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103

Rapid analysis of ^{226}Ra in mine waters by gamma-ray spectrometry

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Contents

Figures

Tables

Abstract

Techniques for the determination of ^{226}Ra in uranium mine waters by γ-ray spectrometry are examined, with an emphasis on methods capable of completion within 1 to 3 days of receipt of the sample. Methods discussed utilise either: (i) the 186 keV ^{226}Ra γ-ray, with the contribution from ^{235}U being subtracted after a separate uranium determination, or (ii) measurement of ingrowing ^{222}Rn progeny, either by two successive counts or by a single count (together with an assumption that radon was not present at the time of sample preparation). A full analysis of the statistical uncertainties and systematic errors associated with each technique is presented.

Rapid analysis of ^{226}Ra in mine waters by gamma-ray spectrometry

1 Introduction

A number of techniques have been reported in the literature for the determination of ^{226}Ra activity concentrations in water samples. The most commonly used of these are radon emanation (Greenberg et al 1992), liquid scintillation (Cooper & Wilks 1981; Schönhofer 1989), γ-ray spectrometry (Lucas & Markun 1992; Kahn et al 1990) and α-particle spectrometry. The first three of these methods normally rely upon an ingrowth period of at least six ^{222}Rn half-lives (~23 days; $t_{1/2}$=3.824 days) to allow radon and its progeny to achieve secular equilibrium with the parent ^{226}Ra. Such delays are of no great consequence in the routine analysis of environmental samples collected for research purposes or in the analysis of water samples collected as part of a regular monitoring program. However, the need for a more rapid analysis of ^{226}Ra in water occasionally arises at uranium mine sites either to verify that standards are met by water proposed for discharge or to enable assessment of the significance of accidental discharges.

Alpha-particle spectrometry allows analysis of ^{226}Ra without an ingrowth period for ^{222}Rn. In addition, measures of the isotopes ^{223}Ra, ^{224}Ra and, after an ingrowth period of some months, ^{228}Ra can be obtained by this method (Hancock & Martin 1991). However, preparation of the source disk is generally time consuming and requires chemistry laboratory facilities and operator expertise which are not always available. The method described by Sill (1987) alleviates these problems to some extent, but still requires some chemical separations, relies on an isotope of barium as a tracer for radium, and does not give an accurate measure of any radionuclide except ^{226}Ra without further processing of the sample.

The use of γ-ray spectrometry has the advantage that activity concentrations of a number of radionuclides can be obtained in addition to ^{226}Ra. These include ^{235}U from the actinium series, ^{234}Th, ^{230}Th and ^{210}Pb from the uranium series and ^{228}Ra, ^{228}Th and ^{224}Ra from the thorium series. In addition, sample preparation is much simpler for this method than for α-particle spectrometry methods.

In this report, emphasis is placed on the adaptation of γ-ray spectrometry techniques that are currently used by the Environmental Research Institute of the Supervising Scientist (***eriss***) and by the Environmental Laboratory at the Ranger Uranium Mine. The method previously suggested by ***eriss*** for use by Ranger was a combination of γ-ray spectrometry and direct measurement of uranium by chemical analysis; one reason for this choice was that the company had fully established facilities for both techniques at the Ranger Environmental Laboratory. The method was quite appropriate because, although it involves a subtraction of the uranium concentration to a particular γ-ray line, precise values for the radium concentration could be obtained. However, since the original development of this method there has been a marked rise in the uranium concentration in the water of two of the retention ponds at Ranger without a significant increase in ^{226}Ra concentrations. For this reason the method requires further assessment.

The objective of this report is to review the various γ-ray spectrometry methods available for the rapid analysis of ^{226}Ra in mine waters, to explore their limitations quantitatively, and to recommend methods that should be used by companies in future. For regulatory purposes, for example to determine whether or not a concentration meets a required standard or to assess the significance of an unplanned discharge, an overall uncertainty of about 30% would normally be considered adequate, and this has been taken as determining the limit of acceptance for the purposes of the following discussion.

2 Analysis of ^{226}Ra by gamma-ray spectrometry

2.1 Normal procedure

The procedure followed by ***eriss*** in the routine analysis of ^{226}Ra in water by γ-ray spectrometry is described by Murray et al (1987). In summary, samples of water (either filtered or unfiltered) are acidified to 1% with Analar grade nitric acid before extraction of the natural series radionuclides by manganese dioxide precipitation. Recently, a second precipitation stage using ferric hydroxide has been added to minimise fluctuations in uranium recovery. The precipitate is removed by filtering through Whatman's No. 42 ashless filter papers and ashed. The precipitate is then cast in a standard geometry using polyester resin, the principal objective of which is retention of radon arising in the radioactive decay of ^{226}Ra. After a delay period of 23 days or more to allow radon concentrations in the sample to achieve secular equilibrium with ^{226}Ra, the sample is analysed using high γ-ray spectrometry and the ^{226}Ra concentration is obtained using the short-lived radon progeny lines (see fig 1) at 295 keV (^{214}Pb), 352 keV (^{214}Pb) and 609 keV (^{214}Bi).

One gamma-ray, energy 186.0 keV, is emitted following the direct decay of ^{226}Ra. This γ-ray could, in principle, be used to measure ^{226}Ra concentrations without the need to wait for ingrowth of radon. However, the decay of ^{235}U gives rise to a line at 185.7 keV; with germanium detectors these two lines cannot be resolved. Use of the radon progeny lines yields a precise measurement of the ^{226}Ra concentration and allows an accurate subtraction of the ^{226}Ra contribution to the peak at 186 keV. The residual intensity of this peak is then used to determine the ^{235}U concentration in the sample.

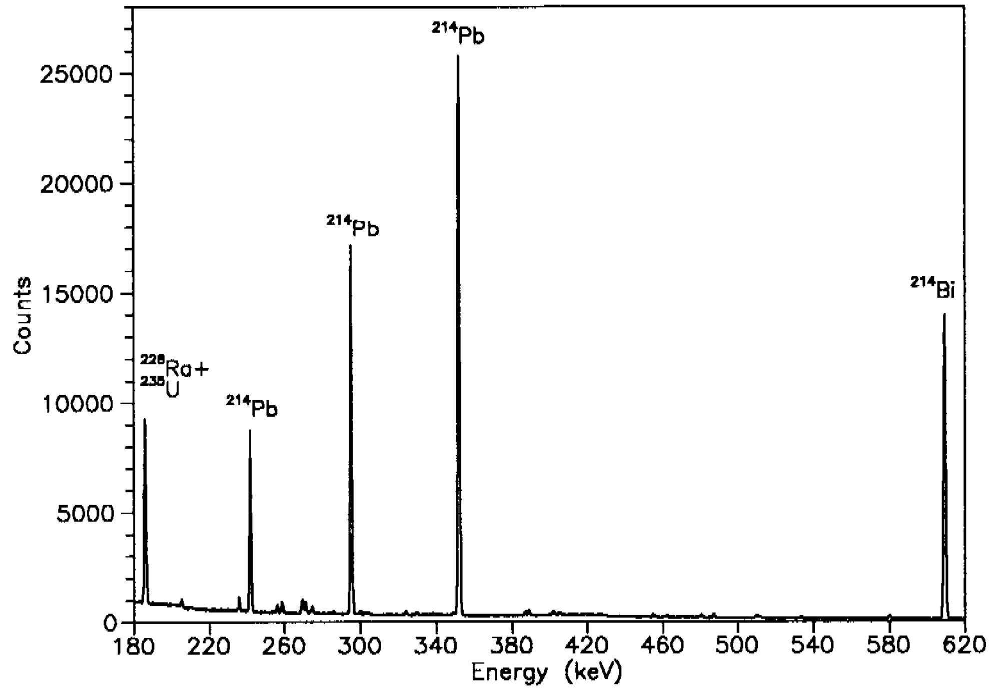

Figure 1 Gamma-ray spectrum of a uranium ore, showing the main peaks of interest from ^{226}Ra, ^{235}U and the radon progeny ^{214}Pb and ^{214}Bi

Where the uranium may be assumed to be of natural origin (ie neither depleted nor enriched in ^{235}U), the normal ^{235}U/^{238}U ratio of 0.046 may then be used to obtain the ^{238}U concentration. Measurement of ^{238}U may also be made via the intensity of the 63.3 keV line arising in the decay of ^{234}Th ($t_{1/2}$ = 28 days), but use of this method assumes that equilibrium exists between ^{238}U and ^{234}Th. For soils and sediments this assumption is usually considered justified but it is not a reasonable assumption for water samples and should not be used unless an ingrowth period of greater than 150 days has been allowed since casting of the sample.

Interference from uranium to the measurement of ^{226}Ra could be avoided by using a precipitation technique which does not co-precipitate uranium, such as $BaSO_4$ (Kahn et al 1990) or $BaSO_4$/$PbSO_4$ (Jiang & Holtzman 1989). However, the use of a relatively non-selective precipitation technique is desirable in order to utilise the ability of γ-ray spectrometry to detect a number of radionuclides at one time. In addition, the simplest and most rapid technique, that of placing the sample in a container directly on a detector, does not involve any radium/uranium separation. For these reasons, we discuss here possible techniques for the rapid determination of ^{226}Ra in water samples without separation of uranium.

2.2 Analysis using the 186 keV line: precipitation method

The routine method for measurement of ^{226}Ra concentrations in water by γ-ray spectrometry requires a delay of at least 23 days between casting of the precipitate and analysis of the sample. The technique can, however, be adapted to provide a rapid analysis of ^{226}Ra if an independent measurement of the uranium concentration of the sample is made by, for example, routine analytical chemistry techniques. Such a measurement allows the subtraction of the ^{235}U contribution to the 186 keV line; the residual intensity of this line can then be used to determine the ^{226}Ra concentration.

For a sample in which the ^{238}U and ^{226}Ra activities are equal the uranium and radium contributions to the 186 keV line are approximately equal. As a result, the uncertainty in the ^{226}Ra measurement using this technique will be small provided that the ratio of uranium to radium in the sample is not too large. In recent years, however, this ratio has increased substantially in the waters of RP2 and RP4 at Ranger. For this reason a full analysis of the statistical and systematic errors arising from the use of this procedure has been carried out as a function of the uranium-radium ratio. This analysis enables a determination of the limitations of the technique when applied to waters from the mine site.

2.2.1 Statistical uncertainties

The count rate in the 186 keV line has four components arising from the radium and uranium activities in the sample, A_r (Bq) and A_u (Bq) respectively, the peak background due to impurities in the detector and shield, r_b (counts/ksec), and the continuum underlying the peak, r_c (counts/ksec).

If the sample is counted for a period T (ksec), the total number of counts in the 186 keV peak is given by:

$$\begin{aligned} n_t &= n_r + n_u + n_b + n_c \\ &= k_r A_r T + k_u A_u T + r_b T + r_c T \end{aligned}$$

where k_r and k_u are the calibration constants (counts/Bq/ksec) for the radium and uranium contributions to the 186 keV line for the particular detector and particular geometry used in the measurement.

The values of k_r, k_u, r_b and r_c are given in table 1 for a standard disk sample counted by each of four detectors in use at ***eriss***. The variation in k_r and k_u between detectors is not large. However, the background count rates vary by more than an order of magnitude; calculations have therefore been carried out for the best (G) and poorest (A) of the detectors listed. The continuum count rate cannot be specified uniquely because its magnitude depends upon the concentration of other radionuclides, eg ^{228}Ra, ^{228}Th and ^{224}Ra, in the sample as well as those considered here. In addition there are contributions due to detector and shield impurities and from cosmic rays. However, when radionuclide concentrations are low in the sample, the latter contributions will dominate the continuum and hence provide a detection limit. The continuum count rates listed in table 1 are, therefore, those measured in the absence of any sample.

The net radium count is given by:

$$n_r = n_t - n_u - n_b - n_c$$

and the statistical uncertainty δn_r is given by:

$$(\delta n_r)^2 = (\delta n_t)^2 + (\delta n_u)^2 + (\delta n_b)^2 + (\delta n_c)^2$$

n_c is estimated from the counts observed in regions above and below the peak. If the total number of channels used is twice the number of channels under the peak, then we have:

$$(\delta n_c)^2 \approx \frac{n_c}{2}$$

n_b is estimated from counts made in the absence of the sample. Normally, such counts are made at regular intervals over a long period of time, and the results averaged, in which case δn_b will be small in comparison with δn_t. Similarly, for the purposes of this analysis (where we are approaching detection limits for Ra), we assume that the precision of the independent U measurement is high; hence the random error δn_u is taken to be small, and we have:

$$(\delta n_r)^2 \approx n_t + \frac{n_c}{2} = n_r + n_u + n_b + \frac{3n_c}{2}$$

and the fractional statistical uncertainty, ε_r, in the measured Ra concentration is given by:

$$\varepsilon_r = \left(\frac{\delta n_r}{n_r}\right)$$

$$\approx \frac{\left[k_r A_r + k_u A_u + r_b + 3r_c / 2\right]^{1/2}}{k_r A_r T^{1/2}} \qquad (1)$$

Table 1 Calibration constants, background count rates and continuum count rates for the 186 keV line using four detectors at ***eriss***

Detector[a]	Description	k_r [b] (cts/Bq/ksec)	k_u [b] (cts/Bq/ksec)	r_b (cts/ksec)	r_c (cts/ksec)
A	16% p-type PGT	2.33	1.67	5.95	14.8
D	10% p-type PGT	2.26	1.59	2.92	10.6
G	19% n-type Canberra	2.93	1.97	0.34	7.6
H	15% p-type Ortec	2.06	1.43	2.36	15.7

[a] Nomenclature is that used for identification at ***eriss***

[b] Calibration for standard disk geometry

The fractional uncertainty given by equation (1) has been evaluated for detectors A and G as a function of the activity ratio, *R*, of uranium to radium in the sample. Two sample volumes, 2 L and 10 L, were considered. In each case a counting time of 12 hours was used (to enable results to be available within 24 hours of sampling) and a radium concentration of 1 Bq/L has been assumed, this value being typical of waters in RP2. The results are presented in figure 2. For a 10 L sample the statistical uncertainty is always less than 15% even for uranium to radium ratios as high as 40:1 and the difference in the precision obtained with the two detectors is not large. For a 2 L sample, however, the difference between detectors is more pronounced and, even with detector G, a precision of better than 30% can only be achieved for uranium to radium ratios of less than 30:1.

Taking the limit of acceptance as an uncertainty of about 30% (as discussed in the introduction), useful data could be obtained with respect to statistical precision using this technique with a 2 L sample for the waters typically contained in RP2, RP3 and the tailings dam at Ranger. However, it is no more difficult to collect and process a 10 L sample than a 2 L sample. It is therefore recommended that a minimum sample volume of 10 L is used; this would ensure a statistical uncertainty of less than 5% and the precision obtained would be virtually independent of detector background. For RP4 water, however, in which a radium concentration of 0.25 Bq/L is more typical, a 20 L sample would be more appropriate.

The statistical uncertainty has also been evaluated (fig 3) as a function of the ^{226}Ra concentration in those cases where the uranium-radium ratio is approximately 1:1. The useful detection limit is about 0.1 Bq/L using detector G and a 10 L sample but rises to about 0.6 Bq/L using detector A and a 2 L sample.

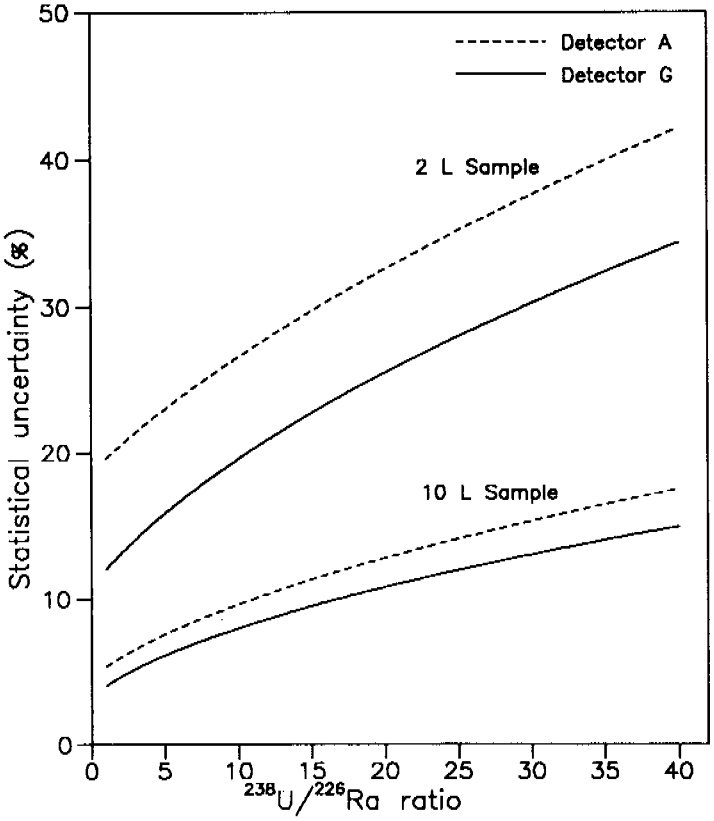

Figure 2 Statistical uncertainties in the measurement of ^{226}Ra concentrations using the 186 keV line with precipitated water samples. Results are shown as a function of the ^{238}U/^{226}Ra ratio for a ^{226}Ra concentration of 1 Bq/L.

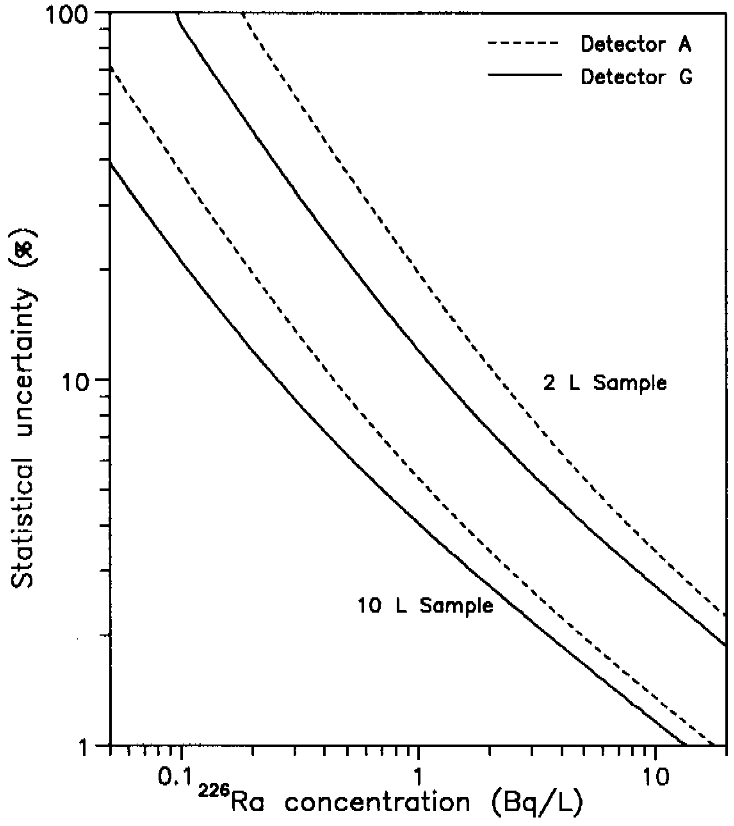

Figure 3 Statistical uncertainties as a function of ^{226}Ra concentration using the 186 keV line with precipitated water samples. Results shown are for a ^{238}U/^{226}Ra ratio of 1:1.

2.2.2 Systematic errors

In the current procedure, a systematic error enters due to errors in the predicted contribution of U to the 186 keV line (for example, errors in calibration standards used or interferences in the uranium measurement process). In the notation of the previous section the number of counts attributable to radium in the 186 keV line is given by:

$$n_r = n_t - n_u - n_b - n_c$$

Hence an error, Δn_u, in the uranium count due to the use of the incorrect value of the uranium concentration gives rise to a corresponding error in the radium count of:

$$\Delta n_r = -\Delta n_u$$

Hence the fractional error in the radium concentration (expressed as a fraction of the *measured* value) is:

$$\varepsilon_r = \left[\frac{\Delta n_u}{(n_r - \Delta n_u)}\right] = \frac{k_u f R}{(k_r - k_u f R)} \qquad (2)$$

where R is the uranium-radium ratio, f is the fractional error in the uranium measurement and k_r and k_u are the calibration constants listed in table 1.

The fractional systematic error has been evaluated as a function of the uranium-radium ratio for two assumed values of the accuracy of the uranium measurement. The results are presented in figure 4. These data show that, even with a uranium accuracy of 5%, a useful measurement of the radium concentration (uncertainty < 30%) can only be obtained if the uranium-radium ratio is less than about 6:1; for a uranium accuracy of 10%, the maximum useful ratio is 3:1. In practical terms this implies that the method is no longer applicable for RP4 and RP2 waters at Ranger but can be used for waters in the tailings dam. At the time at which this work was carried out, the method was applicable for RP3 water, but in general this would not be the case.

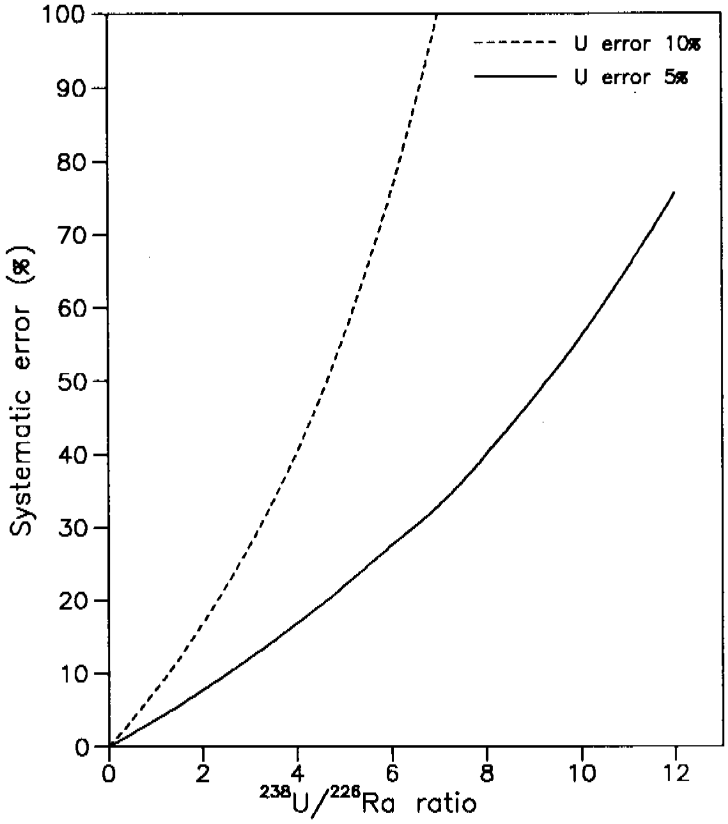

Figure 4 Systematic error in the measurement of ^{226}Ra concentrations using the 186 keV line resulting from uncertainty in the ^{238}U concentration

2.2.3 Application to waters at the Ranger mine

Samples of water were collected from RP2, RP3 and the tailings dam and analysed by a number of techniques at ***eriss*** including that outlined above. Uranium concentrations were measured at the Ranger Environmental Laboratory using laser-induced fluorimetry (Scintrex UA-3 fluorimeter) by the method of standard additions. The sample volumes and uranium concentrations are listed in table 2.

The radium concentrations and statistical uncertainties obtained using the 186 keV line are given in table 2. For the RP3 and tailings dam samples the derived values of the uranium-radium ratio are 0.8 and 0.3 respectively. From the results shown in figure 4 it can be concluded that the maximum error in these results due to uncertainty in the uranium concentration is about 10%. Hence the results obtained for the radium concentration are valid. The statistical uncertainties are about 7% in both cases..

Table 2 Results obtained for ^{226}Ra concentration in mine waters using the 186 keV line analysis technique on precipitated samples. ^{226}Ra uncertainty is one standard deviation due to counting statistics only.

Sample	Volume (L)	Uranium (μg/L)	^{238}U (Bq/L)	^{226}Ra (Bq/L)	^{238}U/^{226}Ra	Validity
RP2	7.1	1100^{a}	13.8	0.28 ± 0.14	50	No
		1000^{b}	12.5	1.17 ± 0.14	11	
RP3	2.2	210^{a}	2.63	3.2 ± 0.2	0.8	Yes
TD	0.7	420^{c}	5.25	18.5 ± 1.4	0.3	Yes

a Measured by laser-induced fluorimetry

b Assumed value to demonstrate the effect of a 10% error in the uranium concentration

c Estimated value deduced from the three most recent measurements

For RP2 water, however, the derived value of the uranium-radium ratio is about 50:1. Even if a maximum uncertainty of 5% is attributed to the uranium concentration, the analysis procedure for radium must be considered invalid. To illustrate the effect of an error in the uranium concentration, the second entry for RP2 in table 2 uses a uranium concentration that is lower than the measured value by 10%. The resulting radium concentration is higher by a factor of four even though the absolute value of the statistical uncertainty remains unchanged.

2.3 Analysis using the 186 keV line: Untreated samples

The high penetrability of γ-rays in matter allows the use of samples of much larger physical dimensions than those of the standard disk used in routine γ-ray spectrometry. It is, therefore, possible to dispense with the sample treatment phase of the analysis procedure and to use an untreated water sample placed directly on the head of the germanium detector. Two convenient containers for the water are a cylindrical vial (sample volume ~200 mL) and a 1000 mL Marinelli cup; the latter has a re-entrant geometry that maximises the solid angle subtended by the sample at the detector.

Such a procedure has several disadvantages associated with it:

- reduction in sensitivity due to the fixed value of the usable sample volume at either 200 mL or 1000 mL compared with a reasonably practicable upper limit of about 500 L for the precipitation technique;
- reduction in sensitivity due to the decrease in effective solid angle of the sample compared with that of the standard disk; and
- increased sensitivity to detector and room background due to the reduced count rate caused by the previous two effects.

Nevertheless, the method may be applicable in some cases where the specific activity of ^{226}Ra in the water is high and where elimination of sample processing is desirable.

The sensitivity of this technique to uncertainties in the uranium concentration in the water is the same as that described in section 2.2.2. Hence the method is only applicable when the uranium-radium ratio is expected to be low. For this reason the analysis presented in this section has been carried out under the assumption that uranium and radium are present in approximately equal concentrations. Statistical uncertainties only are considered.

2.3.1 Statistical uncertainties: 200 mL vial

The expression for the fractional statistical uncertainty in the measured radium concentration is that given as equation (1) in section 2.2.1. However, because of the reduced effective solid angle the calibration constants k_r and k_u are lower than the corresponding values for the standard disk. Variation of these constants is small between detectors and the values used in making uncertainty estimates are those of detector A ($k_r = 0.93$, $k_u = 0.67$ cts/Bq/ksec).

The fractional uncertainty has been calculated as a function of the ^{226}Ra concentration assuming that the uranium and radium concentrations are equal. A counting interval of 24 hours has been assumed since this would provide a direct comparison with results of section 2.2, that is a result 1 day after collection of the sample. The background and continuum counting rates were those listed in table 1.

The dependence of the fractional uncertainty on the ^{226}Ra concentration is shown in figure 5 for detectors A and G. From these data it can be concluded that useful data ($\varepsilon_r < 30\%$) can only be obtained for values of the radium concentration in excess of about 7 Bq/L for detector G and about 11 Bq/L for detector A. In the case of waters at Ranger, this restricts applicability of the technique to tailings dam water.

2.3.2 Statistical uncertainties: 1000 mL Marinelli cup

The absolute detection efficiency for a 1000 mL Marinelli cup at 186 keV is lower than that obtained using a standard disk by about a factor of four (Murray et al 1987): $k_r = 0.58$ and $k_u = 0.42$ cts/Bq/ksec. These calibration constants are lower than the corresponding values for the 200 mL vial by about 30% but this reduction is offset by the increase in sample activity by a factor of five due to the increased sample volume.

The statistical fractional uncertainty for the Marinelli cup has been calculated as a function of the radium concentration assuming, as in the previous section, equal radium and uranium concentrations and a counting interval of 24 hours. The results obtained for detectors A and G are shown in figure 5. The lower limit of detection is about 2 Bq/L for detector G and about 3 Bq/L for detector A. Thus direct measurement of the radium concentration without sample processing is possible using a Marinelli cup for the waters of RP3 and the tailings dam but the technique is not applicable to RP2 and RP4 waters.

2.3.3 Application to waters at the Ranger mine

The water sample collected from the tailings dam at Ranger was analysed by direct measurement of a 200 mL untreated sample using detector H (table 1). Detector G could not be used because it was under repair at the time. The uranium concentration used to subtract the ^{235}U contribution from the 186 keV line was that listed in table 2. The result obtained for the ^{226}Ra concentration was 16 ± 4 Bq/L, in good agreement with that obtained from analysis of the sample prepared by manganese dioxide and ferric hydroxide precipitation, namely 18.5 ± 1.4 Bq/L. The fractional uncertainty in the radium concentration, 25%, is in good agreement with that expected on the basis of the calculations shown in figure 5.

2.4 Analysis using radon ingrowth: Double count

2.4.1 Measurement of ^{226}Ra concentration by radon ingrowth

The results presented in previous sections have shown that the technique for the rapid analysis of ^{226}Ra using the γ-ray line at 186 keV is of limited applicability. Valid results are only obtained for low values of the ratio of uranium to radium in the sample; ie less than about 3:1 when the uranium concentration is known to an accuracy of better than 10%. An alternative method is, therefore, required for waters that do not satisfy this condition. In particular the technique is not applicable to RP4 and RP2 waters at Ranger.

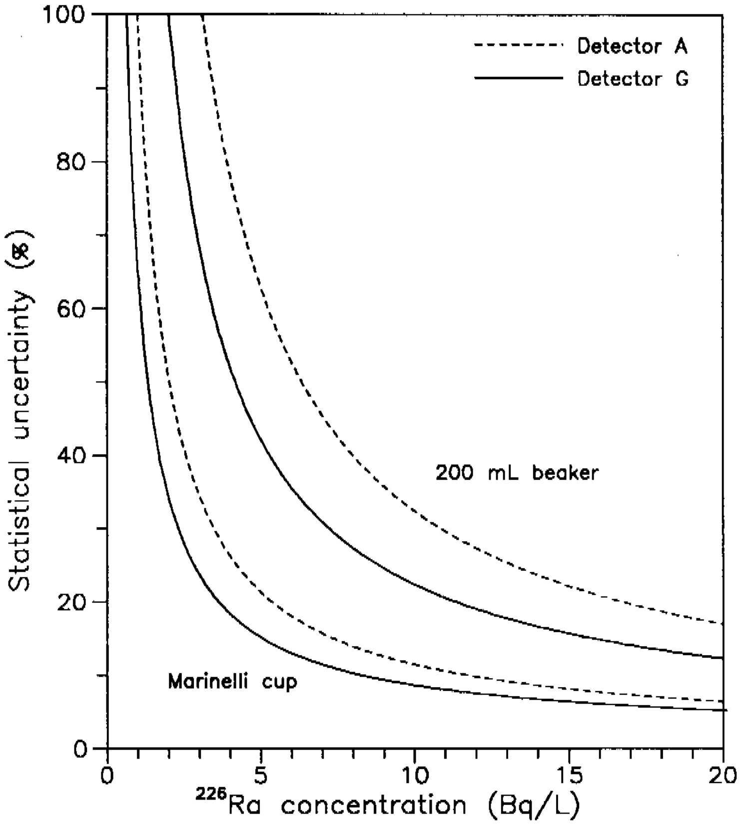

Figure 5 Statistical uncertainties as a function of ^{226}Ra concentration using the 186 keV line with untreated water samples. Results shown are for a ^{238}U/^{226}Ra ratio of 1:1.

The use of the γ-ray lines arising from the decay of ^{222}Rn progeny does not necessarily require delaying analysis until secular equilibrium is achieved between ^{222}Rn and ^{226}Ra. The time dependence of radon ingrowth after casting of the sample is known; it depends only on the half-life of ^{222}Rn, 3.824 days. There are, however, two unknowns: the activity of the parent nuclide, ^{226}Ra, and the initial radon activity in the sample at the time of casting. Two separate measurements are therefore required to obtain an analysis of the ^{226}Ra concentration using the radon progeny lines if counting is carried out before secular equilibrium is achieved. In this section the precision that can be obtained within 2 days of sample collection is investigated. Clearly this precision will not be as good as would be obtained after the full ingrowth period but it may be quite adequate for samples of high specific activity such as those collected from mine site retention ponds.

There are three prominent radon progeny lines that may be used in such an analysis; their energies are 295 keV (^{214}Pb), 352 keV (^{214}Pb) and 609 keV (^{214}Bi). For each of these lines the number of counts recorded, n, between time t_1 and t_2 (each referred to zero at casting time) is given by:

$$n = k\int_{t_1}^{t_2} A(t)\,dt \tag{3}$$

where k is the detector calibration constant for the appropriate line (in counts/Bq/ksec) and $A(t)$ is the radon progeny activity (in Bq) of the sample at time t. Solutions for $A(t)$ for the two progeny of interest, ^{214}Pb ($t_{1/2}$ = 26.8 minutes) and ^{214}Bi ($t_{1/2}$ = 19.7 minutes) may be obtained via the equations of Bateman (1910). In general, the difference between the activity of ^{222}Rn and those of its progeny will be small (eg approximately 2% and 4% respectively at

t = 24 hours if the initial ^{222}Rn activity is zero). For the purposes of the error analysis to follow, this difference is negligible and for simplicity we will consider $A(t)$ to denote the activity of ^{222}Rn. If the activity of the parent ^{226}Ra and the initial radon activity in the sample are denoted A_p and A_0 respectively, $A(t)$ is given by:

$$A(t) = A_0 e^{-\lambda t} + A_p\left(1 - e^{-\lambda t}\right)$$

where λ is the radon radioactive decay probability. Integration of equation (3) yields:

$$n = k\left(t_2 - t_1\right) A_p \left[1 - (1-r) f(t_1, t_2)\right] \tag{4}$$

where the function $f(t_1, t_2)$ is given by:

$$f(t_1, t_2) = \frac{\left(e^{-\lambda t_1} - e^{-\lambda t_2}\right)}{\lambda\left(t_2 - t_1\right)} \tag{5}$$

and $r = A_0 / A_p$ is the initial radon retention coefficient of the sample. The average radon activity in the sample during the counting period is:

$$\begin{aligned} A &= n / k\left(t_2 - t_1\right) \\ &= A_p\left[1 - (1-r) f(t_1, t_2)\right] \end{aligned} \tag{6}$$

Consider two counting intervals a and b, from t_1 to t_2 and from t_3 to t_4 respectively. Then the measured radon activities in these intervals are:

$$\begin{aligned} A_a &= A_p\left[1 - (1-r) f(t_1, t_2)\right] \\ A_b &= A_p\left[1 - (1-r) f(t_3, t_4)\right] \end{aligned}$$

The parent ^{226}Ra activity is therefore given in terms of A_a and A_b by:

$$A_p = \frac{\left[A_b f(t_1, t_2) - A_a f(t_3, t_4)\right]}{\left[f(t_1, t_2) - f(t_3, t_4)\right]} \tag{7}$$

and the radon retention coefficient is obtained from:

$$r = 1 - \frac{\left(A_a - A_b\right)}{\left[A_a f(t_3, t_4) - A_b f(t_1, t_2)\right]} \tag{8}$$

2.4.2 Statistical uncertainties

During the first counting interval the total number of counts recorded in each of the radon progeny lines is given by

$$n_t = n_a + \left(r_b + r_c\right)\left(t_2 - t_1\right)$$

where n_a is given by equation (4), r_b is the background count rate for that line and r_c is the corresponding continuum count rate. Hence the fractional statistical uncertainty in n_a is

$$\varepsilon_a = (\delta n_a / n_a)$$

$$\approx \frac{\left[n_a + (r_b + 3r_c / 2)(t_2 - t_1)\right]^{1/2}}{n_a} \qquad (9)$$

Similarly, the fractional uncertainty for the second counting period is:

$$\varepsilon_b \approx \frac{\left[n_b + (r_b + 3r_c / 2)(t_4 - t_3)\right]^{1/2}}{n_b} \qquad (10)$$

Hence the absolute uncertainties in the measured activities during the two counting periods are:

$$\delta A_a = \varepsilon_a \; A_a$$

$$\delta A_b = \varepsilon_b \; A_b$$

where A_a and A_b are the measured average radon activities. Equation (7) may be re-written as:

$$A_p = K_b \, A_b - K_a \, A_a$$

where

$$K_a = \frac{f(t_3, t_4)}{\left[f(t_1, t_2) - f(t_3, t_4)\right]}$$

$$K_b = \frac{f(t_1, t_2)}{\left[f(t_1, t_2) - f(t_3, t_4)\right]}$$

Then the absolute uncertainty in the derived activity of ^{226}Ra is given by:

$$(\delta A_p)^2 = (K_a \, \delta A_a)^2 + (K_b \, \delta A_b)^2$$

$$= (K_a \, \varepsilon_a \, A_a)^2 + (K_b \, \varepsilon_b \, A_b)^2$$

Finally, the fractional statistical uncertainty in A_p is:

$$\varepsilon_p = (\delta A_p / A_p)$$

The above derivation has been used to estimate the statistical precision obtained in a measurement of ^{226}Ra concentration using two separate measurements of the ^{222}Rn concentration in the cast sample. If a water sample is collected early in the day, around 0900, sample processing (including ashing and casting) can be completed by about 1600 on the same day. Since counting can begin at this time it is appropriate to consider a 12 hour interval for the first count immediately after casting and a second 12 hour counting interval beginning 24 hours after casting. This procedure provides an analysis 48 hours after sample collection.

The calibration constants, background count rates and continuum count rates for each of the radon progeny lines are given in table 3 for four intrinsic germanium detectors used at ***eriss***. As before, results are presented for detectors A and G. In all cases a sample volume of 10 L has been assumed to give direct comparability of the results obtained with those given for the 186 keV line using the sample volume recommended for use with that technique.

Table 3 Calibration constants, background count rates and continuum count rates for radon progeny lines using four detectors at ***eriss***

Energy (keV)	Variable	Detector			
		A	D	G	H
295	k (cts/Bq/ksec)	7.73	6.99	9.39	7.45
	r_h (cts/ksec)	0.96	0.75	0.86	1.44
	r_c (cts/ksec)	9.91	5.29	4.45	7.43
352	k (cts/Bq/ksec)	12.79	11.23	15.33	12.33
	r_h (cts/ksec)	1.58	1.20	1.55	2.33
	r_c (cts/ksec)	8.12	4.09	3.56	6.13
609	k (cts/Bq/ksec)	8.14	6.68	9.67	8.09
	r_h (cts/ksec)	1.09	0.92	1.04	1.92
	r_c (cts/ksec)	5.29	2.12	1.95	3.49

The results obtained for the variation in the percentage statistical uncertainty as a function of the ^{226}Ra concentration using detector G are presented in figure 6. Since a high value of the initial radon activity gives rise to larger statistical uncertainties in the measurement of the parent activity, uncertainty estimates are shown for two values of the radon retention coefficient, $r = 0.0$ and $r = 0.9$. Also shown for comparison are the percentage uncertainties that would be obtained if the full ingrowth period of 23 days were allowed before analysis. In the latter case a 24 hour counting period has been assumed since this would be normal practice.

As will be shown in the next section, radon retention coefficients for the sample preparation techniques used here are quite low, less than 10%. The solid curve in figure 6 is, therefore, the appropriate estimate of statistical uncertainties expected from the use of two separate measurements of radon ingrowth to determine the concentration of ^{226}Ra. Useful results for regulatory purposes are obtained for all concentrations in excess of 0.05 Bq/L. Although this detection limit is approximately one order of magnitude higher than that obtained using the normal analysis procedure with a 10 L sample, it is nevertheless quite adequate for all waters in RP2, RP3, RP4 and the tailings dam at Ranger. Even if the initial radon retention coefficient is as high as 90% the effective detection limit for this technique is about 0.08Bq/L.

The corresponding estimates of uncertainty using detector A are shown in figure 7. This detector has a poorer background performance and a lower sensitivity than detector G. The detection limit for application of this technique is about 0.1 Bq/L, a value that is still adequate for all of the waters on the Ranger site.

An additional advantage of this technique is that, having determined the ^{226}Ra concentration with quite high precision using the radon progeny lines, the uranium concentration can be measured by subtraction of the ^{226}Ra contribution to the 186 keV line. This is particularly the case when the uranium-radium concentration ratio is high, for example in RP2 water.

2.4.3 Application to waters at the Ranger mine

The water samples collected from RP2, RP3, and the tailings dam at Ranger were each analysed using the radon ingrowth method by counting the cast disks twice within a few days of sample collection. Because of the demands on detectors at that time (in particular, their use for other analyses as part of this project) the precise time scale outlined in the previous section was not followed. Nevertheless, the data obtained confirm the applicability of the technique and the uncertainty estimates made in section 2.4.2.

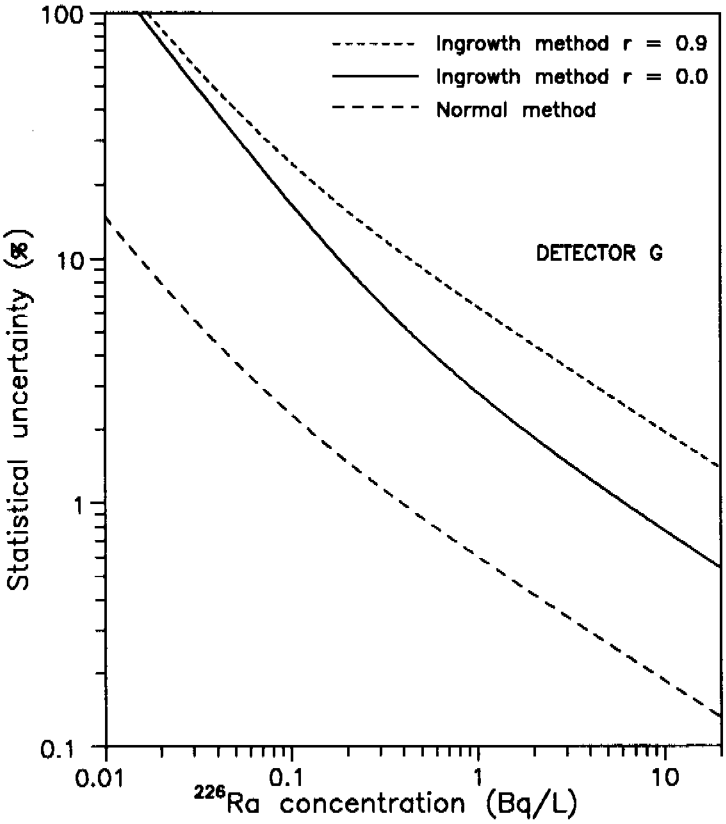

Figure 6 Statistical uncertainties in the measurement of ^{226}Ra concentrations using the radon ingrowth method and two counting periods. Results are for ***eriss*** detector G and a sample volume of 10 L.

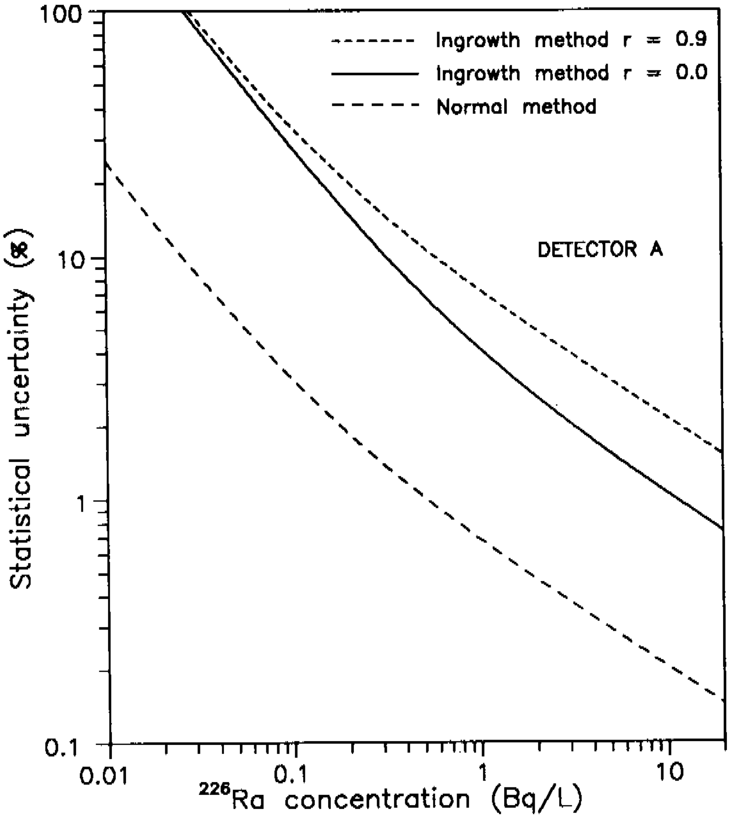

Figure 7 Statistical uncertainties in the measurement of ^{226}Ra concentrations using the radon ingrowth method and two counting periods. Results are for ***eriss*** detector A and a sample volume of 10 L.

The sample volumes used are given in table 4 together with the start and completion time of each counting interval relative to the time of casting. Also listed are the measured average radon concentrations for the first and second counting periods and their associated statistical uncertainties. The concentration of ^{226}Ra was calculated using equation (7) and the radon retention coefficient was obtained using equation (8). The results (given in table 4) were 1.18 ± 0.04 Bq/L, 3.57 ± 0.12 Bq/L and 16.0 ± 0.4 Bq/L for RP2, RP3 and the tailings dam respectively. Thus the precision obtained by this method is excellent for the waters in the storage ponds at Ranger and the observed value of the statistical uncertainties are in good agreement with the estimates obtained using the method outlined in section 2.4.2. The latter estimates are 0.035 Bq/L, 0.11 Bq/L and 0.40 Bq/L for RP2, RP3 and tailings dam samples respectively using the actual sample volumes and counting times rather than those relevant for figures 6 and 7.

The value of the radon retention coefficient (that is, the ratio of the initial radon activity to that of radium) for each sample is also given (in %) in table 4. The low values obtained (all less than 10%) are not unexpected because of the nature of the sample treatment process. Since radon is an inert gas ^{222}Rn atoms are not removed by the precipitation process; in addition, radon is expected to be effectively removed from the water by bubbling. Radon build-up can commence once the precipitate is formed but the precipitate itself is a fine powder that is spread out over the filter paper during the ashing process. Radon loss is, therefore, expected to be high until casting of the precipitate occurs.

Table 4 Results for ^{226}Ra concentrations (Bq/L) in waters from the Ranger mine site using the radon ingrowth method. Times are relative to the time of casting. Uncertainties are one standard deviation due to counting statistics only.

Variable	RP2	RP3	TD
Sample volume (L)	7.07	2.24	0.70
First count start (h)	25.8	30.4	25.2
First count stop (h)	46.3	46.4	30.2
Second count start (h)	74.0	74.0	74.0
Second count stop (h)	91.8	91.8	91.8
First radon concentration (Bq/L)	0.279 ± 0.007	1.020 ± 0.025	3.77 ± 0.14
Second radon concentration (Bq/L)	0.551 ± 0.010	1.750 ± 0.030	7.93 ± 0.10
Double count method			
^{226}Ra concentration (Bq/L)	1.19 ± 0.04	3.58 ± 0.12	16.0 ± 0.4
Radon retention coefficient (%)	-0.4 ± 1.5	4.5 ± 2.0	5.8 ± 1.7
Single count method			
^{226}Ra concentration (Bq/L)	1.17 ± 0.03	4.06 ± 0.10	20.0 ± 0.7

2.5 Analysis using radon ingrowth: Single count

The analysis procedure using radon ingrowth has considerable advantages over that using the 186 keV line; the method yields results with superior statistical precision and which are free of large systematic errors. However, using this procedure analytical results become available about 48 hours after sample collection compared with 24 hours in the method using the 186 keV line.

Results presented in the previous section showed that, for the three samples processed, the initial radon activity was low, of the order of 5% or less. If low radon retention were shown to be a consistent property of the sample preparation technique it is possible that radon ingrowth using only one count of the cast precipitate may be a viable method of measuring ^{226}Ra concentrations in water.

In this section, therefore, estimates are made of the systematic and statistical errors associated with the use of a single count of the radon progeny lines to measure ^{226}Ra activity. The most significant feature of this method is that the systematic error due to initial radon retention in the sample always results in an overestimate of the ^{226}Ra concentration. From a regulatory point of view, therefore, application of the technique may be considered adequate, at least in the first instance, since if the measured concentration meets a required standard the actual concentration must also do so.

2.5.1 Systematic errors

If a single count of the radon activity in the cast sample is carried out between times t_1 and t_2 after casting, the observed radon activity is given by equation (6), that is:

$$A = A_p\left[1 - (1 - r)f(t_1, t_2)\right]$$

where A_p is the ^{226}Ra activity in the sample, r is the radon retention coefficient and the function $f(t_1, t_2)$ is given by equation (5).

If, therefore, the initial radon activity in the cast sample is neglected, the calculated ^{226}Ra activity, A_p', is given by:

$$\begin{aligned} A_p' &= \frac{A}{\left[1 - f(t_1, t_2)\right]} \\ &= \frac{A_p\left[1 - (1 - r)f(t_1, t_2)\right]}{\left[1 - f(t_1, t_2)\right]} \end{aligned}$$

The difference between the measured activity and the true activity is therefore:

$$A_p' - A_p = \frac{A_p r f(t_1, t_2)}{\left[1 - f(t_1, t_2)\right]}$$

and the fractional systematic error, ε_p, is:

$$\varepsilon_p = \frac{r f(t_1, t_2)}{\left[1 - f(t_1, t_2)\right]}$$

If a fixed counting period, T, is chosen the variation of the systematic error with the starting time, t, of the analysis is given by:

$$\varepsilon_p(t) = \frac{r e^{-\lambda t} g(T)}{\left[1 - e^{-\lambda t} g(T)\right]}$$

where the function $g(T)$ is given by:

$$g(T) = \frac{\left(1 - e^{-\lambda T}\right)}{\lambda T}$$

Calculations of the magnitude of the systematic overestimate of the ^{226}Ra concentration have been carried out for three values of the counting interval: 2 hours, 6 hours and 12 hours. The results have been expressed as a ratio with respect to the initial radon retention coefficient and are shown in figure 8 as a function of the starting time of the analysis period after casting of the sample. Since the objective of using the single count method would be to provide an analysis at an earlier time than the double count approach would provide, the latest completion time for analysis that should be considered is 24 hours after casting of the sample. This would provide an analytical result on the day after sample collection. The arrows on each curve of figure 8 indicate the value of ε_p/r for each counting time for completion of analysis within 24 hours.

These results show that if the initial radon activity is 5% of the parent activity or less, the overestimate of the ^{226}Ra concentration would be less than 30% for both the 2 hour and the 6 hour counting periods. For the 12 hour period the overestimate would be about 35%. These values would be considered satisfactory in most regulatory situations provided that the corresponding statistical uncertainty is low. Further work would be needed, however, to provide systematic information on the range of radon retention coefficients that occur using the current sample preparation procedure.

2.5.2 Statistical uncertainties

Estimates of the statistical uncertainties that would arise in the use of the single count method have been made using equations (4) and (9) of section 2.4. The calibration constants, background count rates and continuum count rates used were these given in table 3. A 10 L water sample was considered. The results obtained for detectors A and G are shown in figures 9 and 10 respectively as a function of the ^{226}Ra concentration in the water sample.

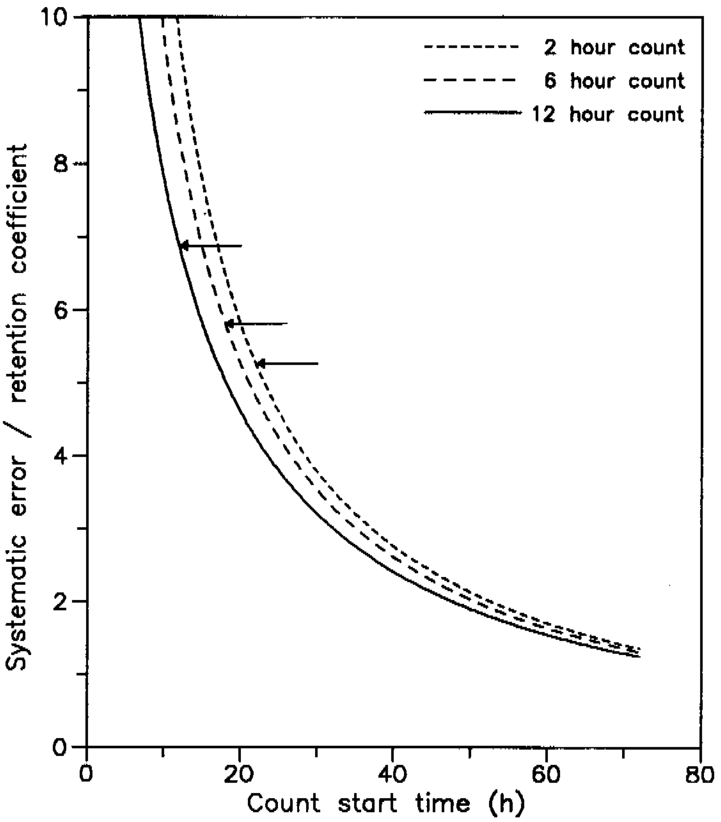

Figure 8 Systematic errors in the measurement of ^{226}Ra concentrations using the radon ingrowth method and a single counting period. Results are expressed as ratios to the initial radon retention coefficient. Arrows indicate results for completion 24 hours after casting.

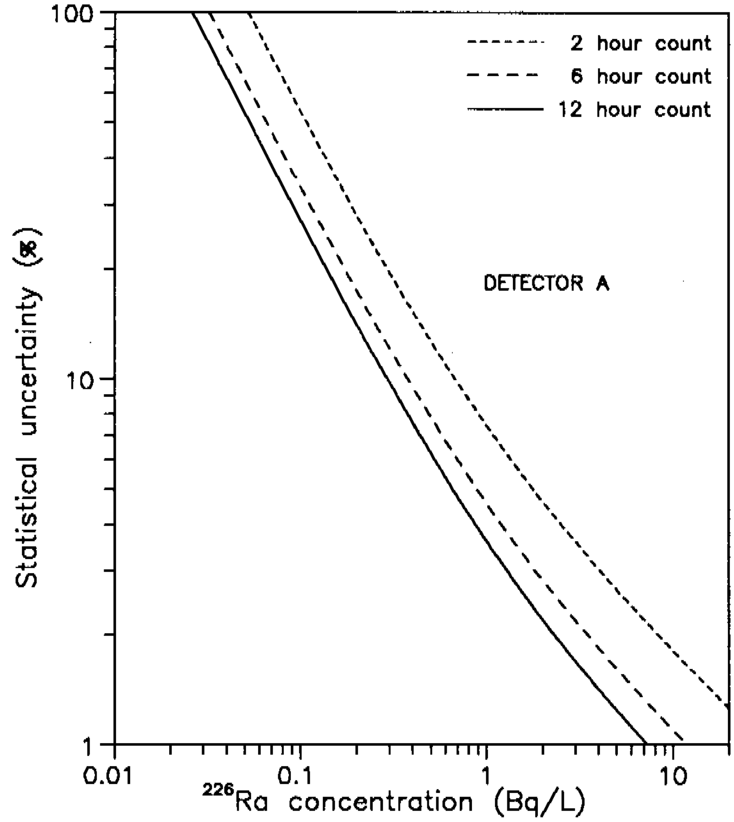

Figure 9 Statistical uncertainties in the measurement of ^{226}Ra concentrations using the radon ingrowth method and a single counting period. Results are for ***eriss*** detector A and a sample volume of 10 L. Each counting period terminates 24 hours after casting.

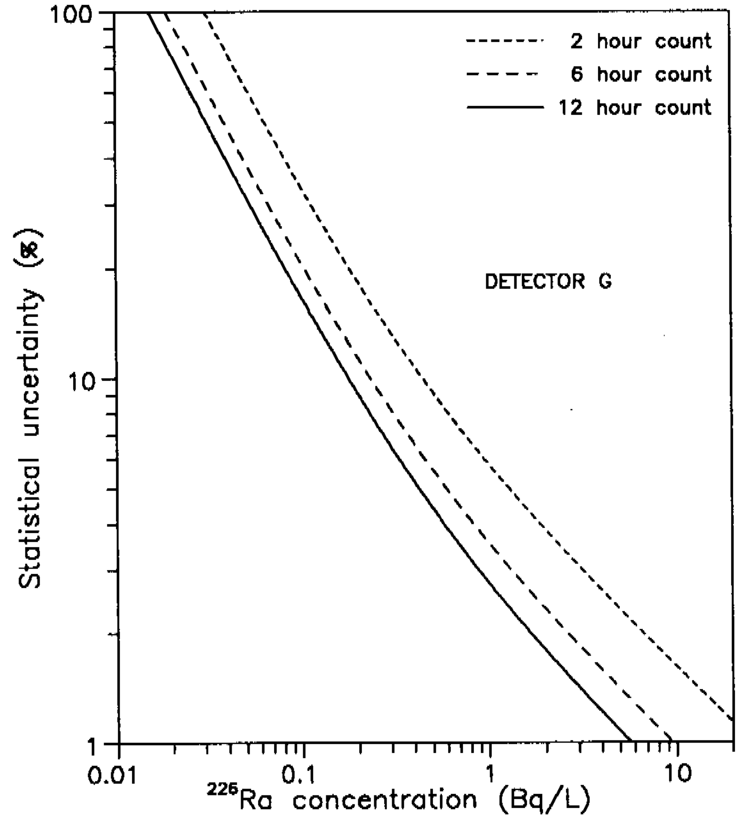

Figure 10 Statistical uncertainties in the measurement of ^{226}Ra concentrations using the radon ingrowth method and a single counting period. Results are for ***eriss*** detector G and a sample volume of 10 L. Each counting period terminates 24 hours after casting.

The detection limits obtained ($\varepsilon_p \sim 30\%$) using a 6 hour counting interval are about 0.1 Bq/L for detector A and about 0.06 Bq/L for detector G. These are quite adequate for measurement of the concentrations of ^{226}Ra in RP2, RP3 and tailings dam water at Ranger, but for RP4 water use of detector G would be preferred. For typical RP2 water (concentration about 1 Bq/L) the statistical uncertainty expected is 4% for detector G and 5% for detector A. Thus the systematic uncertainty would be expected to dominate. Even with the shorter 2 hour counting period, which yields a lower systematic error, the RP2 water concentration would be obtained with statistical uncertainties of 8% and 6% for detectors A and G respectively.

2.5.3 Application to waters at the Ranger mine

The data given in table 4 were used to estimate the concentration of ^{226}Ra in the samples of water collected from RP2, RP3 and the tailings dam using equation (11). The results obtained were 1.19 ± 0.03 Bq/L, 4.09 ± 0.10 Bq/L and 20.4 ± 0.8 Bq/L for RP2, RP3 and the tailings dam respectively. The overestimates of the ^{226}Ra concentration deduced from the values measured from the double count method were 0.0%, 15% and 27% respectively. These values agree with the values calculated using the expressions given in section 2.5.1 and the radon retention coefficients listed in table 4.

3 Conclusions

Techniques have been developed for the analysis of ^{226}Ra in mine waters by γ-ray spectrometry within 1 to 3 days of receipt of the sample. These techniques involve:

1 Analysis using the 186 keV line: Precipitation method

This method requires an independent measurement of the uranium concentration of the sample. Systematic errors in the ^{226}Ra measurement will be small provided that the ratio of uranium to radium in the sample is not too large. For an error of 5% in the uranium contribution, the resulting error in the ^{226}Ra determination will be less than 30% if the ^{238}U/^{226}Ra ratio is less than about 6:1. For a uranium contribution error of 10%, the corresponding ^{238}U/^{226}Ra ratio is 3:1. For samples with a ^{238}U/^{226}Ra ratio of 1:1 or less, counting statistic uncertainties result in a detection limit for ^{226}Ra of about 0.1 Bq/L for a 10 L sample using a 12 hour counting period.

2 Analysis using the 186 keV line: Untreated samples

This method allows for determinations to be carried out without the necessity of precipitation and casting procedures, with the disadvantage of a reduction in sensitivity. For a 200 mL vial geometry, useful data (uncertainty <30%) can be obtained for ^{226}Ra activity concentrations of about 7 Bq/L or above (for detectors with similar background count rates to ***eriss*** detector G). For a 1000 mL Marinelli cup geometry, the sensitivity is improved to about 2 Bq/L. Restrictions on this method for samples with a high 238U/226Ra ratio are similar to those for method (1).

3 Analysis using ^{222}Rn ingrowth

Methods utilising radon progeny are free from uranium interference and hence are applicable to samples with a high uranium/radium ratio. A complication appears due to the possibility that some radon may be present in the sample at the time of casting. This problem may be approached in two ways:

(a) Analysis utilising two counting periods

This method eliminates errors due to any initial radon retention. The uncertainty in the result is essentially due to calibration errors and counting statistic errors. Where the two counts are completed within 2 days of casting, the detection limit is about 0.05 Bq/L for a sample volume of 10 L.

(b) Analysis utilising a single counting period

This method has the advantage that results may be obtained within 24 hours of receipt of the sample. The detection limit for a 10 L water sample and a 6 hour counting interval is about 0.06 Bq/L. A systematic error which leads to an over-estimate of the radium concentration must be accepted with this method. This over-estimate is due to the ^{222}Rn which remains in the precipitate after ashing. If the initial ^{222}Rn activity is 5% of the parent activity or less, the resulting over-estimate in the ^{226}Ra concentration will be less than 30% for a 6 hour counting period.

Table 5 summarises the results obtained for water samples collected from RP2, RP3 and the tailings dam at Ranger and analysed at ***eriss*** within a few days by a number of the techniques outlined above. Results are also given for analysis of these samples by the normal γ-ray spectrometry method and by α-particle spectrometry using ^{225}Ra as a tracer. All of the results using the rapid analysis techniques agree with the best estimates from the normal methods or, in the case of RP3 and tailings dam waters analysed using the single count radon ingrowth method, are over-estimated by an amount consistent with the expected systematic error.

Figure 11 is a decision flow-chart showing the ^{226}Ra analysis methods which are feasible for any situation. In summary, if an analysis is required in less than 23 days, then the standard method cannot be used. If then a ^{238}U analysis is available (eg by laser-induced fluorimetry) and the ^{238}U/^{226}Ra ratio in the water is known to be less than a certain value (3:1 if the ^{238}U value is known to better than 10%) then one of the 186 keV methods can be used. Otherwise, ^{222}Rn ingrowth methods (single or double count) are required.

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Table 5 Summary of results obtained for ^{226}Ra (Bq/L) in Ranger mine site waters by various techniques. Uncertainties are one standard deviation due to counting statistics only.

Method	RP2	RP3	TD
γ-ray *spectrometry*			
186 keV line: precipitation method	n.a.	3.2 ± 0.2	18.5 ± 1.4
186 keV line: 200 mL untreated sample	n.a.	n.a.	16 ± 4
Radon ingrowth: single count	1.17 ± 0.03	4.06 ± 0.10	20.0 ± 0.7
Radon ingrowth: double count	1.19 ± 0.04	3.58 ± 0.12	16.0 ± 0.4
Normal method	1.09 ± 0.01	3.41 ± 0.04	17.1 ± 0.2
α-particle spectrometry			
^{225}Ra tracer	1.14 ± 0.04	3.25 ± 0.14	16.9 ± 0.4

n.a. method not applicable

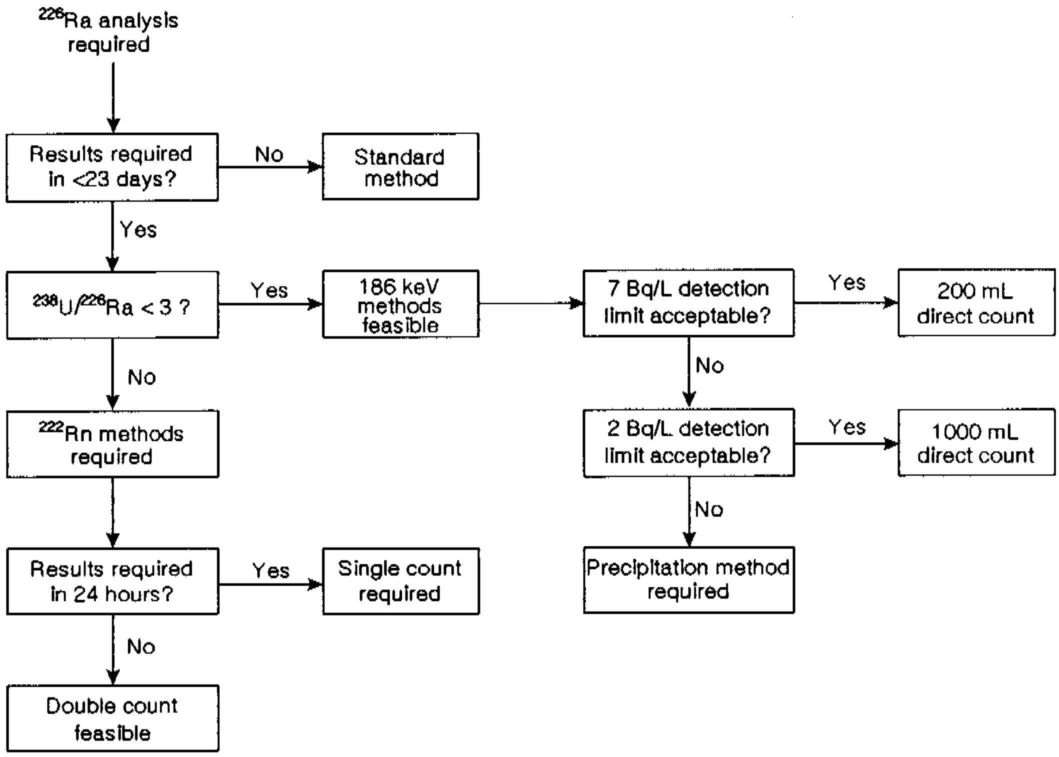

Figure 11 A decision flow-chart showing possible choices of analysis methods. Detection limits given for 186 keV methods are based on a 30% uncertainty in the ^{226}Ra determination, a 10% uncertainty in the ^{238}U analysis, and similar background count rates to ***eriss*** detector G.