

## A RAPID METHOD FOR THE DETERMINATION OF STRONTIUM-90 IN POWDERED MILK

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A method in which  $^{90}\text{Y}$  the daughter product of  $^{90}\text{Sr}$  decay is extracted by tributyl phosphate (TBP) from ashed powdered milk is described. The  $^{90}\text{Y}$  which is in equilibrium with  $^{90}\text{Sr}$  is back-extracted into the aqueous phase and coprecipitated with milligram amounts of ferric hydroxide. The proposed procedure makes it possible to obtain thin planar sources convenient for low level gas counters. The overall detection efficiency of 45.5% for  $^{90}\text{Y}$  (including chemical recovery of yttrium) was achieved. The detection limit for 200 g powdered milk samples and 10 000 s counting time was  $0.065 \text{ Bq} \cdot \text{kg}^{-1}$ . The concentration of  $^{90}\text{Sr}$  in three-year old samples (after Chernobyl accident) ranged from  $0.81$  to  $1.31 \text{ Bq} \cdot \text{kg}^{-1}$ .

### Introduction

Strontium radionuclide  $^{90}\text{Sr}$  is one of the main long-lived components of the radioactive fallout which occurred as a result of previous atmospheric nuclear tests and the recent accident at Chernobyl nuclear power station. The deposited  $^{90}\text{Sr}$  is transferred into humans mainly via food in which milk is a substantial contributor, especially for infants.

In most methods for determination of  $^{90}\text{Sr}$  in milk, this radionuclide or its daughter product  $^{90}\text{Y}$  (after 3 weeks storage to settle an equilibrium) are preconcentrated by ion exchange methods.<sup>1–5</sup> Alternative recommended analytical procedures in routine milk analysis using freeze-drying or evaporation of liquid milk, ashing the solid residue and strontium separation by fuming nitric acid are also time consuming.<sup>6,7</sup> Moreover, all these procedures require the further several-step radiochemical purification of  $^{90}\text{Sr}$  before final beta-counting.

The almost selective extraction of yttrium from concentrated nitric acid solutions ( $> 14\text{M}$ ) by TBP is an attractive method for determination of  $^{90}\text{Sr}$  in the sample where  $^{90}\text{Sr}$ – $^{90}\text{Y}$  equilibrium has already been reached.<sup>8–11</sup>

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Apart from several procedures suggested in the literature, as is evident from inter-comparison studies performed by IAEA and US EPA,<sup>12,13</sup> the determination of strontium radionuclides at low-levels still presents analytical problems.

The aim of the present study was the elaboration of a rapid method for determination of  $^{90}\text{Sr}$  in powdered milk using TBP extraction after dissolving the ashed samples in concentrated nitric acid. Amorphous ferric hydroxide, which is known as an efficient collector of yttrium traces,<sup>14</sup> was used for coprecipitation of  $^{90}\text{Y}$  from solution in order to eliminate the expensive yttrium carrier and to prepare the thin ( $< 1 \text{ mg} \cdot \text{cm}^{-2}$ ) radioactive sources.

### Materials and method

#### *Chemicals*

Nitric acid (sp. gr. 1.42 – AnalaR), sodium hydroxide (AnalaR), ferric chloride (Solution 60% w/v-AnalaR) from BDH chemicals Ltd. Tributyl phosphate (purum), sodium oxalate (puriss, p.a.) yttrium nitrate from Fluka. Ready-solve-liquid scintillation cocktail from Beckman. Standard radioactive solution of  $^{90}\text{Sr}$  with  $^{90}\text{Y}$  (SIZ-44) from Amersham. Powdered milk-TATRA (supplied 1986, Czechoslovakia).

#### *Procedure:*

1. 200 g of powdered milk in porcelain crucible is dried for 2 hours at  $110^\circ\text{C}$  and then placed in a muffle furnace at  $180^\circ\text{C}$  for 4 hours followed by final 16 hours ashing at  $485^\circ\text{C}$ .

2. The ash obtained (10–12 g) is transferred to a 250 ml beaker and dissolved by the gradual addition of 75 ml of 14M  $\text{HNO}_3$ . The solution is then evaporated to 50 ml on a hot plate.

3. The solution is transferred to a 250 ml separatory funnel with 50 ml of TBP (previously equilibrated with 14M  $\text{HNO}_3$ ) and shaken for 5 minutes.

4. After separating the phases, the aqueous phase is transferred to a second funnel and extracted once again with 50 ml of equilibrated TBP.

5. The TBP fractions are combined in one separatory funnel and time is recorded for calculating of the  $^{90}\text{Y}$  decay factor.

6. The organic phase is shaken twice with 50 ml of 14M  $\text{HNO}_3$  to remove possible contamination from other radionuclides with lower distribution coefficients between TBP and 14M  $\text{HNO}_3$ . Aqueous phases are discarded.

7. The organic phase is shaken two times with 50 ml of water and third time with 50 ml of 2M  $\text{HNO}_3$  to strip the yttrium from TBP.

8. To the combined aqueous phases 0.02 ml of 60% w/v ferric chloride solution is added and the pH adjusted to 8 by adding NaOH.

9. After cooling, the amorphous ferric hydroxide precipitated during neutralization of the aqueous phase is filtered by suction on a 4 cm Whatman No. 42 filter paper.

10. Precipitate dried at 110 °C in an oven, is mounted on standard metallic dishes and beta counted in a low level gas GM counter.

In one set of experiments this procedure was changed in order to measure  $^{90}\text{Y}$  activity by Cherenkov counting in a commercial liquid scintillation counter. In that case after step 7 the aqueous solution with stripped  $^{90}\text{Y}$  was evaporated to 10 ml and then transferred to a 20 ml plastic scintillation vial for Cherenkov counting.

#### *Radioactivity measurement*

A Panax low-background counting system of  $2\pi$  flow type 50 mm dia GM counter guarded by an anticoincidence plastic counter was used for determination of radioactivity for  $^{90}\text{Y}$  coprecipitated with ferric hydroxide. The detection efficiency for  $^{90}\text{Y}$  was determined using sources prepared from standard  $^{90}\text{Sr}$ – $^{90}\text{Y}$  solution after separation of  $^{90}\text{Y}$  and was equal to 46.9%. A Beckman 3800 type liquid scintillation counter was used for registration of Cherenkov radiation. The detection efficiency for that method was 63% for aqueous solution of  $^{90}\text{Y}$  and 4.6% for  $^{90}\text{Sr}$  solution. The detection efficiency of 0.1 ml standard solution of  $^{90}\text{Sr}$ – $^{90}\text{Y}$  and 10 ml of Ready-solve scintillation cocktail was 98% for both radionuclides.

The  $^{90}\text{Y}$  sources from milk samples were counted for 10000s several times to check the half-life of the separated radionuclide.

#### **Results and discussion**

On the basis of preliminary experiments with milk samples spiked before ashing with  $^{90}\text{Sr}$ – $^{90}\text{Y}$  (without yttrium carrier), it was observed that 97–98% of  $^{90}\text{Y}$  goes from milk samples to aqueous phase. It means that extraction and back-extraction are almost quantitative and because of the strongly acidic medium during all these operations adsorption losses are negligible. The final coprecipitation of  $^{90}\text{Y}$  traces on amorphous ferric hydroxide depends on the amount of precipitate and pH of the solution. Ferric hydroxide starts to precipitate at about pH 4 but the distribution ratio for  $^{90}\text{Y}$  increases for higher pH values.<sup>14</sup> In order to avoid any competitive adsorption losses on the wall, pH 8 was chosen in all experiments. Table 1 presents the recoveries of  $^{90}\text{Y}$  for dif-

Table 1  
Recovery of  $^{90}\text{Y}$  from milk samples for different amounts of precipitated ferric hydroxide;  
activity added: 15.5 dps

Amount of $\text{Fe}(\text{OH})_3$ , mg	1.45	2.90	5.70	11.45	28.00	57.20
Activity, cps	7.10	7.12	6.94	6.90	7.27	6.97
Overall detection efficiency	0.458	0.459	0.448	0.445	0.469	0.450

Average overall detection efficiency  $E = 0.455 \pm 0.008$ .

ferent amounts of precipitated ferric hydroxide from 150 ml aqueous solution after yttrium stripping from the organic phase.

The overall detection efficiency, which includes also chemical recovery of yttrium traces is within the limits of error constant and close to the true detection efficiency for  $^{90}\text{Y}$  equal to 0.469. Therefore, it proves quantitative collection of  $^{90}\text{Y}$  even for 1.5 mg of the precipitate. From practical reasons in routine experiments 11.5 mg  $\text{Fe}(\text{OH})_3$  was precipitated (0.02 ml of  $\text{FeCl}_3$  solution added), giving after filtering thin sources  $0.9 \text{ mg} \cdot \text{cm}^{-2}$  for counting.

Although TBP extraction from 14M  $\text{HNO}_3$  is selective for yttrium, it is known that some lanthanides (e.g. Pm) and Zr, Nb, U and Th radionuclides may also be partially extracted even after washing the organic phase with fresh concentrated  $\text{HNO}_3$ .<sup>15</sup> As a result for some samples, e.g. soil, the activity of separated  $^{90}\text{Y}$  does not decrease according to the 64-hour half-life. In order to overcome the problem of possible contamination by traces of other radionuclides, a second extraction procedure (second milking) of digested samples is proposed after 3 weeks, when a new equilibrium has settled.<sup>11</sup>

Thorium and uranium radionuclides can also be separated from yttrium by stripping the latter from TBP phase using 3M  $\text{HNO}_3$  instead of pure water (uranium and thorium remain in the organic phase).<sup>9</sup> In the proposed method the concentration of  $\text{HNO}_3$  in the water phases after consecutive washings of TBP (saturated with 14M  $\text{HNO}_3$ ) was 5.7, 2.6 and 1.2M, respectively. Therefore, to avoid back-extraction of U and Th, a third washing with 2M  $\text{HNO}_3$  instead of pure water is proposed.

Two fission products:  $^{95}\text{Zr}$  and  $^{95}\text{Nb}$  cannot be separated from yttrium by this method. However, their transfer coefficients  $F_m$  from feed to milk are three or four orders lower of that for strontium:  $5.5 \cdot 10^{-6}$  for  $^{95}\text{Zr}$  and  $4.8 \cdot 10^{-7}$  for Nb,<sup>16</sup> whereas  $1.3 \cdot 10^{-3} \text{ d} \cdot \text{l}^{-1}$  for Sr.<sup>17</sup> Therefore, their presence in milk is possible in ultratrace amounts and only shortly after accidental release of the remarkable amounts of fission products into the environment.

In order to confirm the purity of the separated  $^{90}\text{Y}$  radionuclide, the half-life was

determined for all samples over a period equal to at least 10 days and it was always close to the accepted value of 64 hours.

Moreover, two consecutive milkings of the digested milk ashes (after 3 weeks each) gave values of  $^{90}\text{Sr}$  content of 0.81 and 0.80  $\text{Bq} \cdot \text{kg}^{-1}$ , almost the same as the initial 0.84  $\text{Bq} \cdot \text{kg}^{-1}$ . It also confirms radiochemical purity of the  $^{90}\text{Y}$  sources obtained.

The proposed method was compared with the EML recommended method (E-Sr-05-01) and Cherenkov counting of the stripped  $^{90}\text{Y}$  from the TBP phase. The detection limits calculated according to Currie's formula<sup>18</sup> for 10000s counting time were: 0.065  $\text{Bq} \cdot \text{kg}^{-1}$  for this method, 0.070  $\text{Bq} \cdot \text{kg}^{-1}$  for EML procedure and 0.13  $\text{Bq} \cdot \text{kg}^{-1}$  for Cherenkov counting.

The detection limit obtained for the method elaborated is sufficient for  $^{90}\text{Sr}$  monitoring in commercially distributed powdered milk. The data for  $^{90}\text{Sr}$  levels in two batches of the TATRA milk are presented in the Table 2.

Table 2  
Determination of  $^{90}\text{Sr}$  in two different portions  
of TATRA milk

Sample No.	Activity, $\text{Bq} \cdot \text{kg}^{-1}$	Average activity $\text{Bq} \cdot \text{kg}^{-1}$
I-1	1.31	$1.12 \pm 0.18$
I-2	1.10	
I-3	0.96	
II-1	0.81	$0.92 \pm 0.09$
II-2	1.02	
II-3	0.92	

Relatively good reproducibility and its consistence with  $^{90}\text{Sr}$  levels in powdered milk determined for Middle European samples after the Chernobyl accident<sup>19</sup> fully confirms the validity of the method. Moreover, this method may also be applied for liquid milk after its evaporation. The detection limit for this method allows the determination of  $^{90}\text{Sr}$  concentration in 2 l liquid milk samples only. However, in that case for fresh milk samples during a post accidental intervention determination of  $^{90}\text{Sr}$ , the final Cherenkov counting of the separated  $^{90}\text{Y}$  is recommended. The threshold energy for detection of beta-emitters by this method is equal to 0.26 MeV for water solutions and possible traces of the interfering soft beta-emitters such as  $^{95}\text{Zr}$  and  $^{95}\text{Nb}$  would be counted with very low efficiency, below 1%.

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