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DETERMINATION OF RADON BY LIQUID SCINTILLATION α/β PARTICLE SPECTROMETRY:
Towards the Resolution of a ^{14}C Dating Problem

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ABSTRACT. Traces of uranium and radium within the ^{14}C sample generate radon (Rn) which gets occluded during the benzene synthesis, thus generating false (extra) counts within the ^{14}C counting window. This, if undetected, gives rise to erroneous ^{14}C age determinations. The application of simultaneous α and β liquid scintillation spectrometry will enable a mathematical evaluation of the ^{14}C signal unaffected by α and β particle emissions from radon decay daughters.

INTRODUCTION

Samples such as charcoal, bone, shell, and soil organic matter, can incorporate uranium (^{238}U, hence radium (^{226}Ra), while stored in the archives of nature. The first radioactive daughter element of ^{226}Ra is ^{222}Rn, a noble gas of relatively high abundance in nature. It is, for all practical purposes, ubiquitous. It was discovered, early in the history of radiocarbon dating by gas proportional counting (de Vries, 1957), that CO_2 prepared from a ^{226}Ra containing sample by combustion of organic matter or acid hydrolysis of carbonates will occlude radon but not its parent ^{226}Ra. Thus, gas purification techniques involving cryogenic distillation, chromatographic separation, or decay of radon prior to counting are practiced by all gas proportional ^{14}C daters.

The effect on gas proportional counting was detailed by Nydal (1983) who endorses the common method of storing the counting gas for several weeks (or months if necessary) until radon naturally decays to ^{210}Pb. However, Nydal includes the warning that, when severe contamination has occurred, the residual activity of ^{210}Pb may be significant and adversely affect the ^{14}C age determination.

Early experiments relating to liquid scintillation (LS) counting gave rise to the generally accepted notion that radon is eliminated quantitatively during the rigorous heating, under vacuum, of lithium carbide to ca 900°C prior to its hydrolysis to acetylene, which is the precursor of all modern benzene syntheses (Barker, 1953; Noakes, Kim & Stipp, 1965; Tamers, 1965). Nevertheless, checking for the presence of radon and/or storing the sample benzene for several weeks prior to counting is the normal procedure in all ^{14}C laboratories using the LS counting method.

The delay in counting a sample is not always acceptable and it was determined at the ANU Radiocarbon Laboratory, early in the 1970s that, in the presence of a significant sample contamination by radon, neither the heating of lithium carbide nor the delay of 2–3 weeks after synthesis and prior to counting, eliminated the radon contaminant. Thus, a suspect sam-

ple was often recounted after a 2–3 month delay and, if this was not possible, a mathematical correction was applied based on the observed decrease in count rate of a sample over a period of several weeks, involving 10^3 minute weekly counting times (Gupta & Polach, 1985, p 109).

This paper deals with the recognition of radon and its decay daughters by simultaneous α and β particle liquid scintillation spectrometry.

EXPERIMENTAL

Uranium Decay Series

When a CO_2 sample contains radon (^{222}Rn), short lived daughter elements are produced. Two of these are α-emitting elements, ^{218}Po and ^{214}Po, and two are β-emitting elements, ^{214}Pb and ^{214}Bi. Since the radon daughters all have considerably shorter half-lives they are found in secular equilibrium with their parent after several hours. The decay series ends, from the radiocarbon dating point of view, with β-emitting element ^{210}Pb with a 22.3 yr half-life (Table 1).

In gas proportional counting, the counts generated by α particles can be independently determined and, thus, subtracted from the observed ^{14}C

TABLE 1
Uranium decay series of significance to ^{14}C dating

Element	Half-life	Particle	Energy MeV	Comment
^{238}U	4.468×10^9y	α	4.196	77%, Decays via ^{234}Th, ^{234}U and ^{230}Th
		α	4.149	23%
		γ	0.496	~0.3%
^{226}Ra	1600 y	α	4.785	and 5% 4.6 MeV; deemed not to be present in CO_2 prepared for ^{14}C dating
		γ	0.186	~0.5%
^{222}Rn	3.824 d	α	5.489	Equilibrates with its daughters in 3.3 h
		γ	0.51	<0.1%
^{218}Po	3.05 m	α	6.002	RaA
		$\beta-$	0.33-1.03	~6%
^{214}Pb	26.8 m	$\beta-$	0.73	RaB, $\beta-$ spectrum overlaps ^{14}C
^{214}Bi	19.7 m	α	5.61	0.02%, RaC
		$\beta-$	0.4-3.3	~100%, $\beta-$ spectrum overlaps ^{14}C
		γ	~0.61	
^{214}Po	163.7 μs	α	7.69	RaC', 99+%
		γ	0.8	<0.1%
^{210}Pb	22.26 y	$\beta-$	0.015-0.061	RaD, 99+%
		γ	8.04	
^{210}Bi	5.01 d	α	~4.7	RaE
		$\beta-$	1.16	99+%
^{210}Po	138.8 d	α	5.305	RaF, 100%
		γ	0.08	
^{206}Pb	Stable			

Structure based on: Ivanovich and Harmon (1982, Table 1.2, p 22) with data from Lederer and Shirley (1978)

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count rate. However, the counts generated by the β particles cannot be distinguished from ^{14}C β pulses nor can a detailed spectral analysis be performed. Nydal (1983) thus concludes that the count rate contribution to ^{14}C, due to the presence of radon and its daughters in the counting gas, cannot be determined.

Liquid scintillation counting, on the other hand, enables a full spectral resolution of β isotopes in terms of pulse height (PH), and therefore energy. The recently developed LS pulse shape (PS) analysis (Oikari, Kojola, Nurmi & Kaihola, 1987) enables the counting of α particles in the presence of β particle emissions and an important application could be the resolution of a ^{14}C signal in the presence of ^{222}Rn.

Equipment and Procedure

A commercial high resolution low-level LS spectrometer (LKB-Wallac, Quantulus™) capable of both α and β particle simultaneous energy spectra definition was used for the experiment at Wallac Oy. The same type of counter, without the α particle detection facility was used at ANU. ^{222}Rn was injected into a ^{14}C-free benzene sample containing 15g/L butyl-PBD scintillant and the resulting spectrum determined after the equilibrium with radon daughters was reached. Then two differential energy spectra were plotted: one, PH spectrum only (at ANU) and two, simultaneous alpha/beta (PH/PS) determinations resulting in discrete β and α emission spectra (Figs 1 & 2). Superimposed onto these were, for interpretation purposes, pure ^{14}C (no radon contaminant) spectra determined in a separate run at ANU.

For the experiment, a 100% ^{14}C modern (~65 dpm for 5mL of benzene) and approximately equivalent radon count rate were selected. The signal to noise (modern/background) for ^{14}C at ~75% efficiency is 210 in the low-level laboratory of Wallac Oy and 135 in a normal environment at

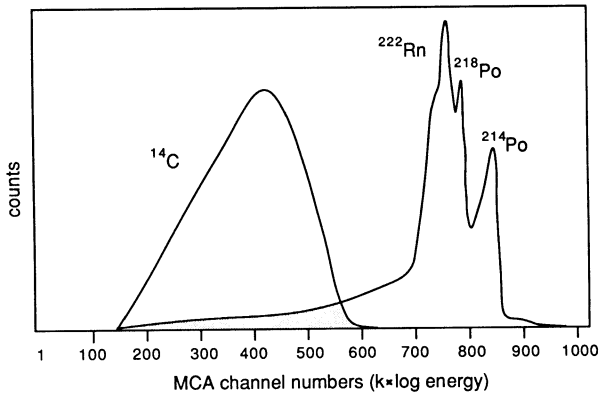

Fig 1. Pulse height spectra of ^{14}C and ^{222}Rn superimposed, showing good resolution of ^{222}Rn daughters and significant overlap with ^{14}C (shaded area).

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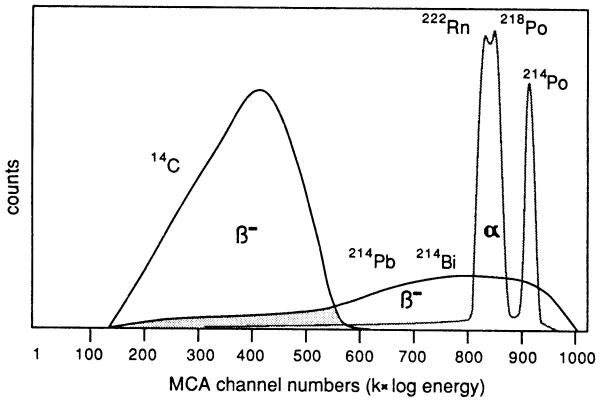

Fig 2. ^{14}C β emission spectrum superimposed on simultaneous radon α and radon β emission spectra. In practice, if ^{222}Rn is present, the ^{14}C β and ^{214}Pb and ^{214}Bi β spectra would merge. Simultaneous α/β emission spectra analysis will enable a more precise multi-isotope resolution.

ANU (Polach, 1987, Table 1). The background thus does not enter our considerations.

Results

We can confirm Nydal's experiment showing that 99.3% equilibrium with daughters of ^{222}Rn was reached in 3.3 hours (Nydal, 1983, p 504). Natural decay of daughters then occurred and can be monitored in the PH spectrum (Fig 1) and the simultaneous and separate α and β emission spectra (Fig 2).

The relative contribution of α-producing particles can be resolved in the PH (pulse height) mode alone (Fig 1) but the spectrum is attenuated (most likely due to the different counters used), in relation to PS (α) spectrum in Figure 2, as well as pooled with the expected β particle producing elements and the Compton electron scatter due to γ emitting daughters. The latter contribution however cannot be very significant as γ particles are of minor abundance (Table 1). The overlap with ^{14}C spectrum (free of ^{222}Rn) is seen to be significant and radon count rate dependent. In practice, under the worst conditions at ANU, this resulted in a contamination equivalent to 2% modern (160 yr) which, as we will demonstrate in a later paper, was negligible (within statistics) after 3 weeks delay in counting. This is essentially due to the fact that ^{210}Pb emits low energy β particles and X-rays, the emission spectra of which fall outside the ^{14}C region of interest in radiocarbon dating by LS spectrometry.

The relative contribution of α-producing particles of ^{222}Rn and of their β-producing daughters can be resolved by simultaneously acquiring an independent α and β energy emission spectrum, here superimposed in Figure 2. The α and corresponding β daughters (Table 1) are well resolved. Both of these are seen to overlap, in the expected manner, the ^{14}C spectrum (free of ^{222}Rn), which was determined during another experimental run.

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CONCLUSION

Liquid scintillation multiparameter spectrometry is capable of resolving spectral contributions of multi-labelled samples, in this case, ^{14}C, ^{222}Rn and its daughters. In the absence of simultaneous and separate α particle emission spectra the contribution to ^{14}C must be judged in terms of the observed total count rate in the region of interest above the ^{14}C spectrum. Thus, the precision of determination of the interference (additional ^{14}C counts) will be count rate dependent in both the ^{14}C and ^{222}Rn window. Thus, subject not only to Poisson counting errors but also to errors associated with the assessment of the β contribution from ^{214}Pb and ^{214}Bi and associated β and γ particle transitions.

In the presence of a pure α particle emission spectrum, the contribution of the β-emitting daughters, ^{214}Pb and ^{214}Bi, can be quantitatively determined from the sharp and 100% detection efficiency α particle emission spectral peaks. This will enable a spectral subtraction to be carried out in the multi-isotope, software based analysis mode. It is anticipated that while still subject to count rate defined Poisson errors, the simultaneous α/β particle emission resolution will give more precise results than is presently possible.

It is not clear, from the spectral evidence presented, what count rate is induced by the γ Compton scatter. Some events involve β and γ particle transitions in prompt succession. Therefore, some β energy is added to the Compton electron energy which is variable and smaller than the true γ particle transition energy. As some γ particles will escape the counting vial without producing fluorescence we predict that multi-isotope resolution will be vial specific and not general.

We will pursue the collaborative development of software and propose to test the applicability of a mathematical correction on precisely determined ^{14}C samples prior to their contamination with radon as well as on contaminated field samples prior to and after radon decay.

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