Procedure for determining the strontium-90 content of milk (tri-butyl phosphate method)

F-Sr-90-MILCH-02

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Procedures manual for monitoring of radioactive substances in the environment and of external radiation
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1 Scope

The analytic procedure specified in the following for determining the Sr-90 content of milk is comparable in sensitivity to that of procedure F-Sr-90-MILCH-01. It is suitable for examining all samples of milk that are to be routinely monitored according to the Precautionary Radiation Protection Act and the Guideline for the Monitoring of Emissions and Immissions of Nuclear Installations. Compared to the approach outlined in procedure F-Sr-90-MILCH-01, it has the advantage of being much less demanding as to effort and time. One person should be able to conduct simultaneously a minimum of six Sr-90 analyses within 1,5 days. A precondition for applying the procedure is that Sr-90 and its daughter nuclide Y-90 in the ash to be analysed are in radioactive equilibrium. This will usually be ensured by the time elapsing between sampling, preparing the samples and the ashing process or can be ensured by inserting a waiting period of a few days if necessary.

2 Sampling

The sampling process is described in detail in procedure F-γ-SPEKT-MILCH-01.

3 Analysis

3.1 Principle of the procedure

The Y-90 is extracted from the ash dissolved in concentrated nitric acid with n-tri-butyl phosphate that has been saturated with HNO_3. The Y-90 content is then measured with an anti-coincidence beta detector following an interim precipitation as hydroxide and its transformation into oxalate. The yttrium yield is determined by complexometric means.

3.2 Sample preparation

Preparing the samples, including producing milk ash, is described in procedure F-γ-SPEKT-MILCH-01.

3.3 Radiochemical separation

3.3.1 15 g of milk ash are weighed into a 400 ml-glass beaker to which are added by pipette the following aqueous carrier and hold-back carrier solutions, respectively:

5 ml of yttrium solution (= 10 mg of Y^{3+})

1 ml of barium solution (= 1 mg of Ba^{2+})

1 ml of strontium solution (= 1 mg of Sr^{2+})

1 ml of caesium solution (= 1 mg of Cs^{+})

1 ml of lanthanum solution (= 1 mg of La^{3+})

The respective nitrate salts of the elements in diluted nitric acid (1 mol·l^{-1}) are used to prepare these solutions. The yttrium solution must be prepared and pipetted precisely because it is used in the yttrium yield determination.

3.3.2 The milk ash is boiled with 300 ml of concentrated nitric acid (65 %) (14 mol·l^{-1}) and boiled until nitrous gasses cease to emanate (10 minutes to 15 minutes). The solution is allowed to cool to room temperature and filtered through a pleated filter of 150 mm in diameter (e. g., SS No. 595½) into a 500 ml-separation funnel (slim shape). The filter is washed with a small amount of concentrated nitric acid (14 mol·l^{-1}).

3.3.3 The nitric acid solution of the ash is shaken three times with 20 ml of tri-butyl phosphate that has been previously saturated with concentrated nitric acid (14 mol·l^{-1}) by shaking for 1 minute with a fresh portion of this acid. The point of time when extraction commences is to be recorded. Thereafter, the tri-butyl phosphate extracts collected in the first separation funnel are washed by shaking for 0,5 minutes with each of 5 fresh portions of 20 ml of concentrated nitric acid (14 mol·l^{-1}).

3.3.4 The purified tri-butyl phosphate extract is split in two halves in two 250 ml-centrifuge beakers (use graduated centrifuge beakers). To each centrifuge beaker are then added 60 ml of ethanol (denatured), *immediately* followed by 40 ml of concentrated ammonium hydroxide solution (13 mol·l^{-1}) under vigorous stirring. It is recommendable to add the concentrated ammoniac solution rapidly in one dash. Thereafter the solution is warmed in a water bath for a *maximum* of 10 minutes until the yttrium hydroxide flocculates. As the precipitate is difficult to recognize, it is advisable to observe the solution for several minutes until a proper flocculation is visible. Warming in a water bath for periods exceeding 10 minutes are to be avoided, as the precipitate will easily form a colloidal dispersion again.

Warning
The ethanol addition must be followed instantly by the addition of the ammonium hydroxide solution. Failing to add ammonium hydroxide may cause the residual nitric acid in the tributyl phosphate to react explosively with the ethanol within a very short period of time, especially when warmed in a water bath! Furthermore, waste products containing nitric acid (e. g., those obtained in step 3.3.3) must not be collected in the same waste container as those containing ethanol (e.g., from step 3.3.5) as this creates a risk of serious accidents from explosions!
The analysis becomes much less dangerous at this stage, if the same amount of methanol is used instead of ethanol. However, the flocculation of the yttrium hydroxide will then be even more difficult to recognize. It takes some experience to discern the flocculation.

3.3.5 The yttrium hydroxide precipitate is separated by centrifuging. After decanting the supernatant solution, the yttrium hydroxide is dissolved with 25 drops of diluted nitric acid (6 mol·l^{-1}) in each centrifuge beaker and precipitated as yttrium oxalate by adding 10 ml of 2 % oxalic acid (0,16 mol·l^{-1}). By warming it briefly in a water bath, the oxalate precipitate is transformed into a coarser, readily filtered form.

3.3.6 The yttrium oxalate from the two centrifuge beakers is filtered under suction through a blue-band filter (Hahn's suction apparatus) and washed with methanol.

3.3.7 The filter with the precipitate is immediately laminated between two lengths of sticky tape (e. g., Sellotape) and fixed in a central position to a circular disk made of V4A-steel. This counting source can now be measured with a beta anti-coincidence counter of low background count rate (< 0,008 s^{-1}).

3.3.8 To determine the yttrium yield, the filter with the yttrium oxalate precipitate is cut out of the sticky tape after measuring has been completed and placed in a 250 ml-titration flask (with the upper layer of sticky tape attached). 20 ml of EDTA solution (0,01 mol·l^{-1}) are added and the flask is placed in a water bath (90 ºC) until the precipitate has completely dissolved. Then, 20 ml of borate buffer (pH 8,4) and a spatula's tip worth of the indicator mix Eriochrome-black T and sodium chloride (1 + 99) are added. The solution has to show a pure blue colouration. The surplus EDTA is determined by titrating with zinc sulphate solution (0,01 mol·l^{-1}) (colour change from green to red).

Calculating the yttrium yield:

20 ml	EDTA solution (0,01 mol·l^{-1})
- a ml	consumption of $ZnSO_4$ solution (0,01 mol·l^{-1})
x ml	consumption of EDTA solution (0,01 mol·l^{-1})

The consumption *b* of EDTA solution corresponding to 100 % of the yield, will be known from determining the yttrium content of the carrier solution with a similar titration procedure.

$$\eta_Y = \frac{\text{x ml consumption of EDTA} \cdot 100}{\text{b ml consumption for the yttrium standard}} \ \%$$

The yttrium yield obtainable ranges between 85 % and 95 %.

4 Measuring the activity

The Y-90 activity is quantified with a low-level beta anti-coincidence counter with a background count rate of < 0,008 s^{-1} for at least $1{,}2 \cdot 10^4$ s (200 minutes). The actual measuring period depends on the activity of the sample. The equipment is calibrated with a Y-90 standard of known activity that has been precipitated with the same amount of carrier as the sample that is to be measured. The background effect and count rate of the equipment have to be monitored all the time. For verifying the count rate, a Sr-90/Y-90 standard in radioactive equilibrium will be suitable.

5 Calculation of the results

The following symbols are used in the equations of sections 5 and 6:

c	Sr-90 activity concentration, in Bq·l^{-1};
R_g	gross count rate, in s^{-1};
R_0	background count rate, in s^{-1};
R_n	net count rate of the Y-90 counting source, in s^{-1};
t_0	duration of the background measurement, in s;
t_m	duration of the counting source measurement, in s;
t_A	period of time between sampling and start of analysis, in s;

t_Y period of time between the separation of the yttrium and start of analysis, in s;

φ_A activity-related calibration factor, in Bq·s;

$k_{1-\alpha}$ quantile of the normal distribution (type I error);

$k_{1-\beta}$ quantile of the normal distribution (type II error);

ρ_M proportion of milk ash, in g·l^{-1};

η_{Sr} chemical yield of strontium;

η_Y chemical yield of yttrium;

m_A mass of ash, in g;

$f(t_A)$ decay factor for the period between sampling and start of the analysis: $f(t_A) = e^{\lambda_{Sr-90} \cdot t_A}$;

$f(t_Y)$ decay factor for the period between the separation of the yttrium and start of the measuring process: $f(t_Y) = e^{\lambda_{Y-90} \cdot t_Y}$;

$f(t_m)$ factor for the decay of the Y-90 during the measuring period:

$$f(t_m) = \frac{\lambda_{Y-90} \cdot t_m}{1 - e^{-\lambda_{Y-90} \cdot t_m}};$$

λ_{Sr-90} decay constant of Sr-90, in s^{-1}: $\lambda_{Sr-90} = \ln 2 / t_{Sr-90}$;

t_{Sr-90} half-life of Sr-90, in s;

λ_{Y-90} decay constant of Y-90, in s^{-1}: $\lambda_{Y-90} = \ln 2 / t_{Y-90}$;

t_{Y-90} half-life of Y-90, in s.

$f(t_A)$ takes into consideration the decay of Sr-90 during the period between sampling and start of the analysis. $f(t_Y)$ is used to correct the decay of Y-90 between the separation of the yttrium and the start of the measuring process. This correction is not required if the interval is not too long (t_Y < 1 hour). $f(t_m)$ accounts for the decay of Y-90 during the measuring period.

s_n standard deviation of the net count rate R_n, in s^{-1};

s_g standard deviation of the gross count rate R_g, in s^{-1};

s_0 standard deviation of the background effect count rate R_0, in s^{-1};

s_c standard deviation of the activity concentration c at time of sampling, in Bq·l^{-1};

G detection limit of the activity A, in Bq;

$G(t_A)$ detection limit of the activity A at time of sampling, in Bq;

$g_c(t_A)$ detection limit of the activity concentration c at time of sampling, in Bq·l^{-1}.

The calculation assumes that Sr-90 and Y-90 in the milk ash are in radioactive equilibrium. The Sr-90 activity in Bq per litre of milk is then calculated with the following formula:

$$c = \frac{f(t_A) \cdot f(t_Y) \cdot f(t_m) \cdot \varphi_A \cdot \rho_M \cdot R_n}{\eta_Y \cdot m_A}$$

The statistical counting uncertainty, s_n, of the net count rate, R_n, is:

$$s_n = \sqrt{s_g^2 + s_0^2}$$

and the standard deviation, s_c, of the activity concentration, c, at time of sampling is obtained from:

$$s_c = \frac{f(t_A) \cdot f(t_Y) \cdot f(t_m) \cdot \varphi_A \cdot \rho_M \cdot s_n}{\eta_Y \cdot m_A}$$

Results are reported as the activity concentration, c, of the sample and the standard deviation, s_c, both at time of sampling, in $Bq \cdot l^{-1}$ ($c \pm s_c$).

5.1 Worked example

R_g	$= 7{,}69 \cdot 10^{-2}\ s^{-1}$;	ρ_M	$= 8{,}0\ g \cdot l^{-1}$;
R_0	$= 0{,}68 \cdot 10^{-2}\ s^{-1}$;	η_Y	$= 0{,}900$;
R_n	$= 7{,}01 \cdot 10^{-2}\ s^{-1}$;	m_A	$= 15{,}0$ g;
t_m	$= 7{,}8 \cdot 10^4$ s;	$f(t_A)$	$= 1{,}000$;
t_0	$= 5{,}76 \cdot 10^4$ s;	$f(t_m)$	$= 1{,}022$;
t_A	= 0 (negligible) ;	$f(t_Y)$	$= 1{,}033$;
t_Y	$= 1{,}08 \cdot 10^4$ s;	φ_A	$= 2{,}062\ Bq \cdot s$.

$$c = \frac{1{,}000 \cdot 1{,}033 \cdot 1{,}122 \cdot 2{,}062 \cdot 8{,}0 \cdot 7{,}01 \cdot 10^{-2}}{0{,}900 \cdot 15{,}0}\ Bq \cdot l^{-1} =$$

$$= 99{,}0 \cdot 10^{-3}\ Bq \cdot l^{-1} = 99{,}0\ mBq \cdot l^{-1}$$

$$s_g = \sqrt{R_g / t_m} = \sqrt{7{,}69 \cdot 10^{-2} / 7{,}8 \cdot 10^4}\ s^{-1} = 1{,}0 \cdot 10^{-3}\ s^{-1}$$

$$s_0 = \sqrt{R_0 / t_0} = \sqrt{0{,}68 \cdot 10^{-2} / 5{,}76 \cdot 10^4}\ s^{-1} = 3{,}4 \cdot 10^{-4}\ s^{-1}$$

$$s_n = \sqrt{\left(1{,}0 \cdot 10^{-3}\right)^2 + \left(3{,}4 \cdot 10^{-4}\right)^2}\ s^{-1} = 1{,}1 \cdot 10^{-3}\ s^{-1}$$

$$s_c = \frac{1{,}000 \cdot 1{,}033 \cdot 1{,}122 \cdot 2{,}062 \cdot 8{,}0 \cdot 1{,}1 \cdot 10^{-3}}{0{,}900 \cdot 15{,}0}\ Bq \cdot l^{-1} =$$

$$= 1{,}6 \cdot 10^{-3}\ Bq \cdot l^{-1} = 1{,}6\ mBq \cdot l^{-1}$$

Thus, the Sr-90 content of the sample of milk at time of sampling in this example is:

$$c = (99{,}0 \pm 1{,}6)\ mBq \cdot l^{-1}$$

5.2 Consideration of uncertainties

The above example took into consideration only the statistical counting uncertainties incurred during measuring the activity, but not uncertainties in the chemical separation and yield determination processes. As numerous round robin test and experiences with comparative analyses have shown, the total uncertainty of this method ranges from 5 % to 10 % for activities between 30 mBq per litre and 100 mBq per litre of milk and measuring periods of several hundreds of minutes.

6 Characteristic limits of the procedure

The formula applicable here for calculating the detection limit is described as equation (2.4) in chapter IV.5, section 2.1.2 of this procedures manual. This formula still needs to be completed by adding three correctional functions to obtain the detection limit, $G(t_A)$, at time of sampling:

$$G(t_A) = f(t_A) \cdot f(t_Y) \cdot f(t_m) \cdot G$$

To calculate the detection limit of the activity concentration, $G(t_A)$ must be divided by the chemical yield of yttrium, η_Y, and the mass of ash, m_A, and multiplied with the proportion of ash per litre of milk, ρ_M:

$$g(t_A) = \frac{f(t_A) \cdot f(t_Y) \cdot f(t_m) \cdot G \cdot \rho_M}{\eta_Y \cdot m_A}$$

6.1 Worked example

R_0	= 4,2·10^{-3} s^{-1};	η_Y	= 0,900;
t_0	= 5,76·10^4 s;	m_A	= 15,0 g;
t_m	= 2,16·10^4 s;	$f(t_A)$	= 1,000;
t_A	= 0 (negligible);	$f(t_m)$	= 1,033;
t_Y	= 0 (negligible);	$f(t_Y)$	= 1,000;
φ_A	= 2,109 Bq·s;	ρ_M	= 8,0 g·l^{-1}.

$$G = 2{,}109 \cdot \left[4{,}645 \cdot \sqrt{4{,}2 \cdot 10^{-3} \cdot \left(\frac{1}{5{,}76 \cdot 10^4} + \frac{1}{2{,}16 \cdot 10^4} \right)} + 0{,}25 \cdot 4{,}645^2 \cdot \left(\frac{1}{5{,}76 \cdot 10^4} + \frac{1}{2{,}16 \cdot 10^4} \right) \right] \text{Bq} =$$

$$= 5{,}79 \cdot 10^{-3} \text{ Bq}$$

$$g(t_A) = \frac{1{,}000 \cdot 1{,}033 \cdot 1{,}000 \cdot 5{,}79 \cdot 10^{-3} \cdot 8{,}0}{0{,}90 \cdot 15{,}0} \text{ Bq} \cdot \text{l}^{-1} = 3{,}5 \cdot 10^{-3} \text{ Bq} \cdot \text{l}^{-1}$$

The detection limit of the method is about 3,5 mBq per litre of milk when 15 g of ash and a measuring period of 2,16·10^4 s (6 hours) are used.

7 Catalogue of chemicals and equipment

7.1 Chemicals

— Concentrated nitric acid 65 % by weight (14 $mol \cdot l^{-1}$);
— Dilute nitric acid (6 $mol \cdot l^{-1}$);
— Oxalic acid 2 % aqueous solution (0,16 $mol \cdot l^{-1}$);
— Concentrated ammonium hydroxide solution 25 % by weight (13 $mol \cdot l^{-1}$);
— n-tri-butyl phosphate;
— Ethanol (denatured);
— Yttrium aqueous carrier solution, 2 mg of Y^{3+} per ml;
— Barium carrier solution, 1 mg of Ba^{2+} per ml;
— Strontium carrier solution, 1 mg of Sr^{2+} per ml;
— Caesium carrier solution, 1 mg of Cs^{+} per ml;
— Lanthanum carrier solution, 1 mg La^{3+} per ml;

All carrier solutions are the nitrate salts in nitric acid (1 $mol \cdot l^{-1}$).

7.2 Equipment

— Cylinder-drier, alternatively spray-drier, or other equipment fit for desiccating milk;
— Ashing furnace;
— Fused silica dishes;
— Basic equipment of a radiochemical laboratory with glass vessels, centrifuges etc.;
— Beta anti-coincidence measuring station;
— Calculator (preferably programmable).