used for correcting the peak shape function to emulate the experimental peak shape, for example non-symmetry, short and long tails, etc. The HYPERMET function [3] was used in quite a number of software:

$$F_i = A * \exp\left(- \frac{(i - i_0)^2}{2\sigma^2} \right) + B * \exp\left(\frac{i - i_0}{\beta} \right) * \frac{1}{2} erfc\left(\frac{i - i_0}{\sigma\sqrt{2}} + \frac{\sigma}{\beta\sqrt{2}} \right) \tag{2}$$

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[12] *Prepared by WANG LI-YU, China Institute of Atomic Energy, China*

in which 5 parameters need to be fitted. Some more complex functions were designed, for example Kern [4] suggested following function:

$$F_i = A * \exp\left(-\frac{(i-i_0)^2}{2\sigma^2}\right) * \left(1 + p_3\left(\frac{(i-i_0)}{\sigma}\right)^4 + p_4\left(\frac{(i-i_0)}{\sigma}\right)^{12}\right) \tag{3}$$

$$+\frac{A}{\sigma} * \left(1 + \frac{1}{\left((i-i_0)^2 / \sigma^2 + 1\right)}\right) * \left[p_2 + p_3 \exp\left(\frac{p_6(i-i_0)}{\sigma}\right)\right]$$

The function with more parameters to be fitted emulates the peak in experimental spectrum more closely, but the fact that more parameters have to be fitted leads to a more complicated calculation, and increases the probability of a failure. Some analytical functions were designed to fit the baseline continuum under the peak. For the cases shown in formulas (2) or (3) and additional function describing the continuum need to be fitted as well. Thus, the fitting calculation will be even more complicated. For example, suppose there are 4 peaks in a multiplet; taking above-mentioned formulas, each peak has 6 parameters, and then the continuum has 3 parameters, so ending in a total amount of 27 parameters to be fitted. It is not an easy task to calculate 27 x 27 array. Besides, the peak shape is not only depended on the detector and amplifier, but also depends on sample conditions, such as dimension, thickness, etc. Therefore only one analytical peak shape function is not suitable to describe all these conditions.

Under these circumstances, I came to the idea that why not to use directly the *experimental peak shapes* to fit multiplets. This numerical method can be used to fully resolve the problem. Under this concept, some new techniques and algorithms have been developed in the software packages SPAN and SPAN/XRF, they are:

(1) Integral peak baseline.

(2) Experimental peak shape.

(3) Complex peak shape.

Due to the application of these techniques, the analysis of spectral data becomes very fast and the accuracy is satisfactory. These techniques are discussed below.

8.3. INTEGRAL PEAK BACKGROUND

To describe the baseline under peak correctly is the key to get an accurate net peak area. Watching a g ray or X ray spectrum, we can find the baseline levels are different before and after a peak, especially for a strong peak, see Fig.1.

It is quite evident that a straight line or a quadratic curve can not satisfactorily describe the baseline continuum. Some step functions were designed, such as arc tangent function etc.; but these functions are also not satisfactory because they lack of continuity with the "outside-peak" baseline and sometimes they are not acceptable, see Fig.2. W.Watzig [5] in 1978 designed the "integral peak background" method, with which the baseline can be directly subtracted. I improved this technique and it has been satisfactorily used in the software SPAN [6].

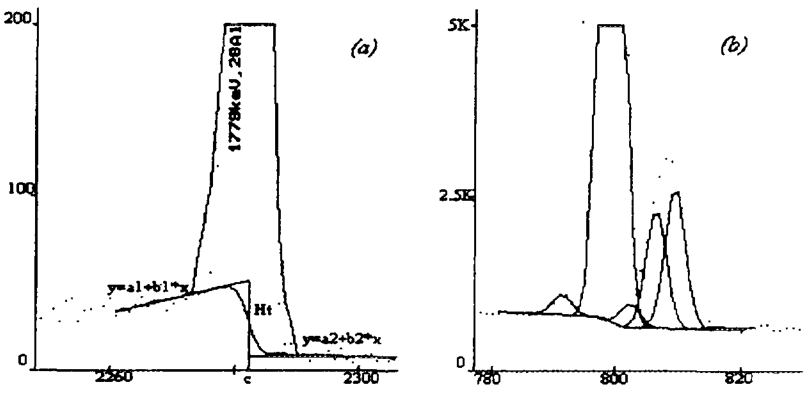


FIG 1. The integral peak background under singlet and multiplet

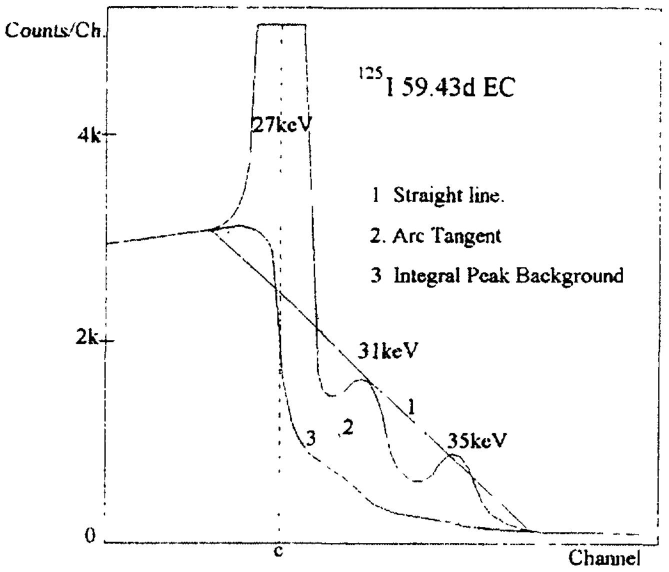


FIG. 2. Comparison of several baseline functions

The principle of the technique is described as below:

(1) The peak causes the baseline step.

(2) The baseline step height depends on the peak height and the peak energy. At the same energy the step is proportional to the net peak area of the peak. In the case of multiplets, for example, the stronger peak causes a larger step baseline.

(3) From items 1 and 2 we can make an important inference: the change of the baseline per channel under a peak(s) is proportional to the net count of the relevant channel, that is:

$$dH = \frac{(A_i - B_i) * H_t}{S} \tag{4}$$

where dH is the change of the baseline,

H_t is the total step height,

A_i is the count in channel i,

B_i is the baseline in channel i.

S is the net peak area of the peak(s) in the peak region, that is:

$$S=\sum_{i=l}^{r}\left(A_i - B_i\right) \tag{5}$$

where l and r are the left and right limits of the peak region, respectively.

The equations (4) and (5) are available for both singlet and multiplet. The slope of the baseline plateau before the peak is usually not zero, and after the peak the baseline is also slanting. We need to design a continuous baseline curve in the whole spectra region, that means at the peak left and right limit the integral baseline under the peak should be equal to the baseline outside the peak, and the slopes should be identical. We can find a baseline region out of the left or the right side, as shown in Fig.1 we can fit out a straight line in each continuum region:

$$y_1 = a_1 + b_1 * x \qquad \text{(left side)} \tag{6}$$

$$y_2 = a_2 + b_2 * x \qquad \text{(right side)} \tag{7}$$

Extending the straight lines to the center of the peak(s), we can get the total step amount:

$$H_t = a_1 + b_1 * c - a_2 - b_2 * c \tag{8}$$

Where c is the center of the peak(s), it may be expressed as:

$$c = \sum_{i=l}^{r}\left[\left(A_i - B_i\right) * i\right] \Big/ \sum_{i=l}^{r}\left(A_i - B_i\right) \tag{9}$$

Thus, we can express the background under the peak as:

$$B_i = a_1 + b_1 * i - \frac{H_t}{S} * \left[\left\{\sum_{k=l}^{i}\left(A_k - B_k\right)\right\} - \frac{A_i - B_i}{2}\right] \tag{10}$$

Of course, dH, B_i, c and H_t are interrelated each other, but not arbitrary. The initial B_i in a region is assumed by equations (6) and (7). The final values for B_i are obtained iteratively by using appropriate computer techniques. In detail the final values for B_i are obtained after following steps:

(1) To find a baseline region out of the left or the right side and fit out a straight line for each of these baseline regions as equations (6) and (7), assuming the peak(s) top as the center for the peak(s).

(2) To extend the straight lines (6) and (7) to the center of the peak(s), the initial B_i can be obtained.

(3) Calculate the area of the peak according to equation (5).

(4) According to equation (9), get the center of the peak(s).

(5) To get new values of B_i according to equation (10).

(6) To repeat steps 2 to 5, until all the parameters converged.

The convergence of the parameters is rather fast, only after 3-5 loops the calculation could be finished. Using this technique we can subtract the baseline before resolving multiplet, thus the parameters are decreased for resolving multiplet, so it can accelerate the data processing. It is more important that this technique can result in an acceptable baseline under both singlet and multiplet.

8.4. EXPERIMENTAL PEAK SHAPE

For getting a better fitting we do not try to increase the parameter number of the analytical peak shapes, instead it is replaced with a numerical method, hereafter called *experimental peak shape*, to perform the multiplet fitting. The experimental peak shape is different from traditional analytical ones at following points:

We use a set of data to replace the traditional analytical peak shape function, the set of data was got from an experimental spectrum:

$$P_j = \frac{A_i - B_i}{S} \qquad P_j = \sum_{i=k}^{l} \left(F_{ij} * P_i \right) \tag{11}$$

where P_j is the distribution factor of the peak in channel j (in experimental peak shape library) or channel i (in the spectrum), and $j = i$ - *left-limit.*

A_i is the counts in channel i.

B_i is the baseline in channel i.

S is the net peak area, got by equation (5).

A peak shape may be well described with 64 points of the data, meanwhile the peak center x_0, the peak width σ and peak energy E are also saved in the library as parameters. Then we can use the experimental peak shapes to fit the peaks in any other spectra, in which the peaks have different center x_0', width $\sigma'$and area S, the experimental peak shape will be projected on the spectrum to be fitted. The projection shift depends on the peak centre x_0 and x'_0, the projection amplification is calculated from peak width σ and σ', peak height depends on the peak area S. The projection can be expressed as following:

$$P_j = \sum_{i=k}^{l} \left(F_{ij} * P_i \right) \tag{12}$$

where P_j is the distribution factor in channel j in the spectrum to be fitted.

P_i is the distribution factor in channel i in the experimental peak shape library.

F_{ij} is the conversion factor.

k and l are the channels, on which the left and right limits of channel j are projected.

The accurate projection points are at x_1 and x_2. The conversion factor can be calculated as follows and shown in Fig. 3:

$$F_{ij} = \begin{cases} 1-[x_1-1] & \text{for } i=k \\ 1 & \text{for } k< I <l \\ x_2-1 & \text{for } i=l \end{cases} \tag{13}$$

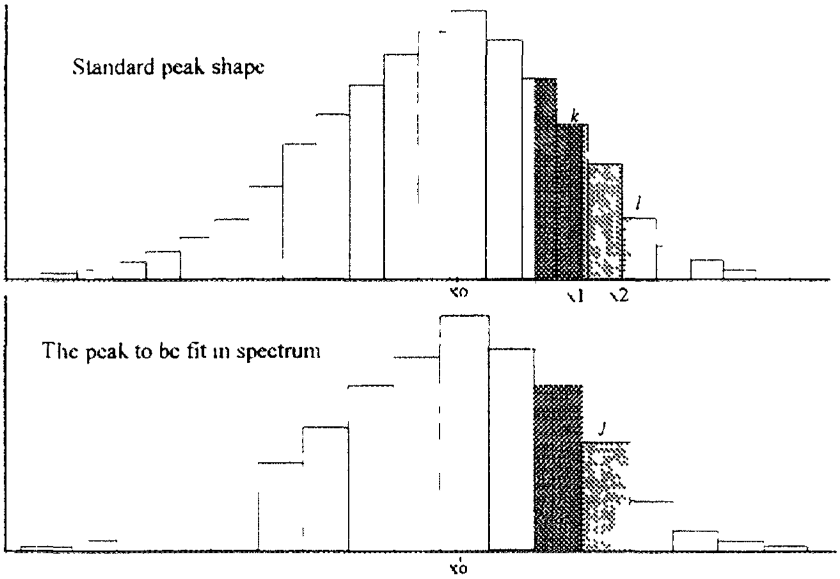


FIG 3 The projection of the experimental peak shape onto spectrum

The non-linear least square fitting is required to calculate the differential of peak shape, while traditionally this is performed by the analytical expression, here in the experimental peak shape it is done by the numerical method:

$$\frac{\partial f(x_0.\sigma,x)}{\partial x_0} = \frac{f(x_0+\Delta x_0,\sigma,x)-f(x_0,\sigma,x)}{\Delta x_0} \tag{14}$$

$$\frac{\partial f(x_0,\sigma,x)}{\partial \sigma} = \frac{f(x_0,\sigma+\Delta\sigma,x)-f(x_0,\sigma,x)}{\Delta\sigma} \tag{15}$$

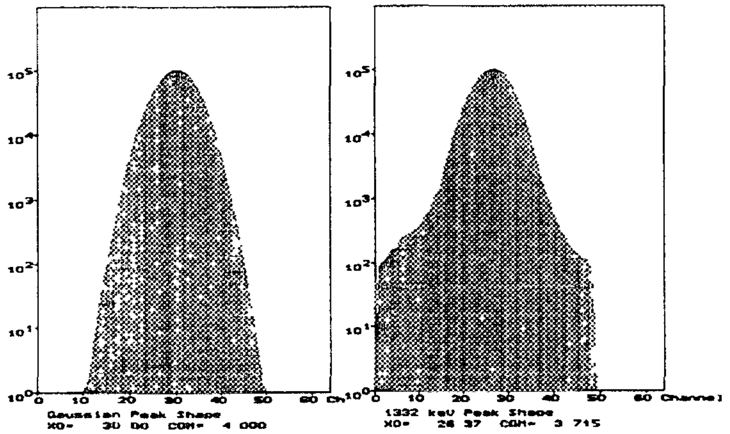
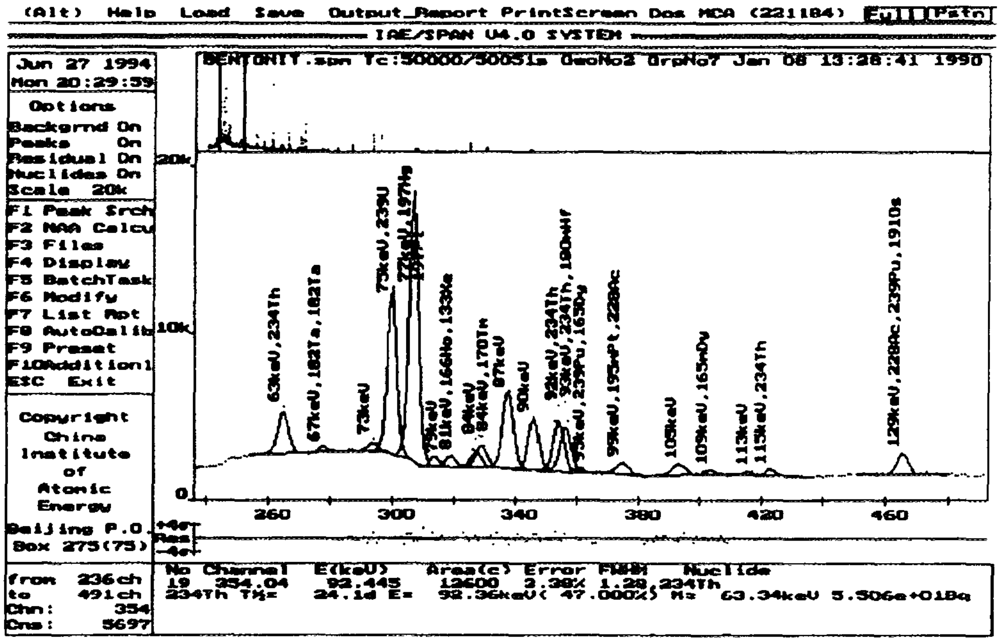


FIG 4 The comparison between experimental peak shape and Gaussian peak shape

The experimental peak shape has following advantages:

- The experimental peak shape is much similar to the peak shapes of the spectrum to be processed, because they are obtained from the same detector, so the fitting will be the best one if the experimental peak shape is accurate enough extracted.
- Only 3 parameters are needed to be fitted; they are: peak's centre, width and area. Much less than those needed when using analytical peak shape functions.
- The calculation of the experimental peak shape is much easier than the one for an analytical expression; the formal is just some simpler mathematical calculations.

Summing up above 3 points, we can say that the experimental peak shape can get a better and faster fit, and the result is much accurate. Figure 5 is an example of using experimental peak shape to fit multiplet. By the experimental peak shape, very much complex and overlapped multiplets, peaks with tails and non-symmetry peaks can be satisfactorily processed. In addition it does not increase any additional fitting parameters.



```
Jun 27 1994
Mon 20:29:59
Options
Backgrnd On
Peaks    On
Residual On
Nuclides On
Scale   20k
```

```
BENTONIT.spn Tc:50000/50051s GeoNo2 GrpNo7 Jan 08 13:28:41 1990
```

```
No Channel    E(keV)     Area(c) Error FWHM    Nuclide
19   354.04    92.445     12600  2.38% 1.28,234Th
234Th T½=     24.1d E=   92.36keV( 47.000%) M=  63.34keV 5.506e+01Bq
```

```
from   236ch
to     491ch
Chn:     354
Cns:    5697
```

FIG. 5. An example of resolving multiplet with experimental peak shape.

8.5. THE KNOW-HOW IN PROCESSING X RAY SPECTRUM

The X ray spectrum is quite different from the γ ray spectrum in which the peaks are much more complex and overlapped. In X ray spectrometry some peaks are very close to each other, they can not be resolved one by one even with any mathematical methods. Moreover, if they could be resolved, the results would have a large inaccuracy. Because a lot of peaks jam up in the X ray spectrum, sometimes it is difficult to automatically find the peaks and the background regions, so some special methods have been developed in the software SPAN/XRF for X ray spectrum.

8.5.1. Preset peak position using the data in X ray data library

When the peaks are very crowded in X ray spectrum, to find every peak in the spectrum is difficult by normal peak searching program. Fortunately the elements in the X ray spectrum are not too many, and they usually have been known, or they could be assumed, so we can build up a sub-library, in which the known or assumed elements are included. According to the energy region of the spectrum section and the X ray energy in sub-library, all the possible peaks could be preset. Then the spectra can be fitted taking in consideration the preset peaks. If there is no peak at the preset position, the peak area should be near to zero and it could be deleted by the program. If there is a peak in the spectrum, but no relevant X ray line in the sub-library, the peak is called no-named peak, on which just mark an energy value without X ray and element name. If large residues are found after fitting the spectrum, that may be due to shortage of an element in the sub-library. Fig.6 is an example using the presetting method to analyse X ray spectrum.

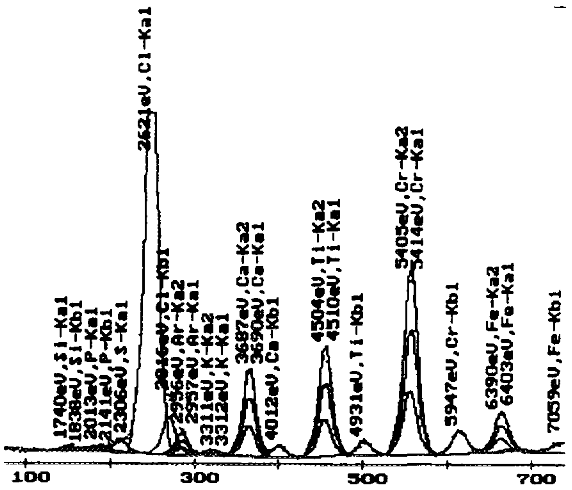


FIG. 6. An example using the presetting method to analyze X ray spectrum.

8.5.2. Complex peak shape

For some X rays in spectrum, their correspondent energies are very closed to each other, making it very difficult to resolved by mathematical method. If these X rays are of the same element, usually it is not necessary to resolve them, they can be processed as a complex peak. The complex peak can be expressed as following:

$$f_m(x_0,\sigma,x)=\sum\left[\Psi_i^{*}\varepsilon_i^{*}f_i(x_{0i},\sigma,x)\right]/\mathrm{Y}_0 \tag{16}$$

where $f_m(x_0,s)$ is the complex peak,

Ψ_i is the emission probability of X ray i,

ε_i is the detection efficiency of X ray i,

$f_i(x_{0i}, \sigma, x)$ is the mono-energy peak shape function of X ray i,

x_{0i} is the centre of the peak of X ray i, which is calculated from X ray data library,

σ is the peak width of the mono-energy peak, it needs to be fit, calibration value is used as the initial.

$\Psi_0 = \sum \Psi_i * \varepsilon_i$, is the normalization factor.

Figure 7 is an example of using complex peak shape, in which 15 X rays peaks have been synthesized into 5 complex peaks for processing easily.

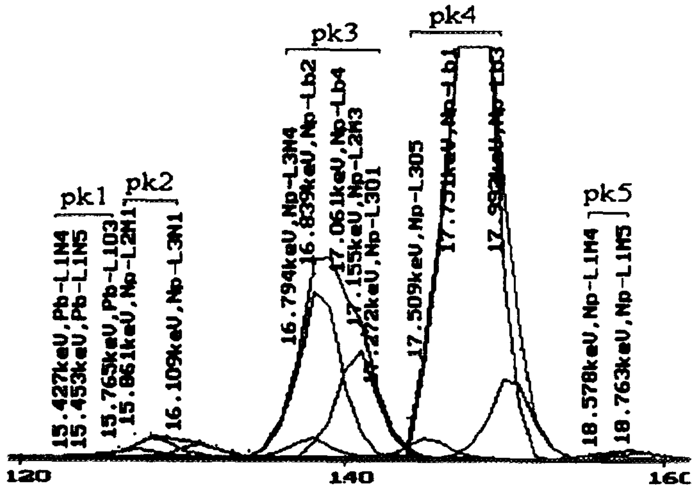


FIG. 7. An example using complex peak shape.

8.5.3. Manual setting of baseline region

The software SPAN analysing γ ray spectra finds the spectrum baseline automatically. But for X ray spectrum this performance is usually not successful due to the large amount of peaks. In order to resolve this problem, a method to set the baseline region was developed in X ray spectrum software SPAN/XRF, by which the spectrum could be processed satisfactorily.

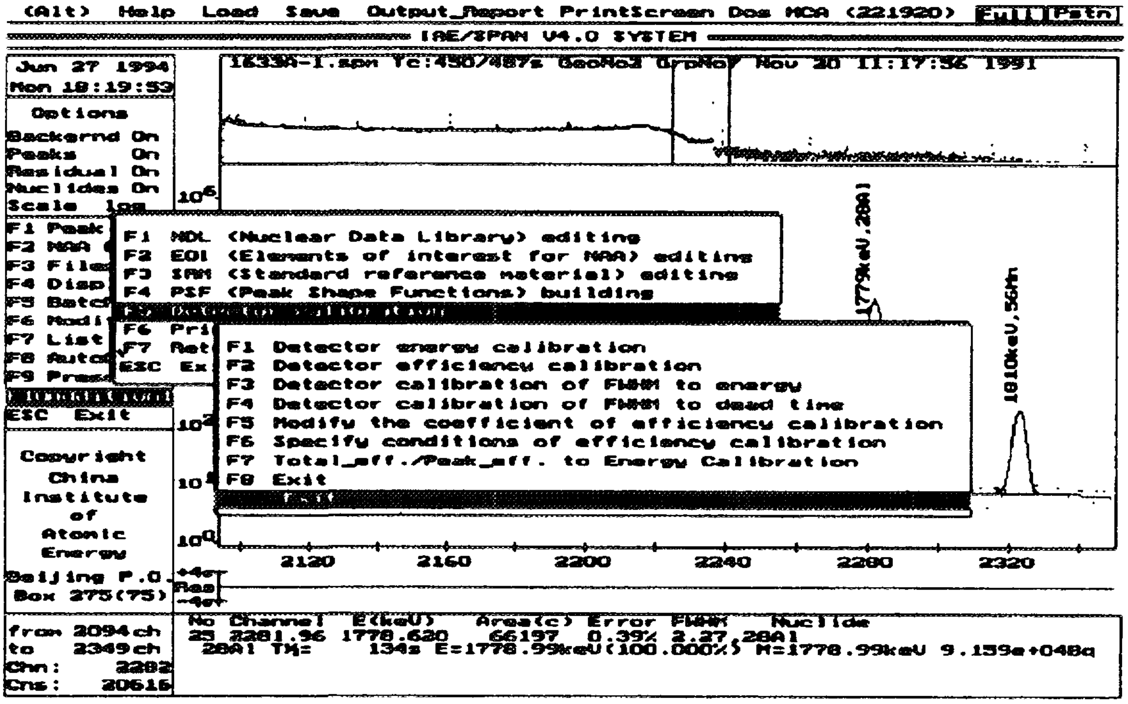
8.6. THE OTHER CHARACTERISTICS OF SOFTWARE SPAN AND SPAN/XRF

Good software not only should possess accurately the spectrum, but also be convenient to use. A lot of auxiliary functions have been designed in the software SPAN and SPAN/XRF, including files management (load, save and convert), report output (peak analysis report, isotope report, neutron activation analysis report), detector calibration (energy, efficiency and FWHM calibration), library editing (nuclear data library, elements of interest and standard reference material), spectrum (original data, background, peaks and residual) and curves (calibration curves and peak shapes) displaying. Now some distinguished features are described here.

8.6.1. Good-looking and useful graphical capabilities

After processing the spectra, the analysis results: including baseline, peaks and residuals, and original spectrum data; are displayed on screen in different colours. The energy and relevant nuclide are marked on the top of each peak, so the analysis results are clearly seen at a glance. Several convenient possibilities were implemented in the software, by which the user can change the content and view of it; for example, fast and slow cursor movements, jumps from peak to peaks, window movements and different spectrum scales.

Furthermore the energy, FWHM and efficiency calibration curves; and the standard peak shapes can also be displayed on the screen. Screen capture capability has been implemented into the software so a spectra plotting can be pasted into a file or printed (black and white or coloured) into a plotter or printer.



```
from 2094ch   No Channel  E(keV)    Area(c) Error FWHM    Nuclide
to   2349ch   25 2281.96  1778.620   66197   0.39% 2.27,28Al
Chn:   2282    28Al T½=      134s E=1778.99keV(100.000%) M=1778.99keV 9.159e+04Bq
Cns:  20616
```

FIG. 8. The pop menus of the SPAN software.

8.6.2. Pop menu and mouse control

The software is operated by menu options and mouse (see Fig.8); so its operation is rather easy and without the necessity for reading the user's manual.

8.6.3. Batch mode operation

The software can operates in batch modes, meaning it can process several spectra (84) without the direct intervention of the user. After editing a batch sequences for a task, the spectra can be processed automatically with the corresponding analysis reports. Of course the batch mode operation can be interrupted or exited manually.

8.6.4. Easy energy calibration and efficiency calibration

A large γ ray data library (obtained from IAEA TECDOC-564[7]) and an X ray data library (from IAEA-TECDOC-619[8] and others) are included in the software SPAN and SPAN/XRF, respectively.

The energy and efficiency calibrations are easy to perform in these software. They are based on the data in the library and on the analysis results, only a few operations are required for the calibrations. For example only a few nuclides need to be entered for energy calibration, all the data are retrieved from software's library and the analysis results. The efficiency calibration is also rather easy, only the nuclide radioactivity, the decay time and spectrum file name are required to be entered. Then the selection of the user's choice peaks for this calibration. The efficiency calibration is performed using quadratic spline function on the two logarithmic coordinates (efficiency and energy). The calibration is shown in the screen, see Fig.9, which could be printed as well.

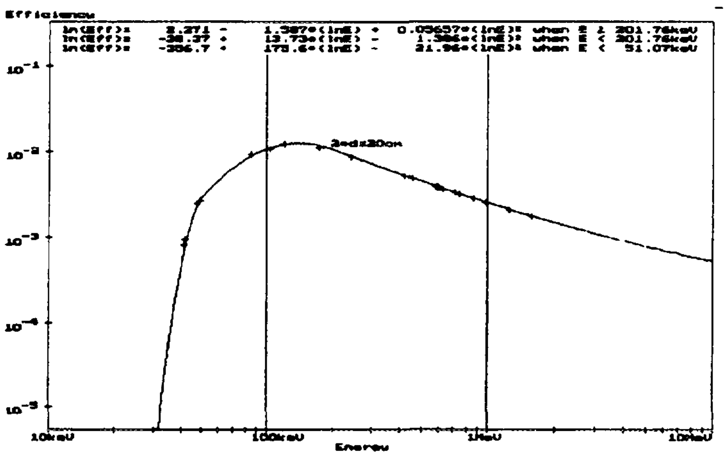


FIG. 9. Efficiency calibration curve of an HPGe detector

8.7. CONCLUSIONS

The software packages SPAN and SPAN/XRF use different approaches like "experimental peak shape", "integral background" and "complex peak shape" among others, with which the spectra can be processed quickly and accurately. The software SPAN is useful in neutron activation analysis, isotope identification, and environment radioactivity monitoring, as well. The software SPAN/XRF is used for X ray fluorescence analysis. Practice has proved that the techniques used in the software are successful and the analysis results are satisfactory.

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9. A PROCEDURE FOR INCORPORATING GAMMA RAY ATTENUATION CORRECTIONS INTO GERMANIUM EFFICIENCY CALIBRATIONS[13]

9.1. SUMMARY

Quantification of radionuclide concentrations by gamma ray spectrometry is often complicated by the need to make self-absorption corrections. These corrections become especially important when the matrix composition or density of the calibration source is different from the samples that are being analyzed. At our laboratory attenuation corrections are being done by means of a computer program. Here a brief explanation of it is presented.

9.2. DISCUSSION

At the Environmental Measurements Laboratory the tedium of determining attenuation corrections by direct measurement has been replaced by computer calculations. Attenuation corrections are computed and applied to the calibration data to obtain a matrix free and weightless set of efficiency versus energy data points. These data points are then adjusted using the attenuation corrections computed for the sample bring analysed. This results in an efficiency calibration that matches both sample composition and density.

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[13] *Prepared by C G Sanderson. Environmental Measurements Laboratory, United States of America*

The correction required for the difference in self-absorption between calibration standards and sample matrices is usually small for intermediate and high-energy photons, but it is not negligible at low energies where the photoelectric effect is the most important mode of attenuation. The photoelectric process varies approximately as Z^{4-5} (Z is the atomic number of the elements in the matrix) so that a change in the elemental composition of a sample relative to a calibration standard can require a correction factor for detector efficiency as high as a factor of 2. The method for self-absorption correction at various energies requires that the linear attenuation coefficient, μ, of the sample matrix be known. Knowledge of μ usually requires that the elemental composition of the matrix be determined.

A computer program was written for IBM PCs and compatibles to calculate μ/ρ for various compounds when the percent elemental composition of the compound is known. μ/ρ is computed as a linear combination of the mass attenuation coefficients of the composite elements

$$\mu/\rho=\sum(\mu_i/\rho_i)P_i$$

where P_i is the percent by weight of the i^{th} element in the compound. Values of mass attenuation coefficients, μ/ρ, for various elements from standard reference tables were used as input data. The program also calculates the percent attenuation of the beam, A, when gamma photons of a certain energy pass through a medium of a given density.

The input parameters required to run the program are:

(1) percent by weight of elemental composition

(2) matrix density

(3) gamma ray path length

(4) photon energy

When a gamma ray passes through a homogenous sample of mass attenuation coefficient, μ/ρ, density, ρ, and average gamma ray path length, D, the gamma ray attenuation, A, is given by

$$A=\frac{I_0-I}{I_0}=1-e^{-(\mu/\rho)D\rho}$$

For radioactive samples, these corrections are integrated for a path length of. 0 to D.

The accuracy of the computer program in determining μ/ρ for known compounds was tested for H_20 and $Si0_2$. The percent deviation between the computed μ/ρ values and those given in standard tables is insignificant at 60, 600 and 1000 keV, the energies tested.

TABLE 1. COMPARISON OF COMPUTED μ/ρ AND STANDARD TABLE μ/ρ

	Water		SiO_2	
Energy (keV)	computed	standard table	computed	standard table
60	0.206	0.206	0.253	0.252
600	0.0895	0.0896	0.0808	0.0808
1000	0.0706	0.0707	0.0636	0.0636

TABLE 2. TYPICAL ENVIRONMENTAL SAMPLE COMPOSITIONS

Element/ Compound	% by Weight			
	Soil	Bone	Vegetation	Epoxy
Al	7.1			
Fe	3.2			
O	11.0	41.0		42.0
H				8.0
C	1.2		90.0	50.0
Ca		39.0		
P		20.0		
SiO_2	67.5		10.0	
H_2O	10.0		10.0	

TABLE 3. DETECTOR EFFICIENCY (%)

Energy KeV	Epoxy Standard P=1.15	Weightless Standard P=0	Vegetation Sample P=0.5	Soil Sample P=0.7	Soil Sample P=2.0
60	5.76	7.72	6.84	6.00	3.99
88	5.90	7.64	6.87	6.40	4.73
122	5.44	6.90	6.25	5.94	4.59
166	4.45	5.53	5.06	4.86	3.88
279	3.04	3.65	3.38	3.28	2.72
392	2.23	2.62	2.45	2.39	2.03
514	1.65	1.91	1.80	1.76	1.52
662	1.39	1.58	1.50	1.47	1.29
898	0.97	1.09	1.04	1.02	0.91
1173	0.79	0.87	0.84	0.83	0.75
1333	0.71	0.78	0.75	0.74	0.67
1836	0.52	0.57	0.55	0.54	0.50

TABLE 4. DETECTOR EFFICIENCY (%).

Energy KeV	Epoxy Standard P=1.15	Water Sample P=1.00	Vegetation Sample P=1.15	Bone Sample P=1.15	Soil Sample P=1.15
60	5.76	5.89	5.88	4.32	5.15
88	5.90	6.04	6.00	5.38	5.73
122	5.44	5.57	5.52	5.27	5.41
166	4.45	4.55	4.51	4.44	4.48
279	3.04	3.10	6.07	3.07	3.07
392	2.23	2.27	2.25	2.25	2.25
514	1.65	1.68	1.67	1.67	1.67
662	1.39	1.41	1.40	1.40	1.40
898	0.97	0.98	0.98	0.98	0.98
1173	0.79	0.80	0.80	0.80	0.80
1333	0.71	0.72	0.71	0.71	0.71
1836	0.52	0.53	0.52	0.53	0.52

TABLE 5. DETECTOR EFFICIENCY (%) WITH SOIL SAMPLES CONTAINING

Energy keV	7% Al 0% Th	6% Al 1%Th	5% Al 2% Th	4% Al 3% Th	3% Al 4% Th	2% Al 5% Th	1% Al 6% Th
60	5.65	5.17	4.74	4.36	4.03	3.73	3.47
88	6.13	5.91	5.70	5.50	5.31	5.14	4.97
122	5.81	5.64	5.48	5.32	5.18	5.03	4.90
166	4.73	4.59	4.46	4.33	4.21	4.09	3.98
279	3.21	3.18	3.16	3.13	3.10	3.08	3.05
392	2.33	2.33	2.23	2.31	2.30	——›	
514	1.76	1.75	——›				
662	1.43	——›					
898	1.00	——›					
1173	0.81	——›					
1333	0.72	——›					
1836	0.54	——›					

TABLE 6. DETECTOR EFFICIENCY (%) AT Eγ = 122 keV. COMPOSITION OF SOIL SAMPLE: 68% SiO_2, 3% Fe, 11%O, 1%C, 10%H_2O

Composition (Al. Th)	Efficiency
7%Al. 0%Th	5.81
6%Al. 1%Th	5.64
5%Al. 2%Th	5.48
4%Al. 3%Th	5.33
3%Al. 4%Th	5.18
2%Al. 5%Th	5.03
1%Al. 6%Th	4.90
0%Al, 7%Th	4.76

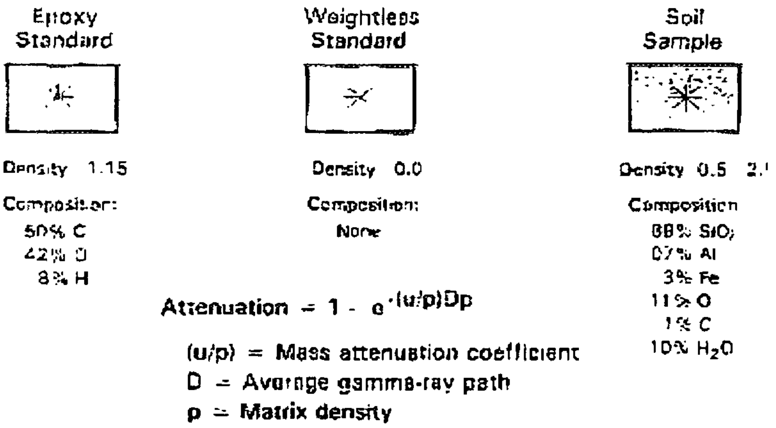

FIG. 1. Detector calibration procedure.

10. COMPARISON OF Pu ISOTOPIC COMPOSITION BETWEEN GAMMA AND MASS SPECTROMETRY: EXPERIENCE FROM IAEA-SAL[14]

10.1. SUMMARY

About 2000 Pu containing samples have been analysed during the last 8 years at SAL using gamma spectrometry (GS) in parallel with mass spectrometry (MS). Four different detectors have been used for the measurement of gamma-ray spectra and several versions of the MGA program have been used for spectra evaluation. The results of Pu isotopic

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[14] *Prepared by J.L Parus and W. Raab, IAEA.*

composition obtained by both methods have been systematically compared. Attempts to improve the agreement between GS and MS are described. This was done by adjustment of the emission probabilities for some gamma energies and the development of a new correlation equation for ^{242}Pu. These improvements have been applied for evaluation of two sets containing 320 and 404 samples, respectively analysed in 1991 and in 1992-93. The mean differences and their standard deviations between MS and GS were calculated, showing mean relative differences for $^{238-241}$Pu isotopes in the range from 0.1 to 0.5% with standard deviations within ± 0.4 to ± 1%. For ^{242}Pu these values are about 0.5% and ±5%, respectively.

10.2. INTRODUCTION

The MGA programme was implemented at SAL by R. Gunnink in the middle of 1986 in the framework of the US support program to the IAEA. Since then all samples containing plutonium without fission products have been measured as received after unpacking from their transportation containers. In the beginning the accumulated spectra contained 4096 channels comprising the energy range from 0 to 307 keV (75 eV per channel). The planar detector used initially had 1500 mm^2 active area and 560 eV FWHM at 122 keV. The results contained in addition to the isotopic composition of Pu, also the ^{241}Am and ^{237}Np concentration in relation to plutonium. Each spectrum was evaluated twice: 1) immediately after measurement, assuming arbitrarily a 5 year time period between discharge from the reactor and reprocessing, and 2) after MS isotopic analysis with substitution of the ^{242}Pu abundance. The results of the first evaluation were delivered to the wet chemistry laboratory and were used to select a suitable analytical scheme (IDMS vs. titration when significant amount of ^{237}Np was present, choice of Pu spike).

From the very beginning the results of both MGA evaluations and MS measurements (^{238}Pu was measured by alpha spectrometry) have been mutually compared, thus increasing the quality of the final analytical results. The results for ^{241}Am after validation with isotope dilution gamma spectrometry [1], are routinely reported as analytical results.

A particular concern was to measure the isotopic composition of plutonium in comparison to mass spectrometry. It was very important to find rather a simple mathematical procedure to perform this comparison. After several approaches we selected the comparison of the paired observations where a set of differences is treated as a separate distribution with a mean, d, and a variance, s_d^2 .

10.3. MEASUREMENT

All measurements discussed in this paper were performed using three different HPGE planar detectors with 1000, 800 and 500 mm^2 active area and energy resolution of 530, 600 and 550 eV at 122 keV respectively with 6 μs shaping constant of the main amplifier. Spectrum stabilisation was used throughout and the peaks of 59.5 keV and 208 keV were selected for zero and gain stabilisation, respectively. All spectra contained 8196 channels, 75 eV/channel, covering the energy range from 0 to 614 keV. The measurement time was variable. The region of interest (ROI) was set for 129 keV energy of ^{239}Pu and 10^5 net counts were accumulated for each spectrum. The dead time of the ADC did not exceed 15 %. Cadmium absorbers of adequate thickness to suppress the 59.5 keV peak to approximately the same height as the 100 keV peak grouping were applied. Most of the measurements were performed with the use of sample changers. The shielding was sufficient to eliminate degradation of the measured sample spectrum by the neighbouring samples. The accumulated spectra were transferred from the MCA to the Micro VAX II computer for evaluation.

10.4. SPECTRUM EVOLUTION

All spectra whose results are reported here have been evaluated in a batch mode and the results of Pu isotopic composition were calculated to the date of MS measurement. For samples containing uranium the MGA/U option was used.

10.5. SAMPLES

All samples were measured, as received, in containers doubly bagged in a plastic foil. The description of analysed material, the sample size and the sample container are given in Table I. Only the samples with ^{239}Pu content below 71% are considered in this comparison. The number of samples with ^{239}Pu content above 71% constituted about 5% of the total number compared (36 against 724). The deleted samples had low ^{242}Pu content and the relative differences against MS were very high with the algorithms used. This group of samples should be treated separately.

TABLE 1. ANALYSED MATERIALS

Material symbol	Material characterisation	Sample size	Sample container
MNH	Mixed U-Pu nitrate, hydrated. U/Pu ratios range 1:1 to 100:1	4 mg Pu	Penicillin vials
MOX	Mixed U-Pu oxide in powder or pellet form. U/Pu ratios range 1:1 to 100:1	1 - 10g max 1g Pu	Erlenmayer flasks, BC4,scintillation vials
PNH	Plutonium nitrate, hydrated	4 mg Pu	Penicillin vials
POX	Plutonium oxide in powder form	0.1 - 1 g	BC4 or Erlenmayer flasks

The analysed materials were of very different origin. The division into four groups in Table 1 is based on chemical form in which the samples were received but does not indicate in which chemical or physical form the material was during the sampling. For example, PNH (plutonium nitrate hydrated) can be relatively fresh material from the spent fuel reprocessing or a rather old Pu oxide dissolved for sampling and later evaporated.

10.6. ADJUSTMENT OF BRANCHING RATIOS

To characterise the performance of MGA, two quantities have been studied on relatively large sets of results: 1) the mean difference between MS and GS, and 2) the standard deviation of this difference. The former is a measure of the bias and the latter of the precision of measurements. It was observed that the relative differences between MS and GS results were strongly correlated for the pairs of isotopes: ^{239}Pu/^{240}Pu and ^{238}Pu/^{241}Pu. To study these differences in detail the ^{242}Pu abundance was taken from the MS measurement. The set of 112 samples was used to minimize the mean differences by changing the branching ratios for some energies [2, 3]. These differences decreased significantly with the emission probabilities given in Table 2.

TABLE 2. OLD AND NEW BRANCHING RATIOS

ENERGY (KEV)	ISOTOPE	GUNNINK [2]	THIS WORK
99.864	^{238}Pu	7.10×10^{-5}	7.13×10^{-5}
129.296	^{239}Pu	6.29×10^{-5}	6.30×10^{-5}
104.242	^{240}Pu	6.96×10^{-5}	6.92×10^{-5}

Using these branching ratios the average differences and their standard deviations (RSD) for the set of 112 samples were as given in Table 3.

TABLE 3. AVERAGE DIFFERENCES AND RELATIVE STANDARD DEVIATIONS FOR TEST SAMPLES (112)

ISOTOPE	REL. DIFF.%	RSD%
238Pu	0.08	0.93
239Pu	- 0.08	0.40
240Pu	0.13	0.92
241Pu	0.29	0.60
240Pu eff	0.10	0.69

These branching ratios were consistently used in all comparisons presented in this paper.

10.7. CORRELATION EQUATION FOR ^{242}Pu

As can be seen in Fig. 1, 2, 3 and 4 the atomic ratio of the $^{242}Pu/^{239}Pu$ (I242) is strongly correlated with the isotopic ratios of other isotopes: $^{238}Pu/^{239}Pu$ (I238), $^{240}Pu/^{239}Pu$ (I240), $^{241}Pu/^{239}Pu$ (I24 1) and with the product of I240*I241. All ratios presented in these Figures are atomic ratios measured by MS. To find an alternative method of I242 calculation several simple linear equations have been devised and the regression coefficients were calculated using multiple regression analysis. The coefficient of variation was used as a measure of fit quality. The best equation has the following form:

$$I242 = a_0 + a_1\, I238 + a_2\, I241 + a_3\, I240 \times I241$$

where: a_0, a_1, a_2, a_3 are regression coefficients,
I238, I240, I241, I242 are respective atomic isotopic ratios.

Table 4 shows regression coefficients calculated for all 320 samples and for individual materials.

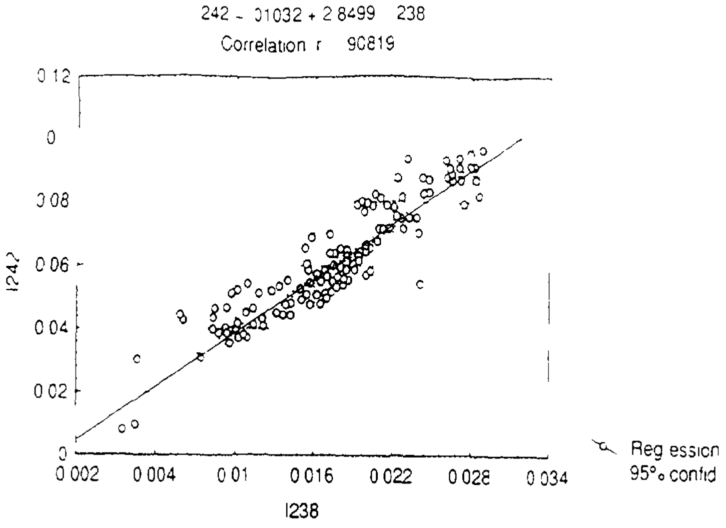

FIG 1 MS atomic ratio of ^{242}Pu/^{239}Pu vs ^{238}Pu/^{239}Pu

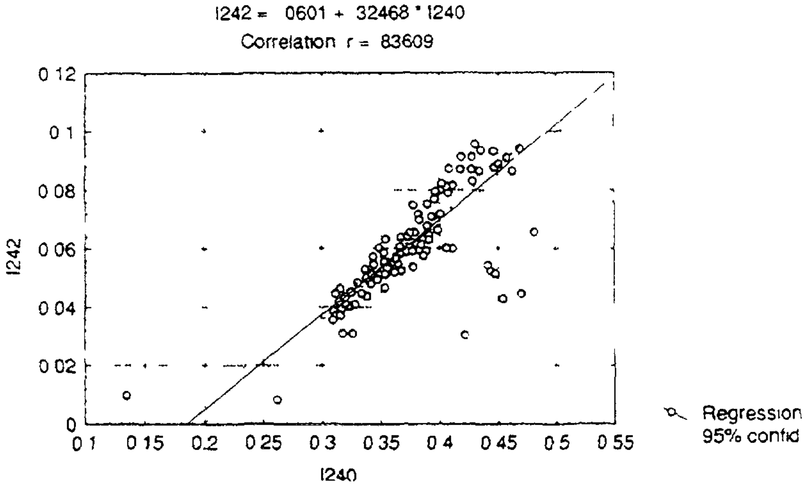

FIG 2 MS atomic ratio of ^{242}Pu/^{239}Pu vs ^{240}Pu/^{239}Pu

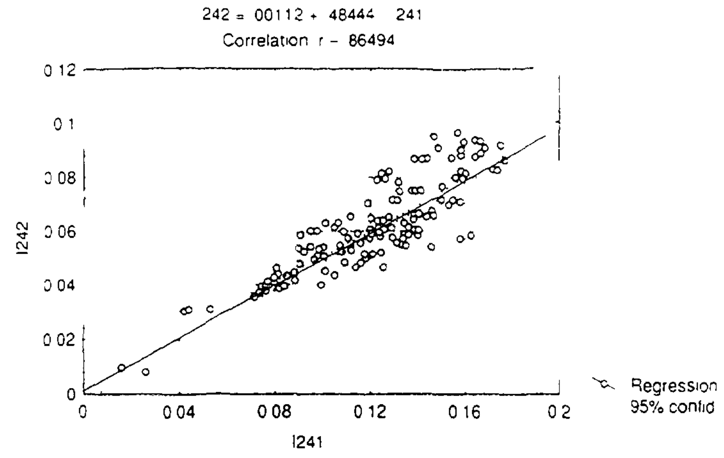

FIG 3 MS atomic ratio of ^{242}Pu/^{239}Pu vs ^{241}Pu/^{239}Pu

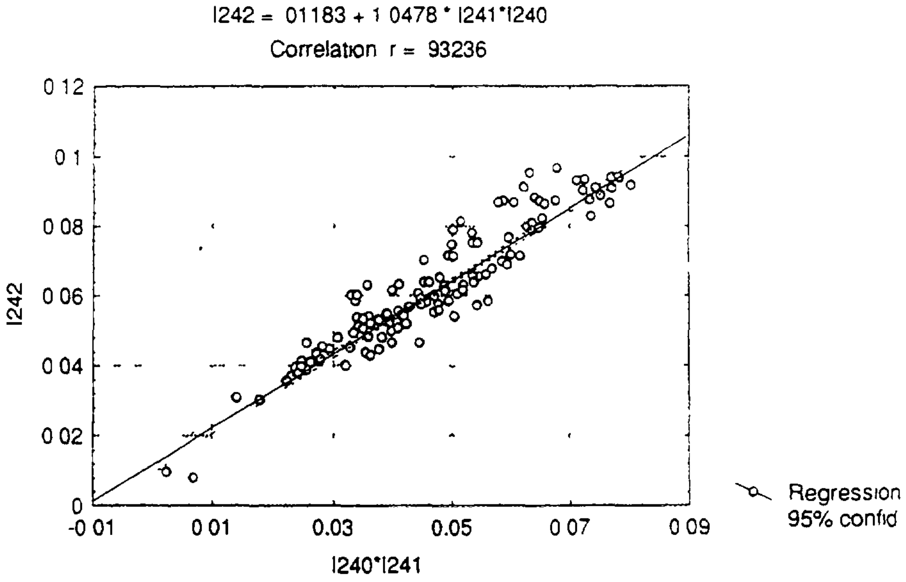

FIG. 4. MS atomic ratio of $^{242}Pu/^{239}Pu$ vs $(^{240}Pu/^{239}Pu)*(^{241}Pu/^{239}Pu)$

TABLE 4. MULTIPLE REGRESSION COEFFICIENTS. SET I - 320 SAMPLES

Material	a_0 Intercept	a_1 I238	a_2 I241	a_3 I240 x I241	Equation
ALL	0.0198	1.4424	-0.3886	1.3530	(1)
MNH	0.0362	1.0619	-0.7971	2.2281	(2)
MOX	0.0172	1.6708	-0.4332	1.4521	(3)
PNH	0.0218	1.1345	-0.3286	1.2229	(4)
POX	0.0198	1.1426	-0.2582	1.2078	(5)

10.8. CALCULATION OF ^{242}Pu ABUNDANCE

All spectra were evaluated with MGA (version 8). Only for calculation with so called "old algorithm" the discharge time of 5 years from reactor to reprocessing was assumed. Then the atomic isotopic ratios in relation to the ^{239}Pu abundance wore calculated for ^{238}Pu, ^{240}Pu, and ^{241}Pu isotopes. These ratios have been substituted to the correlation equations: (1) - for all samples of the set and to equations (2), (3), (4), and (5) according to Pu-material and the $^{242}Pu/^{239}Pu$ ratios were calculated. In the next step, using the ratios for ^{238}Pu, ^{240}Pu, ^{241}Pu , and ^{242}Pu the weight percents of all five Pu isotopes were computed. Then the relative differences between MS and GS were found and averaged and the standard deviation of the differences calculated.

10.9. COMPARISON OF RESULTS

Two series of results from GS and MS, containing 320 and 404 measurements, respectively, were compared in two ways:

(1) with ^{242}Pu, taken from MS, and

(2) with ^{242}Pu calculated from different correlation equations.

Additionally, Pu effective values have been compared.

10.9.1. Results with ^{242}Pu from MS

In Table 5 the relative mean differences and their relative standard deviations are shown for $^{238-241}$Pu isotopes. The 320 sample group was split into material subgroups and was also evaluated according to which Ge detector was used in the measurements. The smallest bias was achieved for 239Pu and 240Pu, with the biggest detector (1000 mm^2) which also had the best energy resolution (530 eV). The mean difference for all Pu isotopes is in the range from 0.1 to 0.5% and the RSD in the range from ±0.3 to ±1%. The differences for ^{239}Pu and ^{240}Pu are very strongly correlated with each other (Fig. 5) and the same is observed to a lesser degree for ^{238}Pu and ^{241}Pu (Fig. 6). The mean differences and the RSDs for the group of 404 samples are similarly distributed. Only the results for the whole group are given. Figures 7, 8, 9, and 10 show the distribution of differences for all isotopes of 320 samples.

TABLE 5. RELATIVE MEAN DIFFERENCES AND RELATIVE STANDARD DEVIATIONS (RSD) FOR 4 Pu ISOTOPES [%}. ^{242}Pu VALUES FROM MASS SPECTROMETRY

Samples/ Detectors	No. of meas.	^{238}Pu		^{239}Pu		^{240}Pu		^{241}Pu	
		Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
All samples I set.	320	0.24	0.77	-0.14	0.39	0.25	0.90	0.36	0.64
MNH	63	0.29	0.69	-0.17	0.34	0.32	0.84	0.41	0.59
MOX	151	0.29	0.69	-0.23	0.36	0.45	0.82	0.50	0.67
PNH	61	-0.13	0.63	0.11	0.31	-0.27	0.65	0.05	0.56
POX	45	0.50	0.77	-0.11	0.51	0.14	1.20	0.22	0.52
Detector 1 800 mm^2	85	0.30	0.75	-0.24	0.36	0.48	0.79	0.49	0.64
Detector 2 500 mm^2	128	0.23	0.82	-0.13	0.41	0.28	0.91	0.18	0.67
Detector 3 1000 mm^2	107	0.19	0.75	-0.06	0.38	0.02	0.91	0.46	0.55
All samples II set	404	0.16	0.78	-0.07	0.40	0.03	0.86	0.43	0.55

10.9.2. Results with calculated ^{242}Pu abundance

The mean relative differences and their RSDs are presented in Table 6. The new algorithm (G), in the second row, which was used in version 8 of MGA, shows a high bias of about 19% for ^{242}Pu. Four remaining isotopes are all negatively biased by about 1%. The old algorithm in MGA and the algorithm (PR) developed at SAL give comparable means and RSDs. The algorithm (PR) applied to a second set of 404 samples shows also similar differences.

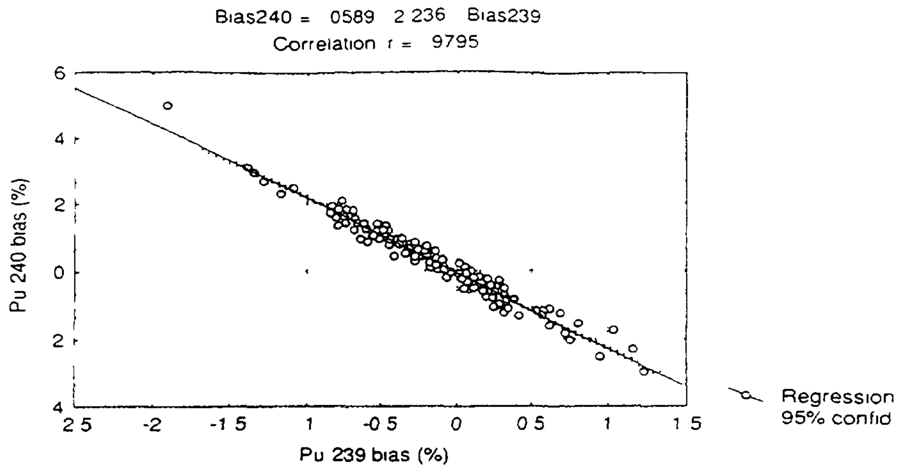

FIG 5 Correlation of biases, ^{240}Pu/^{239}Pu

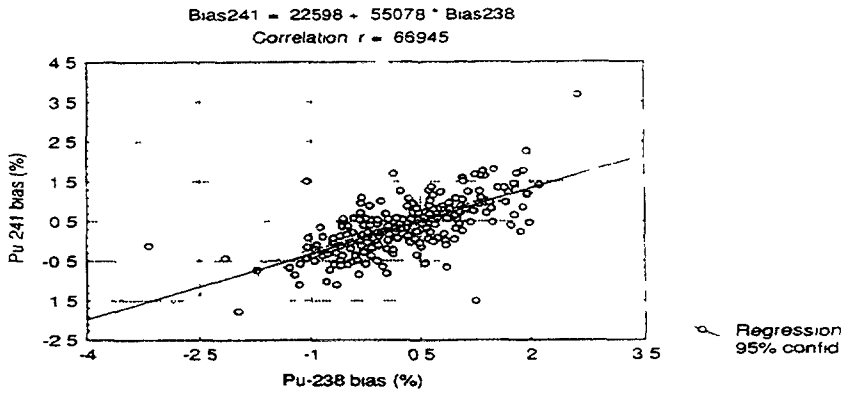

FIG 6 Correlation of biases, ^{241}Pu/^{238}Pu

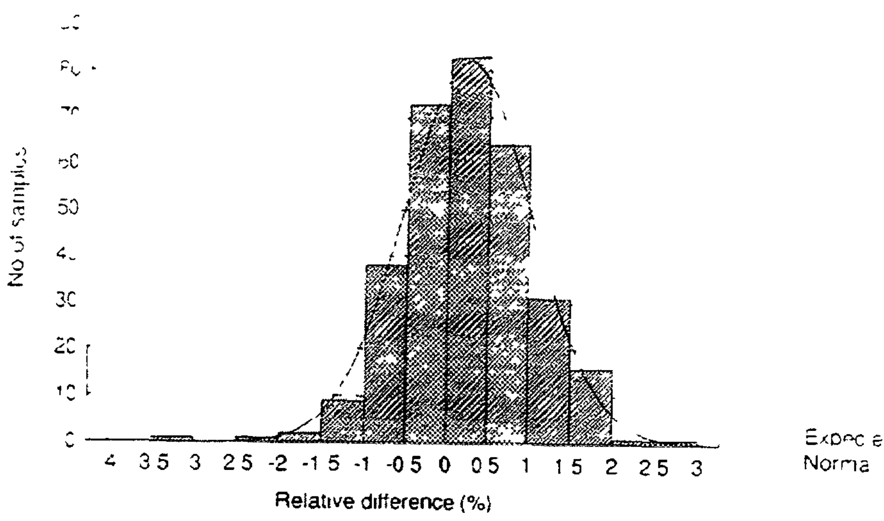

FIG 7 ^{238}Pu Distribution of differences (MS-GS)*100/MS

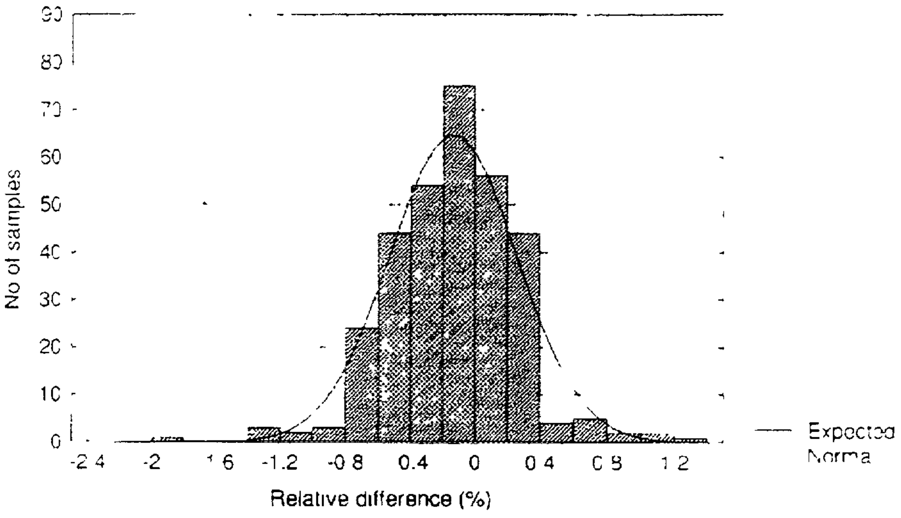

*FIG 8. ^{239}Pu. Distribution of differences (MS-GS)*100/MS*

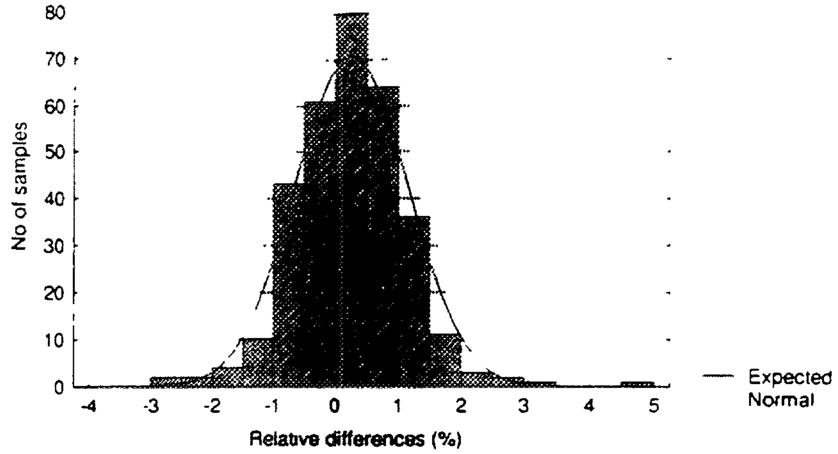

*FIG. 9. ^{240}Pu Distribution of differences (MS-GS)*100/MS.*

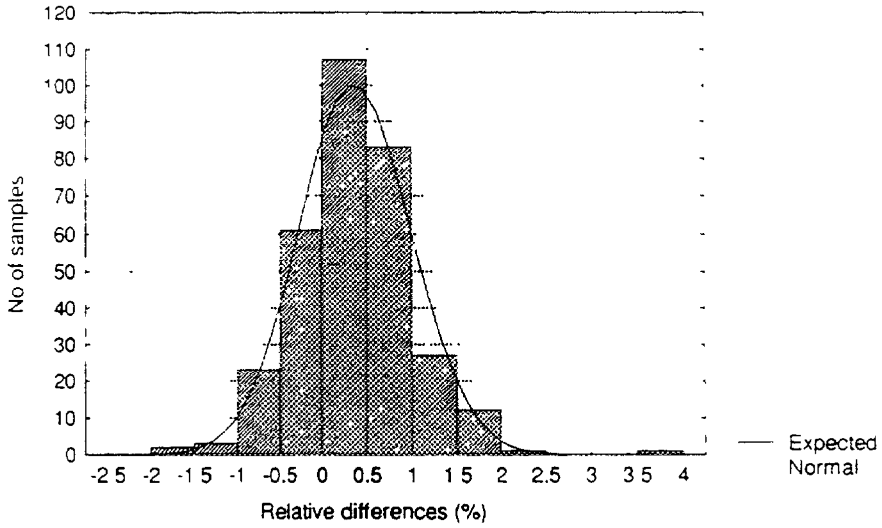

*FIG 10. ^{241}Pu. Distribution of differences (MS-GS)*100/MS.*

TABLE 6. RELATIVE MEAN DIFFERENCES AND RELATIVE STANDARD DEVIATIONS (RSD) FOR 5 Pu ISOTOPES [%]. 320 SAMPLES, VARIOUS ALGORITHMS FOR ^{242}Pu CALCULATION

MGA version ^{242}Pu algorithm	238Pu		239Pu		240Pu		241Pu		242Pu	
	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
8I, old algorithm (G)	0 34	0 86	-0 20	0 48	0 26	0 97	0 37	0 70	1 05	5 87
8I, new algorithm (G)	-0 38	0 81	-0 92	0 50	-0 46	0 96	-0 35	0 70	19 15	6 49
8I, algorithm (PR) one parameter set	0 21	0 76	-0 16	0 52	0 22	0 86	0 33	0 65	0 51	5 68
8I, algorithm (PR) material parameter set	0 21	0 78	-0 16	0 50	0 22	0 86	0 33	0 64	0 54	4 66
					404 samples					
8I, algorithm (PR) one parameter set	0 08	0 78	-0 14	0 64	-0 04	0 73	0 34	0 63	1 42	6 51
8I, algorithm (PR) material parameter set	0 06	0 80	-0 17	0 54	-0 07	0 80	0 32	0 61	1 79	4 18

The distributions of differences for ^{242}Pu in 320 samples set are presented in Figures 11–14.

10.9.3. ^{240}Pu effective

This comparison was performed only for the 320 sample set. The following mean differences and RSDs were calculated:

(1) for ^{242}Pu taken from MS,

(2) for ^{242}Pu derived from our own algorithm comprising all 320 samples, and

(3) for all samples using the equations for the subgroups of materials.

The resents are presented in Table 7.

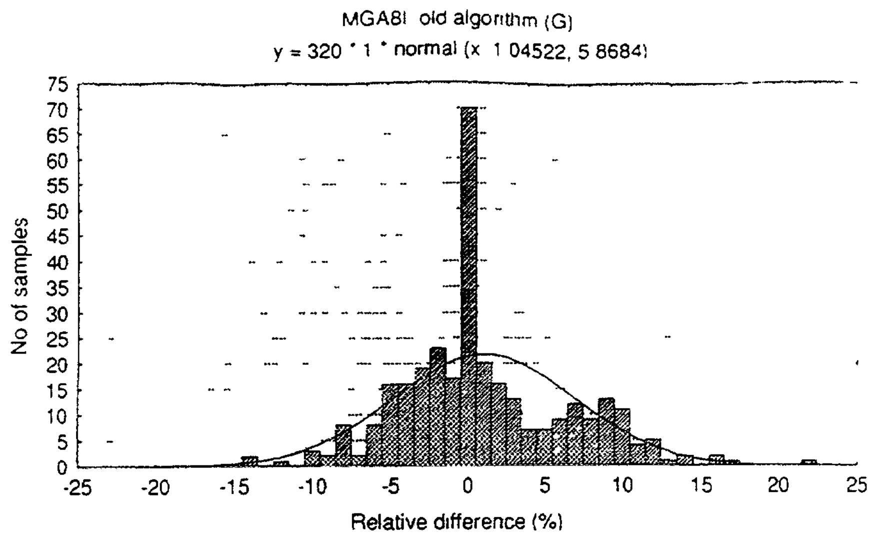

*FIG. 11 ^{242}Pu. Distribution of differences (MS-GS)*100/MS*

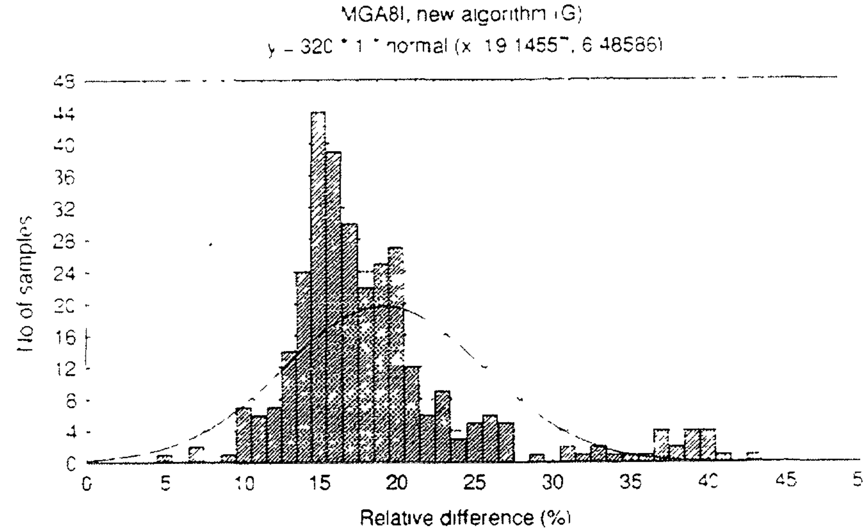

FIG 12. ^{242}Pu. Distribution of differences (MS-GS)*100/MS

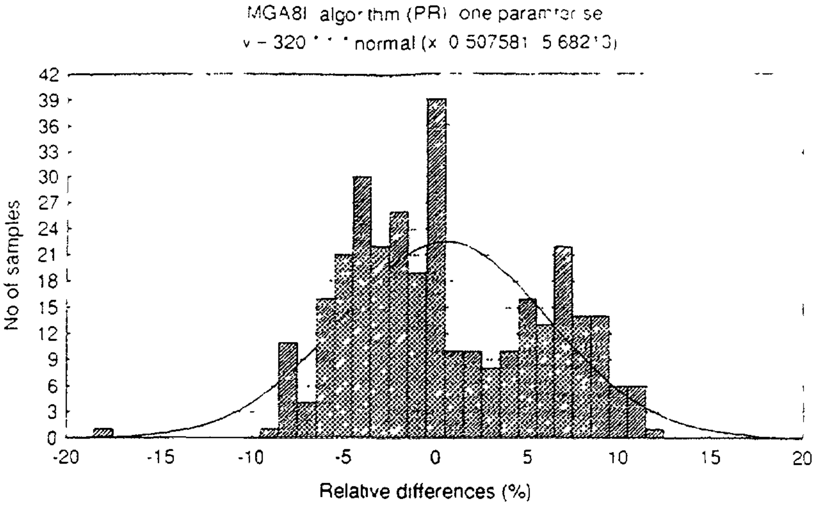

FIG. 13 ^{242}Pu Distribution of differences (MS-GS)*100/MS

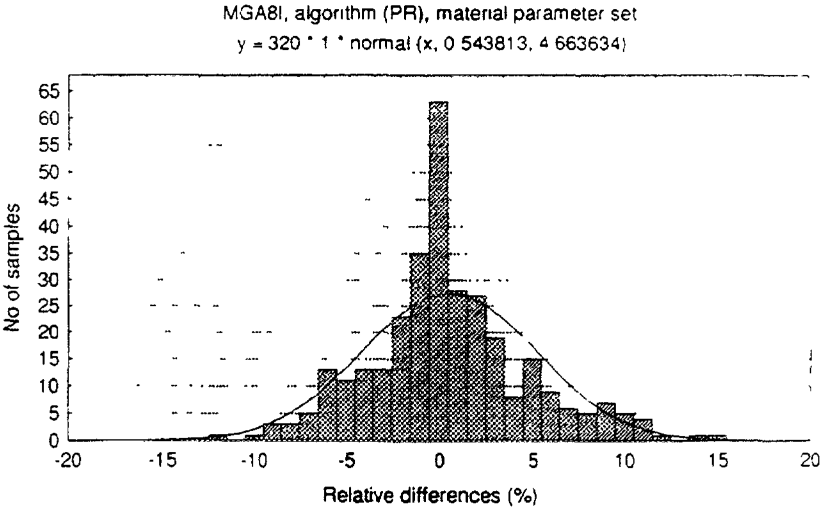

FIG. 14. ^{242}Pu. Distribution of differences (MS-GS)*100/MS

TABLE 7. COMPARISON OF ^{240}Pu EFFECTIVE FROM MS AND GS

Data used	Mean difference (%)	RSDs (%)
^{242}Pu from MS	0.03	0.64
^{242}Pu from own general algorithm	-0.29	1.34
^{242}Pu from own material algorithms	-0.29	1.19

The RSD for the calculated ^{242}Pu content is about twice of this value when ^{240}Pu effective is calculated with ^{242}Pu taken from MS. The negative bias of about 0.3% results from the mean bias of ^{242}Pu calculated from correlation equations which is about 0.5% (see Table VI). The RSD calculated from equations for individual materials is about 10% lower.

10.9.4. Quality control measurements

In 1992-93 systematic measurements at regular time intervals were performed with the same sample of NBS 947 standard reference material. The sample was evaporated in a penicillin vial. Altogether, 452 measurements were recorded. The mean differences and RSDs are shown in Table 8. All results were decay corrected to a common date and the ^{242}Pu was taken from the certificate.

TABLE 8. MEAN BIAS AND RSD FOR QUALITY CONTROL MEASUREMENTS (%)

Measurement type	No. of meas.	^{238}Pu		^{239}Pu		^{240}Pu		^{241}Pu	
		Mean	RSD	Mean	RSD		RSD		RSD
All meas.	452	-0.37	0.86	0.28	0.18	-1.17	0.70	0.40	0.74
Detector 1 800 mm^2	101	-0.33	0.96	0.29	0.19	-1.23	0.75	0.66	0.90
Detector 2 500 mm^2	159	-0.66	0.78	0.30	0.17	-1.24	0.69	0.19	0.72
Detector 3 1000 mm^2	192	-0.15	0.79	0.26	0.17	-1.09	0.68	0.44	0.60

There is a high negative bias for ^{240}Pu (in routine samples it was positive and at least 4 times lower, see Table 5). Also the bias for ^{238}Pu is negative (in Table 5 positive) and the bias for ^{239}Pu negative (previously positive). The RSD for ^{239}Pu is lower (0.18 vs. 0.39) but for other isotopes it is practically the same as for routine samples. The detector used does not seem to have a significant influence on the quality of results.

10.10. CONCLUSION

(1) The relative differences between MS and GS for isotopes $^{238-241}$Pu are in the range of ±1% for ^{239}Pu and ±2% for the other 3 isotopes; the differences for ^{242}Pu are in the range ±10%.

(2) The samples with a high abundance of ^{239}Pu require a separate algorithm for calculation of ^{242}Pu. Such samples constitute no more than 5% of the total number of samples routinely analysed at SAL.

(3) It was possible to lower the mean bias by adjusting the gamma ray emission probabilities. The spread of differences for directly measured isotopes, except ^{239}Pu, is, however, 2 to 3 times larger than it would have been expected from the counting statistics. This seems to come from the instability of the deconvoltition procedures.

(4) The presence of correlated bias for the pairs of isotopes ^{239}Pu - ^{240}Pu and ^{238}Pu - ^{241}Pu can indicate some systematic errors in the calculation of the number of counts from deconvoluted spectra or errors in the intrinsic efficiency calibration.

(5) In terms of bias the materials show some differences, for example, the change in sign of the bias for PNH material (mostly freshly separated Pu with low ^{241}Am). However, the fluctuations of differences (RSD) remain practically the same, independent of the material subgroup. The same can be said when different detectors are used.

(6) The quality control measurements performed on the same sample (NBS 947), with the same detector, in the same 2 year time-span show similar bias and RSD as the routine samples compared for the same period of time.

(7) In a few cases the MGA calculation failed completely. Without identifiable reason the spectra could not be evaluated.

(8) All results considered here were obtained with the version 8 of MGA. The version 9, which is at SAL since about 1 year, was not implemented for routine work because it produces unacceptable errors, particularly for ^{239}Pu and ^{240}Pu.

(9) It was assumed that the MS were free of errors. From quality control measurements with the use of reference materials the following mean bias and RSD for isotopic ratios were estimated (in%): ^{238}Pu (α spectrometry): -0.21 and 0.21, ^{240}Pu: from -0.03 to 0.02 and 0.06, ^{241}Pu: 0.08 and 0.14, ^{242}Pu: -0.36 and 0. 14.

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ABBREVIATIONS

ADC	analog to digital converter
ADSP	analog to digital signal processor
AQCS	analytical quality control services
FWHM	full with–half maximum
IEC	International Electrochemical Committee
MCA	multi-channel analyser
MS	mass spectrometry
NAA	neutron activation analysis
NPP	nuclear power plant
PIXE	particle induced X ray emission
P/Z	pole/zero
RDS	relative standard deviation
ROI	region of interest
QA	quality assurance
QC	quality control
QXAS	quantitative X ray analysis software
SAL	Safeguards Analytical Laboratory
STD	standard deviation
XRF	X ray fluorescence

CONTRIBUTORS TO DRAFTING AND REVIEW

Aarnio, P.A.	Helsinki University of Technology, Finland
Abani, M.C.	Bhabha Atomic Research Centre, India
Ala-Heikkil, J.J.	Helsinki University of Technology, Finland
Capote Noy, R.	Center of Applied Studies for Nuclear Development, Cuba
Debertin, K.	Physikalisch-Technische Bundesansalt, Germany
Desdin, L.F.	Center of Applied Studies for Nuclear Development, Cuba
Fazinic, S.	International Atomic Energy Agency
Hakulinen, T.T.	Helsinki University of Technology, Finland
Heydorn, K.	Risø National Laboratory, Denmark
Nikkinen, M.T.	Helsinki University of Technology, Finland
Osorio, V.	International Atomic Energy Agency
Parus, J.L.	International Atomic Energy Agency
Perez, R.	Center of Applied Studies for Nuclear Development, Cuba
Raab, W.	International Atomic Energy Agency
Sanderson, C.G.	Environmental Measurement Laboratory, United States of America
Sarria, P.	Center of Applied Studies for Nuclear Development, Cuba
Van Espen, P.	University of Antwerp, Belgium
Wang Li-Yu	China Institute of Atomic Energy, China
Westmeier, W.	Gessellschaft für Kernspektrometrie, Germany