

## APPLICATION OF THE EICHROM-LSC METHOD FOR DETERMINING $^{90}\text{Sr}$ IN FINNISH LAKE WATERS

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**ABSTRACT.** A method for determining  $^{90}\text{Sr}$  based on the separation of Sr with Eichrom resin and measurement with a Quantulus<sup>TM</sup> liquid scintillation spectrometer was applied to lake water samples. Samples of 10 L each, collected from 31 lakes during the summer of 1998 and/or 2002, were included in the study. The samples were concentrated by evaporation and then ashed to remove the organic material. The ashed samples were dissolved, transferred to 3M  $\text{HNO}_3$ , and placed on a column of Sr-specific Eichrom (SrSpec) resin. Strontium was eluted from the resin with 0.05M  $\text{HNO}_3$ , precipitated as carbonate, and dissolved in 1M HCl. Scintillation solution (Ultima Gold<sup>TM</sup> AB) was added and  $^{90}\text{Sr}$  with ingrowing  $^{90}\text{Y}$  was measured with a Quantulus liquid scintillation spectrometer. The chemical yield of strontium was determined by atomic absorption spectrophotometry (AAS). Our Quantulus calibrations allow us to carry out the measurements at any point in time after Sr-Y separation during the ingrowth of  $^{90}\text{Y}$ . The effectivity is almost 200% if the counting is performed 18 d after Sr-Y separation, when equilibrium has been reached. The validity of the calibration was tested by measuring the samples at various times during the ingrowth of  $^{90}\text{Y}$ . The results of the intercomparisons in which we have participated have confirmed the high quality of our analysis and calibration method.  $^{90}\text{Sr}$  in lakes in Finland originates from nuclear weapons tests carried out mainly in the 1960s and from the Chernobyl deposition in 1986. The importance of  $^{90}\text{Sr}$  is emphasized regarding radiation doses via drinking water derived from surface water.  $^{90}\text{Sr}$  decreases slowly in water after deposition and it is not significantly removed by the commonly used treatment processes in water plants. Activity concentrations of  $^{90}\text{Sr}$  in lake waters in 1998 and 2002, respectively, varied from 5 to 23  $\text{Bq/m}^3$  and 6.3 to 17  $\text{Bq/m}^3$ .

### INTRODUCTION

An extraction chromatographic method is used at the Laboratory of Ecology and Foodchains of Radiation and Nuclear Safety Authority (STUK), Finland, for determining  $^{90}\text{Sr}$  in environmental samples. In this method, a sample dissolved in 3M  $\text{HNO}_3$  is placed on a column containing Sr-specific (SrSpec) resin (Eichrom). This retains Sr, which is then eluted from the column with diluted  $\text{HNO}_3$ . Many reports have dealt with the basic method (Alvarez et al. 1995; Gjeççi 1996; Hewitt and Bronisława 1994; Vajda et al. 1992). Before adoption, the method was tested at STUK with dozens of surface water and other environmental samples. The results were compared with those obtained using the much slower method previously used in our laboratory for  $^{90}\text{Sr}$  determinations, in which the separation of Sr from Ca is based on precipitation with concentrated  $\text{HNO}_3$  (Bryant et al. 1959; Osmond et al. 1959). The results agreed well with each other. The basic method, with additions due to the removal of disturbance caused by Pb in some cases, was reported by Saxén (2002). This paper reports on the application of the Eichrom separation method combined with Quantulus liquid scintillation counting (LSC) for lake water samples, with special emphasis on the calibration method used. Using LSC for the measurement of  $^{90}\text{Sr}$  was first reported at STUK by Salonen (1978), and it has served as a basis for the development of the LSC measurement included in the method reported here.

### LAKE WATER SAMPLES

Water samples were collected from 31 lakes in 1998 and/or 2002. The locations and surface areas of the lakes are given in Figure 1.

### SAMPLE TREATMENT, SEPARATION OF $^{90}\text{Sr}$ WITH EICHROM RESIN, AND MEASUREMENT

After arrival at the laboratory, lake water samples were acidified and 20 mg of Sr carrier was added. The samples were then evaporated to dryness (Figure 2) and ashed to remove the organic material. Next, a melt was made with  $\text{Na}_2\text{CO}_3$  at 900 °C for 30 min. The melt was then boiled with water, cen-

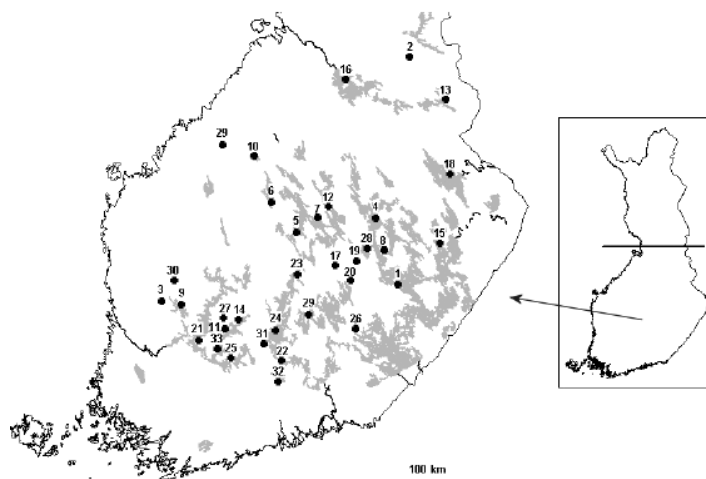


Figure 1 Location and areas of the lakes sampled for water in 1998 and/or 2002. Areas of the lakes are taken from Raatikainen and Kuusisto (1988). Points 22, 23, and 24 are sampling points of 1 large lake, Päijänne.

Lakes corresponding to sampling points in Figure 1 (above):

	km <sup>2</sup>		km <sup>2</sup>		km <sup>2</sup>
1. Haukivesi	620	12. Nilakka	163	23. Päijänne (Jyväsk. mlk)	1054
2. Hyrynjärvi	18.3	13. Ontojärvi	95	24. Päijänne (Kuhmoinen)	1054
3. Jämijärvi	9.2	14. Oriselkä	<10	25. Pälkänevesi	45.9
4. Kallavesi	513	15. Orivesi	536	26. Saimaa (Mikk.mlk)	1147
5. Keitele	500	16. Oulujärvi	893	27. Siikajärvi	0.96
6. Kivijärvi	155	17. Pieksänjärvi	25	28. Sorsavesi	50.8
7. Konnevesi	187	18. Pielinen	868	29. Ullavanjärvi	13.3
8. Kuore-Kaita	<1	19. Pieni Ahveninen	<1	30. Vahojärvi	<10
9. Kyrösjärvi	96.2	20. Pyhäjärvi (Pieks. mlk)	10.9	31. Vehkajärvi	24.6
10. Lestijärvi	65	21. Pyhäjärvi (Pirkkala)	124	32. Vesijärvi (Hollola)	108
11. Längelmävesi	178	22. Päijänne (Asikkala)	1054	33. Vesijärvi (Kangasala)	40.2

trifuged and the solution was discarded; the residue was dissolved in  $\text{HNO}_3 + \text{H}_2\text{O}_2$ . The solution was evaporated nearly to dryness and dissolved into  $3\text{N HNO}_3$ . In this form, the sample was put onto the column of resin (3 g, Eichrom, SrSpec, 100–150  $\mu\text{m}$ ). A wash was done with  $8\text{N HNO}_3$  to remove Ba, and thereafter the resin was eluted with  $3\text{N HNO}_3$  to remove Y. The end of the wash was noted as the final time point for the separation of Y from Sr. Sr was finally eluted from the column with  $0.05\text{N HNO}_3$ , precipitated as carbonate, and dissolved in 1.7 mL of  $1\text{N HCl}$ . An aliquot of 0.15 mL was taken from the final solution by weighing to determine the chemical yield of Sr, which was carried out by atomic absorption spectroscopy (AAS). The amount of stable Sr in the lake water samples was so low that it did not need to be taken into account in the yield determination. The chemical yield of the determinations for surface water samples has been good ( $77 \pm 4\%$ ,  $n = 38$ ). In the absence of  $^{89}\text{Sr}$ , as in the case with lake water samples, no Cerenkov counting is needed but only measurement with scintillation solution. Before measurement, 6 mL of Ultima Gold™ AB scintillation solution was added to the samples and then measured with a Quantulus 1220™ liquid scintillation spectrometer (Wallac). The counting time for lake water samples was 300 min. The measurement can be done at any time after Sr-Y separation. If the samples are measured 18 d after the separation, when the equilibrium between  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  is reached, the effectivity is close to 200%.



Figure 2 Concentration of lake water samples by evaporation. A thin film makes it easy to take the evaporation residue off of the crucible.

## CALIBRATION OF THE QUANTULUS FOR $^{90}\text{Sr}$ DETERMINATIONS AS A FUNCTION OF TIME SINCE Sr-Y SEPARATION

### Preparation of the Calibration Samples (Standards)

For  $^{90}\text{Sr}$  measurements with the Quantulus, we performed calibrations that allow the sample measurements to be carried out at any time after Sr-Y separation, not only after waiting for equilibrium to be reached with the daughter nuclide  $^{90}\text{Y}$ . For this type of calibration, a few (we usually use 3) parallel aliquots of standard solution ( $^{90}\text{Sr}+^{90}\text{Y}$  in equilibrium) are taken precisely and  $^{90}\text{Y}$  is separated from  $^{90}\text{Sr}$  by iron hydroxide precipitation. Activity concentrations of the calibration samples should be high enough (usually  $\sim 500$  dpm) to allow good counting statistics, even with short (60 min) counting times. The time of the separation is noted exactly (time 0). Sr is precipitated as carbonate, filtered, washed, and dried. The precipitate is dissolved in 1.5 mL of 1N HCl. Thereafter, 6 mL of Ultima Gold AB scintillation solution is added and mixed well. The measurement is started immediately and performed repeatedly at first with short counting times (60 min) over 3 d, then with a longer counting time over 15 d, until the equilibrium between  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  has been reached.

### Determination of Chemical Yield of the Calibration Samples

The Sr yield of the calibration samples is obtained by comparing the count rates for the Sr-Y separated calibration samples (separation with iron hydroxide precipitation) after 18 d, i.e. after reaching equilibrium, with the results for the standards (3 parallel) measured directly in equilibrium without separation of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$ . The yield of strontium (Sr) is

$$Sr = a_1/a_2 \quad (1)$$

where  $a_1$  is the average cpm/g for the calibration sample, calculated from the standard solution through Sr-Y separation (Y precipitated with iron hydroxide) after reaching the equilibrium between  $^{90}\text{Sr}$  and  $^{90}\text{Y}$ ; and  $a_2$  is the average cpm/g for the standard solution sample measured directly in the equilibrium between  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  (without Sr-Y separation).

### Calculation of Effectivities for $^{90}\text{Sr}$ , $^{90}\text{Y}$ , and $^{90}\text{Sr}+^{90}\text{Y}$

Effectivity rates are calculated for every measurement of the 3 calibration samples, which are carried out via Sr-Y separation. For the calculations, the exact value is needed of the  $^{90}\text{Sr}$  activity in the calibration samples measured,  $A(\text{Sr})$ :

$$A(Sr) = \text{added activity}(dpm) \times Sr \times e^{[(-\ln 2 \times t_1)/(28.5 \times 365)]} \quad (2)$$

where  $t_1$  is time between the reference date and the midpoint of the measurement, and  $Sr$  is the yield of Sr after Sr-Y separation of the calibration samples (cf. "Determination of Chemical Yield of the Calibration Samples").

Measurements of the calibration samples then give:

$$E(Sr + Y)(t) = (a - b)/A(Sr) \quad (3)$$

where  $a - b$  is net count rate of the calibration sample (standard), cpm.

Values of  $E(Sr + Y)(t)$  for all measurements of the calibration samples are plotted as a function of time since Sr-Y separation. A curve describing the ingrowth of  $^{90}\text{Y}$  as a function of time is obtained by fitting a curve to the empirical points (Figure 3). From this curve, effectivities for the sample measurements are taken according to the time since Sr-Y separation up to the midpoint of the measurement. An example is given in Figure 4 of the spectra of calibration sample measurements at various times after Sr-Y separation and the corresponding effectivities. On the other hand, this time-dependent effectivity of the calibration samples consists of the effectivity of  $^{90}\text{Sr}$  plus that of the ingrowing  $^{90}\text{Y}$  according to the equation:

$$E(Sr + Y)(t) = E(Sr) + E(Y) \times (1 - e^{-\ln 2 * t_1 / 2.69}) \quad (4)$$

where  $t_1$  is time between separation of Sr and Y to the midpoint of the measurement:

$$E(Y) = [(cpm Sr + Y) - (E(Sr) \times A(Sr))]/dpm Y \quad (5)$$

Effectivity of  $^{90}\text{Sr}$  at time 0,  $(E(Sr)(0))$ , is determined by extrapolation of count rates of the first few measurements of the calibration samples and divided by the added activity of  $^{90}\text{Sr}$ .

After determining the effectivity of  $^{90}\text{Sr}$  (without  $^{90}\text{Y}$ ) [ $= E(Sr)(0)$ ], the effectivity of  $^{90}\text{Sr} +$  ingrowing  $^{90}\text{Y}$  and of  $^{90}\text{Y}$  (Equations 4 and 5) can be calculated for all the measurements. The calculated values can be compared with the empirical values obtained directly from the measurements according to Equation 3. The results are consistent and the curves are an excellent match (Figure 3). It is important to start the counting of the calibration samples immediately after the separation in order to obtain the zero point of the curve as accurately as possible. The application of Microsoft Excel® software for the calculations demands the use of the values for Equations 4 and 5; for manual use of the calibration, only the curve determined by the measurements (Equation 3) is needed.

## CALCULATION OF THE RESULTS FROM THE SAMPLE MEASUREMENTS

The effectivity of each sample measurement is taken from the calibration curve according to the time between Sr-Y separation and the midpoint of the measurement time of the sample. The activity concentration of  $^{90}\text{Sr}$  in the sample is calculated using the following equation:

$$A = (a - b) \times L_{tot} / [60 \times L_{quant} \times Sr \times V \times E(Sr + Y)] \quad (6)$$

where  $A$  is activity concentration of  $^{90}\text{Sr}$  in the sample, Bq/L or Bq/kg;  $a - b$  is net count rate of the sample measurement, cpm;  $L_{tot}$  is total volume of the sample solution (before taking the subsample for AAS), g;  $L_{quant}$  is volume of the sample in the Quantulus measurement, g;  $Sr$  is chemical yield of Sr in the analyses;  $V$  is weight or volume of the original sample, L or kg; and  $E(Sr + Y)$  is effectivity, cpm/dpm, taken from the calibration curve.

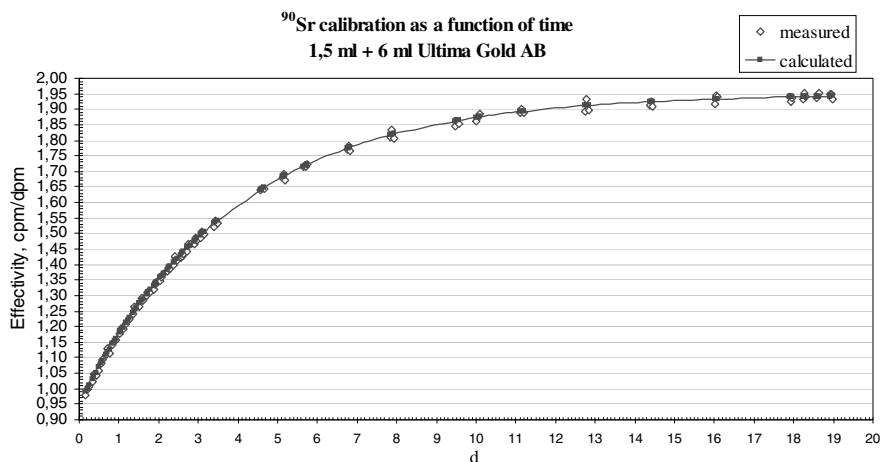


Figure 3  $^{90}\text{Sr}$  calibration as a function of time since Sr-Y separation. The time (in days [d]) from Sr-Y separation to the midpoint of each measurement is indicated on the x axis and the corresponding effectivity (cpm/dpm) is on the y axis.

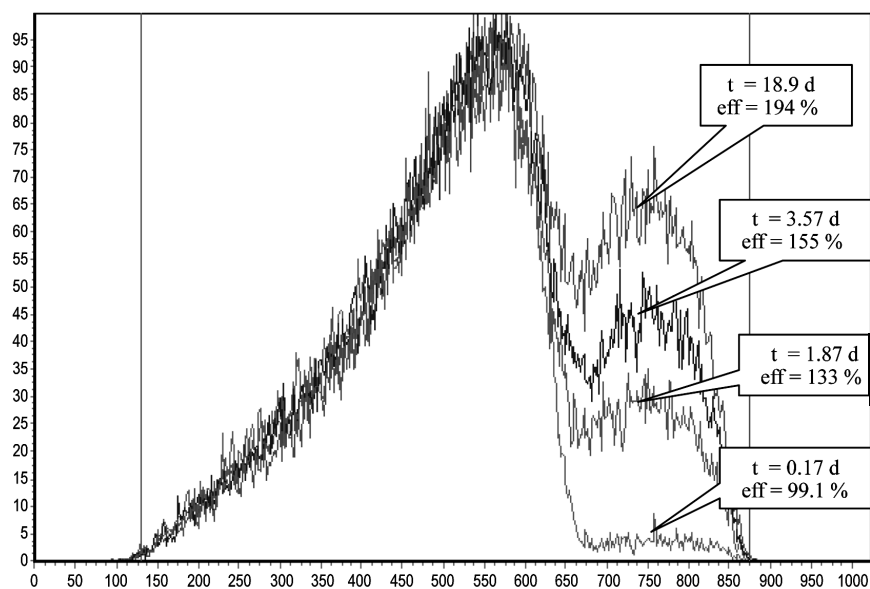


Figure 4 Spectra of  $^{90}\text{Sr}$  and ingrowing  $^{90}\text{Y}$  at various time points after Sr-Y separation. The times from separation to the midpoint of the measurement and the corresponding effectivity values are given for each measurement.

We tested the repeated use of the same resin for several samples by analyzing aliquots of one and the same surface water sample using the same resin. Our experience is that the same resin can be used at least 10 times without a marked decrease in the chemical yield of Sr or other disturbances. After using the resin 15 times, the chemical recovery decreased by  $\sim 10\%$ . Multiple use of the resin decreases the cost of the method significantly.

To check the accuracy and reliability of the method, we participated in various intercomparisons using the method described. The latest intercomparison involving water samples in which we participated was an intercalibration program, Environmental Radioactivity 2003, organized by the National Physical Laboratory (NPL; United Kingdom). The result for  $^{90}\text{Sr}$  obtained by STUK was  $11.9 \pm 0.6 \text{ Bq/kg}$ , and the value reported for the sample by the organizer was  $11.942 \text{ Bq/kg}$  with an uncertainty of  $0.035 \text{ Bq/kg}$ .

## RESULTS

The activity concentrations of  $^{90}\text{Sr}$  in lake water samples varied from 5 to  $23 \text{ Bq/m}^3$ . The total uncertainty of the determinations ( $2\sigma$ ) was  $+(8\text{--}10)\%$ , depending on the total net count rate of the sample. The activity concentrations decreased by 16–28% over 4 yr (1998–2002), but in 1 lake by only 6% (Figure 5). As a comparison,  $^{90}\text{Sr}$  in the waters of the Techa (upper parts and mouth)–Iset–Toboll–Irtyshev river system varied from 30 to  $12,000 \text{ Bq/m}^3$  (Kryshev and Kryshev 2005).

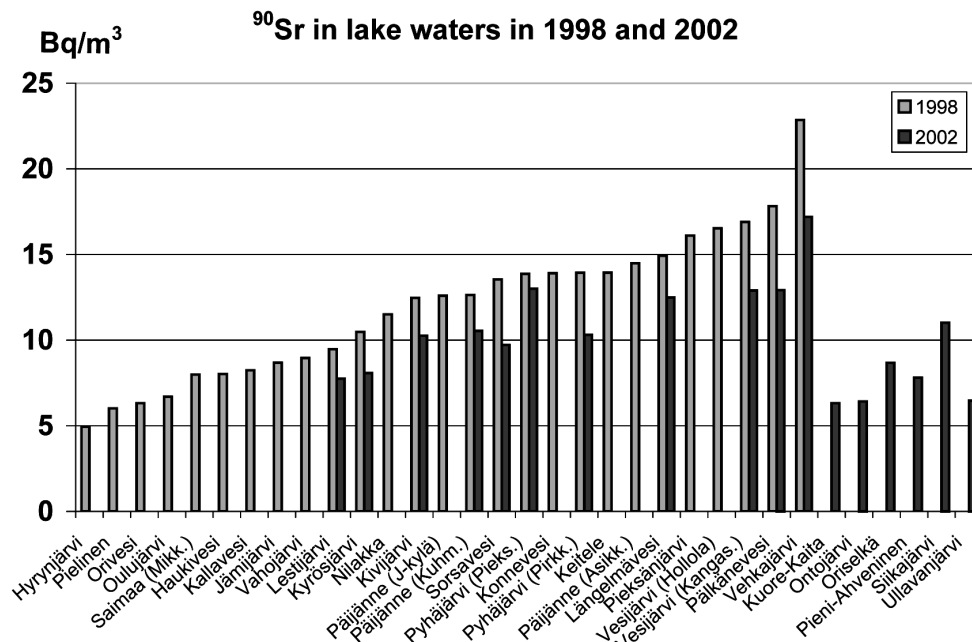


Figure 5  $^{90}\text{Sr}$  in water of various lakes ( $\text{Bq/m}^3$ ) in 1998 and/or 2002. Locations of the lakes are given in Figure 1.

The logarithm-transformed data were close to the normal distribution (Figure 6). The average activity concentration of  $^{90}\text{Sr}$  in lake waters was  $10.7 \text{ Bq/m}^3$  and the standard deviation  $1.4 \text{ Bq/m}^3$  in 1998. If the lake waters studied were used as drinking water, radiation doses via  $^{90}\text{Sr}$  would have been around  $0.1\text{--}0.2 \mu\text{Sv}$  in 1998 and even lower thereafter. Variation in  $^{137}\text{Cs}$  in the water of these lakes was much greater than that of  $^{90}\text{Sr}$ . The contribution of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  to the internal radiation dose via drinking water would be only a few  $\mu\text{Sv/yr}$ , even in the case of the highest water activity concentrations of these radionuclides (Saxén 2005).

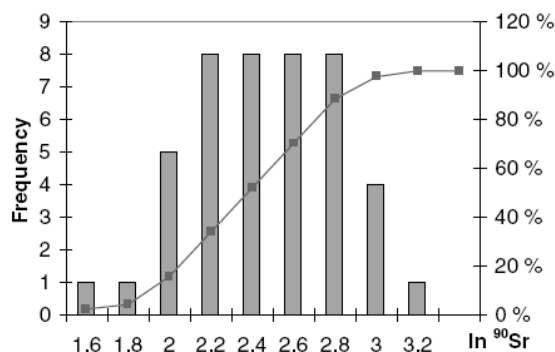


Figure 6 Frequency distribution of ln-transformed activity concentrations of  $^{90}\text{Sr}$  in lake water. The average was  $10.7 \text{ Bq/m}^3$  and the standard deviation was  $1.4 \text{ Bq/m}^3$ .

## ACKNOWLEDGMENTS

Special thanks are due to Ms Ulla Yli-Arvo and Ms Ulla-Maija Hanste, who carried out the  $^{90}\text{Sr}$  analyses of the samples and the calibration measurements.

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