

A Radon-in-Water Monitor Based on Fast Gas Transfer Membranes

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ABSTRACT

In Earth Sciences there is a growing interest in simple, field usable radon-in-water monitors with temporal resolutions of hours or less. They can be used to study fast transport processes with radon as a natural tracer.

Separating air and water by a diffusion membrane and then measuring the radon concentration in the gaseous phase is an easy method to determine radon in water. Thin plastic foils used for this purpose show a slow diffusion and are delicate. However thick-walled, mechanically stable, watertight membrane tubes developed for microfiltration let radon pass easily. The radon concentration in the tube reaches 90% of the saturation value after only 10 min. A few meters of this tube and a flow-through radon-in-air detector make a simple radon-in-water monitor with a temporal resolution below 1h.

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INTRODUCTION

^{222}Rn (radon), a noble gas from the ^{238}U decay series, is present at Bq/liter levels in groundwaters worldwide. Its half-life of 3.8d makes it a potential natural tracer to study transport processes with characteristic times below 10 days. Infiltration from a river to groundwaters [1] as well as flow dynamics in a karst system [2] are examples where radon has been used successfully to gain additional information. Changes in groundwater radon concentrations have been observed prior to earthquakes, showing its potential as a precursor [3,4].

Batch sampling and eventual lab analysis is common practice, but continuous radon monitoring in the field is rare. This may be due to the lack of simple and cheap monitors with a good temporal resolution.

Radon in water can be determined by measuring radon in an air circuit coupled to the water. The coupling may be done by separating air and water by a membrane, or by bubbling (a very old method [5]) air through the water. Monitors with plastic foils as diffusion membranes generally have a slow response due to the small exchange surface possible with delicate thin foils. Bubbling air through the water allows for a fast exchange, but efficient bubblers consume a lot of power. One is always short of electric energy in the field. If there is a water head of at least 1m, the water to be measured can drive a water jet pump that circulates the air and acts as a bubbler [6], but that water head is not always available.

The membrane tube described below has none of these problems. With a wall thickness of 1.5 mm there are no mechanical problems, and despite the thick wall radon diffusion is fast.

Either bubbling or diffusion lead to an air saturated with water vapor. Most semiconductor-based radon monitors use electrostatic collection of radon daughters (no collection means poor count rate), and therefore don't work properly at high humidity levels. The same holds for monitors using ionization chambers. The air has to be dried. Drying with Peltier elements is smart, but is impossible far from a mains supply. Changing desiccant once a week or every other week is no problem in the lab, but is excluded for remote field stations that should work unattended for months.

Lucas-cell based instruments have high count rates per Bq/liter even for small cells (100-200 ml), and no desiccant is needed as long as there is no condensation inside the cell. A disadvantage is their lack of energy resolution. Alphas from ^{222}Rn , ^{218}Po and ^{214}Po decaying inside the cell all contribute to the count rate. Mainly ^{214}Po 's slow buildup and decay smooth out fast radon concentration changes. However, the high count rate, meaning good statistics, makes it possible to still detect small changes. The monitor described below consists of a Lucas-cell detector coupled to a few meters of the membrane tube. At a mean radon-in-water concentration of 1 Bq/liter and an integration time of 30 min, variations of 0.25 Bq/liter can still be detected with this monitor. Its small volume, low power consumption, and the fact that there is no need for a desiccant, make it an ideal field instrument either for batch measurements or for continuous monitoring.

THEORY

For batch samples in a closed system the relation between the air radon concentration and the initial radon in water concentration is at a steady state, independent of the method used to couple air and water (bubbling or diffusion) :

$$c_a(\infty) = c_w(0) * (1 / (V_a / V_w + k)) \quad (1)$$

with

$c_w(t)$ = radon in water concentration

$c_a(t)$ = radon in air concentration

k = radon's water solubility (Ostwald coefficient, see Fig.1), defined as the steady state ratio c_w/c_a

V_a = air volume, V_w = water volume

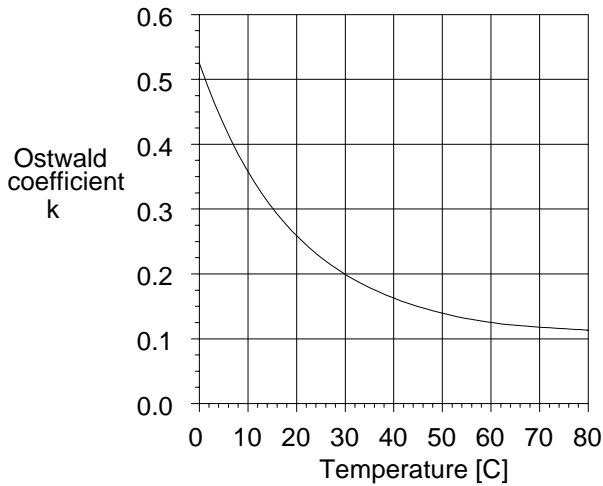


Fig.1 : Radon water solubility vs. temperature (Ostwald coefficient k) [7].

To calculate the dynamic behavior, it is useful to introduce a third compartment V_i , the air volume in contact with the water, i.e. the air volume inside the membrane tube or the total bubble volume.

The air activity increase Δc_a for one pass of the air volume V_a through the interface volume can be expressed as :

$$\Delta c_a = \varepsilon * (c_w/k - c_a) \quad (2)$$

with

$\varepsilon = (1 - \exp(-\lambda_d * t_c))$, the transfer efficiency

λ_d = radon diffusion rate at air-water interface

t_c = residence time at air-water interface = $(V_i / V_a) / \lambda_{ex}$

λ_{ex} = air exchange rate , number of V_a exchanges per unit time

Using the fact that no activity is lost in a closed system (neglecting radon decay), the corresponding differential equation has the solution

$$c_a(t) = c_a(\infty) * (1 - \exp(-\lambda * t)) \quad (3)$$

with

$$\lambda = (\varepsilon / k) * (V_a / V_w + k) * \lambda_{ex} \quad (4)$$

To monitor the radon-in-water concentration continuously, the air/water exchange unit (bubbler or diffusion unit) is either placed directly into a large volume of the water to be measured or into a vessel with the water flowing through. The air circulates in a closed system. Assuming that the water flow rate or the volume is high enough to compensate for losses to or for gains from the air circuit, the term V_a / V_w can be neglected.

With

$$c_a(0) = 0 \text{ and } c_w(t) = \text{const.} = c_w$$

the radon concentration in the air circuit then reacts to a c_w step like

$$c_a(t) = (c_w / k) * (1 - \exp(-\lambda * t)) \quad (5)$$

with

$$\begin{aligned} \lambda &= \varepsilon * \lambda_{ex} \\ &= (1 - \exp(-\lambda_d * t_c)) * \lambda_{ex} \\ &= (1 - \exp(-(V_i / V_a) * (\lambda_d / \lambda_{ex}))) * \lambda_{ex} \end{aligned} \quad (6)$$

For $V_i * \lambda_d \ll V_a * \lambda_{ex}$, e.g. at a small interface volume, a slow diffusion and a high exchange rate, this reduces to

$$\lambda = (V_i / V_a) * \lambda_d \quad (7)$$

The other limit, $V_i * \lambda_d \gg V_a * \lambda_{ex}$, i.e. a large exchange volume and a fast diffusion leads to

$$\lambda = \lambda_{ex} \quad (8)$$

The radon solubility is temperature dependent. Between 10 °C and 20 °C the solubility decreases by about 3% / °C. For precise continuous measurement it is therefore recommended to monitor the water temperature simultaneously with the radon concentration. Temperature has less influence on batch measurement results, where temperature dependence is reduced by a factor (V_a / V_w) . For batch measurements and for continuous measurements in still water λ is considerably reduced by the slow radon diffusion in the water. For batch measurements using the membrane tube Eq.4 is valid only if the water or the tube coil are moved constantly.

EXPERIMENTAL

The monitor is composed of a few meters of the membrane tube coupled to a Lucas-cell based radon detector, a small pump, some pulse shaping electronics, a power supply and a data logger (Figs.2 and 3). Electronics and detector are housed in a thermally insulated box. Heat produced by the electronics thus keeps the cell at a temperature slightly higher than outside temperature. This avoids condensation inside the cell if the outside temperature is not considerably lower than the temperature of the water to be measured.

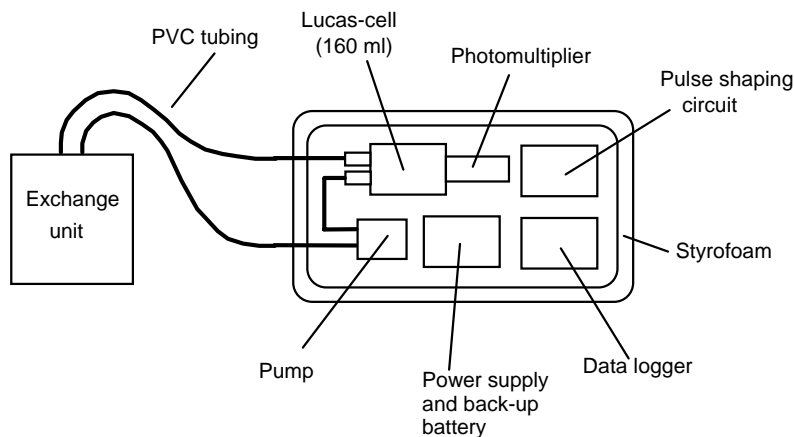


Fig. 2 : Monitor setup. Components are described in text below. Details of exchange unit are shown in Fig.3. Optionally there is a water temperature sensor connected to the data logger.

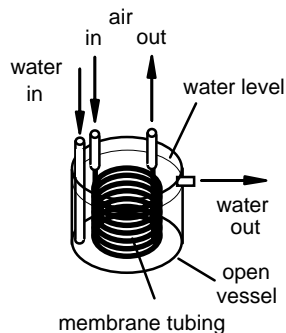


Fig 3 : Air-water exchange unit. Membrane tube is 4 m Accurel V8 [8]. The open vessel holds approx. 4 liters. For batch measurements the vessel is closed.

The monitor's components are :

Membrane tube : a commercially available permeable polypropylene tube, developed for microfiltration [8]. With an inside diameter of 5.5 mm and a wall thickness of 1.5 mm, it holds 24 ml/m. At a mean diameter of 7 mm, it has an exchange surface of 220 cm²/m. The material is quite stiff, but with some precaution coils with a diameter of 10 cm can be formed.

Pump : micro-membrane pump type NMP02 L/U [9], nominally for 3 to 6 V it operates well at 1.5 V, pumping 80-100 ml /min and consuming only 15 mA.

Lucas-cell : commercially available 160 ml cell [10].

Photomultiplier : H5783-00 [11], 8 mm active area diameter, includes HV-supply driven by 12 V DC, consuming 10 mA. Photomultiplier and HV-supply are housed in a 50 mm *22 mm * 22 mm box.

Pulse shaping circuit : contains 2 Op-Amps (CA3140) and 2 Schmitt-Triggers (74C14) to produce uniform square pulses 1 ms wide for the data logger. It consumes 3 mA at 12V.

Data logger : Tattletale Lite, Type S [12]. Works on 6 to 15V and consumes about 1 mA at 12V. This data logger includes an RS232 interface and can be programmed in a BASIC dialect.

Other tubing : soft PVC. Silicone tubing cannot be used. It shows a very strong radon adsorption.

RESULTS

The diffusion rate λ_d through the membrane can be calculated from the data in Fig.4 using $\lambda = (V_i/V_a)*\lambda_d$ (Eq. (7), approximation for large λ_{ex} and small V_i/V_a ratio). With $(V_i/V_a) = 0.1$ and $\lambda = (0.022 \pm 0.002) \text{ min}^{-1}$ from the fit in Fig.4 one gets :

$$\lambda_d = (13 \pm 2) \text{ h}^{-1}, \text{ or a "half-live" of approx. 3 min.}$$

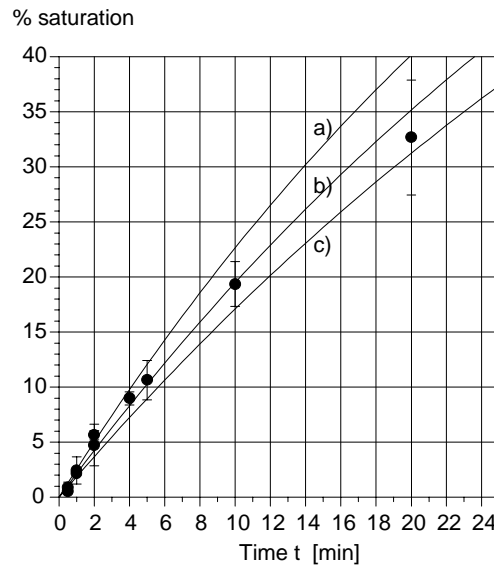


Fig. 4 : Determination of radon diffusion rate. 4m of the membrane tube Accurel V8 are submerged for time t at constant water temperature and coupled to a radon-in-air monitor. $V_a = 1000 \text{ ml}$, $V_i = 100 \text{ ml}$, $\lambda_{ex} = 60 \text{ h}^{-1}$. Radon-in-air concentrations measured with a RAD7 [13] radon monitor after complete mixing of air inside tube with total air volume. Radon-in-water concentration measured with the RAD7-H2O [13] method, using 250 ml bottles. " % saturation " = $100 * c_a / (c_w/k)$. Fits are $100 * (1 - \exp(-\lambda * t))$ with a): $\lambda = 0.693/27\text{min}$, b): $\lambda = 0.693/32\text{min}$., c): $\lambda = 0.693/37\text{min}$. Error bars are 2σ counting statistics.

Thus, the diffusion process alone would allow for a temporal resolution on the order of 10 min. A more limiting factor is the (exchange volume V_i) / (total volume V_a) ratio. Figure 5 shows measurements done with two different V_i/V_a ratios.

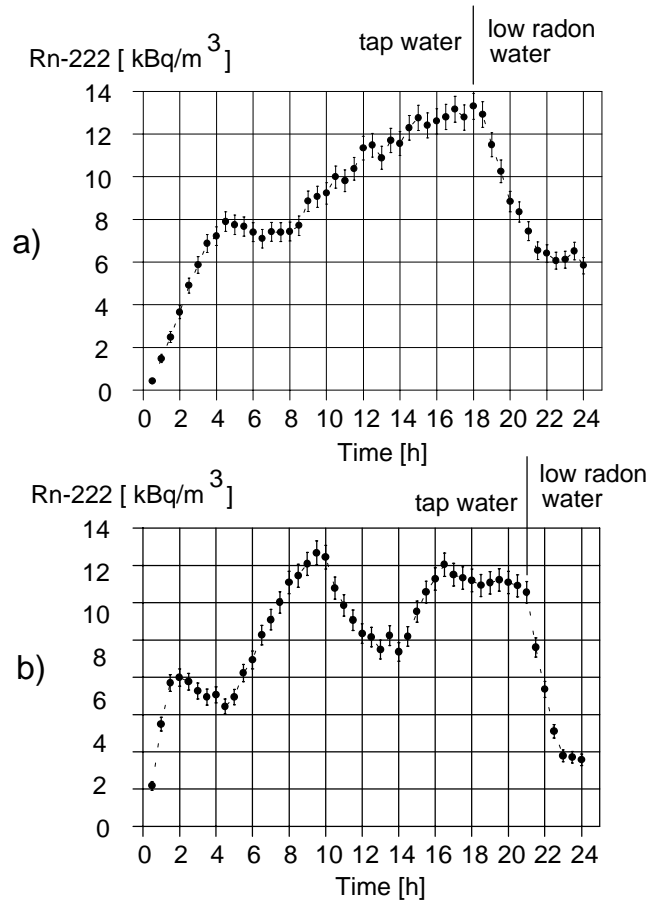


Fig. 5 : ^{222}Rn concentrations vs. time in air circuit coupled to a membrane tube submerged in tap water (constant temperature). Open 2 liter vessel setup similar to Fig.2. Radon monitor : RAD7 [13], ^{222}Rn values are calculated from counts in the ^{218}Po energy window. a) 1.9 m Accurel V8, $V_a = 1700 \text{ ml}$, $\lambda_{\text{ex}} = 7 \text{ h}^{-1}$, b) 5.4 m Accurel V8, $V_a = 1800 \text{ ml}$, $\lambda_{\text{ex}} = 6.7 \text{ h}^{-1}$. Membrane tube submerged at $t = 0$. Initial ^{222}Rn concentration in air of measuring circuit : $< 100 \text{ Bq/m}^3$. Average radon-in-water concentration approx. 3.5 Bq/liter. Water flow rate $> 1 \text{ liter/min}$. Near the end of each run, tap water has been replaced by low-radon water (tap water stored for some days) at a rate of 2 liters / 30 min during 150 min. Data in a) and in b) are for different periods. Error bars are 2σ counting statistics.

For the two examples in Fig.5, λ can be calculated using Eq. (6)

$$\lambda = (1 - \exp(-(V_i/V_a) * (\lambda_d/\lambda_{ex}))) * \lambda_{ex}$$

With $V_i = 46$ ml (1.9 m tube), $V_a = 1700$ ml, $\lambda_{ex} = 7$ h⁻¹, $\lambda_d = 13$ h⁻¹ (Fig.5 a)
 $\lambda = 0.34$ h⁻¹ or $T_{1/2} = 2.0$ h

or with $V_i = 130$ ml (5.4 m tube), $V_a = 1800$ ml, $\lambda_{ex} = 6.7$ h⁻¹, $\lambda_d = 13$ h⁻¹ (Fig.5 b)
 $\lambda = 0.88$ h⁻¹ or $T_{1/2} = 0.79$ h,

well in agreement with the experimental data (see initial increase and also decay after addition of low-radon water).

For detectors with small cell volumes like Lucas-cell detectors neither the V_i/V_a ratio nor λ_{ex} are the limiting factors.

With

$$V_i = 100 \text{ ml (4 m Accurel V8), } V_a = 300 \text{ ml (160 ml Lucas-cell + membrane tube + connection tubing)}$$

and

$$\lambda_d = 13 \text{ h}^{-1} \text{ (from above)}$$

one gets for some exchange rates, using Eq. (6) :

$$\lambda_{ex} = 5 \text{ h}^{-1} \text{ (25 ml/min pump) } \rightarrow \lambda = 2.9 \text{ h}^{-1} \text{ or } T_{1/2} = 14 \text{ min.}$$

$$\lambda_{ex} = 10 \text{ h}^{-1} \text{ (50 ml/min pump) } \rightarrow \lambda = 3.5 \text{ h}^{-1} \text{ or } T_{1/2} = 12 \text{ min.}$$

$$\lambda_{ex} = 20 \text{ h}^{-1} \text{ (100 ml/min pump) } \rightarrow \lambda = 3.9 \text{ h}^{-1} \text{ or } T_{1/2} = 11 \text{ min.}$$

$$\lambda_{ex} = 40 \text{ h}^{-1} \text{ (200 ml/min pump) } \rightarrow \lambda = 4.4 \text{ h}^{-1} \text{ or } T_{1/2} = 10 \text{ min.}$$

This means that a flow-through radon detector still working properly at high humidity levels, having high count rates and good energy resolution at a measuring volume of not more than 200 ml, coupled to 4m of the membrane tube by a 100 ml/min pump, would make an ideal monitor. A temporal resolution well below 1h would be possible.

A Lucas-cell flow-through detector has some of the properties required. It properly works at high humidity levels. It has a measuring volume below 200 ml. It shows high count rates. Unfortunately alphas from radon and radon daughters cannot be distinguished. This leads to a slow response (Fig.6).

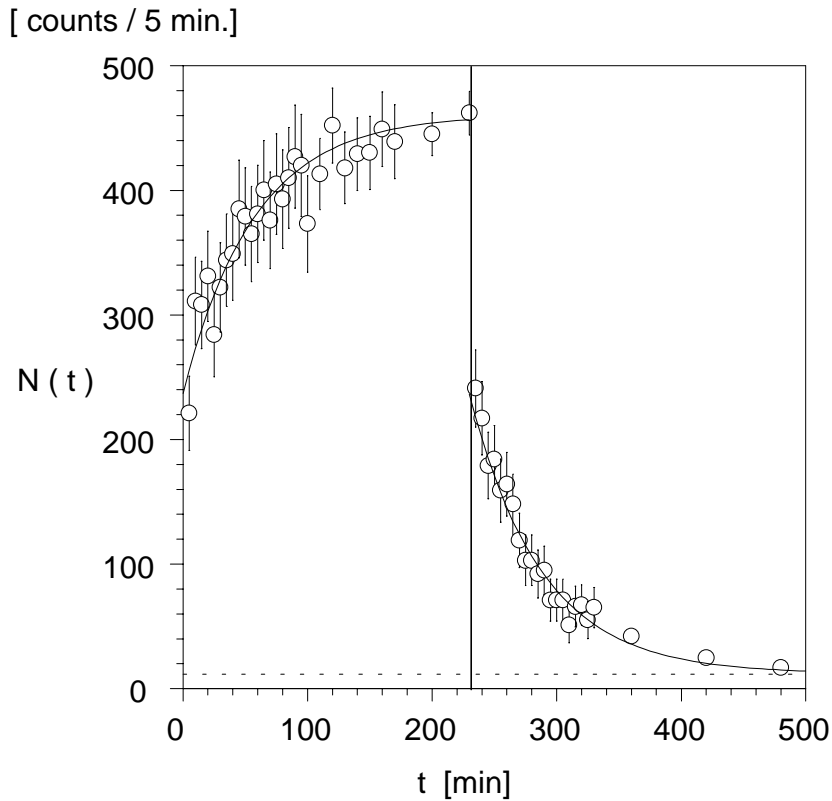


Fig. 6 : Count rate vs. time for a 160 ml Lucas-cell [10]. At $t = 0$ the cell has been purged for 2 min at 1 liter/min with moist air (R.H. > 90%, non condensing) having a radon concentration of approx. 4.5 kBq/m^3 , at $t = 230$ min for 2 min at 1 liter/min with outside air (R.H. approx. 60%, radon concentration < 50 Bq/m^3). Error bars represent 2σ -counting errors. Solid line : calculated buildup and decay (see equations in text). Dotted line : background (^{210}Po).

For integration times of 5 min buildup and decay in Fig.6 can be approximated by :

$$\begin{array}{ll}
 N(t) = N_{\max} * (1-0.5*\exp(-\lambda_1*t))*\exp(-\lambda_2*t) & \text{buildup} \\
 N(t) = N_{\max} * 0.5*\exp(-\lambda_1*t)*\exp(-\lambda_2*t) & \text{decay} \\
 \text{with } \lambda_1 = 0.693 / 40 \text{ min and } \lambda_2 = 0.693 / 3.8 \text{ d} &
 \end{array}$$

Radon decay during the experiment in Fig.6 has nothing to do with the detector. The detector response, that can be used to unfold data, thus becomes :

$$\begin{array}{ll}
 N(t) = N_{\max} * (1-0.5*\exp(-\lambda_1*t)) & \text{buildup} \\
 N(t) = N_{\max} * 0.5*\exp(-\lambda_1*t) & \text{decay} \\
 \text{with } \lambda_1 = 0.693 / 40 \text{ min} &
 \end{array}$$

Combined with a 4m membrane tube and a 100ml/min pump this Lucas-cell detector will make a radon-in-water monitor with a reaction time ($T_{1/2}$) of just below one hour (Fig.7).

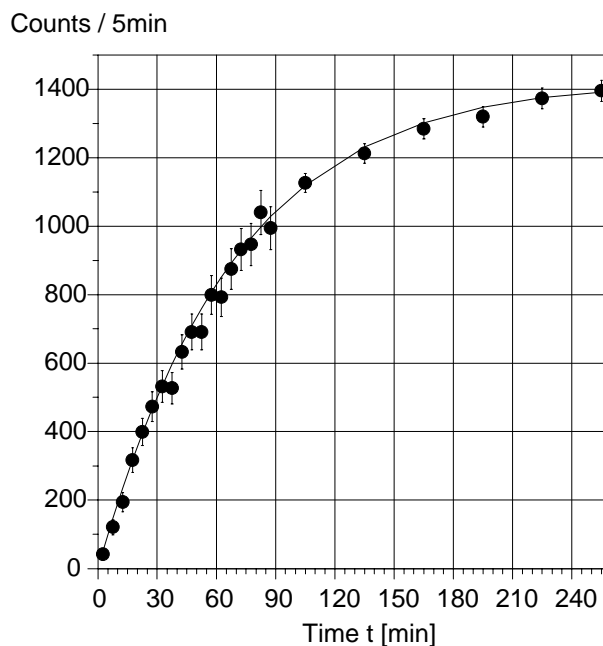


Fig. 7 : Count rate vs. time for the Lucas-cell in Fig.6 coupled to 4 m Accurel V8 placed in a 4 liter vessel. Water flowing through at a rate of 4 liter/min is tap water with an initial radon concentration of 4.2 Bq/liter and a constant temperature of 18 °C. During the experiment the radon-in-water concentration decayed with the ^{222}Rn half live. The line is a fit with a half-live of 50 min, taking into account radon decay. Error bars are 2σ counting statistics.

The monitor response to a step function in Fig.7 can be described by a single exponential. It behaves like a low pass filter with a time constant of 72 min (increase to $(1-1/e)$). This behavior greatly simplifies unfolding experimental data, if needed.

Counting statistics is as important as the time constant. It determines unfolding procedure cutoff frequency and the detection limit for small variations. For the monitor described, 1 Bq/liter in the water gives about 2000 counts / 30 min at saturation. Taking into account the instrument response in Fig.7, a 1 Bq/liter peak-to-peak square wave with a period of 1 h leads to an amplitude of 680 counts/30min. Two values can be considered significantly different if they are 4σ apart (179 counts/30 min at 1 Bq/liter background). This means that at a mean concentration of 1 Bq/liter, variations of 0.25 Bq/liter are still detectable with a temporal resolution of 1 h.

An example of measurements made with the monitor described can be seen in Fig.8. It shows variations in the radon concentration in a drinking water supply. The diurnal pattern is mainly due to a refilling of the municipal storage tank starting around noon and a subsequent radon decay in the tank. Mainly between midnight and noon the decay is close to the radon decay. It is not yet known why the initial decay is faster.

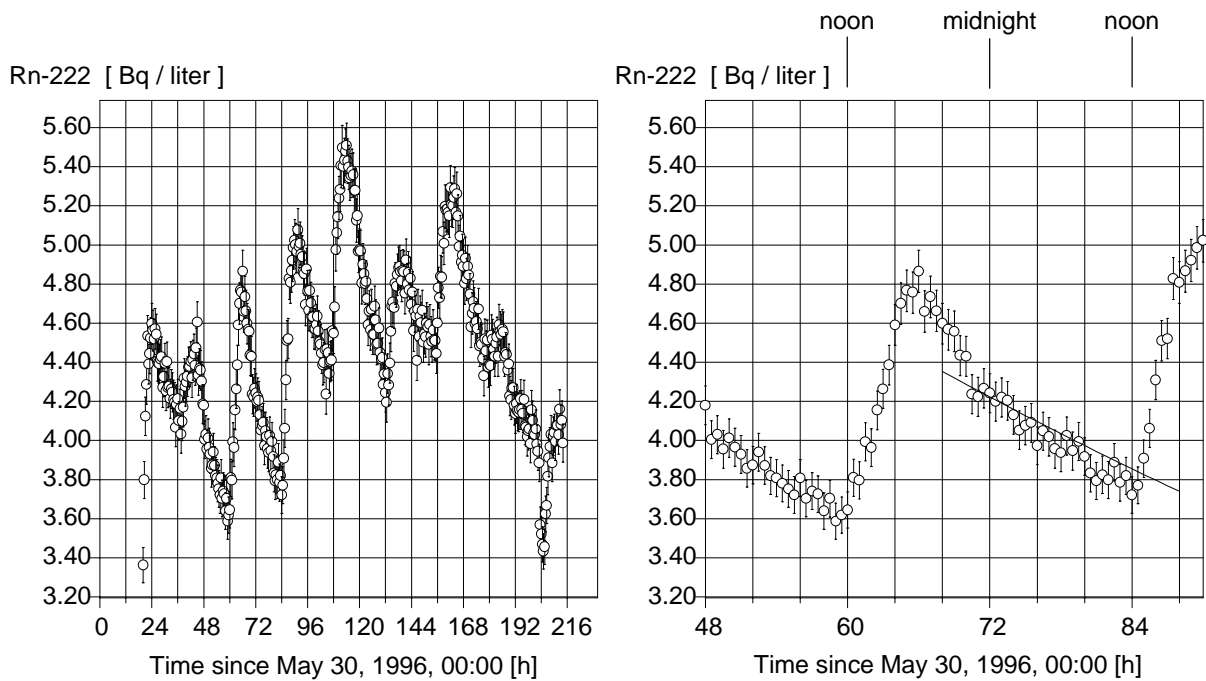


Fig. 8 : ^{222}Rn concentration in tap water measured with the monitor described. $V_i = 100$ ml (4 m Accurel V8), $V_a = 300$ ml, air flow rate = 80 - 100 ml / min. Integration time : 30 min. 4 liter vessel. Water flow rate : 4 liter/min, started at May 30, 1996, 17:30. Line in zoomed part (right) shows decay with ^{222}Rn half live. Error bars are 2σ counting statistics.

REMARK

Radon diffusion through the membrane tube turned out to be very fast ($T_{1/2}$ approx. 3 min). It is to be expected that other noble gases diffuse at least as fast as radon. A submerged coil of some 10 m of the membrane tube would thus make an efficient device to extract noble gases from surface waters or groundwaters, replacing large and power-hungry bubblers.

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