Procedure for determining radionuclides in samples of animal feed and animal feed raw materials by gamma spectrometry

F-γ-SPEKT-FUMI-01

Author:

A. Wiechen

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)

ISSN 1865-8725 Version November 1998

Procedures manual for monitoring of radioactive substances in the environment and of external radiation
(Messanleitungen für die „Überwachung radioaktiver Stoffe in der Umwelt und externer Strahlung")

Procedure for determining radionuclides in samples of animal feed and animal feed raw materials by gamma spectrometry*

1 Scope

The procedures described in the following are to be applied for examining all animal feeds and animal feed raw materials that are to be routinely monitored in accordance with the Precautionary Radiation Protection Act and the Guideline for the Monitoring of Emissions and Immissions of Nuclear Installations (REI).

2 Sampling

2.1 General

Samples of animal feeds should be obtained at the same sampling sites that are also scheduled to serve for collecting samples of soil. Sampling should be repeated every year on the same farmland, but at least within one and the same topographical area.

Collecting samples of animal feeds properly requires some experience. It should therefore be commissioned preferably to institutions that are experienced in this field. An expert in animal feed science has to train sample-collecting staff. Agricultural laboratories and/or research institutions or feed science departments of universities should be asked for assistance or expert advice.

The areas to be sampled must be distant from potential obstacles (buildings, trees, etc.) by a minimum of twice the height of the obstacle. The position and demarcation of the sampled area are to be documented clearly and precisely to create a basis for sampling the exact same area every year. As the utilisation of an area might change over time thus changing the characteristics of the original sampling area, potential replacement areas in the immediate vicinity should be reserved. Considering that it is common agricultural practice to rotate crops it makes sense to fix a number of sampling areas within the same area from the beginning in order to have a sufficiently large number of alternative sampling areas later. The person collecting samples should be equipped with detailed maps in which both the primary and the alternative sampling areas are clearly marked. A sampling area must be between 0,1 ha and 1,0 ha in size. Only in exceptional cases in which there are no suitably large areas available may the minimum area to be reduced to 100 m². This may apply, for example, in the case of a nuclear installation that lacks larger areas in the surroundings of the maximum receiving point.

Areas bordering roads, paths and ditches should not be sampled, as they will typically exhibit an unrepresentative soil composition; the respective areas are marked in Figure 1 of procedure F-γ-SPEKT-BODEN-01 of these measuring instructions. The individual sampling spots are to be distributed evenly throughout the entire sampling area. An example for a perfectly even distribution of sampling spots is illus-

*These procedures have been worked out in collaboration with Dr. H. Weller, LUFA Speyer and the VDLUFA (Verband der Landwirtschaftlichen Untersuchungs- und Forschungsanstalten), Expert group XI, Workgroup «Radioanalysis».

trated in Figure 1 of procedure F-γ-SPEKT-BODEN-01 of these measuring instructions as well. The person collecting the samples should move along a zigzag-course through the designated area and strive to achieve the ideal sampling pattern as much as possible.

Sampling of green forage plants should be timed so that they can be processed immediately without the risk of their decomposing or growing mildew from storage in unsuitable conditions.

2.2 Vegetation of pastures and meadows (clover, lucerne, green cereals)

Sampling areas in meadows or pastures should be representative of areas that serve the harvesting of animal feeds and are therefore tended and fertilized regularly. Areas bordering bodies of water, margins of fields, or fallow land etc. are unsuitable for sampling. Sampling should take place at the time of the first harvest of hay or forage. The selected area needs to be sampled every year anew. Changing sampling areas should be avoided if possible, but potential alternative areas should be designated right from the beginning, as it cannot be ruled out that e.g., meadows and pastures might be converted into land used for other purposes in the future. It is expedient to demarcate collecting spots in various places by placing a V2A-steel or plastic frame of 70 cm x 70 cm (= 0,5 m²) on the ground and cut off the vegetation about 2 cm above the ground (e.g., with lawn shears), then combine the cuttings to a mixed sample of 10 kg to 15 kg in a plastic bag. The sampled spot should be approximately representative of the plant variety that is typical of the area. Being precise with regard to the dimensions of the spots sampled and collecting all sample material without loss is necessary if the results of the subsequent analysis are to be related to a specific area unit. Contaminating the sample with soil and roots must be avoided.

2.3 Maize (whole plants)

At the corn kernel ripening stage, one plant is cut off some 5 cm above the ground at each of altogether 15 spots distributed evenly over a designated sampling area within a maize field. The subsamples are roughly chopped up and then combined in plastic bags for transport and storage. Contaminating the sample with soil must be avoided here as well.

2.4 Feedgrain

During or after the harvesting of cereals, a total of ten subsamples are collected from the combine harvester, transport vehicle, or granary of the farmer and consolidated to form a mixed sample of 2 kg in weight. All samples should be largely free of impurities (alien grains, seeds of weeds, straw etc.).

2.5 Feeder potatoes, turnip

Sampling should be carried out at farms that grow feeder potatoes or turnip regularly every year in fields that are homogeneous in character and situated as closely as possible to each other. It is of advantage if one and the same variety of potato or turnip is cultivated for several years in succession. In the case of potatoes, early varieties are not sampled, as these are intended almost exclusively for human consumption. Samples are collected from the stores of the farmer in late autumn. Subsamples are taken from ten spots and combined to a mixed sample. The size distribution of the potatoes or turnips should be representative of that of the spec-

imens in entire store. The subsamples are combined to a mixed sample of at least 10 kg in the case of potatoes and at least 25 kg in the case of turnip.

2.6 Animal feed raw materials (imports)

Imported raw materials serving the production of animal feeds are collected from the manufacturers of animal feed mixes by official samplers in accordance with the Ordinance for the Official Monitoring of Animal Feeds ("Verordnung für die amtliche Futtermittelüberwachung") (1), who usually act on behalf of, or are officially affiliated with, the High Offices of the Ministries of Economy or Agriculture of the respective federal state ("Wirtschafts- or Landwirtschaftsoberbehörden").

The characteristics of the tools used for sampling, collection methods and constitution of samples, number of individual and mixed samples to be taken in relation to the type and extent of the stock to be sampled, as well as sample processing prior to analysis are all described in detail in this Ordinance. Deviating from the Ordinance, the minimum amount of specimens for radioactive monitoring must be 1,5 kg.

3 Analysis

3.1 Principle of the procedure

The sample material is typically roughly chopped up, dried to constant weight at 105 ºC, ground, and then gamma spectrometrically analysed in this form. If only a gamma spectrometer with a low efficiency and/or relatively high background is available, it might be necessary to ash the samples at temperatures not exceeding 400 ºC and measure the resultant ash to achieve the required detection limits. A significant portion of iodine radioisotopes may be lost during the drying process and during the ashing process in particular, so that these can no longer be quantified after processing the sample.

3.2 Sample preparation

3.2.1 Vegetation of pastures and meadows (clover, lucerne, green cereals)

If the collected plant material is very crude, the samples may need to be shredded prior to drying them. It is general practice to dry the sample at 105 ºC till constant weight, then crush it in a cross-beater mill fitted with a 1 mm-sieve or another device serving the same purpose, and mix it thoroughly until homogenous.

3.2.2 Maize (whole plants)

The total amount of the sample collected is shredded as finely as possible and mixed thoroughly. A subsample of 10 kg is processed as described in section 3.2.1. The remainder is discarded.

3.2.3 Feedgrain

The samples are dried and milled as described in section 3.2.1. If the gamma spectrometric analysis is to take place with measuring vessels of 1 l or more, milling is superfluous.

3.2.4 Feeder potatoes, turnip

In potatoes, the remnants of stolons and foliage as well as all other dirt are removed. Turnips need to be cut cleanly. The bases of roots with soil attached have to be scraped off with a knife. Both potatoes and turnip are then washed thoroughly twice with water. They are not peeled. The samples are then shredded not too finely, dried at 105 ºC, and milled with a cross-beater mill fitted with a 1 mm-sieve.

3.2.5 Animal feed raw materials (imports)

The samples are dried and ground as described in section 3.2.1.

3.2.6 Ashing

Laboratories with access to a semi-conductor detector with only a low response probability and/or lead shielding with a high background, which would render the required detection limits achievable only with excessive measuring periods, may resort to ashing according to sections 3.2.1 through 3.2.5 and measuring the resultant ash.

This requires that the dried and fragmented sample material be ashed in quartz dishes or similar vessels at a furnace temperature of less than 400 °C. To this end, the quartz dishes are placed in the furnace when it is still cold. The air supply is reduced to the minimum possible in order to carbonise the sample material and prevent it from igniting. The ventilation openings of the furnace are opened only after this carbonisation process has been completed to obtain ash that is as light in colour as possible. After the ash has cooled down, it is crushed in a tumbling- or 3D-mixer filled with ceramic or agate balls and homogenized.

To avoid deposits of carbonisation products in the chimney, with the attendant fire risk and to minimize the emission of pollutants to the atmosphere, it is advisable to use an ashing furnace with a catalytic afterburner when ashing larger amounts of biological materials. 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 have proven particularly useful.

The yield of ash needs to be recorded so that the analysis results can be calculated relative to the dry mass (DM).

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 to a 3" x 3" NaI(Tl)-detector for the 1,33 MeV-line of Co-60) in 1 l-Marinelli beakers or, in the case of ash, in flat-bottomed, screw-capped vessels of 50 cm^3 in volume.

The procedures to be applied for quantitatively calibrating a gamma spectrometer are outlined in detail in procedure F-γ-SPEKT-MILCH-01, where notes on the correction of summation and self-absorption losses can be found that may also be relevant when measuring samples of animal feeds.

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 specific activities of all major radionuclides, but can also calculate decision thresholds and detection limits according to chapter IV.5 of this procedures manual (see also section 6) and employ the decision threshold as a criterion in the search algorithms to decide whether or not a line is distinct from the background.

Measuring results of specific activities or their detection limits are always, also in the case of ash, to be given in $Bq \cdot kg^{-1}$ (DM).

6 Characteristic limits of the procedure

The characteristic limits of gamma spectrometric measurements of animal feed samples are not only determined by the response probability of the detector used and the nuclear-physical data of the radionuclides to be measured, but also and particularly so by the radionuclide spectrum of the measured sample. The background spectrum of the measuring configuration plays only a minor role in this case, because animal feeds contain particularly large amounts of potassium (K-40). These K-40 concentrations vary substantially with the type of animal feed. Corresponding variations must also be expected for the detection limits of Co-60 and other radionuclides that have gamma lines below the K-40 line. Table 1 provides some average values of the specific K-40 activity encountered in animal feeds that are to be monitored. Individual values may range as much as 50 % above or below these average values.

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

Tab. 1: Average values of the specific activity of K-40 in animal feeds to be monitored, in $Bq \cdot kg^{-1}$ (DM)

Animal feed	Specific K-40 activity
Green feeds	
Pasture vegetation	1130
Meadow vegetation	880
Red clover	730
White clover	1000
Lucerne	620
Green oats	1080
Green maize	880
Green rye	840
Maize, whole plant	
Maize, dough stage	710
Feeder cereals	
Barley	170
Oats	150
Maize	140
Rye	190
Wheat	160
Tubers and roots	
Potatoes, raw	700
Substantial turnips	970
Mass-produced turnips	1040
Imported feeds	
Maize products	
Maize sprout grist	30
Maize meal (commeal)	70
Maize gluten feed	420
Maize bran	120
Tapioca flour	250
Oilcakes and grists	
Cotton seed cake (8 % fats)	480
Cotton seed grist, extract	490
Peanut cake (< 8 % fats)	400
Peanut grist, extract	430
Coconut cake (8-12 % fats)	620
Coconut grist, extract	710
Linseed cake (8-12 % fats)	340
Linseed grist, extract	470
Palm kernel cake (< 8 % fats)	230
Palm kernel grist, extract	240
Raps cake (< 8 % fats)	400
Raps grist, extract	610
Sesame cake (< 8 % fats)	220
Sesame grist, extract	340
Soy grist, extract	640
Sunflower cake (8 % fats)	370
Sunflower grist, extract	410

As an indication for detection limits that can be achieved may serve the following values obtained from measuring a dried and milled sample of vegetation from a meadow (300 g in a Marinelli beaker) on a detector (25 % relative efficiency, low-level shielding and detector, measuring period: 12 hours). The meadow vegetation sample that was used for determining the detection limit contained no other gamma emitters in significant concentrations other than natural K-40 at a specific activity of 910 $Bq \cdot kg^{-1}$ DM. The values provided in Table 2 for detection limits of the reference nuclide Co-60 and artificial radionuclides that may be found in vegetation samples are given in $Bq \cdot kg^{-1}$ DM.

Tab. 2: Detection limits for meadow vegetation

Radionuclide	Detection limit in $Bq \cdot kg^{-1}$ (DM)
Be-7	0,24
Mn-54	0,04
Co-57	0,02
Co-58	0,04
Co-60	0,07
Zn-65	0,12
Zr-95	0,07
Nb-95	0,04
Ru-103	0,03
Ru-106	0,29
Ag-110m	0,03
Te-132	0,03
Cs-134	0,03
Cs-136	0,04
Cs-137	0,04
Ba-140	0,11
La-140	0,02

7 Catalogue of chemicals and equipment

7.1 Chemicals

No chemicals are required.

7.2 Equipment

The equipment required is listed in procedure F-γ-SPEKT-MILCH-01. Preparing of samples furthermore requires a shredder, and large drying cabinet (convection drying cabinet), and a cross-beater mill.

References

(1) Verordnung für die amtliche Futtermittelüberwachung vom 21.03.1978, Bundesgesetzblatt (BGBl.) Part I, 1978, p. 414,
Amended on 28.10.1980, BGBl. Part I, 1980, p. 2035,
Amended on 05.05.1982, BGBl. Part I, 1982, p. 604,
Amended on 18.10.1984, BGBl. Part I, 1984, p. 1290