

CHAPTER 49

A New Simplified Determination Method for Environmental ^{90}Sr by Ultra Low-Level Liquid Scintillation Counting

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ABSTRACT

^{90}Sr is a bone seeker and when in equilibrium with its short-lived, hard-beta-emitting daughter ^{90}Y , it may cause damage to the bone marrow. There is considerable interest in determining ^{90}Sr in a wide variety of environmental material, particularly food.

Normally, time-consuming chemical separation steps for isolation and decontamination from interfering radionuclides are necessary. Using a commercially available ultra low-level liquid scintillation counter, the required time for analysis could be reduced to a minimum. Extremely low LLDs allow for very small samples, and the entire separations can be performed in centrifugation tubes. The LLD achieved depends on the measurement method (Cerenkov or LS counting), and is between 50 and 90 fCi/sample (1.7 to 3.0 mBq/sample), based on 3σ of the background and 500 min counting time. The method has been tested with certified reference materials, and some results from analysis of food contaminated by Chernobyl fallout will be given.

INTRODUCTION

^{90}Sr is of considerable interest in radiation protection. It is produced by nuclear fission, and its fission yield is approximately the same as for ^{131}I or ^{137}Cs (5.7%). ^{90}Sr , originating from atmospheric bomb tests, has been spread all over the world and found its way to man through the food chain; there is direct deposition on plants and root uptake from the soil. The main source is milk. Transfer from soil to plants is normally about four times higher for ^{90}Sr as compared to ^{137}Cs ; transfer in the cow to milk is lower. ^{90}Sr is incorporated into bone tissue and therefore has an extremely long biological half-life. ^{90}Sr is a pure β -emitter with a maximum energy of 0.546 MeV and a half-life of 28.5 years. Its daughter ^{90}Y is a pure β -emitter as well, with a maximum energy of 2.27 MeV and a half-life of 64.1 hours, so it is very fast in equilibrium with ^{90}Sr . The high energetic β -particles may damage bone marrow. Since ^{90}Sr is a

highly radiotoxic nuclide maximum permissible levels in food are very low, and sensitive methods are needed for its determination.

Since the ban of atmospheric nuclear weapons testing in 1962 the ^{90}Sr concentration in food has decreased considerably. In the case of the nuclear accident at Chernobyl, ^{90}Sr was emitted to a much lower fraction than ^{137}Cs because it is less volatile. In Western Europe the total ^{90}Sr deposition was much lower than the one originating from the atmospheric bomb tests.¹ Nevertheless measurement of ^{90}Sr is necessary both for radiation protection purposes and public interest. It has been shown for Austria, by measurements with a conventional method, that in 1986 the additional intake of ^{90}Sr was equal to the intake of remaining ^{90}Sr from atmospheric bomb tests.²

This paper will deal only with ^{90}Sr , in the absence of short lived fission products, and ^{89}Sr (half life 50.5 d). Analysis of ^{90}Sr and ^{89}Sr will be the next step in development of fast measurement methods for the case of a nuclear accident.

STRATEGY FOR THE DEVELOPMENT OF THE METHOD

The traditional "nitrate method"³ has some serious disadvantages, the most important is handling the large amounts of fuming nitric acid for repeated precipitations. It was therefore attempted to avoid or at least reduce the number of purification steps with fuming nitric acid.

Liquid scintillation counting has been used for ^{90}Sr determinations since at least 1965 (an overview is given in Dehos⁴). The determination of low levels of ^{90}Sr has been considered by Salonen,⁵ who also gave a first comparison between LSC and gas flow counters. In LSC the sample has a 4π geometry, a very high efficiency compared to gas flow counters.

Before choosing a separation method it was necessary to determine the lower limits of detection of the liquid scintillation counters for ^{90}Sr .

The equipment used was the commercially available ultra low-level liquid scintillation counter "Quantulus" (Pharmacia – Wallac, Turku, Finland). This instrument exhibits extremely low background due to heavy passive and an active shielding.

The concentration of ^{90}Sr can be determined by several methods. In samples where ^{90}Y is in equilibrium with ^{90}Sr , the former can be extracted by, e.g., HDEHP, and measured either by Cerenkov counting or after mixture with a suitable scintillation cocktail. (This method was first applied to cheese, but interference by an unidentified radionuclide with a half-life of approximately 6 hours was found.) ^{90}Sr can be measured directly after separation and mixture with a suitable cocktail and it can be remeasured after ingrowth of ^{90}Y for control. ^{90}Y also can be measured in the final solution after ingrowth by Cerenkov counting followed by scintillation counting. Data from Cerenkov counting can be obtained only after some waiting time, but then possible

interferences from lower energy beta emitters and gamma emitters can be excluded.

First tests were conducted at the low-level laboratory ("LOLA") of Wallac OY in Turku, Finland. On one hand the environment shows high background radiation due to granite rock, on the other hand the laboratory has heavy concrete shielding. For all measurements, PTFE coated polyethylene vials (Zinsser, Frankfurt) were used. Cerenkov measurements were done in 10 ml 0.5 M hydrochloric acid; in LSC measurements 4 ml of 0.5 M hydrochloric acid solution were mixed with 6 ml Quickszint 400 (Zinsser).

Figure 1 shows the obtained pulse height spectra from Cerenkov counting both for background and standard. The window was optimized for highest figure of merit, using standard software for Quantulus. Efficiency was 69.25%, background 0.753 cpm. In Figure 2 ^{90}Sr and ^{90}Y are in equilibrium and mixed with cocktail. The window is adjusted for the sum of the radionuclides, giving an efficiency of 184.57% and a background of 1.988 cpm. If the window is adjusted for the part of the ^{90}Y spectrum above the maximum energy of ^{90}Sr (Figure 3), then an efficiency of 58.12% and a background of 0.603 cpm results.

Table 1 is a summary of the results obtained in terms of figure of merit (E^2/B) and lower limit of detection both for counting times of 100 and 500 min. The LLD is based on 3σ of the background.

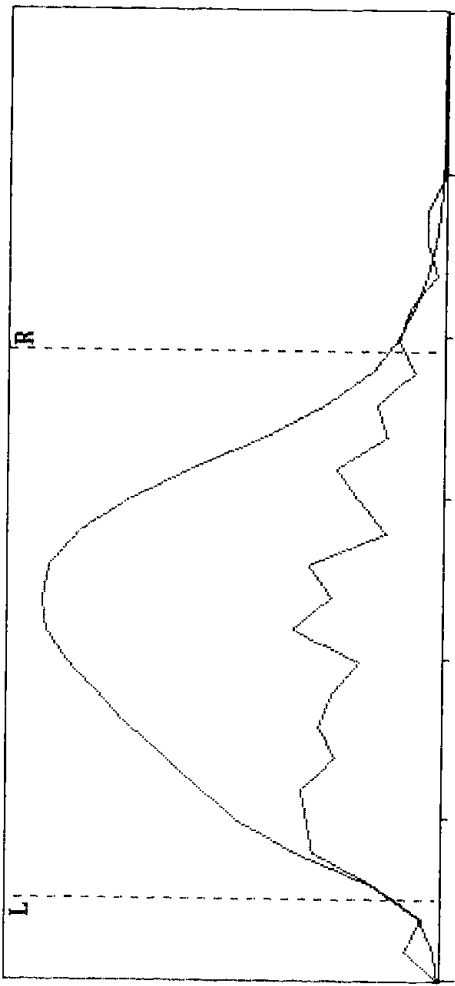
DETERMINATION OF ^{90}SR

The extremely low LLDs achievable with our equipment makes it possible to use considerably lower amounts of material than in conventional methods. In the conventional nitrate method described, 20 g milk or cheese ash are used. We have used for our analysis between 1 and 2 g of ash. The following procedure was tested and is now used in routine work:

The ash of dairy products is dissolved in dilute nitric acid; carrier solutions of strontium, barium, iron, and chromate are added. The resulting volume in the first step is about 120 mL. Upon addition of ammonium acetate and adjustment to pH 5, barium chromate, iron phosphate, and basic iron acetates are precipitated and centrifuged. Phosphate is thus removed from the sample. Radium is also removed and it can be recovered and isolated from the precipitation. After precipitation with ammonium carbonate, work can be continued in small volumes of 10 to 20 mL. After dissolution in nitric acid, hydrogen peroxide, and yttrium carrier, the hydroxides of chromium and yttrium are removed. The final solution can be either acidified and measured directly or have one carbonate precipitation step added.

The use of fuming nitric acid is avoided completely. The chemical recovery, which is determined by atomic absorption spectroscopy, is in the range of 70%, which is regarded as sufficient compared with the ease of the procedure. In three days 20 samples of cheese ash have been processed. The limiting and

[AJ 750.000 CPM/ch 3.81 min A:\SR\BUCHT-FS\CERI\Q056001N.000 SP#12
 [B] 0.010 CPM/ch 394.87 min A:\SR\BUCHT-FS\CERI\Q040401N.000 SP#12

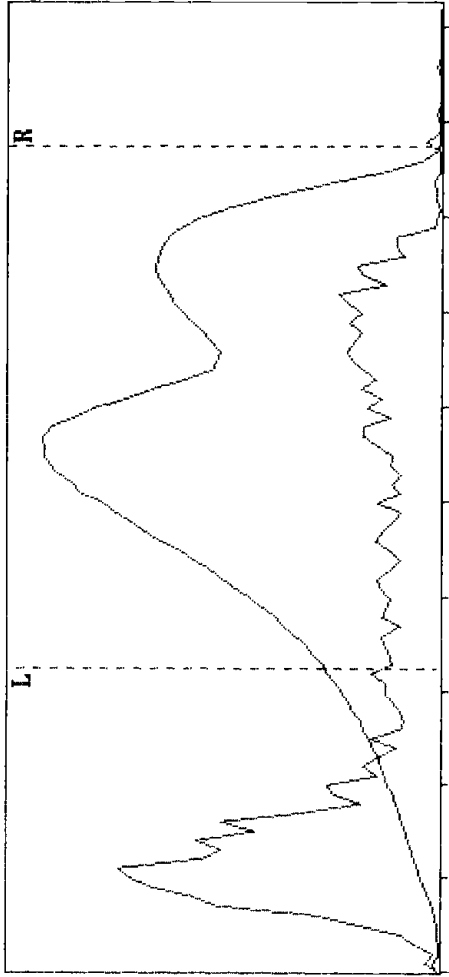


1 100 200 300 400 500 600
 INTEGR (50- 390) [AJ]153771.641 CPM [B] 0.753 CPM
 BUNCH=10 * FM * (222026.42 DPMco) FM {[AJ],[B]}= 6367 (E= 69.26 %)

Isotope: Half Life = 28.5 Y
 STANDARD preparation date = 01.03.79 00:00 284160.00 dPM
 measurement date = 20.04.89 00:00 222026.42 DPM (decay corr.)
 decay ratio (A/Ao) = 0.7813

Figure 1. Pulse height spectra of ⁹⁰Sr standard and background, and Cerenkov counting in 0.5 M hydrochloric acid, with window optimized.

[A] 1300.000 CPM/ch 3.39 min A:\SR\BUCHT-FS\LSC1\Q056001N.000 SP#12
 [B] 0.030 CPM/ch 394.87 min A:\SR\BUCHT-FS\LSC1\Q040401N.000 SP#12

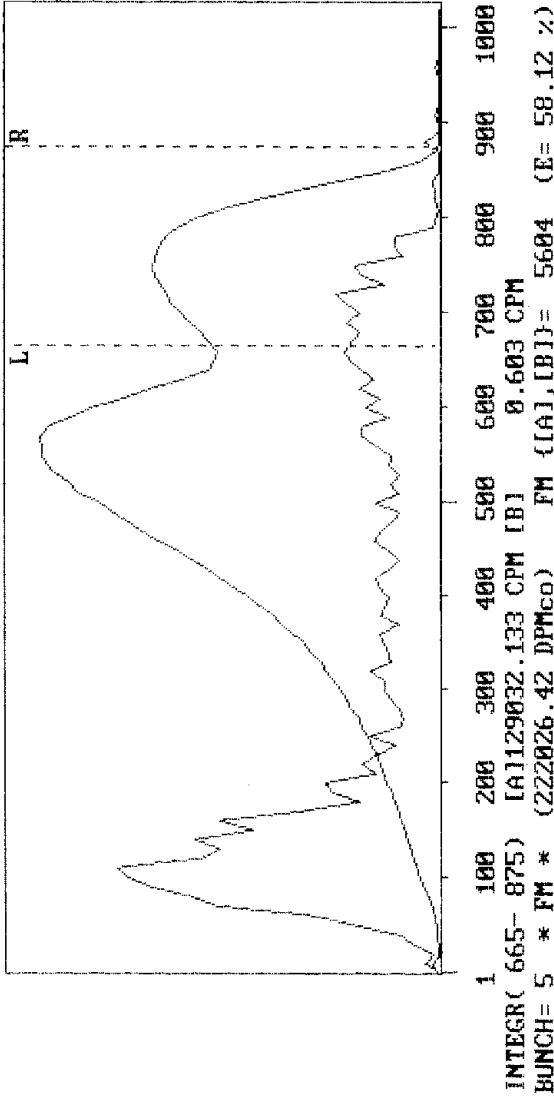


1 100 200 300 400 500 600 700 800 900 1000
 INTEGR (324- 875) [A]409800.530 CPM [B] 1.988 CPM
 BUNCH= 5 * FM * (222026.42 DPMco) FM {[A],[B]}= 17136 (E=184.57 %)

Isotope: Half Life = 28.5 Y
 STANDARD preparation date = 01.03.79 00:00 284160.00 DPM
 measurement date = 20.04.89 00:00 222026.42 DPM (decay corr.)
 decay ratio (A/Ao) = 0.7813

Figure 2. Pulse height spectra of ⁹⁰Sr standard and background, and mixture with Quicksint 400, with window optimized for sum of ⁹⁰Sr and ⁹⁰Y.

[A] 1300.000 CPM/ch 3.39 min A:\SR\BUCHT-FS\LSC1\005600IN.000 SP#12
 [B] 0.030 CPM/ch 394.87 min A:\SR\BUCHT-FS\LSC1\004040IN.000 SP#12



Isotope: Half Life = 28.5 Y
 STANDARD preparation date = 01.03.79 00:00 284160.00 JPM
 measurement date = 20.04.89 00:00 222026.42 DPM (decay corr.)
 decay ratio (A/Ao) = 0.7813

Figure 3. Pulse height spectra of ^{90}Sr standard and background, and mixture with Quickszint 400, with window optimized for ^{90}Y alone.

Table 1. Performance of Quantulus for ^{90}Sr for Different Conditions

Measurement Condition	Figure of Merit	LLD (mBq) (100 min)	LLD (mBq) (500 min)
Cerenkov counting	6,367	6.3	2.8
LS counting, open window	17,136	3.8	1.7
LS counting, ^{90}Y window	5,604	6.7	3.0

most time consuming step is ashing the samples. In the case of fresh milk, ion exchangers for concentrating strontium are planned, thus avoiding ashing.

RESULTS

The liquid scintillation method has been applied to a large variety of food samples collected after the Chernobyl accident. They are predominantly measured for ^{137}Cs and ^{131}I . Figure 4 shows the results for ^{137}Cs in emmental cheese from Salzburg—a highly contaminated area. Since ^{137}Cs is concentrated in whey, its activity concentration in cheese is low compared with milk. Figure 5 shows the activity concentration of ^{90}Sr for some of the cheese samples. Not all of the samples which had been measured for ^{137}Cs were available for ^{90}Sr analysis, so the increased speed of activity concentration in milk cannot be concluded. As in the case of ^{137}Cs a slow decrease can be seen about two weeks after the contamination occurred. The activity of directly deposited ^{90}Sr per kg grass ingested by the animals decreased due to dilution by plant growth. Samples from March 1987 showed concentrations of ^{90}Sr in cheese between 1.5 and 3.6 Bq/kg fresh weight (40 to 97 pCi/kg).

Concerning meat, another important source, concentrations were low—from below LLD to 0.1 Bq/kg freshweight (2.7 pCi/kg), with some exceptions in highly contaminated areas of up to 0.4 Bq/kg (2.5 pCi/kg).

The analyses of many samples collected after Chernobyl is going on and a report on the impact of the nuclear accident regarding ^{90}Sr is under preparation.

CONCLUSION

A method has been developed to analyze environmental samples and especially milk products for ^{90}Sr without using fuming nitric acid. Due to the extremely low LLDs of the used liquid scintillation counter, a very small sample amount can be used, and the whole separation procedure can be carried out in centrifuge tubes. The chemical yield is about 70% and it is determined by AAS. Twenty cheese ashes were processed within three days. The only limiting step is the ashing of the samples. The method saves time, chemi-

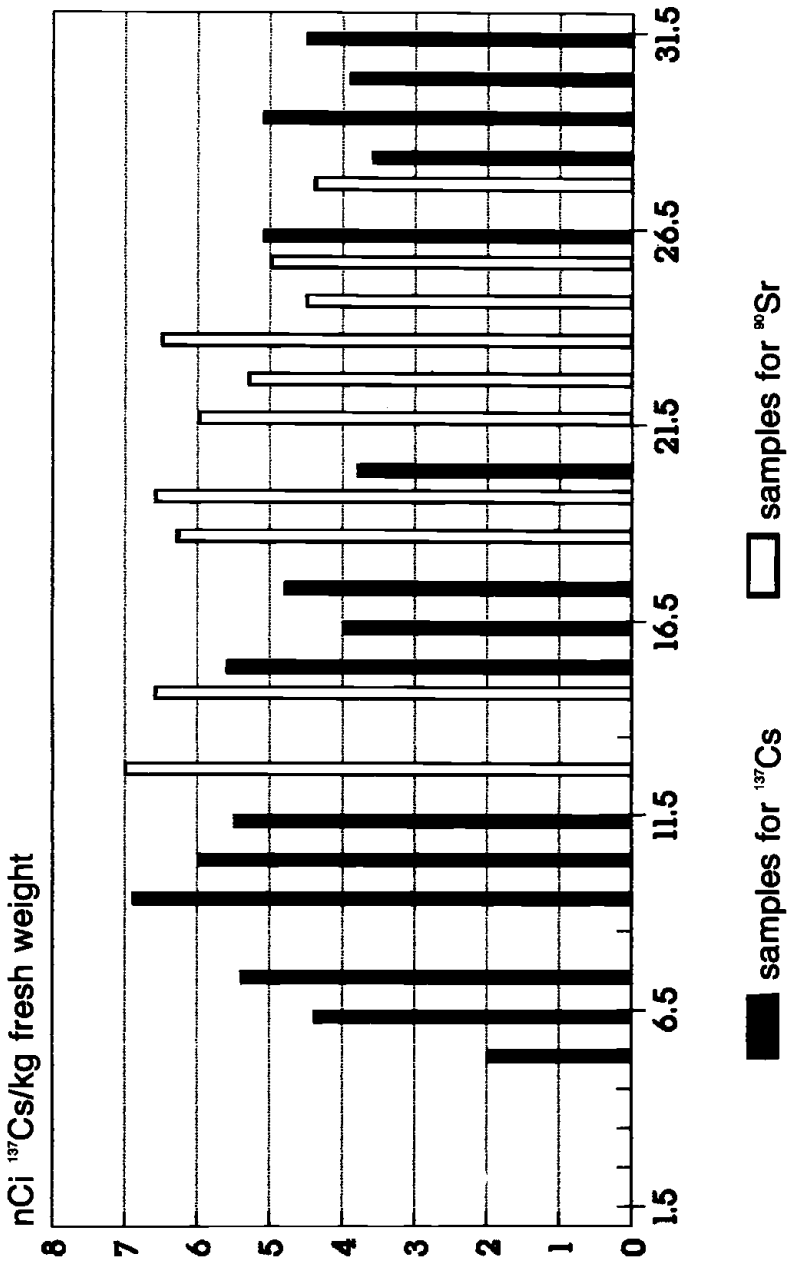


Figure 4. Contamination of emmental cheese from Salzburg with ¹³⁷Cs following the nuclear accident at Chernobyl. Values are given for fresh weight.

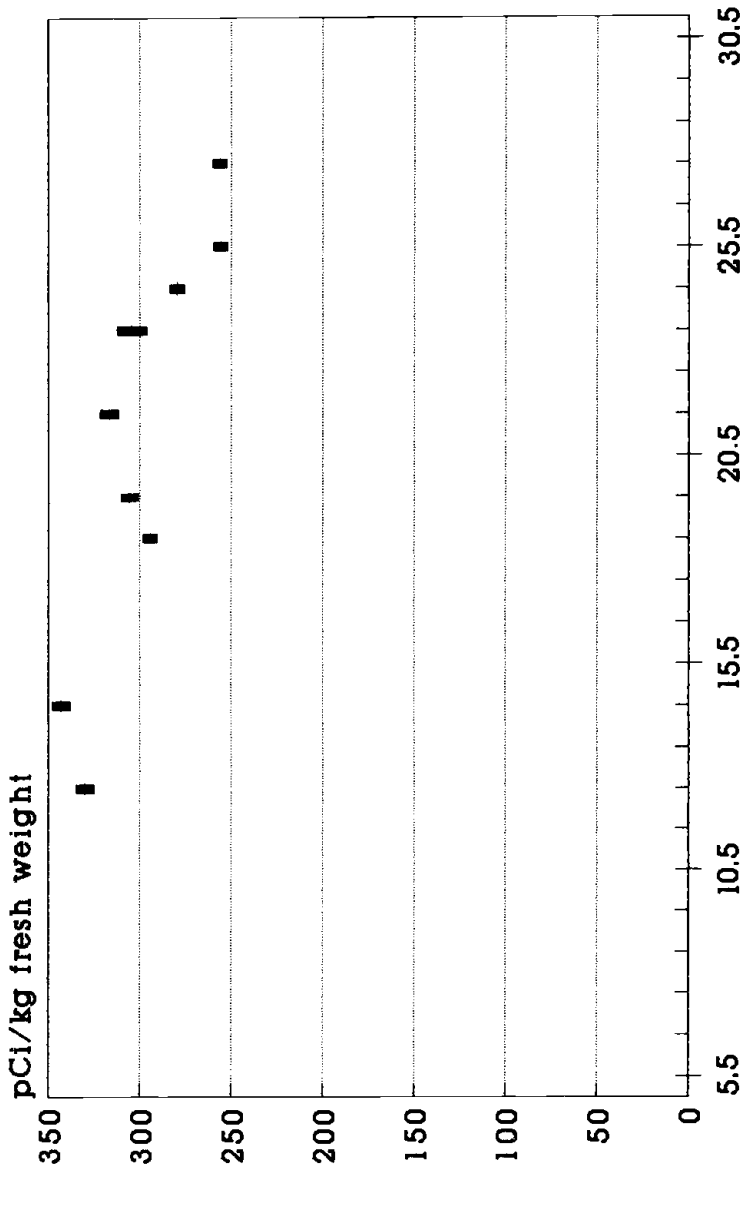


Figure 5. Contamination of some emmental cheese samples from Salzburg with ⁹⁰Sr. Values are given for fresh weight.

cals, and equipment, and it is accurate as was proved with certified reference material.

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REFERENCES

1. Schönhofer, F., W. Ecker, H. Hojesky, W. Junger, K. Kienzl, H. Nowak, A. Riss, P. Vychytil, and J. Zechner. *Chernobyl and Its Impact on Austria*, Austrian Ministry of Health and Environmental Protection, Nov. 1986 (in German).
2. Mück, K.S. Striet, F. Steger, and K. Mayr. *The Contribution of ^{90}Sr to the Ingestion dose after the reactor accident in Chernobyl*, Austrian Research Center Seibersdorf, OEFZS-4452, ST-157/88, June 1988.
3. *Methods of Radiochemical Analysis*. (Geneva: World Health Organization, 1966), p. 52 ff.
4. Dehos, R. *Determination of ^{90}Sr in Human Bones, Tissues and Excretion*. STH-Berichte 13/1979, (Federal Republic of Germany: Bundes gesundheitsamt [Federal Health Authority], 1979), in German.
5. Salomen, L. "Determination of ^{90}Sr and ^{89}Sr in Environmental Samples by Liquid Scintillation Counting," paper presented at the International Symposium on Scintillation Counting and Related Techniques, Bath, England, September 13-16, 1977.