# THE DETERMINATION OF LOW LEVELS OF RADIUM ISOTOPES AND RADON BY DELAYED-COINCIDENCE LIQUID SCINTILLATION SPECTROMETRY

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**ABSTRACT.** I describe a new liquid scintillation (LS) method to determine extremely low levels of $^{222}$Rn (*e.g.*, contaminating a $^{14}$C sample), $^{226}$Ra, $^{228}$Ra and $^{224}$Ra *via* the short-lived decay products, $^{214}$Po and $^{212}$Po. The background for $^{222}$Rn is in the order of one Rn decay per day. In this method, a separate pulse-height spectrum is recorded from pulses that occur within a fixed, short interval following a preceding pulse. This method can be applied in conventional LS spectrometers with little supplementary electronics.

## INTRODUCTION

The short-lived Po isotopes, $^{214}$Po ($t_{½}$ = 164 $\mu$sec, $E_\alpha$ = 7.69 MeV) and $^{212}$Po ($t_{½}$ = 0.30 $\mu$sec, $E_\alpha$ = 8.78 MeV) are found in the natural decay chains of $^{238}$U and $^{232}$Th (Fig. 1). An atom of such a short-lived Po isotope decays within a few half-lives from the moment of its production, *i.e.*, its decay is "delayed coincident" with the decay of its mother, $^{214}$Bi or $^{212}$Bi. Liquid scintillators are excellently suited to detect these delayed coincidences, because they have high efficiencies for both the alpha decays of the short-lived Po isotopes and the high-energy beta decays of $^{214}$Bi and $^{212}$Bi (<0.5% of the $\beta$ decay branches have an endpoint energy below 0.4 MeV, <8% below 1.0 MeV).

When a fixed, short time window of 5–10 half-lives of a short-lived Po isotope is opened after each pulse in a liquid scintillation (LS) counter, nearly all decays of this Po isotope will occur in this window, and may be counted with a separate scaler (Assaf & Gat 1967). At low total decay rates, only a small fraction of counting time is actually occupied by short time windows, so that only small fractions of the randomly distributed decays and background events will coincide with such windows.

## METHODS

Buheitel (1989) showed that recording a separate pulse-height spectrum of the delayed coincident pulses (instead of counting them with a separate scaler) results in an extremely sensitive, though simple and robust, method. Accordingly, I assembled a simple delayed-coincidence LS spectrometer. It comprises a single photomultiplier tube (PMT) that views the 2.8-ml quartz vial containing the sample. The PMT is sufficient to detect >97% of the high-energy $^{214}$Bi and $^{212}$Bi $\beta$ decays well above the noise level. Quenching has only moderate influence on this high detection efficiency for the precursors of the short-lived Po isotopes. PMT and sample are shielded with 5 cm of lead. A PMT output pulse is amplified linearly (unipolar, 2 $\mu$sec shaping time), and its height is converted by an analog-to-digital converter (ADC) to an n-bit address. However, the multichannel analyzer (MCA) memory address for the pulse is represented by n + 2 bits.

A "delayed-coincidence detection unit" opens two time windows after each PMT pulse that exceeds a discriminator level (these window settings are not optimal): 1) the $^{212}$Po window, 15 nsec–1.6 $\mu$sec, and 2) the $^{214}$Po window, 16 $\mu$sec–1.35 msec. When a subsequent pulse coincides with one of these windows, the delayed-coincidence detection unit switches one of the bits, n + 1 and n + 2, which defines the section of the MCA memory where the pulse is to be counted. The n bits at the ADC output define the channel number within the section. Thus, in addition to the common

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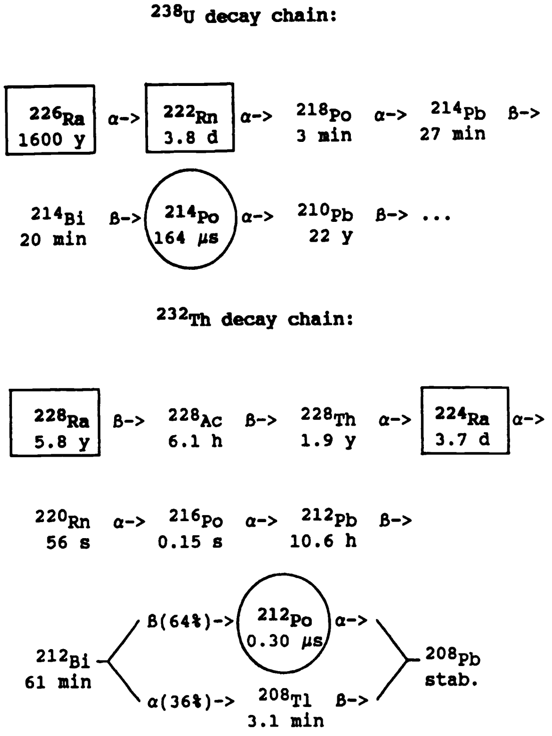

Fig. 1. Relevant parts of the decay chains of $^{238}$U and $^{232}$Th

pulse-height spectrum, two separate spectra of delayed coincident pulses are recorded, having the same relation between pulse height and channel number.

In the separate spectrum corresponding to the $^{214}$Po time window, the $^{214}$Po α peak appears (Fig. 2B). For the sake of simplicity, no effort was made to obtain a similarly undisturbed α peak of the very short-lived $^{212}$Po by separating the $^{212}$Po PMT pulse from the preceding $^{212}$Bi pulse (*e.g.*, by gating and delaying) before ADC processing. On the contrary, I chose an extra-long amplifier-shaping time, so that the ADC always handles the $^{212}$Bi plus $^{212}$Po pile-up pulse as a single pulse (Fig. 3A). This simple configuration is sufficient for practical purposes.

## SAMPLE PREPARATION AND COUNTING

The preparation of Rn is not discussed here. $^{222}$Rn is counted after growth of the decay products to $^{214}$Po. Its activity is calculated from the content of the $^{214}$Po α peak in the corresponding separate spectrum, which is similar to the spectrum shown in Figure 2B.

Ra is separated from a sample using ~60 mg Ba as a carrier and ~5 Bq $^{133}$Ba (electron capture, $t_{½}$ = 10.7 yr, 356 keV γ radiation) as a yield tracer. It is then converted to the chloride and simply mixed as a 1.0-ml aqueous solution with 1.8 ml of an appropriate scintillator. The full-width half maximum (FWHM) of the $^{214}$Po α peak is ~11% in this mixture and ~9% in the pure scintillator.

First, $^{224}$Ra is measured about 2–3 days after preparation, when all the daughter activity present in the counting vial will have grown in since the vial was closed. The $^{224}$Ra activity is calculated

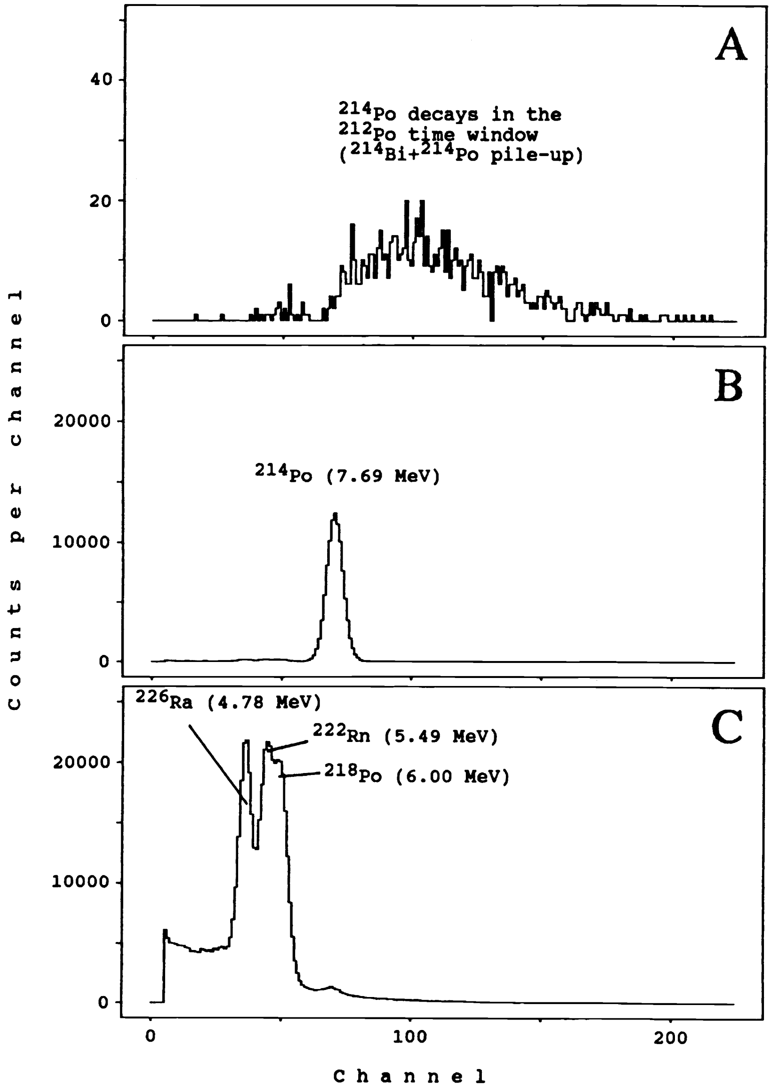

Fig. 2. Pulse-height spectra of $^{226}$Ra with daughters down to $^{214}$Po in equilibrium (linear pulse-height scale). $^{226}$Ra activity = 1.0 Bq. Sample composition = 1.8 ml scintillator plus 1.0 ml aqueous barium chloride solution. Counting time = $1 \times 10^5$ sec. A. Pulses in the $^{212}$Po time window. B. Pulses in the $^{214}$Po time window; C. Pulses in no time window.

from the content of the $^{212}$Bi plus $^{212}$Po pile-up peak in the corresponding separate spectrum (Fig. 3A). About 0.7% of the $^{214}$Po atoms from the $^{238}$U series also decay within the $^{212}$Po time window after the decay of their parent nuclide. These decays contribute to the count rate in the separate $^{212}$Po spectrum (Fig. 2A). The value of this contribution is readily calculated from the content of the $^{214}$Po $\alpha$ peak in the other separate spectrum (Fig. 2B).

$^{226}$Ra is measured when $^{222}$Rn is sufficiently grown in. Its activity is calculated from the content of the $^{214}$Po $\alpha$ peak in the corresponding separate spectrum (Fig. 2B). If $^{223}$Ra ($t_{½}$ = 11.4 d) from the weak $^{235}$U series is not allowed to decay before the $^{226}$Ra measurement, its short-lived decay product, $^{215}$Po ($t_{½}$ = 1.8 msec, $E_\alpha$ = 7.39 MeV) slightly disturbs the $^{214}$Po peak.

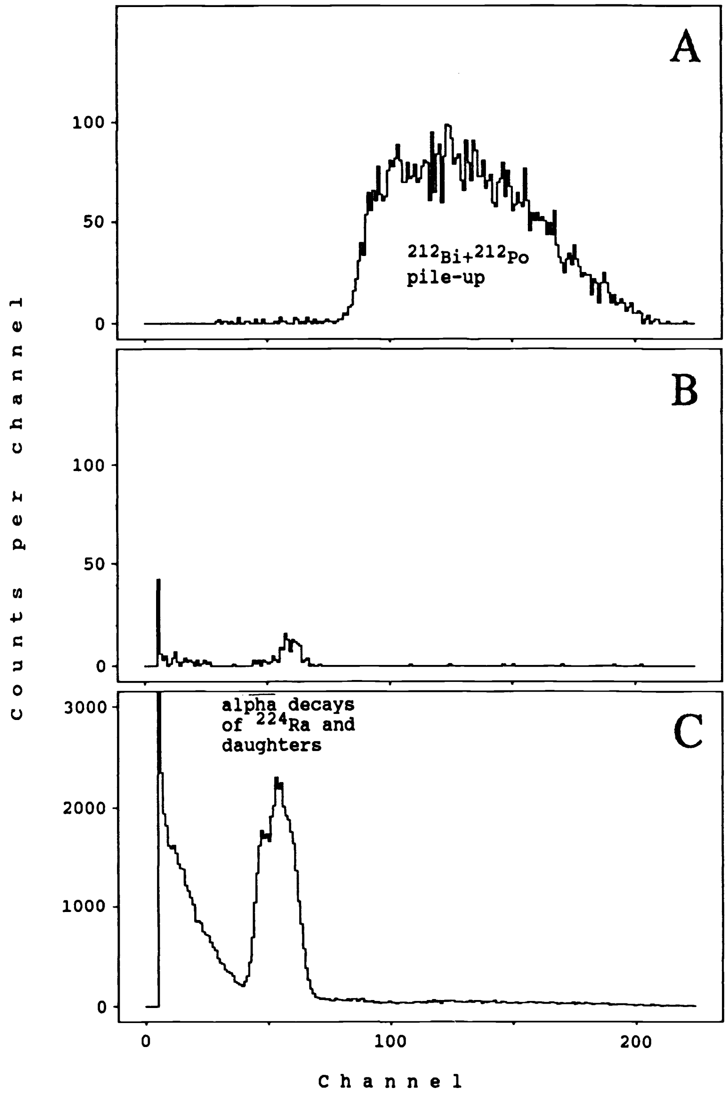

Fig. 3. Pulse-height spectra of $^{224}$Ra with daughters in transient equilibrium (linear pulse-height scale). Initial $^{224}$Ra activity = 0.10 Bq. Sample composition = 1.8 ml scintillator plus 1.0 ml aqueous barium chloride solution. Counting time = $1 \times 10^5$ sec. A. Pulses in the $^{212}$Po time window; B. Pulses in the $^{214}$Po time window; C. Pulses in no time window.

Finally, $^{228}$Ra is measured after two or more months' growth of $^{228}$Th ($t_{½}$ = 1.9 yr) and its decay products to $^{212}$Po. In this measurement, $^{226}$Ra is obtained again, now no longer disturbed by $^{223}$Ra.

A two-week ($1.2 \times 10^6$ sec) measurement of a blank (scintillator only) yielded six counts in the region of the $^{214}$Po peak (3 × FWHM) in the corresponding separate spectrum (Fig. 4B). An earlier one-week measurement yielded four counts. In the presence of a $^{133}$Ba tracer, the $^{214}$Po time windows following decays of $^{133}$Ba allow additional random delayed coincidences. As a consequence, 5 Bq $^{133}$Ba increase the background of a blank (scintillator mixed with water) in the region of the $^{214}$Po peak in the corresponding separate spectrum by three counts per day.

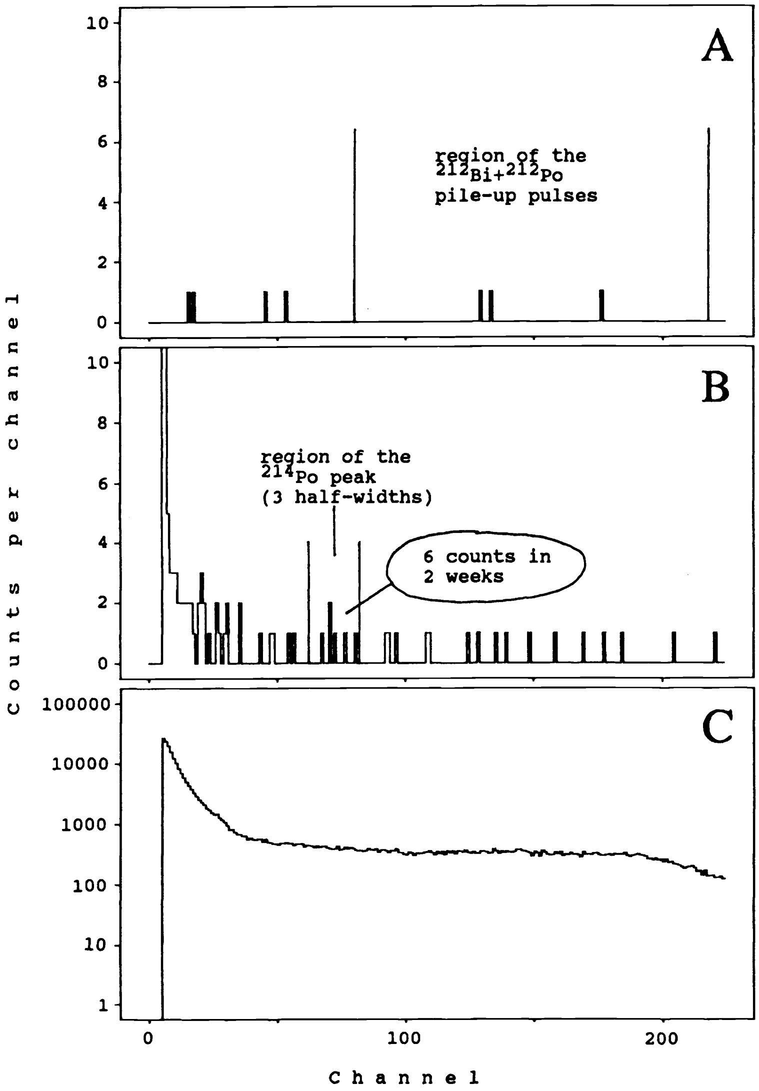

Fig. 4: Pulse-height spectra of a blank (linear pulse-height scale). Sample composition = 2.8 ml scintillator. Counting time = 1.2 x $10^6$ sec (~2 weeks). A. Pulses in the $^{212}$Po time window; B. Pulses in the $^{214}$Po time window; C. Pulses in no time window.

## DISCUSSION AND CONCLUSIONS

In a $^{222}$Rn measurement, the decays of a single daughter nuclide are detected with a probability close to 100% by the present method. In contrast, according to integral counting methods, such as those of Lucas (1957) and Prichard and Gesell (1977), decays of $^{222}$Rn and of several daughters are detected with a probability close to 100%, so that one $^{222}$Rn decay results in several counts. This high yield is no real benefit over the present method when the counting period is much longer than the half-lives of the $^{222}$Rn daughters down to $^{214}$Po (Sarmiento, Hammond & Broecker 1976). In such a case, the counts of $^{222}$Rn and its daughters are strongly correlated, so that the accuracy of the measured $^{222}$Rn activity is limited by the number of $^{222}$Rn decays during the counting period.

Due to the extremely low background, the delayed-coincidence LS spectrometry method allows measurement of extremely low activities of $^{222}$Rn, $^{226}$Ra, $^{228}$Ra and $^{224}$Ra. As an example, the method is ideally suited to measure the $^{222}$Rn contamination of a low-level $^{14}$C sample while performing the $^{14}$C measurement. The preparation of Ra is simple, as quenching has little influence on the counting efficiency, and the Ba carrier and the $^{133}$Ba tracer accompany it into the counting sample.

In α LS spectrometry, the α energy scale is easily calibrated by adding $^{222}$Rn to a sample after the measurement, performing another measurement and observing the position of the single $^{214}$Po α peak. The composition of the sample is hardly changed by adding a gas, and after the decay of $^{222}$Rn, only little activity of $^{210}$Pb ($0.0005 \times$ $^{222}$Rn activity) and its daughters remain.

Recently, I modified my apparatus to measure $^{223}$Ra in addition to the other Ra isotopes. $^{223}$Ra disintegrates to $^{219}$Rn, which itself disintegrates to the short-lived $^{215}$Po by α decay. I use a third time window (1.35 msec–2.9 msec) to record a third separate spectrum of delayed coincident pulses. An α peak appears in this spectrum that contains 26% of the $^{215}$Po decays. The discriminator level for the opening pulses of this window is set closely below the pulse heights of the $^{219}$Rn α decays to keep low the rate of opened windows not originating from $^{219}$Rn decays. After correcting the $^{215}$Po peak area for random delayed coincidences and true delayed coincidences of the $^{214}$Bi/$^{214}$Po and $^{220}$Rn/$^{216}$Po pairs, a fairly accurate value for the $^{223}$Ra activity is obtained, provided that the $^{223}$Ra/$^{226}$Ra and $^{223}$Ra/$^{224}$Ra activity ratios are not far below the average natural value of ~0.05. The result for $^{226}$Ra obtained a few days after preparation can now be corrected for the influence of $^{223}$Ra.

This delayed-coincidence LS spectrometry method can be applied in conventional low-cost LS spectrometers, as well as high-performance low-level and pulse-shape devices, by adding few supplementary electronics.

## REFERENCES

Assaf, G. and Gat, J. R. 1967 Direct determination of short-lived radon daughter products on air filters by liquid scintillation counting using a delayed-coincidence technique. *Nuclear Instruments and Methods* 49: 29–37.

Buheitel, F. 1989 European Patent Application No. 89114850.4, Publication No. 0 412 194 A1.

Lucas, H. F. 1957 Improved low-level alpha-scintillation counter for radon. *The Review of Scientific Instruments* 28(9): 680–683.

Prichard, H. M. and Gesell, T. F. 1977 Rapid measurements of $^{222}$Rn concentrations in water with a commercial liquid scintillation counter. *Health Physics* 33: 577–581.

Sarmiento, J. L., Hammond, D. E. and Broecker, W. S. 1976 The calculation of the statistical counting error for $^{222}$Rn scintillation counting. *Earth and Planetary Science Letters* 32: 351–356.