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# ACCOUNTING FOR OVERCOUNTING INDUCED BY <sup>222</sup>Rn CONTAMINATION IN <sup>14</sup>C MEASUREMENTS PERFORMED WITH LIQUID SCINTILLATION COUNTING

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Received 25 June 2023

Accepted 03 November 2023

#### Abstract

This research paper introduces a methodology for estimating overcounting resulting from uranium series radionuclides, with a specific focus on <sup>222</sup>Rn contamination. The method is demonstrated using the Quantulus 1220<sup>™</sup> spectrometer. Exponential fitting is employed for the calculations, utilizing a custom algorithm developed in MATLAB® R2022b. The proposed method allows for the determination of the sample count rate correction, F<sup>14</sup>C and radiocarbon age without the need for additional chemical treatment or specialized electronics during liquid scintillation counting (LSC) measurements with the Quantulus 1220<sup>™</sup> spectrometer. However, the method does have certain limitations. It requires a significant number of cycles and extended measurement time per cycle, but it can be applied to samples with significant <sup>222</sup>Rn contamination that require rapid <sup>14</sup>C analysis.

#### Keywords

overcounting estimation, uranium series radionuclides, <sup>222</sup>Rn contamination, Quantulus 1220<sup>™</sup> spectrometer, exponential fitting, liquid scintillation counting

## 1. Introduction

Radiocarbon dating utilizes two methods to determine the <sup>14</sup>C content in a sample: count rate measurement and concentration measurement. The count rate measurement involves the detection and counting of  $\beta^-$  particles. This method is used in the gas proportional counting (GPC) technique and the liquid scintillation counting (LSC) technique. In contrast, the concentration measurement method is employed in the accelerator mass spectrometry (AMS) technique.

In the count rate measurement method, one of the sources of uncertainty arises from the presence of other radionuclides in the sample that emit  $\alpha$  or  $\beta^-$  particles, which can be detected in the <sup>14</sup>C counting window. This issue is well known in radiocarbon dating, particularly due to the presence of the radionuclide <sup>222</sup>Rn from the uranium series, as documented by Nydal (1983), Polach and Kaihola (1988), Horvatinčić *et al.* (1995) and Pawlyta *et al.* (1997). The presence of <sup>222</sup>Rn distorts the <sup>14</sup>C measurements. Thus far, various approaches have been suggested to address this issue.

## 1.1. Aging Process

The half-life of <sup>222</sup>Rn is relatively short, so the waiting time needed for 7–10 half-lives to elapse is not very long. Based on exponential decay, <sup>222</sup>Rn levels can be reduced to background levels over this time period. Therefore, a common method to eliminate <sup>222</sup>Rn contamination is the 30-day aging process, in which the sample is stored in a freezer. This method is based on the principle that approximately 99.6% of <sup>222</sup>Rn will decay over that time.

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ISSN 1897-1695 (online), 1733-8387 (print)

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#### **1.2.** Gas Proportional Counters Methods

Historically, the first methods of  $^{222}$ Rn removal were dedicated to removing radon from CO<sub>2</sub>, such as by slow fractional distillation at controlled temperatures (de Vries, 1957). There was also the application of gas proportional counters to monitor  $^{222}$ Rn concentration in the Rn–CO<sub>2</sub> mixture (Pazdur, 1979).

### **1.3. Liquid Scintillation Counters Methods**

There are several methods of purifying benzene, involving vacuum pumping at low temperatures. Hood *et al.* (1989) reported that <sup>222</sup>Rn can be removed during dynamic vacuum recovery of benzene at -78°C. Tudyka *et al.* (2021) described a method of removing <sup>222</sup>Rn using four freeze–pump–thaw cycles at either -20°C (with a H<sub>2</sub>O ice and NaCl mixture) or -72°C (with a dry ice and ethanol mixture) to bring <sup>222</sup>Rn contamination to the background level.

Another method involves calculating the correction based on additional measurements. This method uses the very short half-life of <sup>214</sup>Po, and if two consecutive counts are registered within a certain time window, they can be interpreted as <sup>214</sup>Bi and <sup>214</sup>Po decays, respectively, referred to as a <sup>214</sup>Bi/<sup>214</sup>Po pair decay event (Theodórsson, 2005b; Tudyka *et al.*, 2015). A liquid scintillation counter with the ability to measure pulse height, pulse shape, and time between subsequent pulses, such as the ICELS system (Theodórsson, 2005a) equipped with a multichannel analyser that records amplitude of pulse and time between pulses (Tudyka and Bluszcz, 2011), or the Multicell spectrometer (Tudyka *et al.*, 2017), is required for this method.

#### 1.4. Mathematical and Computational Methods

The literature lacks mathematical or computational methods that do not require additional measurements or chemical treatment, except for the linear regression fitting method described by Gupta and Polach (1985). By using the radioactive decay equation, one can obtain:

$$a_{\rm Rn} = a_{s+b+Rn} - a_{s+b} = a_{Rn_0} e^{-\lambda_{Rn}t}, \qquad (1.1)$$

where:

- $-a_{s+b+Rn}$  represents the measured count rate of the sample, background, and radon and its daughter radionuclides present in the sample, obtained from results from the liquid scintillation counter, measured over time *t*;
- the decay constant  $\lambda_{Rn} = 0.1813 \text{ day}^{-1}$  is known;
- the initial count rate of radon and its daughter radionuclides in sample,  $a_{Rn_0}$ , is unknown;
- the sought-after value is the count rate of the sample and background without radon and daughter nuclides,  $a_{s+b}$ , which is unknown and constant.

After taking natural logarithm, Eq. (1.1) can be written as

$$\ln\left(a_{s+b+Rn} - a_{s+b}\right) = -\lambda_{Rn}t + \ln\left(a_{Rn_0}\right),\tag{1.2}$$

which corresponds to the equation of a line, y = mx + c, where x = t,  $y = \ln(a_{s+b+Rn} - a_{s+b})$ ,  $m = -\lambda_{Rn}$ , and  $c = \ln(a_{Rn_0})$ . Hence, the values of y are partially known. Gupta and Polach (1985) suggest estimating  $a_{s+b}$  through 'guesstimation' until the slope of the determined curve corresponds to  $-\lambda_{Rn}$  with an acceptable level.

However, this method should be interpreted with caution and can only be used as a means of verifying the presence of <sup>222</sup>Rn in the sample. It is not suitable for modern-day processing standards. Firstly, the transformation of data from exponential form to linear form through linearization alters the probability density distribution (Box and Cox, 1964). Secondly, introducing the variable decay constant  $\lambda$  for <sup>222</sup>Rn adds an additional degree of freedom to the calculations, which should be avoided.

Therefore, there is a lack of mathematical methods for estimating overcounting induced by daughter isotopes of <sup>222</sup>Rn. In this paper, direct exponential fitting is proposed, taking advantage of efficient modern-day numerical calculations.

#### 1.5. Uranium Series Radionuclides

The uranium series, named after its parent isotope <sup>238</sup>U, is one of three naturally occurring decay chains. A detailed table of the uranium series, starting from <sup>226</sup>Ra (a parent radionuclide of <sup>222</sup>Rn) and ending with <sup>210</sup>Pb, is presented in **Table 1**, along with the <sup>14</sup>C radionuclide for comparison. Uncertainties are provided in parentheses, and they refer to the last digit or the last two digits of the presented value.

Within this chain, two isotopes of interest are <sup>226</sup>Ra and <sup>222</sup>Rn, which can be found in underground water, as well as in drinking water (Cothern and Rebers, 1990) and construction materials of buildings (Nero and Nazaroff, 1984). As a result, these isotopes can be present in the atmosphere of a laboratory and in water used for chemical pretreatment, which can lead to sample contamination.

The first of the aforementioned radionuclides, <sup>226</sup>Ra, has a half-life comparable to that of <sup>14</sup>C. As such, if it contaminates a sample, it will remain there indefinitely from a radiocarbon dating standpoint.

It is worth noting that the daughter radionuclides of <sup>222</sup>Rn, namely <sup>218</sup>Po, <sup>214</sup>Pb, <sup>214</sup>Bi and <sup>214</sup>Po, all have very short half-lives of less than an hour. As a result, one decay of <sup>222</sup>Rn is followed by four additional decays (**Table 1**).

The next isotope in the uranium chain, <sup>210</sup>Pb, has a relatively long half-life and typically its contribution within the <sup>14</sup>C counting window is considered negligible.

Parent isotope	Decay mode	Daughter isotope	Percentage of decay mode (%)	Half-life T <sub>1/2</sub>	Weighted mean β⁻ decay energy, keV	Q value (max energy), keV	Major decay branches (>0.5%)		
							Mean β⁻energy, keV	End-point energy, keV	Branching percentages (%)
<sup>14</sup> C	β-	<sup>14</sup> N	100	5700(30) year	49.47(10)	156.475(4)	49.47(10)	156.475(4)	100
<sup>226</sup> Ra	α	<sup>222</sup> Rn	100	1600(7) year	-	4870.62(25)	4601(1) 4784.34(25)	-	6.16(3) 93.84(11)
<sup>222</sup> Rn	α	<sup>218</sup> Po	100	3.8222(9) day	-	5590.4(3)	5489.48(30)	-	99.920(10)
<sup>218</sup> Po	α	<sup>214</sup> Pb	99.980(2)	3.097(12) min	-	6114.75(9)	6002.55(10)	-	99.9789(20)
<sup>218</sup> Po	β-	<sup>218</sup> At	0.020(2)	3.097(12) min	-	259(12)	-	-	-
<sup>218</sup> At	α	<sup>214</sup> Bi	99.95(5)	1.27(6) s	-	6876.1(26)	6654(5) 6693(3)	-	6.90(10) 92.7(5)
<sup>218</sup> At	β-	<sup>218</sup> Rn	0.05(5)	1.27(6) s	-	2883(12)	-	-	-
<sup>218</sup> Rn	α	<sup>214</sup> Po	100	33.75(15) ms	-	7262.5(19)	7129.1(19)	-	99.870(4)
<sup>214</sup> Pb	β-	<sup>214</sup> Bi	100	27.06(7) min	224(5)	1018(11)	48.0(32) 142.8(37) 205.1(39) 225.3(40) 334.5(42)	179(11) 484(11) 666(11) 723(11) 1018(11)	2.75(8) 1.063(18) 44.5(7) 39.0(5) 12.7(9)
<sup>214</sup> Bj	β-	<sup>214</sup> Po	99.9790(13)	19.71(2) min	641(6)	3269(11)	$\begin{array}{c} 161.4(38)\\ 247.8(40)\\ 260.5(41)\\ 317.8(42)\\ 355.8(42)\\ 356.1(43)\\ 384.7(43)\\ 424.2(44)\\ 426.7(44)\\ 426.7(44)\\ 433.1(44)\\ 474.5(44)\\ 474.5(44)\\ 524.9(43)\\ 539.0(45)\\ 566.8(45)\\ 614.9(46)\\ 667.6(46)\\ 683.3(46)\\ 1007.1(47)\\ 1268.4(48)\\ \end{array}$	$\begin{array}{c} 540(11)\\ 787(11)\\ 821(11)\\ 976(11)\\ 1005(11)\\ 1076(11)\\ 1252(11)\\ 1258(11)\\ 1258(11)\\ 1274(11)\\ 1379(11)\\ 1422(11)\\ 1504(11)\\ 1539(11)\\ 1504(11)\\ 1726(11)\\ 1854(11)\\ 1854(11)\\ 1891(11)\\ 2660(11)\\ 3269(11)\\ \end{array}$	0.542(22) 1.28(4) 2.78(6) 0.563(16) 5.56(5) 0.866(12) 4.33(4) 2.459(15) 1.433(11) 1.192(21) 1.589(17) 8.16(5) 16.90(11) 17.55(10) 0.57(5) 3.09(4) 0.90(5) 7.22(8) 0.55(8) 19.2(4)
<sup>214</sup> Bi	α	<sup>210</sup> TI	0.0210(13)	19.9(4) min	_	5621(3)	5273(9) 5452(3) 5516(3)	-	5.8(5) ª 54(4) ª 39(3) ª
<sup>214</sup> Po	α	<sup>210</sup> Pb	100	163.6(3) μs	-	7833.46(6)	7686.82(7)	-	99.9895(6)
<sup>210</sup> Tl	β-	<sup>210</sup> Pb	100	1.30(3) min	1.18(16) ·10³	5482(12)	477(13) 568(14) 674(10) 743(11) 877.1(69) 1635(18) 1762.6(54)	1380(30) 1600(30) 1860(24) 2020(30) 2413(17) 4210(40) 4386(12)	2.0(10) 7.0(20) 24(5) 10(3) 10(3) 30(6) 20.0(20)
<sup>210</sup> Pb	β-	<sup>210</sup> Bi	100	22.20(22) year	6.1(6)	63.5(5)	4.16(13) 16.16(13)	17.0(5) 63.5(5)	84(3) 16(3)
<sup>210</sup> Pb	α	<sup>206</sup> Hg	1.9(3)·10 <sup>-6</sup>	22.20(22) year	-	3792(20)	3720(20)	-	-

# Table 1. Subsequent decays of the uranium series from <sup>226</sup>Ra to <sup>210</sup>Pb.

<sup>a</sup>Recalculated.

The highlighted decays are more likely to affect the radiocarbon dating in Quantulus 1220<sup>™</sup>. <sup>14</sup>C radionuclide is shown for comparison. Data retrieved from NuDat 3.0 database and IAEA NDS database.

The energy of decay is another factor of importance in radiocarbon dating with the LSC technique. <sup>14</sup>C decays through  $\beta^-$  decay, with a continuous energy spectrum and a weighted mean energy of 49.47(10) keV and a maximum or endpoint energy of 156.475(4) keV. As a result, isotopes that undergo  $\alpha$  decay, namely <sup>226</sup>Ra, <sup>222</sup>Rn, <sup>218</sup>Po and <sup>214</sup>Po, usually will be separated from the radiocarbon energy spectra (see major decay branches in **Table 1**).

Isotopes that undergo  $\beta^-$  decay, such as <sup>214</sup>Pb and <sup>214</sup>Bi, have much greater weighted mean  $\beta^-$  decay energy that <sup>14</sup>C. Therefore, they are mostly separated from the radiocarbon energy spectra. However, statistically some decays will have energy that overlap the <sup>14</sup>C energy spectra. The overcounting of uranium series radionuclides in the <sup>14</sup>C window is therefore the result of <sup>214</sup>Pb and <sup>214</sup>Bi decays (other rare decay modes mentioned in **Table 1** are negligible).

# 2. METHODS

## 2.1. Quantulus 1220<sup>™</sup> Spectrometer

Quantulus 1220<sup>TM</sup> is a commonly used ultra-low background spectrometer. Ultra-low level background is obtained by using a passive shield (asymmetrical 630 kg lead shield), active shield (allowing subtraction of scintillations registered simultaneously by photomultipliers in anticoincidence shield filled with mineral oil liquid scintillator and registered by photomultipliers directed onto sample), radio frequency noise discriminator and pulse amplitude comparator (allowing subtraction of pulses whose amplitude is highly different in both photomultipliers directed onto sample; Pawlyta *et al.*, 1997). Measured spectra on the Quantulus 1220<sup>TM</sup> are spread with logarithmic conversion into 1024 channels (**Fig. 1**). Hence, radionuclides from uranium series are measured in  $\alpha/\beta$  spectra. The Quantulus 1220<sup>TM</sup> spectrometer can be used to many experiments such as for determining content of these radionuclides in drinking water (e.g., Schönhofer, 1989; Salonen and Hukkanen, 1997) or for determining <sup>210</sup>Pb and <sup>210</sup>Po count rates in the sample (Kim *et al.*, 2008).

The spectra in the Quantulus  $1220^{\text{TM}}$  at the Gliwice Laboratory are divided into three windows, after Tudyka and Pazdur (2010): the <sup>3</sup>H window (channels 1–290), the <sup>14</sup>C window (channels 291–580) and the radon and daughter products window (channels 580–1024), as shown in **Fig. 1**.

#### 2.2. Exponential Function Fitting Method

We propose a contemporary approach, distinct from linear regression fitting, which involves direct weighted



Fig 1. Alpha and beta particle spectra of radioactive nuclides in a Quantulus 1220<sup>™</sup> liquid scintillation counter with counting windows used at the Gliwice Laboratory (Poland). In most cases, peak from <sup>210</sup>Pb would not be observed in radiocarbon dating due to its low probability.

exponential function fitting utilizing a numerical algorithm to Eq. (1.1).

In most cases, the count rate induced by radon and daughter radionuclides in the <sup>14</sup>C window is too small to directly fit an exponential function to the <sup>14</sup>C window. However, in the radon and daughter products window, presence of <sup>222</sup>Rn and its daughter isotopes is usually noticeable if the sample is measured soon enough after benzene synthesis. Therefore, two fittings into two different windows can be performed using the following formulas:

$$a_{s+b+Rn}^{C+Rn} = a_{Rn_0}^{C+Rn} e^{-\lambda_{Rn}t} + a_{s+b}^{C+Rn} ,$$
  

$$a_{s+b+Rn}^{Rn} = a_{Rn_0}^{Rn} e^{-\lambda_{Rn}t} + a_{s+b}^{Rn} .$$
(2.1)

Here, the C + Rn superscript denotes the combined <sup>14</sup>C and radon and daughter products window, and the Rn superscript represents the radon and daughter products window.

The radon and daughter nuclides-free count rate in the <sup>14</sup>C window is calculated as

$$a_{s+b}^{C} = a_{s+b}^{C+Rn} - a_{s+b}^{Rn} .$$
(2.2)

This calculation, subtracting two independent values, will be referred to as the subtraction approach later in the paper.

Since some values in Eq. (2.1) are interdependent, a different approach is more suitable, which involves calculating the values in the radon and daughter products window and the combined <sup>14</sup>C and radon and daughter products window as a system of equations:

$$\begin{cases} a_{s+b+Rn}^{Rn} = a_{Rn_0}^{Rn} e^{-\lambda_{Rn}t} + a_{s+b}^{Rn} \\ a_{s+b+Rn}^{C+Rn} = E a_{Rn_0}^{Rn} e^{-\lambda_{Rn}t} + a_{s+b}^{Rn} + a_{s+b}^{C} \end{cases}$$
(2.3)

This approach, treating some values as interdependent, will be referred to as the system of equations approach later in the paper. Here, E represents the correction constant, which accounts for the count rate of the radon and daughter radionuclides measured in the <sup>14</sup>C window compared to the count rate of the radon and daughter radionuclides measured in the radon and daughter products window. Specifically,  $a_{Rn}^{Rn}(E)$  represents the part of initial count rate of radon and daughter radionuclides measured in the <sup>14</sup>C window. The count rate of radon and daughter nuclides at time zero,  $a_{Rn_0}^{Rn}$ , is sample-dependent, while the value of the constant E is related to the specific measurement conditions, including settings of the liquid scintillation beta spectrometer. Therefore, if the *E* constant is determined for the spectrometer, correction in the  ${}^{14}C$  window can be calculated as:

$$a_{s+b}^{C} = a_{s+b+Rn}^{C} - (E-1)a_{Rn_0}^{Rn}e^{-\lambda_{Rn}t},$$
(2.4)

and  $a_{Rn_0}^{Rn}$  can be calculated from the radon and daughter products window as

$$a_{s+b+Rn}^{Rn} = a_{Rn_0}^{Rn} e^{-\lambda_{Rn}t} + a_{s+b}^{Rn} \,. \tag{2.5}$$

This approach is suitable because most of the time, the overcounting induced by <sup>222</sup>Rn and daughter isotopes can be distinguished from the naturally occurring randomness of radioactive decay only in the radon and daughter products window. It is primarily in this window where it is possible to fit an exponential function with statistical parameters at an acceptable level, such as  $\chi^2$ . This attempt, which involves calculating the correction constant, will be referred to as the correction constant approach later in the paper.

## 3. Results

Measurements were performed on the sample of bog wood. Approximately 50 g of material were prepared with the standard ABA pretreatment protocol (after Michczyńska *et al.*, 2018 and references therein). On the next day, benzene synthesis was performed. The sample was pyrolyzed in a cylindrical reactor at 750°C for 15 min with limited oxygen available. To the pyrolyzed sample about 5 g lithium was added, and the reaction was conducted at 700–750°C for 30 min under vacuum, in order to form Li<sub>2</sub>C<sub>2</sub>. Upon hydrolysis of the lithium carbide to produce C<sub>2</sub>H<sub>2</sub>, trimerization was facilitated by the use of a Cr<sub>2</sub>O<sub>3</sub> catalyst. On the third day, measurements were performed on the Quantulus 1220<sup>TM</sup> Liquid Scintillation Beta Spectrometer at the Gliwice Laboratory on the 2 mL counting geometry (Pawlyta *et al.*, 1997; Pazdur *et al.*, 2003).

The sample, labelled as GdS-4657, was measured for a longer duration than a typical sample in order to obtain good statistics. Specifically, the sample was measured for 49 cycles, with each cycle consisting of 6 repetitions, and each repetition involving 40 min of measurement. Simultaneously, the background sample was measured for 49 cycles, and each cycle consisted of 2 repetitions, and each repetition consists of 30 min of measurement. For both samples, the SQP(E) parameter was measured after each repetition for 1 min. Thus, the sample was measured for approximately 11 days, which allowed for coverage of almost 3 half-lives of <sup>222</sup>Rn.

The measured spectra for the GdS-4657 sample clearly show three visible peaks (**Fig. 2**). The main peak is connected to the <sup>14</sup>C decay, while the two smaller peaks are associated with radionuclides undergoing alpha decay. The first smaller peak represents <sup>222</sup>Rn and <sup>218</sup>Po decays, and the third peak represents <sup>214</sup>Po decay.

In a subsequent section of the paper, the count rate is normalized by dividing it by the mass of the sample. This normalization procedure allows us to obtain the count rate per gram of sample. By expressing the results in this manner, we ensure that the count rate values are easily interpretable and comparable, as they are standardized to a consistent unit of measurement.

#### 3.1. Subtraction Approach

Calculations were performed using a custom program written in MATLAB<sup>®</sup> R2022b, employing direct exponential fitting. Fitting was carried out in two separate windows: the radon and daughter products window (channels 580–1024) and the combined <sup>14</sup>C and radon and daughter products window (channels 291–1024). Regarding the GdS-4657 sample, the fitted exponential regression exhibited favourable  $\chi^2$  value in both windows, as depicted in **Fig. 3**. The count rate  $a_{s+b}^{Rn}$  was found to be 0.180(22) min<sup>-1</sup> · g<sup>-1</sup> in the radon and daughter products window and  $a_{s+b}^{C+Rn} =$ 6.452(51) min<sup>-1</sup> · g<sup>-1</sup> in the combined <sup>14</sup>C and radon and daughter products window. The count rate in the <sup>14</sup>C window was calculated by subtracting the count rates obtained in the two previously mentioned windows, resulting in  $a_{s+b}^{C} = 6.272(55) \text{ min}^{-1} \cdot \text{g}^{-1}$ .

## 3.2. System of Equations Approach

The second exponential fitting method involving solving of a system of equations was performed in MATLAB<sup>®</sup> R2022b and also in two separate windows: the radon and daughter products window (channels 580–1024) and the combined <sup>14</sup>C and radon and daughter products window (channels 291–1024), as depicted in **Fig. 4**. Regarding the GdS-4657 sample, the count rate in the <sup>14</sup>C window was calculated as  $a_{S+b}^{C} = 6.275(24) \text{ min}^{-1} \cdot \text{g}^{-1}$ .

The correction constant *E*, obtained as 1.166(26), can potentially be utilized in the future to assess the contamination of <sup>222</sup>Rn and its daughter isotopes in samples in Gliwice Laboratory. This approach, labelled as the correction constant approach, relies on the definition of the boundary between windows and, consequently, the sample quality parameter (external), abbreviated as SQP(E), which is related to a specific gamma source Compton electrons counts, and quantifies the number of channels above which 1% of the pulses from the external  $\gamma$  radiation source occur, and it corrects for spectral shifts caused by varying levels of quenching in synthesized benzene and instrument gain changes (McCormac, 1992). In order to obtain a comprehensive understanding of the influence of this parameter



Fig 2. Counts spectra for the GdS-4657 sample with counting windows used at the Gliwice Laboratory.



Fig 3. Exponential function fitted into (A) – radon and daughter products window, (B) – combined <sup>14</sup>C and radon and daughter products window. Fitted functions are shown with a 68.3% confidence band.



Fig 4. The results of the solved system of equations for the GdS-4657 sample. (A) – Equation corresponding to the radon and daughter products window. (B) – Equation corresponding to the combined <sup>14</sup>C and radon and daughter products window. The fitted functions for both equations are shown with a 68.3% confidence band.

on the correction constant E, it is necessary to measure it across a larger sample series.

## 3.3. Dating Results

To assess the efficacy of the method, we performed supplementary measurements on the GdS-4657 sample, which was labelled as GdS-4684 after undergoing an aging process for more than a month, as described earlier. The F<sup>14</sup>C and <sup>14</sup>C age values (**Table 2**) were calculated by taking into account background correction and the SQP(E) correction. Results obtained from both correction methods are in agreement with results obtained for GdS-4684 sample within statistical significance (determined using a *t*-test). The uncertainty obtained using the system of equations approach is smaller.

## 3.4. Required Number of Measurement Cycles

To evaluate the need for extended measurements of the GdS-4657 sample, we analysed the uncertainties in the count rate,  $a_{s+b}^{C}$ , under the assumption that the sample was measured for a specific number of cycles, starting from

Sample ID	$a_{s+b}^{C}$ , min <sup>-1</sup> · g <sup>-1</sup>	SQP(E)	F <sup>14</sup> C	Radiocarbon age, <sup>14</sup> C year
GdS-4657 Immediate, without correction	6.420(18)	806.35(30)	0.8318(45)	1480(43)
GdS-4657 Exponential correction Subtraction approach	6.272(55)	806.35(30)	0.8120(79)	1673(78)
GdS-4657 Exponential correction System of equations approach	6.275(24)	806.35(30)	0.8124(48)	1669(48)
GdS-4684 After aging process	6.345(31)	809.89(44)	0.8115(54)	1678(53)

Table 2. The measurement results for sample without correction, with both methods of exponential corrections, and after aging process.

SQP(E), sample quality parameter (external).



**Fig 5**. Evolution of determined count rate, with a  $\chi^2$  value versus  $\chi^2_{crit}$  at  $\alpha = 0.05$ . Each data point represents a hypothetical scenario where measurements were terminated after a specific cycle, starting from the 10th cycle for the first point, the 11th cycle for the second point, the 12th cycle for the third point, and so on. (A) – Subtraction approach. (B) – System of equations approach.

10 cycles (see **Fig. 5**). Each data point in the graph represents a different population size, therefore the  $\chi^2$  value versus  $\chi^2_{crit}$  is depicted, at  $\alpha = 0.05$ . The uncertainties reach an acceptable level only after around 35 cycles. It is worth noting that this measurement duration of 35 cycles is generally longer than the standard measurements conducted in the Gliwice Laboratory, which typically involve 24 cycles.

# 4. Conclusions

The method presented offers the advantage of determining the count rate and <sup>14</sup>C age of a sample correction for misestimating resulting from the contamination by <sup>222</sup>Rn without the need for additional treatment or electronics during LSC measurements using the Quantulus 1220<sup>TM</sup> spectrometer. Moreover, the calculations using the described method can be performed in just a few seconds. However, it is essential to acknowledge the limitations of this method. Firstly, it requires a relatively large number of cycles (35 or more) and a lengthy measurement time in each cycle (around 3–4 h). Consequently, the overall measurement time for a single sample is longer than what is typically used. Furthermore, it is important to note that this method is specifically applicable to freshly prepared benzene samples with a significant level of <sup>222</sup>Rn contamination. The count rate within the radon and daughter products window needs to be sufficiently high to overcome the inherent randomness of decay.

# Acknowledgements

This research was supported by the Silesian University of Technology subsidy for the maintenance and development of research potential (14/020/BK\_23/0028) and a project for young scientists (14/020/BKM23/0038).

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