Procedure for determining the strontium-90 content of milk (Chelite P/crown ether method)

F-Sr-90-MILCH-03

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1 Scope

The analytic procedure specified in the following for determining the Sr-90 content of milk is about as sensitive as procedures F-Sr-90-MILCH-01 and F-Sr-90-MILCH-02. Like these, 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 approaches outlined in the mentioned procedures, it has the advantage of being even less demanding as to effort and time, as desiccating and ashing of the milk are not applied. Similar to procedure F-Sr-90-MILCH-01 and in contrast to procedure F-Sr-90-MILCH-02, it has the disadvantage of the strontium yield being determined with the aid of Sr-85 and requiring that the Sr-90 concentration be determined by measuring the daughter nuclide Y-90. This incurs a storage period to allow the ingrowth of Y-90 following the separation of strontium.

2 Sampling

The sampling parameters are detailed in procedure F-γ-SPEKT-MILCH-01.

3 Analysis

3.1 Principle of the procedure

Alkaline earths including strontium are adsorbed to a chelate forming resin directly from the liquid milk after the tracer (Sr-85) for the strontium yield determination has been added. The resin is eluted with diluted nitric acid and the strontium isolated by extracting the eluate with crown ether solutions (dicyclohexyl-18-crown-6 in chloroform). Thereafter, the strontium is extracted back into an aqueous phase and precipitated as carbonate. The strontium carbonate is then stored until Sr-90 and the daughter Y-90 attain radioactive equilibrium (at least 15 days). The carbonate is then dissolved and dispersed in a liquid scintillator cocktail. The mixed beta spectrum of Sr-85, Sr-90 and Y-90 is recorded with a liquid-scintillation spectrometer and the net count rate calculated in an energy range that is free of contributions from Sr-85. The Sr-85 added as a tracer for determining the yield is measured by gamma spectrometry of the scintillation cocktail.

3.2 Sample preparation

No particular preparation of samples is required.

3.3   Radiochemical separation

3.3.1   1000 ml of the sample of milk are poured into a 2000 ml-Erlenmeyer flask followed by the addition of 10 Bq to 15 Bq of Sr-85 as a tracer for determining the yield. The temperature of the sample is adjusted in a water bath to 65 °C-70 ºC. Following the addition of 150 g of Chelite P in its Na$^+$-form (wet volume, as supplied, ca. 220 ml), the mixture is stirred with a paddle-mixer submerged in the milk from above at 65 °C-70 ºC for 30-40 minutes.

3.3.2   After stirring, the milk is decanted and discarded. The resin is washed three times with 300 ml of hot (70 °C) distilled water, and then transferred to a glass column (inner diameter: ca. 3 cm, length: ca. 60 cm) fitted with a glass frit (porosity grade 2). To remove even the last traces of milk constituents from the resin, the column is washed with hot (90 °C), distilled water (ca. 1 litre to 1,5 litres). The runoff water must be clear with no traces of turbidity.

3.3.3   The column is then cooled by flushing it with cold distilled water. The water is allowed to elute from the column completely.

3.3.4   The top of the resin column is covered with some glass wool to prevent disturbance of the upper layers of the column when it is subsequently eluted with acid.

3.3.5   The alkaline earth cations are eluted with 270 ml of nitric acid (5 mol·l^{-1}). The acid is added to the column in 4 or 5 portions, and the flow rate through the column of each portion is adjusted to 10 ml to 20 ml per minute. The first 30 ml (approximately corresponding to the dead volume of the column) of the eluate are discarded, while the remaining 240 ml are collected. The final portion of acid is allowed to drain from the column completely.

3.3.6   The collected eluate is filtered through a glass frit (porosity grade 4) and then transferred to a 500 ml-separation funnel (separation funnel 1).

3.3.7   100 ml of a solution of dicyclohexyl-18-crown-6 in chloroform (0,025 mol·l^{-1}) are added to the eluate in separation funnel 1, and the mixture is shaken for 2 minutes. Following the phase separation, the chloroform (lower phase) is drained into another separation funnel (separation funnel 2). The aqueous nitric acid phase in separation funnel 1 is shaken twice more with fresh 100 ml portions of dicyclohexyl-18-crown-6 in chloroform (0,025 mol·l^{-1}) for 2 minutes each. The chloroform phases of these extraction processes are likewise transferred to separation funnel 2. The aqueous nitric acid phase is then discarded.

3.3.8   75 ml of an aqueous solution containing sodium acetate and acetic acid (both 0,1 mol·l^{-1}) as well as strontium chloride (0,133 mg·ml^{-1} of Sr-carrier) are added to the chloroform phase in funnel 2 and the mixture is shaken for 2 minutes. Following the phase separation, the chloroform (lower phase) is transferred to a third separation funnel (separation funnel 3). The aqueous phase is kept in separation funnel 2 whereas the chloroform phase in separation funnel 3 is shaken with another 75 ml portion of the aqueous solution of sodium acetate, acetic acid and strontium chloride (2 minutes of shaking). The chloroform phase is then discarded.

3.3.9   The aqueous phases are combined in a 200 ml-centrifuge beaker and the pH-value is adjusted to about 12 by dropwise addition of aqueous sodium hydroxide (10 mol·l^{-1}). Then, 1 g to 2 g of ammonium carbamate is added and the mixture is heated for at least 40 minutes in a boiling water bath. After the solution has cooled down, it is centrifuged and filtered under suction through a blue-band filter of 3 cm in diameter (Hahn's suction apparatus). The precipitate on the filter is

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washed first with some distilled water, then with methanol. Thereafter, the filter is dried at ca. 80 ºC in a drying cabinet for 2 to 3 minutes.

3.3.10 The strontium carbonate on the filter paper is for the largest part transferred to a 20-ml scintillation vial made of low potassium glass. The margins of the filter paper that have had no contact with the strontium carbonate are cut off with a pair of scissors and discarded. The core of the filter with the remaining traces of strontium carbonate is added to the precipitate in the scintillation measuring vial which is stored for a minimum of 15 days to allow the ingrowth of the daughter nuclide Y-90.

3.3.11 When Sr-90 and Y-90 have attained radioactive equilibrium, 2,0 ml of a 25 %-toluene sulfonic acid solution containing 10 mg of Y-carrier are added to the measuring vial. As soon as the carbonate has dissolved, 19,0 ml of Instant-Scint. gel (Canberra-Packard) are added and the measuring vial is shaken vigorously. After some 10 minutes, a clear, homogeneous scintillator solution forms. As an alternative to shaking, the solution may be mixed in an ultrasonic bath. In this case, it must be ensured that the cap of the measuring vial is not firmly screwed on, as this might cause the vial to burst. It must thereafter also be ensured that the scintillation solution is saturated with atmospheric air (e. g., by briefly shaking it).

3.3.12 To determine the yield of strontium, the measuring vial containing the precipitate is measured at 514 keV with a gamma spectrometer. The net count rate is compared to that of a standard source that contains the same Sr-85 activity as that which was added to the sample at the beginning of the analysis. This standard source is produced in the same type of measuring vial as that used for the sample and consists of a corresponding aliquot of the aqueous Sr-85 parent solution and 20 mg of strontium carrier in the form of an aqueous solution, which are then diluted with distilled water to a total of 21 ml and mixed well.

The strontium yield is calculated as follows:

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

Note

Alternatively, the Y-90 may be separated according to step 3.3.10 of this procedure, precipitated first as hydroxide and then re-precipitated as oxalate, and measured by means of a proportional counter tube (low-level measuring station with anti-coincidence shielding). For the separation of the Y-90, steps 3.3.11 through 3.3.15 of procedure F-Sr-90-MILCH-01 of this procedures manual apply analogously. For measuring the activity and calculating the results of the analysis as well as the detection limits, sections 4 through 6 of procedure F-Sr-90-MILCH-01 provide the necessary details.

4   Measuring the activity

The total scintillation spectrum of the scintillation solution is recorded with a low-level liquid-scintillation spectrometer.

For calibrating the equipment and analysing the sample spectrum, the spectra of the background and a calibration source that contains Sr-90 and Y-90 in equilibrium need to be measured. This requires that the exact Sr-90 activity will be known. With the tracer Sr-85 contributing to the low-energy segment of the scintillation spectrum, an area must be found that is free of contributions by Sr-85. To this end, a counting source is measured that has the same activity of Sr-85 as that required for determining the yield. This counting source must of course not contain any Sr-90/Y-90. The sources needed for measuring these spectra are produced as follows:

1. Background: A 20 ml-scintillation vial made of potassium-deficient glass is filled with 35 mg of strontium carbonate (corresponding to 20 mg of strontium) dissolved in 2,0 ml 25 %-toluene sulphonic acid in water, and the solution is then mixed with 19,0 ml Instant-Scint gel.

2. Sr-90/Y-90 standard: 100 µl to 500 µl of aliquot portions of an aqueous Sr-90/Y-90 standard (diluted to a few hundred $Bq \cdot ml^{-1}$) and 1,0 ml of a 50 % toluene sulphonic acid solution in water containing 10 mg Y-carrier, as well as 20 mg of Sr-carrier (added in the form of strontium carbonate), are filled into a 20-ml scintillation vial made of low-potassium glass. The volume is adjusted with distilled water to a total of 2,0 ml, and the solution is then mixed with 19,0 ml of Instant-Scint gel.

3. Sr-85: The same Sr-85 activity should be used as that required for determining the Sr-yield of the samples. To this end, 0,1 ml to 1,0 ml of aliquot portions of an aqueous Sr-85 solution (diluted to 10 $Bq \cdot ml^{-1}$ to 100 $Bq \cdot ml^{-1}$) are treated exactly like the Sr-90/Y-90 standard source in step 2 above.

Experience shows that in the energy range above 220 keV, scintillation counting sources containing 10 Bq of Sr-85 produce the same count rates as counting sources used for measuring the background. An optimal measuring range from 220 keV to 860 keV was found for measuring Sr-90 samples containing 10 Bq of Sr-85, employing the low-level scintillation counter 2260 XL manufactured by Canberra-Packard. It is nevertheless advisable to identify the optimal measuring range if different equipment or a different Sr-85 activity is used.

The quench conditions achieved are approximately equal in all measuring processes. Differences with regard to quench factors (tSIE-value according to Packard) of > 12 % indicate that errors have been incurred during the sample preparation. Smaller differences in the quench behaviour of the sample and the standard may be corrected with the aid of quench curves in which the count yield is plotted against the quench factor if and when necessary. To obtain reliable values for the quench factor of the measuring sources, the scintillation cocktail has to be of the same temperature as the ambience inside the measuring instrument, and the measuring period for the external standard of the measuring instrument needs to be sufficiently long. For the low-level liquid-scintillation counter 2260 XL from Canberra-Packard, a measuring period for the external standard of at least 240 seconds is recommended.

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};
     all count rates relate to the selected energy range;
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 the analysis, in s;
φ_A activity-related calibration factor (as a function of the quench value), in $Bq \cdot s$;
$k_{1-\alpha}$ quantile of the normal distribution (type I error);
$k_{1-\beta}$ quantile of the normal distribution (type II error);
η_{Sr} chemical yield of strontium;
$f(t_A)$ decay factor for the period between sampling and start of the analysis:
$$f(t_A) = e^{\lambda_{Sr-90} \cdot t_A} \; ;$$

     $f(t_A)$ takes into consideration the decay of Sr-90 during the period between sampling and the start of the analysis. This correction is necessary only if the interval is relatively long ($t_A > 0{,}5$ years).

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;
V bolume of the sample of milk used, in l;
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 sample activity c at the 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 the time of sampling, in Bq;
$g_c(t_A)$ detection limit of the activity concentration c at the time of sampling, in $Bq \cdot l^{-1}$.

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

$$c = \frac{f(t_A) \cdot \varphi_A \cdot R_n}{\eta_{Sr} \cdot V}$$

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 the time of sampling is obtained from:

$$s_c = \frac{f(t_A) \cdot \varphi_A \cdot s_n}{\eta_{Sr} \cdot V}$$

The result is reported as the activity concentration, c, of the sample and the standard deviation, s_c, of the activity concentration, both calculated with reference to the time of sampling, in Bq·l⁻¹ ($c \pm s_c$).

5.1   Worked example

R_g = 0,228 s⁻¹; φ_A = 1,978 Bq·s;

R_0 = 0,147 s⁻¹; η_{Sr} = 0,850;

R_n = 0,081 s⁻¹; V = 1,0 l;

t_m = 6,0·10⁴ s; $f(t_A)$ = 1,000;

t_0 = 6,0·10⁴ s; t_A = 0 (negligible).

$$c = \frac{1{,}000 \cdot 1{,}978 \cdot 0{,}081}{0{,}850 \cdot 1{,}0}\ \mathrm{Bq \cdot l^{-1}} = 0{,}19\ \mathrm{Bq \cdot l^{-1}}$$

$$s_g = \sqrt{R_g/t_m} = \sqrt{0{,}228/6{,}0 \cdot 10^4}\ \mathrm{s^{-1}} = 1{,}9 \cdot 10^{-3}\ \mathrm{s^{-1}}$$

$$s_0 = \sqrt{R_0/t_0} = \sqrt{0{,}147/6{,}0 \cdot 10^4}\ \mathrm{s^{-1}} = 1{,}6 \cdot 10^{-3}\ \mathrm{s^{-1}}$$

$$s_n = \sqrt{\left(1{,}9 \cdot 10^{-3}\right)^2 + \left(1{,}6 \cdot 10^{-3}\right)^2}\ \mathrm{s^{-1}} = 2{,}5 \cdot 10^{-3}\ \mathrm{s^{-1}}$$

$$s_c = \frac{1{,}000 \cdot 1{,}978 \cdot 2{,}5 \cdot 10^{-3}}{0{,}850 \cdot 1{,}0}\ \mathrm{Bq \cdot l^{-1}} = 5{,}8 \cdot 10^{-3}\ \mathrm{Bq \cdot l^{-1}}$$

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

$$c = (0{,}19 \pm 0{,}01)\ \mathrm{Bq \cdot l^{-1}}$$

5.2   Consideration of uncertainties

The above example considers only the statistical counting uncertainties incurred during measuring the activity, but not uncertainties in the chemical separation, yield-determination process, and calibration of the measuring instruments. Five analyses of milk powder reference standards (milk powder A-14 of the IAEA) produced a mean value of 1,46 (standard deviation 0,18) Bq·kg⁻¹ of powder for the Sr-90 activity. The reference value recommended by the IAEA is 1,5 Bq·kg⁻¹ for this material.

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 one correctional function in order to obtain the detection limit, $G(t_A)$, at the time of sampling:

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

For calculating the detection limit of the activity concentration, $G(t_A)$ must be divided by the chemical yield of strontium and the volume of the sample used:

$$g(t_A) = \frac{f(t_A) \cdot G}{\eta_{Sr} \cdot V}$$

6.1   Worked example

R_0 = 0,146 s^{-1}; η_{Sr} = 0,850;

t_0 = 6,0·10^4 s; V = 1,0 l;

t_m = 6,0·10^4 s; $f(t_A)$ = 1,000;

t_A = 0 (negligible) ; φ_A = 1,978 Bq·s.

$$G = 1{,}978 \cdot \left[4{,}645 \cdot \sqrt{0{,}146 \cdot \left(\frac{1}{6{,}0 \cdot 10^4} + \frac{1}{6{,}0 \cdot 10^4} \right)} + 0{,}25 \cdot 4{,}645^2 \cdot \left(\frac{1}{6{,}0 \cdot 10^4} + \frac{1}{6{,}0 \cdot 10^4} \right) \right] \text{Bq} =$$

$$= 2{,}05 \cdot 10^{-2} \text{ Bq}$$

$$g(t_A) = \frac{1{,}000 \cdot 2{,}05 \cdot 10^{-2}}{0{,}850 \cdot 1{,}0} \text{ Bq} \cdot \text{l}^{-1} = 2{,}4 \cdot 10^{-2} \text{ Bq} \cdot \text{l}^{-1}$$

The detection limit of the method is about 24 mBq per litre of milk when 1 l of milk and a measuring period of 6,0·10^4 s (1000 minutes) are used. This value was obtained by analysing the energy range from 220 keV to 860 keV in the spectrum of a blank sample that contained no Sr-90 and therefore no Y-90.

If necessary, the detection limit may be reduced by about half by doubling the sample volume and the amount of Chelite P-resin and correspondingly increasing the volume of nitric acid (5 mol·l^{-1}) used for elution to 350 ml. In this case, the initial 60 ml-70 ml of the eluate from eluting the resin column with nitric acid (5 mol·l^{-1}) can be discarded.

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7 Catalogue of chemicals and equipment

7.1 Chemicals

All chemicals used should be of the purity grade "*pro analysi*":

— Chelite P in Na^+-form (available from: Serva, Heidelberg);

— Nitric acid (5 mol·l^{-1});

— Aqueous sodium hydroxide solution (10 mol·l^{-1});

— Sodium acetate/acetic acid solution (both 0,1 mol·l^{-1}) with 0,133 mg·ml^{-1} of Sr-carrier;

— Ammonium carbamate, solid;

— Strontium carbonate, solid;

— Dicyclohexyl-18-crown-6 in chloroform (0,01 mol·l^{-1}) (crown ether available from: Merck, Darmstadt or Serva, Heidelberg);

— Toluene sulphonic acid solutions 25 % by weight and 50 % by weight, respectively, in water, containing appropriate amount of Y-carrier (5 mg/ml and 10 mg/ml, respectively;

— Liquid scintillator cocktail
(Instant-Scint gel, by Canberra-Packard, Frankfurt a. M.).

7.2 Equipment

— Basic equipment of a radiochemical laboratory;

— Liquid-scintillation measuring vials made from low-potassium glass;

— Liquid-scintillation spectrometer, if possible as a low-level model, with multi-channel analyser.

References

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