

ALPHA SPILLOVER DEPENDS ON ALPHA ENERGY: A NEW FINDING IN ALPHA/BETA LIQUID SCINTILLATION SPECTROMETRY

Laina Salonen

Radiation and Nuclear Safety Authority (STUK), PO Box 14, FIN-00881 Helsinki, Finland. Email: laina.salonen@stuk.fi.

ABSTRACT. The calibration of the alpha/beta liquid scintillation (LS) spectrometric measurement is rather complicated for samples having variable chemical and radionuclide compositions if rather accurate results are required. Variable quenching can be a significant source of uncertainty if it is not considered in the calibrations because variable quenching affects alpha and beta spillovers, the optimum pulse-shape analyzer (PSA), and alpha and beta backgrounds. It is known that the beta spillover to the alpha window also depends on the energy of the beta particle, but until now it has been assumed that the alpha spillover to the beta window does not depend on the energy of the alpha particle. The present study demonstrates that the alpha spillover depends also on the energy of the alpha particle. The alpha spillover of lower energy alpha particles is larger than the spillover of higher energy alpha particles when the sample is measured at a constant PSA. This is established by preparing sample series from radon-bearing water, quenching some samples to different degrees, and measuring the samples at various PSA levels. The large energy difference between radon and its alpha-emitting daughters, ^{218}Po and ^{214}Po , allows one to see the dependence of alpha spillover on the alpha energy. The significance of the new finding is evaluated with a few examples of determinations of uranium and radium in groundwater samples. The too-low uranium results by alpha/beta LS spectrometry can be partly explained by increased quenching when the samples are measured at the PSA level set according to an unquenched sample. Because of the low alpha particle energies of uranium isotopes, their alpha spillovers to the beta window are clearly larger for quenched samples than the spillovers of ^{222}Rn , ^{218}Po , and ^{214}Po .

INTRODUCTION

The use of alpha/beta liquid scintillation (LS) spectrometry for measuring natural and artificial radionuclides in environmental samples has increased considerably during the past 10 yr. In many laboratories, alpha/beta LS spectrometry has replaced methods based on gas proportional counting and has become a useful alternative to alpha-spectrometric methods. Alpha/beta separation using commercial LS counters became possible in the late 1980s (Oikari et al. 1987). Instruments were equipped with electronic circuitry capable of identifying alpha and beta events by the length of the light pulse and separating them into their own spectra (Oikari et al. 1987; Dodson 1991; Passo et al. 1992). Because the backgrounds of the LS counters were also reduced by incorporating into them passive and active shields, low-level analysis by LS counting (LSC) became possible.

Prior to the use of commercial LS counters for alpha/beta separation, alpha/beta separation was carried out using the PERALS[®] (Photon/Electron-Rejecting Alpha Liquid Scintillation) spectrometer, which was designed for alpha spectrometry and not for the simultaneous measurement of beta activities (Thorngate et al. 1974). Its electronic circuitry is able to reject at least 99.95% of beta/gamma pulses, and the background over the alpha energy region (4–7 MeV) is as low as 0.001 cpm when extractive scintillation cocktails are used (McDowell et al. 1994). Like PERALS, low-background LS spectrometers permit the measurement of low alpha activities in the presence of high beta/gamma activities due to their high alpha efficiency and low background (often below 0.1 cpm).

Until now, alpha/beta LS spectrometry has been applied in a wide range of radionuclide analyses, many of which are reviewed by Pates et al. (1996a) and Cook et al. (2003). These include the analysis of natural series radionuclides and transuranium elements in various environmental matrices, in bioassay, in effluents from mining and milling industries, and in primary coolant water. Radon, radium, and gross alpha and beta analyses in water samples, especially drinking waters, are the most common applications, having many alternative sample preparation procedures. Direct measurements, where water is mixed with the cocktail, are often used with pure groundwaters that are screened by gross alpha and beta measurements. If waters are highly acidic or saline, like the wastes and effluents in nuclear facilities, it is better to separate the radionuclides from the sample matrix in

order to enable alpha/beta separation (Bickel et al. 1992; Dewberry et al. 1998; Eikenberg et al. 2004).

Several studies have shown that it is important to consider the effects of variable quenching when a new application based on alpha/beta separation is developed (Sanchez-Cabeza et al. 1995, 1998; Pates et al. 1998; Burnett et al. 2000; Warwick et al. 2002). Quenching has many effects on alpha/beta separation: 1) with increased quenching the alpha spillover to the beta window increases, whereas the beta spillover to the alpha window decreases (Sanchez-Cabeza et al. 1993; Pates et al. 1996b; DeVol et al. 1996; Warwick et al. 2002); 2) the optimum pulse-shape analyzer (PSA) is influenced by a chemical quencher (Pates et al. 1998) and color quenching (Villa et al. 2003); and 3) the alpha background increases and beta background decreases with increasing quenching when samples are measured at their optimum PSAs (DeVol et al. 1996). Furthermore, the beta spillover is influenced by beta particle energy; the effect is more significant for higher energy beta emitters (Pates et al. 1998; Warwick et al. 2002; Villa et al. 2003). Consequently, the exact efficiency, spillover, and background corrections for real samples with variable quenching are rather complicated (Warwick et al. 2002; Cook et al. 2003). They assume that the PSA level should be optimized according to each sample quench level using the same energy beta emitter and same quenching agents as in real samples. The composition of the standard and real samples should be as similar as possible.

Until now, it has not been shown that the alpha spillover depends on the alpha particle energy. In an earlier study performed using ^{233}U and ^{241}Am , no dependence of alpha spillover on alpha energy was observed (Yang 1996). The alpha particle energies of these 2 nuclides are between 4.8 and 5.5 MeV. However, the present study did establish a dependence using radon-bearing groundwater. The much larger differences between the alpha-particle energies of radon (Rn) (5.5 MeV) and its alpha-emitting daughters, ^{218}Po (6.0 MeV) and ^{214}Po (7.7 MeV), is probably the main reason why the effect was confirmed in this study (Table 1). Additional advantages in using Rn and its daughters were: 1) they could be measured in the same sample under equal conditions, and thus possible small differences between different standard compositions or quench levels could not prevent observation of the effect; and 2) due to the equal activities of these nuclides, the comparison could be made on the basis of the count rates, and the uncertainties of different standard activities had no effect on the results. The disadvantage in using Rn is that its beta-emitting daughters, ^{214}Pb and ^{214}Bi , are in the same sample, and thus they can affect the results. The dependence of alpha spillover on alpha energy is demonstrated here with a series of Rn samples quenched to different degrees and then measured at various PSA levels. The significance of the new finding is evaluated with a few examples of the determination of uranium and radium in groundwater samples.

EXPERIMENTAL

The groundwater used in this study originated from a drilled well and was sampled into a 4-L glass bottle and stored for 4 hr at room temperature (22 °C) before sample preparation. The Rn concentration of the water at the time of sampling was 33,000 Bq/L, which enabled the measurement of the sample series during several days using short counting times. The concentrations of other natural radionuclides (^{238}U , ^{234}U , ^{226}Ra , ^{210}Pb , and ^{210}Po) were 4 orders of magnitude lower than the Rn concentration, and, consequently, they did not interfere with Rn measurement. The sample composition was the same (10 mL water and 12 mL cocktail) as used in measuring Rn concentrations in water (Salonen 1993a; Salonen et al. 1997). Our Rn measurement method differs from the most commonly used method originally described by Prichard and Gesell (1977). We mix water with the cocktail to provide a homogeneous sample, while Prichard and Gesell's (1977) method is based on

Table 1 Some members of the natural decay series of ^{238}U .

| Radio-nuclide | Half-life | α -decay energy (MeV) and intensity (%) | β -decay energy (MeV) and intensity (%) | γ -emission energy (keV) and intensity (%) |
|-------------------|------------------------|--|--|--|
| ^{238}U | 4.468×10^9 yr | 4.198 (79.0), 4.151 (20.9) | — | 49.5 (0.06), 113.5 (0.01) |
| ^{234}U | 2.455×10^5 yr | 4.775 (71.4), 4.722 (28.4) | — | 131.3 (0.03), 53.2 (0.12) |
| ^{226}Ra | 1600 yr | 4.784 (94.5), 4.601 (5.5) | — | 186.2 (3.59) |
| ^{222}Rn | 3.82 d | 5.490 (99.9), 4.986 (0.1) | — | 510.0 (0.076) |
| ^{218}Po | 3.11 min | 6.002 (100) | — | — |
| ^{214}Pb | 26.8 min | — | 0.728 (42.2), 0.670 (48.9), 1.030 (6.3) | 351.9 (37.6), 295.2 (19.3), 242.0 (7.43) |
| ^{214}Bi | 19.9 min | — | 3.275 (18.2), 1.542 (17.8), 1.508 (17.0), 1.425 (8.2), 1.894 (7.4) | 609.3 (46.1), 1764.5 (15.4), 1120.3 (15.1), 1238.1 (5.8), 2204.2 (5.1) |
| ^{214}Po | 164 μs | 7.687 (100) | — | — |

a 2-phase system where water underlies an organic cocktail. The homogeneous sample is very stable for extended time periods.

Sample and Background Preparation

Four parallel samples were prepared from Rn-bearing groundwater using the standard procedure of our laboratory. Three of these samples were quenched with a few drops of carbon tetrachloride (CCl_4). Similar samples series were also prepared using other quenching agents (HCl , HNO_3 , or EDTA), but the results for these are only commented on here very briefly. The Rn samples were prepared in the following way:

- The glass vial containing the cocktail (12 mL Ultima Gold™ XR) was weighed with an analytical balance.
- A 10-mL subsample of water was transferred with a 20-mL glass pipette from the sampling bottle into the LS vial. No pipette filler was used to avoid suction and Rn release. The tip of the pipette was simply placed near the bottom of the bottle so that water slowly entered the pipette up to the 10-mL level. Thereafter, the water was released on the cocktail in the LS vial.
- A few drops of CCl_4 were added to 3 samples. Every vial was sealed tightly and shaken vigorously before the preparation of the next sample.
- The vials were weighed, cleaned with ethyl alcohol, and placed into the LS counter prior to measurement, which started 4 hr later.

The parallel Rn samples prepared in this way have had very similar Rn contents (Salonen 1993a). The standard deviations have varied between 1.3–2.1% in various experiments performed over the course of years. The amount of water added to each vial is presented in Table 2. The amount of CCl_4 added to the 3 vials was subtracted when the water volumes were calculated. This was performed by separately weighing the corresponding amounts of CCl_4 .

The background sample was prepared from the same groundwater after aerating the water for 4 hr. During this time, all Rn was removed from the water, and its short-lived daughters completely decayed.

MEASUREMENT

The measurements were performed with a Quantulus™ using alpha/beta separation. The Quantulus is a low-background LS spectrometer equipped with a PSA, an anticoincidence guard counter (G), and 2 multichannel analyzers (MCA). It can produce 4 spectra simultaneously, 1 in each half of the 2 MCAs. The optimum PSA level of the Quantulus was established using ^{241}Am and ^{36}Cl standard samples. These were prepared from distilled water and contained a small amount (0.1 g) of standard solution in 2M hydrochloric acid. Figure 1 presents the alpha and beta spillovers as a function of the PSA level. The optimum PSA is 85 if it is taken from the point where alpha and beta spillover curves cross each other and spillovers are equal.

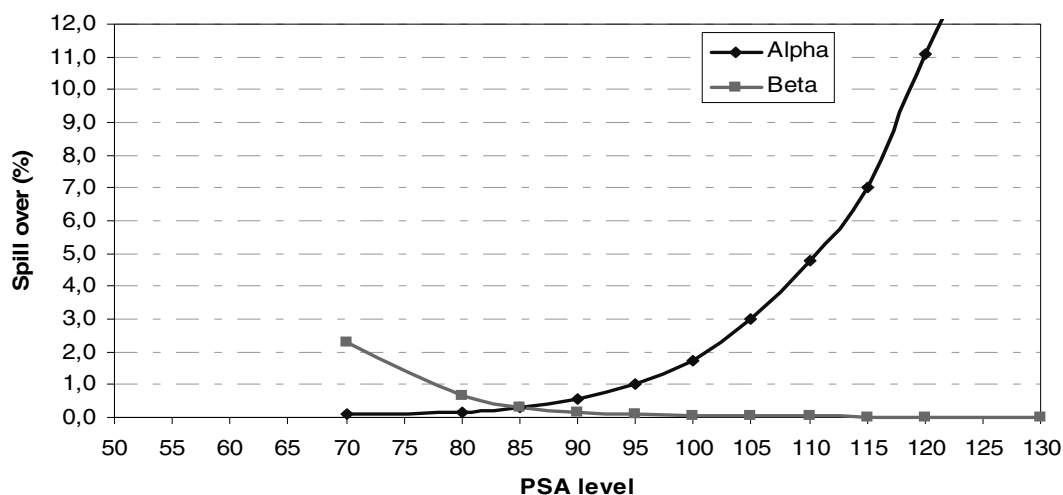
Alpha and beta spillovers in the opposite windows

Figure 1 The PSA level of the Quantulus is set using ^{241}Am and ^{36}Cl standards prepared with a similar composition (10 mL water + 12 mL UltimaGold XR) to the real samples.

When Rn in water is measured using the Quantulus or the Guardian, the count rates are lower than those obtained with other LS counters that have no external G counter (Salonen 1993a; Salonen et al. 1997). This is due to the very short half-life of ^{214}Po ($T_{1/2} = 164 \mu\text{s}$; Table 1). The anticoincidence G counter eliminates part of the ^{214}Bi counts because it observes the gamma photons of ^{214}Bi simultaneously with the alphas of ^{214}Po in the detector. This was easily recorded by the Quantulus using quasi-simultaneous counting, program mode 6, in which the settings of both MCAs can be selected separately. The G counter was set to operate only with MCA 1, but the PSA operated with both MCAs. Two alpha and 2 beta spectra were produced simultaneously, and the effect of the Q counter on the count rates could be calculated. The settings were as follows:

| MCA | Input | ADC Trigg | Inhibit | Memory split |
|-----|-------|-----------|---------|--------------|
| 1 | LRsum | L*R | G | PSA |
| 2 | LRsum | L*R | | PSA |

| MCA | Half | Spectrum | |
|-----|------|----------|------|
| 1 | 1 | Beta | SP11 |
| 1 | 2 | Alpha | SP12 |
| 2 | 1 | Beta | SP21 |
| 2 | 2 | Alpha | SP22 |

Figure 2 shows the spectra of an unquenched Rn sample (number 1) in equilibrium with its daughters at the PSA level of 85 and 90. The figure indicates that the beta count rates of MCA 2 (SP21) are higher than those of MCA 1 (SP11) and that the increase occurs in the energy region of ^{214}Bi . The count rate in the wide beta windows (channels 1–1024) is 23% higher when G is not operating, but only 0.1% higher in the alpha window (channels 520–720). The small increase in the alpha window occurs in the ^{214}Po peak region. The background of the alpha window (channels 520–720) is 0.07 cpm higher when G is not operating, but 20 cpm higher in the beta window (channels 1–1024).

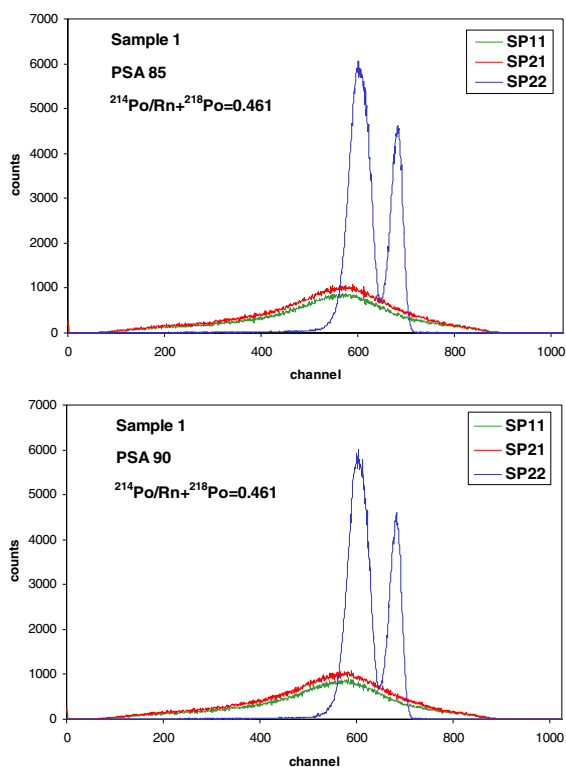


Figure 2 The alpha (SP22) and 2 beta spectra (SP11 and SP21) of an unquenched Rn sample (number 1) measured at the PSA level of 85 and 90 with and without the use of the anticoincidence guard counter.

Figure 2 shows that the alpha/alpha ratio ($^{214}\text{Po}/^{222}\text{Rn} + ^{218}\text{Po}$) of sample 1 is 0.461 at the PSA level of 85 and 90 when no tail corrections for the 2 adjacent peaks were performed. The theoretical value is 0.5 if all 3 alpha particles are observed with $\sim 100\%$ efficiency. According to the previous calibrations based on ^{226}Ra standard solution and on the measurement with an older Quantulus, the effi-

ciency of ^{214}Po was 86%, while other alphas were observed with ~100% efficiency (Salonen 1993b). The lower efficiency of ^{214}Po compared with other alphas could not be understood completely. One possible explanation is the short half-life (164 μs) of ^{214}Po . For this reason, some of its counts are lost during the dead time, which is 8.1 μs for the new Quantulus used in this study. Using this time for the dead-time correction, the efficiency of ^{214}Po would be 96.6% and, consequently, the $^{214}\text{Po}/\text{Rn}+^{218}\text{Po}$ ratio will be 0.483. This value differs from the experimental value (0.461). The calibration of the new Quantulus with ^{226}Ra standard will help to assess whether the disagreement is mainly due to the dead time or other reasons as well. Regardless, the ratio of these 2 alpha peaks can be used in assessing whether the PSA level has been adjusted properly for Rn measurement. It also indicates if Rn-bearing water contains significant amounts of ^{226}Ra or other alpha-emitting nuclides.

RESULTS AND DISCUSSION

Four Rn samples and a background sample were measured at various PSA levels from 60 to 120 using the settings of the Quantulus reported above. All results were calculated from the counts of MCA 2, because it is a better alternative when the alpha/beta ratios are calculated and compared to the theoretical values or to the results with other counters. As all nuclides have the same activity, the results were compared on the basis of the count rates after correcting these for background, decay of Rn, and sample weight. However, none of these corrections were applied for the spectra presented in various figures because the quench effects on alpha/beta separation were obvious without them. Consequently, the reduced count rates between the spectra are partly due to the decay of Rn.

The background correction actually had no effect on most results because the count rates were rather high (1800–58,000 cpm) in all windows. The alpha background, prepared from the drilled well water, was the same, 9.7 cpm, for MCA 1 and MCA 2 (channels 520–720), and the beta background was 46.4 cpm for MCA 2 and 26.0 cpm for MCA 1 (channels 1–1024). Most of the background counts were due to uranium, and only a minor proportion were due to ^{226}Ra , ^{210}Pb , or ^{210}Po .

Figure 3 presents the alpha and beta spectra of 3 Rn samples (numbers 1–3) measured at a constant PSA of 85. The spectra indicate that increased quenching shifts the alpha peaks to the left towards lower energies and increases the alpha spillover to the beta window, which has been well demonstrated by earlier studies (Suontausta et al. 1996; Yang 1996). However, a new finding is that the alpha spillover of lower energy alpha particles is larger than the spillover of higher energy alpha particles when the sample is measured at a constant PSA. The effect can be observed in alpha and beta spectra; the peak heights of the lower and higher energy alpha peaks become more equal with increased quenching, and the spillover increases over the continuous beta spectra are visible.

The count rates of the 4 Rn samples in a wide alpha and beta window (channels 1–1024) are summarized in Table 2. The table shows that although the quench variation between sample 1 (SQP[E] = 816) and 4 (SQP[E] = 607) is large, the total (alpha+beta) counts decrease by only 6.9%. The reduction is due entirely to the decrease in beta counting efficiencies. The effect was established with a ^{241}Am standard sample prepared similarly to the Rn samples and then measured at the PSA of 90. When it was measured before and after adding the quenching agent (CCl_4), its total count rate in the alpha and beta windows remained the same, although the spectral quench parameter for the external standard (SQP[E]) decreased from 735 to 475. At the same time, the alpha efficiency decreased from 97.1% to 20.5% due to the alpha spillover into the beta window. Figure 3 verifies the same; the beta spectra have shifted to the left and the count rates have decreased more than the decay of Rn assumes. Table 2 shows that the alpha efficiencies decrease rapidly with increased quenching due to increased alpha spillover to the beta window.

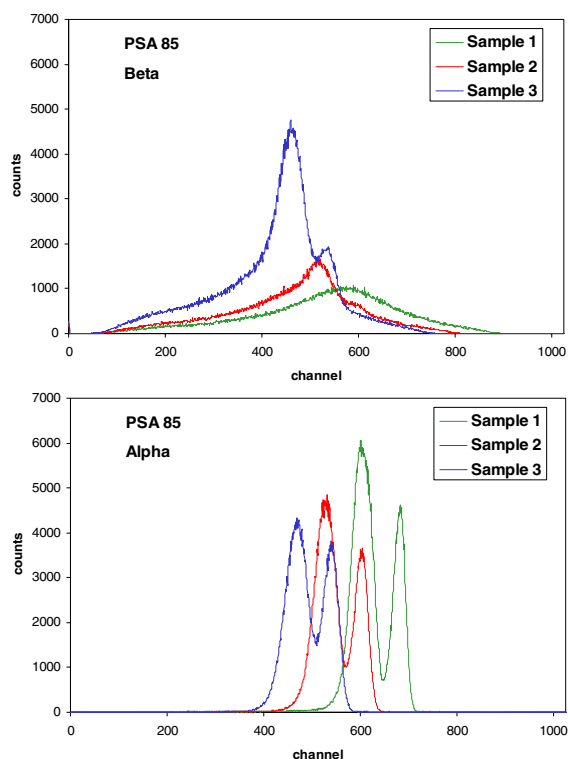


Figure 3 The beta and alpha spectra of 3 Rn samples (numbers 1–3) measured at a constant PSA level of 85 adjusted according to an unquenched sample (number 1).

Table 2 Series of quenched Rn samples measured at PSA 85 that was adjusted according to an unquenched sample (number 1). Count rates (cpm/g of water) were corrected for Rn decay to correspond to the same reference time. The uncertainties (%) of the various count rates vary between 0.2–0.5%, and those of the reduction percentages vary between 0.4–0.9%

| Sample number | Water (g) | CCl ₄ (drops) | SQP(E) | Counts in α and β windows | | | Reduction (%) compared with sample 1 | |
|---------------|-----------|--------------------------|----------|--|----------------|-------------------------|--------------------------------------|-----------------|
| | | | | α 1–1024 | β 1–1024 | $\alpha + \beta$ 1–1024 | $\alpha + \beta$ 1–1024 | α 1–1024 |
| | | | | cpm/g | cpm/g | cpm/g | % | % |
| 1 | 9.8374 | — | 816 ± 16 | 5495 | 3741 | 9236 | 0 | 0 |
| 2 | 9.7596 | 3 | 719 ± 14 | 4679 | 4081 | 8760 | 5.2 | 14.9 |
| 3 | 9.6703 | 8 | 676 ± 13 | 3204 | 5499 | 8703 | 5.8 | 41.6 |
| 4 | 9.8024 | 12 | 607 ± 12 | 1280 | 7315 | 8595 | 6.9 | 76.7 |

Figure 4 illustrates the alpha and beta spectra of 3 Rn samples (numbers 1–3) when each sample was measured at 3 different PSA levels. The alpha and beta spectra mostly affirm the same effects as observed in Figure 3. The dependence of alpha spillover on alpha energy can be observed for all samples, and quenching has a strong effect on alpha spillover. Figure 4 demonstrates that in the case

Table 3 Count rates of samples 1 and 2 in alpha (SP 22) and beta (SP21) windows as measured with the Quantulus using different PSA levels. Rn and its short-lived daughters were in equilibrium, and the count rates (cpm/g of water) were corrected for the decay of radon to correspond to the same reference time. The uncertainties (%) of the various count rates vary between 0.2–0.8%, and those of the count rate reduction percents vary between 0.5–1.2%.

| Count rates in various α and β windows (cpm/g water) | | | | | | Count rate reduction (%) compared to the value at an optimum PSA* | |
|---|----------|------------------------|-------------------|----------|-------------|---|----------|
| Sample 1 (unquenched) SQP(E) = 816 ± 16 | | | | | | | |
| PSA | α | α | α | β | a + β | α | α |
| Chan. | 1–1024 | 500–645 | 645–720 | 1–1024 | 1–1024 | 500–645 | 645–700 |
| | | Rn + ^{218}Po | ^{214}Po | | | | |
| 60 | 5763 | 3690 | 1712 | 3481 | 9244 | | |
| 70 | 5579 | 3752 | 1720 | 3655 | 9234 | | |
| 80 | 5509 | 3717 | 1715 | 3718 | 9226 | | |
| 85* | 5495* | 3715* | 1716* | 3741* | 9236* | 0 | 0 |
| 90 | 5459 | 3692 | 1704 | 3764 | 9223 | 0.6 | 0.6 |
| 95 | 5420 | 3659 | 1714 | 3798 | 9219 | 1.5 | 0.1 |
| 100 | 5395 | 3649 | 1705 | 3829 | 9224 | 1.7 | 0.6 |
| 110 | 5179 | 3474 | 1674 | 4038 | 9217 | 6.5 | 2.4 |
| 115 | 4993 | 3335 | 1630 | 4214 | 9207 | 10.2 | 5.0 |
| 120 | 4739 | 3153 | 1561 | 4480 | 9219 | 15.1 | 9.0 |
| Sample 2 (quenched with 3 drops of CCl_4) SQP(E) = 719 ± -14 | | | | | | | |
| PSA | α | α | α | α | a + β | α | α |
| Chan. | 1–1024 | 500–645 | 645–720 | 1–1024 | 1–1024 | 500–645 | 645–700 |
| 60* | 5268* | 3597* | 1595* | 3490* | 8758* | 0 | 0 |
| 70 | 5987 | 3472 | 1570 | 3641 | 8728 | 3.4 | 1.5 |
| 75 | 4984 | 3379 | 1570 | 3758 | 8743 | 6.1 | 1.5 |
| 80 | 4843 | 3263 | 1553 | 3884 | 8728 | 9.3 | 2.6 |
| 85 | 4679 | 3131 | 1527 | 4081 | 8760 | 12.9 | 4.3 |
| 90 | 4435 | 2934 | 1482 | 4299 | 8734 | 18.4 | 7.1 |
| 95 | 4125 | 2690 | 1423 | 4608 | 8733 | 25.2 | 10.8 |
| 100 | 3772 | 2428 | 1335 | 4973 | 8745 | 32.5 | 16.3 |
| 110 | 2955 | 1869 | 1079 | 5770 | 8725 | 48.0 | 32.4 |
| 115 | 2527 | 1585 | 938 | 6202 | 8729 | 55.9 | 41.1 |

should be), sample 2 should have at its optimum PSA the same alpha count rate as sample 1 (5495 cpm/g). Because sample 2 has a lower alpha count rate (5268 cpm/g) at 60 PSA, its optimum PSA is obviously below this value.

Table 3 presents the count rate reductions (%) under the combined peak of Rn and ^{218}Po and under the ^{214}Po peak when the count rates at various PSA levels are compared to the value at an optimum PSA. These percentages also illustrate the increase in alpha spillover from its value at the optimum PSA and, consequently, enable the numerical assessment of the spillovers under the 2 alpha energy peaks. Table 3 shows that the alpha spillover difference between the 2 alpha energies is clear when the PSA level exceeds its optimum value. It is ~1% at the PSA level nearest to the optimum, but over

5% if the PSA level is 30 units higher. These estimates are approximate because the alpha peak asymmetries and tails of 2 adjacent peaks are not considered.

The possible interference of the ^{214}Pb and ^{214}Bi beta particles with the observation of the dependence of alpha spillover on the alpha energy was examined by the spectra measured on each side of the alpha peaks. Figure 5 illustrates the alpha spectrum (SP22) of sample 1 in the windows that have been set on the lower and upper side of the alpha peak region. The counts in these spectra are mainly due to beta spillover to the alpha window. Figure 5 shows that beta spillovers are 3 to 5 times higher on the lower side (5a) of the alpha peak region than the upper side (5b) when both windows include 50 channels, and the difference was quite similar when the window included 10, 20, or 100 channels. However, the beta spillover should be higher on the upper side of the alpha peak because the beta spillover to the alpha window is larger for higher energy beta particles than for lower energy beta particles (Pates et al. 1998; Warwick et al. 2002). The opposite result is caused here by the higher beta count rate on the lower side of the alpha peak region than on the upper side. Figure 5 indicates that the beta spillover is larger at a lower PSA level than at higher levels, as the beta spillover curve assumes (Figure 1). These 2 factors therefore have an opposite effect on the alpha spillover difference between the 2 alpha energies, as observed here. It can be concluded that the interference from the beta particles of ^{214}Pb and ^{214}Bi had no significant effect in observing the dependence of alpha spillover on alpha energy.

The effect of alpha energy on the alpha spillover was observed when HCl, HNO_3 , or EDTA was used as a quenching agent. The sample quench levels were then much lower than when using 3 drops of CCl_4 , although 3 mL of Rn-bearing water was replaced with a 0.5M solution of HCl or HNO_3 or with a 0.2M solution of EDTA. The lowest SQP(E) value using these quenching agents was 760, and the alpha spectra were shifted to the lower energy region with 5–10 channels only. Nevertheless, the dependence of alpha spillover on the alpha energy was clearly visible. The spill differences between the 2 alpha energies were quite similar (Table 3).

Examples of Determining Uranium and Radium In Groundwater Samples

We have determined the gross alpha and beta activities in groundwater samples since 1988 by alpha/beta LS spectrometry using a relatively simple sample preparation procedure (Salonen 1993b). Our method has mostly been used to screen whether the gross alpha and gross beta activities in drinking water samples are below certain limits and to determine whether further analyses using nuclear-specific procedures are necessary. The method has, however, permitted the uranium and radium contents to be calculated quite accurately in most groundwater samples. The ^{226}Ra content has been calculated from the ^{214}Po peak and the total uranium ($^{234}\text{U}+^{235}\text{U}+^{238}\text{U}$) content simply by subtracting the ^{226}Ra content from the gross alpha content. This uranium content also includes ^{210}Po , but because of the relatively much lower content of the latter (Salonen et al. 2002; Vesterbacka et al. 2005), it usually causes only a small error in the uranium content estimate. However, if the ^{210}Po content is known from radiochemical analysis, it can be subtracted together with the ^{226}Ra content. The method has been calibrated with ^{226}Ra , natural uranium, and ^{210}Pb standards and a ^{40}K sample. The alpha and beta efficiencies have been nearly equal (98–100%) with all these standards except for ^{214}Po (86% efficiency) (Salonen 1993b).

We have applied constant efficiency percentages for all samples and measured them at a constant PSA, which has been an adequate approach for most groundwaters. There is usually good agreement between the results from the radiochemical analysis of ^{226}Ra and uranium and from those calculated from the gross alpha spectra of the Quantulus (Salonen 1993b). This is mainly due to the good water quality and low mineral content that are characteristic of Finnish groundwaters (Tarvainen et al.

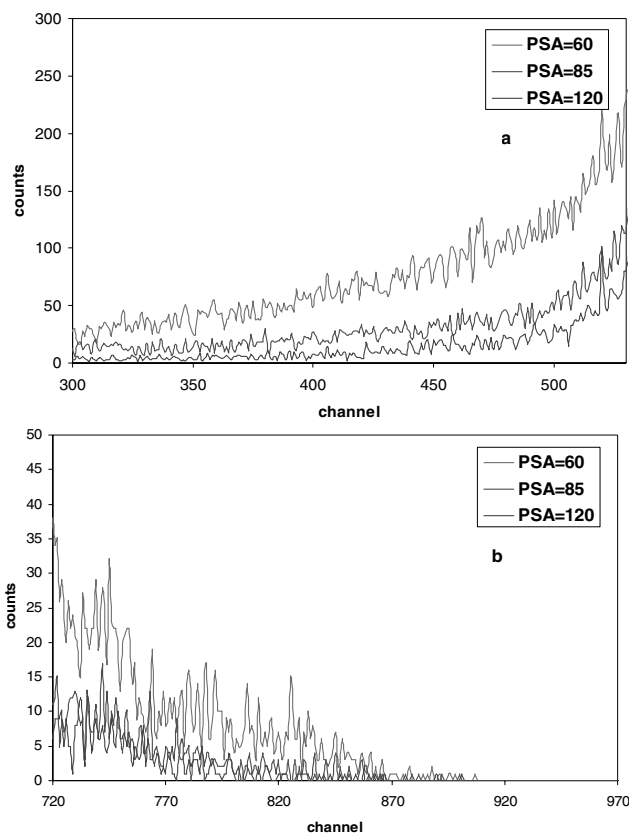


Figure 5 The count rates in the alpha window (channels 450–500) were 565, 204, and 120 cpm measured at PSA levels of 60, 85, and 120, respectively, and the respective count rates in the alpha window (channels 720–770) were 107, 47, and 37 cpm. The count rates (cpm) were corrected for the decay of Rn to correspond to the same reference time.

2001). Samples prepared from such waters have a relatively consistent composition, and they are nearly unquenched because the small residues produced by water concentration (19–38 mL) are dissolved into 1 mL of 0.5M HCl and then mixed with 21 mL of OptiPhase HiSafe 2. Therefore, SQP(E) values, as well as alpha and beta spillovers, are often nearly the same (0.1%) as those of the unquenched standard samples.

Figure 6 illustrates a good correlation between the uranium concentrations in 1350 drinking water samples determined by radiochemical alpha spectrometry and low-background LS spectrometry. However, for a small proportion of the samples, the results for the 2 methods differ considerably from each other. The gross alpha and beta spectra of the Quantulus from 4 drilled well waters are presented in Figure 7. Three of them (Figure 7a–c) are typical bedrock waters in Finland; when the gross alpha activity of water is elevated, it is usually due to uranium, whereas elevated ^{226}Ra contents are very unusual (Figure 7d).

The gross alpha and beta spectra of the Quantulus (Figure 7a–c) show that the main alpha peak is high compared to the ^{214}Po peak, which means that these waters have a high uranium content compared to the ^{226}Ra content. For these samples, the uranium contents derived from the gross alpha

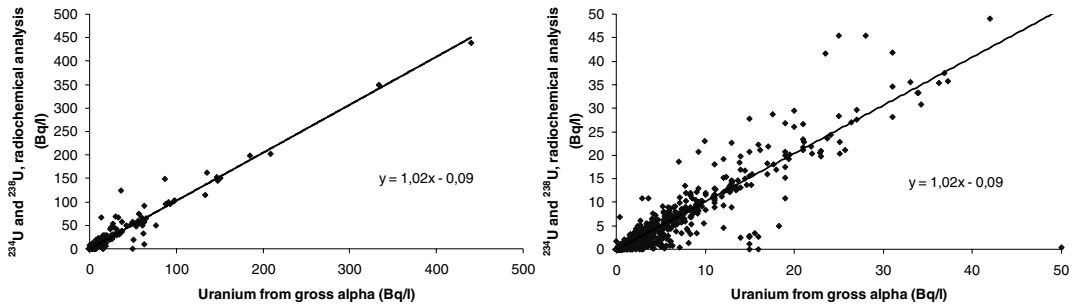


Figure 6 Correlation between the uranium contents of 1350 drinking water samples obtained by 2 methods: radiochemical alpha spectrometry and low-background LS spectrometry with the Quantulus.

spectrum of the Quantulus are 4–30% lower than from radiochemical analysis. It seems obvious that a part of the deviating results are due to the increased quenching, which has caused greater spillover of uranium alphas to the beta window than was considered in the calibrations. The increased quenching is indicated by the SQP(E) values; the spectra have shifted to the left at a different degree and alpha spillovers to the beta window in the energy region of uranium are visible. Owing to the low alpha energies (4.2–4.8 MeV, Table 1) of uranium isotopes, their spillovers to the beta window can clearly be larger than expected on the basis of the spillovers of Rn, ²¹⁸Po, and ²¹⁴Po. Consequently, the uranium results depend more closely on adjusting the PSA level according to each sample quench level than the ²²⁶Ra results that are calculated from the ²¹⁴Po peak.

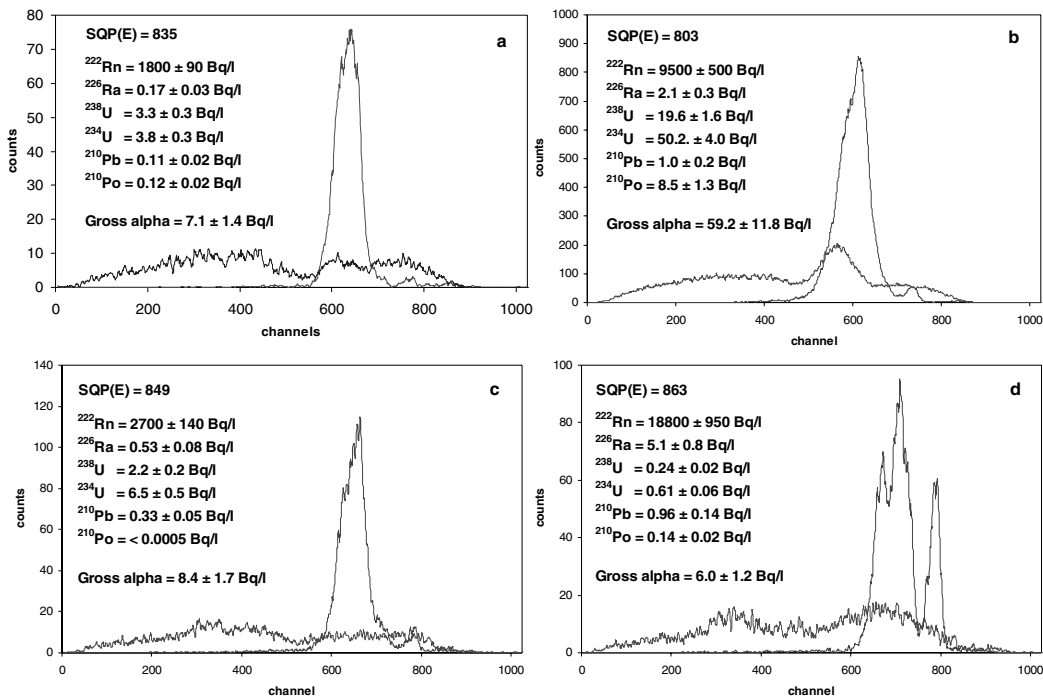


Figure 7 The gross alpha and beta spectra of the Quantulus from 4 drinking water samples originating from drilled wells

These few examples show that the dependence of alpha spillover on the alpha energy in measuring uranium and ^{226}Ra in groundwater samples with various chemical compositions needs to be studied more thoroughly in order to assess its effect on the results and to identify measures to consider it in the calibrations.

CONCLUSIONS

The dependence of alpha spillover on the alpha energy was readily demonstrated using sample series prepared from Rn-bearing water. A selection of samples were quenched to different degrees and measured at various PSA levels. The large difference between the alpha particle energies of Rn and its alpha-emitting daughters, ^{218}Po and ^{214}Po , establish the effect. The alpha spillover to the beta window was larger for lower energy alpha particles than for higher energy alpha particles in quenched samples when the PSA level was not adjusted properly. Under such circumstances, the lower energy alpha emitters will have larger uncertainties in their results than the higher energy emitters if variable alpha spillovers are not considered in the calibrations. The new effect observed in this study suggests that comprehensive studies are needed to assess its significance in the analyses of different radionuclide matrixes under variable quench conditions. The simultaneous determination of uranium and radium in quenched samples belongs to those analyses where variable alpha spillover can cause erroneous results.

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