BETA-SPECTROMETRIC DETERMINATION OF ^{90}Sr IN WATER, MILK AND OTHER SAMPLES WITH AN ULTRA-LOW-LEVEL LIQUID SCINTILLATION COUNTER

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ABSTRACT. We have developed a beta-spectrometric method and software for rapid determination of ^{90}Sr in milk, water, urine, soil, ash, hot particles and soil. We used a Wallac 1220™ Quantulus low-level liquid scintillation (LS) spectrometer and several types of standard cocktails for this purpose. Minimum detectable activities are as follows: milk = 3.7 Bq liter^{-1}; water = 0.1 Bq liter^{-1}; urine = 4.5 Bq liter^{-1}; soil = 50 Bq kg^{-1}; hot particles = 0.05 Bq per particle. Soil and ashes from foodstuff and grass must be dissolved in 1M HCl or 2M HNO$_3$. For hot-particle measurement, gel cocktails are used. In some cases, results of the determination of other radionuclides in the samples are also available, *e.g.*, ^{137}Cs, ^{134}Cs and ^{40}K in milk. To confirm the reliability and accuracy of the method, we made several sets of intercomparison measurements with radiochemical and other methods. Our β-spectrometric method has been routinely used for continuous monitoring of ^{90}Sr in Dnieper River water near water supply stations, in direct measuring of milk, in studies of hot particles and in experiments on ^{90}Sr metabolism in cows.

INTRODUCTION

Time-consuming radiochemical methods are widely used for the determination of the beta emitters ^{90}Sr, and its daughter, ^{90}Y. The contribution of ^{90}Sr in the environment from accidental fallout is comparable with that from other natural β emitters, *e.g.*, ^{40}K, which allows β-spectrometric determination of ^{90}Sr without radiochemical preparation of samples. The classical method for ^{90}Sr determination in liquid samples is radiochemical extraction with subsequent radiochemical measurement (Johnson 1966; Schönhofer & Henrich 1987). This method has several shortcomings: 1) it is laborious, with a lengthy isolation process (several days); 2) highly toxic reagents and concentrated acids are required, thus special labs are needed; 3) several qualified radiochemists are required; and 4) chemical yields must be high to minimize loss of radionuclides.

Another method for ^{90}Sr determination is based on the measurement of total β activity, and subtraction of other radionuclide contributions according to the results of gamma-spectrometric measurement. However, this method is restricted by the sensitivity of γ-spectrometric measurement, which is noticeable especially when γ-radionuclides with low intensity have to be measured (^{40}K, 10.7%; ^{144}Ce, 10.8%) in a small amount of sample.

Some methods of β-spectrometric determination of ^{90}Sr use different types of solid detectors (Dementyev 1967; Los' *et al.* 1987; Knat'ko *et al.* 1989; Bondarenko, Zelensky & Repin, in press). "Solid" β spectrometry usually has low sensitivity due to low counting efficiency, narrow energy range of detection and low spectral resolution.

METHODS

Spectrum Processing

Samples and scintillants (Optiphase HiSafe™ 3 and Lumagel®) in ratios ranging from 1:9 to 2:3 were counted in 20-ml plastic vials. To decompose the spectrum into components, we performed a linear least squares regression

$$X(j) = B(rng,1:J) \setminus S(rng) \tag{1}$$

where

X(j) = count rate of j nuclide in the sample

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B = matrix containing calibration spectra (vectors) of the samples
j = number of nuclides to be determined (number of columns in matrix B)
rng = spectrum region of interest between channels N1 and N2 (number of rows in matrix B)
S = spectrum of sample (vector).

All equations are presented in a matrix and vector form, where B\S is the matrix division of B into S, which is the same as INV(B) × S; and : without range indication means the use of all vector, elements or all the lines (columns) of the matrix.

When an "extra" nuclide is present in the sample, or in the event of uncontrolled spectrum shift, the system will be solved incorrectly. To control the result, we restore spectral form using separate components received as a result of decomposition. Apart from visual comparison of restored (calculated) and real spectra of a sample, we use a quantitative assessment of correctness:

$$\mathrm{Diff} = \frac{\left(\sum_{i=N1}^{N2} (S(i) - S1(i))^2\right)^{1/2}}{\sum_{i=N1}^{N2} S(i)} \times 100\% \qquad (2)$$

where S(i) = the content of the i channel of sample spectrum, and S1(i) = the content of the i channel of restored spectrum.

The selection of a region of interest to be analyzed is based on the optimization of counting efficiency, background and matrix stability. The upper (right) boundary of the range of the spectrum usually coincides with the maximum energy of the β spectrum of the sample. To select the lower (left) boundary, we use a "generalized parameter", which we determine according to

$$\mathrm{Opt}(i) = \frac{\mathrm{Cond}(i)}{\mathrm{FM}(i)} \qquad (3)$$

where Cond(i) = parameter of B matrix stability (Condition number) (Forsayt, Malkom & Mouler 1980; Moler, Little & Baugert 1987), FM(i) = Figure of Merit, and i = channel number at the lower boundary of the region of interest. In its turn, quality ratio is widely used for optimization of radiometric measurements of one radionuclide (Schönhofer 1989) and is determined as follows

$$\mathrm{FM}(i,j) = \frac{(\mathrm{Eff}(rng,j))^2}{\mathrm{BG}(rng)} \qquad (4)$$

where Eff = counting efficiency of j nuclide in the region of interest, BG = background in the region of interest, and rng = given region of interest between channels i and Nmax. The lower boundary of the region of interest is selected by finding the minimum of Opt(i,j). The use of Equation 3 will be examined below in selecting the lower boundary of the region of interest on the example of ^{90}Sr determination in milk.

Spectrum Standardization

An obstacle in the method described above is the quenching of the sample resulting in the change of spectrum shape and counting efficiency. This phenomenon depends upon chemical composition, sample color and sample/scintillator ratio. We used the spectral quench parameter-external (SQP(E)) to control and standardize the spectrum. This parameter is determined in the Quantulus 1220™ with an external standard. Calibration and background spectra for a number of fixed values of SQP(E) quench should be prepared in order to cover the working interval of sample quenching.

Thus, the transformed spectrum of the sample, background and spectra of the calibration matrix (matrix B) are brought to the same quench parameter. This allows decomposition of the sample's spectrum and calculation of the specific radionuclide activity.

The specific activity of a nuclide in the sample is determined according to Equation (1)

$$A(j) = \frac{1000 \times X(j)}{V \times Eff(rng,j)T} \tag{5}$$

where V = volume of the sample (ml), T = time of sample measurement (sec), X(j) = count rate of the j radionuclide (cps), and Eff(rng,j) = counting efficiency of the j radionuclide (cps Bq^{-1}).

Our method assumes a simultaneous determination of a radionuclide mixture. To calculate statistical error, we used an equivalent background value for each component (Bondarenko, Zelensky & Repin, in press)

$$BGO(j) = \sum_{i=N1}^{N2} BG(i) + \left(\sum_{i=N1}^{N2} S(i) - X(j) \right) \tag{6}$$

where X(j) = count rate of the j component (cps).

Calculation of the statistical error of j nuclide determination is determined according to Bondarenko, Zelensky and Repin (in press)

$$Error(j) = \frac{(X(j) + 2 \times BGO(j)T)^{1/2}}{X(j)T} \ . \tag{7}$$

The minimum detectable activity (MDA) for j radionuclide is estimated according to Bondarenko, Zelensky and Repin (in press)

$$MDA(j) = \frac{2000(BGO(j)T)^{1/2}}{V \times T \times Error \times Eff(j)} \times 100 \tag{8}$$

where Error = given statistical error. Equations (6)–(8) give only conservative assessments of MDA and statistical error.

RESULTS

At the collection site, milk samples were injected into counting vials that contained scintillation cocktail. Samples with scintillation cocktails, Optiphase HiSafe™ 3 and Lumagel®, retained stability while stored for several weeks at 10°C. The principal radionuclides in milk are ^{40}K, ^{134}Cs, ^{137}Cs and ^{90}Sr+^{90}Y. Spectra of these nuclides determine the matrix of sample spectra (Fig. 1). Considering possible chemiluminescence in a spectrum of milk sample, channel 300 is assumed to be the lower boundary of the region of interest. Accuracy and sensitivity of measurements depend on the relative proportions of radionuclides in the mixture, which vary considerably in real samples.

^{90}Sr in milk or milk products is normally measured in ashed samples. Sample preparation requires dissolution 0.5–1 g of ash in 4–5 ml of 2M nitric acid solution, then addition of scintillator. Measurement and analysis are performed as described earlier. Ashing has the following advantages for β spectrometry: 1) concentrates activity up to 25–30 times, which increases the sensitivity of the method; and 2) alters the relative proportions of radionuclides in favor of ^{90}Sr through loss of the more volatile Cs isotopes.

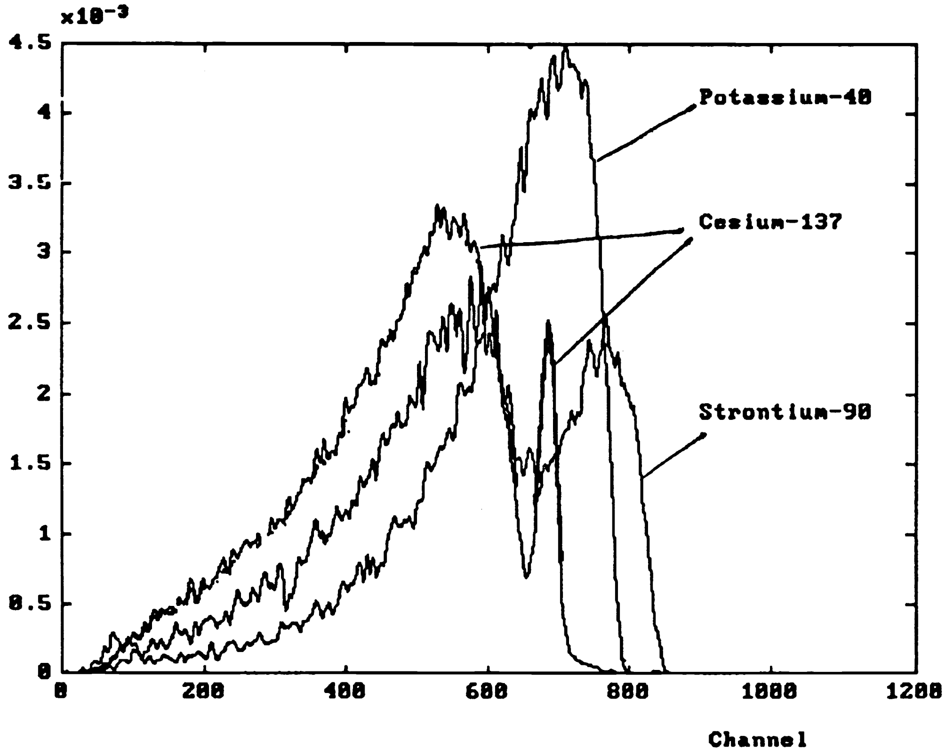

Fig. 1. Normalized calibration β spectra of the chief radionuclides that occur in milk

Equations (6)–(8) trace the alteration of sensitivity and error measurement by using an ash sample, *e.g.*, for fresh milk with a specific activity of ^{137}Cs = 1200 Bq liter^{-1}, MDA of ^{90}Sr determination 7.5 Bq liter^{-1}, measuring time of 100 min (error 50%). While using a sample based on 0.5 g ash, where Cs activity is ten times lower due to thermal loss, the MDA of ^{90}Sr decreases by a factor of only 1.5 Bq liter^{-1} for the same measuring time. To ascertain the reliability of the method, we used the radiochemical method of ^{90}Sr determination, γ spectrometry and a combined γ-β method. Table 1 shows results of all radionuclide activity measurements obtained from one sample using different methods.

TABLE 1. ^{90}Sr Concentration Measurements in Milk Using Three Methods (Bq liter^{-1})

Method	Volume (ml)	^{137}Cs	^{134}Cs	^{40}K	^{90}Sr
γ spectrometry	1000	137.1	17.9	60.2 (1.0)	--
β-γ decomposition*	1000	--	--	--	33.1 (10%)
β spectrometry	4	134.5	19.2	58.3	36.3
β spectrometry	4	137.1	19.6	60.4	32.9
β spectrometry	4	134.8	19.3	58.7	34.5
Radiochemistry	1000	--	--	--	27.0 (20%)

*The result was obtained by subtraction of the β part of γ-emitting radionuclides from the sample's gross β activity. The average variance of results from our method compared with the results of radiochemistry is 20.2%, and for samples with specific activity >7.0 Bq liter^{-1} is 10.7%.

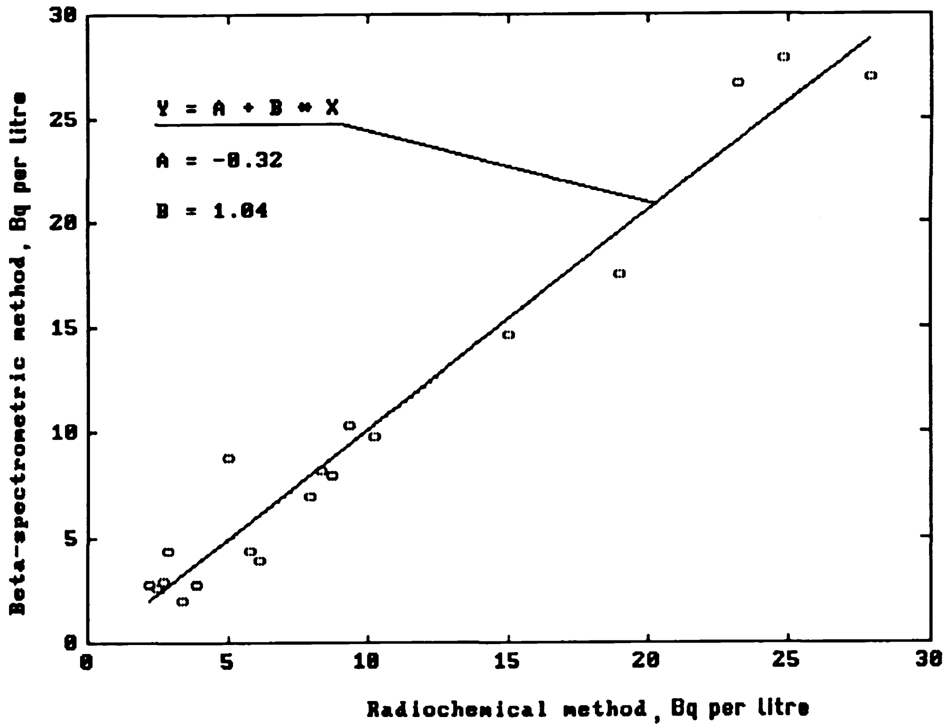

Fig. 2. Comparison of the results of ${}^{90}Sr$ determination in milk (Bq liter^{-1}) obtained with two different methods

Figure 2 shows the results of ${}^{90}Sr$ measurement in 19 milk samples. The average variance of results from our method compared with the results of radiochemistry is 20.2%, and for samples with specific activity >7.0 Bq liter^{-1} is 10.7%. ${}^{90}Sr$ is in the activity interval from 2.0–27.9 Bq liter^{-1}.

To measure ${}^{90}Sr$ in "hot particles", the sample is prepared with a scintillation cocktail in gel form. Separated particles are suspended in cocktail gel (10 ml Lumagel® + 10 ml distilled water). We select β components using preliminary information of γ spectrometry, taking into account the possible availability of nuclides in the blend. Table 2 shows the results of β-component activity in some "hot particles". For these, the lower boundary of the region of interest cannot be <100 keV, because β decays <100 kev lose considerable energy within the particles.

TABLE 2. Radionuclide Concentrations in Hot Particles, Determined by Spectrometry (Bq)

Hot particle	${}^{137}Cs$	${}^{134}Cs$	${}^{90}Sr$	${}^{144}Ce$	${}^{106}Ru$
hp6	*				430.30
hp2				2.82	130.95
hp3				4.26	57.16
hp4	9.02	1.29	9.73	5.99	29.69
hp1	29.60	4.23	93.64	26.55	26.12
hp5	5.83	0.83	56.39	13.88	19.60
135404	290.89	41.56	20.95	5.40	58.81
804802	13.16	1.88	21.96	6.23	8.08

*Blanks = MDA 0.5–1.0 Bq

We tested the LS β-spectrometric method during the IAEA-90 intercomparison runs (IAEA 1991) for ^{90}Sr determinations in air filters. We obtained results for a range of sample activities. Numerous γspectrometric measurements, radiochemical analyses of ^{90}Sr and measurements of gross β activity of water samples confirm that the main contributors to the β spectrum of Dnieper River water are ^{90}Sr+^{90}Y, ^{137}Cs, ^{134}Cs and ^{40}K.

The contribution of natural uranium, radium and daughter radionuclides in concentrated water samples was determined by α spectra. This is estimated at ≤0.04 Bq liter^{-1}, which is ≤15–20% of the ^{40}K concentration in Dnieper River water. It is known that ^{137}Cs preferentially adsorbs onto sediment particles, whereas ^{90}Sr prefers the dissolved phase. The share of dissolved fraction for ^{90}Sr is 90–95%, for ^{137}Cs, 60–70%. To concentrate sample activity, we evaporated 100 ml of water to dryness and then dissolved the residue in 2 ml 0.5 M HCl or HNO_3. Several drops of concentrated H_2O_2 solution added to the sample at the later stage of evaporation destroys suspended organic matter. Both evaporation and sample measurement should be carried out in Teflon vials; it prevents losses of activity and helps to minimize background count rate. The sample is prepared for counting by adding 18 ml of LS Optiphase HiSafe™ 3 to the 2-ml acid solution of the dried water sample. The MDA for determining ^{90}Sr for 120 min of measurement is about 0.1 Bq liter^{-1}. Reducing sample preparation and counting to 1–2 h enabled us to monitor in real time, scale, which is important in studying such dynamic water supply systems as rivers. MDA is considerably lower than the temporarily permissible level of ^{90}Sr in drinking water (3.7 Bq liter^{-1}).

We monitored ^{90}Sr concentrations in drinking water in Kiev because of its increase during spring floods of the Prip'at River. We collected tap water samples twice a week. Water activity from the Desna River was almost always below the MDA level (0.1 Bq liter^{-1}). As Figures 3 and 4 show, the main change in ^{90}Sr concentrations was observed during spring floods and is described by an exponential curve. Figure 3 shows the correlation of β-spectrometric and radiochemical data. Water from the Dnieper River was refined and diluted with Desna River water. Figure 4 shows that specific activity of ^{90}Sr in tap water was much lower than that in Dnieper River water. We observed the greatest difference during spring floods and took measures to purify the water.

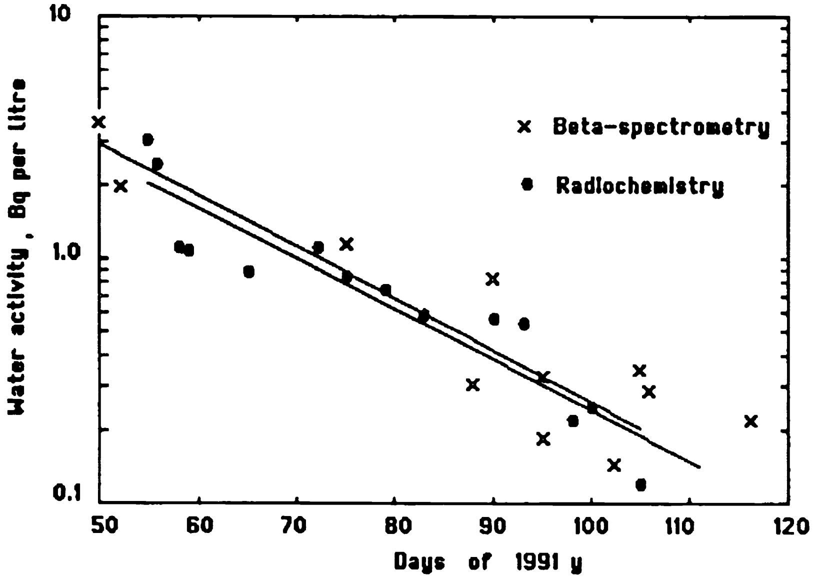

Fig. 3. Comparison of results of ^{90}Sr content determination in Dnieper River water near Kiev with β-spectrometric and radiochemical methods (Bq liter^{-1})

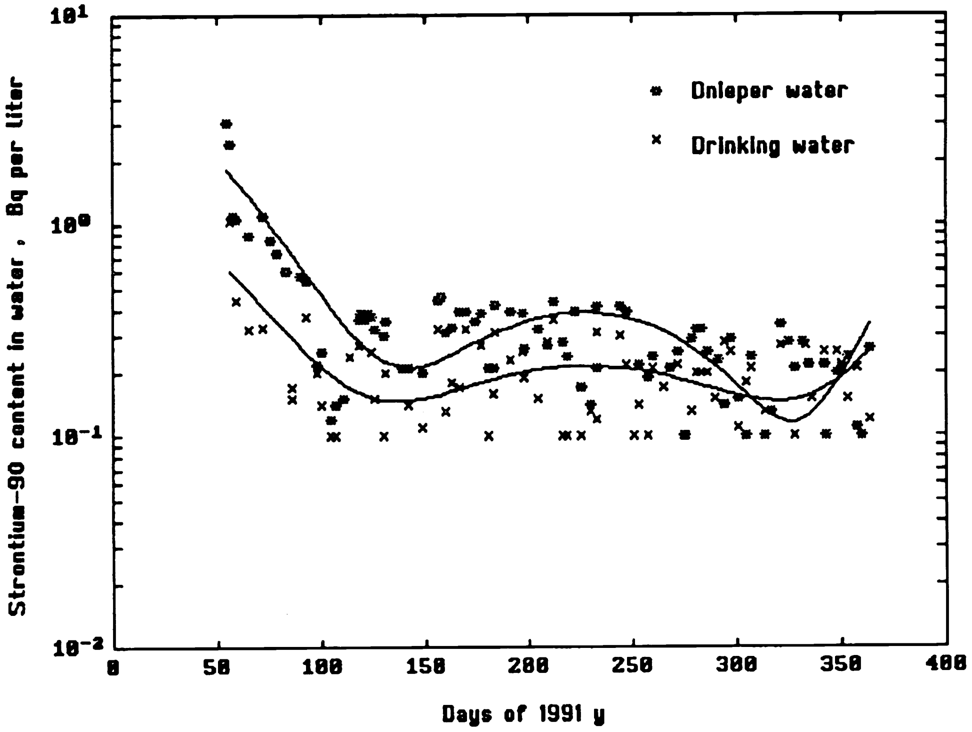

Fig. 4. ^{90}Sr content in Dnieper River and drinking water during 1991 near Kiev

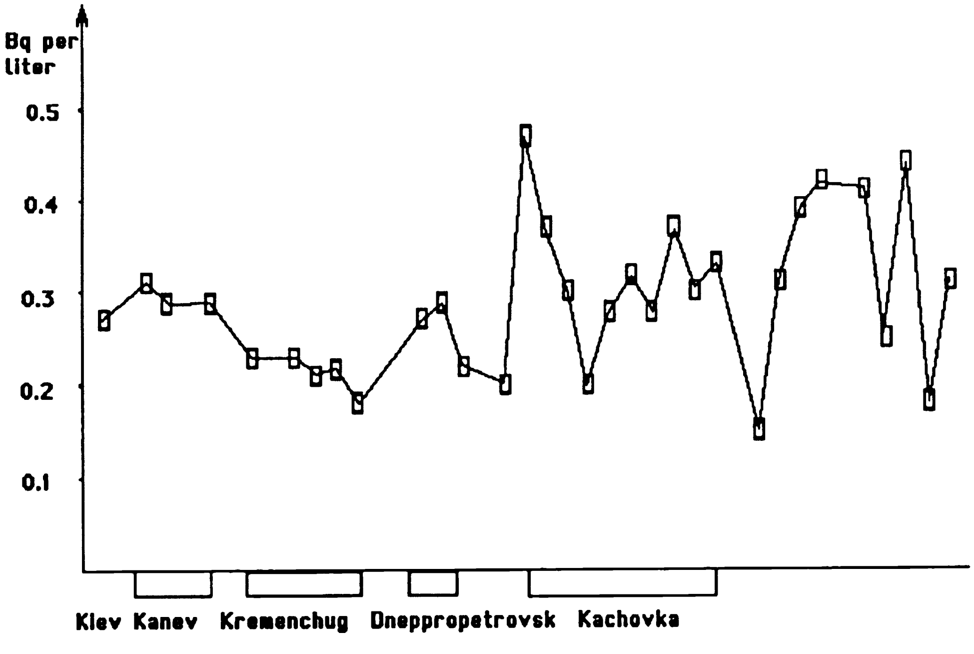

Fig. 5. ^{90}Sr content in Dnieper River water in September 1991

TABLE 3. Specific Activity of ^{137}Cs and ^{90}Sr in Water Samples in a 30-km Zone

Sample	Site	^{137}Cs	^{90}Sr
3877	Chernobyl NPP, Channel 1	2.93	5.83
3878	Chernobyl NPP, Channel 2	6.44	9.16
3879	Prip'at River	0.16	0.23
3880	Chernobyl NPP, reservoir	12.60	4.92
3881	Prip'at R., near Otashev	3.20	8.35
3882	Drilled well, Otashev	0.53	<0.10

We checked for ^{90}Sr in Dneiper River water from 30-km zones (Table 3) during September and October 1991. Our results show that ^{90}Sr activity significantly exceeded the MDA (Fig. 5). These data enable us to use LS β spectrometry to monitor ^{90}Sr in Dnieper water contaminated by Chernobyl fallout.

CONCLUSION

Our β-spectrometric method offers a unique possibility for measuring of ^{90}Sr in fresh milk and other liquids with no chemical preparation in a wide range of quench. The data confirm that our estimation of MDA and error is conservative. The comparison of characteristics (MDA and error in ^{90}Sr measurement) for LS β-spectrometry and radiochemistry showed definite advantages of using LS counting.

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