PECULIARITIES OF USING ISOTOPIC DILUTION IN LS SPECTROMETRY

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ABSTRACT. In this proposed isotopic dilution method, the activities of target isotope-analytes are determined relative to the known activity of an isotope tracer that is added in the initial stage of analysis in order to determine the chemical yield. A key aspect of activity calculation, undertaken on the basis of new mathematical approaches, is the splitting of a complex spectrum obtained by liquid scintillation (LS) counting into its separate individual reference spectra, corrected for the sample quenching parameter. This method avoids applying alternative techniques for chemical yield determination, such as gravimetry, various modifications of optical methods (SF, AAS, AES), or γ spectrometry. Based on our experience, it is possible to formulate the following criteria to select tracer isotopes for LS spectrometry: absence (or negligible content) in analyzed samples, sufficiently long half-life (at least 1 month), and, most importantly, minimal overlapping of the spectra of the isotopes to be determined. Because of the poor energy resolution of the LS spectra, it is necessary to optimize the amount of the isotope tracer in order to minimize the statistical uncertainties when determining the activities of target isotopes. In the present work, we present methods for identifying and quantifying the individual isotopic activity, and for evaluating the components of uncertainties resulting from the analysis of complex LS spectra. A few examples of the analytical procedures and corresponding calculations are considered.

INTRODUCTION

Liquid scintillation counting (LSC) has a number of advantages compared to other radiometric methods, namely the registration of nuclear emission in 4π geometry, simultaneous registration of various types of radiation in correlation with energy, and the simplicity of sample preparation.

Because LSC can determine some beta and alpha emitters by the isotopic dilution method, it is possible to use, as monitor of chemical yield, isotopes whose LS spectra have a minor overlap with the spectra of the isotopes to be determined. Isotopes that have basic components of particulate radiation that are represented by low-energy electrons preferably should be used (see Table 1).

Table 1 Characteristics of basic particulate emission for certain isotopes.

Tracer	E_{e-} (keV)	Emission probability	Target isotope	E_{max} (keV)
^{85}Sr	11.4	0.29	^{89}Sr	1491
			^{90}Sr	546
^{88}Y	12.1	0.27	^{90}Y	2284
^{95m}Tc	2.3	0.95	^{99}Tc	294
	14.8	0.20		
^{143}Pm	4.2	0.72	^{146}Pm	162
	30.5	0.07		795
			^{147}Pm	223
^{237}Pu	10.1	0.38	^{241}Pu	20.8
	10.8	0.12		
	27.5	0.04		

So, for example, the following determinations are possible:

- ^{85}Sr for determining ^{89}Sr and ^{90}Sr;
- ^{88}Y for determining ^{90}Y;
- ^{95m}Tc for determining ^{99}Tc;

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- ^{143}Pm for determining ^{146}Pm, ^{147}Pm;
- ^{237}Pu for determining plutonium isotopes, including ^{241}Pu.

Determining ^{228}Th, ^{230}Th, and ^{232}Th in solid samples via ^{234}Th in secular equilibrium with existing ^{238}U is possible as well.

A technique for radiostrontium (^{89}Sr, ^{90}Sr) determination via an ^{85}Sr tracer has found a recent practical application (Heilgeist 2000; Ermakov et al. 2002; Kriuchkova et al. 2004; Eikenberg et al. 2006). Attempts to determine ^{99}Tc via ^{95m}Tc were undertaken as well (Lee et al. 2002). All tracers listed above are gamma emitters; thus, scintillation caused by Compton scattering results in overlapping of the spectra of the tracer and the target isotope in a wide energy region. This makes the correct calculation of isotope activities via LS spectrometry problematic.

To solve this problem, a method is proposed based on new mathematical approaches for decoding complex LSC spectra. Identification and activity calculation of the components in counting sources (e.g. ^{85}Sr, ^{89}Sr, ^{90}Sr, and ^{90}Y during radiostrontium determination) are done using an algorithm that includes the optimized convolution of the spectra into groups, and by modeling the superposition of individual reference spectra shaped to a sample quenching parameter (Kashirin et al. 2003). To determine the individual emitters, a fitting process for the whole spectrum is used, not for just the counts in certain energy windows. This fitting process increases the sensitivity of the measurements.

MATERIALS AND METHODS

Reagents and Tracers

All the following chemicals were of reagent grade: LS cocktails Ultima Gold™ AB, Ultima Gold F, Insta-Fluor were from PerkinElmer (USA), OptiPhase HiSafe 3 (PerkinElmer Life Sciences). All measurements were carried out with low-diffusion 20-mL polyethylene vials.

Standard radioactive solutions used for creating the spectral library were obtained from the stocks of various institutions: All-Russian Scientific Research Institute of Metrology (St. Petersburg, Russia): (^{90}Sr+^{90}Y), ^{89}Sr, ^{99}Tc, ^{147}Pm; Joint-Stock Company "Cyclotron" (Obninsk, Russia): ^{85}Sr, ^{88}Y; and LNP of Joint Institute of Nuclear Research (Dubna, Russia): ^{95m}Tc, ^{143}Pm, ^{237}Pu.

Instruments

Tri-Carb 2550 TR/AB and Guardian 1414 (PerkinElmer) LS analyzers were used in this study. The software RadSpectraDec (Tri-Carb and Guardian versions) was used to identify radionuclides and calculate their activities.

Separation Procedures

The following techniques were used for the separation and radiochemical purification of certain elements. Brief descriptions are given below.

- Strontium: 2 methods were applied: 1) Separation and purification using a number of precipitation procedures: preconcentration of the 2nd group with sulfates, elimination of polyvalent elements and ^{210}Pb with hydroxides, separation of Ra isotopes and ^{140}Ba by precipitation of chromates, precipitating strontium sulfate in the presence of EDTA, and transformation into carbonate form by metathesis; 2) Column sorption chromatography using VS-15 material (Ermakov et al. 2002).

- Technetium: Anion-exchange chromatography with TEVA resin (Eichrom, USA): sorption in 0.1M HCl medium, washing with 0.5M HNO_3, and elution with 10M HNO_3. To avoid elimination of technetium, evaporation of the eluate should be carried out at 50–60 °C.
- Yttrium: Separation of yttrium from brine waters consists of the following stages: separation from bulk salts and preconcentration by coprecipitation with hydroxides; anion-exchange separation of impurities in HCl; separation of Ac, Pb, and Th by coprecipitation with $KLa(SO_4)_2$ in saturated K_2SO_4 solution; and hydroxide precipitation.

LS Spectra Processing

A key aspect of this mathematical approach is the splitting of a complex spectrum, obtained via LSC, into its individual reference spectra, and corrected for the sample quench parameter.

A model spectrum is created as a linear combination of normalized spectra of various radionuclides:

$$M_i = \sum_{i=1}^{J} c_j M_{i,j}(T) \tag{1}$$

where M_i is the model spectrum, $M_{i,j}(T)$ is the spectrum library of each nuclide, and c_j is the proportion of each species. The weight coefficients (c_j) are adjusted so that the model spectrum will coincide with the sample spectrum to the maximum degree. Each spectrum is a function of the quench parameter (T) of the sample. The solution is found by recursive minimization of a special function representing the difference between a model spectrum and the experimental spectrum.

Due to problems with the correct fitting of LS spectra by certain elementary functions for creating the nuclide library, direct measurements of the spectra of each radionuclide were used. Therefore, the analytical database (the library of quenched spectra) for each radionuclide was obtained by measuring standard solutions for at least 10 quenching levels, using CCl_4 as the chemical quenching agent.

The statistical content of only 1 channel is very low. To increase the statistical information, the initial experimental spectra are combined into groups (Figure 1), and the algorithm of grouping depends on the nature of the spectrometer amplifier. For spectrometers with a linear analog-to-digital converter (ADC) (Tri-Carb series), the optimum algorithm for binding reference spectra into groups is a quasi-arithmetic progression.

For spectrometers with a logarithmic ADC (Quantulus and Guardian from PerkinElmer and Triathler from Hidex) and a detailed low-energy region of the spectrum, the usual linear combination gives good results (e.g. a combination of 10 channels in a group). Based upon values of c_j obtained after the spectrum model, the activity of a component (radionuclide A_j) in a sample may be determined as follows (for $T_{sample} = T_{bkg}$):

$$A_j = \frac{(N - N_{bkg})c_j}{T\varepsilon_j} = \frac{N_j}{T\varepsilon_j} = \frac{N - N_{bkgj}}{T\varepsilon_j} \tag{2}$$

where c_j is the contribution of the j-th isotope to the integrated spectrum counts; j is the counting efficiency of the j-th isotope for the quenching parameter of the sample; N_{bkg} is the number of background counts integrated over all channels; and $N_{bkgj} = N - N_j$ is the total integral account of all radionuclides in the sample including the blank sample background, after subtraction of the j-th radionuclide.

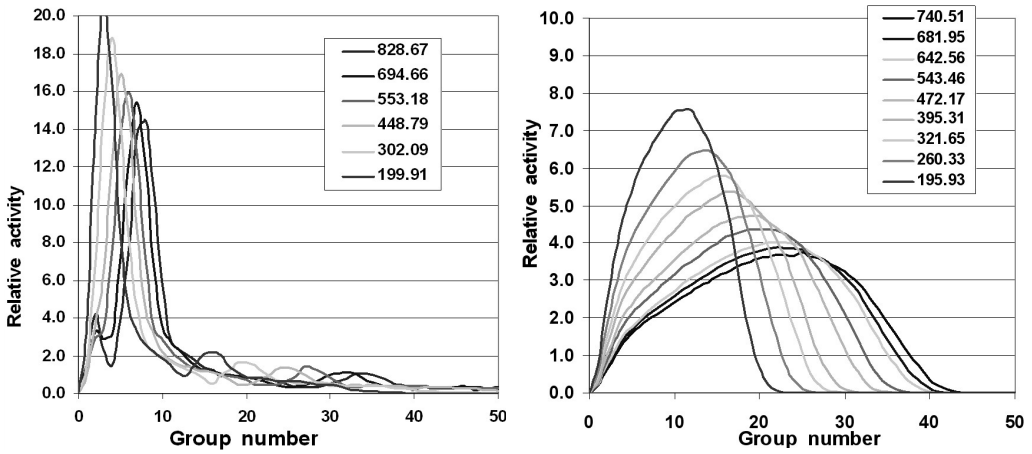

Figure 1 Sets of reference library LS spectra of the tracer and target isotopes obtained for different quenching levels after conversion into group form (measured with LSC Tri-Carb). Left: ^{95m}Tc; Right: ^{99}Tc.

The combined standard uncertainty of *j*-th isotope activity (for $T_{sample} = T_{bkg}$) is

$$\frac{\sigma_{A_j}}{A_j} = \sqrt{\frac{N + (N - N_j)}{N - (N - N_j)^2} + \frac{\sigma_{\varepsilon_j}^2}{\varepsilon_j^2} + \frac{\sigma_{c_j}^2}{c_j^2}} = \sqrt{\frac{2N - N_j}{N_j^2} + \frac{\sigma_{\varepsilon_j}^2}{\varepsilon_j^2} + \frac{\sigma_{c_j}^2}{c_j^2}} \quad (3)$$

where $N_j = (N - N_j) \times c_j$ is the contribution of radionuclide *j* to the integral count of the sample, σ_{cj} is the uncertainty resulting from the fitting procedure, and σ_{ε_j} is the uncertainty resulting from the counting efficiency determination.

Assuming that for the *j*-th isotope the radiation caused by other isotopes is considered to be a background effect (Babenko et al. 2002), the lower limit of detection (LLD) at the 95% confidence level based on Currie's (1968) detection limit L_D can be expressed as:

$$LLD_j = \frac{2.71 + 2 \cdot K\sqrt{2 \cdot N_{bkgj}}}{\varepsilon_j T} \quad (4)$$

Taking into account that $N_j << N$, the LLD when the background and sample are counted at the same time can be expressed (according to Prichard et al. [1992]) as:

$$LLD_j = \frac{4.65\sqrt{N}}{\varepsilon_j T} \quad (5)$$

RESULTS AND DISCUSSION

Minimizing the Statistical Uncertainty for Processing Multicomponent LS Spectra

In the above-stated formulas, the counts N, N_{bkg}, and N_j are integrated in the full range of the channels of the analyzer. However, when measuring low-activity samples ($N - N_{bkg} << N_{bkg}$) with a known radionuclide composition or when determining the low activity of a radionuclide over a high total activity of the sample ($N_j << N$), this approach leads to decreased measurement precision.

When analyzing the ratio of background/useful counts applied to the ^{90}Sr LS spectrum (Figure 2), it is clear that in the low-energy region, the background considerably exceeds the contribution by radionuclide emission. In the medium-energy area, the background and the nuclide counts are comparable, and in the high-energy area, the examined relationship again has a tendency to grow.

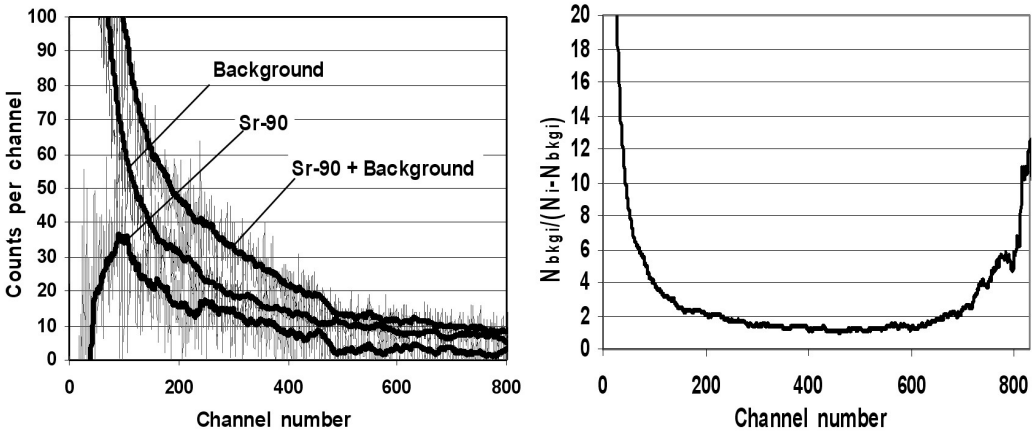

Figure 2 LS spectra obtained with Tri-Carb 2550 counter. Left: a low-level sample containing ^{90}Sr, background, and ^{90}Sr after background subtraction; Right: relationship of background/useful counts for the above spectrum.

Taking into account the above arguments, it is rational to use the middle area of the spectrum with the optimal useful counts/background ratio for minimizing and calculating the statistical uncertainty. Using Equation 3 for the statistical uncertainty instead of N, N_{bkg}, and N_j, we can use the sum only in an optimized region of channels (from the left to right boundaries):

$$\frac{2\sigma_{A_j}}{A_j}(l,r) = 2\sqrt{\frac{2\sum_{i=l}^{r} N_i - \sum_{i=l}^{r} N_{ji}}{\left(\sum_{i=l}^{r} N_{ji}\right)^2}} \tag{6}$$

When searching for the scope of the optimized region, the 2-σ uncertainties for A_j are investigated at the right-hand boundary of the calculation region, from the maximum number of channels up to the first channel, and then at the left-hand boundary line, from the obtained channel with minimum value of uncertainty up to the maximum number of channels.

In accordance with the described algorithm, an optimized region for processing the ^{90}Sr LS spectra obtained with a Tri-Carb ranges from 100 to 540 channels (Figure 3). The results were obtained for 999-min measurements of ^{90}Sr (just after separation from ^{90}Y) with an activity of ~30 mBq.

Boundaries of optimized regions for a spectrum depend on different factors: the energy distribution of emission of radionuclides, the ratios of radionuclide activities, and the quenching parameter. For analyzing samples with complex radionuclide compositions, especially when using the isotopic dilution method, the parameters of optimization depend both on the spectrum of the target radionu-

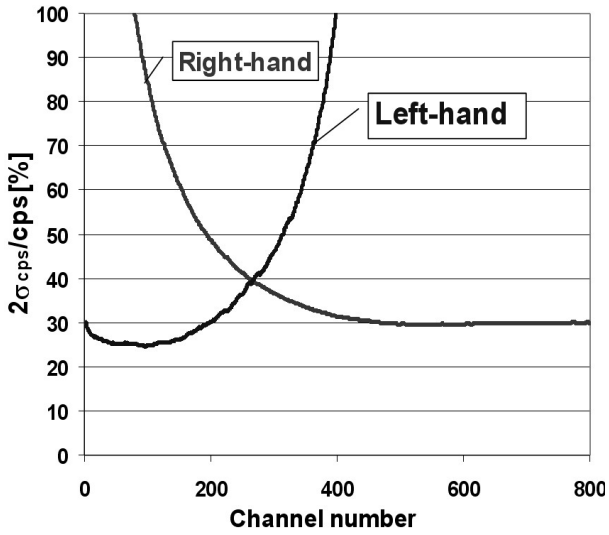

Figure 3 Dependence of statistical $k = 2$ expanded uncertainties on boundaries of the region of optimization for a ^{90}Sr spectrum.

clide and on the whole spectrum of the mixture. In most cases, the proposed approach allows us to carry out the determination of low activities with much smaller uncertainties. The LLD for LS spectrometry according to Equation 5, optimized in the same manner, is much lower as well:

$$LLD_J \cong \frac{4.65\sqrt{\sum_{i=l}^{r} N_i}}{\varepsilon_j T} \tag{7}$$

When determining the radionuclides with high-energy emission against the background of radionuclides with smaller energies of emission, the decreasing LLD value is considerable due to the optimization of the calculation region. Results of LLD calculations for certain isotopes when spiking their short-lived tracers with a scope optimization are given in Table 2.

Table 2 LLD (with optimization) of certain isotopes in mixture with their tracers ($p = 0.95$), Tri-Carb 2550 TR/AB, sample tSI(E) ~400, counting for 1000 min.

	LLD (mBq)	
	Isotope-tracer activity (mBq)	
Composition of the radionuclide mixture	50	500
^{90}Sr (just after separation) + ^{85}Sr	14 (94–535)[a]	19 (99–672)
^{90}Y + ^{88}Y	16 (406–2112)	20 (303–2231)
^{95m}Tc + ^{99}Tc	13 (28–274)	19 (33–295)

[a]In parentheses: boundaries of domains, channel numbers.

Calculation of Activity and Evaluation of Uncertainty Components

Applying our method of LS spectra processing, the activity of an isotope in the sample A_{jsmp} may be calculated via tracer activity as:

$$A_{jsmp} = \frac{N_{trref}}{N_{trsmp}} \cdot \frac{V_{trref}}{V_{trsmp}} \cdot \frac{N_j}{\varepsilon_j \cdot T} \tag{8}$$

where N_{trsmp} and N_{trref} are the net counts related to the determination of the tracer in the sample and in the standard solution (corrected to a sample measurement date); V_{trref} and V_{trsmp} are the volume of the tracer solution for determining the target isotope activity in the reference solution and the sample solution, respectively; N_j is the net counts related to the j-th isotope, calculated from LSC data with optimization; and ε_j is the counting efficiency related to the quenching parameter of the sample.

The specific activity is

$$a_{jsmp} = \frac{A_{jsmp}}{V_{sample}} \qquad or \qquad a_{jsmp} = \frac{A_{jsmp}}{m_{sample}} \tag{9}$$

Taking into account (8) and (9), the combined standard uncertainty of the activity is

$$\delta_{A_j} = \sqrt{\delta_{N_j}^2 + \delta_{\varepsilon_j}^2 + \delta_K^2 + \delta_V^2} \tag{10}$$

where δ_{N_j} is the statistical uncertainty for the j-th isotope determination (from Equation 6); δ_j is the uncertainty of the counting efficiency determination (including counting statistics, standard solution certification, standard solution mass, and quenching parameter determination uncertainty); δ_K is the uncertainty of the chemical yield determination (combined); and $\delta_V(\delta_m)$ are the uncertainties of measuring the volume (mass) of the sample, $\delta_V(\delta) = 1–2\%$.

The combined standard uncertainty of the chemical yield determination when using a tracer is

$$\delta_K = \sqrt{\delta_{trref}^2 + \delta_{trsmp}^2 + 2 \cdot \delta_{V_{tr}}^2} \tag{11}$$

where δ_{trref} and δ_{trsmp} are the statistical uncertainties of tracer activity determination in the standard solution and in the sample, respectively, and $\delta_{V_{tr}}$ is the uncertainty of the tracer volume.

In order to minimize the combined statistical uncertainty for a target isotope activity determination, the amount of tracer isotope should be increased, but this causes the opposite effect for the counting statistics of the isotope to be measured due to the ratio of the Compton electron spectrum to the background counts. Thus, the tracer activity should be adjusted according to the expected activity of the radionuclide to be determined (Table 3).

The described isotopic dilution method has been used for radiostrontium determination with a ^{85}Sr tracer in the SIA Radon analytical department since 2000. The method was introduced in 2003 in the laboratory for environmental monitoring of the nuclear power plant (NPP). Since then, hundreds of analyses of the radiostrontium content in samples of environmental objects of various origin have been carried out.

Table 3 Statistical uncertainties (for $P = 0.95$) for ^{90}Sr determination using a ^{85}Sr tracer, Tri-Carb 2550 TR/AB, sample tSI(E) ~400, counting for 999 min.

		Isotope-tracer activity (Bq)			
	Uncertainty	0.1	0.3	1	3
Isotope	component	Uncertainty ± %			
^{90}Sr, $A^{90}_{Srsmp} = 0.1$ Bq	$\delta_{A^{90}Srsmp}$	15	17	21	30
^{85}Sr	δ_{trsmp}	17	7	2.1	1.7
Combined, expanded relative uncertainty ($k = 2$) %	$\delta_{A^{90}Sr}$	23	18	21	30

The typical experimental spectra obtained in the analysis of different samples, and also their decomposition in elementary components by processing with RadSpectraDec software (Figures 4–6), are described below. Results of the activity calculations are presented in Tables 4–5.

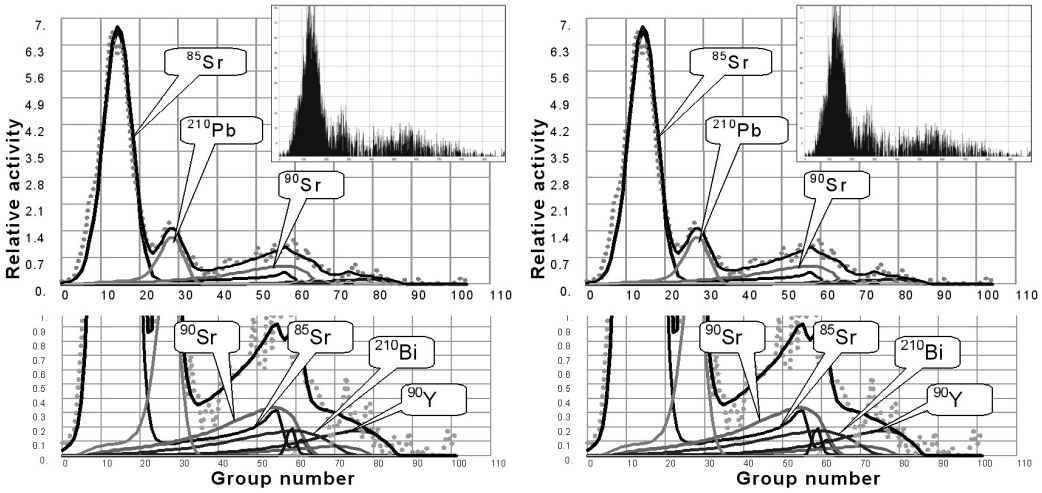

Figure 4 LS spectra obtained from air filters. Left: remote zone of environmental monitoring around NPP; Right: Moscow. Initial (inset) and decoded (lower) spectra using RadSpectraDec-Guardian and RadSpectraDec-Tri-Carb program.

The proposed method of LS determination was verified by analyzing synthetic mixtures of radionuclides prepared from reference certified solutions and also by interlaboratory comparison exercises (De Regge 2000; IAEA 2005).

CONCLUSION

The proposed method allows for the determination of both ^{89}Sr and ^{90}Sr in samples. In the analyzed samples, the ^{89}Sr/^{90}Sr ratio varied from 0.2 to 30. Measurements may be carried out at any time after Sr separation, as the growth of ^{90}Y daughter activity is taken into account in the spectrum analysis process. When the source contains radioactive impurities like ^{210}Pb, ^{210}Bi, ^{226}Ra, or ^{140}Ba/^{140}La, it is possible to discriminate and to subtract these impurities using spectrum processing software.

It is rational to use the area of the spectrum with the optimal ratio of useful counts/background for minimizing and calculating the statistical uncertainty of each radionuclide from the spectrometric data. In order to minimize the combined statistical uncertainty for a specific isotope activity deter-

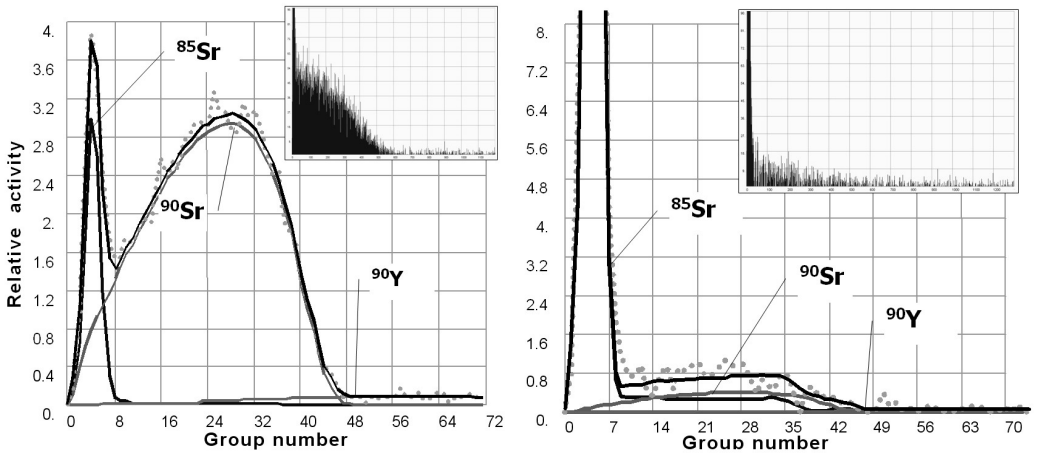

Figure 5 LS spectrometric determination of ^{90}Sr using ^{85}Sr in soils at different contamination levels (A^{85}_{Sr} = 0.42 Bq in each sample, m_{sample} = 10 g). Left: a^{90}_{Sr} = 245 ± 90 Bq/kg; Right: a^{90}_{Sr} = 5.2 ± 2.2 Bq/kg.

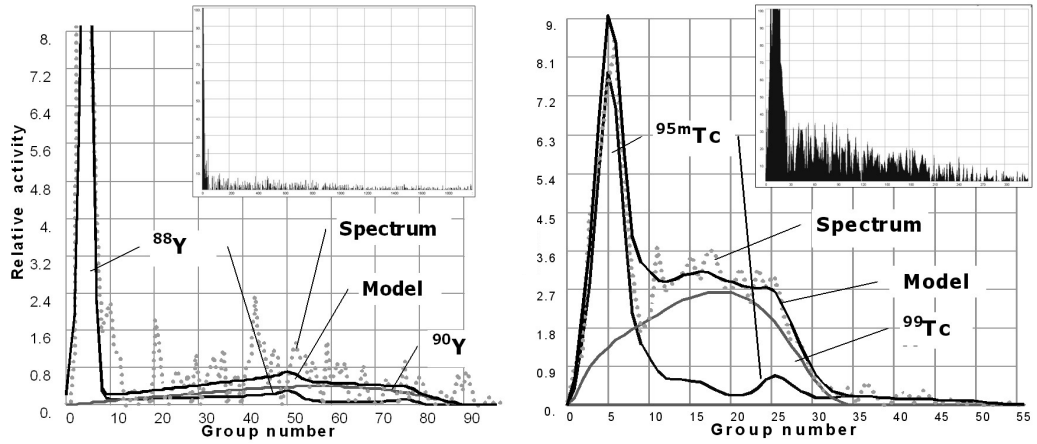

Figure 6 LS spectrometric determination of low-level activities of certain radionuclides by isotopic dilution method. Left: determination of ^{90}Y via ^{88}Y tracer in brines; Right: determination of ^{99}Tc via ^{95m}Tc tracer in technological leakages.

Table 4 Results of ^{90}Sr determination in air aerosol filters (background level of the ^{90}Sr activity concentrations).

Location of sampling	Activity Bq/sample	Concentration (Bq/m^3)	Expanded relative uncertainty (k = 2) %
Remote zone of NPP monitoring	0.022	3.8E-10	33
City of Moscow, north	0.094	3.5E-10	26

Table 5 Results of LS analysis of liquid samples using isotopic dilution method.

Sample	Isotope	Activity (Bq/sample)	Tracer activity (Bq/sample)	Expanded relative uncertainty (k = 2) %
Brines, nuclear test site	^{90}Y, ^{88}Y	0.022	0.076	37
Technological leakages	^{99}Tc, ^{95m}Tc	0.094	0.084	22

mination, the amount of tracer isotope should be adjusted to the expected activity of the radionuclide to be determined. For determining ^{90}Sr via ^{85}Sr, the optimal activity ratio in the sample should be 1:3.

When using an isotope tracer, the analytical procedure may be simplified by excluding a separate step of chemical yield determination (e.g. by gravimetry); not using a stable carrier reduces the amount needed of sorption materials and extractants.

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