

### 10.3.3 *In vitro* measurements: excretion analyses

#### 10.3.3.1 Introduction

In section 7.5.1.2 “Analysis of excreta and other biological materials” the general recommendations of the ICRP in its Publication 78 [78ICRP] on excreta monitoring programmes are summarized.

The selection, use and interpretation of various bioassay approaches are based on the physical and biokinetic characteristics of the particular radionuclides considered. *In vitro* analysis refers to the identification and quantification of radionuclides in the body by analysis of material excreted or removed from the body. The main sources of bioassay data are urine, faeces, breath and blood. Other samples such as hair, teeth, saliva and nails have been employed in special cases. These biological samples provide an indirect measure of the internal radionuclide deposition because there is no direct information about the body or organ burdens. Proper interpretation of these results requires knowledge of the relationship between the presence of a radionuclide in the various bioassay samples and the organ radionuclide burdens of interest.

Various factors influence the applicability of any particular type of sample:

- The chemical element involved,
- Its physical and chemical form,
- The magnitude of internal deposition,
- Biological and physical half-lives of the radionuclides involved,
- Time elapsed since the intake occurred, and
- Sensitivity of the analytical and measuring method used.

For radionuclides emitting non-penetrating radiation, i.e. radiation being absorbed in the body, excretion analysis is the common method for monitoring workers exposed to radioactive material. This is the case with radionuclides with alpha particle radiation (such as thorium, uranium, plutonium, americium, curium) and radionuclides with soft beta particle radiation ( $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{35}\text{S}$ , and others).

*In vitro* techniques for evaluating the internal contamination include also time-consuming procedures for processing urine or faeces samples. Therefore, this technique should be used when *in vivo* methods are not applicable and the exposure is at low levels.

A critical point of the *in vitro* analysis is the sampling. For the application of common assessment models the excretion samples have to be collected in a well defined time interval. Another important point is that the collected bioassay samples have to be free of contaminations from outside.

For the interpretation of the data the biological variability of the excretion of a person, which can lead to different fractions of total body activity to be excreted in daily samples, must be considered. Consideration should be also given to whether medical interventions (chelating therapy, administration of diuretics, blocking agents and so on) could have influenced the pathway or excretion rates of radionuclides.

#### 10.3.3.2 Urine samples

Analysis of urine samples for excreted radionuclides is the method used most frequently for routine monitoring and assessment of internal contamination. Urine samples are easy to collect and rather reliably interpreted for material readily absorbed in the gastrointestinal (GI) tract.

A radionuclide in a relatively transferable (soluble) form entering the body reaches the bloodstream and a fraction of it is deposited in various body organs. The remainder is excreted predominantly in the urine. This biokinetic behaviour depends on the chemical form of the radionuclide involved entering the body, and from its metabolic behaviour in the body after incorporation. Typical radionuclides which will be monitored routinely via urine samples are for example  $^3\text{H}$ ,  $^{32}\text{P}$ ,  $^{35}\text{S}$ ,  $^{89}\text{Sr}$ ,  $^{147}\text{Pm}$ , thorium, americium and other alpha-emitting radionuclides (see also Table 10.24).

The nominal daily excretion rate of urine amounts to 1.2 l for females and 1.6 l for males [89ICR]. The individual excretion rate depends strongly on physiological and environmental conditions but also on individual nutritional habits. Therefore, the general sampling practice for routine monitoring is to collect 24-h-urine samples or equivalent. Repetitive sampling helps determining the time-dependent rate of excretion of a radionuclide after intake of the radionuclide into the body.

Radioactive material can be lost from solution by adsorption onto surfaces of some containers, and so on. For this reason samples must often be stabilised until analysis by refrigeration or freezing. Other methods are the addition of a carrier or of an acidic, basic or other preservative as is appropriate for the particular situation.

### 10.3.3.3 Faeces samples

Collection and analysis of faecal samples is another means of obtaining an indirect assessment of possible internal contamination. For routine monitoring, faeces are not used as often as urine, but analysis of faeces can provide at least qualitative information, particularly for relatively insoluble radionuclides.

Faeces samples are also very helpful for the quick assessment in the case of an extraordinary situation: The excretion of radionuclides by faeces specifically of those with low gastrointestinal absorption (see Chapter 7) is very often faster than by urine.

When an intake occurs by ingestion, the quantity of a radionuclide being excreted soon after ingestion represents the fraction of the radionuclide that has not been absorbed during the passage through the GI tract. In the case of inhalation there are two fractions; one fraction which is absorbed from the respiratory tract enters the bloodstream and is partly deposited in various organs. A part of it is subsequently excreted from the liver into the GI tract via the bile into the faeces. The second contribution comes from radionuclides translocated by swallowing from the respiratory tract directly into the GI tract and is partly retained from the small intestine or excreted via the faeces (see Chapter 7).

Long-term excretion of a radionuclide by faeces after its intake into the body is originating from delayed clearance of insoluble material from the pulmonary region of the respiratory tract or from the clearance of material that has entered the bloodstream and is excreted from the liver into the GI tract via the bile.

There are only few radionuclides for which a routine monitoring should be based on faecal excretion analysis:  $^{90}\text{Y}$ ,  $^{147}\text{Pm}$  (inhalation type S), thorium, curium and other alpha-emitting radionuclides (see also Table 10.24). Such a monitoring is adequate to identify incorporations which occurred just before sampling. Additionally, annual or biannual monitoring by faecal sampling may be used to check the reliability of air monitoring. On the basis of air monitoring results of a hypothetical faecal excretion rate can be derived; the comparison of measured faecal analysis can help to exclude a significant underestimation.

The general sampling practice for routine monitoring is to collect 24-h-faecal samples. The nominal transit time for material passing directly through the GI tract is about two days [30ICR], but this varies considerably with diet, health of the individual, and other factors. For this reason also a collection time of three consecutive days for faecal samples is recommended, in order to obtain reliable estimates of daily excretion rates.

Faecal samples are particularly subject to biodegradation. Therefore, they should be analysed promptly, ashed or preserved by deep freezing.

### 10.3.3.4 Exhalation

Breath samples can be useful in the case of incorporation monitoring for determining the amount of a radionuclide leaving the body by exhalation, i.e. in gaseous form such as  $^{222}\text{Rn}$ ,  $^{220}\text{Rn}$ ,  $^{14}\text{C}$ -labelled carbon dioxide or tritiated water vapour.

In the case of tritiated water about one third of an intake is excreted via breath, whose specific activity rapidly reaches equilibrium with that in body water [00IAE].

For example,  $^{220}\text{Rn}$  exhalation measurement [00Eis] allows the individual determination of  $^{228}\text{Th}$  body burdens without chemical preparation. That means,  $^{228}\text{Th}$  will be measured by its decay product  $^{220}\text{Rn}$  (daughter of  $^{224}\text{Ra}$ ) in the exhaled air of a person with thorium burden. So the worker has for breath sampling only to breathe into a collecting apparatus for up to 30 minutes, depending on the volume required. The detection limit of this method is about 1 Bq of  $^{228}\text{Th}$  in the lung and thus comparable to that of urinary excretion analysis. So this exhalation measurement method is best used to complement other assessment methods.

Quantification of  $^{232}\text{Th}$  by measurement of  $^{220}\text{Rn}$  in exhaled air requires additional information about the nuclide spectrum because of the unknown activity ratio between  $^{228}\text{Th}$  and  $^{232}\text{Th}$  in the body. For example, the diet and the mineral water could lead via  $^{228}\text{Ra}$  to an increased  $^{228}\text{Th}$  burden.

### 10.3.3.5 Other biological samples

Other biological samples, such as blood, hair, teeth, nails and nose blows can be used only as indicators for intake of radionuclides. Due to lack of biokinetic models or uncertainties in those models and data used for qualitative assessment of any internal contamination the results of assessments are generally not useful as a basis for quantitative dose estimations.

Blood samples provide the most direct source for estimating circulating internal contamination. But the majority of radionuclides are rapidly cleared from the blood. So, and because of recirculation in the body, measurements of activity in blood are generally only poor indicators of the total systemic content.

The analysis of nose blow samples can supplement monitoring for the purpose of screening for intakes, and give valuable information on the nature of the inhaled contaminant. Usually this method triggers other types or complementary analyses, such as urine or faeces samples.

Hair samples have been analysed for plutonium [81Too]. Caution is needed to ensure that hair care products have not resulted in contamination with naturally occurring radionuclides, such as uranium.

Teeth incorporate many of the bone-seeking elements, such as strontium, and may provide an indication of long-term, e.g. childhood exposures [95Hen].

### 10.3.3.6 Radiochemical analyses

A large number of different *in vitro* techniques have been developed for the detection and quantification of low-level activity of radionuclides in excreta. Table 10.24 gives an overview on some typical radionuclides and the complexity of the analytical procedure needed.

**Table 10.24.** Examples for some typical radionuclides for monitoring by *in vitro* techniques (U = urine, F = faeces)

Radio-nuclide	Inhalation type, Chemical compound	Biological sample	Analytical procedure
$^3\text{H}$	HTO	U	simple
$^{14}\text{C}$	org.	U	simple
$^{32}\text{P}$	F, M	U	simple
$^{90}\text{Sr}$	F, S	U	elaborate
		F	elaborate
$^{131}\text{I}$	F	U	simple
$^{147}\text{Pm}$	M	U	elaborate
$^{232}\text{Th}$	M, S	U	elaborate
		F	elaborate
$^{239}\text{Pu}$	M	U	elaborate
		F	elaborate

Explanation

Radionuclide:	The radionuclide possibly suitable for incorporation monitoring.
Inhalation type:	Inhalation type of the appropriate radionuclide specified as F = fast lung absorption, M = moderate lung absorption, and S = slow lung absorption.
Biological sample:	Determination of the activity in urine (U) samples or in faeces (F) samples.
Analytical procedure:	A rough overview on the extent of the analytical procedure (simple, elaborate) necessary to determine the radionuclide in the appropriate sample.

In general it is possible to classify the procedure for the determination of the activity concentration of the radionuclides in the following four main groups:

- Alpha particle spectrometry of urine samples, using elaborate and time consuming radiochemical procedures, e.g., for  $^{232}\text{Th}$ ,  $^{241}\text{Am}$ ,  $^{239}\text{Pu}$ ;
- Beta counting of urine samples without or with simple radiochemical procedures, e.g., for  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{32}\text{P}$ ;
- Beta counting of urine or faecal samples using elaborate and time consuming radiochemical procedures, e.g., for  $^{90}\text{Sr}$  and  $^{147}\text{Pm}$ ; and
- Gamma counting of urine samples without or with simple preceding radiochemical procedures, e.g., for  $^{60}\text{Co}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$  and  $^{131}\text{I}$ .

Regardless of which *in vitro* technique is used, the sample activity is calculated after the measurement by the equation

$$A_c = \left( \frac{N_s}{t_s} - \frac{N_b}{t_b} \right) \cdot \frac{1}{R} \cdot \frac{1}{E} \cdot \frac{1}{V} \quad (10.3.3.1)$$

where

$A_c$  = sample activity concentration in Bq per volume unit

$N_s$  = number of counts observed in the sample during the counting time  $t_s$

$N_b$  = number of counts of the background during the counting time  $t_b$

$t_s$  = sample counting time

$t_b$  = background counting time

$R$  = chemical recovery, expressed as a fraction

$E$  = counting efficiency, expressed as a fraction

$V$  = sample size as volume unit

If the counting times are equal the equation above will reduce to

$$A_c = \frac{1}{t} \cdot (N_s - N_b) \cdot \frac{1}{R} \cdot \frac{1}{E} \cdot \frac{1}{V} \quad (10.3.3.2)$$

When an internal tracer is added, e.g., in the case of alpha particle spectrometry, the activity may be calculated using this equation

$$A = A_t \cdot \left( \frac{N_s - N_b}{N_t - N_{b'}} \right) \cdot K \quad (10.3.3.3)$$

Where

$A$  = sample activity

$A_t$  = activity of the internal tracer added to the sample

$N_t$  = number of counts observed in the tracer region of interest (ROI)

$N_{b'}$  = number of counts of the background in the tracer ROI

$K$  = calibration factor applicable for the sample volume

In this case it is not necessary to know the chemical recovery and the efficiency.

The minimum detectable activity (MDA) corresponds to the level of activity which is required to ensure with some chosen level of confidence that the net signal will be detected. The definitions and equations are specified in the Safety Standards Series No. RS-G-1.2 [99IAE] and Safety Reports Series No. 18 [00IAE]. See also Section 10.3.2.8.

$$\text{MDA} = 3.3 \cdot \sqrt{\frac{N_b}{t_s} \cdot \left(1 + \frac{t_s}{t_b}\right)} \cdot \frac{1}{R} \cdot \frac{1}{E} \cdot \frac{1}{V} \quad (10.3.3.4)$$

When  $\alpha$ , the probability of a type I error (false positive), and  $\beta$ , the probability of a type II error (false negative), are both set equal to 0.05, MDA may be calculated in most cases as shown above (the symbols are the same as in the equations before).

In excretion analysis samples usually contain only low activities of a radionuclide. To ensure the reliable detection of such small activities low detection limits are essential. Therefore the following technical items have to be taken into consideration:

- The radiochemical recovery must be as high as possible.
- In general the counting or detection efficiency for alpha or beta particles cannot be higher than 50 % in the case of measuring flat source discs, because the solid angle seen by the detector cannot be more than  $2\pi$ . On the other hand the counting efficiency is a function of the distance between detector and source and varies for alpha particle spectrometry from a few percent up to 40 %. Therefore it is necessary to get an optimal adjustment between counting efficiency and energy resolution needed.
- A higher volume of the sample leads to a lower MDA per volume unit (see equation (10.3.3.4)).
- A lower number of background counts will result in a lower MDA. A main point to ensure this requirement is the careful radiochemical separation of the radionuclides which have to be determined.
- The MDA is inversely proportional to the counting time. That means the sample counting time should be as long as possible, but it depends on the time available.

Equations for the calculation of MDA for more complicated cases will be found in the Safety Reports Series No. 18 [00IAE].

Whatever technique is used for counting, most of the radionuclides analysed and especially the actinides, need to be isolated from the matrices. Numerous analytical procedures have been developed. They all are based on the same principle which consists of

- Sample preparation,
- chemical separation, and
- source preparation.

The sample preparation for urine involves wet ashing or co-precipitation of calcium phosphate, calcination and dissolution of the precipitate. Faeces are ashed and dissolved in acid. Insoluble materials such as silica are treated with fluorhydric acid. Similar procedures are used for tissue samples.

The chemical separation of the radionuclide to be analysed includes separation and purification on ion-exchange resin or by solvent extraction, or a combination of these two techniques.

The type of source preparation used is a function of the following measuring technique needed for the analysis.

For the alpha particle spectrometry of actinides the source is prepared by

- Direct evaporation,
- co-precipitation with lanthanide fluoride, or
- electrodeposition.

For beta counting with a proportional counter, the source is generally obtained by precipitation and filtration of the insoluble salt. For liquid scintillation counting (LSC) the purified radionuclide solution is mixed with an appropriate cocktail for the measurement.

The radiochemical analyses carried out routinely in the laboratory for monitoring potential incorporations of occupationally exposed workers has to be documented [00ISO2]. These written procedures shall include all steps starting with the receipt of the sample at the laboratory to measurement of the sample, or of an aliquot of the sample, and should contain all radiochemical procedures used.

For example, the description of the procedures can be very different:

- In the simple case of analysing tritium (see Table 10.24) it is only necessary to describe how to make the aliquot of the urine sample and the adding of an appropriate scintillation substance to be ready for the measurement by liquid scintillation counter.
- But in most cases the analytical procedure is more complicated and time-consuming, as seen in Table 10.24. In connection with the sample preparation (urine, faeces, tissue, blood etc.) and after adding an internal tracer to determine the chemical recovery, several nuclide-specific radiochemical separation steps have to be done. After electrodeposition on a stainless steel disk the radionuclide activity in the sample can be determined, e.g., by alpha particle spectrometry.

A lot of different analytical procedures have been published. A very fundamental publication in this field is the HASL-300 (Health and Safety Laboratory) document [97HAS]. It is well known as „The procedure manual of the Environmental Measurements Laboratory (EML)“ and covers the existing technology and procedures currently in use at EML (older procedures are updated and new procedures are added). This voluminous manual is also available as CD-ROM. The main task of this document is the analytical chemistry to be used for a wide range of radionuclides (e.g.,  $^3\text{H}$ , Fe, Sr, Tc, Pb, Po) with different matrices and measuring techniques. Detailed descriptions for the determination of thorium in urine and faeces, used in different laboratories in Germany, are given by Riedel et al. [93Rie]. The contribution of Harduin et al. [96Har] describes the analytical determination, especially for actinides in biological samples. Instructions about sequence analysis of actinides and  $^{90}\text{Sr}$  are found in the work of Wihlidal et al. [98Wih]. A fundamental and very informative technical note about the electrodeposition of actinides is given by L. Hallstadius [84Hal].

An important application of these analytical procedures and measuring techniques is the monitoring of workers involved in the decommissioning of nuclear facilities, because of the great variety of the radionuclides present and the conditions of the exposure. Establishing appropriate monitoring programmes and procedures is currently in progress. Due to the presence of transuranic radionuclides the analysis of excretion samples is required. So, for example, the contribution of Robredo et al. [00Rob] describes an excellent radiochemical procedure for the determination of americium and plutonium in urine samples. Neudert et al. [99Neu] present a very fast and closely method by using inductively coupled plasma-mass spectrometry (ICP-MS).

In case of monitoring potential incorporations of occupationally exposed workers, in some cases consideration has to be given to radionuclides incorporated from natural sources via food, especially drinking water. These intakes result in contributions of activities measured when monitoring workers and may mislead the dosimetry of occupationally exposed workers. Therefore it is necessary to have information on the natural contents, especially of thorium and uranium in human urine and faeces; see for example [97Rot] and [98Bey].

### 10.3.3.7 Measuring techniques

There exists a wide field of different measuring techniques to determine the activity of alpha and beta emitting radionuclides (alpha particle spectrometry, beta counting, liquid scintillation counting (LSC), fluorimetry, laser induced fluorimetry, gamma spectrometry, inductively coupled plasma-mass spectrometry (ICP-MS), neutron activation analysis (NAA) and delayed neutron activation analysis (DNAA)).

Table 10.25 gives a rough overview of these different techniques for the determination of radionuclides in excreta, including the values for the minimum detectable activity (MDA). The main measuring techniques for the determination of radionuclides in excretion samples are summarised below.

### Alpha particle spectrometry

This technique is the most commonly applied technique for measuring the isotopes of the different alpha emitters, such as thorium, uranium, plutonium, americium and curium. Alpha particle spectrometry is used to identify the isotopes and to quantify their activities.

Because of the non-penetrating radiation of the alpha emitter, the alpha particle spectrometry requires prior to the measurement an elaborate and time-consuming radiochemical procedure, as described above. For a quantitative nuclide-specific separation a very thin source is very important to get a good energy resolution of the alpha particle spectrum. So the common source preparation technique used is the electrodeposition on a stainless steel disk. This flat source will be measured in an alpha chamber in connection with a multichannel analyser to determine the different isotopes [84Hol].

By using internal tracers such as  $^{229}\text{Th}$ ,  $^{232}\text{U}$ ,  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  the radiochemical recovery is simple to determine. This also allows to measure all isotopes of the element analysed in the same spectrum with the same MDA.

### Beta counting

Radionuclides such as  $^{32}\text{P}$ ,  $^{89}\text{Sr}$ ,  $^{90}\text{Sr}$  or  $^{131}\text{I}$  can be measured after the chemical separation with a low background proportional counter. The technique is applicable for beta emitters of relatively high energy. As for alpha particle spectrometry, this technique requires the same type of radiochemical procedure as described before. The preparation of the source is generally obtained by precipitation and filtration of the insoluble salt.

**Table 10.25.** Measuring techniques for the analyses of excreta

Measuring technique	Radionuclide	Analytical procedure	Typical MDA
Alpha particle spectrometry	Th, U, Pu, Am, Cm	elaborate	1.0 mBq/l
Beta counting	$^{32}\text{P}$ , $^{89}\text{Sr}$ , $^{90}\text{Sr}$	elaborate	<80 mBq/l
LSC	$^3\text{H}$ , $^{14}\text{C}$ , $^{63}\text{Ni}$ , $^{241}\text{Pu}$	no elaborate	5 Bq/l 15 mBq/l
	$^{32}\text{P}$ , $^{89}\text{Sr}$ , $^{90}\text{Sr}$	elaborate	120 mBq/l
Gamma spectrometry	$^{60}\text{Co}$ , $^{134}\text{Cs}$ , $^{137}\text{Cs}$	no	200 mBq/l
Fluorimetry	U nat	simple	25 mBq/l
Laser-induced fluorimetry	U nat	simple	2 mBq/l
ICP-MS	$^{232}\text{Th}$ , $^{238}\text{U}$ , $^{239}\text{Pu}$ , $^{240}\text{Pu}$	no no elaborate elaborate	0.05 mBq/l 0.1 mBq/l 0.1 mBq/l 0.4 mBq/l
NAA	$^{238}\text{U}$ , $^{232}\text{Th}$	elaborate elaborate	0.0025 mBq/l 0.1 mBq/l
DNAA	$^{235}\text{U}$ , U nat, U nat	no no simple	60 mBq/l 25 mBq/l 0.5 mBq/l

Measurement with a low background proportional counter will lower the MDA as compared to measurement by liquid scintillation counting (LSC).

**Liquid scintillation counting** is especially useful for beta emitters of weak energy such as  $^3\text{H}$ ,  $^{14}\text{C}$  and  $^{63}\text{Ni}$ . For these radionuclides a direct measurement can be performed by mixing a small volume of the urine sample with the scintillation cocktail. Internal standards are often used to measure low-level radioactivity.

Liquid scintillation counting is also used to determine pure beta emitters like  $^{32}\text{P}$ ,  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$ . For the measurements of these radionuclides an elaborate radiochemical procedure is needed for separating the analyte from the matrix.

### Fluorimetry

Fluorimetry is a simple and fast technique for the determination of uranium in urine. Uranium is determined by the fluorescence produced when exposed to ultraviolet light. The urine sample may directly be fused in a platinum dish and measured with a fluorimeter. The limitation of this technique is its poor sensitivity and the measurement of total uranium only, mainly  $^{238}\text{U}$ .

### Laser-induced fluorimetry

The laser-induced fluorescence excitation technique needs some treatment of the urine like co-precipitation and calcination, or wet ashing before measuring the uranium content.

### Gamma spectrometry

In many cases gamma spectrometry can be directly applied on the urine samples. It should be noticed that for gamma emitters such as  $^{60}\text{Co}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$  and  $^{131}\text{I}$  *in vivo* measurements are mainly performed.

### Inductively coupled plasma-mass spectrometry (ICP-MS)

The sample is introduced into a mass spectrometer by means of a nebuliser in a plasma torch, and afterwards in a magnetic field that separates the atoms in their different masses and producing thus results for each of the isotopes of the element analysed. This technique has been used for uranium and thorium analyses in urine and human tissues. In fact, this technique is very sensitive for radionuclides with very long half-life such as  $^{235}\text{U}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$ . Beside acidifying the urine sample no other treatment is needed.

This mass spectrometry is also a very sensitive technique for measuring isotopic composition of plutonium. For plutonium analysis a radiochemical procedure is needed to separate plutonium from the bulk of inorganic material and from  $^{238}\text{U}$  which causes interferences at the mass 239, before being subjected to the mass spectrometric analysis. This technique is capable of measuring  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  separately, which is not possible by alpha particle spectrometry.

A clear advantage of ICP-MS is its rapidity. After treatment of the sample, if needed, the results can be obtained in a few minutes; see for example [98Kre], [02Sch] and [03Bou].

### Neutron activation analysis (NAA)

The neutron activation analysis has been used for the rapid determination of thorium in urine and in biological fluids, like serum. The technique involves some radiochemical procedures before and after irradiation of thorium with thermal neutrons, see for example [94Hub]. The photons of  $^{233}\text{Pa}$  obtained by irradiation of  $^{232}\text{Th}$  are counted. This technique is sufficiently sensitive to detect the natural content of  $^{232}\text{Th}$  in the environment, especially in food.



The NAA technique has also been reported for the determination of  $^{238}\text{U}$  in urine. In this case the photons of  $^{239}\text{Np}$  will be counted.

#### Delayed neutron activation analysis (DNAA)

Delayed neutron assay has been used for measuring  $^{235}\text{U}$ . As a screening method for uranium in urine, the evaporated urine was directly irradiated by thermal neutrons in a nuclear reactor. Then the delayed neutrons resulting from fission of uranium were counted. Good compilations about this measuring technique are found in [84Gab], [89Gla] and [94Hub]. For the determination of uranium in urine there is nearly no sample preparation necessary.

$^{232}\text{Th}$  could be fissured only by epithermal neutrons. For the analysis of thorium in urine samples a radiochemical separation technique is required.

DNAA is a very fast technique but measures only  $^{235}\text{U}$ , requiring information concerning the isotopic composition of uranium. For natural uranium a lower MDA can be achieved if uranium is isolated by adequate radiochemical separation.

### 10.3.3.8 Quality assurance

Quality assurance (QA) is an essential and integral element of the routine work in a laboratory to ensure the reliability of the bioassay data yielded in this laboratory. The QA practice in the laboratory can be achieved, e.g., by:

- Establishing a certified quality management system
- Accreditation of all analytical procedures and measuring techniques used in the routine work of this laboratory.

The normative requirements on a certified quality management system are laid down in EN ISO 9001: 2000 [00ISO1]. For the accreditation normative requirements exist for testing laboratories (i.e. „producing activity values“) in EN ISO/IEC 17025: 2000 [00ISO2]. In the case of laboratories performing inspections (i.e. „producing activity values including interpretation, e.g., dose values“) normative criteria are specified in ISO/IEC 17020: 1998 [98ISO]. General and helpful support is given in the paper „Quality management systems for technical services in radiation safety“ [03IAE].

The laboratory has to establish an in-house quality assurance plan to prove its organisational and technical competence. This plan should consist of two sections: the more formal part of „administration support“, and the technical part of „quality control“. In the first section the plan should include, among others, the following items:

- Organisational responsibilities
- Corrective actions
- Personnel qualifications
- Adequate operational environment
- Documentation of all aspects of the bioassay monitoring programme.

The technical part of the QA plan should include procedures as follows:

- Sample registration procedures
- Administrative procedure for each sample
- Procedure manuals for the radiochemical analyses and measuring techniques
- Instrumentation and calibration manuals
- Use of control charts and testing materials
- Participation in intra- and interlaboratory comparisons.

More detailed instructions are given in IAEA Safety Reports Series No. 18 [00IAE] and in ISO 12790-1 [01ISO]. The design and implementation of a QA plan is described in the Safety Guide No. RS-G-1.2 [99IAE].

In order to avoid systematic errors and ensure the quality of the analyses and techniques used, many additional measurements and methods have to be performed in the laboratory. For example, routine checks are necessary on:

- Radiochemical recovery
- Energy calibration
- Efficiency calibration
- Background measurements
- Blind analyses (blanks).

Based on the laboratory practice of many years, particularly the following problems have to be considered.

### **Uncritical observance of analysis procedures**

Generally analysis procedures are given for a defined matrix, e.g. for urine samples with an average content of mineral salt. In practice, however, the salt content is occasionally very high, e.g. from the administration of calcium tablets or excess consumption of lemonades with high phosphate content. In this case procedures should be modified by introducing additional separation steps or by using more efficient separation methods.

### **Avoiding cross-contamination**

Cross-contamination, particularly in monitoring incorporations of alpha emitters, may lead to error analyses with serious consequences. They occur when samples with very different concentrations are measured with the same laboratory equipment. When uranium and thorium isotopes are determined it is appropriate to conduct the measurement of urine and faeces samples in separate locations and with different equipment, because their natural excretion is quite different.

### **Errors during internal standardisation**

In the course of internal standardisation being commonly used in radiochemical analyses, the standard may contribute to the lasting inaccuracy of whole series of measuring results. This may be caused from, among others, errors of production or inappropriate storage and application. In some cases a “cleaning” of the standard from daughter nuclides is required immediately before it is used for analysis procedures.

### **Interference due to blind values from chemicals**

To assess natural  $^{232}\text{Th}$  excretions in urine, identification limits of a few  $\mu\text{Bq}$  excretions per day are required. In this range even p.A. qualities of the used chemicals may lead to relevant contamination. Thus in concentrated hydrochloric and nitric acid (each at p.A. quality) up to a maximum of 3 mBq  $^{232}\text{Th}$  per litre have been proved.

### 10.3.3.9 Examples for dose estimations from *in vitro* measurements

#### Case 1: Routine monitoring of depleted uranium ( $^{238}\text{U}$ )

Handling: Depleted uranium, ICRP inhalation type M,  
routine monitoring by analysis of the urine,  
two times per year (every 180 days)

Measured value  $m = 21 \text{ mBq/d}$  (24 h urine)

Dose assessment by using the following standard assumptions:

- Route of intake: acute inhalation
- Date of incorporation: in the middle of the monitoring interval
- AMAD:  $5 \mu\text{m}$
- Biokinetic and dosimetric data: ICRP 68 and ICRP 78.

The committed effective dose is calculated by the equation:

$$E = \frac{e(50) \cdot m}{E_E(\Delta t)} \quad (10.3.3.5)$$

where

$E$  = committed effective dose in Sv

$e(50)$  = dose coefficient for the effective dose in Sv/Bq

$m$  = value of the 24 h excretion in Bq/d, corrected at the end of the collecting period

$E_E(t)$  = excretion rate ( $E_E = E_U$  for urine), at the day  $t$  in Bq/d after acute inhalation of 1 Bq

$\Delta t$  = in the case of dose assessment by using standard assumptions half-time of the monitoring interval in days

#### Result:

$\Rightarrow$  Committed effective dose  $E = 0.28 \text{ mSv}$  half-yearly, calculated for  $^{238}\text{U}$   
with

$E_U(t) = 1.2 \cdot 10^{-4} \text{ Bq/d Bq}^{-1}$  at  $t = 90$  days for  $^{238}\text{U}$ , tabulated in [03Nos]

$e(50) = 1.6 \cdot 10^{-6} \text{ Sv/Bq}$  for  $^{238}\text{U}$ , tabulated in [78ICRP]

#### Case 2: Practical estimation of the date of incorporation of $^{35}\text{S}$

Handling:  $^{35}\text{S}$ , ICRP inhalation type F,  
routine monitoring by analysis of the urine monthly, i.e. every 30 days

Data from the 1<sup>st</sup> monitoring measurement:

Date of collecting the urine: 30.04./01.05.2001, 24 h urine.

Collected urine sample: 1100 ml, measured value 37 Bq/5 ml urine.

Measurement result  $m = 8.1 \text{ kBq/d}$

Dose assessment by using the same standard assumptions as in case 1, but intake and committed effective dose will be calculated in two steps, derived from the equation (10.3.3.5) in case 1:

intake  $I = m/E_U(t) = 7.4 \text{ MBq}$

and

committed effective dose  $E = I \cdot e(50) = 0.59 \text{ mSv}$  monthly

with

$E_U(t) = 1.1 \cdot 10^{-3} \text{ Bq/d Bq}^{-1}$  at  $t = 15$  days, tabulated in [03Nos]

$e(50) = 8.0 \cdot 10^{-11} \text{ Sv/Bq}$  for  $^{35}\text{S}$ , tabulated in [03Nos]

Problem: Notice of a significant content of  $^{35}\text{S}$  in the urine of one worker, but there was no remarkable irregularity (contamination, accident and so on) happened in the laboratory during the monitoring interval.

Therefore further measurements were done to try an estimation of the date of the incorporation and the amount of the intake to get, on this basis, a more realistic effective dose value:

Collecting date	Amount of urine [ml]	Collecting time [h]	Measured value [Bq/5 ml urine]	Remarks
30.04./01.05.01	1100	24	37	1 <sup>st</sup> monitoring
03.05./04.05.01	1300	24	2.1	special
07.05./08.05.01	600	12	2.1	measurements
02.06./03.06.01	1050	24	0.75	2 <sup>nd</sup> monitoring

To obtain the date of incorporation and the amount of the intake of  $^{35}\text{S}$  the following information of the radiation protection officer were used for the interpretation:

- acute inhalation, and
- inhalation type F and AMAD  $5\ \mu\text{m}$  of the  $^{35}\text{S}$  compound involved.

The procedure consists of the following steps:

1. Variation of the date of the incorporation.
2. Calculation of the belonging intake for each of the four measured values.
3. Calculation of the mean intake and the standard deviation.

The mean value with the minimum standard deviation SD should be the realistic time of incorporation.

	1. Measurement	2. Measurement	3. Measurement	4. Measurement	Mean value	SD*)
Measured value	8140 Bq/d	546 Bq/d	504 Bq/d	158 Bq/d		
27.04.2001:						
Time $\Delta t$	4 d	7 d	11 d	36 d		
$E_U(\Delta t)$	$0.0019\ \text{d}^{-1}$	$0.0016\ \text{d}^{-1}$	$0.0014\ \text{d}^{-1}$	$0.0005\ \text{d}^{-1}$		
$I = m/E_U(\Delta t)$	4284 kBq	341 kBq	360 kBq	316 kBq	1325 kBq	130 %
28.04.2001:						
Time $\Delta t$	3 d	6 d	10 d	35 d		
$E_U(\Delta t)$	$0.0035\ \text{d}^{-1}$	$0.0017\ \text{d}^{-1}$	$0.0014\ \text{d}^{-1}$	$0.0005\ \text{d}^{-1}$		
$I = m/E_U(\Delta t)$	2326 kBq	321 kBq	360 kBq	316 kBq	831 kBq	104 %
29.04.2001:						
Time $\Delta t$	2 d	5 d	9 d	34 d		
$E_U(\Delta t)$	$0.028\ \text{d}^{-1}$	$0.0017\ \text{d}^{-1}$	$0.0015\ \text{d}^{-1}$	$0.0005\ \text{d}^{-1}$		
$I = m/E_U(\Delta t)$	291 kBq	321 kBq	336 kBq	316 kBq	316 kBq	5.1 %
30.04.2001:						
Time $\Delta t$	1 d	4 d	8 d	33 d		
$E_U(\Delta t)$	$0.29\ \text{d}^{-1}$	$0.0019\ \text{d}^{-1}$	$0.0015\ \text{d}^{-1}$	$0.0005\ \text{d}^{-1}$		
$I = m/E_U(\Delta t)$	28 kBq	287 kBq	336 kBq	316 kBq	242 kBq	52 %

\*) standard deviation

Result of the measurements:

The date of incorporation is 29.04.2001, as shown in the table above (the standard deviation is minimal at this date).

The mean value of the intake  $I = 320$  kBq.

The committed effective dose  $E = 0.25$  mSv

Using this practical procedure in many cases it is possible to get information about the date of incorporation (as shown in the example above), the route of intake and the value for the AMAD.

### Case 3: Accidental inhalation of $^{239}\text{Pu}$ [99Kau]

Situation: A worker inhaled contaminated aerosol for approximately 10 minutes,  $^{239}\text{Pu}$ -oxide is involved

The following measurement results were achieved:

Time after the incident [d]	Faecal activity [Bq]	Urinary activity [mBq]
1	160	1.6
2		-
3		1.1
10	0.62	-
15	0.44	-

Each measurement value will be interpreted in terms of intake using the ICRP Publication 78 [78ICRP]:

- The first faecal measurement was a measurement of the pool of all faecal excretion during the first three days after the incident. To interpret this it is necessary to compare this value with the sum of the parameters for the first three days given in [78ICRP].
- Unfortunately for 15 days no value is tabulated in [78ICRP]. However, in the table for routine monitoring the value for the measurement period 30 days is suitable for this purpose because for routine monitoring an acute intake in the middle of the monitoring interval is assumed, i.e. 15 days before the measurement for a monitoring interval of 30 days.
- Because  $^{239}\text{Pu}$  has been inhaled as an oxide, inhalation type S is assumed.

With these assumptions the following intake values were derived, using equation (10.3.3.5):

- for fecal excretion measurements
 
$$I_1 = m / [E_F(1) + E_F(2) + E_F(3)] = 452 \text{ Bq}$$

$$I_2 = m / E_F(10) = 954 \text{ Bq}$$

$$I_3 = m / E_F(15) = 898 \text{ Bq}$$
- for urinary excretion measurements
 
$$I_4 = m / E_U(1) = 696 \text{ Bq}$$

$$I_5 = m / E_U(3) = 1320 \text{ Bq}$$

Using the following data for  $E_F(t)$  and  $E_U(t)$ , tabulated in [78ICR]:

Time after intake [d]	Urinary excretion [Bq/d Bq <sup>-1</sup> ]	Faecal excretion [Bq/d Bq <sup>-1</sup> ]
1	$2.3 \cdot 10^{-6}$	$1.1 \cdot 10^{-1}$
2		$1.6 \cdot 10^{-1}$
3	$8.3 \cdot 10^{-7}$	$8.4 \cdot 10^{-2}$
10		$6.5 \cdot 10^{-4}$
15*)		$4.9 \cdot 10^{-4}*)$

\*) Data for routine monitoring with an time interval of 30 days

Results:

In this case urinary and faecal excretion analyses give similar results. If several successive results are available, the best estimation of the intake  $I$  is obtained by taking the geometric mean of the  $I_i$  values established from these measurements. So in this case the geometric mean of all intake values is 810 Bq.

⇒ Committed effective dose  $E = 6.7$  mSv

with

$e(50) = 8.3 \cdot 10^{-6}$  Sv/Bq for  $^{239}\text{Pu}$ , tabulated in [78ICR]

In the case that there would have been an excretion enhancement by DTPA it would be necessary to consider this by some modifications, for example by division of the measurement values by an appropriate number.

**10.3.3.10 References for 10.3.3**

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