FAST AND SENSITIVE DETERMINATION OF SR-90 AND SR-89 ACTIVITY IN MILK BY ION-CHROMATOGRAPHY AND LIQUID SCINTILLATION

V. Figueiredo and A. Herrmann
Food Control Laboratory, Basel, Switzerland

1. ABSTRACT

A method for fast and exact determination of both strontium isotopes in milk and other foodstuffs, combinating high performance ion chromatographic separation with by liquid scintillation counting, which enables the desired results to be obtained with very satisfactory precision and reproducibility within 24 hours, has been developed. The lowest detectable activity lies by 3 Bq/liter for Sr-90 and 1 Bq/liter for Sr-89 which is satisfactory for assessing a situation in a time of crisis.

2. INTRODUCTION

After the accident in Chernobyl, the old problem of Sr-90 and Sr-89 activity measurements became topical once more. Again it was evident that the public as well as the authorities expected quick and reliable information after the event from the responsible laboratories. Due to the wide bands of energy emited by the beta-radiation, a chemical separation of the nuclides to be measured is unavoidable. The methods used at the moment [1,2,3] involve tedious separations and reliable results require waits of several to 20 days. The method described here, a combination of high performance ion chromatography and liquid scintillation, enables us to obtain the necessary strontium preparation purity and to determine the activities of both Sr-90 and Sr-89 correctly and exactly within a working-day.

3. EXPERIMENTAL

After the removal of the milk protein with trichloroacetic acid, the alkaline earth metal ions are precipitated as oxalates, converted to carbonates by ashing and the strontium as well as the barium ions precipitated as nitrate salts. An aliquot of the nitrate salt is put through a chromatographic system, the strontium peak-volume collected and the activity of both strontium isotopes measured by low-level liquid scintillation. The chemical manipulations require approximately 7 hours and the counting 3 hours.

3.1. ISOLATION OF STRONTIUM FROM MILK

The isolation of strontium is performed according to [4], using 1 liter of milk and adding 40 mg each of strontium and barium carrier. The procedure is interrupted at the level of the nitrate precipitation. The precipitate dissolved in 5 ml water (sample solution) is then used for the ion chromatography.

3.2. FINE CLEANUP OF STRONTIUM BY ION-CHROMATOGRAPHY

250 µl of the sample solution are injected into the chromatographic system described below. After the detection by conductivity the strontium peak-volume is collected in a counting vial, mixed with PICO-AQUA cocktail and counted as soon as possible.

Column	: DIONEX HPIC-CS3 and HPIC-CG3
Eluent	: HCl 48 mM, diaminopropionic acid hydrochloride 16 mM
Flow-rate	: 1 ml/min
Detection	: Suppressed Conductivity

3.3. CHEMICAL YIELD

The chemical yield of the precipitation is also determined by ion chromatography after adequate dilution of the sample solution. The concentration of the sample solution and thereby the chemical yield are determined using an external standard.

3.4. MEASUREMENT OF SR-90/SR-89 ACTIVITIES BY LIQUID SCINTILLATION

The scintillation spectra are measured on a TRICARB 2250CA low level liquid scintillation analyzer from PACKARD. The activities of Sr-90 and Sr-89 of the collected fraction are determined by dual label DPM analysis with AEC (Automatic Efficiency Control) in the following optimized energy windows: 5-200 keV for Sr-90 and 200-1200 keV for Sr-89.

Preparation of the Quench Curves:

As commercially obtained Sr-90 is in equilibrium with its daughter Y-90, it is necessary to purify the Sr-90 standard solution by chemical separation [2] before preparing the quench sets.

Sample measurement:

The sample activity must be measured directly after the eluate is collected, but after a few minutes equilibration in the cooled sample collector. The samples are counted over a period of 180 minutes.

4. RESULTS AND DISCUSSION

At the present time adequate preparative columns are not available: the DIONEX HPIC-CS3 is an analytical column. However the quantities and volumes given here result in a good recovery rate of added strontium. Starting with one liter of milk, with the stated amounts of strontium and barium added, a chemical yield of 68 % ± 2 % (n = 10) was obtained.

Under the given conditions of the ion-chromatographical purification the alkaline earth metal ions are separated, while the alkaline metal ions are eluted with the water peak. Trivalent ions such as lanthanides, yttrium and the transitional metals are held back by the column. If in the case of milk, the calcium is not removed with nitric acid separation,

a large excess of calcium will be present which prohibits a separation of the peaks. One single nitric acid separation completely eliminates any alkali ions that may possibly be present and reduces the calcium concentration by a factor of 1000.

Although the analytical chromatography column is clearly overloaded, the strontium-peak is well resolved from the barium-peak. The addition of barium carrier solution permits a well timed interruption of the collection of the strontium fraction.

With the possibility of dual label DPM counting, spectral separations of both radiations (max. energies: 0,546 keV for Sr-90, 1,492 keV for Sr-89), activity ratios of Sr-90/Sr-89 from 1:50 to 50:1 can be measured well. The two established quench curves in the chosen energy windows for Sr-90 and Sr-89 give a constant spill-up and spill-down. The efficiencies for both isotopes lie by 70 % for Sr-90 and 67 % for Sr-89.

Due to the ingroth of Y-90, after a counting time of 180 minutes only an Y-90 activity of approximately 3 % of the Sr-89 activity will be present. The Beta-radiation from Y-90 appears mainly in the Sr-89 window and so can simulate Sr-89 activity.

5. QUALITY CONTROL OF THE METHOD

At the end of 1990 we received several food samples from Chernobyl, whose activity had been determined with gamma-spectrometry. In 5 samples, the Sr-90 activity was determined with the up to then applied method [2], which is based on the measurement of the chemically separated Y-90 using a gas-proportional counter. The direct determination of the Sr-90 activity of these samples was likewise carried out using the method described above, also only 250 ml of milk and 500 ml of water could be used (Table 1).

Table 1: comparison of the methods: Sr-90 in milk and water samples from Chernobyl (Bq/liter)

sample	method [2]	this method	difference
milk 1	5,6 ± 0,1	5,7 ± 0,6	+ 1,8 %
milk 2	8,4 ± 0,1	7,6 ± 0,8	- 9,5 %
milk 3	10,9 ± 0,2	13,8 ± 1,4	+26,6 %
milk 4	9,9 ± 0,2	10,0 ± 1,0	+ 1,0 %
pond water	46,9 ± 4,5	52,0 ± 2,6	+10,9 %

The difference in the results varies between 1 and 27 %, with a mean value around 10 %. In view of the given degree of pure statistical error (1 sigma), the differences are not significant except in milk sample 3. With the limited volume available, the results are very satisfactory.

A further comparison, on the basis of an interlaboratory test organized by the Berlin Ministry of Health (BGA) is shown in table 2.

Table 2: Interlaboratory test, BGA Berlin 1990 (Bq/liter)

nuclide	method [2]	this method	nomial value
Sr-90	4,3 ± 0,2	4,4 ± 0,4	4,2
Sr-89	-	7,0 ± 0,7	5,3

The sample (water) contained, apart from the two Sr-isotopes, also H-3, Co-60, Zn-65, Cs-134, Cs-137 and Ce-141. The strontium activities measured with both the tested methods agree very well with the expected value. The Sr-89 activity found by the method described here actually deviates by 30 % from the value given by the BGA, but with an activity of only 2,7 Bq/liter at the time of measurement (70 days after the reference date) it is not surprising.

6. CONCLUSIONS

The method described here has shown to be very reliable: the ion chromatography allows a maximum purity of the strontium fraction to be obtained, and the liquid scintillation permits a simultaneous determination of both strontium isotopes. The detection limit lies by 3 Bq/liter for Sr-90 and 1 Bq/liter for Sr-89. Even when this method, at the moment has only been tested by means of some samples from Chernobyl and spiked samples, it can be used for other foodstuffs with the appropriate preparation, without further ado, or in nuclear plant laboratories for their own control of waste water.

Thus it is possible to perform quick and reliable strontium analyses after an event and take the necessary precautionary measures or issue recommendations promptly.

7. REFERENCES

[1] Wilken, R.D. and Diehl, R., 1989, Überwachung der Sr-89/Sr-90-Aktivität von Kuhmilch, Empfehlungen zur Ueberwachung der Umweltradioaktivität, Fachverband für Stahlenschutz e.V., Loseblattsammlung FS-78-15-AKU

[2] Erard, M. and Zimmerli, B., 1988, Bestimmung von Strontium-90 in Milch, Mitt. Gebiete Lebensm. Hyg.,79, pp. 48-56.

[3] Baratta, E.J. and Knowles, F.E., 1973, Ion Exchange Determination of Strontium-89 and Strontium-90 in Milk, Journal of the AOAC, 56, 1, pp. 213-218

[4] Morre, J., Janin-Caufment, F. and Mazer, J.P., 1971, Analyse radiobiologique rapide et complete d'un lait, Rapid Methods for Measuring Radioactivity in the Environment, Proceedings of an International Symposium held in Neuherberg, 5-9 July 1971,International Atomic Energy Agency, Vienna, pp. 233-239 (IAEA-SM-148/46)