RADIOCARBON, Vol 48, Nr 2, 2006, p 197–204

DETERMINATION OF ^{90}SR/^{90}Y IN WHEAT GRAINS, SOIL, AND DEPOSITION SAMPLES BY TBP EXTRACTION AND CERENKOV COUNTING

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ABSTRACT. Within the framework of radioecological studies, ^{90}Sr was determined in wheat grains, soil, and deposition samples. The radiochemical purification of ^{90}Y consisted of liquid-liquid extraction by tributyl phosphate (TBP), followed by hydroxide and oxalate precipitations and, if necessary, the removal of thorium by anion exchange chromatography. The procedure proved to be very robust and reliable, having yttrium yields of 92.7 ± 4.6% for 1-kg wheat samples, 90.9 ± 4.2% for 50-g soil samples, and 90.6 ± 3.2% for wet and dry deposition samples. ^{90}Y was determined by Cerenkov counting and proportional counting. By optimizing the Cerenkov counting window, a figure of merit (FOM) of 4750 could be reached using a Quantulus™ 1220 system. Minimum detectable activities were in the range of 10 mBq.

INTRODUCTION

^{90}Sr is one of the most important anthropogenic radionuclides from a long-term radiological point of view. It decays with a half-life of 28.8 yr by emitting beta radiation with a maximum energy of 546 keV into ^{90}Y, which decays with a half-life of 64.1 hr into stable ^{90}Zr, emitting beta radiation with a maximum energy of 2.28 MeV:

$$^{90}\mathrm{Sr} \xrightarrow[\beta_{max}\ 546\ \mathrm{keV}]{28.8\ \mathrm{yr}} {}^{90}\mathrm{Y} \qquad {}^{90}\mathrm{Y} \xrightarrow[\beta_{max}\ 546\ \mathrm{keV}]{64.1\ \mathrm{hr}} {}^{90}\mathrm{Zr}$$

The chemical analogy of strontium and calcium, leading to the long-term storage of ^{90}Sr in bones, combined with the high-energy beta radiation of ^{90}Y, is responsible for the high radiological impact of ^{90}Sr. For this reason, ^{90}Sr is monitored regularly in many types of environmental samples related to the human food chain.

The ^{90}Sr activity of a sample can be determined either by analyzing either ^{90}Sr itself or its daughter nuclide, ^{90}Y. Since both nuclides are pure beta emitters, both types of analysis require radiochemical processing of the sample. Three principle strategies can be applied. The first method involves the purification of ^{90}Sr, e.g. by the traditional fuming nitric acid method. After the purification of ^{90}Sr, ^{90}Y is isolated and measured after waiting for 2 or more weeks to allow ^{90}Y to reach equilibrium with ^{90}Sr. The second strategy involves the purification and direct determination of ^{90}Sr. This method became more common due to the increasing availability of liquid scintillation (LS) counters in radioanalytical laboratories and the commercial availability of SrSpec resin (Eichrom Ind.) for extraction chromatography. A third method is based on the direct isolation of ^{90}Y instead of ^{90}Sr. This method avoids the difficulties arising from the separation of strontium in the presence of the large amounts of calcium that are often found in environmental samples. In this paper, we will focus our attention on the third strategy.

Radiochemical separations of ^{90}Y can be performed by liquid-liquid extraction with di(2-ethylhexyl) phosphoric acid (HDEHP), cation exchange chromatography, anion exchange of $[Y(dipic)_3]^{3-}$ (dipic = pyridine-2,6-dicarboxylate), sorption on HDEHP-impregnated filter beads, yttrium oxalate precipitation, and liquid-liquid-extraction with tributyl phosphate (TBP). The latter

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https://doi.org/10.1017/S003382220006639X Published online by Cambridge University Press

method has been applied for decades to many types of samples, including an aerosol filter (LaRosa et al. 1992), bones (Baratta and Ferri 1967), flesh (Ghods et al. 1991; Mirna et al. 1990), grass (LaRosa et al. 1992), milk (Bem et al. 1991; BMU 2000; Mercer et al. 1965; Velten and Goldin 1961), sediment (Tinker et al. 1997), soil (LaRosa et al. 1992; Shawky and El-Tahawy 1999; Tinker et al. 1997), and spices (Ghods et al. 1994; Mirna et al. 1990). Reported chemical recoveries of yttrium by TBP extraction were generally high.

The extraction of yttrium with TBP is performed from concentrated HNO_3. Table 1 shows the distribution coefficients of some elements for the system 100% TBP/14M HNO_3 reported by Tinker et al. (1997 and literature cited therein). After washing the organic phase, yttrium is either stripped with water or with diluted HNO_3 or is precipitated as a hydroxide by the addition of ammonia and ethanol (BMU 2000; LaRosa et al. 1992; Tinker et al. 1997). The most serious problem related to the extraction of ^{90}Y with TBP is the coextraction of thorium isotopes, some of them having short-lived daughter nuclides emitting high-energy beta radiation. Different approaches have been reported to reduce the contamination of the counting samples with thorium. For example, when yttrium is stripped from the TBP phase with 2M HNO_3 instead of water, thorium stripping will be reduced (Baratta and Ferri 1967; Bem et al. 1991). Tinker et al. (1997) reported that thorium can effectively be removed prior to TBP extraction with 5% TOPO (trioctyl phosphine oxide) in toluene. Borcherding and Nies (1986) removed thorium after the TBP extraction by cation exchange chromatography or by coprecipitating it with $Zr_3(PO_4)_4$. Another promising approach is to discard the first TPB extract and perform a second extraction after ^{90}Y is in equilibrium with ^{90}Sr again. It is possible to repeat the TBP extraction many times since the amount of ^{90}Sr extracted with TBP is negligible. Another possibility to remove thorium isotopes would be by anion exchange chromatography from HNO_3 solution.

Table 1 Distribution coefficients of selected elements between 100% TBP and 14M HNO_3 (Tinker et al. 1997).

Element	Distribution coefficient
Th	400
Pa	150
Y	80
Fe	15
Po	0.2
Bi	0.05
Cs	0.002
Pb	0.0004
Sr	0.0002

Another difficulty encountered when purifying ^{90}Y by TBP extraction is related to iron, which is partially extracted. Fe(III) can interfere with Cerenkov counting due to its intense yellow color, resulting in lower counting efficiencies. Thus, if the sample solutions appear to be yellow, ^{90}Y has to be purified by additional oxalate precipitations with access oxalic acid, which will build a soluble Fe(III) complex that does not precipitate.

Proportional, liquid scintillation, and Cerenkov counting are the 3 principle detection methods used in low-level analysis of ^{90}Sr by counting ^{90}Y. Cerenkov radiation is produced by charged particles moving through a transparent medium with a speed greater than the speed of light in the medium. The threshold energy of a particle for producing Cerenkov radiation in water is 263 keV. Cerenkov

radiation has a spectrum from UV to the visible light region and can be detected with a conventional LS spectrometer. In water, the radiation is emitted with a maximum angle of 41.3° to the direction of the particle, depending on its energy. The counting efficiency is always smaller than 100% and can be raised slightly by the use of wavelength shifters. In contrast to LSC, there is no need for organic scintillation cocktails, and thus there is no chemical quench effect. In general, measurements are performed in 20-mL plastic scintillation vials containing the purified ^{90}Y in diluted nitric or hydrochloric acid. Counting solutions should be colorless; otherwise, careful color quench corrections have to be done. For a detailed and comprehensive review, see L'Annunziata (2003 and references therein).

The counting efficiencies of ^{90}Y and ^{90}Sr and the background largely depend on the LS counter, counting mode, and counting vial type. The PerkinElmer/Wallac Quantulus™ 1220 proved to have the best counting properties. Counting efficiencies of about 70% for ^{90}Y and background below 0.5 cpm have been reported. Many authors have shown that the use of plastic scintillation vials leads to higher efficiencies in Cerenkov counting and lower background. However, Mirna et al. (1990) reported the background to be lower when using glass vials in a TriCarb 2250 CA.

The main advantages of Cerenkov counting compared to liquid scintillation counting are the following:

1. No organic waste is produced in sample preparation;
2. Alpha and low to medium energy beta emitters do not interfere;
3. There is no chemical quench effect;
4. The background is lower; and
5. The sample volume can be higher because there is no need for mixing it with a LS cocktail.

On the other hand, the counting efficiency is lower in Cerenkov counting than in LSC. Compared to proportional counting, the main advantage of Cerenkov counting is the easy preparation of the counting sample, which has no self-absorption effects.

The aim of this work is to investigate and optimize a robust method for the determination of ^{90}Sr in wheat grain, soil, and deposition samples. It was known prior to the analysis that the activity of ^{90}Sr in some of the deposition samples would be below the detection limits. Thus, the monthly collected samples had to be combined. On the other hand, the sampling time was kept as short as possible to have the maximum amount of information about the seasonal variation of the deposition. For this reason, the method by which samples could be combined for additional ^{90}Sr analysis was preferred.

EXPERIMENTAL

About 1 kg of fresh wheat samples were ashed at 400 °C followed by the determination of ^{137}Cs via gamma spectrometry (Schimmack et al. 2004). The samples were ashed again at 600 °C, mostly resulting in a white clean ash with a mass of about 20 g. This ash was dissolved in 300–400 mL 65% HNO_3 (80 °C, stirring for 1 hr) containing 10 mg of strontium and yttrium carrier. ^{90}Y was extracted 4 times with 20 mL TBP, which was saturated immediately before with 65% HNO_3. The organic phase was discarded. After adding the new yttrium carrier, the aqueous phase was stored for at least 2 weeks, and the TBP extraction was repeated. The organic phase was washed 5 times with 20 mL 65% HNO_3. Yttrium was precipitated as hydroxide by adding 90 mL ethanol and 60 mL 25% NH_3. (For safety reasons, never forget to add NH_3.) Precipitate and solution were separated by centrifugation. All wheat samples were analyzed by proportional counting; however, 19 samples were processed a second time after complete ^{90}Y ingrowth and were analyzed by Cerenkov counting. Propor-

https://doi.org/10.1017/S003382220006639X Published online by Cambridge University Press

tional counting was done with a low-level anticoincidence counter, Berthold LB 6030, as described previously (Bunzl and Kracke 1990, 1991; Bunzl et al. 1996). Samples for proportional counting were prepared by yttrium oxalate precipitation at pH = 2.0. Samples for Cerenkov counting were prepared by dissolving the hydroxide precipitate in 15 mL 2M HNO_3.

Soil samples (50 g) were ashed at 600 °C for 15 hr. The resulting ash was leached twice with 100 mL 65% HNO_3 (80 °C, stirring for 1 hr), filtered, and processed as described above. In addition, after the TBP extraction, the yttrium hydroxide precipitate was dissolved in a few mL HNO_3 and diluted with water to a volume of 1200 mL. After adding 10 g of oxalic acid and 1.85 g of calcium nitrate (corresponding to 1 g Ca^{2+}), yttrium was coprecipitated with calcium oxalate at pH = 2.0. If the precipitate was not colorless due the presence of iron, which was rarely the case, the oxalate precipitation was repeated or Fe(III) was masked by phosphoric acid. The precipitate was ashed at 600 °C, dissolved in 10 mL 8M HNO_3, and passed through an anion exchange column (5 mL, nitrate-form, Bio-Rad or Eichrom 1X4, 100–200 mesh) to remove traces of thorium. The column was washed with 3 column volumes of 8M HNO_3. The combined effluent and washing solutions were evaporated to dryness. Counting samples were prepared by dissolving the residue in 15 mL 2M HNO_3.

Wet and dry deposition samples were collected monthly in a wet-dry sampler at the campus of the Forschungszentrum für Umwelt und Gesundheit (GSF) research center from October 1991 to December 2000 (Rosner et al. 1996). After determining the gamma emitters, the samples were wet ashed with HNO_3, HCl, and $HClO_4$; dissolved in 35 mL 9M HCl; and stored. Since the ^{90}Sr activities in monthly samples were expected to be below detection limits, they were combined with Quaternary samples. After the addition of ^{85}Sr, plutonium was removed by anion exchange chromatography (Rosner et al. 1990). Since large amounts of hydrochloric acid evaporate during determination of ^{90}Sr via the fuming nitric acid method (Rosner et al. 1990), this method should be avoided. ^{90}Sr/^{90}Y were recovered by 2 calcium oxalate precipitations at pH 5.6–6.0. By measuring ^{85}Sr using gamma spectrometry, it was assured that strontium was recovered to 99 ± 1%. The oxalate was decomposed at 600 °C and dissolved in 65% HNO_3. ^{90}Y was purified and determined by Cerenkov counting as described above for soil samples (with the exception that the anion exchange column had a volume of only 1.5 mL).

The chemical yields of yttrium were determined after counting by complexometric titration with EDTA and determined gravimetrically. Cerenkov radiation was measured with a Quantulus 1220. Twenty-mL PE liquid scintillation vials (Zinsser Analytik) were used. If the counting sample solutions were not completely colorless, 20 µL of phosphoric acid was used to complex traces of iron. The counting efficiency was determined using a ^{90}Sr standard solution from the Physikalisch-technische Bundesanstalt (PTB), Braunschweig. The best settings for the counting window were determined by recording the Cerenkov spectra of ^{90}Sr/^{90}Y in 15 mL diluted HNO_3 and also that of a blank sample. The window settings with the highest figure of merit (FOM) were determined by varying the window settings with the Microsoft Excel Visual Basic® program. The contribution of ^{90}Sr to the Cerenkov spectrum of ^{90}Sr/^{90}Y was determined by preparation of a pure ^{90}Sr sample and observation of the ^{90}Y ingrowth via repeated measurements of the Cerenkov spectrum of the sample. An aliquot containing 7.4 Bq ^{90}Sr/^{90}Y was evaporated to dryness and taken up in 10 mL 65% HNO_3. ^{90}Y was removed by 3 TBP extractions. The aqueous solution was evaporated nearly to dryness, and the invisible residue was dissolved in 15 mL 2M HNO_3 and transferred to a counting vial. The ^{90}Y ingrowth was observed via repeated measurements of the Cerenkov spectrum of the sample.

In general, 2 environmental samples were chemically processed in parallel. The 2 resulting counting samples were measured 10 to 20 times for 2 hr alternating. After 1 to 2 weeks, the samples were

measured once more to control the decay curve of ^{90}Y and the background of the samples. Sample activities were calculated by taking into account the decay of ^{90}Y from the time of extraction to the beginning of measurement and also during the measurement time. The amount of ^{90}Y ingrowth between the first and second set of TBP extractions was also taken into account. Some counting samples showed higher counting rates at the beginning that did not fit to the ^{90}Y decay curve and thus were rejected. If the counting rate had not reached the blank counting rate within 3 weeks, the real background rates of the counting samples were used for evaluation.

Quality assurance was done by analyzing 19 wheat samples using 2 independent counting methods (see above). We participated successfully in several national quality control programs. During this investigation, we repeatedly determined ^{90}Sr in bread crumbs (100 g) obtained from the Federal Dairy Research Center (BAfM, Kiel) and in an aerosol filter from the Federal Office for Radiation Protection (BfS, Berlin).

RESULTS AND DISCUSSION

Figure 1 shows the Cerenkov spectrum of a ^{90}Sr/^{90}Y standard solution. Figure 2 shows the FOM calculated based on these spectra with different window settings. The FOM is defined as:

$$FOM = \varepsilon^2 / R_0 \quad (1)$$

with ε = counting efficiency (in %) and R_0 = background (in counts per minute, cpm). One can see that when setting the left channel to 0, the FOM will be larger than 4000 for a wide range of the right channel setting. However, the highest FOMs are obtained when setting the left channel to ~100 and the right one to ~335. This region is marked in Figure 1. These channel settings were used for all future Cerenkov measurements. The counting efficiency for ^{90}Sr/^{90}Y in this window was 58.5%; the background was 0.72 cpm, resulting in a FOM of ~4750. The counting efficiency, background, and FOM over the whole spectrum were 70.0%, 1.20 cpm, and 4080, respectively. Figure 3 shows the netto counting rates R_n of a purified ^{90}Sr solution. The data were fitted with the function:

$$R_n = (\varepsilon_{Sr} + \varepsilon_Y(1 - e^{-\lambda t}))a_0 \quad (2)$$

with ε_{Sr} and ε_Y being the counting efficiencies of ^{90}Sr and ^{90}Y, λ = decay constant of ^{90}Y (3.004E-06), a_0 = activity of ^{90}Sr, and t = time since the separation of ^{90}Sr and ^{90}Y. Since a little loss of ^{90}Sr during the separation cannot be avoided, the counting efficiencies were only used to determine the ratio $\varepsilon_Y/\varepsilon_{Sr}$, which was found to be 70. Thus, the Cerenkov counting efficiency for future experiments was estimated to be 57.7%. For calculating the uncertainty budget, an overall calibration uncertainty of 2% was estimated.

Table 2 shows the number of samples that were analyzed, the activities contained in the processed sample amount, the combined standard uncertainties, and the mean chemical yields of yttrium. Minimum detectable activities (MDA) were calculated according to BMU (2000). Typical MDA were in the range of 7 to 12 mBq. The uncertainty budget was calculated taking in account the uncertainties of chemical yield, counting efficiency, and counting rates (ISO 1995). For all types of samples, the mean Y yield was slightly above 90% with a very small variance. The lowest yield ever achieved was 74.4%. These results show that this method is very robust for many types of samples. The decontamination of the counting sample of interfering beta emitters was generally good, which could be shown by the ^{90}Y decay curve. In a few analyses, the counting rate did not reach the background level (0.72 cpm). In these cases, the real background of the samples had to be used. Some

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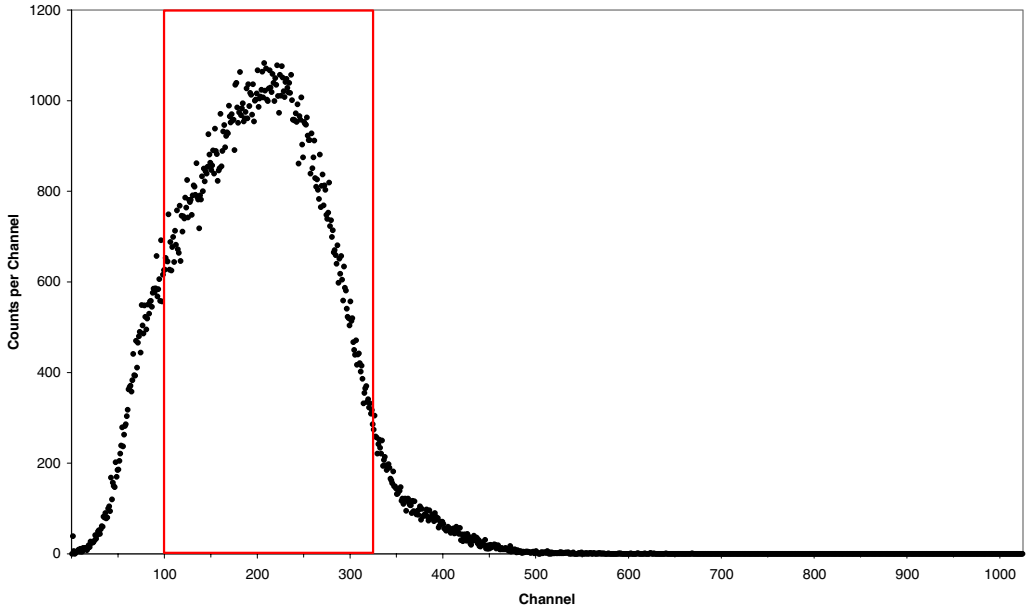

Figure 1 Cerenkov spectrum of $^{90}Sr/^{90}Y$ (in 1 mL 65% HNO_3 + 14 mL H_2O). The optimized counting region is marked.

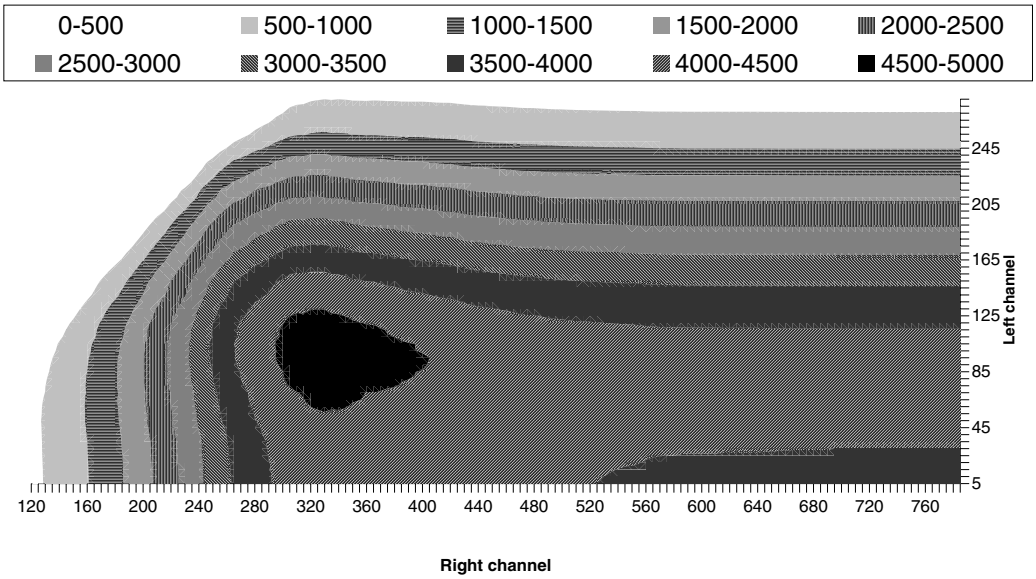

Figure 2 Dependency of the figure of merit (FOM) and the channel settings used for the determination of sample and background counts.

counting samples from soil showed high counting rates during the first 2-hr measurement, which did not fit the ^{90}Y decay curves. It was expected that this was caused by ^{212}Bi ($t_{1/2}$ = 60.55 min) and its daughter ^{208}Tl ($t_{1/2}$ = 3.05 min). However, even when neglecting these first measurements, the data from the following measurements were still of sufficient quality for evaluation.

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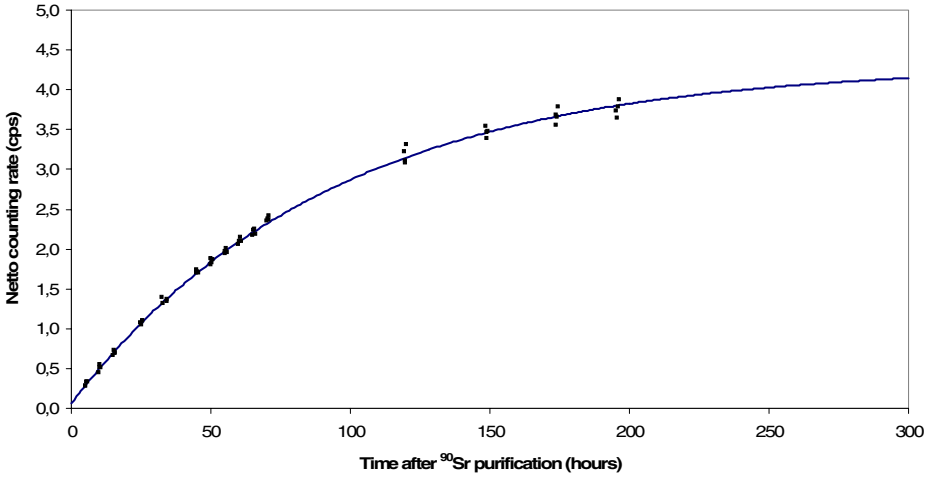

Figure 3 Time dependency of the netto counting rate of a purified ^{90}Sr solution (7.4 Bq in 1 mL HNO_3 + 14 mL H_2O) in a Wallac 1220.

Table 2 Number and chemical yields (± standard deviation) of yttrium of the analyzed samples.

Sample type	Number of samples	Activity per sample (Bq)	Combined standard uncertainty (%)	Yttrium yield (%)
Wheat, 1 kg	98	0.1–0.35	3.5–5.0	92.7 ± 4.6
Soil, 50 g	33	0.035–0.085	6.0–12.0	90.9 ± 4.2
Deposition, 0–300 L	76	<0.007–0.065	5.0–>50	90.6 ± 3.2

Figure 4 shows the results of 16 wheat samples that were analyzed by proportional and Cerenkov counting. With only 1 exception, all results matched very well within the 95% confidence level.

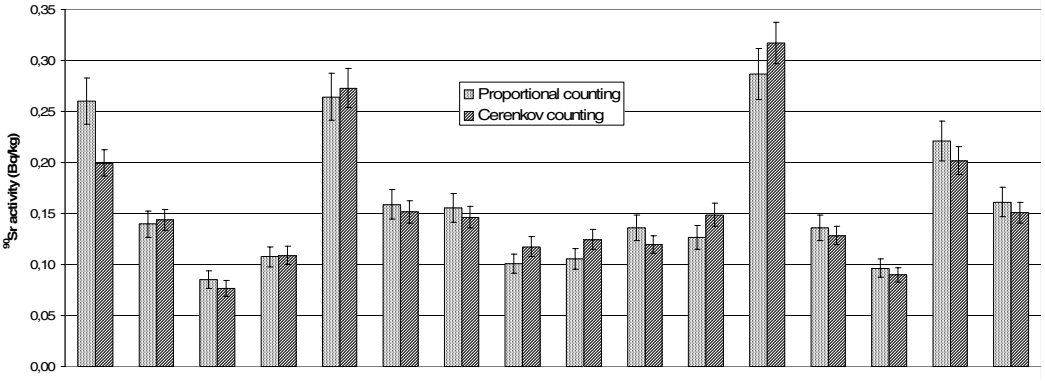

Figure 4 Comparison of ^{90}Sr activities in 16 wheat samples determined by proportional and Cerenkov counting. Error bars show the 95% confidence levels.

CONCLUSION

In summary, the determination of ^{90}Sr by the extraction of ^{90}Y with TPB, followed by Cerenkov counting, has proven to be very robust and reliable with different types of samples. The main advantage of the direct isolation of ^{90}Y is that the original sample solution can be reprocessed many times.

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For example, the ^{90}Sr content of the Quaternary deposition samples was often in the range of, or below, the detection limit. These samples now are combined to half-year samples and will once more be analyzed for their ^{90}Sr content.

ACKNOWLEDGMENTS

Drs K Schneider and J Tschiersch are warmly acknowledged for revising the manuscript.

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