INTERNATIONAL STANDARD

ISO 13161

First edition
2011-10-01

Water quality — Measurement of polonium 210 activity concentration in water by alpha spectrometry

Qualité de l'eau — Mesurage de l'activité du polonium 210 dans l'eau par spectrométrie alpha

Reference number
ISO 13161:2011(E)

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Published in Switzerland

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13161 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radiological methods*.

Introduction

There are different techniques to measure ^{210}Po activity concentration in water: alpha spectrometry, liquid scintillation counting, alpha proportional counting.

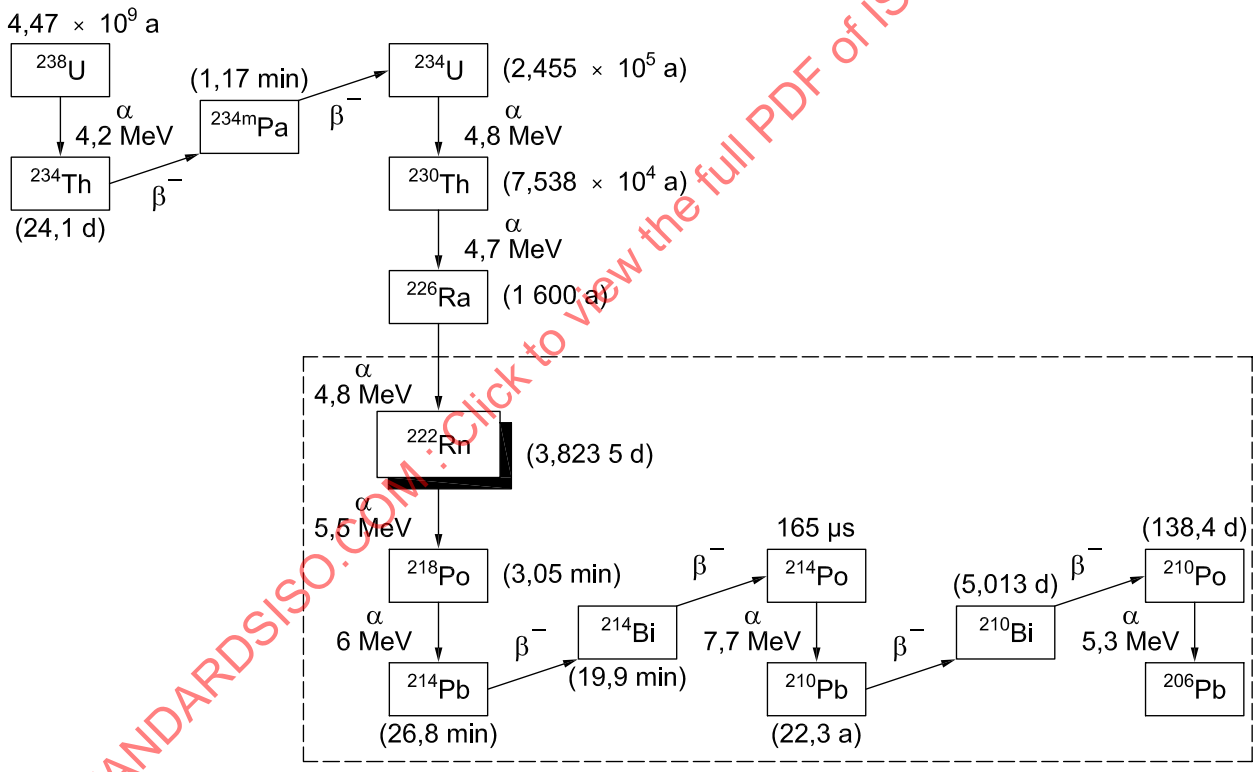
This International Standard describes a method for measuring ^{210}Po activity concentration in natural waters by alpha spectrometry.

Polonium 210 (^{210}Po) is a natural alpha-emitting radionuclide with a half-life of 138 d. It appears in the natural chain of uranium 238 (^{238}U) (see Figure 1). It is a long-life decay product of radon 222 (^{222}Rn) through lead 210 (^{210}Pb) (see References [5] to [9]).

Precautions are required when manipulating radioactive materials such as polonium isotopes.

The activity concentration ranges of ^{210}Po, in drinking waters for example, are generally very low, usually ranging from 1 mBq l^{-1} to 30 mBq l^{-1}.

This International Standard is applicable to all types of water, including sea water, and usually allows the measurement of ^{210}Po activity concentrations greater or equal to 5 mBq l^{-1}.



NOTE ^{206}Pb is stable.

Figure 1 — Uranium 238 and its decay products

Water quality — Measurement of polonium 210 activity concentration in water by alpha spectrometry

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies the measurement of ^{210}Po activity concentration by alpha spectrometry in all kinds of natural waters.

The detection limit of this method depends on the volume of the sample, the counting time, the background count rate and the detection efficiency. In the case of drinking water, the analysis is usually carried out on the raw sample, without filtration or other pretreatment.

If suspended material has to be removed or analysed, filtration at 0,45 µm is recommended. The analysis of the insoluble fraction requires a mineralization step that is not covered by this International Standard (see NF M 60-790-4[4]). In this case, the measurement is made on the different phases obtained. The final activity is the sum of all the measured activity concentrations.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 11929, *Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation — Fundamentals and application*

ISO 80000-10, *Quantities and units — Part 10: Atomic and nuclear physics*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms, definitions, symbols and units

For the purposes of this document, the terms, definitions, symbols and abbreviations given in ISO 80000-10 and the following apply.

3.1 Terms and definitions

3.1.1
certified reference solution
solution of known concentration traceable to primary or secondary certified reference solution standards of radioactivity

3.1.2
tracer solution
usually a secondary standard or reference material, such as ^{208}Po or ^{209}Po, employed to determine the chemical yield of the analysis

3.1.3
quality control standard
radioactive source used to demonstrate that the measurement equipment employed performs within defined limits

NOTE Quality control is usually carried out by the regular measurement of a suitable radioactive source in accordance with ISO 7870-1[1], ISO 7870-2[2], and ISO 7871[3].

3.2 Symbols, definitions and units

A	activity of the tracer added	Bq
c_A	activity concentration of ^{210}Po	Bq l^{-1}
c_A^*	decision threshold	Bq l^{-1}
$c_A^\#$	detection limit	Bq l^{-1}
$c_A^\triangleleft, c_A^\triangleright$	lower and upper limits of the confidence interval	Bq l^{-1}
R_c	chemical yield	1
R_T	total yield	1
r_0	background count rate in the ^{210}Po region of interest	s^{-1}
r_{0T}	background count rate in the tracer region of interest	s^{-1}
r_g	gross count rate of the sample in the ^{210}Po region of interest	s^{-1}
r_T	gross count rate in the tracer region of interest	s^{-1}
t_0	background counting time	s
t_g	sample counting time	s
U	expanded uncertainty calculated by $U = k \cdot u(c_A)$ with $k = 1, 2 \ldots$	Bq l^{-1}
$u(c_A)$	standard uncertainty associated with the initial measurement result	Bq l^{-1}
V	volume of the test sample aliquot	l
ε	counting efficiency	1

4 Principle

4.1 General

After sampling, the test sample undergoes a treatment which leads to an extremely thin deposit of the polonium on a metal disc, for measurement by alpha spectrometry.

^{210}Po has a half-life of 138,376 d ± 0,002 d (see Reference [11]).

The sample shall be analysed as soon as possible to give an activity concentration on the sampling date. If the time elapsed between sampling and measurement is long, the activity concentration measured requires correction and it is then necessary to know the ^{210}Pb and ^{210}Bi activity concentrations of the sample to adjust the ^{210}Po activity concentration on the sampling date.

4.2 Treatment

The main steps of the sample treatment are:

— filtration if necessary;

— acidification with concentrated hydrochloric acid or nitric acid and addition of a polonium tracer (^{208}Po or ^{209}Po) solution;

NOTE The polonium isotopes ^{208}Po (5,11 MeV alpha emission) or ^{209}Po (4,88 MeV alpha emission) can be used as tracers since interference with ^{210}Po (5,31 MeV alpha emission) is minimal for sources displaying good resolution (<50 keV FWHM); ^{209}Po is preferred, but ^{208}Po is acceptable.

— addition of a reducing agent (e.g. ascorbic acid);

— spontaneous deposition of a thin layer on to a metal disc.

The activity concentration measurement as well as the determination of the total yield is carried out by alpha spectrometry.

4.3 Principle of alpha spectrometry

The thin layer deposited on the metal disc allows the detection of alpha particles. The interaction of alpha particles and detector results in a change in (bias) current that is proportional to the energy of the particles.

The electronic pulses generated by the detector are amplified, and displayed as an energy spectrum using an analogue-digital converter, multiple channel analyser, and computer processing. The spectrum display enables the radionuclides present in the source to be identified and integration of counts enables the determination of activity concentration of the test sample, taking into account the background counting rates and/or the blank test and the total yield.

A blank test should be carried out with the same reagents replacing the water sample by water complying with ISO 3696, grade 3 previously used for the preparation of the reagents without tracer.

To ensure the acceptable performance of the detector system, a quality control standard shall be measured.

The chemical yield of ^{210}Po measurement is determined by adding a radioactive tracer. The total yield is a product of the chemical yield and the detection efficiency.

5 Reagents and equipment

5.1 Reagents

During chemical treatment and cleaning of the metal disc, use only reagents of recognized analytical grade. Use only reagents with no measurable ^{210}Po concentration.

5.1.1 Water, complying with ISO 3696, grade 3.

5.1.2 Tracer solution.

^{208}Po ($T_{1/2}$ = 1 058,5 d ± 0,7 d) or ^{209}Po ($T_{1/2}$ = 37 300 d ± 1 800 d) tracer solution of known activity; the spike is adjusted to the ^{210}Po activity concentration expected in the test sample (References [12][13]).

When ^{208}Po is used, its decay shall be taken into account in accordance with the information given on the calibration certificate.

NOTE The half-life of ^{209}Po and its associated uncertainty commonly used was subjected to a recent investigation that suggests an uncertainty of ±25 % instead of 4,8 % (Reference [14]).

5.1.3 Concentrated hydrochloric acid, 37 % mass fraction, or **concentrated nitric acid**.

5.1.4 Dilute hydrochloric acid or **dilute nitric acid**, to adjust the pH at the beginning of the treatment.

5.1.5 Ascorbic acid or **hydroxylamine hydrochloride**.

5.1.6 Ethanol.

5.2 Preparation material and treatment

The preparation material should be appropriate for the operating method used (Clause 7).

5.2.1 Standard laboratory equipment, including filtration material, hot plate, pH meter or pH paper.

5.2.2 Analytical precision scale.

5.2.3 Stirrer.

5.2.4 Equipment for the preparation of the thin layer deposit.

5.2.5 Metal disc, of a metal that allows reductive deposition of polonium (e.g. stainless steel [304L type], silver, nickel or another metal displaying this property).

5.3 Alpha spectrometry measuring equipment

The alpha spectrometry counting can be carried out using either gridded ionization chambers or thin semiconductor detectors.

A spectrum display is essential.

6 Sampling and samples

It is important that the laboratory receives the test sample as soon as possible.

Carry out sampling, handling, and storage as specified in ISO 5667-1 and ISO 5667-3.

7 Chemical treatment and deposit process

7.1 General

The volume of the test sample is variable; the usual quantity is between 150 ml and 2 000 ml.

Where necessary, the test sample can be filtered on a filter of 0,45 µm porosity (the use of a single-use filtering device is recommended).

Acidify the filtrate, preferably with dilute hydrochloric acid (5.1.4), to ensure that the pH of the test sample is below 1,5.

All reasonable precautions should be taken during handling and storage of the test sample to avoid contamination or degradation.

The verification that any contamination of reagents and residual contamination in the analytical equipment are below the detection limit for the analysis shall be carried out and documented (blank analysis).

The analysis shall be carried out under a fume-extracting hood.

NOTE If large test samples are used, or if a special study is being carried out, it is possible that a preliminary concentration prior to the first step of chemical treatment is necessary, e.g. co-precipitation of $Fe(OH)_3$ adding Fe^{3+} can be used. If this co-precipitation is used, the volume of analysed sample can be large and the detection limit decreases in the same proportion.

7.2 Chemical treatment

Take an aliquot of volume V from the test sample, e.g. 500 ml.

Adjust the pH with concentrated hydrochloric acid or concentrated nitric acid (5.1.3) in order to reduce the pH below 1,5. Add a known quantity of tracer solution (5.1.2) in order to enable the determination of the chemical yield without introducing large measurement uncertainties and avoiding contamination of the laboratory equipment. Ideally the ^{210}Po and the tracer peaks should be of the same magnitude (an ideal aim is the acquisition of between 400 counts and 10 000 counts in the tracer peak).

At this stage, a concentration step [dry evaporation and addition of dilute hydrochloric acid (5.1.4)] can be carried out by slow evaporation at a temperature lower than 80 °C (to avoid losses of Po) to dryness and then add, for example, 20 ml of 6 mol/l HCl.

Adjust the volume of the solution to approximately 100 ml with water (5.1.1).

A final HCl concentration between 0,1 mol/l and 3 mol/l and consistent use of the same concentration in order to maintain the repeatability level are recommended. The final volume can vary from 50 ml to 100 ml.

7.3 Disc cleaning

The disc shall be thoroughly cleaned in order to remove deposits of organic impurities, e.g. using ethanol; it may also be necessary to remove surface oxide deposits with dilute hydrochloric acid.

NOTE In the case of unprotected silver discs, the oxide and sulfur deposits present on the surface can be eliminated by polishing or by washing with dilute ammonia solution.

Rinse the disc with water.

7.4 Deposition phase

Transfer the solution to the deposition equipment (Annex A) and add an excess of the reducing agent, e.g. 0,1 g of ascorbic acid or hydroxylamine hydrochloride (5.1.5).

During the deposition phase, the metal disc catalyses the reduction of the polonium from Po^{4+} or Po^{2+} to metallic polonium. The addition of a reducing agent in the solution prevents the reoxidation (and therefore redissolution) of the deposited polonium on the disc by any oxidants that may be present in the solution, e.g. Fe^{3+}.

Stir the solution continuously using an automatic stirrer during the entire deposition phase.

The reduction kinetics of Po^{4+} or Po^{2+} to metallic polonium are slow at room temperature. The deposition rate can be accelerated by heating the solution to a maximum of 90 °C, making sure that the solution is in permanent contact with the metal disc, without excessive bubbling. Therefore, it is advisable to limit evaporation losses by keeping the acidity of the solution low. This phase shall be long enough to allow a good deposition yield and in normal circumstances is complete within 3 h.

Add ascorbic acid carefully as it can interfere with the spectral resolution. The quantity needed depends on the amount of Fe present in the sample, especially when an $Fe(OH)_3$ co-precipitation has been used.

On completion, polonium is deposited as a thin source on the disc. Rinse the disc with water (5.1.1) and wait until it is dry before measuring it by alpha spectrometry.

Depending on the deposition equipment used (e.g. hanging the disc in the solution), it is important to get the deposition on only one side of the disc. Cover one side of the disc with tape if necessary.

8 Measurement by alpha spectrometry

8.1 General

The counting time depends on the data quality objectives, uncertainty and detection limit to be achieved.

8.2 Quality control

Equipment quality control sources shall be measured (see 3.1.3) to verify that the measurement equipment is performing within agreed limits (see Reference [10]).

A thin source of $^{239/240}$Pu may be employed for this purpose as well to estimate the detection efficiency; the alpha emissions are in the 5,10 MeV to 5,20 MeV energy region, and there is no appreciable decay over the working life of the source.

The chemical yield of the process can be calculated using Equation (1):

$$R_c = \frac{R_T}{\varepsilon} \tag{1}$$

See 3.2 for definitions of the symbols. In general, the chemical yield obtained is greater than 90 %.

— The background rate of each detector is determined with an empty source support (cleaned disc); this shall take at least as much time as the counting of a sample.

NOTE The optimum time for the measurement of the background source can be shown to be equal to that of the source from very low activity sources (see Reference[12]).

— The blank analysis [i.e. analysis carried out with water (5.1.1) containing no detectable ^{210}Po without adding tracer solution (5.1.2)] value shall be compared to the totality of the background values obtained from the same detector. This value shall be comparable to the background value measured with an empty source support (cleaned disc) in the energy region of ^{210}Po and of the tracer to make sure that there is no reagent or laboratory equipment contamination.

— The background value of the detector is r_0. A “blank” value significantly larger than r_0 demonstrates either the presence of polonium in the reagents and/or equipment, or a cross-contamination.

8.3 Measurement

The source is measured using grid ionization chambers or thin semiconductor detectors (See Annex B).

9 Expression of results

9.1 General

See 3.2 for definitions of the symbols used in the following.

Measurement results are expressed as activity concentrations, in becquerels per litre, with associated uncertainty, presented in a test report. The coverage factor for the expanded uncertainty is specified in the presentation of results.

Note that the expression of results is an estimation of the “true” value, associated to an uncertainty, which is itself a combination of elementary uncertainties.

Where alpha spectrometry is used to measure radionuclide activity concentration, only the standard uncertainties of the following parameters are taken into account:

a) gross counting and background, integrating the number of counts into the corresponding peak;

b) mass of the added tracer (or volume of the tracer solution);

c) activity and possible impurities of the tracer;

d) volume of the test sample.

Other uncertainties are small in comparison to the parameters listed in a) to d) and may be disregarded, unless there is reason to include them.

Note also the recommendations in the following three paragraphs.

When ^{209}Po is used as a chemical yield tracer, ^{209}Po activity should be corrected for the decay probability of 99,52 ± 0,04 % and also according to his half-life and the elapsed time. Verification that the uncertainty associated with the half-life of ^{209}Po does not lead to significant bias in the result is recommended.

When the tracer quantity is added by volumetric method, it is necessary to know the exact volumetric activity of the tracer solution. Use of a gravimetric method to add the tracer is recommended.

When ^{210}Pb is known to be present, the calculation of the activity at the sample reference date can be complex. When ^{210}Po deposition and measurement are not done immediately, ^{210}Pb and/or ^{210}Bi activities should also be measured in order to make the proper corrections.

9.2 Total yield

Total yield is the product of the chemical yield and the counting efficiency.

The chemical yield can be considered as a quality control parameter.

Total yield, R_T, is calculated from the sample spectrum using Equation (2):

$$R_T = \frac{(r_T - r_{0T})}{A} \tag{2}$$

See 3.2 for definitions of the symbols. Decay correction is not taken into account in Equation (2), but shall be done if necessary.

9.3 Activity concentration of ^{210}Po in the sample

In all the equations, counting time is taken to be identical for the measurement of the sample and the measurement of the background.

The activity concentration, in becquerels per litre at the date of measurement, of ^{210}Po of the sample is calculated using Equation (3):

$$c_A = \frac{(r_g - r_0)}{V\ R_T} = (r_g - r_0)w \tag{3}$$

where

$$w = \frac{1}{V\ R_T}$$

Note the following remarks on the need for corrections.

If ^{208}Po or ^{209}Po are used as tracers, a correction due to impurities is necessary only if these have been declared by the supplier or are otherwise known to be present.

The decay correction of the ^{210}Po activity concentration is made if necessary, e.g. for a very long counting time or a delay between the plating date and the counting time.

9.4 Combined uncertainties

According to ISO/IEC Guide 98-3, the combined uncertainty of c_A can be calculated using Equation (4):

$$u(c_A) = \sqrt{w^2\left[u^2(r_g) + u^2(r_0)\right] + c_A^2\, u_{rel}^2(w)} = \sqrt{w^2\left(\frac{r_g}{t_g} + \frac{r_0}{t_0}\right) + c_A^2\, u_{rel}^2(w)} \quad (4)$$

where the uncertainty of the counting time is neglected and the standard uncertainty of w, $u_{rel}(w)$, is calculated using Equation (5):

$$u_{rel}^2(w) = u_{rel}^2(R_T) + u_{rel}^2(V) \quad (5)$$

The relative standard uncertainty of R_T, $u_{rel}(R_T)$, is calculated using Equation (6):

$$u_{rel}^2(R_T) = u_{rel}^2(r_T - r_{0T}) + u_{rel}^2(A) = \frac{\left(r_T / t_g\right) + \left(r_{0T} / t_0\right)}{\left(r_T - r_{0T}\right)^2} + u_{rel}^2(A) \quad (6)$$

where $u_{rel}^2(A)$ includes all the uncertainties related to the tracer activity, i.e. in the standard solution, preparation of the tracer solution, and the addition of the tracer solution to the sample.

For the calculation of the characteristic limits, $\tilde{u}(\tilde{c}_A)$ is required, i.e. the combined uncertainty of c_A as a function of its true value (see also ISO 11929), calculated using Equation (7):

$$\tilde{u}(\tilde{c}_A) = \sqrt{w^2\left[\frac{(\tilde{c}_A / w + r_0)}{t_g} + \frac{r_0}{t_0}\right] + \tilde{c}_A^2\, u_{rel}^2(w)} \quad (7)$$

9.5 Decision threshold

The decision threshold c_A^*, expressed in becquerels per litre, is obtained from Equation (7) for $\tilde{c}_A = 0$ (see ISO 11929).

This yields:

$$c_A^* = k_{1-\alpha}\, \tilde{u}(0) = k_{1-\alpha}\, w \sqrt{\frac{r_0}{t_g} + \frac{r_0}{t_0}} \quad (8)$$

where $\alpha = 0{,}05$ with $k_{1-\alpha} = 1{,}65$, a value often chosen by default.

9.6 Detection limit

The detection limit $c_A^\#$, expressed in becquerels per litre, can be calculated using Equation (9):

$$c_A^\# = c_A^* + k_{1-\beta}\, \tilde{u}(c_A^\#) = c_A^* + k_{1-\beta} \sqrt{w^2\left[\frac{(c_A^\# / w + r_0)}{t_g} + \frac{r_0}{t_0}\right] + c_A^{\#2}\, u_{rel}^2(w)} \quad (9)$$

The detection limit can be calculated by solving Equation (8) for $c_A^\#$ or more simply by iteration with a starting approximation $c_A^\# = 2c_A^*$ in terms of the right side of Equation (9).

One obtains $c_A^{\#}$ with $k_{1-\alpha} = k_{1-\beta} = k$:

$$c_A^{\#} = \frac{2c_A^{*} + \left(k^2\, w\right)/t_g}{1 - k^2\, u_{rel}^2(w)} \tag{10}$$

Values $\alpha = \beta = 0{,}05$ and therefore $k_{1-\alpha} = k_{1-\beta} = 1{,}65$ are often chosen by default.

9.7 Confidence limits

The lower, $c_A^{\triangleleft}$, and upper, $c_A^{\triangleright}$, limits of the confidence interval are calculated by using Equations (11) and (12) (see ISO 11929):

$$c_A^{\triangleleft} = c_A - k_p\, u(c_A);\ p = \omega\left(1 - \frac{\gamma}{2}\right) \tag{11}$$

$$c_A^{\triangleright} = c_A + k_q\, u(c_A);\ q = 1 - \frac{\omega\gamma}{2} \tag{12}$$

where

$$\omega = \Phi\left[\frac{c_A}{u(c_A)}\right]$$

Φ being the distribution function of the standardized normal distribution and $1 - \gamma$, the probability that the true value of c_A is situated in the confidence interval.

Set $\omega = 1$, if $c_A \geq 4\, u(c_A)$. In this case:

$$c_A^{\triangleleft\triangleright} = c_A \pm k_{1-\gamma/2}\, u(c_A) \tag{13}$$

Values $\gamma = 0{,}05$ with $k_{1-\gamma/2} = 1{,}96$ are often chosen by default.

10 Test report

The test report shall conform to ISO/IEC 17025 requirements. It shall contain at least the following information:

a) the test method used, with reference to this International Standard (ISO 13161:2011);

b) all information necessary for the complete identification of the sample;

c) units in which the results are expressed;

d) ^{210}Po activity concentration reference date — if the reference date is not the deposition date, then the equilibrium between ^{210}Po, ^{210}Pb and ^{210}Bi shall be taken into account to correct the activity concentration;

e) test result, $c_A \pm u(c_A)$ or $c_A \pm U$, with the associated k value.

Complementary information can be provided such as:

f) probabilities α, β, and $(1 - \gamma)$;

g) decision threshold and detection limit;

h) date of deposition and date of measurement;

i) dependent on the customer request, there are different ways to present the result:

   1) when the activity concentration c_A is compared with the decision threshold (see ISO 11929), the results of the measurement should be expressed as $\leq c_A^*$ when the result is less than or equal to the decision threshold,

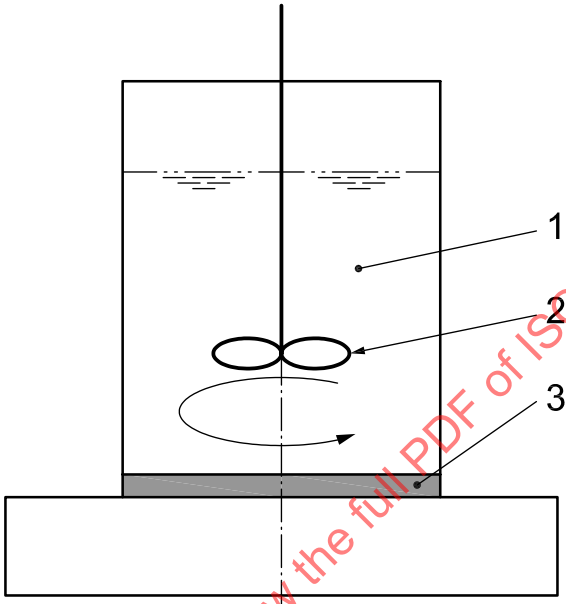
   2) when the activity concentration c_A is compared with the detection limit, the result of the measurement can be expressed as $\leq c_A^\#$ when the result is less than or equal to the detection limit.

NOTE Note that $U = k\,u(c_A)$ with $k = 1$ or 2.

In accordance with ISO/IEC 17025, additional information can be provided, e.g. sampling details (date, etc.).

Annex A
(informative)

Cell deposit examples



Key
1 solution
2 stirrer
3 metal disc

Figure A.1 — Room temperature deposit system