Journal of Environmental Radioactivity 157 (2016) 52–59

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Optimized measurement of radium-226 concentration in liquid samples with radon-222 emanation

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ARTICLE INFO

Article history:
Received 21 December 2015
Received in revised form
3 March 2016
Accepted 6 March 2016

Key words:
Scintillation
Mineral water
Groundwater
Tap water
Wine
Pollution

ABSTRACT

Measuring radium-226 concentration in liquid samples using radon-222 emanation remains competitive with techniques such as liquid scintillation, alpha or mass spectrometry. Indeed, we show that high-precision can be obtained without air circulation, using an optimal air to liquid volume ratio and moderate heating. Cost-effective and efficient measurement of radon concentration is achieved by scintillation flasks and sufficiently long counting times for signal and background. More than 400 such measurements were performed, including 39 dilution experiments, a successful blind measurement of six reference test solutions, and more than 110 repeated measurements. Under optimal conditions, uncertainties reach 5% for an activity concentration of 100 mBq L^{-1} and 10% for 10 mBq L^{-1}. While the theoretical detection limit predicted by Monte Carlo simulation is around 3 mBq L^{-1}, a conservative experimental estimate is rather 5 mBq L^{-1}, corresponding to 0.14 fg g^{-1}. The method was applied to 47 natural waters, 51 commercial waters, and 17 wine samples, illustrating that it could be an option for liquids that cannot be easily measured by other methods. Counting of scintillation flasks can be done in remote locations in absence of electricity supply, using a solar panel. Thus, this portable method, which has demonstrated sufficient accuracy for numerous natural liquids, could be useful in geological and environmental problems, with the additional benefit that it can be applied in isolated locations and in circumstances when samples cannot be transported.

1. Introduction

Radon emanation was the first method used, as early as 1904, to evidence and measure the radioactivity of geothermal spring waters (Curie and Laborde, 1904; Strutt, 1904). Now, while the various sources of radioactivity are well understood, the radium-radon couple remains of particular interest, with radium confined in solid or dissolved phases, while radon, a rare gas, tends to escape from porous media and liquids (Nazaroff, 1992). Radium also can be transported from its production place in rocks and soils to the surface environment, for example from volcanic vents, but more commonly it is released in water solutions from natural aquifers, with a concentration that can vary over orders of magnitude (Przylibski et al., 2014; Girault and Perrier, 2014). When a water sample is ventilated, cleared of its original radon, and placed in a sealed container, then the radon activity at radioactive equilibrium is equal to the radium activity. In the case of radium-226 (half-life ~1600 years), the activity is approximately constant while equilibrium is reached with radon-222 (half-life ~3.82 days), a situation achieved after about three weeks. In this case, the measurement of radon-222 activity concentration is actually a measurement of radium-226 activity concentration.

As techniques for radon-222 measurement in air are numerous and easily available at moderate cost, radon emanation is still a technique used for routine measurements of radium-226 concentration in water samples (Köhler et al., 2002; Stringer and Burnett, 2004). Other methods, such as liquid scintillation (Aupiais et al., 1998; Aupiais, 2005), alpha spectrometry (Morvan et al., 2001; Jia and Jia, 2012), and mass spectrometry (Dosseto et al., 2006; Copia et al., 2015), tend to be now favored because they have detection

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http://dx.doi.org/10.1016/j.jenvrad.2016.03.006
0265-931X/

limits as low as 0.074 mBq L^{-1}, in the latter case, after separation, pre-concentration, and counting in mass spectrometer (Copia et al., 2015).

In comparison with these techniques, radon emanation has the disadvantage of the long time necessary to establish the equilibrium with radium-226. However, it has the advantage of being selective, as the detection of radon-222 can be made unambiguous, and it comes as a free addition when the necessary equipment is already available for radon-222 concentration measurement in the original sample. Furthermore, radon-222 measurements can be performed directly in natural sites, without the need for electrical distribution power, as we demonstrated for example in remote locations of the Nepal Himalayas (Girault and Perrier, 2014). In that particular instance, to simplify the method for field conditions and to avoid leakage, we had revisited emanation methodologies by suppressing the pipes, air or gas circulation proposed routinely in standard kits (Genitron, 1997).

In this paper, we show that this simplified method, originally operated for radon concentration measurements, can also provide, when optimized, high-precision radium-226 measurements. This improved method makes use of two optimizations of the standard radon emanation methodology. The first is the optimization of the water to air volume ratio. The second is the optimization of the precision of the measurement of the radon concentration in air.

2. Materials and methods

A volume V_w of the liquid sample to measure, having a radium activity concentration C_{Ra}, is placed in a container of total volume V_0, thus leaving a free air volume $V_a = V_0 - V_w$. After the container is closed, decay of original radon-222 proceeds and radon-222 is produced from radium-226 decay. Radioactive equilibrium can be considered reached to better than 1% after 21 days. In the case of some natural samples, the initial radon-222 concentration can be extremely large, in excess of 1000 Bq L^{-1} (Przylibski et al., 2014), it is then necessary to ventilate the water sample, for example by repeated shaking with fresh air, to reduce initially the radon-222 concentration, otherwise the time to reach sufficiently small original radon-222 concentrations can be larger than several months.

After radioactive equilibrium is reached, the container is shaken manually, so that the radon concentration becomes in chemical equilibrium between the liquid phase (activity concentration C_w) and the air phase (C_a). We used a shaking duration of 10 min, as was found appropriate for the measurement of radon concentration in water (Girault and Perrier, 2014).

The ratio C_w/C_a is constrained by the solubility of radon:

$$\frac{C_w}{C_a} = \kappa_w(T) \cong 0.105 + 0.405e^{-0.0502T}, \quad (1)$$

which, under normal salinity conditions, depends only on temperature T. This temperature variation can be approximated by the parameterization given above, referred to as the Weigel equation, where T is expressed in °C (Schubert et al., 2012). This equation, which gives $\kappa_w(T) \cong 0.25$ for $T = 20$ °C and $\kappa_w(T) \cong 0.14$ for $T = 46$ °C, was found adequate by a recent compilation (Girault and Perrier, 2012a), which only introduced a minor revision. In the case of solutions with large ionic forces, such as seawater, significant modifications of the Weigel equation Eq. (1) must be taken into account (Schubert et al., 2012). In the following, for solutions with salinity smaller than 1% NaCl and temperatures larger than 20 °C, the Weigel equation will be considered sufficiently accurate.

After radioactive and chemical equilibrium, we have (Girault and Perrier, 2014):

$$C_{Ra} V_w = C_a V_a + C_w V_w = C_a [V_a + V_w \kappa_w(T)], \quad (2)$$

and the radium concentration in the liquid sample C_{Ra} can be inferred from the measurement of the radon concentration in air C_a:

$$C_{Ra} = C_a \left[\frac{V_a}{V_w} + \kappa_w(T) \right]. \quad (3)$$

Radon concentration in air is measured using 125 mL scintillation flasks (Lucas, 1957; Girault and Perrier, 2012b) with doped ZnS(Ag) from Algade (Bessines-sur-Gartempe, France). The flask is previously evacuated using a hand pump to a pressure of 50–60 hPa, and put into contact, using a filter and needles, with the container equipped with a pre-perforated natural rubber stopper (Girault and Perrier, 2014). The initial and final pressures in the container and in the flask are measured to correct for the air dilution in the flask (Girault and Perrier, 2012b, 2014). The photon activity of the scintillation flask is then counted using a CALEN™ photomultiplier from Algade. The validity of this methodology was checked by changing the water volume in the case of radon-222 concentration (Girault and Perrier, 2014), and similarly in the case of radium-226 concentration (see Supplementary Material Fig. S1).

According to Eq. (3), radon concentration in the air volume of the container increases when the air volume decreases. However, when the air volume becomes too small, of the order of the flask volume, then the radon concentration transferred to the scintillation flask is more significantly diluted. Consequently, there is an optimal water volume in the accumulation container to maximize the radon concentration in the scintillation flask. This effect is illustrated in Fig. 1 which shows the radon concentration in the flask versus water volume, for a V_0~1 L glass bottle and a V_0~2 L glass container. A clear and rather sharp optimal water volume, maximizing detection, is obtained at about 90% of the container volume. In addition, when the solution is heated, for example from 20 °C to 46 °C, because of the reduction of radon solubility with temperature, there is a substantial, albeit less dramatic, gain in the radon concentration.

Consequently, the first optimization was to adequately select the water volume for a given container volume, or properly select the container for an available water volume. This optimal water volume

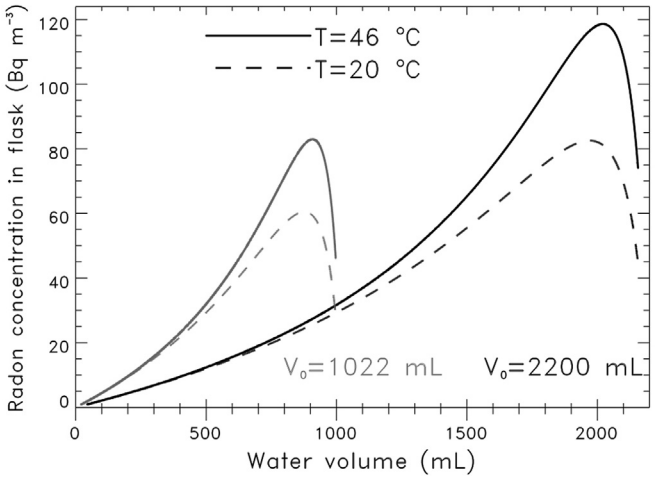

Fig. 1. Calculated radon-222 concentration in a 125 mL scintillation flask, sampling air from an accumulation container of total volume V_0 and varying water volume, and at two equilibrium temperatures. The radium-226 concentration is assumed to be 50 mBq L^{-1}.