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**A PROGRAM FOR AUTOMATIC RADIOELEMENTAL ANALYSIS: DISCUSSION OF THE
METHOD AND RESULTS ON A TEST SPECTRUM.**

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ABSTRACT.

A computer program capable of qualitative and quantitative radioelemental analysis with high accuracy, high degree of automatism and great easy in the utilization, is presented. It has been realised to be used for Ge(Li) gamma-ray spectroscopy and can be used for X-ray spectroscopy as well.

This program provides for: a) automatic search of peaks with the second derivative method; b) nonlinear peak-fitting in terms of a gaussian function superimposed to a linear or parabolic background; c) energy and absolute intensity determination of γ -rays; d) identification of the radioisotopes present in the sample and calculation of the corresponding activities.

The last step is carried out by using a library containing lifetimes and decay schemes of the radionuclides expected to be present in the examined sample. The problem of a gamma line being assigned to more than one nuclide, is solved by searching the least-squares solution of a set of equations for the isotopes activities.

Two versions of this program have been written. The first to be runned batchwise using a medium size computer (UNIVAC 1106) and a second interactive version for the on-line analysis by means of a small computer (HP 2100 A).

Results on a spectrum, due to a water sample from the primary circuit of the Garigliano BWR nuclear power plant, are presented and discussed.

1. - INTRODUCTION.

The extensive utilization of radionuclides in several fields, such as medicine, biology, industry, etc. besides the nuclear power production, has given rise to the need of sensible and precise methods for the determination of the kind and the amount of radioactive contamination both in the environment and at the sites of production and utilization of radioelements.

It is often needed to perform a radioelemental qualitative and quantitative analysis of a large number of samples in a limited amount of time. Moreover, the analysis has to be carried out by users not always fully acquainted with the methods involved. It is then very desirable to have at one's disposal a completely automatic procedure. On the other hand, some degree of interactivity can be useful to the more skilled users, in order to obtain better results.

As far as high-resolution gamma-ray spectra analysis is concerned, the various steps of the data reduction have been well established in nuclear spectroscopy work. In particular, peak-searching and -fitting have been the object of a great amount of works. Many programs have been written for precise analysis of gamma-ray spectra, with large memory requirements and long processing times⁽¹⁻⁷⁾ or for fast but less accurate analysis⁽⁸⁻¹³⁾. Concerning qualitative and quantitative radioelemental analysis, only few automatic high-accuracy programs are at present available⁽¹⁴⁾.

The aim of the present work has been to realize a program for high-resolution qualitative and quantitative analysis capable to be used in fully automatic mode or with a degree of interactivity depending on the user's will. Following this line, the program CERNUC has been written that can be run batchwise using a medium size computer. A preliminary version has been presented in ref. (15). Then a modified version of the code (ICREA) for an interactive analysis using a small computer has been developed.

The method of analysis will be described in Section 2. In Section 3 the description of the two versions of the code and some results are given.

2. - METHOD OF ANALYSIS.

The main steps of the analysis are five: 1) the search of the peaks present in the spectrum; 2) the fitting of the data for extraction of the gamma-lines parameters; 3) the energy and absolute intensity determination; 4) the identification of the radionuclides responsible for the emission of the observed gamma-rays, and 5) the calculation of the activities of the identified radionuclides.

The analysis is carried out splitting the pulse-height spectrum in region where the width of the peaks is assumed constant (512 channels in a 4096-channels spectrum with about 0.5 keV/ch).

The knowledge of the position and width of two calibration-lines allows the calculation of an "external" linear energy-calibration and an estimate of the FWHM (to be assigned to each region) by interpolation of a linear relationship of resolution vs. (energy)^{1/2}. For each region of the spectrum peak-searching and line-fitting are iteratively carried out; partial overlap between regions is provided in order to avoid border-peak missing.

Peak searching is performed by means of the well known second derivative method⁽¹⁶⁾.

The iterative gradient least-squares method has been applied for the fitting of the spectrum in terms of a superimposition of gaussian functions on linear or parabolic background utilizing a slight modification of the program CERPI⁽⁴⁾. The selection of the fitting intervals and of the number of components included in each fit is made automatically on the basis of the peak positions as resulting from the search routine, and of the initial guess for the FWHM.

The free parameters for each multiplet are: the peak centroids and heights, their width and the background coefficients. The convergence of the minimization is controlled by performing, after each iteration, a set of significance tests on the fit parameters: the comparison of the current value of peak centroids and width with the initial guesses, the control of the distance between neighbouring peaks, the evaluation of the ratio between peak heights and underlying background. In case at least one test gives a negative answer, the fit on the corresponding multiplet is reinitialized with different starting values of the nonlinear parameters or adding or removing peaks.

This procedure provides for fast convergence so that no restriction on the number of iteration steps was set.

When the whole spectrum has been analysed in such way, the centroid and area of each peak are converted into energy and intensity. An "internal" energy-calibration is calculated in this way: on the basis of the external calibration, some "internal calibration" lines are identified out of twenty, whose accurate energies are stored in a properly chosen calibration-library. If the number of the recognized calibration-points is greater than six, a least-squares fit with a polynomial of fourth degree is performed taking into account both peak-centroid and energy errors. The polynomial degree is reduced down to a minimum of two if the calibration points are less than six. An iterative procedure based on the test of the chi-square value is provided in order to eliminate calibration points probably badly identified. Finally, the energies of the lines in the spectrum and the errors resulting from the centroids uncertainty and from calibration accuracy, are calculated.

For the intensity determination, an absolute intrinsic efficiency-curve of the detector has to be provided to the program. The actual efficiency-curve is obtained applying distance and finite sample size-factors relative to experimental arrangement.

The identification of the nuclides present in the sample is performed on the basis of a radio-nuclides-library containing lifetimes and decay schemes of the expected radioisotopes. The first step of the identification concerns with the comparison between the calculated energies of the spectrum lines and the energies stored in the library. If the energy of at least one gamma-transition belonging to a given radionuclide agrees with the energy of a spectrum line, that radionuclide is considered "candidate", and the gamma-peak is attributed to it. The good determination of the peak energies and of their errors, resulting from the accuracy of the energy calibration procedure, provides for reliable identification adopting the 3σ criterium. If the agreement occurs for more than one library energy, all the corresponding nuclides are considered candidates and labeled as "interfering".

The "not interfering" candidates are treated separately and their activities are expressed in terms of the intensities y_j of the identified emission lines as

$$C_i = \frac{\sum_j y_j b_{ij} / \sigma_{y_j}^2}{\sum_j b_{ij}^2 / \sigma_{y_j}^2} ;$$

where b_{ij} is the number of gamma-transition of energy E_j per decay of the i -th nuclide, and σ_{y_j} is the standard deviation of y_j .

If not all the gamma-transitions included in the library for a given candidate i are identified in the spectrum, the expected intensities for the not identified branches are calculated as

$$\bar{y}_k = C_i b_{ik}$$

and compared with the detection limit at energy E_k . This is computed taking into account the contents of a number of channels equal to three times the expected FWHM around the expected peak position. Such a procedure has been preferred to that based on an "a priori" estimate of the detection limit vs. energy, because it takes into account, at least partially, the chance that a peak has been missed by the automatic search routine. If the expected intensity of at least one of the not observed branches is greater than the detection limit, the nuclide is considered "uncertain".

For each group of interfering nuclides a branching matrix is built, where the i - j element b_{ij} is given by the branching ratio of the gamma-ray transition of energy E_j in the i -th candidate nuclide. The set of equations

$$Y_j = \sum_{i=1}^{NNU} b_{ij} C_i \quad j=1, \dots, NGAM \quad (1)$$

can be solved if the number NGAM of gamma-lines in the group is greater or equal to the num-

ber NNU of nuclides, and the least-squares solution, given by the minimization of

$$\chi^2 = \sum_{j=1}^{NGAM} (Y_j - \sum_{i=1}^{NNU} b_{ij} C_i)^2 / \sigma_{y_j}^2$$

provides for the activities of the candidate nuclides. Then the expected intensities of the unobserved branches are calculated and compared with the detection limit. If an expected intensity is greater than the detection limit, the corresponding nuclide is rejected before the final calculation of the activities of the remaining nuclides in the group.

Sometimes, although $NGAM > NNU$, the set of equations (1) cannot be solved, being two or more of the least-squares equations linearly dependent. In these cases only upper limits can be given for the activities of the nuclides involved.

Finally, the list of gamma-lines observed in the spectrum but not assigned to any nuclide, is given for helping the improvement of the radionuclides library.

3. - CODE DESCRIPTION.

The method of analysis described in the previous Section can be used in fully automatic mode. Only position and width of two calibration lines, besides an internal calibration library, an intrinsic efficiency curve for the detector and a radionuclides library are needed for carrying out all the steps of the analysis without any action of the user.

Following this method two computer codes have been written: CERNUC, which can be runned batchwise using a medium size computer and ICREA, which has been implemented on an interactive computer.

Table I shows typical data to be supplied as input to both programs.

The first version has been implemented on a UNIVAC 1106 computer, with magnetic tape or punched cards input. The maximum number of components for each fitting interval of maximum 150 channels, has been set to 6. With this configuration the program storage requirement is 45 K, 36 bit words and typical CPU time is 10 min for a 4096 channels spectrum with about 150 peaks.

In the second version, which can also be runned automatically, a reasonable compromise between automatism and flexibility has been reached. Such version allows the interaction of the user with the computer in some steps of the analysis. In particular at each iteration step of the fitting procedure, both experimental counts and fitted data relative to a multiplet can be displayed on a CRT and the user can eventually change the starting value of the width, the number and position of the gaussian functions and the type of background. This version has been implemented on a HP 2100 A computer with 24 K, 16 bit words memory.

To meet the memory requirement of the code together with the actual features of a small computer, we have split the analysis steps into five linked programs using the disk memory to store both the segments of the program and the data. The radionuclides library was split into five sub-libraries having in mind the advantage of easily performing partial analysis with oriented libraries.

TABLE I - Input table. The values are those used for the analysis of the test-spectrum. The assignment of values to the variables IFIR, ILAS, DELTA, DIS, KPMAX, NF, IGP, is optional. Zero for these variables implies the use of default values.

SPECTRUM LABEL	SP120
NUMBER OF CHANNELS	4096
COUNTING TIME (sec)	1000
COOLING TIME (min)	120
SAMPLE VOLUME (cm ³)	100
SAMPLE-DETECTOR DISTANCE (mm)	130
DETECTOR RADIUS (mm)	25
661 keV POSITION AND WIDTH (channels)	1652.5
1332 keV POSITION AND WIDTH (channels)	3328.6
IFIR, ILAS (first and last channels of the region to be analysed)	0,0
DELTA (defining the fitting intervals)	0
DIS (defining the minimum distance between components in a multiplet)	0
KPMAX (maximum number of components in a multiplet)	0
NF (degree of the background polynomial)	0
IGP (degree of the internal-calibration polynomial)	0

With this configuration, typical CPU time for a fully automatic analysis of a 4096-channel spectrum is 1 h. Using a Fast Fortran Processor (HP 1290 A) the time was reduced to about 20 min.

4. - RESULTS AND DISCUSSION.

The program has been used for the analysis of samples containing a mixture of fission and activation products and has been tested on spectra obtained from water samples from the primary circuit of the BWR Garigliano nuclear-power plant.

Spectra were taken at different cooling times, by means of a $60 \text{ cm}^3 \text{ Ge(Li)}$ detector with a standard electronic chain and a multichannel analyzer Laben 4096.

Fig. 1 shows the comparison between the initial guess of the width for each region and the widths resulting from the fitting procedure, vs. energy. The good agreement proves that the initial values of the width are well estimated, so good fitting convergence is achieved.

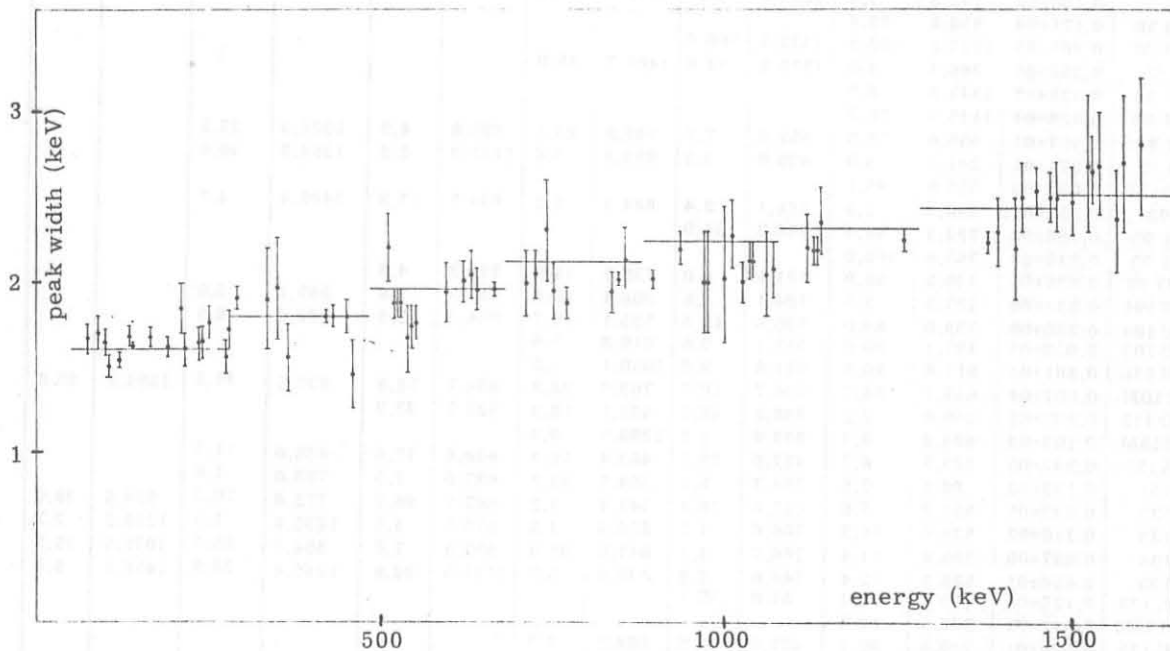


FIG. 1 - Peak width vs. energy. Full lines represent the estimated widths for each region while points and bars are widths and errors resulting from the fitting procedure.

The result of the fitting procedure for a multiplet in the test spectrum is shown in Fig. 2.

Fig. 3 presents the plot of the test spectrum, where the 93 lines resulting from the fitting procedure are drawn by a full line. Among them, 61 lines are assigned by the program to 28 nuclides and are labelled in Fig. 3 by the name of the corresponding nuclide identified on the basis of the library given in Table II.

The library contains 50 radionuclides: for each of them the maximum number of branches included is limited to 6. This number is adequate for an unambiguous nuclides identification and an accurate activity determination, but lines corresponding to low branchings not included in the library, even if found by the searching and fitting routines, cannot be assigned to any nuclide. In particular, in our spectrum this is the case for 30 out of the 34 unassigned lines. They are due essentially to the iodine isotopes and are labelled by an asterisk in Fig. 3.

Two of the 28 candidates i. e. $^{110\text{m}}\text{Ag}$ and $^{115\text{m}}\text{Cd}$, were rejected because the detection limit control gave a negative answer.

As an example of rejection in the case of a set of interfering nuclides, the code output for the interference of ^{92}Sr , $^{110\text{m}}\text{Ag}$, ^{104}Tc , ^{133}I , ^{134}I is given in Table III, where the comparison between the detection limit and the expected intensity of the unobserved transition energies is reported. For the $^{110\text{m}}\text{Ag}$ the detection limit test was negative and its contribution has been dropped for the calculation of the activities of the other nuclides in the group. After this rejection, ^{92}Sr results to be not interfering.

The detail of the final calculation of activities and expected intensities for each branch of ^{92}Sr and of the still interfering nuclides in the group are reported in Tables IV and V.

Finally Table VI summarizes the results relative to all the identified nuclides. Activities at drawing time are evaluated by our program without taking into account the decay relation between isotopes. For this reason the activities at $T = 0$ for $^{91\text{m}}\text{Y}$, ^{92}Y , $^{133\text{m}}\text{Xe}$ and $^{135\text{m}}\text{Xe}$ are not reliable and do not appear in the Table.

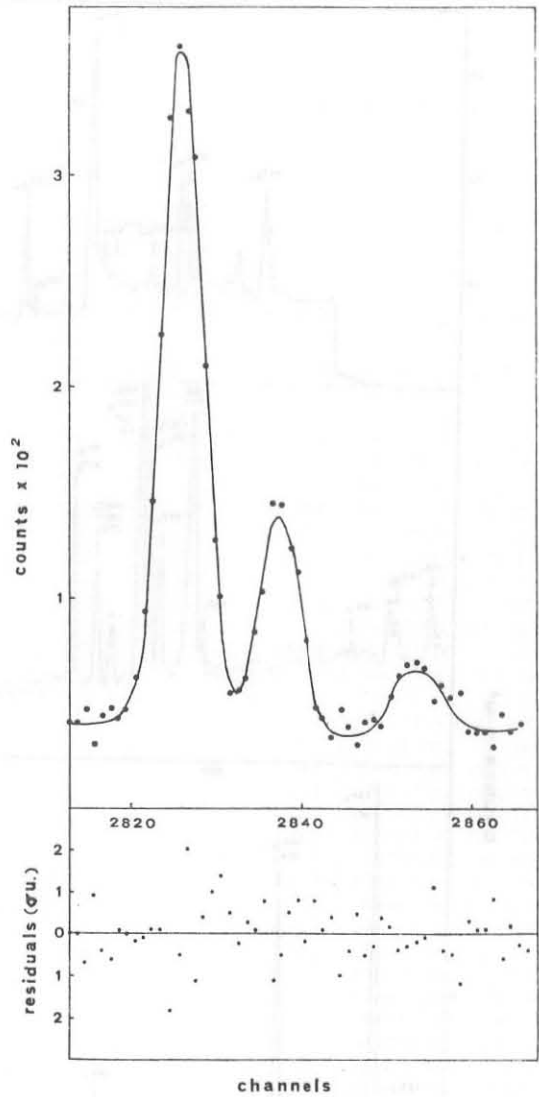


FIG. 2 - A multiplet in the test spectrum resolved by fitting the data with three gaussian functions superimposed to a quadratic background. The residuals are reported in units of standard deviation of the counts.

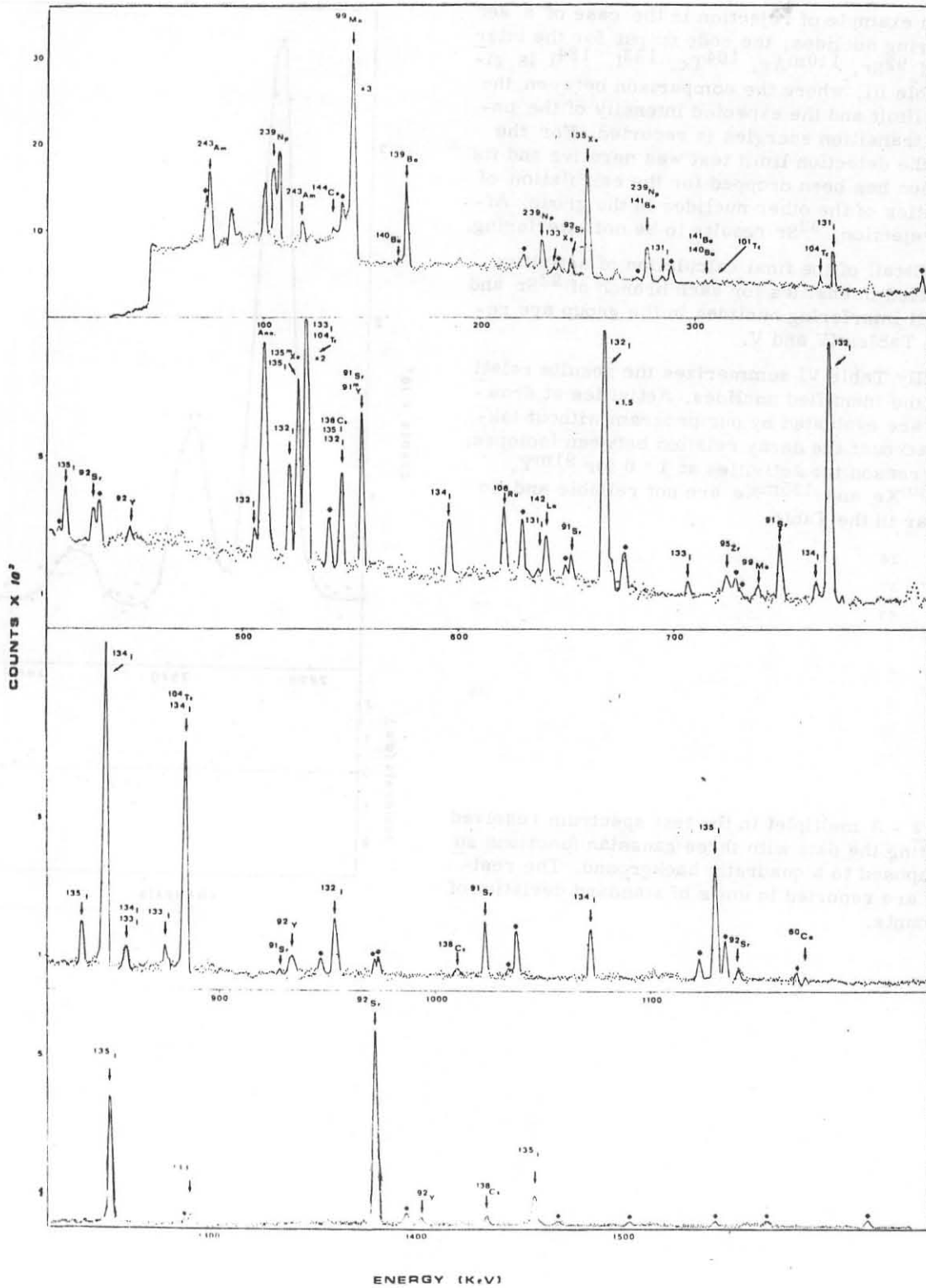


FIG. 3 - Gamma-ray spectrum from a water sample of the primary circuit of the BWR Garigliano nuclear power plant. The spectrum has been counted for 1000 sec, 120 min after the sample drawing, with a 60 cm³ Ge(Li) detector placed at 130 mm from the sample.

TABLE III - Code output relative to the interference of ⁹²Sr, ¹⁰⁴Tc, ^{110m}Ag, ¹³³I and ¹³⁴I.

NUCLIDE	ACTIVITY (PC/CC)		CALCULATED INTENSITIES						
	T = 120 M	T = 0 M	TOTAL	SR92	AG110M	I133	TC104	I134	DET. LIM.
SR92	2112 ± 40	3649 ± 69							
AG110M	56 ± 44	56 ± 44							
I133	1810 ± 24	1942 ± 25							
TC104	35 ± 6	4765 ± 827							
I134	1920 ± 28	10594 ± 152							
ENERGY	EXP. INTENSITY								
241.65	127 ± 12	141	141						
358.14	73 ± 12	69					69		
430.62	159 ± 36	187	155						
529.92	3461 ± 46	3484					3472	12	
595.33	456 ± 26	478							478
707.65	89 ± 19	80		20		60			
766.63	128 ± 22	175							175
847.13	4089 ± 63	4093							4093
857.24	328 ± 29	346					48		298
875.59	236 ± 26	181				181			
884.24	2883 ± 57	2882			90		8		2784
1072.57	734 ± 37	652							652
1142.63	200 ± 30	136	136						
1298.17	160 ± 35	92					92		
1383.87	4259 ± 79	4251	4219	32					
953.3			169						173
657.70					116				111
763.90					28				109
937.50					42				122
1236.60						60			112
535.1							11		104
893.0							7		159
CHISQUARE = 25.7									

TABLE IV - Code output relative to ⁹²Sr radioisotope.

NUCLIDE	ACTIVITY (PC/CC)		INTENSITY		
	T = 120 M	T = 0 M	EXP	CALC.	DET. LIM.
SR92	2143 ± 38	7303 ± 66			
ENERGY					
241.65	127 ± 12		127 ± 12	141	
430.62	160 ± 36		160 ± 36	155	
1142.63	201 ± 31		201 ± 31	136	
1383.87	4259 ± 79		4259 ± 79	4244	
953.3				169	173
CHISQUARE = 5.6					

TABLE V - Code output for the nuclides of Table III still interfering after the rejection of ^{110}mAg .

NUCLIDE	ACTIVITY (PC/CC)					
	T = 120 M	T = 0 M				
TC104	36 ± 6	5300 ± 837				
I133	1812 ± 24	1944 ± 25				
I134	1939 ± 22	10701 ± 123				
ENERGY	EXP. INTENSITY	CALCULATED INTENSITIES				DET. LIM.
		TOTAL	TC 104	I 133	I 134	
358.14	73 ± 12	73	73			
529.92	3461 ± 46	3488	12	3476		
595.33	456 ± 26	482			482	
707.65	89 ± 19	60		60		
766.63	128 ± 22	176			176	
847.13	4089 ± 63	4133			4133	
857.24	328 ± 29	349		48	301	
875.59	236 ± 26	181		181		
884.24	2883 ± 57	2819	8		2811	
1072.57	734 ± 37	659			659	
1298.17	160 ± 35	92		92		
535.1			11			104
893.0			7			159
1236.60				60		112
CHISQUARE = 23.1						

TABLE VI - List of the finally identified radioisotopes in the test spectrum. For each isotope, activities and errors are reported.

	T = 120 M	T = 0
CO60	25 ± 8	25 ± 8
SR91	964 ± 35	1124 ± 41
SR92	2143 ± 38	3703 ± 66
Y91M	701 ± 22	
Y92	1021 ± 89	
ZR95	259 ± 24	239 ± 24
MO99	2019 ± 58	2064 ± 13
TC101	17 ± 5	9709 ± 2730
TC104	39 ± 6	5300 ± 837
RU106	2174 ± 131	2174 ± 131
I131	254 ± 10	256 ± 10
I132	1654 ± 18	3151 ± 35
I133	1812 ± 24	1944 ± 25
I134	1939 ± 22	10701 ± 123
I135	3250 ± 52	4054 ± 65
XE133M	141 ± 36	
XE135	536 ± 10	6301 ± 12
XE135M	69 ± 10	
CS138	75 ± 46	1421 ± 825
BA139	346 ± 8	1012 ± 24
BA140	64 ± 92	65 ± 93
BA141	90 ± 16	12502 ± 2187
LA142	348 ± 27	918 ± 72
CE144	700 ± 47	700 ± 47
NP239	818 ± 23	840 ± 23
AM243	186 ± 8	186 ± 8

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