

Rapid determination of strontium-89 and strontium-90 in food and environmental samples by Cerenkov counting.

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SUMMARY

The method has been developed for emergency situations. Minimum detectable concentrations of 5 Bq/liter, kilogram of strontium-89 and strontium-90 respectively is achievable in the presence of nuclides considered to be released under accidental conditions. Result on the strontium-89 and strontium-90 content in a sample can be obtained within 12 hours. One technician can easily handle 8-10 samples during a working day of eight hours.

The determination of the strontium isotopes is accomplished by monitoring the Cerenkov radiation from strontium-89 and yttrium-90 in a liquid scintillation counter. The later is the daughter product of strontium-90. Prior to the Cerenkov counting the sample is separated from interfering nuclides by oxalate precipitation, chromate precipitation and HDEHP-extraction.

The method has to be further improved and evaluated with respect to different soil types such as forest mineral soil layers, agricultural soils and pastures. Furthermore, the decontamination procedure should be evaluated for a sample containing freshly irradiated uranium.

OUTLINE OF THE METHOD

Sample quantity

The sampling, the transportation and the sample preparation (drying and ashing) is, for the most part, the time limiting step in the procedure. Small sample quantities are therefore preferable. In order to meet the requirements of the detection limit the following sample quantities are recommended ; milk and water 100 ml; other food, vegetation and soil 100 gram fresh weight.

Sample preparation

All samples are prepared in the presence of a carrier solution containing strontium, yttrium and barium.

Samples of milk, vegetation and other foods are dried and ashed before decontamination of interfering nuclides. The ashes are dissolved in dilute hydrochloric acid.

Radionuclides in the soil are extracted by diluted hydrochloric acid were after the extract has to be decontaminated from interfering nuclides.

Concerning water no sample preparation is needed before the decontamination procedure.

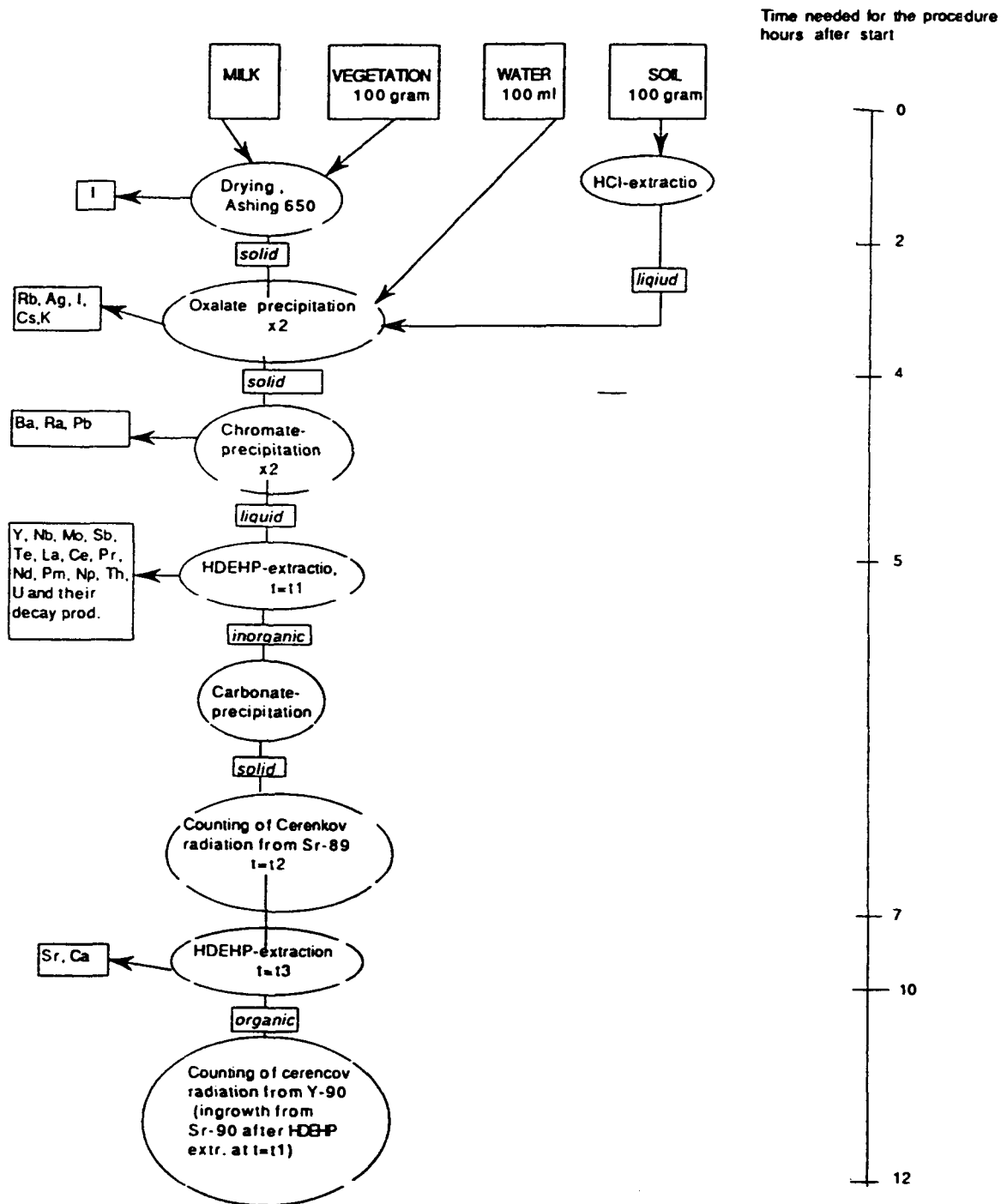
Decontamination of interfering nuclides

Nuclides decaying with high beta energies are considered to cause Cerenkov radiation and with that interfere in the determination of the strontium isotopes (Table 1). These nuclides have to be separated from the matrix before Cerenkov counting of strontium-89 and yttrium-90, the daughter nuclide of strontium-90 (Figure 1).

Table 1. Nuclides considered to be present in the sample matrix after an accidental release of radioactive material.			
NUCLIDES	HALFLIVES	VALENCE	SEPARATED BY
Rb-86	• 18.7d	+1	oxalate precipitation
Sr-89	• 52d	+2	
Y-90	• 64h	+3	HDEHP-extraction
Sr-90	28.7y		
Y-91	• 59d	+3	HDEHP-extraction
Nb-95	35d		
Zr-95	65d		
Nb-96	23h	+3, +5	HDEHP-extraction
Mo-99	• 66.7h	+6	HDEHP-extraction
Ru-103	40d		
Ru-106	1.02y		
Rh-105	35.9h		
Ag-111	• 7.5d	+1	oxalate precipitation
Pd-112	21h		
Cd-115	• 53.5d	+2	?
Cd-115m	• 43d	+2	
Sn-121	27h		
Sn-123	• 42m		?
Sb-124	• 60d	+3,+5	HDEHP-extraction
Sb-125	2.76y		
Sn-125	• 9.4d	+2, +4	?
Sb-127	• 93h	+3, +5	HDEHP-extraction
I-131	(*) 8.7d	+1,+5,+7.	ashing, oxalate precipitation
Te-131m	(*) 30h	+4,+6,-2.	HDEHP-extraction
Te-132	78h		
I-133	• 21h	+1,+5,+7.	ashing, oxalate precipitation
Cs-134	• 2.1y	+1	oxalate precipitation
Cs-136	13d		
Cs-137	• 30y	+1	oxalate precipitation
Ba-140	• 12.8d	+2	chromate precipitation
La-140	• 40h	+3	HDEHP-extraction
Ce-141	33d		
Ce-143	• 33h	+3,+4	HDEHP-extraction
Ce-144	0.8y		
Pr-143	• 13.7d	+3	HDEHP-extraction
Nd-147	• 11.1d	+3	HDEHP-extraction
Pm-147	2.5y		
Pm-149	• 53.1h	+3	HDEHP-extraction
Pm-151	• 28h	+3	HDEHP-extraction
Sm-153	• 46.8h	+2,+3	
Np-239	(*) 2.35d	+3,+4,+5,+6	HDEHP-extraction
Tb-160	73d		
Actinides			
Th,U decay prc*			chromate precipitation, HDEHP-extraction

* nuclide is expected to give Cerenkov radiation

Figure 1. Decontamination of interfering nuclides for determination of Sr-89 and Sr-90 in food and environmental samples



Strontium and other multivalent ions (e.g. barium, yttrium, cerium) are concentrated by precipitation as oxalates. Monovalent cations (e.g. potassium and cesium) will remain in the solution. (Table 2, Sunderman & Townley 1960).

Table 2. Decontamination of interfering nuclides in a water sample
Mean of four replicates.

	initial activity Bq/sample	remaining initial activity (%) in the sample after	
		oxalate precipitation (x2) mean (sd)	oxalate precipitation (x2)+ chromate precipitation (x2) + HDEHP- extraction (x1) mean (sd)
Cs-137	90	<1 (0)	<1 (0)
Ba-133	40	100 (0)	<1 (0)
Sr-85	35	100 (0)	96 (3)
Y-88	55	88 (2)	<1 (0)
Ce-139	15	78 (5)	<1 (0)

The oxalates are ignited and the residue dissolved in dilute acid.

Ions of Barium, Radium and Lead are separated from strontium by precipitation as chromates.

Tri and tetra valent ions such as yttrium, cerium and lanthanum as well as uranium and thorium and their decay products are separated from strontium by extraction with HDEHP (Di(2-ethyl-hexyl)phosphoric acid) (Table 2). The capacity of HDEHP of separating strontium from tri and tetra valent ions has been demonstrated by Peppard et al 1957.

After separation the inorganic phase will contain isotopes of strontium (strontium-89 and strontium-90) and yttrium-90 growing in from strontium-90. The inorganic phase is considered to be decontaminated from any substantial amounts of interfering nuclides.

The amount of strontium-89 is determined by monitoring the Cerenkov radiation in a liquid scintillation counter. If large amounts of strontium-90 compared to strontium-89 are present in the sample, the ingrowth of yttrium-90 has to be taken into consideration in calculating the amount strontium-89 based on the Cerenkov counting (Figure 2).

Strontium-90 is determined by Cerenkov counting of yttrium-90. Yttrium-90 is the decay product of strontium-90 and has been growing into the sample since the first HDEHP-extraction ($t=t_1$ in Figure 1). After a sufficient time of ingrowth, about 5 hours (Figure 3), yttrium-90 is separated from strontium-89 by an additional HDEHP extraction and monitored by Cerenkov counting.

Figure 2. Part of Cerencov counts originating from strontium-89 (%) in relation to the time after separation with HDEHP at $t=t_1$ (Figure 1).

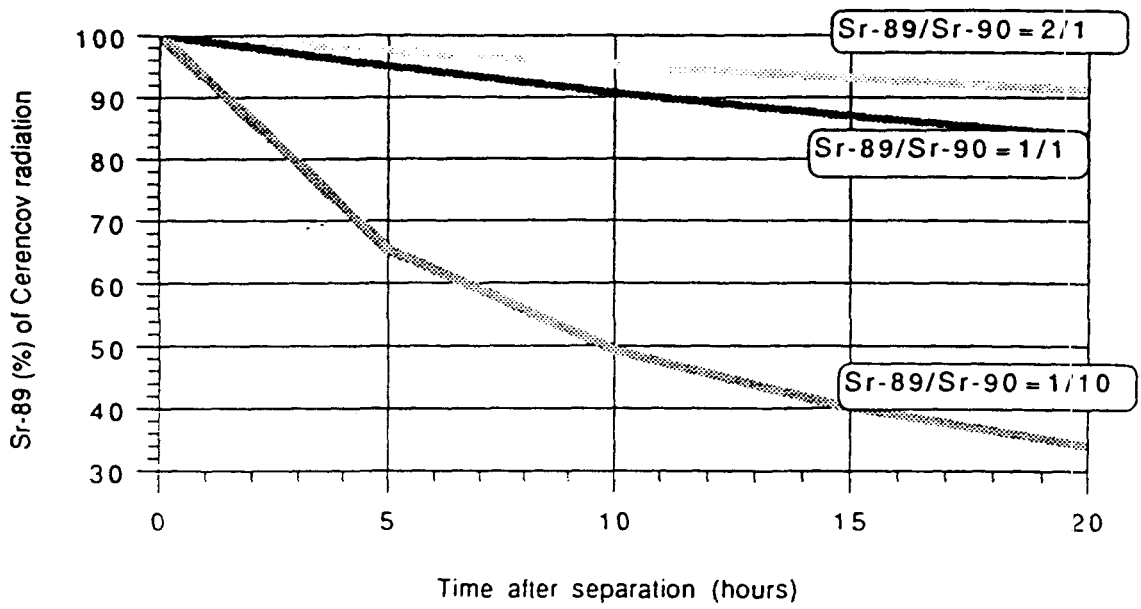
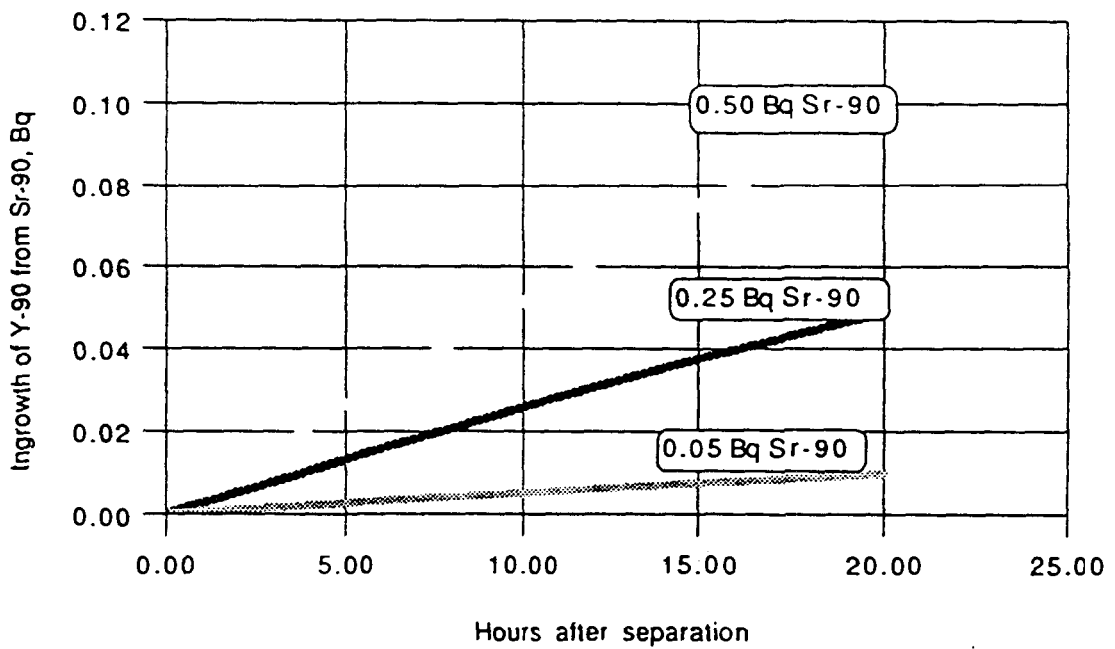


Figure 3. Ingrowth of Y-90 from Sr-90 after separation with HDEHP (Figure 1)



Recovery (yield)

The recovery of strontium or yttrium, for strontium-90 determination, was evaluated in different sample matrixes by using strontium-85 as an internal tracer (Table 2) as well as by titrimetric and gravimetric procedures (Table 3). The recovery of strontium and yttrium varies between 80 and 95% except for acid mineral forest soil layers where the recovery varied between 0-20 %. For emergency situations where an accuracy of ±10%-50% is required an average figure of recovery can probably be used. The determination of recovery can therefore in most occasions be excluded in the routine procedure under emergency conditions. It must however be stressed that the recovery of strontium (yttrium) will vary between the different laboratories and technicians as well as for different sample types. It is therefore necessary to determine an average figure of recovery on each laboratory to be used in the routine procedure of strontium determination. It is also important to evaluate the method for different soil types in order to obtain reliable average figures of recovery.

sample	initial concentration, Bq/liter,kg mean (sd)	recovery, % mean (sd)
milk	0.09(0.03)	0.88(0.02)
water, effluents from nuclear power plants	7.3(22.6)	0.85(0.03)
soil, litter and humus layers of forest soils	62.5(19.7)	0.82(0.05)
soil, acid mineral soil layers of forest soils		0.00-0.28
vegetation, herbs,grass)	36.2(30.4)	0.91(0.2)

CALCULATIONS

Strontium-89

$$\frac{C_{Sr}(t=t_2)}{Eff} = R \times (Sr^{89} + Y^{90})$$

Ekv 1

The contribution of yttrium-90 (Y⁹⁰) to the Cerenkov counting at t=t₂ is caused by the ingrowth from strontium-90 (Sr⁹⁰) after the HDEHP-extraction at t=t₁ (Figure 3). The Cerenkov radiation from yttrium-90 at t=t₂ can in general be disregarded as the Cerenkov counting will be carried out within a couple of hours after the separation step at t=t₁ (Figure 2)) . Furthermore, the proportion between strontium-89 and strontium-90 can be considered to be higher than 1 during the early phase after an accidental release of radioactive material. Ekv 1 can therefore be simplified :

$$S_{r^{89}} = \frac{C_{Sr}(t=t_2)}{Eff \times R}$$

Ekv 2

Strontium-90

$$\frac{\text{Cer}(t=t_3)}{\text{Eff}} = R \times Y^{90}$$

Ekv 3

After separation of yttrium with HDEHP at $t=t_1$ yttrium-90 has been growing into the sample from strontium-90. The amount yttrium-90 in the sample will increase according to:

$$Y^{90} = Sr^{90} \times (1 - e^{-((\ln 2)/T_{1/2}) \times (t_3 - t_1)})$$

Ekv 4

From Ekv 3 and Ekv 4 the amount of strontium-90 in the sample can be calculated according to:

$$Sr^{90} = \frac{\text{Cer}(t=t_3)}{R \times \text{Eff} \times (1 - e^{-((\ln 2)/T_{1/2}) \times (t_3 - t_1)})}$$

Ekv 5

Cer = Cerenkov counts corrected for background, cps

Eff = Counting efficiency, <1

R = Recovery of Sr^{89} and Y^{90}

an average value of R can be used for rapid determination under emergency conditions.

Sr^{89} = Activity of strontium-89 in the sample, Bq/sample

Sr^{90} = Activity of strontium-90 in the sample, Bq/sample

Y^{90} = Activity of yttrium-90 in the sample, Bq/sample

$T_{1/2}$ = halflife for yttrium-90 = 64 hours

$(t=t_1)$ = time at the first HDEHP separation, hours (Figure 1)

$(t=t_2)$ = time at the first Cerenkov counting, hours (Figure 1)

$(t=t_3)$ = time at the second Cerenkov counting, hours (Figure 1)

DETECTION LIMIT

$$DLSR^{89} = \frac{DL}{Sq \times T \times \text{Eff} \times R}$$

Ekv 6

$$DLSR^{90} = \frac{DL}{Sq \times T \times \text{Eff} \times R \times (1 - e^{-((\ln 2)/T_{1/2}) \times (t_3 - t_1)})}$$

Ekv 7

DL = detection limit: $3 \times \sqrt{\text{background}}$, counts

Sq = sample quantity , liter or kg
 DLSR⁸⁹ = Detection limit for Sr⁸⁹, Bq/liter or Bq/kg
 DLSR⁹⁰ = Detection limit for Sr⁹⁰, Bq/liter or Bq/kg
 T = counting time , seconds
 Δt = time for ingrowth of yttrium-90 = t3-t1, hours
 Eff = Counting efficiency, <1
 R = Recovery of Sr⁸⁹ and Y⁹⁰

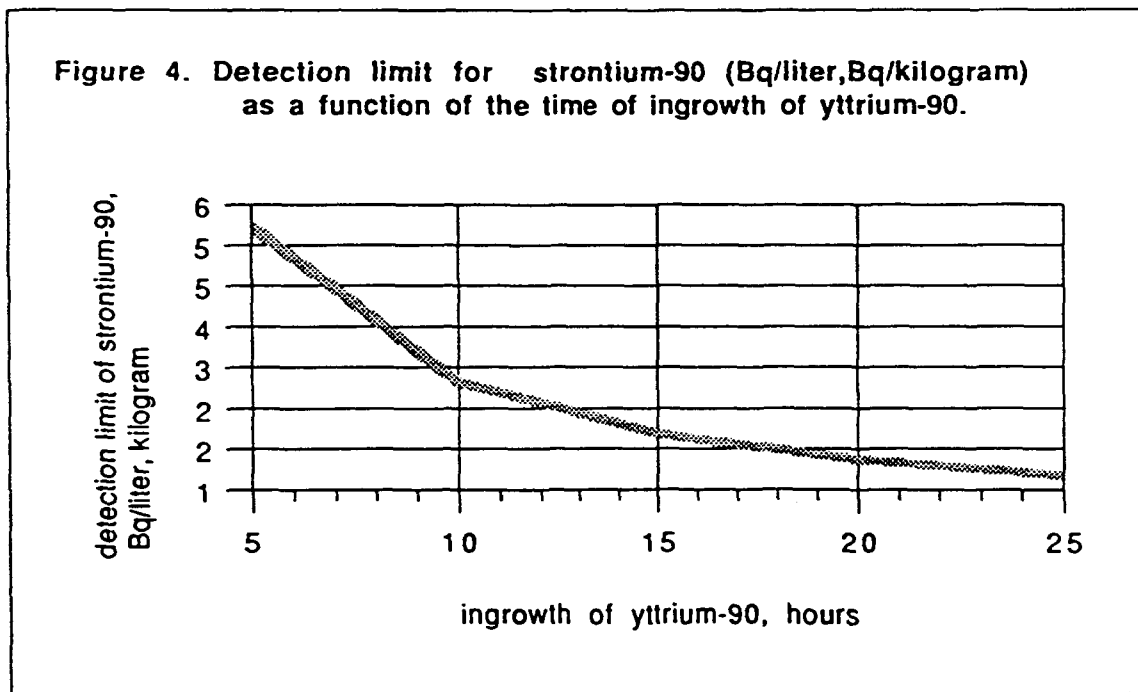
Making the following assumptions:

- Background 5cpm
- Counting time 60 min
- Sample quantity; liquid: 100 ml
solid: 100 gram
- Recovery 0.8
- Counting efficiency 0.6

DLSR⁸⁹ = 0.30 Bq/liter or kilogram

$$DLSR^{90} = \frac{0.30}{(1 - e^{-0.011\Delta t})} \quad \text{Bq/liter or kilogram}$$

In addition to the sample quantity, counting time and prestanda of the instrument (background), the detection limit for strontium-90 will depend on the time during which yttrium-90 is allowed to grow into the sample (Figure 4)., Yttrium-90 should be allowed to grow into the sample for at least five hours in order to meet the requirements of a detection limit of 5 Bq/liter or kilogram at a sample quantity of 100 gram (or 100 ml), a counting time of one hour in a liquid scintillation counter with a background of 5 cpm.



CONCLUSIONS

The method has been shown to be reliable for samples of milk, vegetation, organic soil layers and water. It is however important to further evaluate the method for mineral soils as the method has been shown to give very low and variable values of recovery for this sample matrix.