APPLICATION NOTE

Determination of the ^{3}H, gross α/β and ^{222}Rn activity concentration in drinking water with the Quantulus GCT 6220.

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Introduction

The analysis of drinking water has been the focus of many laboratories throughout Europe since the publication of the European Council Directive 2013/51/Euratom.[1] While the determination of the activity of Tritium (^{3}H), Radon-222 (^{222}Rn) and gross α/β-activity has historically been routine in many laboratories, the drinking water directive contains updated recommendations for sampling rate, detection limits, and other parameters which have forced many labs to upgrade instrumentation and adjust their previous methods.

With this directive, gross α/β-measurements have once again become a measurement of interest. In many cases, the need for additional investigation can be avoided if the activity of the sample measures below 1 Bq/L for α-nuclides and below 0.1 Bq/L for β-nuclides. When the measured gross α/β-activity is below this threshold, it can be assumed that based on the average annual consumption of water, the annual delivered dose will be less than 0.1 mSv/a and therefore the drinking water does not pose a risk to health in terms of ingested radionuclides. Starting with gross α/β-measurements can potentially save laboratories time and hassle by avoiding other measurements based on time-consuming separation technology

While Tritium (^{3}H), Radon-222 (^{222}Rn) and Potassium-40 (^{40}K) are not nuclides that are included in the indicative dose of 0.1 mSv/a, the drinking water directive does include parametric values for both ^{3}H and ^{222}Rn. The requirements of increased sample number and more specific detection limits required by the directive have led many labs to upgrade to more sensitive instrumentation.

Council Directive 2013/51/Euratom does not give detailed information about the required instrumentation and methods - it only stipulates that the method must reach the defined detection limits (see Table 1). Other regulations also exist and provide more precise instructions regarding the determination of radionuclides in drinking water.

In this application note we demonstrate the suitability of the Quantulus™ GCT 6220 liquid scintillation counter (Figure 1) for the analysis of drinking water. Additional regulations and general norms for quality control and sampling were also utilized, including ISO 96982 for the measurement of Tritium, ISO 11704[3] for the gross α/β, ISO 13164-4[4] for the ^{222}Rn measurements, ISO/EC 17025[5], ISO 5667-1[6], ISO 5667-3[7], and ISO 5667-14[8]. The determination of characteristic limits such as decision threshold and detection limits followed ISO 11929.[9]

Table 1: Requirements of council directive 2013/51/Euratom.

Nuclide	Max. activity	Limit Of Quantification (LOQ)
^{3}H	100.0	10.0
^{222}Rn	100.0	10.0
Gross α	0.1	0.004
Gross β	1.0	0.4

Figure 1: Quantulus GCT 6220 liquid scintillation counter.

Data collection and analysis

All measurements were obtained using Quantulus GCT 6220 (Revvity) at 15°C unless stated otherwise.

Ultima Gold™ LLT (Revvity, 6013371) was used as the scintillation cocktail for all ^{3}H and gross α/β-measurements, and Ultima Gold F (Revvity, 6013171) was used for all ^{222}Rn measurements. Vials used in this study include: 20 mL super polyethylene vials (Revvity, 6001085), 20 mL Teflon coated polyethylene vials (Revvity, 6000477), and 20 mL glass vials with low potassium content (Revvity, 6000128).

The determination of the optimum PSA value for α/β-discrimination and efficiency were done with ^{90}Sr, ^{226}Ra and ^{241}Am standards from the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig (Germany). For the ^{3}H measurements, internal standards (Revvity, 6004052) with tritiated water were used. The exact mass of each standard was weighed with an analytical balance (model ME204T, Mettler-Toledo GmbH). The pH measurements were performed using a pH meter (model pH Bench F20 standard kit, Mettler Toledo GmbH), and calibrated with a 3-point calibration.

Tritium measurements

All Tritium measurements were done according to ISO 9698.[2] After distillation, 8 mL of the water sample was mixed with 12 mL of Ultima Gold LLT scintillation cocktail. The sample was then placed in the Quantulus GCT liquid scintillation counter for temperature equilibration. The sample measurement was performed at 15°C in the optimized counting window from 0.5-4.0 keV, three hours after the samples were initially placed inside the instrument. The optimized window was determined using the SpectraWorks 2 software, which allows loading of the spectra obtained from Tri-Carb® and/or Quantulus GCT 6220 systems and for the evaluation of the data.

Spiked water samples, received from the German Federal Institute of Hydrology, were measured to determine the accuracy of the instrument. Three different samples with activity levels of 9.3, 37.3 and 83.9 Bq/L of Tritium in water were measured and activity levels of 9.0, 36.1 and 82.1 Bq/L, respectively, were found (data not shown).

Table 2 shows results from background and standard samples which have been measured with a Tri-Carb 4910TR liquid scintillation counter in normal count mode and a Quantulus GCT in super low-level count mode (SLLCM), in normal count mode with GCT (Guard Compensation Technology) off (NCM GCT off), and in normal count mode with GCT High[24] (NCM GCT high). These results show that the correction, provided by the Quantulus GCT, significantly improves the figure of merit due to the very low background. Furthermore, the loss of efficiency of the former most sensitive SLLCM can be avoided when using the GCT high setting, which improves the background without loss of efficiency compared to the NCM with GCT deactivated.

Table 2: Sensitivity of the Quantulus GCT for the measurement of Tritium activity in different count modes..

Instrument	Count Mode	Efficiency (%)	Background (CPM)	Figure of Merit E^2/B
Tri-Carb 4910	NCM	25.7	1.91	346
Quantulus GCT	NCM GCT Off	23.6	1.00	557
Quantulus GCT	SLLCM	20.4	0.61	682
Quantulus GCT	NCM GCT High	23.6	0.21	2652

Table 3 shows the counting times, in different count modes, needed to reach the required detection limits. The measurement times for the required detection limits were determined according to ISO 11929 for a sample volume of 8 mL and values for $k_{1-\alpha} = k_{1-\beta} = 1.645$. Here we see that improved sensitivity results in much lower counting times to reach the detection limit for Tritium of 10 Bq/L as required by the European Council Directive 2013/51/Euratom.[1] The counting time decreased from 33 minutes on the Tri-Carb 4910TR in NCM to just 8 minutes on the Quantulus GCT in NCM with the GCT high setting.

Table 3: Required counting time to reach a detection limit of 10 Bq/L of Tritium in different count modes on the Quantulus GCT and Tri-Carb 4910 liquid scintillation counters.

Instrument	Count Mode	Counting Time (min)
Tri-Carb 4910	NCM	33
Tri-Carb 4910	ULLCM	28
Quantulus GCT	NCM GCT Off	23
Quantulus GCT	SLLCM	20
Quantulus GCT	NCM GCT High	8

Radon-222 measurement

All ^{222}Rn measurements were done according to ISO 13164-4[4], based on the extraction of radon with a water immiscible scintillation cocktail. In these experiments, Ultima Gold F was used as the scintillation cocktail.

To verify the extraction efficiency and counting efficiency, 10 mL of Ultima Gold F was added to a ^{226}Ra standard of known activity in 12 mL water, into either glass- or Teflon-coated plastic vials. Care was taken to completely fill the vial to avoid the loss of ^{222}Rn into the gas phase. The vials were tightly closed and stored in an inverted position within a refrigerator for one month to reach equilibrium between ^{226}Ra and ^{222}Rn.

After a month, the samples containing Ultima Gold F were shaken for 30 seconds and stored inside the instrument for 3 hours. Measurements were carried out using either both α- and β-counting of ^{222}Rn, ^{218}Po, ^{214}Po, ^{214}Bi, and ^{214}Pb, or α-counting alone of ^{222}Rn, ^{218}Po and ^{214}Po using α/β discrimination. Typically, the exclusive use of the α-measurement leads to very low background values and often better performance. Here, α- and β-counting was done because GCT can be used to significantly reduce background signal to levels typical for α-counting, and in some cases even lower. The setting of the optimum pulse discriminator was obtained via measurements of ^{241}Am and ^{90}Sr standards in glass- and Teflon-coated scintillation vials. The optimum PSA level determined for plastic vials was 116 and for glass vials 150 (data not shown). A typical α-spectrum measured with α/β discrimination is shown in Figure 2.

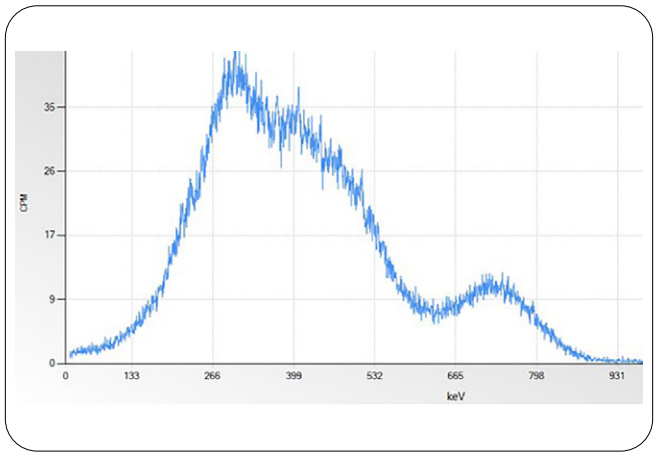

Figure 2: α-spectrum after extraction of 222Rn from a standard sample with Ultima Gold F in glass vials.

Table 4 shows the results of the ^{222}Rn measurements in water. No significant difference in efficiency or background was observed between plastic and glass vials using α/β discrimination. The efficiency and background values noted were measured in the optimized energy window which was again determined using the SpectraWorks 2 software.
Due to the much higher counting efficiency when counting all five nuclides and the reduction in background using GCT low setting, the overall performance was significantly better when avoiding α/β discrimination.

Due to the high counting efficiency and the low background, it was possible to reduce the counting time to reach the required detection limit of 10 Bq/L for ^{222}Rn to 0.25 minutes (data not shown). This detection limit was obtained with 12 mL water and $k_{1-\alpha} = k_{1-\beta} = 1.645$.

Table 4: Sensitivity of the Quantulus GCT for ^{222}Rn measurements with and without α/β-discrimination.

Vial Type	Efficiency (%)	Background (CMP)	α/β Discrimination	Figure of Merit E^2/B
Plastic	186	0.8	Yes	160 – 650
Glass	183	0.8	Yes	145 – 840
Glass	180	0.8	Yes	145 – 840
Glass	264	0.5	No	20 – 840
Glass	275	0.5	No	20 – 840

Gross α/β-measurement

All gross α/β-measurements were done according to ISO 11704.[3] Due to the low salt content of most drinking waters, sample volumes as large as 120 mL were feasible. The sample was acidified with nitric acid and concentrated to a final volume of 8 mL, with a pH of 1.8, and mixed with 12 mL Ultima Gold LLT in a plastic vial. As with ^{222}Rn measurements, reference standards ^{241}Am and ^{90}Sr were used to determine the optimum PSA value for the α/β-discrimination. For this, the standards were dissolved in 8 mL water, at a pH of 1.8, and mixed with 12 mL Ultima Gold LLT, just as the samples were. The optimum PSA value was determined to be 116 (data not shown).

The α-background was 0.53 CPM, with an efficiency of 97.8% in an energy window from 80-400 keV (data not shown). This counting window was selected to ensure that all possible α-emitters were within the chosen energy window. The maximum of the ^{241}Am peak ($\approx$ 5.5 MeV) in these water samples appeared at approximately 200 keV. The β-background was 0.38 CPM and the counting efficiency was 91.7% in the energy window from 12-800 keV (data not shown). An upper level of 800 keV for the β-emitters ensures that all β-nuclides are within the energy window. The ^{90}Sr standard in equilibrium with ^{90}Y had a maximum energy of approximately 2.2 MeV and the spectral endpoint in these samples very close to 750 keV (data not shown).

An α-detection limit of 0.036 Bq/L and a β-detection limit of 0.032 Bq/L could be reached with 120 mL drinking water and $k_{1-\alpha} = k_{1-\beta} = 1.645$ in 200 minutes counting time for both sample and background (data not shown).

Summary

The measurement of Tritium samples resulted in very high values for the figure of merit and very short counting times. This shows that the Quantulus GCT with GCT high setting is a suitable instrument for all water samples containing very low levels of Tritium. The measurements of ^{222}Rn samples using GCT low setting indicates that measurements without α/β-discrimination will give a much better performance compared to samples using α/β-discrimination. The gross α/β-measurements showed very good performance, especially for the gross β-measurement, due to very low background in the β-channel when using GCT low setting. The patented Guard Compensation Technology (GCT) proved to be an excellent tool for ^{3}H, ^{222}Rn, and gross β-measurements resulting in very low background values and high sensitivities for the analysis of drinking water. Overall, GCT is a very suitable tool for low-level applications and can significantly reduce the counting time compared to traditional instruments.

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