Procedure for determining radionuclides in foodstuffs by gamma spectrometry

E-γ-SPEKT-LEBM-01

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ISSN 1865-8725 Version May 1997

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 foodstuffs by gamma spectrometry

1 Scope

The procedures described in the following are to be applied in the analysis of all foodstuffs (except milk and milk products, fish and fish products) that are to be monitored routinely in accordance with the Precautionary Radiation Protection Act (1) and the guideline for the monitoring of emissions and immissions of nuclear installations (2).

The method can be applied to all types of biological matter, including individual foodstuffs of plant and animal origin, composite and baby foodstuffs. It is not suitable for determining the radionuclides of iodine and other volatile radionuclides if the samples have been ashed dry (see procedure E-I-131-LEBMP-01).

2 Sampling

2.1 General

In routine sampling, the type of sample, extent of sampling, and selection of sampling locations are determined by the guideline for the monitoring of radioactivity in the environment according to the Precautionary Radiation Protection Act, part I: Measurement programme for normal operations (routine monitoring programme) (3). Corresponding specifications for the monitoring of the surroundings of nuclear installations are contained in the guideline for the monitoring of emissions and immissions of nuclear installations (2).

In order to exclude the possibility of cross-contamination and avoid the loss of moisture through storage, the sample material should be stored in well-sealed containers already during the sampling stage (e.g., polyethylene containers with screw caps or polyethylene bags).

The mass of a sample should be based on a dual analysis. Sampling should therefore be conducted in a manner as to make available about four to five times as much sample material as will be required for a duplicate analysis. If an analysis turns out to have been faulty, there will be enough sample material to carry out another dual analysis.

If samples cannot be analysed right away, they need to be stored in individual, closed containers at a temperature of at least -18 ºC in a state they can immediately be analysed on demand (see section 3.2).

2.2 Principles of sample selection

It is not quite possible to examine continuously and without exception all agriculturally produced foodstuffs that are available commercially. A suitable selection must provide the required indications of the extent of a possible contamination of foodstuffs by radionuclides (4). It is therefore that preference is given to those plant and animal products that experience has classified as being more prone to being contaminated by, or accumulating, air-, water- and soil-borne radionuclides (indicators) than others. Except for the case of total diet samples, only products at production level are to be examined.

Sampling is conducted on the basis of the sampling schedules that have been fixed by each federal state in cooperation with the Zentralstelle für die Überwachung der Umweltradioaktivität (ZdB).

2.2.1 Foodstuffs of plant origin

Of primary concern are agricultural products with edible parts that are exposed to contamination. As far as vegetables in general are concerned, the highest radionuclide contents are found in leafy vegetables grown in open fields and in particular those with long growth periods and large leaf surfaces (e. g., kale). Mushrooms exhibit a particular behaviour in that they are able to accumulate radioactive caesium. Amongst fruit, those are of particular interest that have a large surface relative to their total mass, as is very often the case with berries.

The foodstuffs of plant origin to be monitored have to be selected so as to ensure the inclusion of the variety of products ready to be harvested, all farming regions relevant to the supply of the human population, and all seasons. For the monitoring of open-land farmed vegetables and fruit it is recommended to limit the selection to those types that dominate the farming industry of a region either by surface area or production volume. This is meant to ensure that sampling is performed on about the same products in relation to the season and state of the vegetation in all federal states.

Analyses of lettuce, spinach, kohlrabi, leek and radish should be given preference during the months from March through May. For the period from June through September, it is recommended that beans, peas, cauliflower, white cabbage, red cabbage, Savoy cabbage, cucumber, carrots and onions be analysed. In October and November, late vegetables such as Chinese cabbage, endives, celery, and beetroot alongside with late cultivars of white and red cabbage and carrots should be investigated. During the winter months, analyses can obviously only focus on the winter-hardy vegetables kale, Brussels sprouts, Savoy cabbage and lamb's lettuce.

As far as fruits are concerned, strawberries and bushberries (black currant in particular), and cherries are focused on in June/July. From August, pip fruits such as apple and pear as well as stone fruits like plum, apricot and peach should be analysed. Amongst the native nuts, the analysis of hazel- and walnuts is of particular interest for monitoring purposes.

Cereals only need to be monitored at the time of harvest, which is when ripe grains of rye, wheat, barley and oats are to be studied. Whole ears or milled products such as flour and bran should not be used for analyses in order to maintain the comparability of measurement results.

Owing to customary German dietary habits, potatoes have also been included into the sampling schedule, even though these plants do not accumulate radionuclides.

In general, the sampling of plant material should only focus on botanically uniform material. Analyses of mixed samples, e.g., mixes of apples and pears or lettuce and iceberg lettuce, are not permissible. Likewise, cultivars should not be mixed.

2.2.2 Foodstuffs of animal origin

The routine monitoring programme (3) prescribes for the monitoring of foodstuffs of animal origin that sampling be performed regularly throughout the year. Samples should preferably be collected from amongst raw products from native livestock animals as these become available in abattoirs. Preference should be given to beef, pork, veal and poultry, and only muscle meat must be selected.

Up to 10 % of the number of samples prescribed in the routine monitoring programme may be used for analyses of game (deer, stag, fallow deer and wild boar) and lamb, which are known to accumulate radiocaesium.

Complying with the monitoring directive requires that the place of origin of the slaughtered animal, i.e., the place where the animal was raised to slaughter age, be recorded accurately.

2.2.3 Total diet samples

The measurement of total diet samples (5) is obligatory for an assessment of the radiation exposure that is caused by the ingestion of radionuclides (ingestion dose). In contrast to measurements taken from individual foodstuffs that will typically be performed using raw products, it will provide information on the radionuclide contents of foodstuffs ready for consumption and the contributions of individual foodstuffs relative to the amounts of food actually consumed by certain groups of the population. Samples of the total diet are to be obtained primarily from communal kitchens, such as hostels, barracks or canteens that offer complete meals.

A daily sample should comprise the entire amount of food a healthy adult would consume for breakfast, lunch, dinner and as in-between meals *including beverages*. Total diet samples are to be randomly collected at weekly intervals.

The weekly sample is gathered in plastic bags or sealable glass or plastic containers. The sample is homogenised immediately (see section 3.2) and stored refrigerated in this state (otherwise it is to be stored unprocessed under the conditions specified above until it can be processed into a weekly sample). If it becomes apparent that a weekly sample cannot be processed within 7 days, it is to be stored at -18 ºC. Four weekly samples are used to produce a mixed monthly sample for analysing the Sr-90 content.

The mass of the total diet is to be recorded prior to processing. If the samples ready for analysis cannot be measured right away, the individual samples are to be stored deep-frozen at -18 ºC. Keeping foodstuffs with a high water content cooled carries the risk of condensation precipitating on the walls of the storage containers. Its quantity needs to be recorded only in cases where the samples have not been prepared for analysis and weighed. A possible loss of water can be quantified by weighing the emptied containers before and after they have been dried. This loss of mass may need to be taken into account for the calculation of the radionuclide content per kg of wet mass (WM).

The daily amount of food consumed by an adult amounts to about 1,8 kg to 2,3 kg (5). This mass is sufficient for both direct gamma spectrometric measurements and gamma spectrometric measurements after ashing. For a weekly sample, the sampling location, date of sampling, mass of the sample, and its main constituents are to be recorded.

2.2.4 Baby and infant foodstuffs

Baby and infant foodstuffs (food and drinks), including milk substitute foods, are to be sampled on a monthly basis. In their case, production facilities for baby and infant food are to be chosen as sampling locations. If there is no such production plant in a country, large consumers, e. g., children's hospitals, nurseries and crèches, may be sampled instead.

Owing to the changes in the amounts consumed during the first year of life, activity data is to be provided per kg wet mass. The types and amounts to be sampled have been specified by the General Administrative Procedure for article 47 of the radiation protection ordinance ("Strahlenschutzverordnung", StrlSchV), Appendix 5, Table 1.

2.2.5 Sampling of imported products

The number of imported products to be monitored corresponds to about 15 % of the number of samples that are to be taken of domestic products. Both foodstuffs of plant and animal origin are to be analysed. Priority should once more be given to vegetables grown in open fields. Otherwise, those products should preferably be monitored that are relevant owing to the quantities they are imported in. Samples are to be collected either at the importers or directly at border crossings. Samples of imported products are to be collected only if the country of origin is known.

3 Analysis

3.1 Principle of the procedure

The prepared samples are directly analyzed with a Ge-gamma spectrometer in a suitable measurement geometry. In cases of detectors with a low efficiency (< 15 % compared to a 3" x 3" NaI(Tl)-detector for the 1,33 MeV-line of Co-60) and samples with a low concentration of radionuclides, it may be necessary to enrich the radionuclide concentration by ashing (see section 3.2.4) in order to achieve the detection limits required (3).

3.2 Sample preparation

3.2.1 General

It is known that aside from the way the sample is taken, the type of preparation of the sample may significantly influence the results of an analysis. It is therefore appropriate to apply standardised sample-processing procedures in order to obtain results that are truly comparable. The German Health Authority ("Bundesgesundheitsamt") has suggested procedures for determining heavy metal concentrations on and in foodstuffs that are also suitable for determining radionuclides (6).

Only those parts of agricultural products and foodstuffs are analysed in the form they are offered in that are indeed intended for consumption, and the results are related to these.

The following preparation procedures are to be used for the various foodstuffs (7):

3.2.2 Individual foodstuffs

Fresh vegetables: Parts that are not intended for consumption, such as spoilt leaves, stalks, bracts, wrapper leaves, husks, substantial deposits of dirt etc., are to be removed

Leafy vegetables:	Weighing of the sample and standardized rinsing (see below).
Sprout vegetables:	Removal of bases of roots and sprouts (e. g., onions) and peeling (e. g., onions and asparagus).
Fruity vegetables:	Removal of stalks, sepals and buds; cutting-off of ends in green beans and removing threads if necessary.
Root vegetables:	Removal of green parts including the bases and roots; scraping if the skin is not normally consumed; weighing of the sample, and standardized rinsing (see below).

Mushrooms: Removal of root base (mycelium) and flawed spots, weighing of the sample, and standardized rinsing (see below).

Potatoes: Removal of buds and possibly adhering crusts of soil, then weighing of the sample and standardized rinsing (see below), peeling, and briefly rinsing once more. Peeling is omitted if it can be expected that the skin will be consumed as well, e.g., new potatoes.

Fresh fruit:

Berries:	Removal of stalks, remnants of blossoms and spoilt berries. Dirty berries or those growing near the ground (e.g., strawberries) are to be weighed and rinsed in a standardized manner (see below).
Pome:	Removal of bases of flowers, stalks and pips (if not consumed as well).
Stone fruits:	Removal of stalks and stones.
Citrus fruits, melons, bananas:	Removal of peels and pips where applicable.

Rotten spots are to be removed in all types of fruit.

Nuts: Removal of the husks.

Cereals: The ripe grains are plucked from the ears. The cereals need to be clean, i.e., free of all constituents that do not form part of perfect basic cereals.

Meat: Muscle meat has to be freed of all bones, thick tendons, ligaments, firm and elastic connective tissues, as well as fatty deposits as far as possible.

Eggs: Removal of the shells.

Canned food: In the case of canned foodstuffs, the entire content of a can is used for analysis if both the filling material and infusion liquid are meant for consumption. If the infusion liquid is not consumed (e.g., in pickled cucumbers), only the filling material is to be examined.

The kitchen-ready product is washed in standing water for about 3 minutes. The ratio between the mass of the product and water should be 1:10. The product is then left to drain on a plastic sieve for about 2 minutes. If the product is heavily soiled, the washing process needs to be repeated in the same manner. Leafy vegetables and cabbages such as kale, parsley, lettuce etc. are slightly beaten dry in a dry towel. The parts that are ready for consumption are generally weighed prior to washing, but potatoes are weighed after the final washing.

3.2.3 Total diet samples

Weekly samples are produced on varying days of the week. These weekly samples may be homogenised according to the following scheme: Solid foodstuffs such as meat, sausage, cheese, bread, rolls, uncooked foods (vegetables, fruit), nuts etc. are to be chopped with a serrated knife before they are pre-homogenised in a kitchen food processor. A cutter may also be used during this step of the preparation process. The pre-homogenised constituents of the daily sample are then transferred to a high-performance blender with a volume of 2,5 litres to 3 litres and blended with the soft and cooked constituents as well as by gradually adding portions of the beverages until they form a homogenous paste. In order to prevent phase separations caused by solid fats (butter, margarine, lard) and plant oils, 1 ml of an emulsifier is to be added during the homogenisation process. Here it is suggested to use poly-oxyethylene sorbitanmono-oleate (TWEEN 80). The emulsifier will at the same time inhibit the frothing of the sample material that may be experienced when the beverages are added during the homogenisation process, in particular if they contain carbon dioxide gas. The beverages can also be used to flush solid constituents from their storage containers. To preserve the sample material (prevention of microbial decomposition) 4 ml of sodium azide as a 5 % aqueous solution should be added. If the volume of the daily sample exceeds the capacity of the mixer, homogenisation may also be performed with halved sample volumes. In order to achieve adequate mixing and prevent the detaching of constituents during the further processing of the sample halves, a suitably large bowl with a mixer attachment is needed.

Aliquots and, if necessary, weighed portions are taken from the homogenised weekly sample and used for the monthly mixed sample. The mass of the random weekly sample should depend on whether the gamma spectrometric analysis is to be performed directly or after dry ashing. It needs to be taken into consideration whether or not the Sr-89/Sr-90 concentration shall be determined as well (see procedure E-Sr-89/Sr-90-LEBM-01). For a direct measurement via gamma spectrometry, a weekly random sample of 1 kg (ca. 1 l) will suffice.

3.2.4 Ashing

The monitoring of foodstuffs for radionuclides often necessitates ashing the samples as an additional step in the preparation process. This is required in order to liberate the radionuclides of interest from the organic and aqueous matrix, which have a mass many orders of magnitude greater than compared to the former. In the case of minor contamination, the use of kilogram quantities of food will be required for analysis if results above the detection limit are to be obtained.

Dry ashing is preferable over other ashing methods when it comes to processing larger quantities of foodstuffs per individual analysis or large numbers of samples, as it is almost "maintenance-free". The disadvantages often discussed in literature, such as the long time required for preparation and the ashing process, loss of volatile radionuclides through uncontrolled reactive processes, the carbon content of

the ash, reactions of radionuclides with the material of the ashing vessel, and foul odours from carbonisation gases, can be largely, if not fully, avoided by taking appropriate measures.

The quantification of radionuclides requires sufficiently large amounts of ash. The following table shows the mean ash contents of many foodstuffs (8). The following rule-of-thumb formula can be used for estimating which mass of a product that is ready for consumption will be required to obtain about 10 g of carbon-free ash:

$$\frac{1}{\text{Ash content in \%}} = \text{Mass of the product in kg wet mass}$$

Considering that mean ash contents are quoted, larger sample quantities should ensure obtaining the mass of ash required.

The table furthermore contains data on mean Ca-contents, which are required for the analysis of Sr-89/Sr-90. With the analysis of Sr-89/Sr-90 typically supposing either 10 g of ash or a mass of ash that does not contain more than 1 g of calcium, corresponding connections between calcium content, mass of ash, and the wet mass of foodstuffs that facilitate the calculation of the required sample size are also included in the following tables (see also procedure E-Sr-89/Sr-90-LEBM-01)

Water content, mass of ash, and calcium content of selected foodstuff samples [according to (8)]

Product	Mean composition			1 g of Ca is contained in	
	Water %	Ash %	Calcium mg per 100 g WM	Wet mass kg	Ash mass g
Foodstuffs of animal origin:					
Meat:					
Mutton (muscle)	75,0	1,13	12	8,3	94,2
Veal (muscle)	76,4	1,19	13,0	7,7	91,5
Beef (muscle)	75,1	1,23	3,5	28,6	351,4
Pork (muscle)	74,7	1,05	3,2	31,3	328,1
Chicken (average)	60,0	0,93	11	9,1	84,5
Duck (average)	63,7	1,00	11	9,1	91,0
Turkey (average)	63,5	0,95	25	4,0	38,0
Game:					
Rabbit (average)	73,3	1,18	9	11,1	131,1
Stag (average)	74,7	1,07	7	14,3	145,7
Deer (dorsum)	72,2	1,19	25	4,0	47,6
Others:					
Calf's liver	71,2	1,37	8,7	11,5	157,5
Calf's kidney	75,0	1,10	10	10,0	110,0
Beef liver	69,9	1,40	7	14,3	200,0
Beef kidneys	76,1	1,17	11	9,1	106,4
Pork liver	71,8	1,25	10	10,0	125,0
Pork kidneys	76,3	1,20	7	14,3	171,4

Product	Mean composition			1 g of Ca is contained in	
	Water %	Ash %	Calcium mg per 100 g WM	Wet mass kg	Ash mass g
Foodstuffs of plant origin:					
Cereals and cereal products:					
Oats	13,0	2,85	80	1,3	35,6
Maize	12,5	1,30	15	6,7	86,7
Rye	13,7	1,90	115	0,87	16,5
Barley	11,7	2,25	38	2,6	59,2
Wheat	13,2	1,80	44	2,3	40,9
Rice (unpolished)	13,1	1,20	23	4,4	52,2
Rye flour, Type 1800	14,3	1,80	23	4,4	78,3
Wheat flour, Type 2000	15,0	2,00	32	3,1	62,5
Mixed wheat bread	37,6	1,54	17	5,9	90,6
Vegetables:					
Root and tuber vegetables:					
Potato	77,8	1,02	9,5	10,5	107,4
Kohlrabi	91,6	0,95	68	1,5	14,0
Carrot	88,2	0,86	41	2,4	21,0
Radish	93,5	0,75	33	3,0	22,7
Beetroot	88,8	1,00	29	3,5	34,5
Black salsify	78,6	0,99	53	1,9	18,7
Celeriac	88,6	0,94	68	1,5	13,8
Leafy, stalked and flowered vegetables					
Cauliflower	91,6	0,82	20	5,0	41,0
Watercress	93,5	1,10	180	0,56	6,1
Chinese cabbage	95,4	0,65	40	7,5	16,3
Endives	94,3	0,90	54	1,9	10,7
Lamb's lettuce	93,4	0,80	35	2,9	22,9
Kale	86,3	1,70	212	0,47	8,0
Lettuce	95,0	0,72	37	2,7	19,5
Leek	89,0	0,86	87	1,2	9,9
Rhubarb	94,5	0,64	52	1,9	12,3
Brussels sprouts	85,0	1,40	31	3,2	45,2
Red cabbage	91,8	0,67	35	2,9	19,1
Asparagus	93,6	0,62	21	4,8	29,5
Spinach	91,6	1,51	126	0,79	12,0
White cabbage	92,1	0,59	46	2,2	12,8
Savoy cabbage	90,0	1,10	47	2,1	23,4
Onions	87,6	0,59	31	3,2	19,0
Fruity vegetables:					
Green bean	90,3	0,72	57	1,8	12,6
Cucumber	96,8	0,60	15	6,7	40,0
Pumpkin	91,3	0,77	22	4,6	35,0
Paprika	91,0	0,57	11	9,1	51,8
Tomato	94,2	0,61	14	7,1	43,6
Legumes:					
White bean	11,6	3,90	106	0,94	36,8
Pea	77,3	0,92	24	4,2	38,3
Lentil, dried	11,8	3,20	74	1,4	43,2

Product	Mean composition			1 g of Ca is contained in	
	Water %	Ash %	Calcium mg per 100 g WM	Wet mass kg	Ash mass g
Mushrooms:					
Slippery Jack	91,1	0,62	25	4,0	24,8
Button mushroom (cultivated)	90,7	1,02	8	12,5	127,5
Chanterelle	91,5	0,77	8	12,5	96,3
Orange bolete	92,3	0,75	30	3,3	25,0
Yellow boletus	88,6	0,81	9	11,1	90,0
Fruit:					
Pip fruits:					
Apple	85,3	0,32	7,1	14,1	45,1
Pear	84,3	0,33	10	10,0	33,0
Stone fruits:					
Apricot	85,3	0,66	16	6,3	41,3
Cherry, sweet	82,8	0,49	17	5,9	28,8
Mirabelle (yellow) plum	82,4	0,46	12	8,3	38,3
Peach	87,5	0,45	7,8	12,8	57,7
Plum	83,7	0,49	14	7,1	35,0
Berries:					
Blackberry	84,7	0,51	29	3,5	17,6
Strawberry	89,5	0,50	26	3,9	19,2
Blueberry	84,9	0,30	10	10,0	30,0
Raspberry	84,5	0,51	40	2,5	12,8
Currant, red	84,7	0,63	29	3,5	21,7
Gooseberry	87,3	0,45	29	3,5	15,5
Grape	81,1	0,48	18	5,6	26,7
Tropical fruits:					
Orange	85,7	0,48	42	2,4	11,4
Banana	73,9	0,83	8,7	11,5	95,4
Tangerine	86,7	0,70	33	3,0	21,1
Lemon	90,2	0,50	11	9,1	45,5
Nuts:					
Hazelnut	5,2	2,44	226	0,42	10,8
Walnut	4,38	1,98	87	1,2	22,8
Other foodstuffs:					
Honey (blossom honey)	18,6	0,22	4,5	22,2	48,9
White wine (med. quality)	89,0	0,24	9	11,1	26,7
Red wine (light quality)	89,8	0,27	7	14,3	38,6
Beer (full-strength)	90,6	0,20	4	25,0	50,0
Coffee, roasted	2,75	4,13	146	0,69	28,3
Tee (black)	7,9	5,60	302	0,33	18,5
Hen's egg (content)	74,1	1,10	56	1,8	19,6
Margarine	18,3	0,25	10	10,0	25,0

The conditions under which optimal ashing results are obtained are outlined in the following procedure, while the basics have been described in detail in the literature (9-11). This method is suitable for use with liquid and solid foodstuffs, agricultural produce, and other biological materials. If deviations from this ashing method must

be made, respective hints are given in the descriptions of individual procedures for the analysis of radionuclides in foodstuffs.

Solid foodstuffs need to be chopped up to a size suitable for ashing. Food processors or cutters can be employed for the shredding of compact foodstuffs (fruits, vegetables, meat, potatoes etc.).

Fine-grained and dry samples (flour, milk powder etc.) are turned into a paste with distilled water in order to prevent them from pulverising during the ashing process.

Pulpy and liquid samples (fruit puree, milk, juice etc.) are not pre-treated but ashed as is. This means that drying or evaporating watery products prior to ashing is unnecessary.

The sample material is ashed in stainless steel trays that are lined to the rim with transparent paper (e.g., Schöllers-Hammer "hochtransparent", No. 205, 90 $g \cdot m^{-2}$ to 95 $g \cdot m^{-2}$). One layer of paper is required for solid samples, two for pulpy samples, and three for liquid samples. Solid sample material (e.g., leafy vegetables) is loosely filled into the bowl at an approximate filling weight of 40 $g \cdot dm^{-2}$ to 50 $g \cdot dm^{-2}$. In the case of total diet samples, which will typically be present as paste for ashing, a filling height of 1 cm in the ashing bowls should not be exceeded; this corresponds to about 100 $g \cdot dm^{-2}$ in filling weight. For liquids, a filling height of 1 cm to 1,5 cm applies. Filling heights of only 0,3 cm should be used for sugar, honey and comparable products in order to prevent the sample from brimming over.

Note
As the thickness of the layer increases, the ashing temperature within the sample will also increase and so will the total ashing time and the volatilisation of some radionuclides.

Approach

1. The ashing furnace is preheated to the required temperature. The optimal furnace temperature is 400 ºC (measured at the position of the ashing tray).

Note
Losses in caesium isotopes and other volatile radionuclides must be expected at ashing temperatures of > 400 ºC. On the other hand, the ashing process will then be quicker and more complete, and the carbon content of the ash will be decreased.

2. Once the predetermined furnace temperature has been reached, the stainless steel trays containing the samples to be ashed are placed in the furnace with the aid of a long pair of tongs or a hoist.

3. The thermo-elements used for measuring the temperature within the material to be ashed are submerged in the sample to the bottom of the stainless steel trays.

Note
The oxidation temperature during the ashing process may rise to 150 ºC above the set furnace temperature for short periods of time.

4. The air supply to the furnace is to be set as to keep the temperature within the sample to be ashed from rising as little as possible and minimize the formation of carbonisation gases and carbon residue.

Note
The optimal air supply must be determined empirically with thermo-elements on the basis of a comparative sample for each type of furnace separately.

5. Ashing takes from 2 hours (products with high water content, e.g., beverages) to 4 hours (dry products). Ashing is complete when the temperature measured by

the thermo-elements specified in point 3 has once more decreased to furnace temperature.

6. The stainless steel trays are removed from the furnace with the long pair of tongs or hoist. During their removal from the rack, the stainless steel trays need to be covered with stainless steel sheets in order to prevent the dispersal of the light ash constituents by air turbulence.

7. In order to prevent the absorption of water from the surrounding air by the ash right after having cooled down to room temperature, the ash is carefully transferred to a previously weighed plastic flask. Ash adhering to the stainless steel tray is removed with a fine-haired brush.

Note
The recovery of the ash is quantitative, because the transparent paper will have prevented the ash from "baking" on the surface of the stainless steel tray. The contribution by the ash of the transparent paper itself is negligible.

8. The ash is sealed in the plastic bottle and stored for subsequent analysis.

3.3 Radiochemical separation

No radiochemical separation is required for the gamma spectrometric procedure outlined here.

4 Measuring the activity

Fundamental aspects of, and aids for, gamma spectrometry are outlined in chapters IV.1.1 through IV.1.3 of this procedures manual.

Gamma spectra are measured with a Ge-spectrometer (> 15 % relative efficiency compared to a 3" x 3" NaI(Tl)-detector for the 1,33 MeV-line of Co-60). Samples are typically measured in flat-bottomed, cylindrical plastic vessels with screw caps (e.g., PE wide-necked, 1 l) with a defined geometry. Ashes are compacted to a defined volume. Liquid and powdery samples can be measured in ring vessels ("Marinelli" beakers).

To prevent rapid microbiological decomposition at ambient temperatures, homogenised samples may be left half frozen and covered with a thin layer of ethanol so that the sample cannot expand during the measurement period.

The sample vessel is placed on, or in front of, the detector. If sample masses vary, the impact of the filling height on the efficiency needs to be known. Routine measurements should be performed with a fixed geometrical arrangement of sample and detector.

To prevent contamination of the detector caps, it is recommended to cover the cap with polyethylene foil (ca. 0,1 mm thick) and fix it in place with adhesive tape. In the case of an external contamination of the foil by liquids or dust from a leak in the sample vessel, such contamination can be easily removed by replacing the foil. Even acidic radionuclide solutions will not very rapidly diffuse through this foil. If in spite of all precautions the detector cap (aluminium) becomes contaminated, the following decontamination procedure is suggested: After removing the protective foil from the detector, its surface or neck is first wiped with absorbent paper soaked with water, then with a solution of hydrochloric acid (1 $mol \cdot l^{-1}$), and finally with an aqueous solution of tetra-sodium salt of ethylene diamine tetra-acetic acid (EDTA) 0,1 %. The use of aqueous EDTA solution is always recommended when

so-called corrosion nuclides, like, e. g., zinc, manganese, iron, cobalt etc., have contaminated the surface of a detector. The procedure is eventually completed by cleaning the detector with water and acetone. The success of the decontamination procedure has to be verified by a measurement of the background spectrum.

The quantitative calibration of the gamma spectrometer can be performed in an energy- or nuclide-specific manner. Corresponding aqueous solutions of individual standards or nuclide mixes are commercially available. The energy specific calibration with solutions of multiple-line nuclides requires corrections for coincidence loss. In this respect, reference is here made to standard literature (12, 13, 14) and chapter IV.1.1 of this procedures manual. Furthermore, self-absorption effects during the measurement, resulting from the lower density of ashed samples compared to calibration solutions, need to be corrected for (see chapter IV.1.1 of this procedures manual).

5 Calculation of the results

High-performance software for the analysis of gamma spectra and for determining the activity of specific nuclides is available from a range of providers. Preference should be given to those programmes that make provision for the calculation of the decision thresholds and detection limits of all major radionuclides according to chapter IV.5 of this procedures manual (see also chapter 6) and use the decision threshold in their search algorithms as the key criterion for deciding whether or not a line is distinct from the background.

Measuring results above the detection limit and the detection limits themselves always have to be stated in $Bq \cdot kg^{-1}$ wet mass (WM), also in the case of a measurement on ash.

In the case of total diet samples, not only the activity of the sample in $Bq \cdot kg^{-1}$ has to be determined, but also the radioactivity in $Bq \cdot d^{-1} \cdot p^{-1}$ ingested by a person (p) per day (d). This value is computed by multiplying the specific activity, $Bq \cdot kg^{-1}$, with the weekly average of the daily amounts consumed ($kg \cdot d^{-1} \cdot p^{-1}$).

The date of sampling serves as the reference point of time.

In the case of energy-specific calibration on the basis of determining the specific activity, a_r, of a radionuclide, r, from the net peak area, the automatic analysis is verified applying the following equation:

$$a_r = \frac{N_n}{\varepsilon_r \cdot m \cdot p_\gamma \cdot t_m}$$

where:

ε_r the detection efficiency for the nuclide r;

N_n net counts (net peak area), $N_g - N_{0;}$

m wet mass of the sample;

p_γ absolute emission probability of the gamma radiation;

t_m measurement period of the sample.

As an example, the specific activity computed from a measurement on an edible mushroom (suede bolete), with the above-mentioned formula and parameters of m = 0,52 kg WM, t_m = 27570 s, p_γ = 0,85, N_g = 753 counts, N_0 = 445 counts, ε_r = 0,005906, yields $a_{Cs\text{-}137}$ = 4,3 $Bq \cdot kg^{-1}$ WM.

5.1 Consideration of uncertainties

The total uncertainty in specific activity of the radionuclides is based on several individual contributions:

— Uncertainties incurred in sampling;
— Uncertainties incurred during preparing the sample;
— Uncertainties incurred in calibration (ca. 5 %);
— Statistical counting uncertainties (1 % to 5 %);
— Uncertainties incurred in the correction of the density;
— Uncertainties incurred in the correction of coincidence loss (e. g., in Cs-134).

Without uncertainties stemming from sampling and preparation of the sample, a total measurement uncertainty of 10 % to 20 % can be expected.

For the calculation of the standard deviation, see chapter IV.5 of this procedures manual.

6 Characteristic limits of the procedure

The characteristic limits of the gamma spectrometric measurement on radionuclides in samples of foodstuffs are determined by the properties of the detector, by the nuclear properties of the radionuclides, and not least by the content of K-40 in the sample and the K-40 background of the measurement setup (see chapter IV.1.2 of this procedures manual).

In total diet samples, the K-40 content will average around 35 $Bq \cdot kg^{-1}$ WM.

Characteristic limits are calculated according to chapter IV.5 of this procedures manual (section 4.5, equation (4.32a)). If the algorithms of the analysis software used for the calculation of detection limits are not based upon the equation in chapter IV.5, corrections are necessary that may need to be applied a posteriori. Examples for the calculation of detection limits in gamma spectrometric procedures can be found in chapter IV.5, sections 6.4 and 6.5. In the present case, these examples can be followed analogously.

Detection limits in a sample of beef ($Bq \cdot kg^{-1}$ WM)

Radionuclide	Wet mass		Ash
Mass:	0,5 kg		50 g
Geometry:	1 l	1 l	0,1 l
E (keV) /	PE bottle	Marinelli	PE bottle
Co-60	1332,5	0,77	0,47	0,18
I-131	364,5	0,95	0,56	-
Te-132	228,2	0,95	0,55	0,16
I-132	667,7	0,82	0,45	-
I-133	529,9	0,95	0,55	-
Cs-134	604,7	0,85	0,46	0,15
Cs-137	661,7	0,98	0,54	0,25
Ba-140	537,4	3,42	1,88	0,57
La-140	1596,5	0,94	0,57	0,19

Values stated in the previous table were obtained from a sample of beef and can act as a guideline for detection limits.

Measurement conditions: direct measurement of beef samples [0,5 kg WM in 1 litre-PE bottles with screw caps (PE bottles) and 1 litre Marinelli beakers, respectively]; ashed sample [50 g ash from 1,4 kg WM (d = 0,7 g·cm^{-3}) in 100 ml-bottle with screw caps]; detector: Ge(Li) with 20 % relative efficiency; shielding: 3 cm lead, steel, aluminium and Perspex each (from the outside to the inside); measurement period: 12 h.

7 Catalogue of chemicals and equipment

7.1 Chemicals

— Homogenisation agent (e. g., TWEEN 80);
— Na-azide solution, 5 %;
— Acetone, techn.;
— Ethanol, techn.;
— EDTA, tetra-sodium salt of ethylene diamine tetra-acetic acid;
— Absorbent paper;
— Transparent paper (e. g., Schöllers-Hammer "hochtransparent", No. 205, 90 g·m^{-2} to 95 g·m^{-2}).

7.2 Equipment

— Household kitchen-type food processor;
— Household kitchen-type mixer;
— Ashing furnace with catalytic afterburner;
— Ashing containers made of non-tindering stainless steel (Remanit 1880 SST, material No. 4571), dimensions of bottom: 200 mm x 400 mm, 90 mm tall;
— Ring vessels (Marinelli beakers) and cylindrical vessels with screw caps for gamma spectrometric measurements;
— Ge- or Ge(Li)-semiconductor detector (> 15 % relative efficiency, half-width < 2,1 keV at 1,33 MeV) with pre-amplifier and high-voltage power supply unit;
— Main amplifier;
— Analogue-to-digital converter;
— Multi-channel analyser of the conventional type or with corresponding external storage with at least 4096 channels;
— PC with software suitable for the analysis of gamma spectra.

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