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APPLICATION NOTE AN-003_EN

Measurement of the Radon concentration of water samples

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This application note introduces a fast and simple method to determine the Radon activity concentration of water samples. Nothing else is required than a Radon monitor and a bubbling flask.

Physical Basics

The measurement of the Radon activity concentration of a water sample is based on the equilibrium state between the Radon air and water activity concentrations which takes place within a sealed system after a certain time.
The ratio between the activity concentrations depends only on the temperature of the water sample. This dependence can be expressed by the so-called Oswald coefficient which points out that the solubility of the Radon in water decreases if the water temperature increases.
That means, higher water temperatures resulting in higher Radon concentrations within the air.

$K_{Oswald} = C_{Rn}(Water)/C_{Rn}(Air)$ (1)

The Oswald-coefficient can be approximated for the temperature range between 0 to 40°C by the following function:

$K_{Oswald} = 0,425 * EXP(0,05 * -Temperature\ in\ °C) + 0,1$ (2)

The absolute concentrations within the sealed system are dependent on the original concentration of the water sample and on the ratio between the water and air volumes. The higher the water volume compared to the air volume the higher is the expected activity concentration within the air volume. Since the total activity within the system can be considered as a constant over the measurement period, the relationship can be stated by the formula:

$A(Water) = A_1(Water) + A(Air)$ (3)

with: A(Water) = Total activity of the water sample before the de-gassing
A_1(Water) = Remaining activity of the water sample after the de-gassing
A(Air) = activity in the air volume

Because of $C_A = A/V$, the following expression can be stated: (4)

$C_A(Water) * V(Water) = C_{A1}(Water) * V(Water) + C_A(Air) * V(Air)$ (5)

with: C_A(Water) = Activity concentration of the water sample before the de-gassing

V(Water) = Volume of the water probe (constant)
C_{A1}(Water) = Activity concentration of the water sample after the de-gassing
V(Air) = Air volume within the sealed system
C_A(Air) = Activity concentration of the air within the system after the de-gassing

Inserting equation (1) in equation (5) results in:

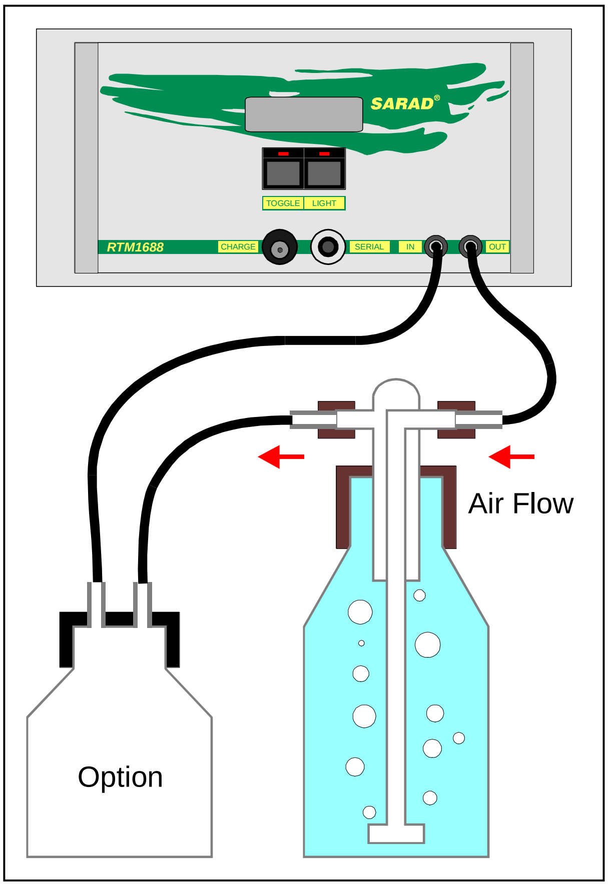
$$C_A(Water) * V(Water) = K_{Oswald} * C_A(Air) * V(Water) + C_A(Air) * V(Air) \quad (6)$$

leading to

$$C_A(Water) = \{C_A(Air) * [K_{Oswald} * V(Water) + V(Air)]\} / V(Water) \quad (7)$$

Sampling Set-up

The Radon gas solved in the water sample will be de-gassed by an air bubbling flask. The bubbling flask has to be connected to the Radon monitor to create a closed air loop. (see graphic). The air volume of the system circulates through the loop drawn by the internal pump of the Radon monitor. The small bubbles will transfer the Radon very efficient because of the large resulting surface of the junction between water and air.
Please make sure that the Radon concentration within the air loop is zero at the begin of each measurement and that the Radon monitor is not longer activated by a former measurement. To ensure this, the monitor, all connection tubes and the optional protection flask have to be flushed with fresh air for at least 15 Minutes.
The equilibrium state between the air and the water activity concentration is given after approximately 30 Minutes.
Therefore, the measurement can be started at the earliest after 30 Minutes of bubbling.



Suitable Radon Monitors

There are some requirements concerning the used Radon monitor which have to be taken in account. The monitor has to provide an internal pressure tight air loop (sealed chamber and tube connectors for inlet and outlet). An internal pump is an advantage. Membrane pumps are more suitable than rotary pumps because membrane pumps offer a much lower leakage rate.
To get a short sample period, a spectroscopic (Alpha spectroscopy) Monitor is required. The internal volume of the monitor should be as small as possible since this volume and the sensitivity of the instrument are the parameters which are defining the detection limits of the sampling method.
The RTM 1688-2 or the RTM 2200 is the most recommended solution for Radon in water analysis. The unit offers a high sensitivity of more than 3 cpm/(kBq/m³) (Fast Mode) obtained from a very small internal volume of only 250 ml.

Both units are working with Alpha spectroscopy and both are equipped with membrane pumps.

Detection Limits

The detection limit depends on the used sampling configuration (volumes) and on the sensitivity of the Radon monitor at the one hand and on the sampling period used for the Radon measurement in the air loop at the other hand. Since the detection limit as well as the statistical error of the measurement corresponds only with the number of detected decays within the sampling period, the configuration can be optimised by the following rules:

- use a water volume as large as possible compared to the internal air volume (generates high air concentrations)
- use a Radon monitor with a high sensitivity
- choose a sampling interval as long as possible

An optimised configuration is a 500 ml bubbling flask in combination with a RTM 1688-2. The sampling period should be chosen not longer than 2 hours. Otherwise the loss of Radon by diffusion through the tube walls etc. becomes significant (even if the air loop is pressure tight). The table below shows a comparison of various sampling configurations with respect to the expected detection limits:

Water-Volume	Air-Volume	Sensitivity of the Radon monitor	Sampling Interval	Detection Limit (2-Sigma)
ml	ml	cpm/(kBq/m³)	min	Bq/l
500	250	3	5	0.096
500	380	3	30	0.033
500	1200	5	5	0.315
100	1200	5	30	0.244

To calculate the detection limit for an arbitrary arrangement, the detection limit of the Radon monitor for the used sampling interval has to be fixed at first. This value can be entered as the „Displayed Radon Concentration“ within the Software „Radon In Water Calculator“. The resulting „Radon in Water Concentration“ is equal to the detection limit of the water measurement.
More detailed information about the detection limit, statistical error and test planning you will find in the application note AN-002 (“Measuring principals - decay statistics - test planning”).

Condensation

A serious problem when analysing water samples is the possible condensation of water vapour inside the Radon monitor. Since the measurement chamber is biased with a high voltage, leakage currents will be generated resulting in a rapid voltage drop. This disturbs the measurement principals of the monitor and reliable readings will not be available. Condensation will not damage the monitor. The instrument can be reused after drying (flushing with fresh and dry air). Please observe the readings of the humidity sensor which is installed in the air loop of the RTM 1688-2 and RTM 2200. If the humidity exceeds 90% you should check the Alpha spectrum after the measurement. It will loose its characteristic shape in case of condensation – otherwise, if the spectrum is good, the measurement is valid.
To avoid condensation, the temperature of the water sample should be slightly lower than the temperature of the monitor. Sometimes it will be necessary to cool down the sample before starting the analysis.

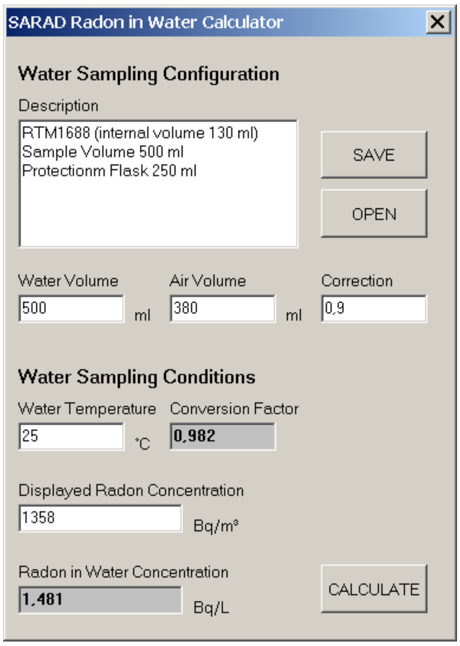
Normally, it is sufficient to store the sample and the monitor for a certain time at the same place. The monitor is always heated slightly because of its own power consumption. In this case you can assume that the reading of the internal temperature sensor gives nearly the temperature of the sampled water (required for the Oswald coefficient).
The usage of moisture absorbers or gas drying units is not recommended because also Radon could be absorbed. Furthermore, drying materials with large pore volumes can lead to an undefined additional volume in the air loop.
To protect the Radon monitor against the direct sucking of water from the bubbling flask, a small and tight glass flask should be inserted between the air inlet of the instrument and the outlet of the bubbling flask.

Standard Operating Procedure

- Flush the Radon monitor and the air loop with fresh air for at least 15 Minutes.
- Fill the bubbling flask completely with the water sample - avoid too much turbulence.
- Close the bubbling flask.
- Cool the water sample down to the ambient temperature of the monitor if necessary (short cut the both tube connectors of the flask by a short piece of PVC tube during this period to avoid Radon exhalation).
- Connect the bubbling flask with the Radon monitor (and the recommended protection flask).
- Start the Radon monitor, to pump the air volume continuously through the air loop.
- The concentration equilibrium between water and air is reached after about 30 Minutes.
- Stop the measurement – discard the recent readings.
- Start the Radon monitor again using the selected sampling interval (e.g. 10 Minutes). Now, the equilibrium concentration in air will be measured.
- Read the Radon concentration and the temperature from the display of the instrument. (possibly measure the water temperature directly if the temperatures of the water sample and the monitor differ)
- Calculate the Radon concentration of the water probe by the software „Radon In Water Calculator“

IMPORTANT HINT: The stated procedure should be performed only under visual control. No water must enter the Radon monitor. This can cause the damage of the pump and the detectors/sensors. Work, if possible, with a protection flask. The flask volume should be large enough to hold back the complete water sample in case of a mistake.

Software „Radon In Water Calculator“



The simple software calculates the Radon activity concentration of a water sample using the formulas stated in the chapter “Physical Basics”. The user has to enter the system configuration and the actual conditions.
Start with the definition of the used volumes:

„Water Volume“:
- volume of the water sample in the bubbling flask

„Air Volume“:
- internal volume of the Radon monitor
- volume of the tubes, connections etc.
- probably not filled volume of the bubbling flask
- additional volumes (e.g. protection flask)

The volumes as well as an additional correction factor are joined to the term “Configuration”. The entered values can be saved into a file together with a short description (memo field “Configuration Description”) using the button SAVE. Use the OPEN button to retrieve the information.
After the definition of the configuration the readings of the Radon concentration and the temperature have to be entered into the edit lines “Water Temperature” and “Displayed Radon Concentration”.
Press the CALCULATE button to obtain the results. The Radon concentration of the water sample as well as the related conversion factor are displayed.
The correction factor (“Correction”) was implemented to take into account that some Radon is lost during sample preparation and that Radon also attaches to the inner surfaces of the air loop. To keep out this influences, set the correction factor to 1. A value of 0.8 indicates that 20% of the Radon is lost by the mentioned processes.

Remarks

Because of the various objective factors affecting the results - and - taking into account that the manual filling of the bubbling flask is always a subjective procedure, a reliable measurement is only possible if the conditions are repeatable. This should be not a problem inside a laboratory but keep in mind that “in situ” measurements with varying conditions will definitely result in a higher uncertainty.
To evaluate the sampling procedure, a calibration measurement should be carried out. Use a water sample with a well defined Radon concentration and keep strictly the standard operating procedure as used later on for the measurements.
Variations from the theoretical values can be compensated by the correction factor within the software.