



Australian Radiation Laboratory

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Radium (^{226}Ra) in Environmental Samples
by the use of Liquid Scintillation Counting

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ABSTRACT

A method is described for the determination of ^{226}Ra in environmental samples utilizing a liquid scintillation counting technique. The procedure involves the isolation of ^{226}Ra from the sample matrix and the extraction of ^{222}Rn into a toluene-based scintillant mixture after a suitable ingrowth period. Results of ^{226}Ra analysis of water samples indicate that the method is applicable to samples having a wide variation in ^{226}Ra concentrations and chemical composition. The detection limit was estimated to be less than 0.005 Bq (0.15 pCi) depending upon the counting system used and counting time.

INTRODUCTION

The advantages of the use of liquid scintillation counting for the measurement of ^{226}Ra activity have been recognized by a number of authors in recent studies¹⁻⁶. In general, the techniques that have been adopted rely on the high solubility of the short-lived daughter of ^{226}Ra , gaseous ^{222}Rn (half-life 3.8 days), in non-polar organic solvents such as toluene or xylene^{3,7}. If the ^{222}Rn is extracted into a toluene or xylene-based scintillant mixture then, under equilibrium conditions, the decay of ^{222}Rn proceeds through four short-lived daughters with the emission of a total of 3 alpha particles and 2 beta particles. The decay scheme is given in Figure 1. The fact that one disintegration of ^{226}Ra will yield 5 particles which can be detected with approximately 90-100% efficiency within the scintillator make the use of liquid scintillation counting for ^{226}Ra determination an attractive proposition.

Published methods vary considerably in their approach to the problem of transferring radon (^{222}Rn) from an aqueous solution containing ^{226}Ra to an organic phase containing scintillants. In one method², radon is bubbled from solution after a suitable ingrowth period and absorbed on silica gel at -200°C . The silica gel is transferred to a toluene-based scintillator. Other methods involve the direct extraction of ^{222}Rn from a large volume of water sample into a small volume of scintillation mixture^{4,6} or the use of a scintillation solution with an emulsifier to solubilize small volumes of aqueous solution³. Another recent publication⁵ describes a rapid technique for the analysis of ^{226}Ra in potable water in which the sample was passed through a small column of cation exchange resin to remove ^{226}Ra . The resin is sealed in a vial with a scintillation mixture and counted after a suitable ingrowth period.

A method is described here for the determination of ^{226}Ra in environmental samples combining a straight-forward procedure to isolate ^{226}Ra from interfering and quenching ions with liquid scintillation counting, after the ingrowth and extraction of ^{222}Rn into a toluene-based scintillant mixture. In this method the difficulties often associated with the transfer of ^{222}Rn from an aqueous solution containing ^{226}Ra are overcome by leaving both phases in contact. This allows ^{222}Rn to diffuse directly into the scintillator solution during the ingrowth period. The sample can be counted then without further treatment. The presence of an

aqueous layer in contact with an immiscible scintillator has been demonstrated⁸ to improve the resolution of liquid scintillation spectra without loss of counting efficiency.

The application of this technique has been demonstrated within this laboratory in recent studies of the ^{226}Ra levels in bottled mineral water and spa water⁹, and in surface and ground-water samples from the vicinity of uranium-bearing ore bodies. Although the emphasis is upon the analysis of ^{226}Ra in water samples, the method has also been applied to other types of environmental samples such as vegetation or soil following preliminary treatment of the particular sample to render it soluble.

EXPERIMENTAL

Chemical Procedure

The chemical procedure is based upon established methods which are known to be effective in isolating ^{226}Ra from the matrix of an environmental sample.¹⁰⁻¹²

It is assumed that following collection of the water sample it has been acidified (pH 1-2) and filtered (0.45 μm membrane filter) prior to analysis. A sample volume of 1.0-1.5 l is taken for analysis. For more sensitive measurements a larger volume, up to 10.0 l, may be analysed. However, as an initial step, it is necessary to reduce the volume to approximately 1.0 l by evaporation.

The aliquot of 1.0 to 1.5 l is heated and 10.0 g of potassium sulphate and 40 ml of sulphuric acid is added to the sample. Lead sulphate is then precipitated upon the dropwise addition of 2 ml of lead nitrate solution (100 ml Pb/ml) to the hot solution. The precipitate is coagulated by heating for approximately 30 minutes and then allowed to settle. The supernate is removed by decanting or aspirating the bulk of the solution and then centrifuging the remaining 100-200 ml. Ten millilitre of alkaline (pH 10) ammonium EDTA (0.2M) are added to dissolve the precipitate. Gentle heating may be required for complete dissolution. The solution is transferred quantitatively to a 20 ml liquid scintillation vial and 1 ml of barium chloride solution (10 mg/ml Ba) is added. The pH of the solution is lowered to 4.6 with 2 ml of 6M Acetic acid. Under these conditions barium sulphate

will precipitate together with any radium present in solution. A small volume (~ 1 ml) of 1.5M sodium sulphate solution is added to ensure complete precipitation. The precipitate of barium (radium) sulphate is isolated by centrifuging, washed with dilute sulphuric acid and then redissolved in 7 ml of alkaline EDTA (0.2M). Gentle heating of the vial may be necessary to obtain a clear solution. Fifteen millilitre of a toluene-based scintillant solution* is added to the vial and nitrogen is carefully bubbled through the two phases for 5 minutes to remove dissolved oxygen and radon. The vials are sealed and set aside to allow for ^{222}Rn ingrowth from ^{226}Ra prior to counting. As a final step it may be necessary to centrifuge the vials to ensure complete separation of the phases.

To carry out this procedure on a batch of 8 water samples takes approximately 3 hours.

Measurement of Radioactivity

Alpha particles from radon and its daughters are observed using the scintillation detector illustrated in Figure 2. The sample is placed on the face of a 50 mm diameter photomultiplier tube (EMI 6097B) and enclosed within a reflecting plastic cover to improve light collection. The detector system is housed within a light-tight lead castle of wall thickness 75 mm to reduce ambient background. Pulses from the detector are amplified and recorded with conventional nuclear counting equipment. A block diagram of the electronic configuration is shown in Figure 3.

Figure 4 illustrates the pulse height distribution obtained with a multi-channel analyser from an aqueous EDTA solution of ^{226}Ra (37 Bq) with the toluene-based scintillant. The spectrum has two well-resolved peaks that can be assigned to alpha particles. The lower peak is a superposition of alpha particles from ^{222}Rn (5.49 MeV) and ^{218}Po (6.00 MeV) and the higher

* The liquid scintillation mixture is prepared from analytical reagent-grade toluene (Merck Scintillation Grade), naphthalene (Beckman Scintillation Grade) and 2-(4-Biphenyl)-6-phenyl-benzoxazole (Fluka purum grade). The scintillator consists of 200g of naphthalene, 4g of PBB0 made to 1.0 l with toluene, following the published results of McDowell et al¹³ on scintillator solutions.

energy peak corresponds to the 7.68 MeV alpha particle from ^{214}Po . These peaks are superimposed upon a continuum of beta particles from ^{214}Pb and ^{214}Bi . With an aqueous volume of 7 ml, there is no evidence of any contribution to the spectrum from the alpha particles from ^{226}Ra alpha particles in the aqueous phase.

For routine analysis we have found it quite satisfactory to use a simpler counting system, consisting of single channel analyser set to cover the range 1-10 MeV of equivalent alpha particle energy, so that both alpha particles and the underlying beta continuum are detected. A separate measurement of the background (Figure 4) from a 7 ml aqueous Ba/EDTA solution and 15 ml of scintillant demonstrated that a lower level discriminator setting equivalent to approximately 1 MeV alpha energy satisfactorily removes most of the background. Scintillation vials with low potassium content (New England Nuclear) are used to reduce the contribution of ^{40}K -induced scintillations to the background.

A commercial liquid scintillation counting system (Searle Analytic 92) in which the detector consists of two face-to-face photomultiplier tubes counting in coincidence was also found to give satisfactory results. The sample-detector configuration described above proved to be the optimum in terms of alpha resolution and counting efficiency for the analysis of ^{226}Ra without resorting to the more sophisticated technique of alpha liquid scintillation spectrometry with pulse-shape discrimination which has been applied extensively by McDowell and co-workers.¹³⁻¹⁵

Calibration

In order to obtain absolute ^{226}Ra activities it is necessary to calibrate the complete system by determining the count rates from reference solutions of ^{226}Ra . These are prepared by accurate dilution of a standard ^{226}Ra solution*. In the present study, calibration solutions were prepared covering the range 0.02 Bq (0.5 pCi) to 3.0 Bq (80 pCi). Each solution is treated in a scintillation vial to precipitate ^{226}Ra on barium sulphate and then dissolved in 0.2 M EDTA. Scintillant is added to the aqueous phase to produce a calibration vial with an identical chemical composition to that of a

* obtainable from the Radiochemical Centre, Amersham, U.K.

sample. Vials are purged with nitrogen and left to allow ^{226}Ra and ^{222}Rn to equilibrate. The scintillator shows excellent stability with time and calibration vials can be retained and used for long periods. For example no reduction in count rates or changes in pulse height spectra were observed over a period of 12 months.

Counting Periods

The selection of a suitable counting time is governed by the sample activity, the background and the accuracy desired. Typical counting times lie in the range of 3000-10000 sec.

Calculation of activity

The procedure to calculate the activity of ^{226}Ra in the sample and its associated uncertainty is outlined in the Appendix.

RESULTS AND DISCUSSION

For routine analysis measurements of activity can be reliably made after 4 days of radon ingrowth (60% of equilibrium). There are obvious advantages in longer periods of ingrowth but this will be dependent on the radium (^{226}Ra) content of the samples and the requirements of the analytical or monitoring program. For the purpose of method development samples were often left for periods up to 14 days (92% of equilibrium) before counting.

Figure 5 illustrates the increase in count rate with time from a scintillation mixture, commencing with a freshly prepared solution of 12 Bq of ^{226}Ra , and follows closely the expected growth of radon from ^{226}Ra in solution. The initial disparity during the first 2 days arises from the diffusion of ^{222}Rn from the aqueous phase into the scintillant. This is more obvious in the first 2 days because the percentage change in ^{222}Rn concentration is greatest during this period. Counting data acquired more than 2 days after preparation of the sample/scintillation mixture can be corrected to obtain an equilibrium value using the factor, $(1 - \exp(-\lambda t))$, where λ is the decay constant for ^{222}Rn and t is the time after preparation.

The fact that all of the radon is dissolved in the toluene phase is readily demonstrated by observing the effects of shaking the mixture. Figure

6a shows the pulse height spectrum from a ^{226}Ra solution approximately 14 days after preparation. After shaking vigorously for 2 minutes, the spectrum (Figure 6b) alters significantly and only the unresolved alpha peaks due to ^{222}Rn and ^{218}Po are observed. There is no beta continuum from ^{214}Pb or ^{214}Bi . After a period of 30 minutes, the alpha peak due to ^{214}Po is apparent together with an increased beta continuum (Figure 6c). Some 160 minutes after shaking the original spectrum is restored (Figure 6d). These results indicate that the radon solubility in the scintillant is undisturbed by agitation and a few minutes after shaking only ^{222}Rn and ^{218}Po are present in the scintillant. Any ^{214}Pb , ^{214}Bi and ^{214}Po present prior to agitation are dissolved in the aqueous EDTA solution and have no influence upon the spectrum. After a period of time, equilibrium between ^{222}Rn and its daughters is re-established within the toluene layer. Likewise the count-rate, as shown in Figure 7, is reduced dramatically by shaking, but returns to its original value 3 hours later.

Variation of the Count Rate with ^{226}Ra Activity

A series of ^{226}Ra solutions was prepared by accurate dilution of a ^{226}Ra standard solution with final activities ranging from 0.02 Bq (0.5 pCi) to 1.5 Bq (40 pCi). Measurements were made on each sample after 5, 14 and 28 days using both the manual system and the commercial liquid scintillation counter. The graph in Figure 8 shows that the count rate varies linearly with the activity of ^{226}Ra in the aqueous phase. Data presented in Figure 8 were taken 28 days after preparation; the results for measurements performed at earlier times also gave linear plots of count rate against ^{226}Ra activity.

The overall efficiency for the extraction of ^{222}Rn into the scintillant and subsequent counting of the ^{222}Rn and its daughters can be derived from the data in Figure 8. Under equilibrium conditions, each disintegration of ^{226}Ra gives rise to 5 particles (3 alpha and 2 beta) within the scintillant and should yield 5 counts per second per Bq of ^{226}Ra . In fact Figure 8 gives a calibration factor of $3.8 \text{ c.s.}^{-1} \cdot \text{Bq}^{-1}$, an overall efficiency of 76%. Similar data, using a commercial liquid scintillation counting system gave an efficiency of 88%. The difference in efficiency is no doubt due to differences in discriminator settings for the two systems.

Limit of Detection

There have been several recent publications¹⁶⁻¹⁸ in which the limit of detection of a radioactive measurement process is presented as a mathematical expression involving the uncertainty in the background of the counting system. One such expression was derived by Currie.¹⁷ The detection limit (L_D , counts) for a specific measurement process is given by

$$L_D = 2.71 + 4.65 \sqrt{B}$$

where B is the background counts over the counting interval. This relationship is based upon uncertainties of 5% for detection of a true signal due to activity in the sample and 5% for the background of the counter. This formula can be applied to the technique described in this present study in order to estimate the sensitivity of the procedure for ²²⁶Ra analysis. Calculated detection limits are given in Table 1 for both the manual counting system and the commercial liquid scintillation counter. These limits are based on counting statistics alone and do not include other random errors or any systematic components of errors in the procedures. Comparison can be made for various counting times. For a one litre water sample, the detection limit of the method lies within the range 0.002 – 0.016 Bq/l depending on the counting time. There is some advantage in terms of higher sensitivity if the counts are integrated over a window limited to the alpha region of the spectrum. Although the commercial counter proved to have a lower sensitivity (because of its higher background), other considerations, such as the advantage of automatic sample changing, may make its use attractive.

With either system a counting period of 5000 to 10000 sec is a reasonable compromise between sensitivity and through-put of samples. As the method can easily be applied to 10 l water samples ²²⁶Ra concentrations below 0.0005 Bq/l should be detectable.

TABLE 1

Detection Limits for Liquid Scintillation Counting
Technique for ^{226}Ra Analysis

Counting System	Background Count Rate (c.s ⁻¹)	Approximate Detection Limit (Bq)		
		Counting Period (Sec)		
		5000	10000	50000
A. Manual LSC.				
(i) Wide window integrated count ^a	0.16	0.008	0.006	0.003
(ii) narrow window integrated count ^b	0.09	0.006	0.004	0.002
B. Searle Analytic 92 Commercial LSC				
	1.1	0.016	0.011	0.005

a. equivalent alpha energy, 1.0 - 10.0 MeV

b. equivalent alpha energy, 4.0 - 8.0 MeV

Chemical Yield

The analysis of 16 water samples to which had been added 0.83 Bq of ^{226}Ra gave a measured average activity of 0.80(4) Bq. This demonstrated that the procedures were both accurate and reliable with an average recovery of 96% for ^{226}Ra . Experiments, in which known amounts of a radioactive tracer, ^{133}Ba , were added to water samples at the commencement of the analyses to determine the radiochemical yield of ^{226}Ra , gave similar consistently high recoveries. Unfortunately for routine analysis it is not possible to use a radioactive tracer to monitor the chemical recovery of ^{226}Ra in each sample. The high γ -activity required for yield determination produces detectable pulses in the scintillant and interferes significantly with the ^{226}Ra measurement. However, because of the high and reproducible

recovery of radium, it is satisfactory to establish the yield of the radiochemical procedures by the use of a set of samples to which a known activity of ^{226}Ra has been added and which have been taken through the full chemical and counting stages. In addition it is good practice to include blank and spiked samples in each batch of field samples to monitor analytical performance.

Examples of ^{226}Ra Analysis of Natural Waters

The application of this technique to the analysis of ^{226}Ra in various types of water samples is demonstrated by the results in Tables 2, 3 and 4.

In Table 2, the ^{226}Ra contents of several samples of bottled natural mineral water are presented. Measurements made by the two types of liquid scintillation counting systems showed good agreement. For the purposes of comparison, the same samples had been analysed by a standard method for ^{226}Ra analysis²³ and the results are also given in Table 2.

TABLE 2

Comparison of Methods of Analysis for ^{226}Ra in
Mineral Water Samples

Sample	Radioactive Concentration of ^{226}Ra (Bq/l)*		
	<u>Liquid Scintillation Counting</u>		ASTM
	Manual System	Commercial Counter	(Reference 23)
A	0.13 (1)	0.16 (2)	0.17 (3)
B	0.29 (2)	0.31 (4)	0.26 (4)
C	0.12 (1)	0.14 (1)	0.16 (3)
D	0.20 (2)	0.19 (2)	0.24 (4)
E	1.58 (4)	1.70 (10)	1.41 (17)
F	0.44 (3)	0.46 (2)	0.52 (7)

* estimated analytical uncertainties corresponding to the 67% confidence interval are given in parentheses and refer to the least significant figure(s).

In an earlier study of natural radioactivity in mineral water ⁹, the radium (²²⁶Ra and ²²⁸Ra) levels in unprocessed spring or spa water had been determined by γ -ray spectrometry. The concentrations of ²²⁶Ra were also determined by liquid scintillation counting and the results are presented in Table 3 to compare two quite different techniques.

TABLE 3

Radium Analysis of Unprocessed Mineral Spring Water - Comparison of Liquid Scintillation Technique and γ -ray spectrometry

Sampling Location	Radionuclide Concentration in Bq/l ⁺		
	γ -ray spectrometry* ²²⁶ Ra	²²⁸ Ra	Liquid Scintillation ²²⁶ Ra
Glen Luce Mineral Springs, Daylesford, Vic.	0.57 (6)	1.06 (5)	0.57 (2)
Sutton Spring, Daylesford, Vic	0.10 (5)	0.08 (3)	0.09 (1)
Sailors Falls, Daylesford, Vic	0.90 (10)	1.03 (5)	0.87 (4)
Helidon District, Queensland	0.21 (1)	0.12 (2)	0.16 (2)

* previously published results, reference 9.

+ estimated analytical uncertainties corresponding to the 67⁰/o confidence interval are given in parentheses and refer to the least significant figure(s).

As a further example of the application of the liquid scintillation method assay results for ^{226}Ra in samples of surface water and ground water are summarised in Table 4 together with analytical results obtained with the ASTM method.²³

TABLE 4

Analysis of ^{226}Ra in Surface and Ground-Water Samples taken from the Vicinity of Uranium-Bearing Ore Bodies

Sample Type and Location	^{226}Ra Concentration in Bq/l*	
	Liquid Scintillation Technique	ASTM Method (Reference 23)
<u>Ground Water, Yellirie, W.A.</u>		
a. Community Bore	0.17 (1)	0.25 (2)
b. Grid Location 431000N/829200E	0.67 (3)	0.63 (3)
c. Grid Location 430750N/830250E	1.21 (4)	1.00 (6)
<u>Surface Water, Mt. Brockman, N.T.</u>		
a. Anomaly 'X'	0.50 (4)	0.48 (5)
b. Leichardt Springs	0.30 (2)	0.27 (3)
c. Radon Creek	0.36 (2)	0.41 (4)

* estimated analytical uncertainties corresponding to the 67% confidence interval are given in parentheses and refer to the least significant figure(s).

Overall the results indicate that the procedures described here are applicable to the analysis of ^{226}Ra in water samples with a wide variation in chemical composition. In addition the agreement between data obtained with the liquid scintillation and that obtained by other techniques of ^{226}Ra assay proved to be quite satisfactory.

Potential Problems

Interferences

The chemical procedure is effective in separating radium from other radioactive elements and potentially-interfering ions. However the aqueous phase contains, in addition to ^{226}Ra , the other naturally-occurring radium isotopes ^{224}Ra and ^{228}Ra if they were present in the original sample.

^{224}Ra is a potential source of interference through its short-lived daughter ^{220}Rn , which may be taken up by the toluene scintillant solution. The efficiency with which this occurs is very small in comparison with ^{222}Rn as can be seen by the spectrum in Figure 9. The maximum net count rate that was achieved with a solution of ^{224}Ra of activity 2.3 Bq (63 pCi) was 0.13 c.s^{-1} . The contribution of ^{224}Ra to the count rate when measuring ^{226}Ra activity is only $0.06 \text{ c.s}^{-1} \cdot \text{Bq}^{-1}$ of ^{224}Ra . The low efficiency for ^{224}Ra is probably due to the short half-life of ^{220}Rn (55.6 s), which prevents the efficient extraction of ^{220}Rn into the toluene phase. The effect of ^{224}Ra interference progressively decreases during ingrowth because of its short half-life ($t_{1/2} \sim 3.6 \text{ d}$).

^{228}Ra and its short-lived daughter ^{228}Ac ($t_{1/2} \sim 6.8 \text{ h}$) both remain in the aqueous phase. The efficiency of the scintillant for detection of high-energy beta and gamma emissions from ^{228}Ac is low. Nevertheless at elevated levels of ^{228}Ra this may become significant. The spectrum displayed in Figure 9 was taken with a ^{228}Ra solution of activity 28 Bq (750 pCi), in contact with the scintillant and the net count rate was 1.19 c.s^{-1} . This gives an efficiency of $0.04 \text{ c.s}^{-1} \cdot \text{Bq}^{-1}$ for ^{228}Ra which is approximately 10% of the observed counting efficiency for ^{226}Ra ($3.7 \text{ c.s}^{-1} \cdot \text{Bq}^{-1}$). It is apparent therefore that significant interference by ^{228}Ra in the measurement of ^{226}Ra will only occur when the concentration ratio of ^{228}Ra to ^{226}Ra in the sample exceeds 10:1. From published data for the concentrations of radium isotopes in natural waters¹⁹⁻²¹ it is extremely unlikely that ratios of this magnitude occur. Even in the processing of minerals containing monazite impurities activity ratios for $^{228}\text{Ra}/^{226}\text{Ra}$ did not approach a value of 10 in process or effluent samples.²²

Quenching in the Scintillator

Quenching effects in the scintillator are not significant for several reasons,

- a. the chemical procedure separates radium from potential quenching agents such as organic or coloured species in the sample,
- b. the presence of EDTA and barium in the aqueous phase was shown to have no effect upon the spectrum of ^{222}Rn and daughters in the scintillation solution,
- c. it was observed that de-gassing the scintillation solution with air instead of nitrogen had no effect upon the spectrum or count rate after the same time for ingrowth; the absence of oxygen is therefore not critical to the behaviour of the scintillator under these conditions, and
- d. the aqueous phase and scintillant solution have the same composition (apart from radium content) for each sample so that any quenching effects are constant.

Comparison with other techniques

In comparison with the radon emanation technique for ^{226}Ra analysis^{24,25} this method appears to have several advantages due to the high counting efficiencies which can be obtained with liquid scintillation counting. For sensitive ^{226}Ra determination ingrowth periods and counting times are shorter; reliable measurements of activity can be made after four days of ingrowth (60% of equilibrium). The method is applicable over a considerably broader range of sample activities and a higher through-put of samples can be achieved, particularly with the use of a commercial liquid scintillation counter equipped with automatic sample changing. Although the chemical procedures involved with this method may be more complex than those associated with sample preparation in the emanation technique, the use of vacuum apparatus for ^{222}Rn transfer is avoided. One additional feature of this method is that repeat measurements on the same sample can be performed during or beyond the ^{222}Rn ingrowth period, if required.

Techniques for ^{226}Ra analysis using alpha spectrometry with solid state detectors^{26,27} are specific for this radionuclide and require no ingrowth

periods for ^{222}Rn . However, in contrast with the method presented here, the chemical procedures are very complex, time-consuming and require a high level of operator skill. Counting efficiencies are low and long counting times are required for sensitive determination of ^{226}Ra . Source preparation is extremely critical due to problems of sample self-absorption.

Methods in which ^{226}Ra is determined by alpha counting of a barium-radium precipitate^{23,28} are not absolutely specific for ^{226}Ra . Problems may arise due to self-absorption and significant losses of precipitate may occur at several stages of the chemical and counting procedures. The time of counting is critical due to the ingrowth of ^{222}Rn and its possible loss from the unsealed counting source. The presence of other radium isotopes requires repeated measurements to determine the ^{226}Ra content. Alpha counting by liquid scintillation avoids these problems and has the advantages of a much higher counting efficiency and less sample manipulation.

SUMMARY

The procedures which are described above overcome difficulties associated with other liquid scintillation methods for ^{226}Ra assay. Losses of ^{222}Rn in transfer to the scintillator are avoided and ^{226}Ra is removed from potential quenching agents and interfering radionuclides in the sample. The results indicate that no significant interferences due to ^{224}Ra and ^{228}Ra in a sample occur and therefore the method is specific for ^{226}Ra .

The manual counter described in this work is a low-cost system and has proved to be entirely suitable for routine assay of environmental samples. There are advantages in the acquisition of liquid scintillation spectra using a multichannel analyser to confirm the presence of ^{226}Ra in the aqueous phase and to selectively integrate the counts over a particular region of the spectrum. A commercial liquid scintillation counter may be used for routine measurements, although it should be noted that such systems are generally optimized for counting low-energy beta emissions from ^{14}C and ^3H and may not be entirely suitable in terms of energy resolution for alpha counting.

This method of analysis for ^{226}Ra has proved to be sensitive and reliable and offers a useful and improved alternative to radon emanation and alpha spectrometry for the routine analysis of ^{226}Ra in environmental samples.

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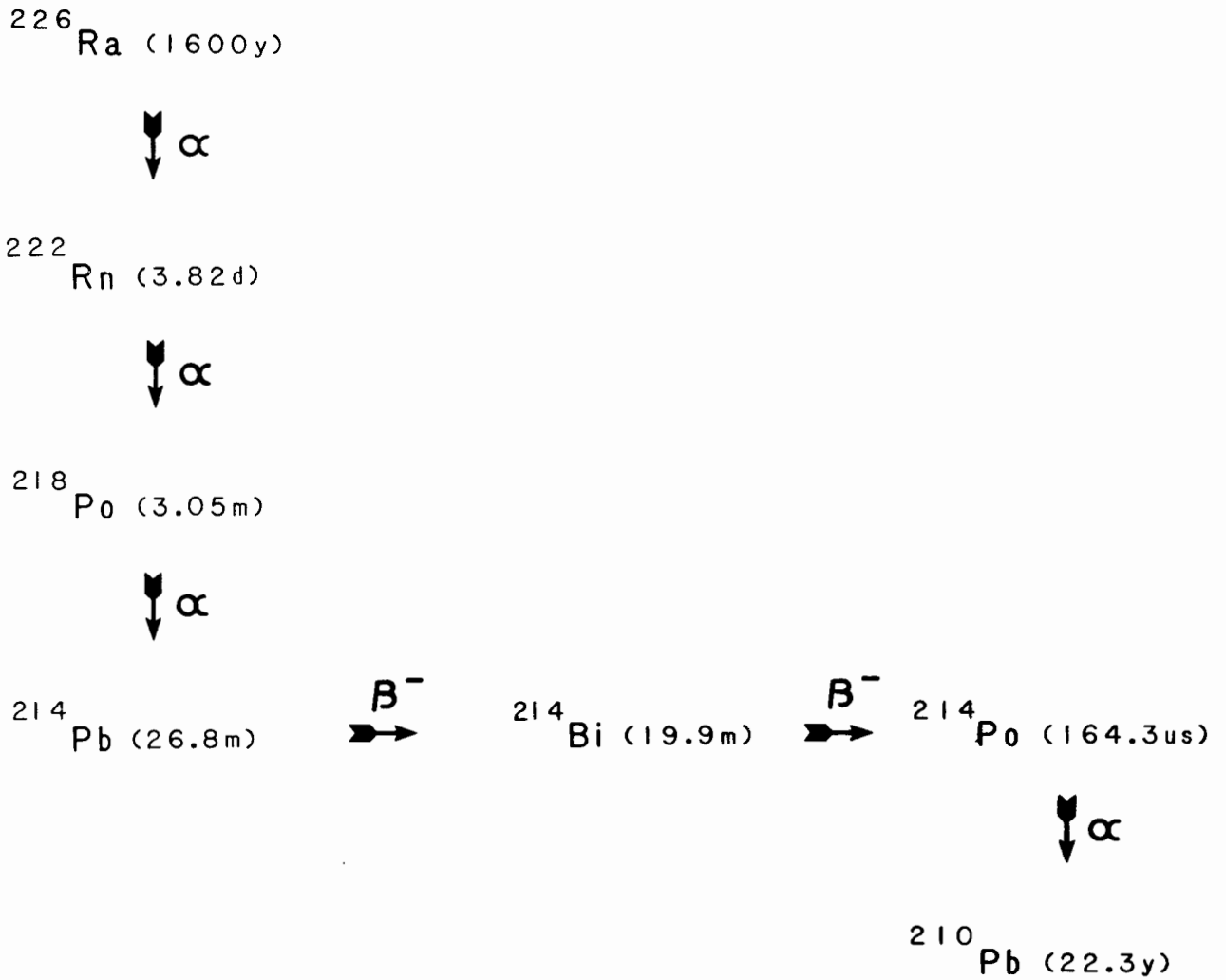


Figure 1. Radioactive decay scheme for ^{226}Ra

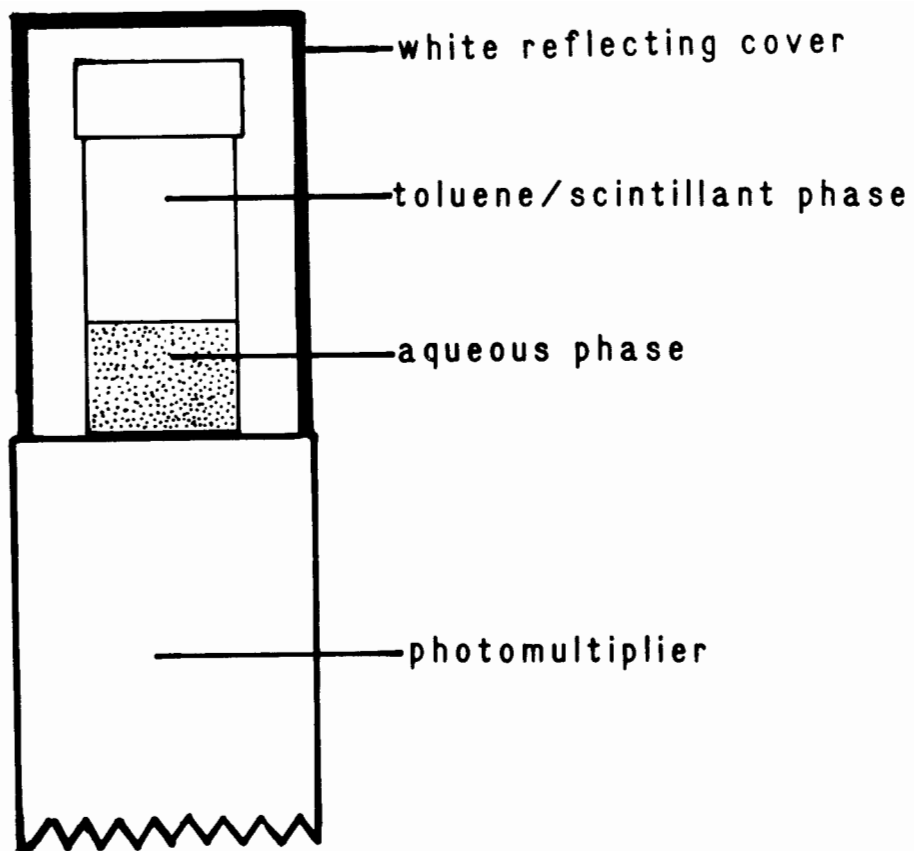


Figure 2. Sample-detector configuration in liquid scintillation counter.

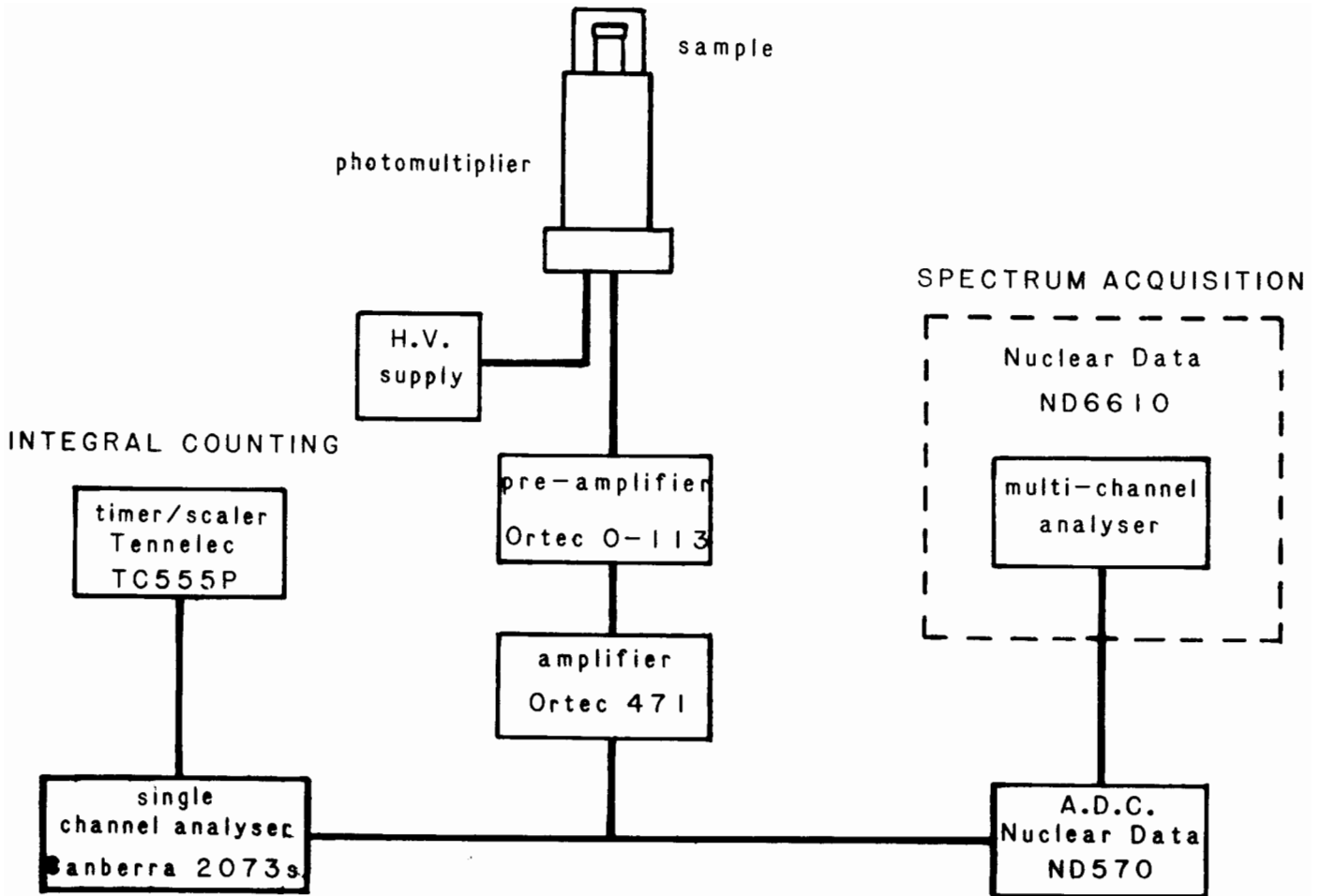


Figure 3. Arrangement of electronic modules for liquid scintillation counting and acquisition of spectra.

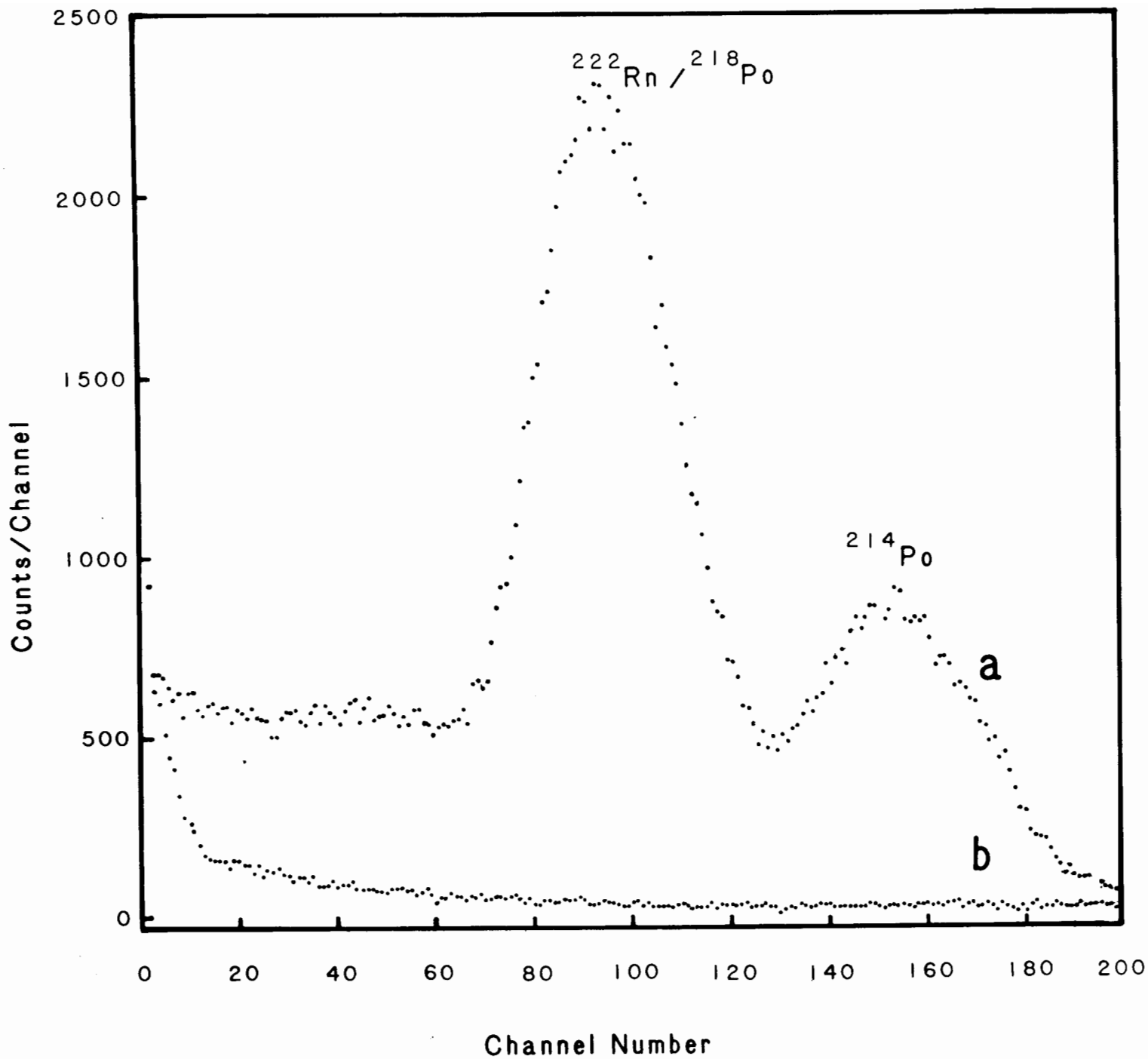


Figure 4. Typical pulse height spectra.
a. ^{226}Ra solution, activity 37 Bq, 1000 s count time.
b. Background, 50000 s count time.

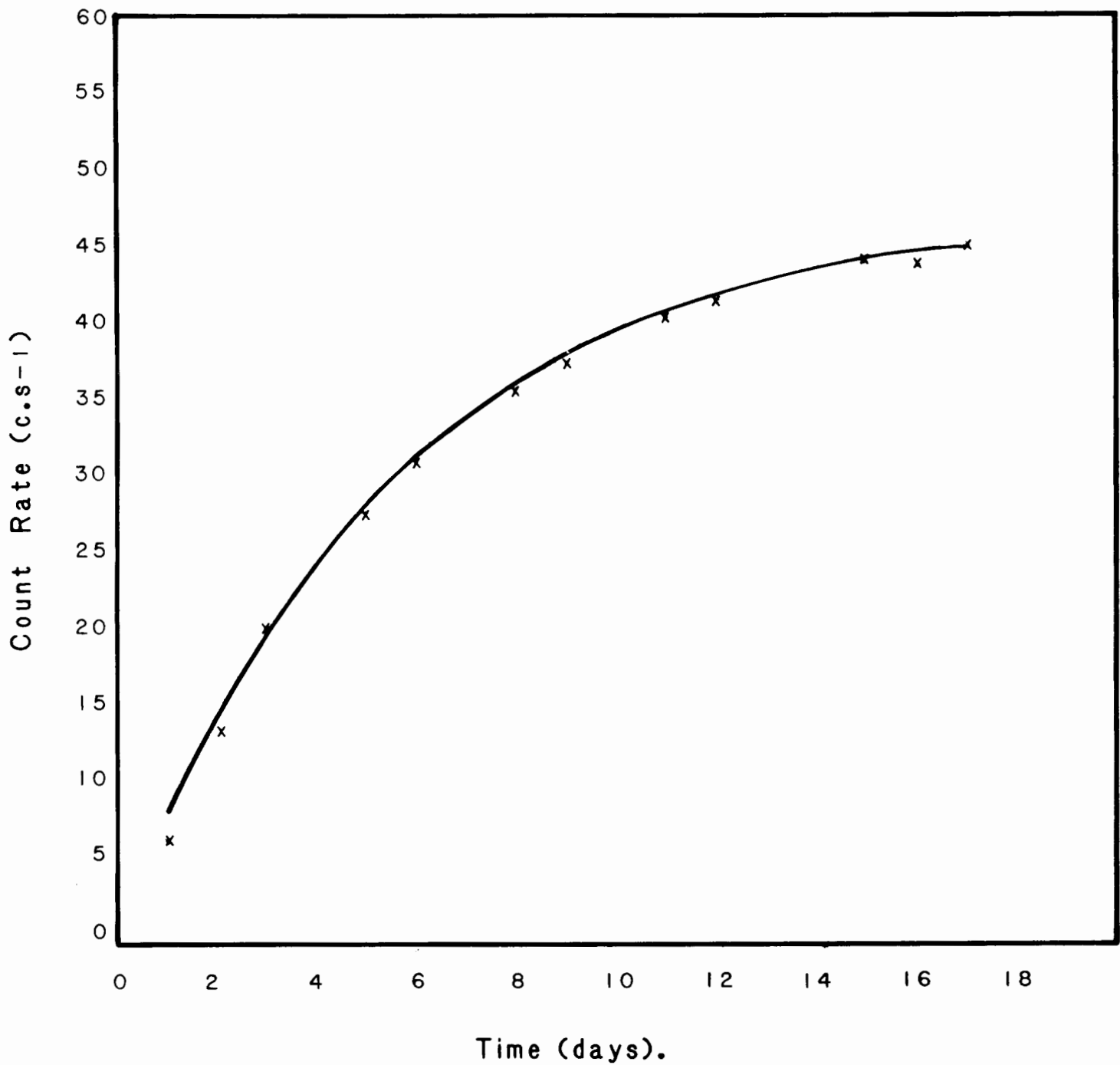


Figure 5. Increase in count rate with time after scintillant mixture was purged with nitrogen, ^{226}Ra activity 12 Bq. Solid line represents count rate calculated using ingrowth expression for ^{222}Rn .

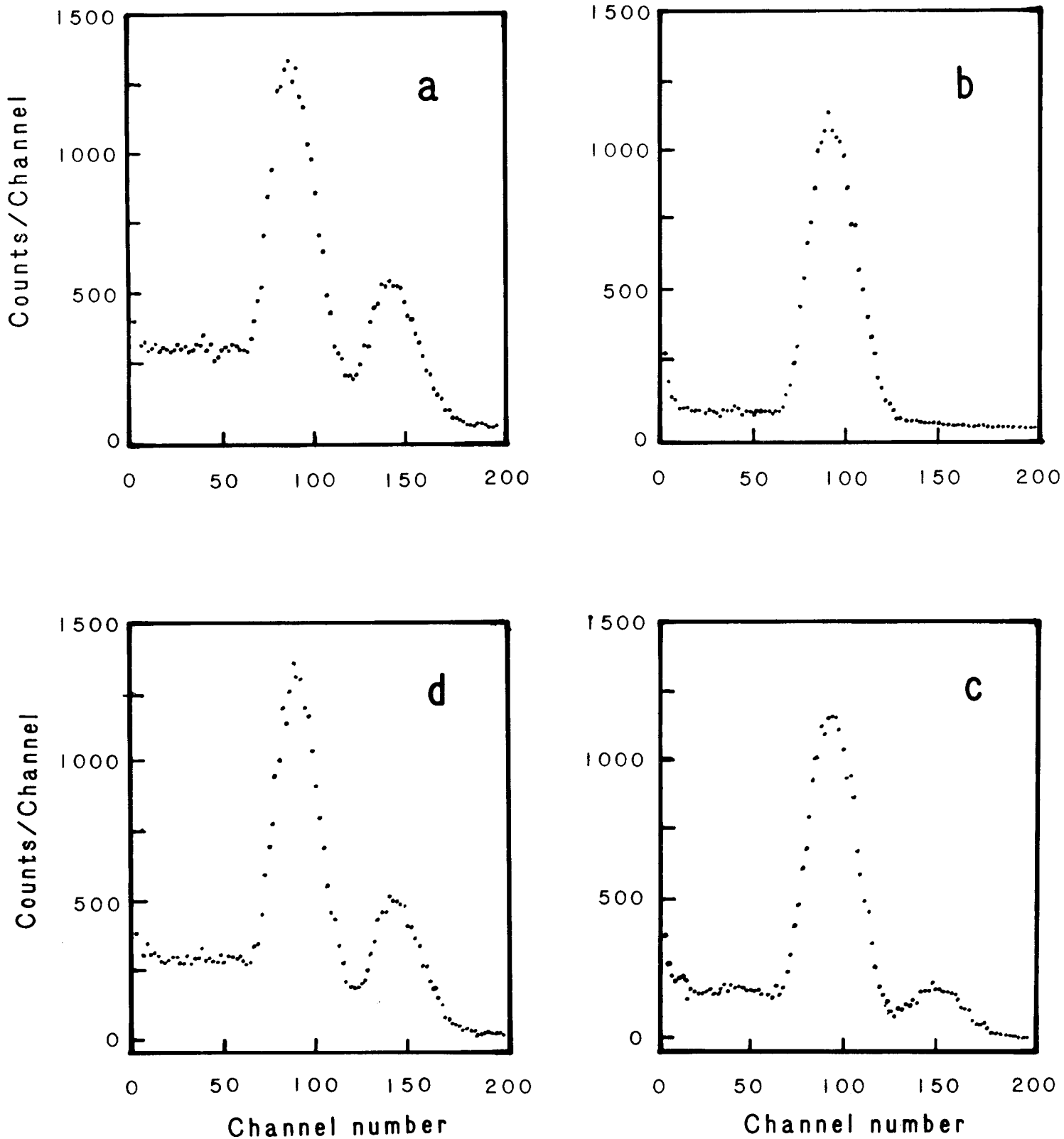


Figure 6. Changes in pulse height spectrum upon agitation of liquid scintillation vial, ^{226}Ra activity 37 Bq, 1000 s count time.

- a. Immediately before shaking
- b. Immediately after shaking
- c. 30 m after shaking
- d. 160 m after shaking

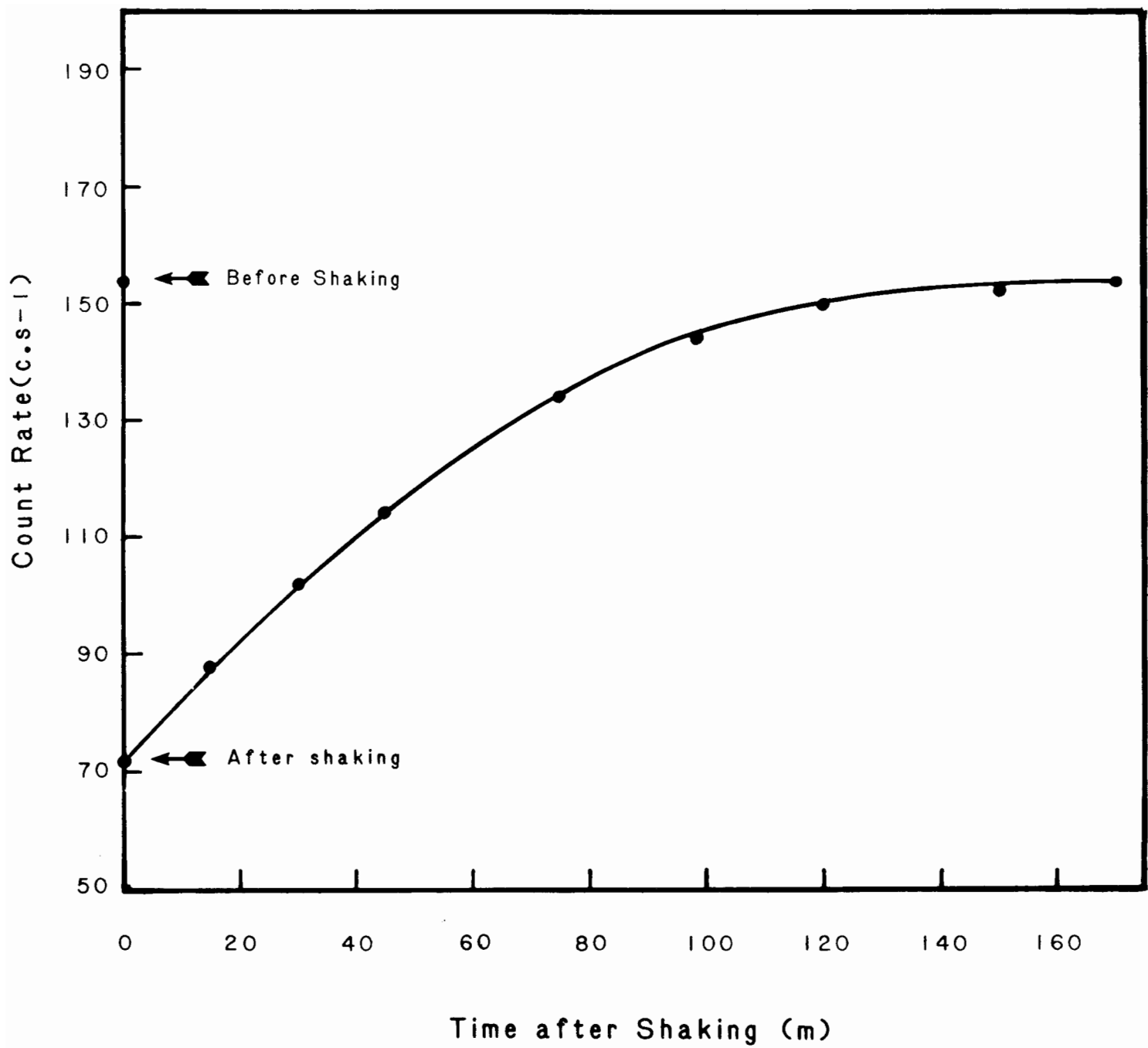


Figure 7. Behaviour in count rate following agitation of liquid scintillation vial, ^{226}Ra activity 37 Bq.

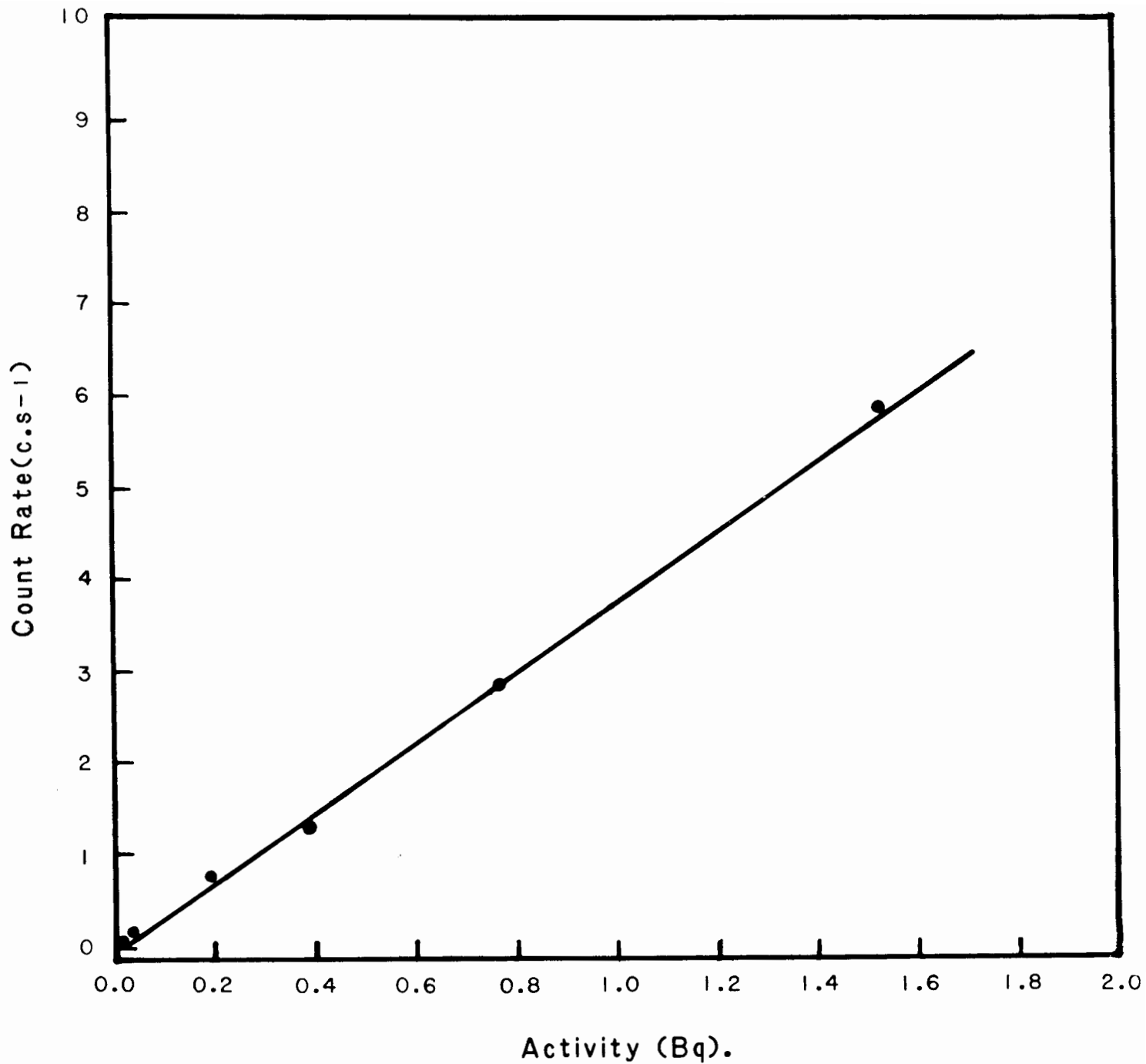


Figure 8. Variation of count rate with ^{226}Ra activity, ingrowth period 28 days.

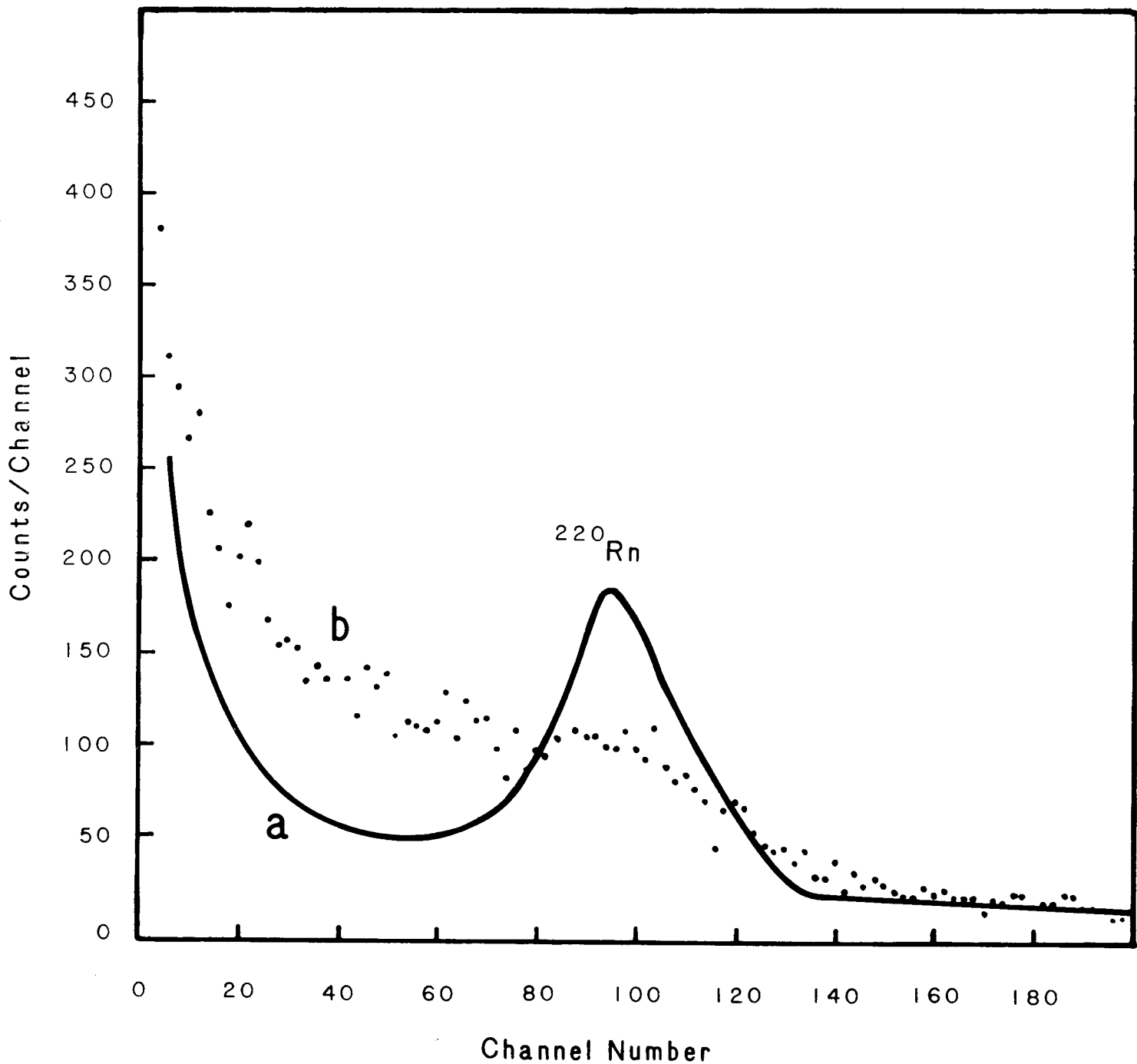


Figure 9. Pulse height spectra with other radium isotopes in aqueous phase; 10000 s count time
 a. ^{224}Ra solution, activity 12 Bq,
 b. ^{228}Ra solution, activity 28 Bq.

APPENDIX

Calculation of ^{226}Ra Activity in Water Sample.

The activity, A(Bq), of ^{226}Ra per unit volume is given by the expression,

$$A = \left(\frac{N - Bt_N}{t_N} \right) \cdot \frac{1}{(1 - \exp(-\lambda t_R))} \cdot \frac{1}{V \cdot F} \cdot \frac{100}{Y}$$

- where
- N is the gross counts accumulated for a counting time of t_N seconds,
 - B is the background count rate in counts per second,
 - λ is the decay constant for ^{222}Rn , i.e. 0.182 (day)^{-1} ,
 - t_R is the time in days for the ingrowth of ^{222}Rn from ^{226}Ra ,
 - F is the calibration factor for the detector in counts per second per Bq of ^{226}Ra activity,
 - V is the volume of sample analysed in litre, and
 - Y is the percentage chemical yield.

The analytical uncertainty (σ_A) in the value of A is calculated by error propagation giving the following expression,

$$\sigma_A = A \sqrt{\left[\left(\frac{N}{t_N^2} + \frac{B}{t_B} \right) / \left(\frac{N}{t_N} - B \right)^2 \right] + \frac{\sigma_V^2}{V^2} + \frac{\sigma_F^2}{F^2} + \frac{\sigma_Y^2}{Y^2}}$$

where t_B is the counting time for the background and σ_V^2 , σ_F^2 and σ_Y^2 are the variances for the independent variables V, F and Y respectively. This derivation neglects uncertainties in counting times and in the calculation of the radon ingrowth factor.