Procedure for determining the strontium-90 content of milk (nitric acid method)

F-Sr-90-MILCH-01

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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 procedure described in the following is to be applied 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. The method has proven adequate for decades and must therefore be viewed as a reference procedure for subsequent approaches.

2 Sampling

Sampling is described in detail in procedure F-γ-SPEKT-MILCH-01.

3 Analysis

3.1 Principle of the procedure

The milk is ashed, the Sr-90 is separated from the ash, and the activity of the daughter nuclide Y-90 is then measured with an anti-coincidence beta detector.

3.2 Sample preparation

The preparation processes for samples including the production of milk ash is described in procedure F-γ-SPEKT-MILCH-01.

3.3 Radiochemical separation

3.3.1 15 g of ash are weighed into a 400 ml-glass beaker to which are then added 10 ml of strontium carrier solution, 1 ml of barium carrier solution, 5 ml of Sr-85 solution corresponding to 30 Bq, 215 ml of distilled water, and 25 ml of fuming nitric acid (23 $mol \cdot l^{-1}$). The solution is warmed and stirred until it becomes clear and then filtered through an acid-proof filter into a 600 ml-glass beaker. Following the addition of 3 ml of phosphoric acid 85 % (14,8 $mol \cdot l^{-1}$), an excess of concentrated ammonium hydroxide solution (13 $mol \cdot l^{-1}$) is added. The precipitate is centrifuged off in two 200 ml-centrifuge beakers and the supernatant solution discarded. The precipitates in both centrifuge beakers are each suspended in 100 ml of wash solution and centrifuged once more. The wash solution is discarded.

3.3.2 The precipitates in each centrifuge beaker are dissolved by adding 20 ml of fuming nitric acid (23 $mol \cdot l^{-1}$). The volume in each centrifuge beaker is measured. A volume of fuming nitric acid (23 $mol \cdot l^{-1}$) corresponding to 2,5 times this volume minus 40 ml are added. The mix is stirred for 30 minutes in a cooling bath of ice water, then centrifuged, and the supernatant solution is discarded.

3.3.3 Adding 40 ml of distilled water, the contents of one centrifuge beaker are transferred to the second one. 90 ml of fuming nitric acid (23 $mol \cdot l^{-1}$) are added. While cooling in ice water, the solution is continuously stirred for 30 minutes, centrifuged, and the supernatant solution is discarded.

3.3.4 The stirring of the nitric acid with a fresh 90 ml portion of fuming nitric acid (23 mol·l^{-1}) is repeated as described in step 3.3.3.

3.3.5 The precipitate is transferred to a 40-ml centrifuge beaker with 20 ml to 30 ml of distilled water. The solution is made alkaline with concentrated ammonium hydroxide solution (13 mol·l^{-1}), then solid ammonium carbamate is added, and the solution warmed in a bath of boiling water to coagulate the carbonate precipitate. The precipitate is separated by centrifugation and the supernatant liquid is discarded.

3.3.6 The precipitate is dispersed with 10 ml of distilled water and (carefully!) dissolved with 22,5 ml of fuming nitric acid (23 mol·l^{-1}), then stirred for 30 minutes while cooling in an ice bath. After separating the precipitate by centrifuging, the supernatant liquid is discarded.

3.3.7 To complete the calcium/strontium separation, step 3.3.6 might need to be repeated once or twice. In the case of milk ash step 3.3.6. is usually sufficient.

3.3.8 The precipitate is dissolved in 10 ml to 15 ml of distilled water. 1 ml of barium carrier solution as well as a few drops of methyl red are added and neutralised with dilute aqueous ammonium hydroxide (6 mol·l^{-1}). 1 ml of acetic acid (6 mol·l^{-1}) and 2 ml of aqueous ammonium acetate solution (25 % by weight) are added, diluted to 30 ml, and heated in a bath of boiling water. 1 ml of sodium chromate solution (30 % by weight) is added, the mix is thus heated for another 5 minutes, centrifuged, and the supernatant liquid is finally filtered through a black-band filter into a second centrifuge beaker.

3.3.9 The filtrate is made alkaline with concentrated ammonium hydroxide solution (13 mol·l^{-1}), solid ammonium carbamate added, and the mixture is heated in a bath of boiling water to coagulate the carbonate precipitate. The solution is centrifuged and the supernatant solution discarded.

3.3.10 The precipitate is dissolved by dropwise addition of dilute nitric acid (6 mol·l^{-1}), then 1 drop of concentrated hydrogen peroxide and 1 ml of iron carrier solution are added. Oxygen is expelled heating and stirring, the solution is diluted to 15 ml to 20 ml then made alkaline with carbonate-free, aqueous ammonium hydroxide solution (6 mol·l^{-1}) until iron hydroxide is precipitated (record the point of time). It is heated for 2 to 4 minutes until the precipitation has been completed, upon which the supernatant liquid is filtered. The filtrate and the distilled water washings are collected in a 40 ml centrifuge beaker.

3.3.11 After adding solid ammonium carbamate, the solution is heated in a water bath until the precipitate has sedimented. It is left to cool down, centrifuged, and the supernatant solution is decanted. The precipitate is dissolved in 2 ml of diluted hydrochloric acid (2 mol·l^{-1}) and transferred with 20 ml of distilled water (measuring cylinder) to a 100 ml-polyethylene bottle. 1 ml of yttrium carrier solution is added, after which the Sr-85 content is measured with a gamma-spectrometer for determining the strontium yield. For determining the strontium yield, two standards are produced prior to the analysis. 5 ml of the Sr-85 solution are pipetted into a 100 ml-polyethylene bottle along with 10 ml of strontium carrier solution and 10 ml of distilled water. These standards are also measured by gamma spectrometry.

Calculating the strontium yield:

$$\eta_{Sr} = \frac{\text{net pulse rate of the sample} \cdot 100}{\text{net pulse rate of the standard}} \ \%$$

3.3.12 The solution obtained from the separation process is stored for about 14 days to allow the ingrowth of Y-90. Thereafter the solution is transferred to a 40 ml-centrifuge beaker, made alkaline with carbonate-free, aqueous ammonium hydroxide solution (6 mol·l^{-1}), warmed and centrifuged. The supernatant solution is decanted into a 100 ml-polyethylene bottle (and may be used to verify the strontium yield and repeating the yttrium separation if necessary). The point of time of precipitating the yttrium hydroxide is recorded. The precipitate is then once more dissolved in nitric acid (6 mol·l^{-1}), diluted to 10 ml to 15 ml with distilled water, then 5 ml of strontium carrier solution are added. Yttrium hydroxide is again precipitated under warming with a fresh portion of ammonium hydroxide solution (6 mol·l^{-1}), centrifuged, and the supernatant liquid is discarded.

3.3.13 The precipitate is then dissolved in as little nitric acid (6 mol·l^{-1}) as possible und warmed in a bath of boiling water. 20 ml of 8 % aqueous oxalic acid (0,6 mol·l^{-1}) are added. To obtain a granular precipitate, the solution is heated in a water bath for 10 to 15 minutes, filtered under suction through a blue-band filter (Hahn's suction apparatus), and the precipitate washed with methanol.

3.3.14 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.

3.3.15 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 titration flask (with the upper layer of sticky tape still 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 assume a pure blue colouration. The surplus EDTA is titrated with zinc sulphate solution (0,01 mol·l^{-1}) (colour change from green to red).

C*alculating 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 of EDTA corresponding to 100 % of the yield, will be known from determining the yttrium content of the ytrrium carrier solution.

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

4 Measuring the activity

The Y-90 activity is measured 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 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 samples that are to be measured. The background effect and efficiency of the equipment have to be monitored repeatedly at regular intervals.

Counting a Sr-90/Y-90 standard in radioactive equilibrium is adequate for regularly verifying the efficiency.

5 Calculation of the results

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

c Sr-90 activity concentration, in $Bq \cdot l^{-1}$;

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 background measurement, in s;

t_m duration of counting source measurement, in s;

t_A period of time between sampling and commencement of analysis, in s;

t_1 period of time between attaining Sr-90/Y-90 equilibrium (period of time between the precipitation of iron and the renewed separation of yttrium for measuring), in s;

t_2 period of time between the separation of the yttrium and start of the measurement, 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 $g \cdot l^{-1}$;

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:
$f(t_A) = e^{\lambda_{Sr-90} \cdot t_A}$;

$f(t_1)$ function for the equilibrium between Sr-90 and Y-90:

$$f(t_1) = \frac{\lambda_{Y-90} - \lambda_{Sr-90}}{\lambda_{Y-90} \cdot \left(e^{-\lambda_{Sr-90} \cdot t_1} - e^{-\lambda_{Y-90} \cdot t_1} \right)} ;$$

$f(t_2)$ decay factor for the period between the separation of the yttrium and start of the measuring process:
$f(t_2) = e^{\lambda_{Y-90} \cdot t_2}$;

$f(t_m)$ 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. This is only required if the interval is relatively long (t_A > 0,5 years). $f(t_1)$ is used to calculate the degree of establishment of equilibrium between Sr-90 and Y-90 subsequent to the precipitation of iron that separated all Y-90. $f(t_2)$ takes into consideration the decay of Y-90 between the separation of yttrium and the start of the measuring process. This may be omitted if the period between separating the yttrium and measuring is not too long (t_2 < 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 count rate R_0, in s^{-1};

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

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 $Bq \cdot l^{-1}$.

The Sr-90 activity in Bq per litre of milk is then calculated with the following formula:

$$c = \frac{f(t_A) \cdot f(t_1) \cdot f(t_2) \cdot f(t_m) \cdot \varphi_A \cdot \rho_M \cdot R_n}{\eta_{Sr} \cdot \eta_Y \cdot m_A}$$

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

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

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

$$s_c = \frac{f(t_A) \cdot f(t_1) \cdot f(t_2) \cdot f(t_m) \cdot \varphi_A \cdot \rho_M \cdot s_n}{\eta_{Sr} \cdot \eta_Y \cdot m_A}$$

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

5.1 Worked example

R_g	= 7,69·10^{-2} s^{-1};	ρ_M	= 8,0 g·l^{-1};
R_0	= 0,68·10^{-2} s^{-1};	η_{Sr}	= 0,850;
R_n	= 7,01·10^{-2} s^{-1};	η_Y	= 0,980;
t_m	= 7,8·10^4 s;	m_A	= 15,0 g;
t_0	= 5,76·10^4 s;	$f(t_A)$	= 1,000;
t_A	= 0 (negligible) ;	$f(t_1)$	= 1,028;
t_1	= 1,21·10^6 s;	$f(t_2)$	= 1,000;
t_2	= 0 (negligible) ;	$f(t_m)$	= 1,122;
φ_A	= 2,062 Bq·s.		

$$c = \frac{1{,}000 \cdot 1{,}028 \cdot 1{,}000 \cdot 1{,}122 \cdot 2{,}062 \cdot 8{,}0 \cdot 7{,}01 \cdot 10^{-2}}{0{,}850 \cdot 0{,}980 \cdot 15{,}0}\ \text{Bq} \cdot \text{l}^{-1} =$$

$$= 0{,}107\ \text{Bq} \cdot \text{l}^{-1} = 107\ \text{mBq} \cdot \text{l}^{-1}$$

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

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

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

$$s_c = \frac{1{,}000 \cdot 1{,}028 \cdot 1{,}000 \cdot 1{,}122 \cdot 2{,}062 \cdot 8{,}0 \cdot 1{,}1 \cdot 10^{-3}}{0{,}850 \cdot 0{,}980 \cdot 15{,}0}\ \text{Bq} \cdot \text{l}^{-1} =$$

$$= 1{,}7 \cdot 10^{-3}\ \text{Bq} \cdot \text{l}^{-1} = 1{,}7\ \text{mBq} \cdot \text{l}^{-1}$$

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

$$c = (107{,}0 \pm 1{,}7)\ \text{mBq} \cdot \text{l}^{-1}$$

5.2 Consideration of uncertainties

The above example took into consideration only the statistical counting uncertainty incurred during measuring the activity, but not uncertainties in the chemical separation and yield determination processes. As numerous round robin 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, G, 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 four correction functions to obtain the detection limit, $G(t_A)$, at time of sampling:

$$G(t_A) = f(t_A) \cdot f(t_1) \cdot f(t_2) \cdot f(t_m) \cdot G$$

For calculating the detection limit of the activity relative to the volume, $G(t_A)$ needs to be divided by the chemical yields of strontium and yttrium and the weight of ash and multiplied with the proportion of ash per litre of milk:

$$g(t_A) = \frac{f(t_A) \cdot f(t_1) \cdot f(t_2) \cdot f(t_m) \cdot G \cdot \rho_M}{\eta_{Sr} \cdot \eta_Y \cdot m_A}$$

6.1 Worked example

R_0	= 4,2·10^{-3} s^{-1};	η_{Sr}	= 0,850;
t_0	= 5,76·10^4 s;	η_Y	= 0,980;
t_m	= 2,16·10^4 s;	$f(t_A)$	= 1,000;
t_A	= 0 (negligible) ;	$f(t_1)$	= 1,028;
t_1	= 1,21·10^6 s;	$f(t_2)$	= 1,000;
t_2	= 0 (negligible) ;	$f(t_m)$	= 1,033;
φ_A	= 2,109 Bq·s;	$k_{1-\alpha}$	= 3,0;
$k_{1-\beta}$	= 1,645;	ρ_M	= 8,0 g·l^{-1}.

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

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

$$g(t_A) = \frac{1{,}000 \cdot 1{,}028 \cdot 1{,}000 \cdot 1{,}033 \cdot 8{,}0 \cdot 5{,}79 \cdot 10^{-3}}{0{,}850 \cdot 0{,}980 \cdot 15{,}0} \text{ Bq} \cdot \text{l}^{-1} = 3{,}9 \cdot 10^{-3} \text{ Bq} \cdot \text{l}^{-1}$$

The detection limit of the method is about 4 mBq per litre of milk when 15 g of ash and a measuring period of 2,16·10^4 s (360 minutes) are used.

7 Catalogue of chemicals and equipment

7.1 Chemicals

— Fuming nitric acid 95-96 % by weight (23 mol·l^{-1});
— Dilute nitric acid (6 mol·l^{-1});
— Dilute hydrochloric acid (2 mol·l^{-1});
— Dilute acetic acid (6 mol·l^{-1});
— Syrupy phosphoric acid 85 % by weight. (14 mol·l^{-1});
— Aqueous oxalic acid solution 8 % (0,6 mol·l^{-1});
— Carbonate-free aqueous ammonium hydroxide solutions, i.e.,
10 % by weight (6 mol·l^{-1})
25 % by weight (13 mol·l^{-1});
— Wash solution: 3 ml of syrupy phosphoric acid and 30 ml of concentrated ammoniac (13 mol·l^{-1}) per 2 l of distilled water;
— Ammonium carbamate, solid;
— Ammonium acetate, aqueous solution (25 % by weight);
— Sodium chromate, aqueous solution (30 % by weight);
— Strontium carrier, aqueous solution, 5 mg Sr^{2+} per ml;
— Yttrium carrier, aqueous solution, 10 mg Y^{3+} per ml;
— Barium carrier, aqueous solution 10 mg Ba^{2+} per ml;
— Iron carrier, aqueous solution 5 mg Fe^{3+} per ml;
— Methyl-red solution: 0,2 % in ethanol;
— Indicator mix: Eriochrome-black T + NaCl (1 : 99);
— EDTA: 0,01 mol·l^{-1};
— $ZnSO_4$ aqueous solution: 0,01 mol·l^{-1}.

7.2 Equipment

— Spray-drier or cylinder-drier, or other equipment fit for desiccating milk;
— Ashing furnace;
— Quartz dishes;
— Basic equipment of a radiochemical laboratory with glass vessels, centrifuges etc. ;
— beta anti-coincidence counter;
— Calculator (preferably programmable).