

**Procedure for determining radionuclides
in samples of milk
by gamma spectrometry**

F- γ -SPEKT-MILCH-01

Authors:

A. Wiechen

D. Tait

Federal coordinating office for soil, vegetation, animal feed and
food of vegetable or animal origin

(Leitstelle für Boden, Bewuchs, Futtermittel und Nahrungsmittel
pflanzlicher und tierischer Herkunft)

Procedure for determining radionuclides in samples of milk by gamma spectrometry

1 Scope

The procedures described in the following are used for the routine monitoring of milk samples according to the Precautionary Radiation Protection Act and the Guideline for the Monitoring of Emissions and Immissions of Nuclear Installations.

2 Sampling

The Precautionary Radiation Protection Act prescribes that samples of raw milk are to be routinely collected from the storage tanks of selected large-scale dairy plants or milk collection points. These dairies or collection points are to be determined in a sampling schedule so that the same places will be sampled every month, creating continuous timelines.

The Guideline for the Monitoring of Emissions and Immissions of Nuclear Installations requires that two random samples each be collected from a dairy farm, preferentially from within the most exposed area, and a nearby dairy processing plant or collection point for milk during the period when cows are fed with green forage. In the case of sampling from a dairy farm, it needs to be ensured by means of a verbal agreement that the samples originate from animals that graze in the main admission area, or are fed with green forage harvested from this sector. Mixed samples from different localities or taken on more than one date are not admissible in this case.

Collecting liquid samples poses no major problems in principle. However, a few details need attention to ensure that the samples are representative of the milk produced by the sampled dairy farm or processed by the dairy plant: The raw milk has to originate from the collection tanks of the farm or stack tanks of the dairy processing plant that have already been filled and in which the milk has been mixed by pumping or stirring. If the samples are taken from a tap or run-off, sampling must be preceded by letting a volume equal to the potentially unmixed dead volume flow off. If a plant uses several large-volume tanks, or if the tanks are filled several times a day, a day's mixed sample should be produced from aliquots taken from all fillings. Depending on the intended type of analysis (liquid milk, milk powder, ash), a total sample volume of between 2 l and 10 l needs to be collected.

Samples of milk should also be preserved prior to transport from the dairy farm or plant to the laboratory by adding 3,5 ml of 5 % sodium azide solution per litre to prevent them becoming sour.

3 Analysis

3.1 Principle of the procedure

If possible, the samples of milk are measured in their original liquid form with a Ge-gamma spectrometer. If only a gamma spectrometer with a low efficiency and/or relatively high background is available, it may be necessary to first dry the samples or even ash them at temperatures not exceeding 400 °C and then to measure the milk powder or ash, respectively, to attain the required detection limits. A significant portion of iodine radioisotopes may be lost during the drying process and the ashing process in particular, so that these can no longer be quantified after the processing of the sample.

3.2 Sample preparation

If the samples of milk can be measured in their liquid form, no further preparation measures are necessary. Laboratories with access only to a semi-conductor detector with a low response probability and/or lead shielding with a high background, which would render conforming to the required detection limits possible only with excessive measuring periods, may resort to drying or, in exceptional cases, even ashing the sample and measuring the resultant milk powder or ash, respectively.

3.2.1 Desiccating

Samples of milk are best converted to milk powder with cylinder or spray driers. Spray driers designed for small volumes of only a few litres are commercially available. If such equipment is not accessible, the samples may be partially evaporated in a water bath or beneath an infrared heater, then desiccated in a drying cabinet at 102 °C. Samples of milk powder have to be ground and homogenised in a fan mixer, particularly so if they have been desiccated in a water bath and a drying cabinet.

An alternative is to thicken the milk with rennet and then desiccate it in a microwave oven. The optimal conditions for the thickening and desiccation processes have to be established experimentally with the rennet compound available and the particular microwave oven used. Subsequent to the desiccation process, the slightly keratinized material needs to be ground in a mortar and homogenised.

The yield of milk powder must be determined to relate the measuring results to liquid milk.

3.2.2 Ashing

The samples of milk powder prepared according to section 3.2.1 may be ashed for gamma spectrometric measurement. However, the detection limit cannot usually be significantly decreased by measuring milk ash rather than milk powder. Ashing is always required for determining the Sr-90 content (see procedures F-Sr-90-MILCH-01 and F-Sr-90-MILCH-02). This requires ashing the milk powder in a quartz dish at a furnace temperature not exceeding 400 °C. To this end, the quartz dishes are placed in the furnace when it is still cold. The air supply is minimized to carbonise the sample material and prevent it from igniting. The ventilation openings of the furnace are opened only after completion of this carbonisation process. The samples need to be stirred once during the ashing process to give atmospheric oxygen sufficient access to completely destroy all organic material. The ash is again homogenised in a tumbling or drum hoop mixer filled with a few agate or ceramic balls.

To avoid deposits of carbonisation products in chimneys with the attendant fire risk and to minimize pollution of the environment, it is advisable to use an ashing furnace with a catalytic afterburner when ashing larger volumes of biological materials. As particularly useful have proven those furnace designs in which the ashing chamber is directly linked via a generously dimensioned connection to a catalytic afterburner unit with a separate heater.

The yield of ash is to be determined for converting the measuring results into values for dry mass (DM) and liquid milk.

3.3 Radiochemical separation

No radiochemical separation is required.

4 Measuring the activity

Basic information on, and aids for, gamma spectrometry are contained in chapters IV.1.1 through IV.1.3 of this procedures manual.

The gamma spectra are measured with a Ge-spectrometer (> 15 % efficiency relative a 3" x 3" NaI(Tl)-detector for the 1,33 MeV line of Co-60). Liquid milk and milk powder are measured in 1 l-Marinelli beakers. Milk ash is compressed to a defined volume (50 cm³) in a flat-bottomed, screw-capped vessel for measuring on a semiconductor detector.

The gamma spectrometer is calibrated with aqueous standard solutions and typically in dependence of the energy, because standard solutions are not available for all radionuclides that can occur in environmental samples. Only mixed or individual solutions of single-line nuclides or those cascade emitters should be used for which summation losses can be neglected. These summation losses may reach values of up to 30 % in some cases for Marinelli beaker geometries measured with the large-volume detector crystals that are available today! Radionuclides suitable for calibration purposes are Am-241, Cd-109, Co-57, Te-123m, Ce-139, Hg-203, Sn-113, Be-7, Sr-85, Cs-137, Mn-54, and Zn-65. I-131 is not normally included in mixed standards, but can be obtained as an individual standard solution. It should be used instead of the unsuitable Ba-133 for obtaining another reference point between the lines of Te-123m and Ce-139, and between those of Be-7 and Cs-137. K-40 may be particularly useful for calibrating above the 1115,55 keV line of Zn-65, if a gamma spectrometer needs to be calibrated that has a low background of K-40. For calibrating up to an energy line of about 1800 keV, avoiding the use of Y-88 will usually be impossible although this cascade emitter shows significant summation losses. It is therefore present in nearly all commercially available mixed standard solutions. The summation losses in the Y-88 line at 1836,06 keV can be corrected by first calibrating to the Zn-65 line at 1115,55 keV without considering the Y-88 lines, then determining a correction factor against the efficiency curve for the 898,4 keV-line of Y-88. This factor is then used to compensate summation losses in the line at 1836,06 keV. This correction is possible because the two Y-88 lines show summation losses that are practically identical. Thereafter, a new calibration curve is approximated by including the corrected efficiency of the higher energy line of the Y-88.

Thus it is possible to establish an accurate calibration curve to an energy line of about 1800 keV even for large detectors. The problem of summation losses is also encountered in the measurement of samples if these contain critical cascade emitters. Cascade emitters that may be found in milk after a nuclear event are I-132, Cs-134 and La-140. Correction factors relative to the calibration curve should be determined in particular for dose-relevant radionuclides, like Cs-134 for example, using the calibration solution that is available for this radionuclide. The factor is then used to correct the count rates of the lines to be analysed. Furthermore, it should be noted that software products are available that estimate with a high level of accuracy correction factors for summation losses in cascade emitters for defined detectors and geometric sample configurations. An overview of these calculation procedures is provided in a report by the PTB, Brunswick (1).

Deviations in the self-absorption losses in the sample to be measured relative to the calibration solutions as a result of different densities may always be neglected when liquid samples of milk are measured, because the density of liquid milk is nearly $1 \text{ g}\cdot\text{cm}^{-3}$ (full-cream milk: $1,030 \text{ g}\cdot\text{cm}^{-3}$, low-fat milk: $1,033 \text{ g}\cdot\text{cm}^{-3}$). The bulk density of milk powder, on the other hand, deviates significantly from 1 and ranges from $0,5 \text{ g}\cdot\text{cm}^{-3}$ to $0,8 \text{ g}\cdot\text{cm}^{-3}$, depending on production procedures and conditions. Owing to the lower self-absorption, the required corrections for radionuclides that can be expected in milk may amount to a few percent at most when measuring powder in 1 l-Marinelli beakers and can usually be neglected during routine monitoring, because the measured values will be slightly overestimated. This also applies to measuring milk ash at bulk densities of $0,50 \text{ g}\cdot\text{cm}^{-3}$ to $0,55 \text{ g}\cdot\text{cm}^{-3}$ that will typically be carried out with very small measuring geometries of 50 cm^3 at maximum and are therefore rather uncritical with regard to self-absorption.

For the purpose of precision measuring, self-absorption corrections against the aqueous calibration solutions may be determined experimentally in dependence of the energy with adequate precision. This is done by measuring the known activities of various single-line nuclides in media at densities varying from $0,3 \text{ g}\cdot\text{cm}^{-3}$ to $2,0 \text{ g}\cdot\text{cm}^{-3}$. Producing media with densities greater than $1 \text{ g}\cdot\text{cm}^{-3}$, into which radionuclides can be infused homogeneously, does not pose a problem. Suitable for this are highly water-soluble salts such as sodium per-chlorate or sodium di-chromate. Salts containing elements with high atomic numbers should be avoided, as the samples to be measured will not contain significant amounts of these elements.

Densities of less than $1 \text{ g}\cdot\text{cm}^{-3}$ can be produced using one of the commercially available silica gels with various, yet always relatively narrow, grain size distributions. One such silica gel is filled in its original moist form into the measuring vessel and the radionuclide solution is dripped on the gel surface, distributing it as evenly as possible. The gel is then desiccated in a drying cabinet, upon which the measuring vessel is fitted with a well-sealing clip-on or screw-on lid and shaken in a tumbling mixer until the radionuclides are homogeneously distributed. Their distribution may need to be checked several times by means of gamma spectrometry.

A method of mathematical correction of self-absorption losses has been described in the literature (2).

5 Calculation of the results

High-performance software for the analysis of gamma spectra is available from a number of software suppliers. Preference should be given to software that not only makes provision for calculating the activity concentrations of all major radionuclides, but also calculates decision thresholds and detection limits according to chapter IV.5 of this procedures manual (see also section 6) and employs the decision threshold as a criterion in the search algorithms for deciding whether or not a line is distinct from the background.

Measuring results of activity concentrations or their detection limits are always to be given, also in the cases of milk powder or ash, in $\text{Bq}\cdot\text{l}^{-1}$ milk.

6 Characteristic limits of the procedure

The characteristic limits of gamma spectrometric analyses of milk (including milk powder or ash) are determined by the efficiency of the detector used, and the nuclear data of the radionuclides to be measured, and in particular by the K-40 content of the sample to be measured, which amounts to about $50 \text{ Bq}\cdot\text{l}^{-1}$ in milk. The background spectrum of the measuring configuration is less important when such K-40 activities are present in the sample.

Characteristic limits are calculated according to equation (4.32a) of chapter IV.5, section 4.5 of this procedures manual. If the algorithms for calculating the detection limits of the software employed do not correspond to the equation in chapter IV.5, corrections have to be applied subsequently. Examples for how to calculate detection limits in gamma spectrometry are also provided in chapter IV.5, sections 6.4 and 6.5. These examples may be applied to the present case analogously.

The values in the following table indicate the achievable detection limits. They were determined by measuring liquid milk (1 l of milk in a Marinelli beaker), milk powder (600 g of powder in a 1 l-Marinelli beaker), and milk ash (30 g of ash in a 50 cm^3 -screw-capped vessel) on a detector with 25 % relative efficiency, which like its shielding is a low-level model, with measuring periods of 12 hours. The milk, as well as the powder and ash produced from it that were analysed for determining detection limits contained no significant activities of radionuclides other than natural K-40 at an activity concentration of $50 \text{ Bq}\cdot\text{l}^{-1}$. The values for detection limits for the reference nuclide Co-60 and radionuclides that may be present in milk have been converted into those for liquid milk also in instances where powder or ash were measured and are given in $\text{Bq}\cdot\text{l}^{-1}$.

Detection limits in milk (Bq·l⁻¹)

Radionuclide	physical state of measured sample		
	Liquid milk	Milk powder	Milk ash
Co-60	0,20	0,06	0,08
I-131	0,14	-	-
Te-132	0,13	0,03	0,03
I-132	0,53	-	-
I-133	0,17	-	-
Cs-134	0,14	0,03	0,04
Cs-136	0,15	0,04	0,04
Cs-137	0,17	0,04	0,04
Ba-140	0,52	0,11	0,08
La-140	0,17	0,03	0,03

The table clearly indicates that measuring milk powder facilitates a lowering of the detection limits compared to measuring liquid milk. Measuring ash, on the other hand, would not normally lower these limits any further, unless a much larger volume of ash could be analysed in an optimised geometric configuration.

7 Catalogue of chemicals and equipment

7.1 Chemicals

Other than sodium azide for preserving samples and possibly rennet for thickening the milk prior to desiccating it in a microwave oven, no chemicals are required because radiochemical separation processes are not required.

7.2 Equipment

- Spray-drier, alternatively cylinder-drier, infrared irradiating lamp, water bath, drying cabinet, microwave oven for desiccating milk (if necessary);
- Ashing furnace with catalytic afterburner, quartz ashing dishes for ashing milk powder (if necessary);
- Fan-mixer, 3D, tumbling or drum hoop mixer, possibly a mortar for homogenising powders or ashes;
- Ring beakers (Marinelli beakers) or screw-capped vessels for gamma spectrometric measuring;
- Ge- or Ge(Li)-semiconductor detector (> 15 % relative efficiency, full width at half maximum of < 2,1 keV at 1,33 MeV) with pre-amplifier and high-voltage power supply unit;
- Main amplifier (NIM module);
- Analogue-digital converter (NIM module);
- Multi-channel analyser of the conventional type or with a corresponding external data storage unit, with at least 4096 channels (NIM module);
- Rack with power supply for NIM modules;
- PC or workstation with software for the analysis of gamma spectra.

References

- (1) Debertin, K. and Schötzig, U.: Bedeutung von Summationskorrekturen bei der Gammastrahlen-Spektrometrie mit Germaniumdetektoren. PTB RA.24, Braunschweig, Mai 1990
- (2) Debertin, K. and Jianping, R.: Measurement of the Activities of Radioactive Samples in Marinelli Beakers. Nuclear Instruments and Methods in Physics Research. A278 (1989), 541-549