

# **Preface regarding requirements for sampling of drinking water and groundwater**

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# Preface regarding requirements for sampling of drinking water and groundwater

On 22 October 2013, the Council of the European Union adopted Council Directive 2013/51/EURATOM laying down requirements for the protection of public health with regard to artificial and natural radioactive substances in water intended for human consumption (drinking water) [1]. This was transposed into German law by the Third Ordinance amending the Drinking Water Ordinance (TrinkwV), which came into force on 26. November 2015 [2]. To ensure the monitoring of drinking water quality with regard to radioactive substances, parameter values were specified for radon (Rn-222), tritium (H-3) and for the reference dose (effective ingestion dose). Requirements for sampling and measurement have been formulated to verify compliance with these parameter values [2]. In the following, established procedures for sampling of groundwater and drinking water specified in various standards and regulations will be summarized and supplemented by recommendations for their practical implementation.

## 1 Basic principles of sampling

The sampling location, the sampling frequency, the sampling technique as well as the sample pre-treatment and analysis are basically defined by the objective of the sampling. The sample must be representative for the target [3].

In the case of groundwater sampling, this means that the hydrogeological and structural conditions on-site as well as the groundwater conditions must be taken into account [4, 5]. These aspects determine the method of representative sampling – pump, sampling bailer or beaker.

When sampling drinking water from municipal or comparable water supply systems, the complexity of the distribution system, the volume of water distributed in the system and the number of consumers affected must be taken into account. Furthermore, the following aspects need to be considered:

- the impact of external factors (e. g. river floods in connection with bank filtration or constructional measures);
- the stability of the system (e. g. time sequences in the mixing ratios of water from different sources);
- technological processes (e. g. filter flushing).

The sum of these factors is decisive for the type of sample, i. e. whether a representative composite sample or grab sample is required for the measurement purpose [6].

Composite samples provide flow-, time- or volume-dependent average data and are suitable to evaluate compliance with established parameters. In contrast, taking grab samples provides spatial and temporal resolved information, which is suitable in case of heterogeneous flow conditions or unstable and unsteady parameters. The collection of grab samples is essential if the conformance of a parameter value based upon average water quality data needs to be verified.

**Note:**

The terminology used for composite and grab samples corresponds to DIN EN ISO 5667-1 and the technical literature [3, 7]. The term "parameter" is used here to refer to all measured variables specified in the Drinking Water Ordinance or in other regulations.

## 2 Sampling procedure

At wells for water supply purposes, the collection of raw water and drinking water samples is usually carried out at regular water supply points of the drinking water installation. Before sample collection, an ample flow must be ensured. In order to remove any pipe deposits and stagnant water, the supply pipe is usually rinsed for two to three minutes at a constant flow rate and then flushed until a constant water temperature is reached [6]. Alternatively, according to [6], five times the determined flushing time can be applied for a water volume to be displaced. If water supply points with continuous outflow are available, they are preferred for sampling, since the constant flow of water largely eliminates chemical and microbiological sources of contamination. Sampling is to be carried out from the continuous water flow.

At groundwater monitoring wells, sampling is usually performed by pump or bailer according to the structural, geohydraulic and hydrochemical conditions. Representative samples can only be obtained from the continuous water flow after a sufficient volume of stagnant water has been exchanged (hydraulic criteria) by pumping. Samples can be collected as soon as the on-site parameters, such as pH value, electrical conductivity or temperature in the water are stable. Under certain conditions sampling via bailer can also be conducted after pumping. Groundwater sampling at springs and water-bearing mining galleries is usually done with a sampling beaker at the point of discharge [4, 5].

For further information on planning and preparation as well as execution and documentation of groundwater sampling, it is referred to the national regulations [e. g. 8, 9], the technical bulletins of the German Technical and Scientific Association for Gas and Water [5] and the corresponding DIN and ISO standards [4, 10].

Specific information on necessary sample volumes (see Section 2.1) and sample storage (see Section 2.2) must be communicated to the sampling technician in advance by the test laboratory or the measuring station in charge.

## **2.1 Sampling volume**

The sample volume to be taken depends on the planned analyses for the parameters to be determined. In general, it should be sufficient to maintain the status of a representative sample and not limiting subsequent analyses.

The necessary sample volume for the parameters to be determined can be estimated based on the given detection limits in [2]. In addition, the number of analyses planned including possible repetitions as well as the necessity of retaining sample material must be taken into account.

While a sample volume of one litre is usually sufficient for screening parameters such as the gross alpha activity concentration, a minimum volume of approximately ten litres is required for a complete analysis of the natural radionuclides U-234, Ra-228, Ra-226, Pb-210 and Po-210 according to [2].

## **2.2 Sample containers, preservation and storage**

The samples are taken in pre-cleaned, unbreakable plastic containers made of polyethylene (PE). Pre-cleaning of the plastic containers with detergents and subsequent rinsing with diluted nitric acid ( $1,7 \text{ mol}\cdot\text{l}^{-1}$ ) and distilled water is recommended.

To stabilize the sample, to avoid microbiological hazards or to prevent radionuclide adsorption on the inner walls of the sample container, it is recommended to add preservatives directly to the sample taken. This allows storage of the sample for one to a maximum of two months [10]. If the use of preservatives is not permitted at the place of sampling for reasons of transport safety or drinking water hygiene, the sample must be transferred to the test laboratory or measuring station as soon as possible – ideally until the following day. In this case, the sample is stabilized in the respective laboratory.

In principle, concentrated nitric acid ( $14,3 \text{ mol}\cdot\text{l}^{-1}$ ) is suitable for stabilizing a water sample, whereby the sample is adjusted to a pH value of less than 2 [10, 11]. For a 10 l sample volume, 30 ml of concentrated nitric acid ( $14,3 \text{ mol}\cdot\text{l}^{-1}$ ) is usually required. Samples intended for the analyses of Rn-222, H-3, C-14 and, if necessary, I-131 are handled differently. The special case of Rn-222 is considered in more detail in Section 2.3; for sample conservation for the determination of the activity concentrations of H-3, C-14 and I-131, reference is made to the corresponding Procedures Manual of the federal coordinating office H [11].

According to [10], a cooling temperature of  $(3 \pm 2) ^\circ\text{C}$  during sample transport and storage is suitable to prevent microbial growth, especially when no preservatives were added to the samples on-site. For the analyses of radionuclides, sample cooling is usually not necessary; the special case of Rn-222 must also be taken into account here (see Section 2.3).

If filtration is required to separate the dissolved fraction from the particulate fraction, this must be done before the addition of preservatives. Filters with a pore size of  $0,45 \mu\text{m}$  are usually used for this purpose. In the case of filtration after the addition of preservatives, it must be considered that fractions of the radionuclide initially bound to the particulate phase may have desorbed into the solution. This might consequently lead to a corresponding overestimation of the dissolved fraction.

If the activity concentrations of the Rn-222 decay products Pb-210 and Po-210 are to be determined, Rn-222 must be completely removed after the sample has been taken either directly on-site or, at the latest, in the test laboratory. In order to drive Rn-222 out of the water, air or nitrogen is uniformly purged through the sample with a diaphragm pump. The necessary duration of the flow depends, among other things, on the ratio of the volume of air flowed through to the volume of water. For a 10 l sample container, for example, an air flow of approx. 14 litres per minute with a uniform distribution of the air over the bottom of the sample container is sufficient for complete de-gassing within approx. 30 minutes. A control measurement to check the Rn-222 content remaining in the sample can provide information on this.

When storing samples, the physical half-lives of the radionuclides of interest must be taken into account as well as the changing activity ratios. For example, a sample intended for measuring the screening parameter gross alpha activity should not be stored for a longer period of time, since the nuclide composition can change due to the decay of short-lived radionuclides and the ingrowth of daughter nuclides, e. g. Po-210 and Th-228. A storage period of about two weeks has proven successful. Experience has shown that this time span is sufficient to avoid detection of any present Ra-224 during the gross alpha activity concentration.

The determination of Po-210 activity concentration with unknown Pb-210 activity concentration is recommended to be started within a few days after collection. Otherwise the ingrowth of Po-210 from Pb-210 additionally need to be considered.

Information on special issues regarding sample storage can also be found in the respective Procedures Manual [11].

### 2.3 Special case: Radon (Rn-222)

Radon-222 is a radioactive noble gas with a half-life of 3,8 days, whose solubility in water decreases with increasing temperature. Due to the volatility of Rn-222, contact and exchange with the surrounding air should be minimized during sampling. The container material and the container closure must be gas-tight for a period of about one week. Usually, a sample volume of 500 ml is taken for Rn-222 analysis.

The ISO standard [10] also recommends cooling during transport and storage of samples and the use of glass bottles as sample containers. In practice, the use of thick-walled bottles made of polyethylene terephthalate (PET), which are used, for example, for pharmaceutical products and as beverage bottles, has also proven successful.

Due to the short half-life of Rn-222, transport and associated short-term storage should not take more than two days in total. For the cooling of samples, commercially available cool boxes that ensure a temperature of about 5 °C to 10 °C are commonly used.

Two procedures are available for taking samples:

- a) If filling on a regular water supply point is possible, a sample container is slowly filled from the bottom to the top using an attached silicone hose. It is important to allow the water to overflow twice the volume of the bottle in order to flush out any bubbles that may be present. The water flow is then reduced, the sample container slowly lowered and the hose carefully pulled out. A turbulent inflow or outflow must be avoided at all times. It must be ensured that there are no air bubbles and that the sample container has a strong, gas-tight seal.
- b) If sampling from a basin or similar is required, the sample container is immersed in the basin, filled with water that is as free as possible of air bubbles and, if possible, sealed under water. In order to avoid microbiological hazards, especially to drinking water, sterile sampling equipment should be used in this case.

Ideally, samples should be taken in the first half of the week to ensure prompt analysis in the testing laboratory.

### 2.4 Sampling protocol

The following information should be noted for each sample in any case:

- Location of sampling;
- Date and time of sampling;
- Name of the sampling technician;
- Classification of the sample: drinking water or groundwater;
- Sample type: grab or composite sample;

- Sampling procedure;
- Sample preparation, including preservation;
- Recording of on-site parameters: pH value, electrical conductivity, redox potential, water temperature.

### 3 Measurement methods

A selection of suitable methods for determining the gross alpha activity concentration and activity concentrations of individual natural radionuclides to be considered according to [2] is compiled in Table 1.

**Tab. 1:** Selection of suitable methods for the determination of total alpha activity concentrations and activity concentrations of individual natural radionuclides, according to [2]

Parameter	Detection limit in Bq·l <sup>-1</sup>	Procedure or Standard	Measurement methods
Gross alpha activity concentration	0,025 or 0,04	H- $\alpha$ -GESAMT-TWASS-02	Liquid scintillation counting
		H- $\alpha$ -GESAMT-TWASS-01	Alpha activity measurement with proportional counter
		ISO 11704:2015-11*	Liquid scintillation counting (determination of both gross alpha and gross beta activity concentration)
		ISO 9696: 2018-04	Low-level-alpha activity measurement with proportional counter (thick source method)
		ISO 10704:2020-12	Low-level-alpha-/-beta activity measurement with proportional counter (thin source deposit method)
Rn-220	10	H-Rn-222-TWASS-01	Liquid scintillation counting
		ISO 13164-2: 2020-12	Gamma-ray spectrometry
		ISO 13164-3: 2020-12	Emanometry
		ISO 13164-4: 2020-12	Liquid scintillation counting
Ra-226	0,04	H-Ra-226-TWASS-01	Emanometry
		K-Ra-226-TWASS-01	Emanometry
		K- $\gamma$ -SPEKT-TWASS-01	Gamma-ray spectrometry
		ISO 10703:2015-12*	Gamma-ray spectrometry
		ISO 13165-1:2020-12	Liquid scintillation counting
		ISO 13165-2:2020-12	Emanometry
		ISO 13165-3:2020-12	Gamma-ray spectrometry (co-precipitation)
	ISO 22908: 2020-01	Liquid scintillation counting	

Parameter	Detection limit in Bq·l <sup>-1</sup>	Procedure or Standard	Measurement methods
Ra-228	0,02	H-Ra-228-TWASS-01	Low-level-beta activity measurement with proportional counter
		H-Ra-228-TWASS-02	Low-level-beta activity measurement with proportional counter
		K-γ-SPEKT-TWASS-01	Gamma-ray spectrometry
		ISO 10703:2015-12*	Gamma-ray spectrometry
		ISO 22908: 2020-01	Liquid scintillation counting
Pb-210	0,02	H-Pb-210/Po-210-TWASS-01	Beta activity measurement with proportional counter / Alpha spectrometry
		K-Pb-210-TWASS-01	Beta activity measurement with proportional counter
		ISO 13163:2020-09	Liquid scintillation counting
		ISO 10703:2015-12*	Gamma-ray spectrometry
Po-210	0,01	H-Po-210-TWASS-01	Alpha spectrometry
		ISO 13161:2016-01*	Alpha spectrometry
U-238, U-234 (respectively)	0,02 (respectively)	H-α-SPEKT-TWASS-01	Alpha spectrometry
		ISO 17294-2:2017-01	Mass spectrometry (ICP-MS)
		DIN 38406-17:2009-10	Voltammetry
		ISO 13166: 2020-08	Alpha spectrometry

\* A new published draft of this standard is available.

## References

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