

# Correction of the effects of carbon dioxide and hydrogen sulfide on electrostatic cell monitors measurements of radon in water

*Robert-Csaba Begy<sup>1,2</sup>, Codrin-Fabian Savin<sup>1</sup>, Alida Timar-Gabor<sup>1,2</sup>*

<sup>1</sup>*Faculty of Environmental Science and Engineering, “Babes-Bolyai” University, Cluj-Napoca, 400084, Romania*

<sup>2</sup>*Interdisciplinary research institute on Bio-Nano-Sciences, “Babes-Bolyai” University, Cluj-Napoca, 400271, Romania*

**Corresponding author:** Robert-Csaba Begy, [robert.begy@ubbcluj.ro](mailto:robert.begy@ubbcluj.ro), St. Treboniu Laurian no. 42, Cluj-Napoca 400000, +40 264 454 554

## Abstract

The present study investigates the effect of two gases, hydrogen sulfide and carbon dioxide, on radon measurements in water using RAD7 electrostatic ion collector device. CO<sub>2</sub> concentrations between 0.65 g/l and 5.19 g/l were generated in water samples containing <sup>222</sup>Rn activities ranging from  $23.4 \pm 0.9$  Bq/l to  $6.7 \pm 0.9$  Bq/l, after which the samples were measured by RAD7 device and the results compared to the radon activity values of the gas-free samples. The same procedure was followed for hydrogen sulfide concentrations from 0.125 mg/l to 3 mg/l. In both cases, a major impact on the radon measured activity was observed, the apparent specific activities decreasing exponentially with gas concentration. For a CO<sub>2</sub> concentration of 1.29 g/l, the apparent specific activity underestimated the true value by 24.5%, while for a concentration of 5.19 g/l CO<sub>2</sub> the decrease was of 57%. For hydrogen sulfide, the radon measured values decreased by 42.5% for concentrations as low as 0.5 mg/l, culminating in a reduction of 86.9% for 3 mg/l H<sub>2</sub>S. We are attributing these effects to <sup>218</sup>Po neutralization processes, which reduces the electrostatic efficiency of the silicon detector system. The results clearly show that application of correction methods are necessary when radon measurements are carried out on CO<sub>2</sub> and H<sub>2</sub>S-rich waters using the RAD7

device. To eliminate the interferences of these gases on RAD7 radon measurements, a sample preparation method was developed and tested. This involves the precipitation and deposition of CO<sub>2</sub> using Ca(OH)<sub>2</sub>, and H<sub>2</sub>S using Pb(NO<sub>3</sub>)<sub>2</sub>.

**Keywords:** *RAD7, radon, water, carbon dioxide, hydrogen sulfide, <sup>218</sup>Po neutralization*

## 1. Introduction

Radon is a radioactive alpha emitting gas belonging to the natural radioactive decay series of uranium. Radon-222 has a half-life of 3.8 days, and, from a radiological point of view is the most important of the three naturally occurring isotopes of radon: <sup>222</sup>Rn (radon), <sup>220</sup>Rn (thoron) and <sup>219</sup>Rn (actinon). Radon gas accounts for about half of the effective radiation dose received from natural sources, the biologic effects being mainly attributed to its short-lived alpha-emitting decay products (<sup>218</sup>Po and <sup>214</sup>Po). Radon in water causes potential health risks first by elevating the radon concentration in indoor air, resulting in inhalation of the gas, and secondly through ingestion (WHO, 2017).

Besides its radiological importance, accurate radon activity estimations can be used to serve other purposes. As a geological tool, the radon monitoring technique can be used in the study of active geological faults and geothermal energy sources (Khattak et. al., 2011). <sup>222</sup>Rn is indicative of geothermal systems and water-rock relationships (Espinosa et. al., 1991), and can also serve as an environmental tracer in single-well tests for estimating groundwater flow velocities (Schubert et. al., 2011). Volcanic activity and magma degassing areas are known to be correlated with groundwater radon anomalies (Segovia et. al., 1991).

In spring and geothermal waters, other naturally-occurring gases can be present besides radon, such as carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S). Carbon dioxide is a

widely occurring gas in groundwater, and its highest concentrations can be found in mineral waters as a result of dynamo- and thermo-metamorphism of carbonate rocks, as well as due to biochemical reactions in sedimentary rocks. CO<sub>2</sub> can also interact with groundwater via leakage pathways, such as direct leaks (abandoned wellbores), faults or fractures and diffuse leaks such as permeable cap rock material and micro-fractures in the cap rock (Siirila et. al., 2012). Depending on partial pressure and temperature, it generally attains a concentration of up to 3 g/l (Komatina, 2004). Hydrogen sulfide, another important gas present in groundwater, can be produced through geothermal, volcanic activity, hot springs, and underwater thermal vents (Giampaoli et. al., 2013). Sulfur gases that are released from the ground can encounter groundwater and form hydrogen sulfide, whose concentration rarely exceeds 50 mg/l (Komatina, 2004). The necessity of studying both the effects of carbon dioxide and hydrogen sulfide on RAD7 <sup>222</sup>Rn activity measurements is justified by the fact that carbonated waters and hydrogen sulfide waters are constituting two out of six categories of mineral waters. These two gasses are commonly found together, forming a third category, namely H<sub>2</sub>S-CO<sub>2</sub> waters (Komatina, 2004).

Several techniques have been used for radon in water measurements, either by using passive methods, such as active charcoal measured by gamma spectrometry, as well as by active measurement techniques such as Lucas cell scintillation (Nita et. al. 2014), liquid scintillation counting (LSC) (Celaya et. al., 2018) and radon electronic detector devices such as DURRIDGE RAD7 H<sub>2</sub>O (Nikolov et. al., 2012) and Alpha GUARD (Elmehdi et. al., 2019).

The DurrIDGE RAD7 device is known to be widely used by researchers worldwide for performing radon measurements in air, soil and water. The relatively low cost and ease of use makes the device popular among researchers. It is important to know the influencing factors

75 which can lead to compromised results and erroneous interpretations. These factors can be  
76 environmental (humidity, pressure, temperature), which have been studied in literature (Chu  
77 and Hopke, 1988; Hopke, 1989; Roca et al., 2004), or other gases, beside radon. The effect of  
78 carbon dioxide was previously investigated in air measurements using RAD7 device (Lane-  
79 Smith and Sims, 2013) and found to be influencing the precision of the results, however no  
80 study concerning its effect in water samples has been yet conducted, nor for the effect of  
81 other commonly found gases. Besides, numerous studies already have been published  
82 concerning the radon levels (measured by RAD7 device) in groundwaters (Duggal et. al.,  
83 2013; Alharbi et al., 2015), geothermal waters and hot springs (Ertuğral et al., 2015; Ismail et  
84 al., 2021) and drinking water (Salih, 2021). Following this statement, the investigation of the  
85 effects of the most abundant gasses in water samples ( $\text{CO}_2$  and  $\text{H}_2\text{S}$ ) are mandatory for  
86 correct and precise measurements performed with RAD7.

87 The aim of this study is to examine and quantify the effects of two gases present in  
88 water, carbon dioxide and hydrogen sulfide, on the performance of DURRIDGE RAD7  
89 electronic radon detector measurements in water, and to suggest a new protocol that increases  
90 the accuracy for radon measurements in gas-rich waters by using this device. The present  
91 study is the first work presenting such research results in the current literature.

## 92 **2. Materials and methods**

93  
94 19 carbonated and 16 non-carbonated spring water samples from Covasna, Harghita,  
95 Maramureş and Cluj counties, Romania were collected for performing routine measurements  
96 of radon in water activity. The measurements were carried out employing two different  
97 methods, namely Liquid Scintillation Counting (LSC) method using a TRICARB 2100 beta  
98 spectrometer and the DURRIDGE RAD7 device.

The principle of the LSC method is based on the capture of  $^{222}\text{Rn}$  in the scintillation cocktail, and counting the scintillations produced by the cocktail due to the interaction of the alpha and beta particles emitted by its short-lived daughters with it. Here, 10 ml of water from each sample was directly inserted in glass vials containing 10 ml ProScint Rn A/B scintillation cocktail. The vials were then shaken, after which the two phases (water and cocktail) dissociated, and the radon gas remained trapped in the cocktail. The calibration of the LSC device was performed using a  $\text{RaCl}_2$  standard solution (NIST) dissolved in water and having an activity of 6 Bq/l.

DURRIDGE RAD7 radon electronic detector is based on electrostatic collection of alpha-emitters and spectral analysis. Both  $^{218}\text{Po}$  ( $T_{1/2}=3.1$  min) and  $^{214}\text{Po}$  ( $T_{1/2}= 164.3$   $\mu\text{sec}$ ) alpha emissions are counted using a passivated ion-implanted Planar Silicon detector (DURRIDGE RAD7 Manual). RAD7 is calibrated for two protocols, WAT40 and WAT250 which enables the user to perform radon measurements in water, using the  $\text{H}_2\text{O}$  accessories. For the present study the WAT 250 protocol was used, which requires a sample volume of 250 ml. For confirmation, an LSC-RAD7 cross-test was performed on a water sample, and identical values were obtained. The sample used did not contain any other gases beside radon. The detection limit for the WAT250 protocol is 10 pCi/l (0.37 Bq/l), as stated in the RAD7  $\text{H}_2\text{O}$  User Manual.

Prior to the radon activity measurements, the gas content of the samples was determined using a simplified Scheibler method. An Erlenmeyer flask was filled with 350 ml of sample and was attached to a Scheibler device, consisting of two graded burettes and a buffer vessel. The instrument ensures constant pressure at the time of degassing. The samples were magnetically stirred for twenty minutes, and as a result of the pressure of the released

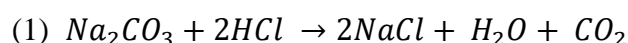
gas, the water level in the burette rises. The volume of the released gas is indicated by the graded burette.

## **2.1. Laboratory procedure**

To quantify the RAD7 measurement efficiency in water samples containing different amounts of gases, different concentrations of carbon dioxide and hydrogen sulfide were generated in the samples. In this regard, water samples were collected from a spring in Cluj County, Romania, which is known to have a relatively constant radon concentration. The samples were collected directly into RAD7 250 ml glass bottles. At the start of the experiment, three samples were measured by RAD7 to determine the radon activity in the absence of other gases. Subsequently, different quantities of CO<sub>2</sub> and H<sub>2</sub>S were generated in water, and three measurements were performed for each concentration. Further experiments were performed for different radon concentrations in water after defined waiting times that allowed radon to decay.

### **2.1.1 Carbon dioxide experiments**

To establish the effect of CO<sub>2</sub> on RAD7 radon activity measurements, carbon dioxide was generated in the water samples with concentrations ranging from 0.65 to 5.19 g/l CO<sub>2</sub>. This was done by adding Na<sub>2</sub>CO<sub>3</sub> and HCl in the water samples, CO<sub>2</sub> being formed, following the reaction:

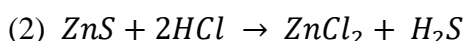


After the reactants were added, the samples were left 20 minutes to ensure that the reaction was complete, then were measured using the RAD7 device, and the results were compared to the activity measured in the absence of other gases in the sample. The

experiment was conducted for samples with four different radon activities ranging from  $23.4 \pm 0.9$  to  $6.7 \pm 0.9$  Bq/l. Eight different CO<sub>2</sub> concentrations were used for each radon activity.

### **2.1.2. Hydrogen sulfide experiments**

H<sub>2</sub>S was generated in samples with five different radon concentrations ranging from  $24.6 \pm 1.4$  to  $6.9 \pm 1.5$  Bq/l, while H<sub>2</sub>S concentrations used ranged from 0.25 to 3 mg/l. Lower H<sub>2</sub>S concentrations of 0.125 to 1 mg/l were generated in an additional sample with a radon activity of 10.8 Bq/l, to further study the effect of low H<sub>2</sub>S concentrations. Hydrogen sulfide was generated by adding ZnS and HCl in the water samples. ZnS was used because the added quantity can be precisely measured, as it is anhydrous. Hydrogen sulfide was formed following the reaction:



All measurements were conducted with an RH% humidity value of under 10% for the RAD7 internal cell, as this is a requirement stated in the DURRIDGE RAD7 user manual. All measured values were subjected to RH% correction, performed by the DURRIDGE CAPTURE RAD7 Data Acquisition and Analysis Software. The device was purged for 20 minutes between measurements to exclude any interference on the values from the previous measurement, and also to allow the short-lived decay products of radon to disintegrate to a level that can no longer influence future measurements.

## **3. Results and discussion**

### **3.1. LSC and RAD7 radon measurements in spring waters.**

From the total of 35 spring water samples that were measured, those containing gas displayed a lack of agreement between the LSC and RAD7 radon measured values. However,

in the absence of a qualitative analysis of the gas, no clear relationship can be established between the gas content of the sample and the difference in measured activities. The gas content in the samples ranged between 5.7 and 860.0 cm<sup>3</sup>/l. The samples that were gas-free showed insignificant differences between values. The difference in radon measured values between LSC and RAD7 had been previously reported in (Stojkovic et. al., 2015). The values obtained using the two methods mentioned above are shown in Figure 1 a) and Figure 1 b).

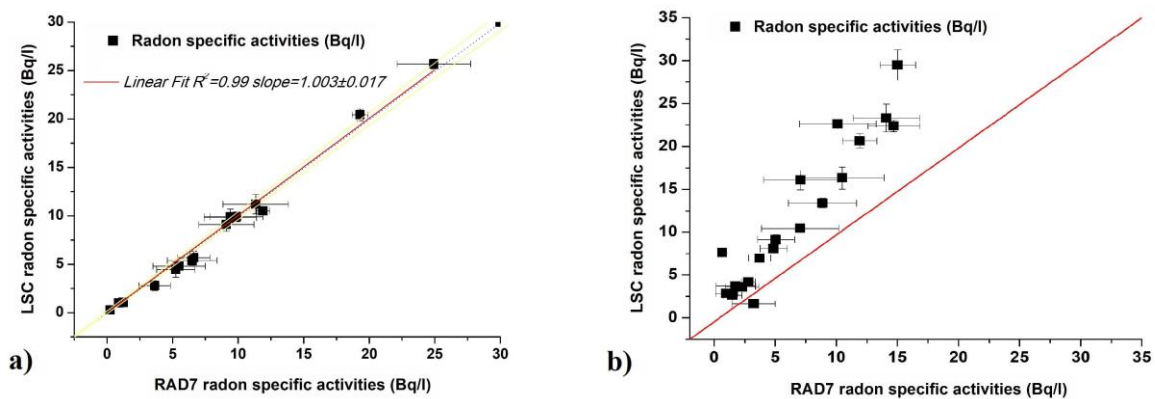


Figure 1. Comparison between LSC and RAD7 radon measured values in natural spring water samples. Panel a) represents the values measured by the two different methods for non-carbonated water samples and panel b) represents the values for carbonated samples. *It can be observed that in panel a) the linear fit perfectly overlaps a 1:1 relationship, while in panel b there are significant deviations from the  $y=x$  function.*

### 3.2. Influence of carbon dioxide on RAD7 measurements

The apparent radon specific activity displays a decrease with increasing gas (H<sub>2</sub>S and CO<sub>2</sub>) concentrations, suggesting a reduction in the detection efficiency of the detector.

For a low CO<sub>2</sub> concentration of 1.29 g/l, which is commonly found in nature (Komatina, 2004), the measured value was 25% lower than the value measured in the absence of added CO<sub>2</sub>. A concentration of 3.24 g/l CO<sub>2</sub> led to a decrease of 43% while for a concentration of



CO<sub>2</sub> of 5.19 g/l the measured activity was 57% lower than the value registered in the absence of gas (Figure 2 a)).

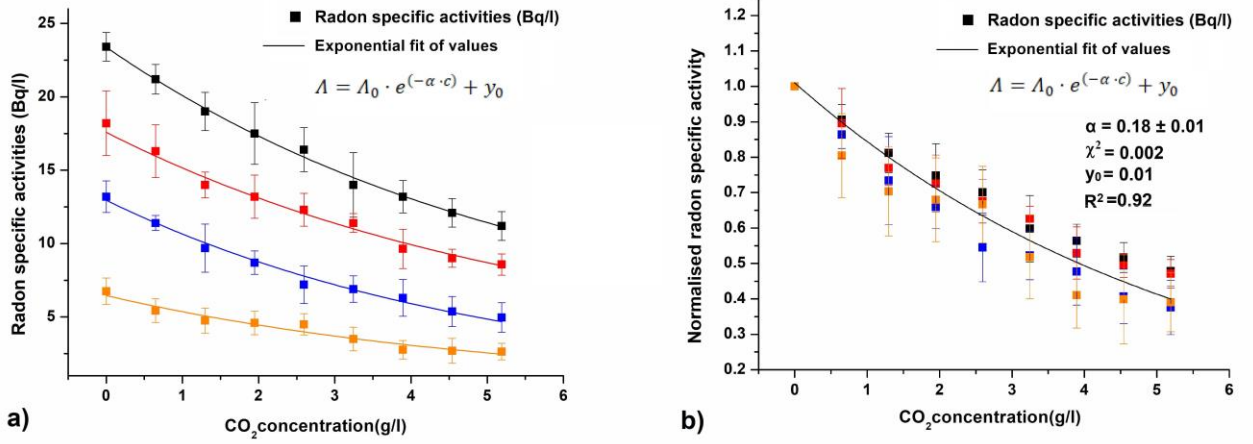


Figure 2. Panel a) represents the dependence of the radon specific activities in water measured by RAD7 in samples with 4 different radon specific activities as function of the concentration of added CO<sub>2</sub>. Panel b) represents the same values normalized to the specific activity measured in the absence of gas.

An exponential dependency of the measured radon activity values as function of the CO<sub>2</sub> concentration can be observed in Figure 2. The data was followed using the following function:

$$(3) \quad \Lambda = \Lambda_0 \cdot e^{(-\alpha \cdot c)} + y_0$$

where:

$\Lambda_0$  is the radon concentration of the sample (Bq/l) measured in the absence of CO<sub>2</sub>

$c$  is the concentration of CO<sub>2</sub> (g/l)

$\alpha$  is the attenuation coefficient (that describes the loss of detection efficiency)

$y_0$  is a residual detectable activity

The parameters obtained by fitting for radon activities measured in the samples enriched in CO<sub>2</sub> are presented in Table 1. It is important to note that values obtained for the  $\alpha$  attenuation coefficient are very similar for all investigated concentrations, the average value obtained being of  $0.18 \pm 0.01$ , at a 95% confidence level.

Measured activity in the absence of CO <sub>2</sub>	Specific activity in the absence of CO <sub>2</sub> obtained by fitting ( $\Lambda_0$ )	Residual activity ( $y_0$ )	$\alpha$	$\chi^2$	R <sup>2</sup>
(Bq/l)	(Bq/l)	(Bq/l)	(l/g)		
<b>23.4±1.0</b>	20.4±1.9	2.9±1.9	0.18±0.03	0.033	0.99
<b>18.2±2.2</b>	15.5±3.0	2.1±0.5	0.17±0.02	0.163	0.97
<b>13.2±1.1</b>	13.0±1.1	0.01±0.1	0.20±0.01	0.066	0.99
<b>6.7±0.9</b>	6.4±0.9	0.06±0.3	0.19±0.03	0.19	0.94

Table 1. Parameters obtained by exponential fitting (eq.3) of data presented in Figure 2.

The interactions of carbon dioxide in soil gas radon measurements were previously studied, including by DURRIDGE company, and a correction factor of 0.3% per 1% CO<sub>2</sub> was suggested to be used for correcting the measured radon values (Lane-Smith and Sims, 2013). Other studies highlighted as well the negative effect of the presence of carbon dioxide on the performance of RAD7 devices in soil gas radon measurements, suggesting that it is not suitable for measurements in CO<sub>2</sub>-rich environments without prior separation of carbon dioxide (Shahrokhi et. al., 2015; Tuccimei and Soligo, 2008). The results of the present study show that an exponential dependency between the measured values for <sup>222</sup>Rn in water and the concentration of CO<sub>2</sub> exists. As such, in principle equation 3 can be used for correcting the measured radon specific activity and obtaining the real radon specific activity, if the concentration of CO<sub>2</sub> in the sample is known. The observed behavior can be explained by

<sup>218</sup>Po ions neutralization processes that is reducing the electrostatic efficiency of the silicon detector system. After the alpha decay of <sup>222</sup>Rn, <sup>218</sup>Po atoms are produced with 88.2% of <sup>218</sup>Po atoms forming singled charged positive ions in dry air (Wellisch, 1913). Chu and Hopke (1988) note two processes that are leading to <sup>218</sup>Po neutralization: electron-scavenging mechanism and water or gas radiolysis. The polonium atom (ionization potential of 8.43 eV) reacts with oxygen to form an oxide species (PoO<sub>2</sub><sup>+</sup>) in dry air atmosphere with an ionization potential in the 10 to 11 eV range (Busigin et al. 1981). This species could then extract electrons from lower ionization potential trace gases such as CO<sub>2</sub>.

Leung and Phillips (1987) observed that the attenuation coefficient in a pure argon atmosphere is relatively independent of radon concentration for low concentrations but high radon concentrations can influence this value. They suggested that the dominant neutralization process at low concentration is charge transfer, and at high radon concentration, it is ion recombination. Because in normal conditions, the CO<sub>2</sub> molecule is an extremely inactive and stable compound (North, 2015), its behavior in the <sup>218</sup>Po neutralization process is similar to that of argon and argon -nitrogen mixture.

### 3.3. Influence of hydrogen sulfide on RAD7 measurements

The influence of H<sub>2</sub>S on RAD7 radon measurements is represented in Figure 3 a) and Figure 3 b). Even for concentrations of H<sub>2</sub>S as low as 0.5 mg/l, there is an average decrease of 43% compared to the values measured when no H<sub>2</sub>S is present. For a concentration of 1 mg/l of H<sub>2</sub>S, the measured activities are 66% lower, while for a concentration of 2 mg/l H<sub>2</sub>S a decrease of 84% is observed. Considering that H<sub>2</sub>S in groundwater can be present in concentrations of up to 50 mg/l (Komatina, 2004), the underestimation of 84% in the

measured radon specific activity observed for a H<sub>2</sub>S concentration of 2 mg/l is extremely concerning. An additional experiment was conducted for lower H<sub>2</sub>S concentrations ranging from 0.1 to 1 mg/l for a sample with a radon activity of  $10.8 \pm 0.8$  Bq/l for studying the dependence in this lower concentration range in greater detail. Figure 3 a) presents the values obtained for radon specific activities in water samples as function of the different hydrogen sulfide concentrations, with the inset focusing on the low concentration range, while Table 2 presents the results obtained by exponential fitting of the data. It can be observed that for concentrations higher than 3 mg/l of H<sub>2</sub>S one is practically unable to perform radon measurements in water using the RAD7 device.

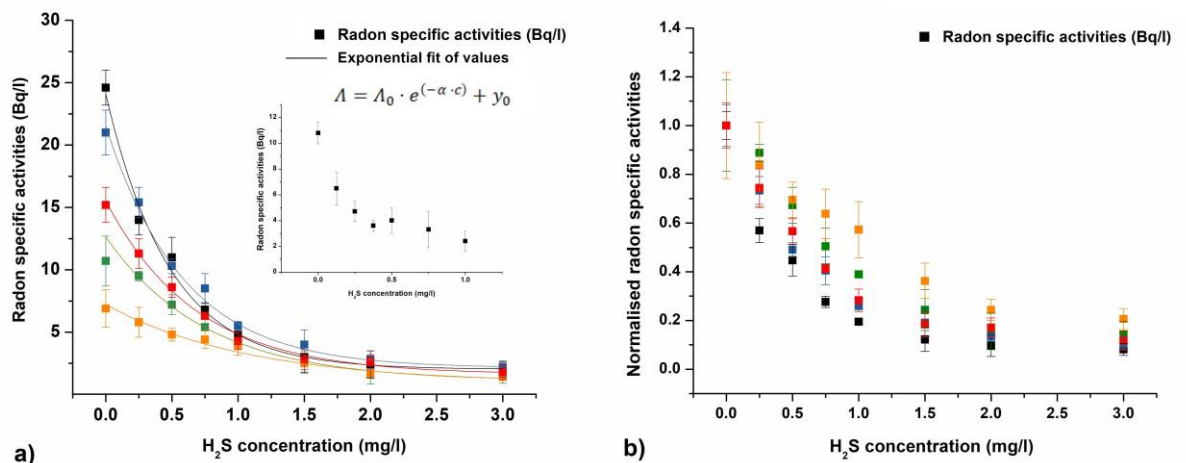


Figure 3. Panel a) represents the dependence of the radon specific activities in water measured by RAD7 in samples with different radon specific activities as function of the concentration of added H<sub>2</sub>S. Panel b) represents the same data normalized to the values obtained in the case of no H<sub>2</sub>S added.

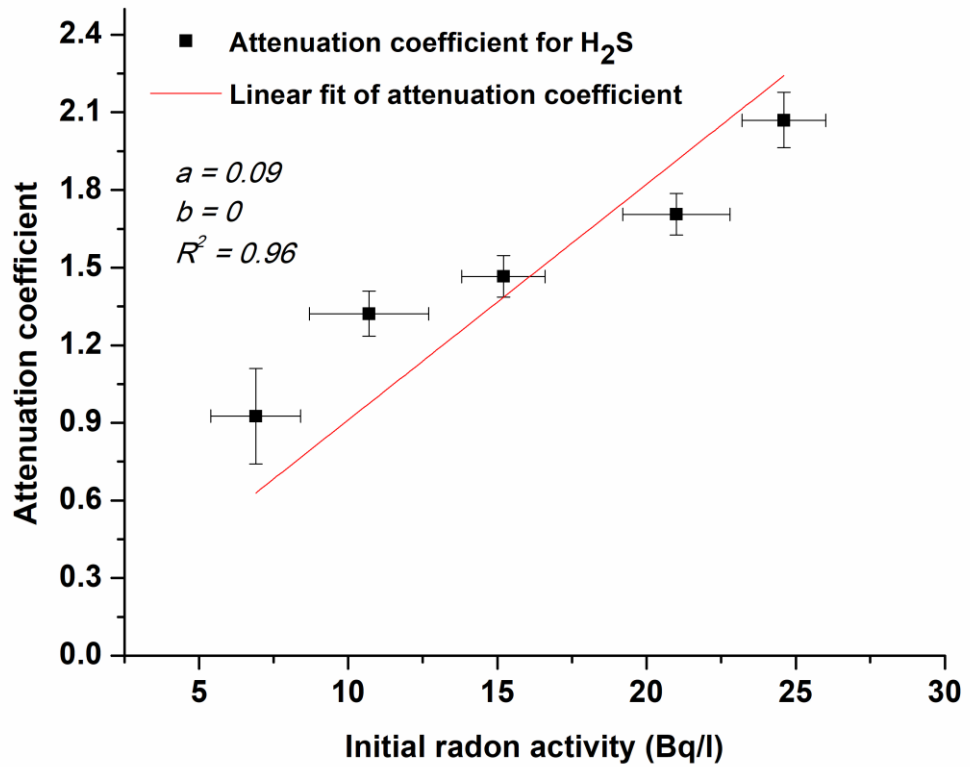
The dependence can be described by the same exponential equation as in the case of CO<sub>2</sub>, in this case the parameter "c" representing the concentration of H<sub>2</sub>S expressed in mg/l. The fitting parameters are presented in Table 2. As in the case of CO<sub>2</sub>, we attribute the

presence of the residual activity ( $y_0$ ) to the signal generated by neutralized  $^{218}\text{Po}$  atoms that are reaching the detector surface even if the electric field in the cell has no guiding effect on them.

Measured activity in the absence of $\text{H}_2\text{S}$	Specific activity in the absence of $\text{H}_2\text{S}$ obtained by fitting ( $\Lambda_0$ )	Residual activity ( $y_0$ )	$\alpha$	$\chi^2$	$\text{R}^2$
(Bq/l)	(Bq/l)	(Bq/l)	(l/mg)		
<b><math>24.6 \pm 1.4</math></b>	$22.1 \pm 0.7$	$2.0 \pm 0.3$	$2.07 \pm 0.11$	0.329	0.99
<b><math>21 \pm 1.8</math></b>	$19.4 \pm 0.7$	$2.1 \pm 0.2$	$1.71 \pm 0.09$	0.259	0.99
<b><math>15.2 \pm 1.4</math></b>	$13.9 \pm 0.6$	$1.6 \pm 0.3$	$1.47 \pm 0.09$	0.232	0.99
<b><math>10.7 \pm 2</math></b>	$11.6 \pm 0.4$	$1.1 \pm 0.3$	$1.32 \pm 0.10$	0.255	0.99
<b><math>6.9 \pm 1.5</math></b>	$6.3 \pm 0.4$	$0.9 \pm 0.3$	$0.93 \pm 0.19$	0.293	0.96

Table 2. Parameters obtained by exponential fitting (eq.3) of data presented in Figure 3

Unlike in the case of  $\text{CO}_2$  enriched samples, for the samples enriched in  $\text{H}_2\text{S}$  the values obtained for the  $\alpha$  attenuation coefficient are not similar for different concentrations of radon in the samples, with the values increasing for the samples with higher radon concentrations. The values range from  $0.93 \pm 0.22$  for  $24.6 \pm 1.4$  Bq/l of  $^{222}\text{Rn}$  to  $2.08 \pm 0.03$  for a specific activity of  $6.9 \pm 1.5$  Bq/l of Rn (Figure 4).



270

271 Figure 4.  $\alpha$  attenuation coefficient (that describes the loss of detector efficiency) as function  
 272 of the radon specific activity in the case of samples where the measurements are interfered by  
 273 the presence of  $H_2S$ .

274 A linear relationship is observed between the attenuation coefficient and the radon  
 275 concentration and the variation of the apparent radon concentration as function of the  $H_2S$   
 276 concentration can be written as:

277 
$$(4) \Lambda = \Lambda_0 \cdot e^{-(a \cdot \Lambda_0 + b) \cdot c}$$

278 Neglecting the intercept for simplicity as within uncertainty it is close to zero, the  
 279 following equation can be applied for performing a mathematical correction of the RAD7  
 280 radon measured activities in water samples in which a known concentration of  $H_2S$  is present:

$$(5) \Lambda_0 = -\frac{1}{a \cdot c} \cdot W(-a \cdot c \cdot \Lambda)$$

Where:

$\Lambda_0$  and represents the true specific activity of the sample

$\Lambda$  represents the apparent (measured) specific activity of the sample

$a$  represents the slope from the linear fit of the alpha coefficient as function of the radon activity reported above

$c$  represents the  $H_2S$  concentration

$W$  is the Lambert  $W$  function

Using the value of the slope given above this equation can be applied if the concentration of hydrogen sulfide and the measured radon specific activity in the sample are known, as the values of Lambert  $W$  function are tabulated or can be obtained using specific software such as Matlab.

Many studies show that the counting efficiency is influenced by humidity (Chu and Hopke, 1988; Hopke, 1989; Roca et al., 2004; Simone, 2016). Hopke (1989) highlighted that the  $^{218}Po$  neutralization in the presence of water molecules occurs because of the radiolysis of water, yielding  $\cdot OH$  and the hydroxyl radicals, which have an electron affinity of 1.83 eV (Drzaic et al. 1984). The phenomenology behind the observed dependency of the apparent radon activity as function of  $H_2S$  concentration can be explain by the similarity of  $H_2S$  and  $H_2O$  molecules as both are polar molecules that can dissociate, creating negative ions. The radiolysis process described for water is also conceivable for  $H_2S$ . The ionization potential of  $H_2S$  (10.45 eV) is close to the ionization energy of the  $PoO_2^+$  ion and its proton affinity of 7.7 eV. During alpha decays,  $H_2S$  can be dissociated into  $HS^-$  or  $S_2^-$ , the dissociation energy of  $H_2S$  (into hydrogen and sulfur) is only 0.2 eV/molecule, compared to water, which has a dissociation energy of 2.9 eV/molecule (Nunnally et al., 2009). Moreover, the water

molecules can act as a catalyst and can themselves dissociate the H<sub>2</sub>S molecule (O'Brien 1991). This can explain the proportionality of the attenuation coefficient with the ionizing radiation activity (Figure 4). These two processes can cause a very strong effect, even at low H<sub>2</sub>S concentrations.

### 3.4. Elimination of CO<sub>2</sub> and H<sub>2</sub>S interference on RAD7 radon measurements

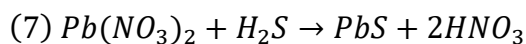
As observed from the results of the experiments presented above, the presence of CO<sub>2</sub> and H<sub>2</sub>S strongly decreases the detection efficiency of the instrument. As such, it is compulsory for correction protocols to be developed and applied for the measurement of radon in natural mineral waters containing gaseous components. Mathematical corrections were presented above, however these corrections rely on having prior information on the type and concentration of the interfering gas. Below we are proposing some experimental procedures that aim at the elimination of the interfering component by chemical precipitation.

To test this approach experiments were conducted on a new set of samples collected from the same location in which CO<sub>2</sub> and H<sub>2</sub>S were generated following the same procedure described above (section 2.1). For eliminating the interference of carbon dioxide on radon measurements in water, Ca(OH)<sub>2</sub> was added in the samples containing CO<sub>2</sub>, before the measurement. The added Ca(OH)<sub>2</sub> quantity was calculated from the reaction (6), with a 10% surplus. The precipitation of CO<sub>2</sub> as CaCO<sub>3</sub> follows the reaction below:



A similar procedure was tested for the water samples with hydrogen sulfide content, by adding Pb(NO<sub>3</sub>)<sub>2</sub> (40 mg of Pb<sup>2+</sup>) as reactant, for converting H<sub>2</sub>S into PbS, that was precipitated and deposited, following the reaction:





Subsequently, after waiting for 20 minutes to ensure that the reaction was complete, the water samples were measured. It was observed that the effect of both gasses was canceled, regardless of their concentration, and the radon measured activity matched the measured activity for sample that were not enriched in  $\text{CO}_2$  or  $\text{H}_2\text{S}$  as it can be seen from the data presented in Figure 5 a) and Figure 5 b), respectively.

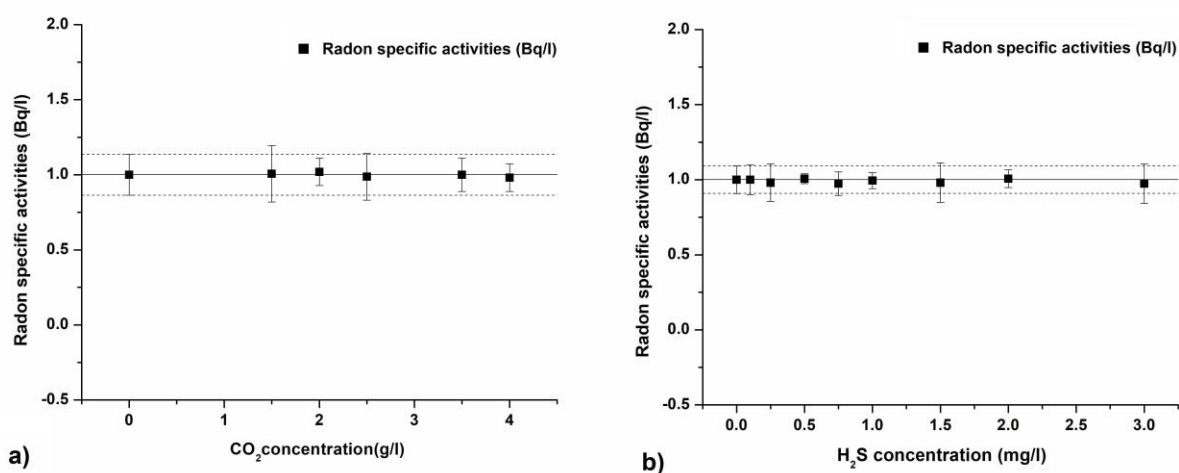


Figure 5. Specific activities of radon measured in samples where no gases were generated, compared to the values measured in samples in which different concentrations of  $\text{CO}_2$  (panel a) and  $\text{H}_2\text{S}$  (panel b) were generated and subsequently neutralized as described above. *All values are normalized to the true value of the specific activity (i.e. measured in the absence of interfering gases). It can be observed that all vales agree within uncertainties and are consistent to unity.*

## 4. Conclusions

In the present study, the effect of the presence of two major gaseous components of natural mineral waters, carbon dioxide and hydrogen sulfide on radon measurements using RAD7 was investigated. For both gases, a decrease of the detection efficiency was reported and an exponential dependence was observed between the apparent activity and the concentration of the interfering gas, suggesting that radon measurements by RAD7 are not accurate when gas-rich waters are analyzed, and a severe underestimation of the true values are expected even in the presence of common concentrations of interfering gases. The findings of the present study are generally applying to all radon measurement devices with electrostatic cells. Mathematical corrections were proposed, however they require independent measurements of CO<sub>2</sub> and H<sub>2</sub>S concentrations. A laboratory method based on the precipitation of H<sub>2</sub>S with Pb(NO<sub>3</sub>)<sub>2</sub>, resulting in HNO<sub>3</sub> and PbS, and the precipitation of CO<sub>2</sub> with Ca(OH)<sub>2</sub> resulting in CaCO<sub>3</sub> and H<sub>2</sub>O was proposed. This procedure, if applied before the RAD7 radon measurements, leads to the removal of the effect of carbon dioxide and hydrogen sulfide on the RAD7 radon measured activities.

Considering the results of the present study, it can be assumed that many published articles on radon measurements in water using electrostatic cell radon monitors, performed on samples containing carbon dioxide and hydrogen sulphide, such as carbonated spring waters and hot springs, could present compromised results. The present study serves as a guide for worldwide researchers using electrostatic cell monitors to perform correct measurements on radon in gaseous water samples, as the effect of the investigated gases cannot be overlooked.

**Acknowledgements:** We acknowledge the financial support from EEA-RO-NO-2018-0126, 3/2019.

The funding source had no involvement in study design; collection, analysis and interpretation of data; writing of the report or in the decision to submit the article for publication.

## 5. References

Alharbi W.R., Abbady A.G.E., El-Taher A., 2015, Radon Concentrations Measurement for groundwater Using Active Detecting Method, American Academic Scientific Research Journal for Engineering, Technology, and Sciences, vol. 14(1), pp. 1–11.

Busigin A., Van der Vooren A.W., Babcock J.C., Phillips C.R., 1981, The nature of unattached RaA ( $^{218}\text{Po}$ ) particles, Health Physics, vol. 40, pp. 333–343.

Celaya S., Fuente I., Quindós L., Sainz C., 2018, Optimization of a portable liquid scintillation counting device for determining  $^{222}\text{Rn}$  in water, Radiation Measurements, vol. 117, pp. 1-6.

Chu K.D, Hopke P.K., 1988, Neutralization kinetics for polonium-218, Environmental Science & Technology, vol. 22 (6), pp. 711-717.

Drzaic P.S., Marks J., Brauman J.I., 1984, Electron photodetachment from gas phase molecular anions, in Gas Phase Ion Chemistry, Vol. 3, Editor: Bowers M.R., New York: Academic Press, pp. 167-211.

Duggal V., Mehra R., Rani A., 2013, Determination of  $^{222}\text{Rn}$  level in groundwater using a Rad7 detector in the Bathinda district of Punjab, India, Radiation Protection Dosimetry, vol.156(2), pp. 239–245. <https://doi.org/10.1093/rpd/nct054>

Duggal V., Sharma S., Mehra R., 2020, Risk assessment of radon in drinking water in Khetri Copper Belt of Rajasthan, India, Chemosphere, vol. 239.

DURRIDGE RAD H<sub>2</sub>O Radon in water accessory for the RAD7 User Manual , (<https://durridge.com/documentation/RAD%20H2O%20Manual.pdf>)

393 (<https://durrige.com/documentation/RAD7%20Manual.pdf>)

394 Elmehdi H. M., Dalah E. Z., BakhronovK., 2019, Measurements of Radon  
395 concentration in water in the United Arab Emirates and the associated health effects,  
396 Advances in Science and Engineering Technology International Conferences (ASET), Dubai,  
397 United Arab Emirates, pp. 1-5.

398 Ertuğral F., Yakut H., Tabar E., Akkaya R., Demirci N., Zenginerler Z., 2015,  
399 Measurements of Radon Content in the Thermal Waters in Sakarya. Acta Physica Polonica  
400 A, vol. 128(2B), pp. 251-254. <https://doi.org/10.12693/aphyspola.128.b-251>

401 Espinosa G., Golzarri J.I., Cortes A., 1991, Radon measurements of groundwater in  
402 Mexico, International Journal of Radiation Applications and Instrumentation. Part D. Nuclear  
403 Tracks and Radiation Measurements, vol.19(1-4), pp. 305-306.

404 Giampaoli S., Valeriani F., Gianfranceschi G., Vitali M., Delfini M., Festa M.R.,  
405 Bottari E., Spica R.V., 2013, Hydrogen sulfide in thermal spring waters and its action on  
406 bacteria of human origin, Microchemical Journal, vol. 108, pp. 210–214.

407 Hopke P.K, 1989, The initial behavior of <sup>218</sup>Po in indoor air, Environment  
408 International, vol. 15 (1-6), pp. 299-308.

409 Ismail N. F., Hashim S., Sanusi M.S.M., Abdul Rahman A.T., Bradley D.A., 2021,  
410 Radon Levels of Water Sources in the Southwest Coastal Region of Peninsular Malaysia,  
411 Applied Sciences, vol. 11(15), pp. 6842. <https://doi.org/10.3390/app11156842>

412 Khattak N.U., Khan A.M., Ali N., Abbas S. M., 2011, Radon monitoring for  
413 geological exploration: A review, Journal of Himalayan Earth Sciences vol. 44, pp. 91-102.

414 Komatina M. M. (Edited by), 2004, Developments in Earth and Environmental  
415 Sciences Medical Geology - Effects of Geological Environments on Human Health, vol. 2  
416 chapter 2: Geological factors, pp. 38–235, DOI: 10.1016/S1571-9197(04)80003-X.

417 Lane-Smith D., Sims K.W.W., 2013, The effect of CO<sub>2</sub> on the measurement of  
418 <sup>220</sup>Rn and <sup>222</sup>Rn with instruments utilising electrostatic precipitation. Acta Geophysica, vol.  
419 61(4), pp. 822–830, <https://doi.org/10.2478/s11600-013-0107-3>

Lane-Smith D., Sims W. W. K., 2013, The effect of CO<sub>2</sub> on the measurement of <sup>220</sup>Rn and <sup>222</sup>Rn with instruments utilizing electrostatic precipitation, *Acta Geophysica*, vol. 61(4), pp. 822–830.

Leung H. M-Y., Phillips C.R., 1987, The Electrical and Diffusive Properties of Unattached <sup>218</sup>Po in Argon Gas. *Radiation Protection Dosimetry*, vol. 18(1), pp. 3-11.

Nikolov J., Todorovic N., Petrovic Pantic T., Forkapic S., Mrdja D., Bikit I., Krmar M., Veskovic M., 2012, Exposure to radon in the radon spa Niška Banja, Serbia, *Radiation Measurements*, vol. 47(6), pp. 443-450.

Nita D., Moldovan M., Cosma C., 2014, Radon measurement in carbonated water with the Lucas cell and charcoal adsorption methods, *Journal of Radioanalytical and Nuclear Chemistry*, vol. 299.

North M., 2014, What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. Editors: Styring P, Quadrelli EA, Armstrong K, *Carbon Dioxide Utilisation: Closing the Carbon Cycle: First Edition*. Elsevier Inc., pp. 3-17.

Nunnally T., Gutsol K., Rabinovich A., Fridman A., Starikovskiy A., Gutsol A., Potter R.W., 2009, Dissociation of H<sub>2</sub>S in non-equilibrium gliding arc “tornado” discharge, *International Journal of Hydrogen Energy*, vol. 34, pp. 7618-7625.

O'Brien M., 1991, Catalytic Oxidation of Sulfides in Biogas, Ventilation Air and Wastewater Streams from Anaerobic Digesters, *Proceedings 1991 Food Industry Environmental Conference*, USA.

Roca V., De Felice P., Esposito A.M., Pugliese M., Sabbarese C., Vaupotic J., 2004, The influence of environmental parameters in electrostatic cell radon monitor response, *Applied Radiation and Isotopes*, vol. 61, pp. 243–247.

Salih N.F., 2021, Determine the Contaminations of Radon in the Drinking Water Using NTDs (CR-39) and RAD7 Detectors, *Arabian Journal for Science and Engineering*, vol. 46(6), pp. 6061–6074, <https://doi.org/10.1007/s13369-020-05267-y>

Schubert M., Brueggemann L., Knoeller K., Schirmer M., 2011, Using radon as an environmental tracer for estimating groundwater flow velocities in single-well tests, *Water Resources Research*, vol. 47(3).

Segovia N., 1991, Radon and volcanic activity: Recent advances, International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements, vol.19(1-4), pp. 409-414.

Shahrokhi A., Burgehele B. D., Fábián F., Kovács T., 2015, New study on the correlation between carbon dioxide concentration in the environment and radon monitor devices, Journal of Environmental Radioactivity, vol. 150, pp. 57–61.

Siirila E.R., Navarre-Sitchler A.K., Maxwell R.M., McCray J.E., 2012, A quantitative methodology to assess the risks to human health from CO<sub>2</sub> leakage into groundwater, Advances in Water Resources, vol. 36, pp. 146-164.

Simone G.D, Lucchetti C., Galli G., Tuccimei P., 2016, Correcting for H<sub>2</sub>O interference using a RAD7 electrostatic collection-based silicon detector, Journal of Environmental Radioactivity, vol. 162-163, pp. 146-153.

Stojkovic I., Tenjović B., Nikolov J., Vesković M., Mrđa D., Todorović N., 2015, Improvement of measuring methods and instrumentation concerning <sup>222</sup>Rn determination in drinking waters – RAD7 and LSC technique comparison, Applied Radiation and Isotopes, vol.98, pp. 117–124.

Tuccimei P., Soligo M., 2008, Correcting for interference in soil radon flux measurements, Radiation Measurements, vol. 43(1), pp. 102–105.

Wellisch E.M., 1913, The distribution of the active deposition of radium in an electric field. II. Philosophical Magazine 6 (XXVI), pp. 623-635.

WHO, 2017, Guidelines for drinking-water quality, WHO publications, Geneva , 4ed., ch. 9, pp. 203–218