Measurement of Alpha and Beta Activity of Water and Sludge Samples. The Determination of Radon-222 and Radium-226. The Determination of Uranium (including General X-ray Fluorescent Spectrometric Analysis) 1985-1986

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £7.00 net

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For information on the use of Gamma Ray Spectrometry see Section 2.4 and references therein.

For information on the determination of specific elements and isotopes consult the specialist literature. See section 2.

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Note: This booklet was approved by the Main Committee of the Standing Committee of Analysts in 1985. It has been completely rechecked and minor additions made in the light of 1986 experience in monitoring the effects of the Chernobyl Nuclear Power Station incident.

About This Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has seven Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No. 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary

1 July 1986

Warning To Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use. Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors, Hartree and Booth), Biochemical Society Special Publication No. 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Service Monograph 6, HMSO, London.

It cannot be too strongly emphasized that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

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Note on the SI Units for the Measurement of Radiation

The General Conference on Weights and Measures has adopted special names for SI units used in connection with radioactivity. The unit for a quantity of radioactivity is called the becquerel (Bq). It is defined as a unit of activity equal to one nuclear disintegration per second. The becquerel has replaced the International Curie (Ci) which was originally based upon the activity of one gram of radium (3.7×10^{10} d/sec). Very much larger numbers are required to express activity in becquerels than were required with curies.

The unit for the quantity of absorbed radiation dose is the gray (Gy). It has replaced the rad. One gray is equal to 100 rads. The quantity absorbed dose is multiplied by modifying factors characteristic of the type of radiation in order to generate a quantity dose equivalent which expresses the biological effect of the radiation. In the old system of units rads were multiplied by modifying factors characteristic of the source and type of radiation and the result quoted in rem. The gray is related to the unit of dose equivalent, the sievert (Sv), in exactly the same way. One sievert is equal to 100 rems.

The same prefixes are used with these units for denoting larger and smaller multiples as are used for other SI units of measurement. The relationship between the new and the old units is summarized as follows:

Physical Quantity	New SI Unit	Old Non-SI Unit	Relationship
Activity	becquerel (Bq)	curie (Ci)	$1\ \text{Bq} = 2.7 \times 10^{-11}\text{Ci}$ $= 27$ pCi $1\ \text{Ci} = 3.7 \times 10^{10}\text{Bq}$
Absorbed Dose	gray (Gy)	rad (rad)	1 Gy = 100 rads 1 rad = 0.01 Gy 1 Gy = 1 Joule Kg^{-1}
Dose Equivalent	sievert (Sv)	rem (rem)	1 Sv = 100 rems 1 rem = 0.01 Sv

Factor	Prefix	Symbol
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	K
10^{-3}	milli	m
10^{-6}	micro	u
10^{-9}	nano	n
10^{-12}	pico	p

The Measurement of Radioactivity in Water

1 Introduction

Water contains a small and variable quantity of natural radioactivity from the decay of uranium and thorium and their daughters, together with ^{40}K. The background radiation has been increased during the past three decades as a result of man's exploitation of nuclear fission. The original, and still the major, artificial input to the hydrosphere is from the fallout of fission products from nuclear weapon testing, and the presence, in UK rain and river waters, of ^{90}Sr and ^{137}Cs (and other radionuclides) has been well documented(1)(2). Other sources of radioactivity now include the discharge of small quantities of liquid radioactive waste from the operation of nuclear powered electricity generating stations and research establishments, the use of radioactive materials in industry(3) and medicine(4), and also from the use of tracers for the investigation of water and sediment movement(5)(6).

The control of the uses of radioactivity, and the limitations of discharges to the environment under the Radioactive Substances Act (1960), ensure that the levels in water are below limits derived from International Commission on Radiological Protection (ICRP) recommendations(7). Where appropriate, the radioactive content of water is measured by the operator who is authorized to discharge radioactivity, and the results are checked by the appropriate authorizing Government Departments; in addition, tracer experiments to follow water movement are usually carried out by specialist groups with the appropriate measuring equipment. The measurement of the radioactive content of water is carried out by some UK Water Authorities as a check on trends and natural levels to be expected in the environment.

The sections that follow are intended to be a general introduction to the problems associated with measurement of radioactivity, and include a discussion on the measurement of radioactivity in water. Further information on the several organizations specializing in the measurement of low levels of radioactivity, and advice on this subject can be obtained from either the *National Radiological Protection Board*, Chilton, Didcot, Oxfordshire, OX11 0RQ, or the Radiochemistry and Tracer Section, *Water Research Centre*, Medmenhan Laboratory, Medmenhan, PO Box 16, Marlow, SL7 2HD (0491 571531).

2 Radioactivity and its Measurement

Radioactive decay is generally accompanied by the emission of α or β particles or alternatively electron capture or isomeric transitions may take place; γ-photon and x-ray emission may also be associated with the decay. Each radionuclide is characterized by its half-life, and type and energy of emission (see Tables 1–5). The different types of emission are affected to different degrees by the sample source and are measured with very different efficiencies by the different detection systems available; furthermore, if there is any significant delay between the collection and analysis of the sample, the correction for radioactive decay will also differ for each radionuclide. It is obvious, therefore, that any attempt to measure directly the total amount of radioactivity in water is fraught with the danger of misinterpretation, and it is generally true to say that the analyst must know what is present *before* attempting such an analysis. However, because this approach can be of use in measuring trends in the levels of activity, a brief description of some of the more generally used techniques follows, with a discussion of the limitations of each method. In addition, these 'total activity' methods are preceded by a general discussion of the principles of radiochemical analysis.

For further information on all analytical aspects of radioactivity, the interested reader could consult the Nucleonics section of the Fundamental Reviews published (biennially) in the American Chemical Society's journal *Analytical Chemistry*. The Water section of the same journal's Application Reviews also contains a summary of recent developments in the measurement of radioactivity in water. Further references on counting techniques are listed at the end of this review(8)(9)(10)(11): the list is not intended to be exhaustive.

2.1 The determination of individual radionuclides

A detailed review of the many analytical techniques used for the separation (where necessary) and measurement of individual radionuclides is neither required nor practicable in this publication, but the following principles are generally applicable and should be borne in mind when carrying out such determinations.

(a) Separations are usually carried out after the addition of a known amount of a stable element analogue or radionuclide tracer to enable the chemical yield of the method to be determined. The former addition also ensures that an adequate quantity of material is available for standard chemical procedures (eg precipitation).

(b) Isotopic equilibration—that is chemical equilibration between the desired radioactive and stable species—must be ensured; this can be achieved by passing the sample through oxidation/reduction cycles or by the formation of very strong complexes with organic or inorganic ligands. Although the presence, in solution, of only one chemical species can often be assumed (in the cases of caesium or strontium, for instance, where the presence in acid solution of only Cs^+ or Sr^{2+} is assured), it is strongly advisable to test this assumption by carrying out the separation process both with and without the equilibration stage.

(c) A single separation from the water matrix is usually carried out to reduce the bulk of the sample. In this step, many other elements and radio-nuclides may be removed, but a specific separation of the radionuclides of interest with an adequate degree of purity may sometimes be achieved at this stage.

(d) Standard radiochemical procedures can be applied to the separated material if necessary.

(e) The chemical yield of the method is determined, usually by a standard quantitative procedure, eg gravimetry (especially if a solid source is used for the final measurement of the separated radioactivity), or spectrophotometry. In some instances, however, the yield can be determined by using, as a tracer, a radioisotope with a different type or energy of emission from that of the isotope being measured; this approach is obligatory where there is no stable isotope, such as is the case in the determination of technetium, promethium, or any element with atomic number greater than or equal to 84, for example of radium, thorium, uranium, plutonium or americium.

(f) *The measurement of radioactivity*

The methods for the measurement of the separated radionuclides depend on the types of emission, their energies and the sensitivity (sections 2.2–2.4).

(g) *Test of radiochemical purity*

The purity of the separated source can be checked in a variety of ways; by measuring the half-life and comparing it with that of the expected value; by measuring the specific activity of the source and comparing it with the specific activity after carrying out a further cycle of purification—a change indicates the presence of a radionuclide of a different element; and by measuring the energies of the emissions present and comparing them with those expected.

(h) *Measurement of reagent blanks*

If very low levels of radioactivity are being measured, the contribution of radioactivity in the reagents must be carefully measured by carrying out the complete separation procedure in the absence of a sample.

There are many papers published in the scientific literature which are concerned with the measurement of radionuclides in environmental materials, but it is possible that the largest concentration of information on this topic exists in the publications of the International Atomic Energy Agency (IAEA) whose headquarters are in Vienna and who publish symposia proceedings, technical reports on reference methods for radioactivity studies and the results of international intercomparison exercises. The World Health Organisation (WHO) has also published manuals of methods(12)(13). In addition, the National Academy of Sciences (USA) Nuclear Science Series of monographs contain much valuable information (although in need of updating): the series includes publications on the radiochemistry of many elements as well as separate monographs on eg 'Low-level radiochemical separations'(14) and 'Chemical yield determinations in radiochemistry'(15). The general principles of radioanalytical methodology are discussed in reference(16), and a manual of methods is published by the US Health and Safety Laboratory (HASL)(17), and others may be found in the joint publication of the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: 'Standard Methods for the Examination of Water and Waste Water'(18, 18A).

2.2 The determination of β-activity

The β-activity of water samples can be measured by the use of either ionization or scintillation techniques. The interaction of β-particles with matter results in the production of ion pairs, and if this ionization occurs in a gas it will become electrically conductive. This principle is used in the proportional and Geiger counters which are commonly used as detectors of β-activity. The application of a suitable voltage across the gas space results in an electrical pulse indicating when a β-particle has caused ionization to occur; these pulses can be counted on a scaler.

Some materials emit flashes of light on absorbing energy, and these solid scintillators can be used as detectors of β-particles. The scintillator is coupled to a photomultiplier, a device which is sensitive to light signals thus converting them to electrical pulses; these can be counted on a scaler as before.

The two systems mentioned above both rely on a sample source placed, externally to the detector, at or near the detector surface or window. However, an alternative application of the scintillation detector—liquid scintillation counting(19)(20)—involves a liquid scintillant intimately mixed with the sample material. The counting of the resultant scintillations is again achieved by the use of a photomultiplier and scaler.

In all these detection systems, the detector is usually shielded by lead from much of the external background radiation (eg cosmic radiation, and radiation from natural uranium and ^{40}K in the surrounding constructional materials). A further reduction in background counting level can be achieved by partially enclosing the main detector in a second, larger, detector and arranging for any simultaneous (or coincident) pulses produced in the two detectors by high energy cosmic radiation to be ignored by the counting system. External source counting methods (using either ionization or scintillation detectors) usually involve evaporating a measured portion of the water sample to dryness on a metal planchette which is then mounted directly below the end-window of the detector and counted for a set period. The measured count rate is corrected for background activity and compared with the activity of a standard identically mounted.

Ideally, the response of the whole system to β-activity should be independent of the nature both of the sample and of activity. In fact, the response of the system depends on the energies of β-emissions in the sample, which will themselves be affected by the components of the system thus:

(a) the source holder material: resulting in a variable amount of back-scatter,
(b) the source itself: variation in thickness (arising from variations in the total dissolved solids) will result in different degrees of self-absorption of the β-particle, and
(c) the detector end-window thickness.

It is obvious, therefore, that care must be taken when evaluating data from β-counting systems.

Two β-counting systems are listed in references(21)(22). In each case the count rate of the sample (corrected for background and if necessary, dead-time) is compared with the activity of a suitable standard source. The former report uses a ^{36}Cl standard (β max emission 0.71 MeV) and corrects for source and end-window absorption losses by counting the sample through different thicknesses of absorber followed by the application of a simple computer program; the latter uses a ^{40}K standard (β max emission of 1.32 MeV), and discusses in more detail than is set out here the limitation of total beta counting.

The advantages of liquid scintillation counting over the other methods may, at first sight, appear overwhelming, for none of the three parameters mentioned earlier which contribute to a variable response by the other systems (viz: back-scatter, self-absorption and external absorption by the detector end-window) are operative. However, there are disadvantages specific to liquid scintillation counting: the scintillation process is extremely sensitive to absorption of the scintillations by a coloured sample (colour quenching), and by the interference of other elements and compounds present in the sample in the energy transfer process before scintillations are produced in the medium (impurity or chemical quenching). Although there are many ways by which these interferences can be minimized it is generally true to say that a more constant response of the system can be achieved by the use of a solid sample source and (usually) a Geiger–Muller detector, and the β counting method given in this booklet is an attempt to balance the requirements of simplicity of operation with the difficulties of variability of response. It is similar to the recently defined WHO reference method(13) which uses a low-background Geiger counting assembly and a source, previously ashed at 350°C, with thickness $50\,\mathrm{mg.cm^{-2}}$, and which compares the count rate of the sample with that of a potassium standard identically mounted. The main differences are: firstly that, if possible, a source thickness of $10\,\mathrm{mg.cm^{-2}}$ is used—this not only is more suitable for UK waters but also results in a smaller effect from self-absorption; and secondly that those other parameters which affect the response of the system (ie detector end-window thickness, planchette material, and source-detector distance) are specified.

2.3 The determination of α-activity

Methods for the determination of α-activity in water involve the evaporation of a sample to low volume and final evaporation to dryness on a tray or disc which is then presented to a detector—usually a zinc sulphide scintillation screen; the total α-activity is then calculated by comparison with a standard similarly prepared. The system is therefore very similar to that used in β counting, but because of the greater degree of interaction between α particles and matter, the problems of absorption are much greater, and care must be taken to apply the appropriate corrections. If, as a result of the evaporation, a large quantity of solid residue is produced, then recourse may need to be made to infinite depth counting: this term describes the situation which exists if the sample source is so thick that particles emitted from the lower portion of the source do not reach the upper surface and therefore are not available for detection: the maximum penetration by α-particles is about $6\,\mathrm{mg.cm^{-2}}$ so any sources thicker than this may be termed infinitely thick. For an explanation of the absorption of α-particles by matter see Kaplan(23). The problems of self-absorption in α-particle measurement have been discussed by Smales and Airey[24]. Two methods for the measurement of total α-activity are given in the list of references(18)(25).

2.4 The determination of γ-activity

Until recently most measurements of total γ-activity were made using, as detectors, NaI crystals activated with thallium: [NaI(Tl)]. The crystal scintillates on absorption of energy from the γ-photon and the technique is very similar to the measurement of β-activity using a plastic phosphor as described in section 2.2. The efficiency of detection of radiation depends to a large degree on the size of the crystal and the energy of photon emission, and therefore the response of such systems will be different for each γ-emitting nuclide. However, γ-photons do not interact with the sample matrix to the same degree as do α or β particles, and self-absorption losses can therefore generally be neglected. In addition the use of radioactive tracers in hydrological studies is generally confined to those radionuclides which emit γ-photons, and the use of NaI(Tl) crystals as detectors is perfectly acceptable because the characteristics of the radiation are constant, resulting in a constant response of the detector.

A more specialized application of NaI(Tl) detectors is γ-spectrometry; this technique involves identification of the γ-emitting radionuclides by assessing the size of the electrical pulse produced from each scintillation (which is proportional to the energy of the incident γ photon if it is totally absorbed in the detector). Hence by this method the amount of each γ emitting radionuclide present can be measured. Alternative γ-spectrometric detector materials now becoming increasingly popular are lithium-drifted germanium-Ge(Li) and the hyperpure or intrinsic germanium detectors. In this system the interaction of γ-photons with the detector material increases its conductivity, and the application of a voltage to the detector allows collection of electrons in the form of an electrical pulse of size directly proportional to the energy deposited in the detector. Although its detection efficiency is not as great as that of the NaI (Tl) detector, its energy resolution is far superior. There are several publications in association with these γ-spectrometric techniques, some of them also serving as very useful introductions to the whole field of γ-photon measurement. Examples are listed in the references(26)(27)(28)(29).

3 Regulations, Guideline Values and Action Levels

It is essential that proper attention be paid to procedures for handling radioactive substances in the laboratory. Regulations governing the use of radioactive materials and the disposal of radioactive wastes in the United Kingdom are set out in another booklet of this series(30).

The type of 'gross' radioactivity measurements recommended in this procedure are primarily of use as screening methods. Implicit in such procedures is the need to decide when more detailed examination is needed and for each situation 'Action levels' should be defined. The report of a WHO working group on the Radiological examination of drinking water is one illustration of how action levels are chosen(31).

As mentioned in the Introduction, the ICRP have recommended dose limits for members of the public. However, these limits do not apply to medical exposures of patients or to normal levels of natural radiation, for example, the occurrence of natural radionuclides in drinking water supplies. A recent publication by the ICRP, however, outlines the principles for limiting exposure of the public to natural sources of radiation(45).

The WHO have recently published guidelines for drinking water quality(31A) which include guideline values for radioactivity in drinking water. These values represent a level below which water can be considered potable without any further radiological examination and are $0.1\ Bq.l^{-1}$ for gross α activity and $1.0\ Bq.l^{-1}$ for gross β activity. These guideline values, which are lifetime consumption values, are specified assuming that only the most toxic radionuclides likely to be present in significant quantities namely ^{90}Sr (beta) and ^{226}Ra (alpha) are contributing to the gross radioactivity of the drinking water.

The action first required when the gross activity approaches the guideline values is to undertake further and specific radiochemical analyses in order to determine and identify the radiochemical contaminants.

The extent and direction of such analyses must depend upon local knowledge and information, but the following radionuclides are identified in a WHO report(31) either as naturally occurring or man-made radioactive contaminants which may be found in the hydrological environment. Of course there are many others.

Beta emitters.	^{40}K, ^{89}Sr, ^{90}Sr, ^{134}Cs, ^{137}Cs, ^{129}I, ^{131}I, ^{60}Co, ^{3}H and ^{14}C.
Alpha emitters.	^{224}Ra, ^{226}Ra, ^{210}Po, ^{232}Th, ^{234}U, ^{238}U (and various radioactive progeny of all the foregoing including isotopes of Radon), $^{239/240}Pu$ and ^{241}Am.

The technology and instrumentation 'state of the art' is highly developed and most radionuclides can be determined at extreme levels of sensitivity.

The advice of appropriate national competent authorities(30) and the services of specialist environmental radiochemistry laboratories should be sought at an early stage, preferably as soon as a significant upward trend in gross activity level(s) becomes apparent. See also Ref 39 and the Radioactive Substances Act itself.

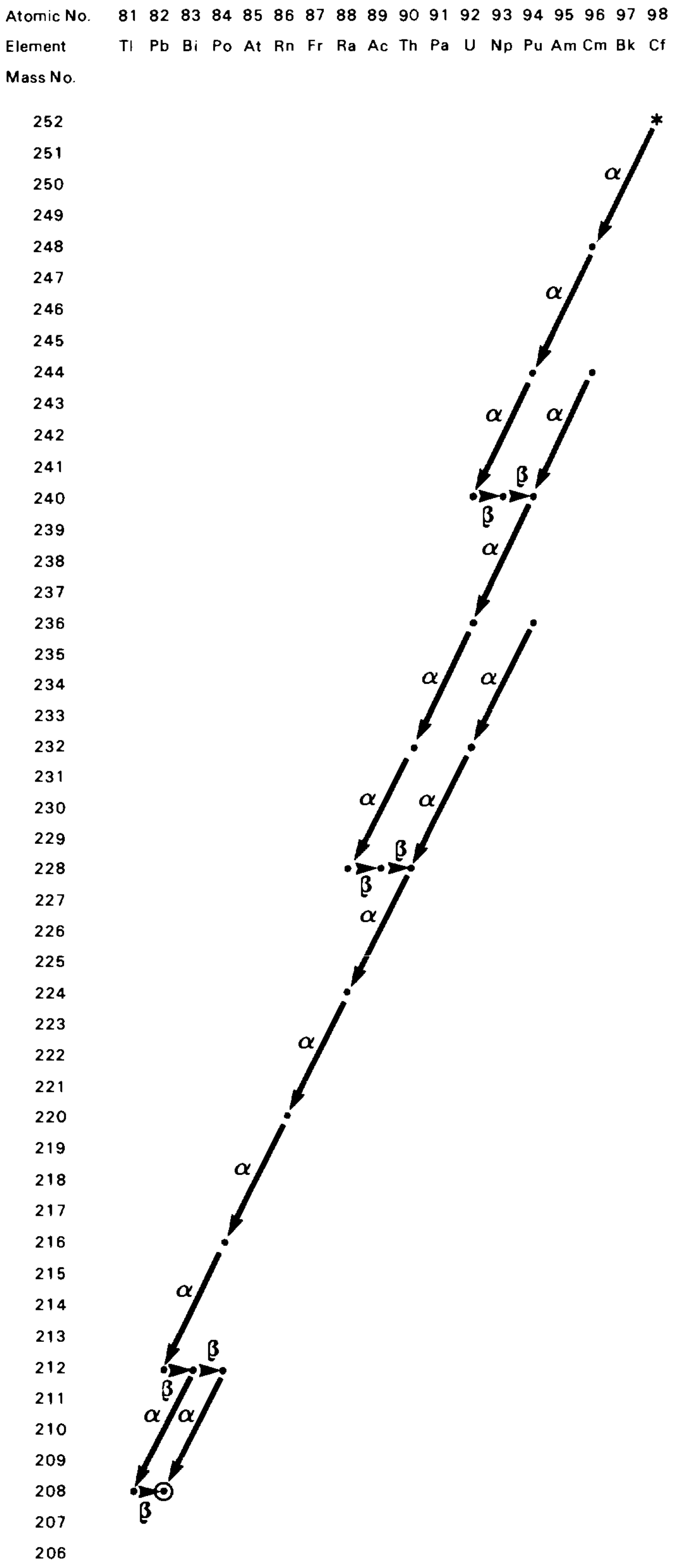
One of the commonest radioactive elements occurring naturally in British waters is radon, chiefly as ^{222}Rn. Radon is a gas and can easily be removed even though appreciably soluble in water; it is not therefore measured with the other alpha emitters in the method for gross alpha radiation. The new WHO guidelines specifically exclude ^{222}Rn. This is because the WHO considers that there is insufficient information available concerning the relationship between the specific activity of ^{222}Rn in drinking water and the resultant doses from inhalation and ingestion. WHO recommend that where high levels of ^{222}Rn are known to be present, reference should be made to the appropriate competent authority. The National Radiological Protection Board have suggested that levels of ^{222}Rn exceeding $40\ Bq.l^{-1}$ at the point of consumption should be referred for further assessment.

3.1 Action in the Event of the Lifetime Values being exceeded

For relatively short terms, it is possible to exceed the above values; but, in taking such a decision, consideration must be given to the isotopes present, their concentration and the local circumstances. *Water Suppliers who are likely to be in this position should consult Her Majesty's Radiochemical Inspectorate*, Mitre House, Church Street, Lancaster for advice (alternatively Her Majesty's Radiochemical Inspectorate may be contacted at the Department of Environment, Romney House, London).

RADIOCHEMICAL DECAY SERIES TABLE 1

THORIUM (4n) SERIES



* Spontaneous fission with emission of neutrons, beta and gamma important

• Isotope in the series

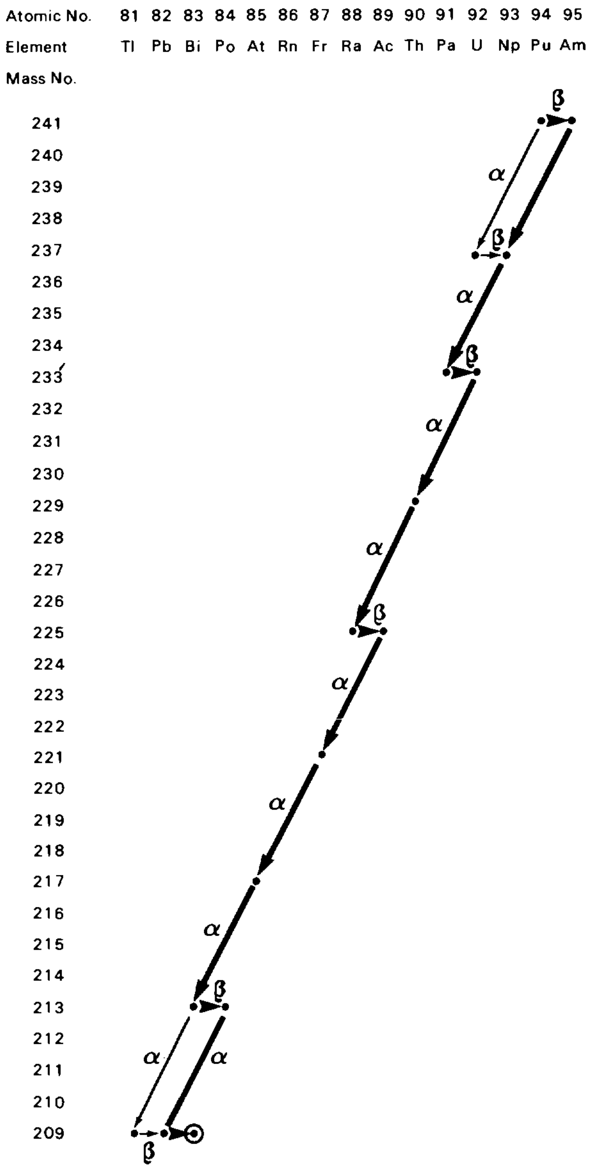
⊙ Stable final isotope

⟶ Main pathway

→ Minor branch

RADIOCHEMICAL DECAY SERIES TABLE 2

AMERICIUM - NEPTUNIUM (4n+1) SERIES



• Isotope in the series

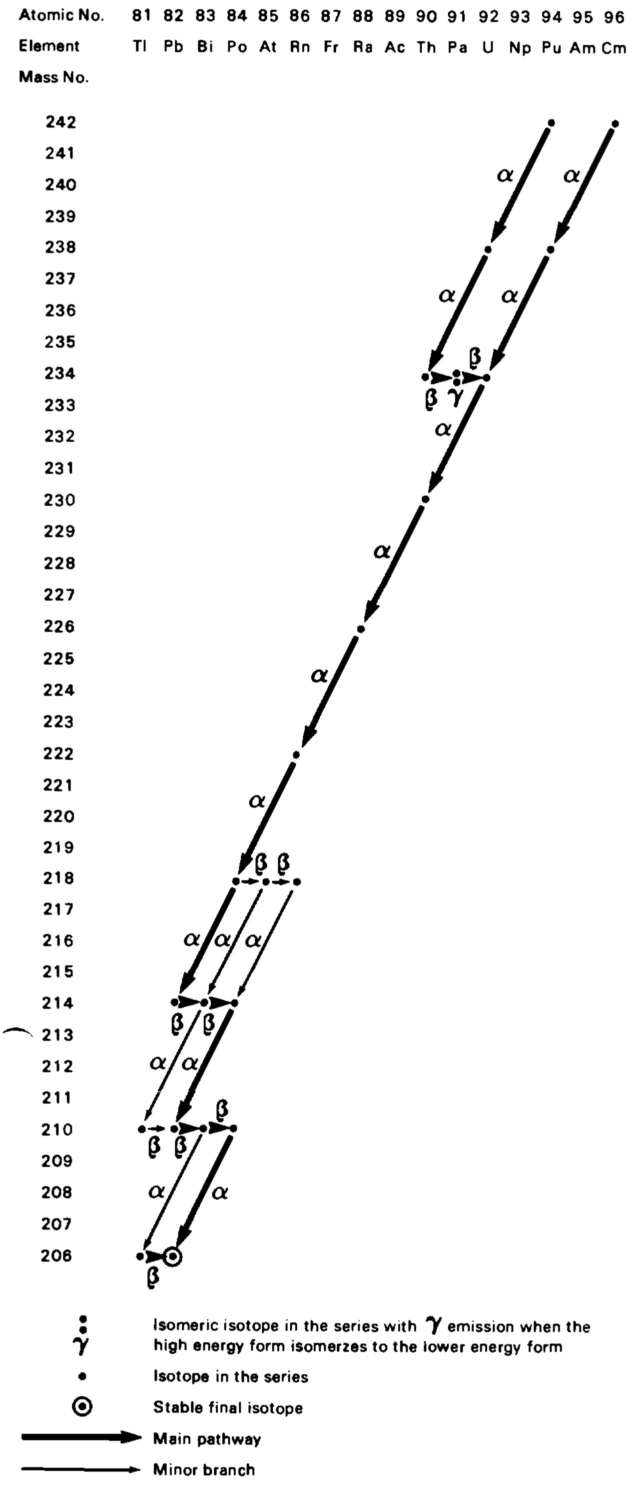
⊙ Stable final isotope

⟶ Main pathway

→ Minor branch

RADIOCHEMICAL DECAY SERIES TABLE 3

URANIUM - RADIUM (4n+2) SERIES



RADIOCHEMICAL DECAY SERIES TABLE 4

URANIUM - ACTINIUM (4n+3) SERIES

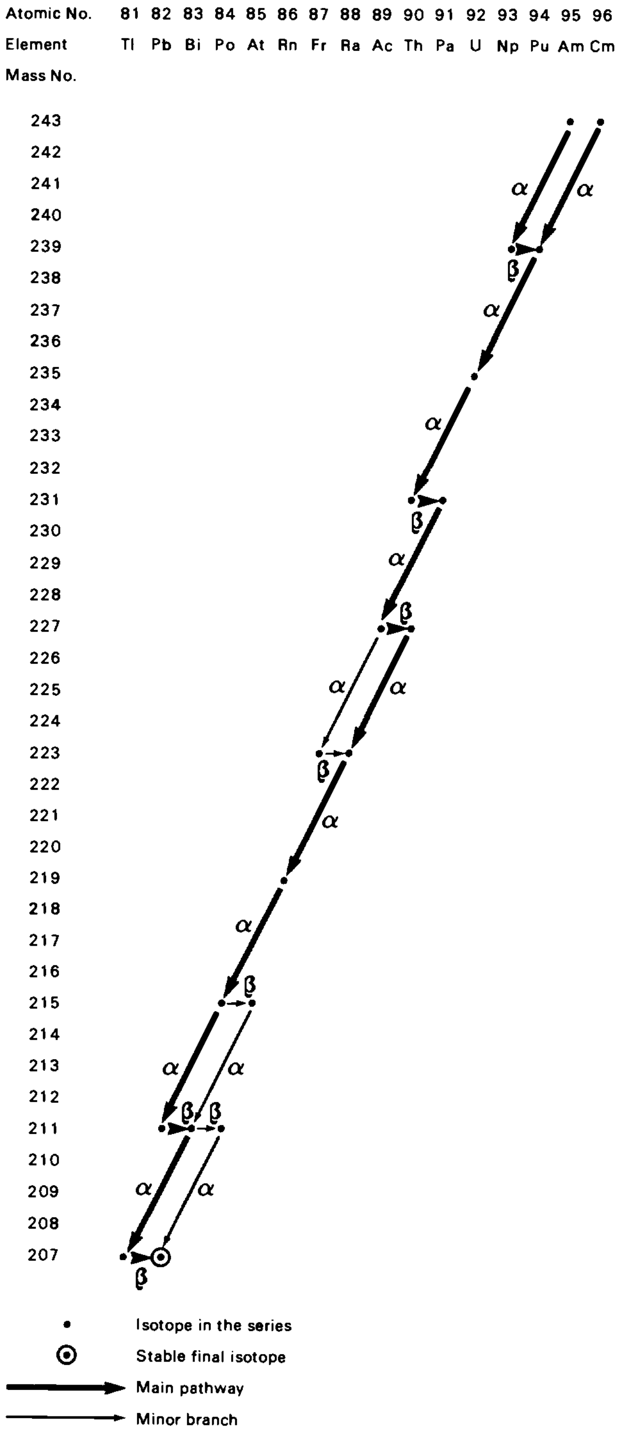


Table 5 Data on some of the Principal Radio Isotopes

(The table below lists isotopes which occur in the four heavy element decay series. Other isotopes decaying into these series are known. The table also lists a selection of other important radioisotopes which occur naturally or are formed either by fission or by irradiation. For more detailed information and for information on gamma emission etc see refs 26 and 60).

Element	Isotope Mass No	Type of Decay	Half Life
Californium	252	αγ + fission	2.638y
Berkelium	247	αγ	1380y
Curium	248	αγ	3.39×10^5y
	246	αγ	4730y
	245	αγ	8500y
	244	αγ	18.11y
	243	αγ	28.5y
	242	αγ	162.8d
Americium	243	αγ	7380y
	242	βγ	16.02h
	242m	αγ	152y
	241	αγ	432.2y
Plutonium	244	αγ	8.26×10^7y
	242	αγ	3.763×10^5y
	241	β(α)γ	14.4y
	240	αγ	6537y
	239	αγ	24065y
	238	αγ	87.74y
	236	αγ	2.851y
Neptunium	240	βγ	7.4m (meta stable) 65m
	239	βγ	2.355d
	238	βγ	2.117d
	237	αγ	2.14×10^6y
	235	αγ	396.1d
Uranium	240	βγ	14.1h
	238	αγ	4.468×10^9y
	237	β	6.75d
	236	αγ	2.3415×10^7y
	235	αγ	7.038×10^8y
	234	αγ	2.445×10^5y
	233	αγ	1.585×10^5y
	232	αγ	72y
Protactinium	234m	γ	1.17m
	234	βγ	6.7h
	233	βγ	27.0d
	231	αγ	3.276×10^4y
Thorium	234	βγ	24.1d
	232	αγ	1.405×10^{10}y
	231	βγ	25.52h
	230	αγ	7.7×10^4y (Ionium)
	229	αγ	7340y
	228	αγ	1.9138y
	227	αγ	18.718d
Actinium	228	βγ	6.13h
	227	β(α)γ	21.773y
	225	αγ	10d
Radium	228	βγ	5.75y
	226	αγ	1600y
	225	βγ	14.8d
	224	αγ	3.66d
	223	αγ	11.434d
Francium	223	βγ	21.8m
	221	αγ	4.8m
Radon	222	α	3.8235d
(or Emanation)	220	αγ	55.65s
	219	αγ	3.96s
	218	αγ	35ms
Astatine	218	αβγ	2s (α94%)
	217	αγ	32.3 ms
	216	αγ	300 ms
	215	αγ	0.1 ms
	211	α, EC, γ	7.214h (EC c 55%)
Polonium	218	α(β)γ	3.05m (α99.9%)
	216	αγ	0.15s
	215	α(β)γ	1.78×10^{-3}s (almost all α)
	214	αγ	164.3 μs

Table 5 *continued*

Element	Isotope Mass No	Type of Decay	Half Life
Polonium contd.	213	αγ	4.2 μs
	212	αγ	0.305 μs
	211	αγ	516 ms
	210	αγ	138.38d
Bismuth	214	β(α)γ	19.9m
	213	β(α)γ	45.65m
	212	α(β)γ	60.55m
	211	α(β)γ	2.14m
	210	β(α)γ	5.012d
	209	—	stable
Lead	214	βγ	26.8m
	212	βγ	10.64h
	211	βγ	36.1m
	210	βγ	22.3y
	209	β	3.253h
	208	—	stable
	207	—	stable
	206	—	stable
Thallium	210	βγ	1.3m
	209	βγ	2.2m
	208	βγ	3.07m
	207	βγ	4.77m
	206	βγ	4.20m
	205	—	stable
	204	β	3.779y
	203	—	stable
Europium	155	βγ	4.96y
	154	βγ	8.8y
Samarium	147	α	1.06×10^{11}y (naturally occurring)
Promethium	147	β	2.6234y
Praseodymium	144	βγ	17.28m
Cerium	144	βγ	284.3d
	141	βγ	32.51d
Lanthanum	140	βγ	40.2h
Barium	140	βγ	12.79d
Caesium	137	βγ	30.0y
	136	βγ	13d
	135	β	2.3×10^{6}y
	134	βγ	2.062y
	132	positron, EC, γ	6.5d
Iodine	132	βγ	78h
	131	βγ	8.04d
	129	βγ	1.7×10^{7}y
	125	EC	60.14d
Tellurium	132	βγ	79h
	129m	βγ	34d
	125m	β	58d
Antimony	125	βγ	2.77y
	124	βγ	60.2d
Silver	110m	βγ	249.9d
Rhodium	106	βγ	29.9s
Ruthenium	106	β	368.2d
	103	βγ	39.28d
Technetium	99	βγ	2.13×10^{5}y
Molybdenum	99	βγ	66.69h
Niobium	95	βγ	35.15d
Zirconium	95	βγ	63.98d
Yttrium	91	β	58.51d
	90	β	64.0d
Strontium	90	β	29.12y
	89	β	50.5d
Rubidium	87	β	4.7×10^{10}y (naturally occurring)
Zinc	65	βγ	243.9d
Nickel	63	βγ	96y
Cobalt	60	βγ	5.271y
	58	positron, γ, EC	70.8d
	57	βγ	270.9d
Iron	60	β	1×10^{5}y
	59	βγ	44.529d
	55	EC, x-ray emission	2.7y

Table 5 *continued*

Element	Isotope Mass No	Type of Decay	Half Life
Manganese	54	EC, γ	312.5d
Chromium	51	EC, γ	27.704d
Calcium	45	β	163d
Potassium	40	$\beta\gamma$	1.28×10^9y (naturally occurring)
Chlorine	36	β	3.01×10^5y
Sulphur	35	β	87.44d
Phosphorus	33	β	25.4d
	32	β	14.29d
Sodium	22	positron	2.602y
Carbon	14	β	5730y
Hydrogen	3	β	12.35y (Tritium)

Note: Stable isotopes can be separated and used as tracers. Nitrogen 15, Carbon 13 and Hydrogen-2 (Deuterium) are the most important. The ratio between the isotopes of certain stable elements can vary either with locality or as a result of natural processes which are very sensitive to differences in atomic weight. Such elements are sometimes used for research especially into events that have happened in the distant past. Among these elements are oxygen, sulphur, the lanthanides and lead.

A

Measurement of Alpha Activity in Non-saline Water Using a Thick Source Method (Tentative Method)

A1. Performance characteristics

A1.1	Determinand	Alpha emitting radionuclides, not volatile at 350°C. Supported volatile radionuclides may be measured to an extent determined by half life, matrix retention (of the volatile species) and the duration of measurement (counting time).
A1.2	Type of Sample	Raw and Potable waters.
A1.3	Basis of Method	The acidified sample is concentrated, sulphated if necessary and ignited at 350 ± 10°C. A relatively thick counting source is prepared from the dried dissolved solids. Alpha activity of the residue is measured using an alpha particle detector system.
A1.4	Range of Application	Dependent on the amount of inorganic material in the water and performance characteristics (background count rate and counting efficiency) of the counter.
A1.5	Standard Deviation	Using ^{238}Pu at a concentration of 0.4 Bq.l^{-1} of water with an ignited residue of 0.5 g.l^{-1}, a 5 cm diameter source and 60000 seconds count duration, a within batch relative standard deviation (1σ) of 5.1% (sulphated), 6.8% (non-sulphated) was obtained (5 degrees of freedom).
A1.6	Limit of Detection	Using a water with an ignited residue of 0.5 g.l^{-1}, a 5 cm diameter source, 60000 seconds count duration and a background count rate of 0.0016 s^{-1} and an efficiency of 6.1% (for ^{239}Pu) the limit of detection is 37 mBq.l^{-1} (sulphated) and 65 mBq.l^{-1} (non-sulphated). These data have 5 degrees of freedom.
A1.7	Sensitivity and Bias	Dependent on the amount of inorganic material in the water, characteristics of the detector and the radionuclides present.

Typical Instrument responses:

	MeV approx.	Counting efficiency	
		Counter A	Counter B
^{241}Am	5.4 – 5.5	—	0.11
^{239}Pu	5.1 – 5.15	0.061	0.071
U natural isotopic	^{238}U = 4.2 ^{234}U = 4.75 ^{235}U = 4.4	0.036	0.064
^{252}Cf	6.12	0.066	0.13

The above figures were calculated from data supplied by LGC using a silver activated zinc sulphide scintillation screen detector. The efficiencies obtained for alpha emitters vary from counter to counter depending on geometry and types of detector. Relative efficiencies for different energy alpha emitters must be checked periodically for

		each counter. The two sets of figures given illustrate this from different counters. Note that measurement of alpha emission is more sensitive to variation than beta.
A1.8	Use of the Method, and Time Required	This method may be used for monitoring background and natural radiation, and also for the screening of samples to select those needing more detailed analysis. Such screening may be achieved in about 12 hours per instrument per sample. Regular monitoring takes longer.

A2. Principle

The sample is acidified to stabilize it, evaporated almost to dryness and ignited at 350°C after conversion to sulphate if necessary. A portion of the residue is transferred to a planchette and the alpha activity measured by counting in an alpha particle detector/counting system previously calibrated against an alpha emitting standard.

A2.1 Sulphation is the preferred technique which should only be omitted if there is prior knowledge that no problem such as hygroscopicity will result from its omission. It should be included if comparison is being made with results obtained using that technique. Variation in counter and planchette size may cause changes in the initial results obtained.

A3. Hazards

See also warning on preparation of alpha standard sources (Step A7.11). High voltages are used in counting equipment; consult manufacturers' instructions.

Strict regulations set out in the Radioactive Substances Act (1960) cover the use of radioactive materials in laboratories. These regulations are enforced by the Radiochemical Inspectorate of the Department of the Environment (ref 39), who should be contacted by prospective users.

A4. Reagents

A method for preparing reagent blanks to check for endemic radioactivity or contamination is given in section A9.1.

All reagents must be checked for activity and in practice no detectable alpha activity can be tolerated; for chemical purity, Analytical grade is a minimum requirement.

A4.1 *A standard solution of* ^{241}Am

Radiochemical standards are available from several sources including Amersham International plc; Atomic Energy Research Establishment (A.E.R.E.) Harwell; British Nuclear Fuels plc (B.N.F.L.) Capenhurst; The US National Bureau of Standards; and International Atomic Energy Agency (I.A.E.A.) Vienna, Austria.

^{241}Am is preferred to ^{239}Pu, because the latter frequently suffers from the presence of ^{241}Pu which leads to ingrowth of ^{241}Am in prepared standard solutions or sources. Although Uranium compounds are more readily available, their isotopic composition is often far from certain.

A4.2 *50% V/V Nitric Acid*

Dilute 100 ± 5 ml of nitric acid (d_{20} 1.42) to 200 ± 10 ml with distilled (or deionized) water.

A4.3 *Sulphuric Acid* (d_{20} 1.84)

A4.4 *Methanol*

(see also A7.9 note (h)).

A4.5 *Calcium Sulphate Dihydrate* $CaSO_4 . 2H_20$

Calcium salts may contain trace amounts of ^{226}Ra and/or ^{210}Pb. Checks should be made and active material should not be used.

A5. Apparatus

A5.1 *Alpha counter*

The simplest type of alpha counter consists of a silver activated zinc sulphide scintillation screen which is optically coupled to a photomultiplier and amplifier/scaler system. The Zn(Ag)S screen and photomultiplier are contained in a light-proof counting head and the sample planchette is introduced via a light-tight drawer or slide. Automatic sample changer systems are also commercially available.

Although the use of other alpha detection systems (silicon surface barrier (SSB) and proportional counters) is not precluded the particulate solids of the prepared sources may give rise to contamination problems in vacuum or gas flow systems.

A5.2 *Planchettes*

The diameter of the planchette (counting tray) to be used is determined by the counter requirements, ie detector diameter and source holder dimensions.

Lipped stainless steel planchettes of thickness at least 250 $mg.cm^{-2}$ should be used and the sources can be presented for either alpha or beta counting.

For thick source preparation it is usually sufficient to degrease the metal by immersion in 1.1.1 trichloroethane (or other suitable solvent) followed by drying with a clean cloth.

Some workers find it easier to produce evenly spread sources on a polished metal surface whereas others prefer to use an etched or roughened planchette (sand blasting and chemical etching have been applied for this purpose). The choice must be left to the individual to determine by practice with mixtures of chemicals which approximate to the composition of local natural water's solids (sulphated or not sulphated as appropriate).

A6. Sample Collection

A6.1 *Stabilization*

To a clean polyethylene bottle add 20 ± 1 ml of 50% v/v nitric acid per litre of sample to be collected, and then collect the sample. The acidification minimizes the adsorption of radioactivity onto the walls of the bottle.

A6.2 *Filtration*

Whether the sample is filtered or not will depend on the purpose of the analysis. Any filtration should be carried out immediately on collection, and before acidification (see section A6.1).

A6.3 *Undue Delays*

Because delay and ingrowth will change the activity of the sample, work should be so planned that samples are examined as soon after collection as possible and all delays timed.

A7. Analytical Procedure

Note: When analysing samples for comparison with past data, it is essential to use the same time intervals and procedure as before, or know how to correct for the differences. Similarly to facilitate comparison with future results it is recommended that all delays be timed and recorded.

Step	Procedure	Notes
	Preliminary	
A7.1	Using a small aliquot from the sample determine the total solids content of the water (Note (a)). Making due allowance for changes in composition due to ignition at 350°C and sulphation of the residue, if appropriate. Calculate the volume of the sample required to produce a mass of solid residue slightly in excess of 10 A mg (where A is the area of the planchette in cm^2). Use this as a guide to the volume of sample required for the concentration stage, which follows.	(a) The procedure for determining the total solids content can be found in 'Suspended, Settleable and Total Dissolved Solids in Waters and Effluents 1980' in this series (Ref 38)

Step	Procedure	Notes
	Concentration Stage	
A7.2	Transfer a measured volume of sample V (±1%) litres (note (b)) to a beaker. Evaporate carefully on a hot plate until the volume is reduced to about 50 mls and allow to cool.	(b) A volume should be chosen such that after ignition there is at least 10A mg of residue, where A cm^2 is the area of the counting tray. See also note (d). With very soft waters it is possible that the volume required to produce 10A mg is impractically large; in these circumstances the largest practicable volume should be used. See also note (g).
A7.3	Transfer the concentrated solution to a tared silica (or glazed porcelain) dish, previously ignited at 350°C. Wash the beaker carefully with the minimum quantity of distilled water and transfer the washings to the dish (note (c)).	(c) If the beaker is large, then it may be convenient to transfer the washings to a smaller (eg 500 ml) beaker; the washings can then themselves be concentrated to low bulk to facilitate transfer to the silica dish.
A7.4	Sulphation stage (note (d)). Allow to cool completely and add 1 ml (±20%) of concentrated sulphuric acid.	(d) Some waters may, on drying and ignition, produce a residue which is unsuitable for the measurement of radioactivity, (hygroscopic or difficult to disperse). A suitable treatment for many such samples is the sulphation as described in section A7.4. The volume of sulphuric acid chosen is capable of sulphating about 1.8 g of calcium carbonate. To allow for an excess of acid, the initial volume of sample should be chosen such that the total solids content does not exceed 1 g. Only omit this stage if prior experience has shown that good planchettes can be prepared without it and the results are not to be compared with results obtained using sulphation.
A7.5	Carefully evaporate the contents of the dish to dryness (note (e)).	(e) To avoid spitting, the dishes should be exposed to top-heat (from say an I.R. lamp) and, if the sulphation stage has been included, heating should continue until fumes of sulphuric acid are evolved; the dishes can then be transferred to a hot-plate and heating continued until no further fumes are evolved.
A7.6	Ignite in a muffle furnace for 1 hour ± 5 mins at a temperature of 350 ± 10°C and allow to cool in a desiccator. Note time and date.	
A7.7	Weigh the dish and residue and obtain the weight of the ignited residue. Let this weight be W mg.	
A7.8	Weigh out 10A mg (±1%) of the ash onto a counting tray, (notes (f) and (g)).	(f) It is essential to produce a fine, evenly spread homogeneous powder. (g) If the volume used (see note (b)) has produced less than 10 A mg of residue then as much as possible should be mounted on the planchette: let this weight be X mg. Because alpha particle counting efficiency is seriously affected by source thickness, it follows that standard sources (section A7.11.7) of the same mass loading, X mg, are required for calibration of the detection system.
A7.9	Disperse the aliquot evenly over the planchette by slurrying with a few drops of methanol and allow to dry (note (h)). Make a note of the time and date of source preparation. Check weight if necessary.	(h) Other volatile organic solvents can be used, eg acetone. Because alpha particle counting efficiency is seriously affected by source thickness, it is essential to produce evenly spread counting sources.

Step	Procedure	Notes
	Counting Stage	
A7.10	Set up the counter in accordance with the manufacturer's instructions.	
A7.10.1	Immediately after drying the source commence measurement of the activity on the planchette by counting for an appropriate time (note (i)). Let the measured count rate be S.sec^{-1}. Note the time, duration of count, and date.	(i) The duration of count depends on the sample and background count rates and the precision required; see section A8. 1000 minutes is the longest time normally used.
A7.10.2	Measure the background activity using an identical clean planchette. Let the measured count rate be B.sec^{-1}.	
A7.10.3	Repeat the counting procedures in A7.10.1 and A7.10.2 periodically over a period of 1 month (note (j)).	(j) Recounting over a period of one month may reveal ingrowth of daughter radionuclides from radium isotopes. The interpretation of such data can be complicated depending on whether uranium and/or thorium series radionuclides are present in admixture, singly or whether one predominates. At normal environmental levels it is rare for these phenomena to be apparent, particularly when long count durations have been employed. However, over a period of 1 month sources from those raw waters which are naturally high in ^{226}Ra may show an increase of about four times the initial count. Some samples show a substantial reduction in emission rate over the month due to the decay of significant amounts of ^{224}Ra.
A7.11	Preparation of the standard for alpha activity measurement. *Warning* This procedure requires the preparation of a dry powder spiked with alpha emitting radionuclides. Accidental ingestion of radioactive particulates must be avoided and the use of a simple closed cabinet glove box is recommended for the preparation of the spiked sources. Alternatively a laboratory fume cupboard may be used provided the extract draught is not excessive and liable to disturb or carry fine powder particles into the air.	
A7.11.1	Accurately weigh approximately 2.5 g of calcium sulphate (A4.5) into a 150 ml beaker. Carefully add 10 ml ($\pm 1\%$) of hot nitric acid d_{20} 1.42, stir and add hot water (up to 100 mls) to dissolve.	
A7.11.2	To the solution, add an accurately known amount of standard [37 Bq of ^{241}Am is suitable].	
A7.11.3	Transfer the solution to a 200 ml silica or porcelain dish, weighed to ± 0.0001 g and take the solution to dryness under an I.R. Lamp.	
A7.11.4	Ignite the dry residue in a furnace at 350 ± 10°C for 1 hour.	
A7.11.5	Calculate the specific activity (Spα) of the $CaSO_4$ using the weight of the ignited residue and the amount of activity added, Bq.g^{-1} as ^{241}Am.	

Step	Procedure	Notes
A7.11.6	(see note k) Crush and grind the solid (with a pestle if necessary) to produce a fine powder in a manner similar to that used for the preparation of the sample.	(k) Possible hazard. See Warning A7.11.
A7.11.7	Prepare planchette sources (10 A mg) on each planchette) in the manner prescribed for samples. Section A7.8 and A7.9.	
A7.11.8	Measure the alpha response of the detector system, to these standard sources. Let the mean of the measured count rates be K.sec^{-1}.	
A7.12	Calculate the activity C of the water sample from the equation $C = \frac{S-B}{K-B} \times Sp\alpha \times \frac{W}{1000} \times \frac{1.02}{V}$ Equation A1	

Derivation of equation A.1

In general, sample activity

$$C = S_{corr.} \times \frac{1}{E} \times \frac{1}{L} \text{Bq.l}^{-1}$$ Equation G1

Where C = alpha activity in becquerels per litre
S_{corr} = sample count rate corrected for background counts (and if necessary for counter dead time), sec $^{-1}$
E = fractional efficiency of counting of the specified radioactive standard
L = volume of sample equivalent to the mass of solid on the planchette, l

Thus $S_{corr} = S - B$

Where S = observed sample count rate, sec^{-1} (see A.7.10.1)
B = background planchette count rate, sec^{-1} (see A.7.10.2)

$$E = \frac{(K-B)}{10A \times Sp\alpha} \times 1000$$

Where K = observed standard count rate, sec^{-1} (see A.7.11.8)
B = background planchette count rate, sec^{-1} (see A.7.10.2)
A = area of planchette, cm^2
[10A = mass of standard solids, mg, on planchette (see A.7.11.7)]
$Sp\alpha$ = specific activity of the standard solids, Bq.g^{-1} (see A.7.11.5)

$$L = \frac{V}{W} \times 10A$$

Where V = sample volume, litres (see A.7.2)
W = mass of ignited residue from volume V, mg (see A.7.7)

And the general equation G.1 becomes:

Step	Procedure	Notes
	$C = (S-B) \times \frac{10A \times Sp\alpha}{(K-B) \times 1000} \times \frac{W}{V \times 10A} = \frac{(S-B)}{(K-B)} \times \frac{Sp\alpha}{1000} \times \frac{W}{V}$ Because 10 ml of nitric acid, (A.4.3), per litre of sample is added as a stabilizer, it is necessary to correct for this addition and 1020 ml of acidified sample is equivalent to an original 1000 ml. The final activity calculation becomes: $C = \frac{(S-B)}{(K-B)} \times \frac{Sp\alpha}{1000} \times \frac{W}{V} \times 1.02$ Bq.l^{-1} (as specified standard)	
A7.13	Report the results, together with the date of counting, indicating whether or not sulphation was used and also the thickness of source in mg cm^{-2}. For example 0.42 ± 0.04 Bq.l^{-1} (^{241}Am equivalent) The confidence level (2σ) quoted is due to counting errors alone. Counting date : February 1982 Source thickness: 10 mg.cm^{-2} unsulphated	

A8. Precision of Counting

The standard deviation, σ, associated with the activity of the sample corrected for background is

$$\sigma_{(S-B)} = \sqrt{\left(\frac{S}{T_S} + \frac{B}{T_B}\right)}$$

where T_S and T_B are the respective durations of the counts of the sample and background. It is usual to ensure that the standard deviation associated with the counting of the standard alpha source is insignificant compared with that of counting the sample, and to quote the result with a standard deviation 'due to counting errors alone'.

Increasing the counting time will lower the limit of detection, limited only by the effects of daughter isotopes. 1000 minutes is the longest time normally used.

A9. Sources of Error

A9.1 Contamination

It is desirable to carry out the analysis in an area where radio-tracers are not used. Contamination of reagents should be checked by evaporating onto separate planchettes appropriate volumes of the reagents and measuring the activities which should be negligible compared with that of the sample. Contamination of the whole system can be checked by processing 1 litre ± 10 ml of distilled water acidified with 20 ml of 50% v/v nitric acid, to which 10A mg ± 1 mg of chromatographic reagent grade silica gel has been added, and measuring the activity. This can be compared with the activity of a direct slurry of 10A ± 1 mg of the silica gel onto a counting tray. Again, the activity should be negligible compared with that of the sample.

A9.2 Losses of Activity

A9.2.1 *Radon Isotopes*

It is obvious that some radionuclides will be lost by volatization in this method. Of the radionuclides in the uranium series, ^{222}Rn would be lost during processing, but with its

α and β-emitting daughters may subsequently grow back in to the counting source from any ^{226}Ra present. A similar effect occurs with radionuclides from the ^{232}Th series.

A9.2.2 *Polonium*

Some alpha emitting Polonium isotopes which occur naturally as members of the uranium and thorium decay series may comprise a significant proportion of the gross alpha activity of some waters. The element and some of its compounds, particularly the halides which sublime at relatively low temperatures, (ref 33) may be volatilized. Nitrates (refs 33 and 34) and sulphates (ref 33) are stable up to temperatures of at least 400–500°C, and losses of polonium are not therefore expected from samples which have been acidified with nitric acid or subjected to sulphation.

A9.3 Variation of Response of the System

The unavoidable effect of self-absorption will result in a variation of counting efficiency depending on the composition of the radioactivity in the water. If necessary, the response of the system to radionuclides which might be encountered can be determined by spiking silica, calcium sulphate or other blank materials with known quantities of standard solutions of these radionuclides. After careful drying and homogenization, sources 10A mg cm^{-2} thick can be prepared and counted. The response of the counter in count rate per unit of activity (counts s^{-1}. Bq^{-1}) can then be calculated.

A10. Quality Control

Apart from the manufacturer's suggestions for instrumental quality control, the standards and background trays should be counted with each batch of samples and a suitable quality control graph prepared refs 35, 36 and 37.

An operator's performance can be checked by the production of at least six counting sources prepared from 1 litre portions of distilled water, to each of which a known amount of an alpha emitting radionuclide and soluble calcium compound has been added; the quantity of the latter added must be sufficient to ensure that, after ignition (following conversion to sulphate form if necessary), at least 10A mg of residue is available to prepare a source for counting. The preparation of a set of standards as in A7.11, is also a useful introductory exercise.

A11. Regulations Covering the Use of Radioactive Materials

Regulations governing the use of radioactive materials and the disposal of radioactive wastes in the UK are set out in another booklet of this series ref 30.

Safeguards Legislation

The acquisition of standard materials described in A4.1 other than Americium, ***however small the amount may be***, will bring the purchaser within the scope of the Euratom Treaty on the non-proliferation of nuclear weapons. EEC countries, as signatories to the Commission Regulation No 3227/76 of 19 October 1976, have to account for the acquisition transfer and usage of 'source materials' (Uranium and Thorium in all forms) and 'special fissile materials' (Plutonium and enriched Uranium at the present time).*

The application of the legislation within individual nations should be ascertained before embarking on the purchase of any of the listed materials.

The responsible body for the UK is:
Safeguards Office
Department of Energy
Atomic Energy Division
Thames House South
Millbank
London
SW1P 4QJ

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*Note that although certain specified small scale exemptions exist as for possession of gas mantles, they are not applicable to materials used in this method.

B Measurement of β-Activity

B.1 Performance Characteristics of the Method

B1.1	Substance determined	Non-volatile β-active radionuclides with β-max energies >0.3 MeV. Very low energy β-emitters including ^{3}H, ^{14}C, ^{35}S and ^{241}Pu will not be determined. See section B1.7, B9.2 and B9.3. See also Section B7, initial note ii.
B1.2	Type of samples	Raw and potable waters.
B1.3	Basis of method	The acidified sample is concentrated, sulphated if necessary and ignited. The activity of the residue is measured with a Geiger counter.
B1.4	Range of application	Sample size is limited by the dissolved inorganic solids content of the water and the size of planchette that can be accepted by the counting equipment in use.
B1.5	Standard deviation	A test sample spiked with 723 mBq.l^{-1} of ^{137}Cs gave the following performance figures with the sulphated residue procedure. The table shows the variable parameters which affect the standard deviation (σ)

Laboratory	Source area cm^{2}	Counting time (s)	Background count rate (c. s^{-1})	Counting efficiency to ^{40}K (counts per disintegration)	Degrees of freedom (n − 1)	Activity found	
						mBq.l^{-1}	%σ
AERE	19.6	1.2×10^{4}	0.014	0.29	5	370	6.9
LGC	20.3	6×10^{4}	0.116	0.29	5	401	3.7
WRC	19.6	6×10^{4}	0.153	0.30	5	409	16.9

* AERE—Atomic Energy Research Establishment (Harwell)
LGC —Laboratory of the Government Chemist (London)
WRC —Water Research Centre (Stevenage)

B1.6	Limit of detection	The Limit of Detection is dependent on the inorganic components of the water, the radionuclides present, the equipment used and the length of counting time. With a sulphated residue the following results were obtained with the 723 mBq.l^{-1} ^{137}Cs test sample. Source area, counting time, background count rate and degrees of freedom are the same as given in the standard deviation table above.

Laboratory	Residue*		Limit of detection mBq.l^{-1}
	W/V	σ W/V	
AERE	522	1.4	40
LGC	578	2.8	70
WRC	535	2.5	114

*See section B7 for definition of W and V

B1.7 Sensitivity

Dependent on the inorganic components of the water, the equipment used and the radionuclides present. Typical instrumental responses have been determined[a].

Nuclide	β Max (MeV) (Ref 26)	%	β Mean (MeV) (Ref 60)	%	Counting efficiency (b) (counts per disintegration)	Relative sensitivity (^{40}K = 1)
^{106}Ru/Rh	3.5	68	1.508	78.8	0.27	1.12
	3.1	11	1.267	8.4	(0.29)	
	2.4	12	0.976	9.7		
^{40}K	1.32	90	0.585	89.3	0.24	1.00
					(0.22)	
^{137}Cs	0.51	94	0.1734	94.6	0.18	0.73
	1.76	6	0.426	5.4	(0.14)	

(a) These figures have been calculated from data supplied by the Fisheries Laboratory, Lowestoft, Suffolk, using a 2-inch diameter anticoincidence Geiger counter. Counting efficiency figures in brackets are supplied by LGC.

(b) The efficiency obtained for beta emitters varies from counter to counter depending on geometry and type of detector. Relative efficiencies should be checked periodically for each counter.

B1.8 Bias

From information given in B1.7 it can be seen that the detector response varies with the β-energy of the radionuclides present. Using ^{40}K as a standard leads to an over estimate of radionuclides decaying with β-max >1.32 MeV and an under estimation of those with lower β-max. Standards should preferably be matched as closely as possible to the mean β-energy of the radionuclides present in the sample.

B1.9 Use of this Method, and Time Required

This method may be used for monitoring natural radioactivity, and also for the screening of samples to select those requiring detailed analysis. Such screening may be achieved in about 12 hours per instrument per sample. Regular monitoring takes longer.

B2. Principle

The sample is acidified to stabilize it, evaporated almost to dryness, converted to the sulphate form if necessary and ignited at a temperature of 350°C. A portion of the residue is transferred to a planchette and the activity measured by counting in a Geiger counting assembly previously calibrated against a potassium standard. (See also Section 7 initial note ii when inclusion of radioiodine is needed).

B2.1

Sulphation is the preferred technique which should only be omitted if there is prior knowledge that no problem such as hygroscopicity will result from its omission. It should be included if comparison is being made with results obtained using that technique.

B3. Hazards

High voltages are used in Geiger counting equipment. Consult manufacturer's instructions.

Strict regulations set out in the Radioactive Substances Act (1960) cover the use of radioactive materials in laboratories. These regulations are enforced by the Radiochemical Inspectorate of the Department of the Environment. For further information, see Reference 39.

B4. Reagents

Analytical grade reagents are a minimum requirement.

B4.1 Water

The water used for blank determinations in the method itself and in the preparation of other reagents should have a radioactive content which is low compared with that of the smallest amount encountered in the samples.

B4.2 Potassium chloride

Dried to constant weight at 105°C.

B4.3 50% V/V nitric acid

Dilute 100 ± 5 ml of nitric acid (d_{20} 1.42) to 200 ± 5 ml with distilled (or deionized) water.

B4.4 Sulphuric acid (d_{20} 1.84)

B4.5 Methanol

(See also B7.9 notes (h)).

B5. Apparatus

B5.1 Low background Geiger counting assembly

The distance of the source from the detector should not exceed 1 cm (1 cm of air ≡ 1 $mg.cm^{-2}$ thickness). The detector system should be capable of presenting an external absorber thickness of 7 ± 2 $mg.cm^{-2}$ to the source: this can be achieved by the use of either the detector end-window alone or a thinner end-window with an added absorber of appropriate thickness. In addition any coincidence/anticoincidence arrangements for background reduction should not affect the response of the system to different energies of emission.

B5.2 Planchettes

These should be of lipped stainless steel of thickness at least 250 $mg.cm^{-2}$; this ensures that saturation backscatter is achieved for energies up to 3.5 MeV. The diameter of the planchette (counting tray) to be used is determined by the counter requirements i.e. the detector diameter and source holder dimensions.

For thick source preparation it is usually sufficient to degrease the metal by immersion in 1.1.1-trichloroethane (or other suitable solvent) followed by drying with a clean cloth.

Some workers find it easier to produce evenly spread sources on a polished metal surface whereas others prefer to use an etched or roughened planchette (sand blasting and chemical etching have been applied for this purpose). The choice must be left to the individual to determine by practice with mixtures of chemicals which approximate to the composition of local natural water's solids (sulphated or not sulphated as appropriate).

B6. Sample Collection

B6.1 Stabilization

To a clean polythene bottle add 20 ± 1 ml of 50% V/V nitric acid per litre of sample to be collected, and then collect the sample. The acidification minimizes the adsorption of radioactivity onto the walls of the bottle.

B6.1.1 If radioiodine is to be determined the sample bottle walls may be iodized. For details, see Ref 63. It is also advisable to add 1 ± 0.1 g of non-radioactive sodium iodide per litre of sample as a carrier. Materials used to iodize the bottle should also be free from radioactivity.

B6.2 Filtration

Whether the sample is filtered or not will depend on the purpose of the analysis, and this should be carried out immediately on collection and before acidification (see section B6.1).

B6.3 Undue Delays

Because decay and ingrowth will change the activity of the sample, work should be so planned that samples are examined as soon after collection as possible and all delays timed.

B7. Analytical Procedure

Notes:

(i) Because it is impracticable to apply decay corrections to unknown mixtures of radionuclides, it is essential when expecting to make comparison with later data, to arrange for consistent relative timing of the sampling, source preparation and counting steps.

Date and time records should be kept.

(ii) **If it is necessary to include iodine radionuclides** in a beta screening measurement, collect a separate sample containing sodium iodide carrier (B.6.1.1). Carry out the procedure with the following amendments. Make the sample just alkaline with sodium hypochlorite solution prior to evaporation at step B.7.2 and omit steps B.7.4 and B.7.6. Data from this modified procedure will not be comparable with results from the standard technique where conditions will lead to some, if not complete, loss of iodine by volatilization.

Step	Procedure	Notes
	Preliminary	
B7.1	Using a small aliquot from the sample determine the total solid content of the water (Note (a)). Calculate the volume of sample required to produce a mass of solid residue slightly in excess of 10A mg (where A is the area of the planchette in cm^2) making due allowance for changes in composition due to ignition at 350°C and sulphation of the residues, if appropriate. Use this as a guide to the volume of sample required for the concentration stage which follows.	(a) The procedure for determining the total solids content can be found in 'Suspended Settleable and Total Dissolved Solids in Waters and Effluents 1980' in this series (Ref 38).
	Concentration Stage	
B7.2	Transfer a measured volume V($\pm$1%) litres to a beaker. (Note (b)). Evaporate carefully on a hot-plate until the volume is reduced to about 50 ml and allow to cool.	(b) The volume should be chosen such that after ignition there is at least 10A mg of residue, where A cm^2 is the area of the planchette. See also note (d). With very soft waters it is possible that the volume required to produce 10A mg is impractically large; in these circumstances the largest practicable volume should be used. If radioiodine is to be determined make just alkaline with sodium hypochlorite prior to evaporation.
B7.3	Transfer the concentrated solution to a tared silica (or glazed porcelain) dish previously ignited at 350°C. Wash the beaker carefully with the minimum quantity of distilled water and transfer the washings to the dish. (Note (c)).	(c) If the beaker is large, it may be convenient to transfer the washings to a smaller (eg 500 ml) beaker: the washings can then themselves be concentrated to a low bulk to facilitate transfer to the silica dish.
	Sulphation Stage. (Note (d)).	
B7.4	Allow to cool completely and add 1 ml ($\pm$20%) of concentrated sulphuric acid.	(d) Some waters may on drying and ignition, produce a residue which is unsuitable for the measurement of radioactivity, (hygroscopic or difficult to disperse). A suitable treatment for many such samples is the sulphation as described in section B7.4. The volume of

Step	Procedure	Notes
		sulphuric acid chosen is capable of sulphating about 1.8 g of calcium carbonate. To allow for an excess of acid, the initial volume of sample should be chosen such that the total solids content does not exceed 1 g. Only omit this stage if prior experience has shown that good planchettes can be prepared without it, or radioiodine is to be included in the count; the results so obtained are not to be compared with results obtained using sulphation.
B7.5	Carefully evaporate the contents of the dish to dryness. (Note (e)).	(e) To avoid spitting, the dishes should be exposed to top-heat (from an I.R. lamp or similar) and if the sulphation stage has been included, heating should continue until fumes of sulphuric acid are evolved; the dishes can then be transferred to a hot-plate and heating continued until no further fumes are evolved.
B7.6	Ignite in a muffle furnace for one hour at a temperature of 350 ± 10°C and allow to cool in a desiccator.	
B7.7	Weigh the dish and residue and obtain the weight of the ignited residue. Let this weight be W mg.	
B7.8	Weigh out 10A mg (±1%) of the ash onto a planchette. (Notes (f) and (g)).	(f) It is desirable to produce a fine, evenly spread, homogeneous powder. (g) If the volume used (see note b) has produced less than 10A mg of residue then as much as possible should be mounted on the planchette: let this weight be X mg.
B7.9	Disperse the aliquot evenly over the planchette by slurrying with a few drops of methanol and allow to dry. (Note (h)).	(h) Other volatile organic solvents can be used, e.g. acetone.
	Counting Stage	
B7.10	Set up the Geiger counting assembly according to the manufacturer's instructions.	
B7.11	Measure the activity on the planchette by counting for an appropriate length of time. (Note (i)). Let the measured count rate be S sec^{-1}. (Note (j)).	(i) The length of count depends on the sample and background count rates and the precision required: see section B8. 1000 minutes is the longest time normally used.
B7.12	Measure the background activity using an identical clean tray. Let this measured count rate be B sec^{-1}.	(j) If standards and samples are recounted after 3 days, any reductions in radiation will be indicative of any short-lived radionucleides However, this is complicated by the possible ingrowth of daughter species such as ^{90}Sr and ^{90}Y.
B7.13	Using potassium chloride instead of sample ash carry out steps B7.8 to B7.11 inclusive. Let the measured count rate be K sec^{-1}.	
B7.14	Calculate the activity C of the solution from the equation: $C = S_{corr} \times \frac{1}{E} \times \frac{1}{L} Bq.1^{-1}$ Equation G1	

Step | Procedure | Notes

where C = beta activity in becquerels per litre.

S_{corr} = sample count rate per second corrected for background counts and if necessary counter dead-time (see $^{-1}$).

E = fractional efficiency of counting of the specified radioactive standard.

L = volume of sample equivalent to the mass of the solid on the planchette. (l)

Thus $S_{corr} = S - B$

where S = observed sample count rate (sec^{-1}) (B7.11)

B = background planchette count rate (sec^{-1}) (B7.12)

And $E = \dfrac{(K - B) \times 1000}{10A \times 14.4}$ (Note k)

where K = observed standard count (B7.13)

B = background planchette count rate (sec^{-1}) (B7.12)

A = area of planchette (cm^2).

10A = mass of potassium solids on planchette (mg) (B7.13)

(k) The β-activity of ^{40}K in natural potassium is 27.4 $Bq.g^{-1}$ and hence in potassium chloride is $\dfrac{14.4}{1000} Bq.mg^{-1}$. One becquerel is one disintegration per second.

Now $L = \dfrac{V}{W} \times 10A$

where V = volume of sample (litres) (B7.2) and W (mg) is the mass of ignited residue from volume V (B7.7).

And the general equation becomes,

$$C = \frac{(S - B) \times 10A \times 14.4 \times W}{(K - B) \times 1000 \times V \times 10A}$$

$$= \frac{(S - B) \times 14.4 \times W}{(K - B) \times 1000 \times V}$$

The final activity equation becomes:

$$C = \frac{(S - B) \times 14.4 \times W \times 1.02}{(K - B) \times 1000 \times V} Bq.l^{-1}$$

(Note (l)).

(l) The factor 1.02 must be included in the final equation to correct for the 20 ml of nitric acid added per litre as stabilizer (see section B6.1).

B7.15 If it is required to express the radioactivity of the sample without that of ^{40}K, its contribution to the original sample can be assessed by measuring the potassium content of the original sample e.g. by flame photometry or atomic absorption spectrophotometry (Note (m)) and deducting this activity, see note (k).

(m) Procedures for the determination of potassium can be found in 'Dissolved Potassium in Raw and Potable Waters Tentative Method 1980'. Methods for the Examination of Waters and Associated Materials in this series. (Ref 44).

Step	Procedure	Notes
B7.16	Report the results together with the date of counting indicating whether or not sulphation was used, and also the thickness of source in mg.cm^{-2}. For example 2.0±0.5 Bq.1^{-1} (^{40}K equivalent); The standard deviation, 2σ, quoted is due to counting errors alone. Counting date 28 Feb. 1982. Unsulphated; source thickness 10 mg.cm^{-2}. (Note (n)).	(n) See also section B8.

B8. Precision of Counting

The standard deviation (σ) associated with the activity of the sample corrected for background is:

$$\sigma_{(S-B)} = \sqrt{\left(\frac{S}{T_s} + \frac{B}{T_B}\right)}$$

where T_s and T_B are the respective durations of the counts of the sample and background. It is usual to ensure that the standard deviation association with the counting of the standard potassium chloride source is insignificant compared with that of counting the sample, and to quote the result with a standard deviation 'due to counting errors alone'.

B9. Sources of Error

B9.1 Contamination

It is desirable to carry out the analysis in an area where radio-tracers are not used. Contamination of reagents should be checked by evaporating appropriate volumes of the reagents on separate planchettes and measuring the activities, which should be negligible compared with that of the sample. Contamination of the whole system can be checked by processing 1 litre ±10 ml of distilled water acidified with 20±1 ml of 50% V/V nitric acid to which 10A±1 mg of chromatographic reagent grade silica gel has been added and measuring the activity. This can be compared with the activity of a direct slurry of 10A±1 mg of the silica gel onto a counting planchette. Again the activity should be negligible compared with that of the sample.

^{60}Co may be encountered as a contaminant in stainless-steel and may therefore affect the background count but not necessarily the sample.

The specification for some ion-exchange resins indicate that ^{90}Sr may be present in the resin (and can be eluted). Hence, if deionized water is used all new supplies should be checked before use.

B9.2 Losses of Activity

It is obvious that some radionuclides will be lost or not measured by this method. For example ^{3}H, ^{14}C and some ^{35}S will be lost on evaporation and ignition; β-emitters of low energy would not be measured (or would be measured with very low efficiency) with 10 mg.cm^{-2} self absorption and 7 mg.cm^{-2} external absorption. Of the radionuclides in the uranium series, ^{222}Rn would be lost during processing but with its β-emitting daughters ^{214}Pb and ^{214}Bi it would subsequently grow back in to the counting source from any ^{226}Ra present.

B9.3 Variation in response of the system

The unavoidable effect of absorption will result in a variation of counting efficiency depending on the composition of the water. If necessary the response of the system to radionuclides which might be encountered can be determined by spiking silica or other blank materials with known quantities of standard solutions of these radionuclides. After careful drying and homogenization, sources 10A mg.cm^{-2} thick can be prepared and counted. The response of the counter in count-rate per unit of activity (counts.s^{-1}.Bq^{-1}) can then be calculated.

B10. Quality Control

Apart from the manufacturer's suggestions for instrumental quality control, the potassium chloride standards and background planchettes should be counted with each batch of samples and suitable quality control graphs prepared (Refs 35, 36 and 37).

An operator's performance can be checked by the production of at least six counting sources prepared from 1 litre portions of distilled water, to each of which has been added a known amount of potassium chloride. The quantity added must be sufficient to ensure that after ignition (following conversion to potassium sulphate if necessary), at least 10A mg of residue is available to prepare a source for counting.

B11. Regulations Covering the Use of Radioactive Materials

Regulations governing the use of radioactive materials and the disposal of radioactive wastes in the UK are set out in another booklet of this series (ref 30).

C

Gross Gamma Measurement Method for Screening Samples for Radon in Natural Water

C.0 Introduction

C.0.1

This method is intended to prevent the overwhelming of expert laboratories. Its prime use is for the elimination of samples too low in radon content to be worthy of analysis. It can be calibrated by having a series of samples with a range of radon contents analysed by this and the following method; then provided there is good analytical control, it can be used for routine analysis for radon.

C.0.2

Radon is a gas, readily soluble in water, the approximate maximum solubilities are 5g.l^{-1} at 0°C, 2g.l^{-1} at 25°C and 1g.l^{-1} at 40°C. Loss during sampling can contribute a relative negative error. Many plastic bottles are permeable to radon. If there is to be any delay in measurement, glass sample bottles are preferred.

C.0.3

^{222}Rn is the most commonly encountered isotope, unless stated, this is the isotope referred to throughout. ^{220}Rn occurs in some thorium-rich areas and ^{219}Rn also exists in the naturally occurring $(4n + 3)$ decay series. If these latter isotopes are suspected seek expert advice.

C.0.4

Radon is formed by the alpha decay of the various radium isotopes which often remain locked in the rocks while the radon escapes through fissures. Hence although all radium solutions eventually acquire an equilibrium concentration of radon, and this can be used as a means of calibrating radon methods, most natural waters, which do contain any radium at all, frequently contain more than the radon-radium equilibrium amount of radon.

C.0.5

Other radioactive isotopes emit gamma radiation, but in natural waters the amounts of these other elements are likely to be small. Potassium-40 and radium are the most common causes of excess gamma activity, which because of its very long half life will remain virtually constant, while the radon activity in excess of that due to the radon-radium equilibrium decays.

C.0.6

Radon can be removed from water by aeration or boiling, but supported radon will grow back in from any radium present (see method D).

C1. Performance Characteristics of the Method

C1.1	Substance Determined	All gamma emitters within the range of the instrument detector system. Radon, when the only measurable gross gamma radiation is due to the pressence of ^{222}Rn and its decay products.
C1.2	Type of Sample	Clear water supply or river samples.
C1.3	Basis of Method	^{222}Rn is not a γ emitter, but due to its short half-life is always accompanied by its

daughters ^{214}Pb and ^{214}Bi which emit γ radiation detected by this method.

A sample is taken at a known time and without further treatment the whole sample counted in the original sample bottle in a gross gamma counting assembly. The time between sampling and counting should be as short as possible, and less than 2 days. Since the decay of ^{222}Rn is a first-order process ($t_{1/2} = 3.83$ days) two gross gamma measurements separated by a reasonable time period (such as 24 hours) will show whether the measured gamma radiation (above background) is due to ^{222}Rn decay products and this allows simple calculation of the level of ^{222}Rn at the time of sampling. This method requires initial calibration against another method that determines absolute ^{222}Rn.

C1.4 Range of Application

This will be dependent upon the sample size and background of the gamma counter used. Samples with counts corresponding to 50–1000 Bq.l^{-1} have been successfully analysed by this method.

C1.5 Standard Deviation

Blank solutions and natural samples (repetitively counted) gave the following performance figures. These figures are dependent upon the sample size and gamma counter assembly. It must be noted that since this method requires calibration against an absolute method, the performance figures of the latter must also be taken into account. (see Method D).

Sample	Sample Volume (litres)	Counting Time (s)	Mean Count rate* (C.s^{-1}) II	Degrees of Freedom (n – 1)	Activity I (Bq.l^{-1}) II	S.D.$^{+}$ Bq.l^{-1}
Blank	1	600	9.88 ± 0.25	9	—	—
1.	1	600	10.95 ± 0.27	9	31 ± 11.6	3.7
2.	1	600	13.09 ± 0.29	13	92 ± 11	3.8

* includes blank/background

I Radon – 222 level using counter efficiency of 3.5% and blank/background corrected.

\+ Within-batch standard deviation of 10 or 14 consecutive counts.

II Based on 2σ.

C1.6 Limit of Detection

Dependent on the counter system, sample size and duration of count used.

C1.7 Bias

A positive bias is present due to the presence of gamma emitters other than radon daughters. A negative bias due to loss of ^{222}Rn gas can occur.

C1.8 Interferences

Other gamma emitters if present in sufficient amount.

C1.9 Time required for analysis

Counting time of 10–20 minutes, or longer for a low level of activity in the sample. Analyst's time ca. 5 minutes per sample including calculations. Does not include time spent on calibration and setting up of the instrument.

Data supplied by South West WA.

C2. Principle

In natural, environmental water samples it is possible that any ^{222}Rn present at a level of interest will be unsupported. In other words, the level of ^{222}Rn will be far above the equilibrium concentration with ^{226}Ra. Should this not be the case, high levels of gross alpha radiation (after ^{222}Rn removal) will be evident.

The sampling time is noted as is the time of counting. A background count may be obtained by filling a bottle identical to the sampling bottle with aged distilled or tap water, having first ascertained the absence of ^{222}Rn. Occasional checks should be made that the environmental samples under investigation reach the typical background level after ^{222}Rn decay (viz after more than 27 days). Since the radioactive decay is a first-order process the level of ^{222}Rn at the time of sampling may be calculated from the first-order rate law knowing the efficiency of the counting system. The initial activity may be determined by recording the counts per second (cps) at the time of counting, and then calculating the cps at the time of sampling (time 0). An independent determination of ^{222}Rn, by an absolute method on replicate samples, allows a calculation of the gross gamma counting efficiency for ^{222}Rn to be made for the particular counting assembly, sample size and bottle geometry and type used. A change in any of these will necessitate a recalibration.

C3. Interferences

Other gamma emitters.

In normal circumstances the only other gamma emitter likely to be encountered is ^{40}K. Potassium can be measured independently and its activity calculated.

C4. Hazards

Radon should not be inhaled. For natural environmental samples laboratory precautions are not necessary unless, for any reason, large volumes of water are aerated to remove Radon from a substantial number of samples over a short-time period. If this is the case the aeration should be performed in a fume cupboard.

High voltages are used in counting equipment. Consult manufacturers' instructions.

C5. Reagents

C5.1 Blank Background Water

Freshly distilled water aged in a closed counting bottle for at least 27 days before use.

C6. Apparatus

C6.1 Counting Equipment

A suitable gamma radiation detector and associated electronics with a simple arrangement which allows the sampling bottle to sit upon the detector with a lead shield fitting snugly against the sides of the bottle holding it centrally on the detector head. A typical arrangement would use 1 litre plastic bottle fitting into a turret of lead shielding. Ideally, the detector and sample container should be enclosed completely in a lead castle. Reproducible sample—detector geometry is essential.

C6.2 Sample bottles

Typically 1 litre plastic bottles would be used. A check can be made that no radon permeates the sides of the bottle chosen by following the radon decay over a period of 3 or 4 half-lives. If first-order decay is observed with an associated half-life of 3.83 ± 0.2 days then it is unlikely that any radon gas is being lost from the bottle.

Standard glass Kilner jars have also proved suitable.

C7. Sampling Procedure

C7.1

The sampling bottles should be filled to the brim by introducing the sample with the minimum agitation possible.

C7.1.1

Provided there is sufficient room, bottles can be filled without aeration or pouring by turning them on the side and gently inserting the lower part of the rim first into the water, displacing the air without any bubble formation. Caps can be similarly immersed and bottles closed under water.

C7.1.2

If filling from a pipe see (ref 40) sampling for dissolved oxygen.

C7.2

The date and time of sampling should be recorded. Where practicable, the sample should be cooled below the water temperature at the time of sampling and kept cool but not frozen until counted.

C7.3

Samples should preferably be analysed within 48 hours of sampling; but not before 5 hours after sampling. The latter is necessary because there is an initial increase in observed c.p.s. with time before the first-order decay curve is followed. This is due to the ingrowth of the Radon-222 daughter products with an eventual equilibrium position being reached.

C8. Analytical Procedure

Step	Procedure	Notes
C8.1	Count the sample in the counting assembly for 10 minutes or as long as is necessary to give an adequate count and record the total count and the starting and finishing times between which the count was carried out.	
C8.2	Count the background sample of freshly distilled water for the same time duration and then record the total count and the times of starting and finishing, as in C8.1.	
C8.3	To ascertain that the observed (above background) gross gamma counts from the sample are solely due to radon-222 and decay products in the sample, the sample should be counted again, typically 24 hours after the first counts. Calculations of the cps at time 0 should be within ±5% for both measurements.	
C8.4	To differentiate between radon from the equilibrium with dissolved radium, and radon leaked from the surroundings, aerate the sample vigorously for a minimum of 2 hours, then stand the sample for a reasonable period (10 or more days) and reanalyse. Then the radon value due to equilibrium with any radium can be calculated. (Note (a)).	(a) Tests by SWWA show that the absolute outgassing of a radon sample by air blowing can be a very lengthy process.

C9. Calculation of Radon-222 activity

Assuming that all the gross gamma activity (above background) is due to the presence of radon-222 and its decay products the following equation may be derived from the first-order decay rate law (using a half-life of 3.83 days).

$$[\mathrm{Rn}]_0 = \frac{100 \times \mathrm{antilog}_{10}\ [(\log_{10} C_t) \times 0.908 \times t \times 10^{-6}]}{\mathrm{Ef}}$$

where $[\mathrm{Rn}]_0$ is the concentration of radon-222 (in $\mathrm{Bq.l}^{-1}$) at time 0 (the time of sampling).

C_t is the observed counts per second (after correcting for background) from the sample.

t is the difference (in seconds) between the time of sampling and the midpoint time of the count.

Ef is the efficiency of the counting assembly (expressed as a percentage) for radon-222. (see either C.10 or Method D).

C10. Calibration against other methods

Preferably using replicate unsupported (radium free) samples, analyse one set either by the above method, and the other set either by a method in the references section (preferably refs 46 or 47 or use method D which follows, which is similar to that given in Ref 46).

Use the data obtained by one of these procedures to calibrate the preceding method.

C11. Instrumental Stability Control

Prepare a standard strength Potassium Chloride solution such as 3 molar by dissolving (223.7 ± 0.1 g for 3M) potassium chloride (predried at 150°C to constant weight) in about 900 ml of warm water, cool and make up to 1 litre in a calibrated flask. Use this solution as a reference sample for analytical quality control with each batch of samples. Investigate any significant change in response.

D Determination of Radon and Radium

D.0 Introduction

The radioactive noble gas radon occurs naturally as three isotopes (see the decay series at the front of this booklet); but, as can be seen from the half-lives of these isotopes, only radon-222 will be determined by this method. Only very minute amounts of ^{220}Rn and ^{219}Rn occur in normal British waters

Most methods for the determination of radon are also intended for the determination of radium. Supported and unsupported radon are normally first removed and determined as total radon. Then a fresh crop of radon daughter is allowed to grow back into the radium-containing sample and the radium content is calculated from a measurement of the in-grown daughter radon. Radium may also be separated from the original sample by co-precipitation with barium sulphate and counted directly, or by ingrowth of radon in this precipitate; but this may be complicated if more than one radium isotope is present.

Radon is usually removed from the sample by bubbling a gas through it, or by solvent extraction into a solvent such as toluene.

References 46–52 refer to methods based on degassing a sample, collecting and measuring the radon. References 53 to 55 refer to methods using solvent extraction and measurement of the radon. Ref 18 contains a method p590ff based on radium precipitation followed by ingrowth of radon intended to measure radium.

The method which follows is based on the outgassing of the radon, collection and measurement of the activity using a scintillation counter technique.

D1. Performance Characteristics of the Method

D1.1	Substance determined	Radon – 222. Radium – 226 may also be determined on the same sample using the same method.
D1.2	Type of Sample	All types of water and aqueous effluent. The radon evolved from porous suspended solids may also be included if not removed by filtration. Radon trapped in solids will not be determined unless the solids are dissolved. This method is suitable for sea water analysis without modification (see Ref 46).
D1.3	Basis of the Method	Separation of radon-222 from samples is achieved either by a closed cycle or a single pass extraction system using helium as the stripping gas. The radon and helium are dried, carbon dioxide removed and the radon absorbed on an activated charcoal trap. At the end of the separation period the radon is desorbed into a Lucas-type low-level alpha scintillation cell and measured radiometrically. If radium-226 is also required, the sample bottle is resealed, stored for up to 30 days and the ingrown radon-222 daughter again measured. From the two radiometric radon-222 measurements the

following can then be mathematically determined:
Radium-226
Radon-222 supported by radium
Radon-222 unsupported by radium

D1.4 Range of Application

This is dependent on the sample size and alpha counter used. Based on published solubility data the expected upper limits for Radon are:
0°C c 5 g.l^{-1} Rn
25°C c 2 g.l^{-1} Rn
40°C c 1 g.l^{-1} Rn
For Radium, element ion solubility is also the limiting factor.

D1.5 Standard Deviation

	Relative Total Standard Deviation	Degrees of freedom	
U.S.N.B.S. Standard			
2.90 Bq ^{226}Ra	c 1.8%	18	(a)(c)
0.041 Bq ^{222}Rn	c 4%	16	(a)(c)

		Activity	Standard Deviation	
2.923 ± 0.0387 Bq	^{226}Ra	2.928 ±	0.14 Bq	(b)(c)
Open Ocean Water	^{226}Ra	0.3580 ±	0.0125 Bq/100 kg	(b)
	^{222}Rn	0.7417 ±	0.0560 Bq/100 kg	(b)

(a) US Government Data Ref 46
(b) MAFF, Fisheries Laboratory, Lowestoft, Typical data.
(c) certified value for sealed sample as supplied.

D1.6 Limit of detection

Dependent on the counting system, sample size, duration of count and background. 0.0009 Bq/100 kg ^{222}Rn is typical (b).

D1.7 Interferences

None known which are not taken care of in the method.

D1.8 Time required for analysis

About 5 hours per sample, but dependent on the level of activity and the amount of counting required for an accurate result. Analytical output can be improved by careful planning with multiple apparatus, samples being started in succession so as to be ready for counting when needed.

General Notes for Figures 1–3

1. Apparatus of this type is commercially available, such apparatus uses modern engineered gas fittings with automatically opening and resealing rapid connections for those pieces of equipment which need to be moved or changed during the analysis. These connections are also available commercially and can be used to simplify the apparatus shown. Even so, the basic operations remain the same, though simplified.

2. All tubing should be made of stainless steel or other materials which do not absorb radon.

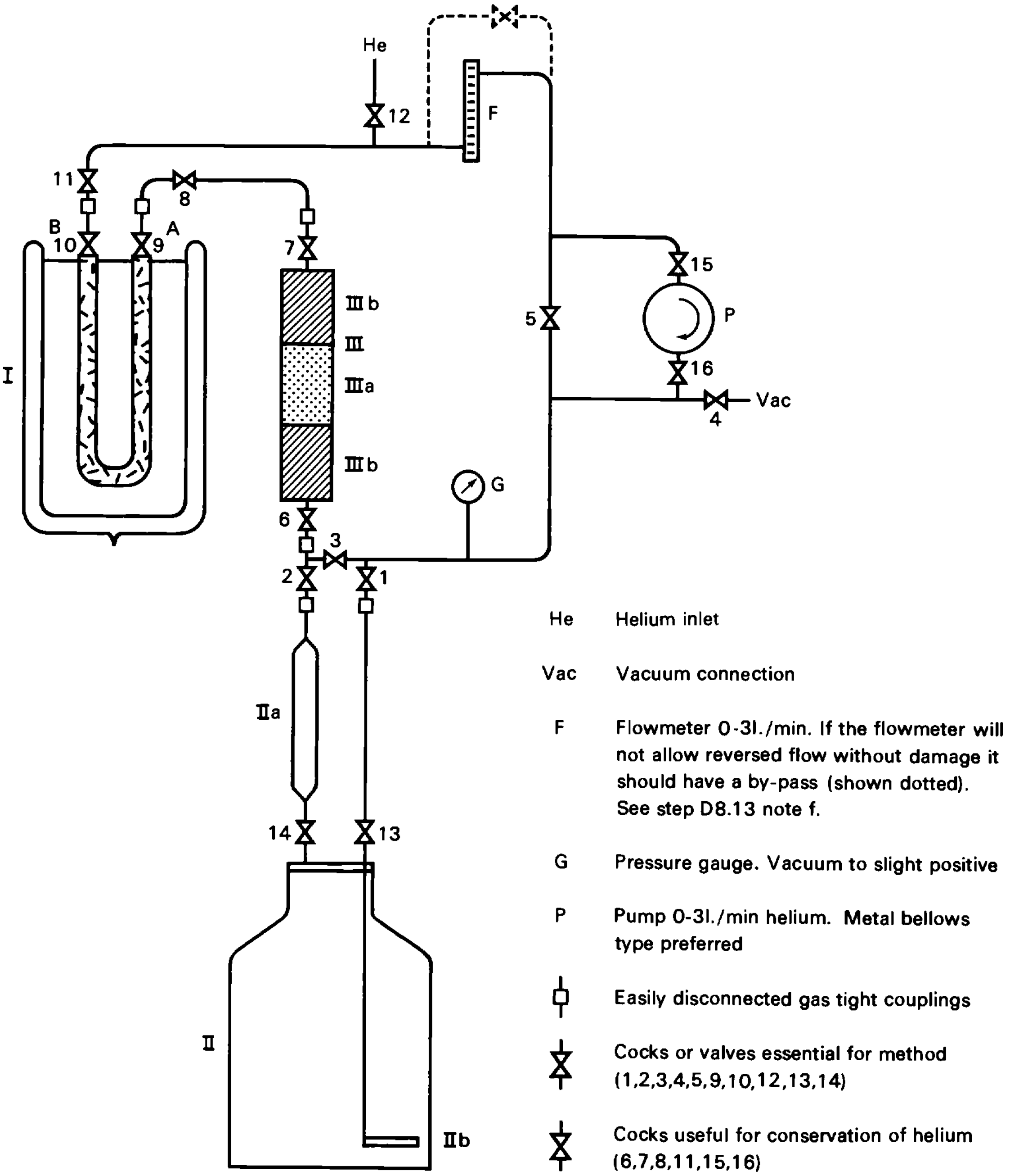
3. During the initial preparative evacuation and purging, gas flow in each apparatus varies in direction, but is never through the actual sample.

3.1 During step D8.10 the circulation in the apparatus shown in Fig. 1 is: pump, 16, 1, 13, sample bottle, 14, 2, 6, 7, 8, 9, absorption tube, 10, 11, flowmeter, 15, pump (roughly clockwise).

3.2 During step D8.23 the flow in the apparatus shown in Fig. 2 is: Helium inlet, Meter valve, 20, 18, 10, absorption tube, 9, 17, 19, (21), counting cell.

3.3 In alternative step D8.34 the flow in the apparatus shown in Fig. 3 is directly in number order from 1 to 6 (but not 7).

Fig 1 Sample Degassing Apparatus - Diagrammatic



He	Helium inlet
Vac	Vacuum connection
F	Flowmeter 0-3l./min. If the flowmeter will not allow reversed flow without damage it should have a by-pass (shown dotted). See step D8.13 note f.
G	Pressure gauge. Vacuum to slight positive
P	Pump 0-3l./min helium. Metal bellows type preferred
□	Easily disconnected gas tight couplings
⧗	Cocks or valves essential for method (1,2,3,4,5,9,10,12,13,14)
⧖	Cocks useful for conservation of helium (6,7,8,11,15,16)

Note arrangement of A and B which are as in Fig 2 and colour coded for quick recognition

All tubing stainless steel or hard glass. Plastic in connections, PVC if possible

Fig. 1 Notes

(a) **I Cold Trap**—Dewar flask containing solid CO_2/n-propanol slurry cooling a stainless steel U-tube filled with 6.5 g of 35–50 mesh absorbent charcoal retained by glass wool filter plugs and stainless steel wire grids. The U-tube is fitted both with stainless steel plug cocks and quick disconnecting joints, which must be workable whether cold or at room temperature. Inlet and exit joints (A and B above) are colour or size coded for quick recognition. (Trap path length 60–65 cm).

(b) **II Sample Bottle**—Preferably of flint glass. Inlet tube (IIb) is fitted with a bubbler. The Exit is flush with the cap to allow complete filling. A small bulb (IIa) above the exit cock prevents water displaced during bubbling from being carried into the gas drier tube (IIIb).

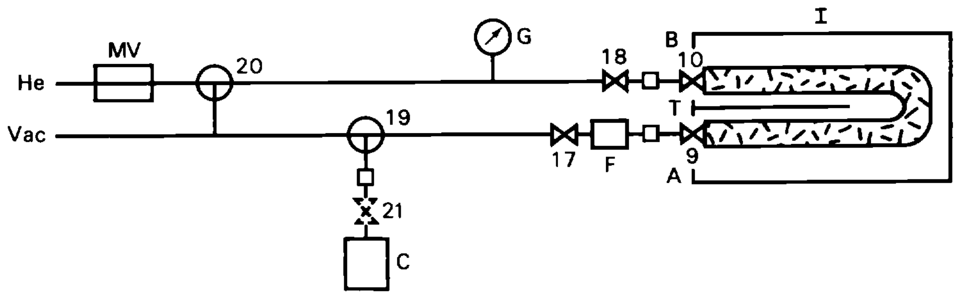
The bottle is fitted with inlet and exit cocks and quick disconnecting joints. A bypass tube with cock joins inlet to exit on the far side of the disconnecting joints.

(c) **III Desiccant-Carbon Dioxide Removal Tube**—The body of the tube is of glass; the end caps and connections are of stainless steel. The tube contains sufficient desiccant (IIIb) and carbon dioxide absorbent (IIIa) to ensure that no water or CO_2 is collected in the cold trap. A second desiccant section after the carbon dioxide absorber improves equipment performance. As a safeguard, indicating reagents are used. The reagents are retained in place and separated by plugs of glass wool and stainless steel wire grids. The tube is changed after each sample and is fitted with quick disconnecting joints.

(d) **Variant for straight through operation** The apparatus illustrated is modified as follows: The return tube from the cold trap to the helium inlet, the pump (but not the pump bypass), and the sample bottle bypass are removed. The vacuum connection is moved to the cold trap outlet and only connected when needed. Helium is replaced by nitrogen or argon which is vented at B. (See Fig 3).

(e) **Pressure Tests** It is essential that all joints and valves be leak free whether under vacuum or slight positive pressure. Pressure test regularly paying special attention to valves and joints used regularly.

Fig 2 Radon Transfer and Counting Apparatus



All tubing stainless steel or hard glass. Plastic in connections, PVC if possible.

He	Helium inlet
Vac	Vacuum connection
MV	Metering valve
G	Pressure gauge. Vacuum to slight positive
F	Gas filter (essential to protect counter from charcoal dust)
C	Scintillation cell (size is dependent on photocell counter but must be sufficient to allow radon to be swept from the trap into it). May have a cock (21) as in Fig 3. The scintillation counter is usually a separate piece of apparatus to which the cell is carried.
I	Stainless steel charcoal filled U tube (I in Fig 1) in an oven capable of heating it to 470°C
T	Temperature measuring device

Note arrangement of joints A and B which are the same ends as in Fig 1 and colour coded for quick recognition. (The direction of flow through the tube is now the reverse of that in Fig 1)

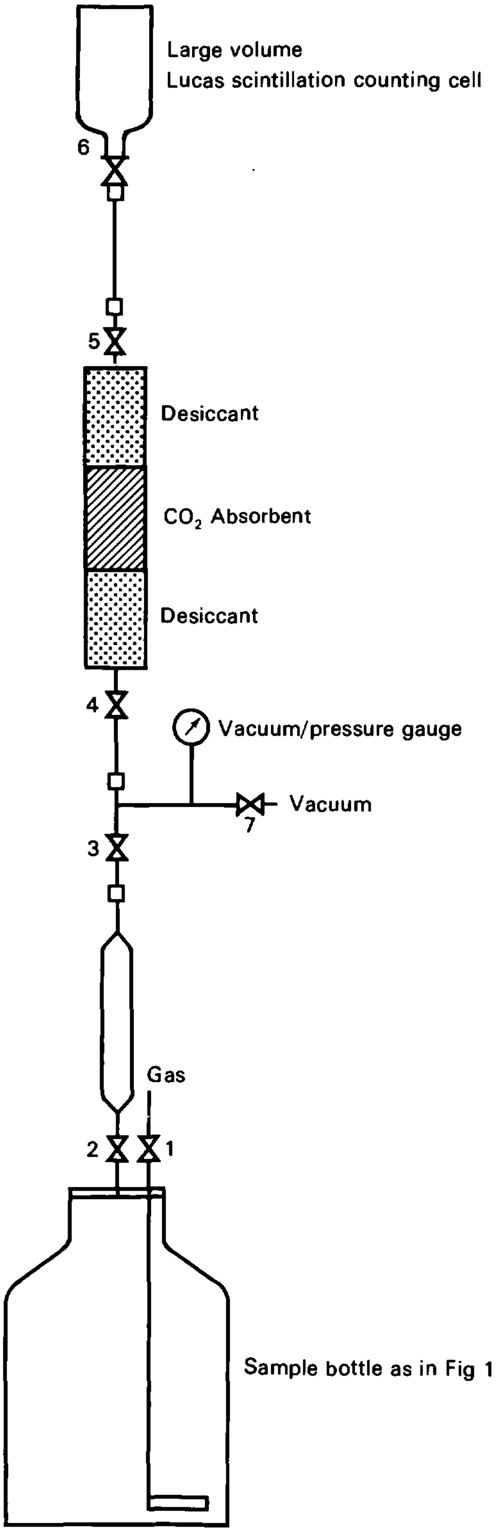
—⋈—	Cocks on charcoal filled U tube
—□—	Easily disconnected gas tight couplings
⊕	Three way cocks

Fig. 2 Radon Measuring Device Notes

21. An additional valve or cock may be added in the side arm between the coupling and the counter cell, or the coupling to the cell may be provided with a sealing plug for the cell side when the cell is disconnected from the system. See step D8.24. Such a valve would remain open when the cell is connected to the transfer device.

Pressure Tests It is essential that all joints and valves be leak free whether under vacuum or slight positive pressure. Pressure test regularly paying special attention to valves and joints.

Fig 3 Single Pass System



D2. Principle (See Refs 46-50)

The sampling time is noted to correct for any decay that occurs prior to analysis. The radon is removed by bubbling helium through the sample (air, argon or nitrogen may be used if helium is not available). The gases are dried, carbon dioxide removed, the radon stripped and collected by adsorption onto charcoal in a cold trap. The trap is cooled by a solid carbon dioxide in propanol bath (liquid nitrogen can be used). The helium is then recycled by means of a pump (once through systems using, argon or nitrogen are possible).

When radon collection is complete, the helium circulation is stopped and the sample bottle resealed. The time is noted. The charcoal trap is disconnected and placed in an oven (cold). It is then connected to the transfer system (see Fig 2) with a silver-zinc sulphide or similar scintillation counting cell fitted. The apparatus is evacuated. Radon is displaced from the trap by heating the trap in the oven to 470°C and the radon is swept into the counter cell by a slow stream of helium. The tube is then allowed to stand for two hours to allow ingrowth of the daughters ^{218}Po and ^{214}Po to equilibrium and then counted. The time is again noted.

A correction for Radon decay prior to determination can be calculated by knowing the time interval between sampling and counting of the original radon. Radon ingrown from radium in the sample is determined by allowing the sample to stand for an appropriate time and repeating the procedure with a new charcoal filled cold trap. The Radium content is determined from this latter reading. The method is standardized using solutions of ^{226}Ra standards as a source of ^{222}Rn.

D3. Interferences

Water and carbon dioxide if not removed will reduce the counting efficiency. Plastic tubing can absorb radon.

D4. Hazards

Radon should not be inhaled. Cleanliness and care are essential not to ingest or inhale alpha emitting substances. Unless abnormally high levels of activity are encountered, only the normal precautions for handling low-level radioactive material are necessary.

Evacuated apparatus should be shielded against risk of implosion.

Equipment and substances at sub zero temperatures should not be handled with bare hands.

D5. Reagents

D5.1 Water

Any water used for making good evaporation losses must be free of radioactive substances. Distilled water, if necessary aged for one month and re-distilled, is satisfactory.

D5.2 Radon Absorbent

Coconut charcoal, or similar gas absorbent charcoal.

D5.3 Desiccant

Fine granular fused calcium chloride or magnesium perchlorate. The desiccant should be of an indicating variety.

D5.4 Carbon Dioxide Absorbent

Soda lime. The absorbent should be of an indicating variety.

D5.5 Solid Carbon Dioxide

If not commercially available, solid carbon dioxide generators are available using gas from cylinders under pressure.

D5.6 n-propanol

D5.7 Liquid Nitrogen

Alternatively Liquid Nitrogen may replace D5.5 and D5.6.

D5.8 A supply of helium

(alternatively nitrogen or argon if not available).

D5.9 A standard Radium-226 solution

(These may be purchased commercially).

When diluting this solution to make working strength standard solutions, additional preservative and added salts must be added equivalent to the volume of dilution water used, in order to maintain the original strength of these substances. This is necessary to prevent organic growth and absorption to the containers. For details of the preservative and added salts used and their concentrations see the supplier's certificate.

D6. Apparatus

D6.1 Sample degassing apparatus

Assemble the apparatus shown in Fig. 1. The sample bottle and charcoal trap connections should be gas tight remakable connections. The charcoal trap should have clearly distinguishable connections, preferably coded with different colours for each end. Any metal or glass joints should be butt joints with the minimum of exposed plastic or rubber.

D6.2 Sample bottles

Sample bottles, 2–20 litre, preferably of flint glass, with stopper fitted with a gas bubbler inlet tube and a gas exit connection, each with gas tight cocks. A small glass bulb should be connected above the exit cock and before the remakable connector large enough to accommodate all liquid displaced during bubbling in order to prevent liquid being blown forward into the drier and lost, also exhausting the drying agent and causing blockages. The sample bottle volume when filled to the cocks should be known to ± 50 ml or better. (See also D7.9). All pressured gas supplies should be connected via a lute. A lute consists of a tee tube dipping into a liquid, usually water, to a sufficient depth that the equipment so guarded can be pressured without bursting and without gas bubbling out through the water, but also to such a depth that gas would so escape at pressures well below bursting pressure.

Note that once assembled, the bottle used for the radium standard solution is not taken apart, but reused indefinitely once filled with a known amount of standard.

D6.2.1 A small funnel

Fitted with a connector suitable for connecting to the gas exit.

D6.2.2 For turbid samples

The bubbler arm should be capable of being removed.

D6.3 Radon Transfer and Counting Apparatus

Assemble the apparatus shown in Fig. 2. Note the carbon trap degassing inlet connection is now the exit connection to the counting cell. The joints should be colour coded accordingly to avoid error. The counting cell is of an internally coated phosphor Lucas type (ref 50). The counting assembly is separate from the transfer apparatus; the cell is carried between the transfer apparatus and the counter, which consists of a photomultiplier tube in a light-tight container, and associated electronics.

D7. Sampling Procedure

D7.1 For detail of the bottles used see D6.2 above.

D7.2 Fill bottles without bubbling or splashing. If there is room, bottles may be filled by turning on their side and lowering slowly and gently into the source of sample turning the bottle upright under the water surface. Then inserting the stopper and bubbler, with the cocks open, under the water surface. If this is not possible, sample gently down the wall of the bottle. If the source being sampled is a tap or pipe, fit a hose which will dip to the bottom of the bottle, flush out the hose and if possible turn off the source, dip the tube into the bottle, right to the bottom, then continue sampling. (See Ref 40 for additional information). Insert the stopper and bubbler with the cocks open. Ensure that the bottle is filled right up to the cocks in the stopper, and that the stopper is tightly in place and does not leak.

D7.3 If only dissolved radon is required turbid samples may be filtered rapidly under gravity (not under vacuum) prior to filling the bottle. This should be avoided if at all possible.

D7.4 Bottles are filled full to the cocks and the cocks closed. Clean samples may be filled through the bubbler arm.

The volume contained in such a filled bottle (V litres) must be predetermined to at least an accuracy of ±0.5% of the volume.

D7.5 Record the time and day on which the sample is taken. This information is needed for the calculation (see D9.3).

D7.6 Samples should be cooled to below the water temperature at the time of sampling and kept below this temperature until analysed. The solubility of radon varies greatly with temperature, (See Section D1.4 above).

D7.7 Samples should be analysed as soon as possible after sampling, and within 48 hours (Radon-222 has a half-life of only 3.8 days).

D7.8 If much suspended matter is present in the sample and it is probable that it contains radon either trapped in the crystal lattice, or dissolved, or absorbed in such a way that it will not outgas in the following procedure, and it is desirable that this radon be included in the analysis preliminary tests must be made to find a suitable solvent for this insoluble matter which will dissolve the solid in the sample bottle, preferably without heating or gas evolution. Such solvent may preclude the use of certain types of sample bottle.

D8. Analytical Procedure

The method consists of three distinct operations: Radon Extraction from the Sample, (Steps D8.1-D8.16 or D8.33) Radon Transfer to the Counting Cell, (Steps D8.17-D8.26) Radon Counting (steps D8.27 to D8.29).

Two procedures are normally used for Radon Extraction: a closed cycle system, (Steps D8.1 to D8.32) and a single pass system. (Step D8.33 with steps D8.27 to D8.32). The same transfer and counting procedures are used with both extraction system. Differences in apparatus are minimal between the two systems. Blank correction and a procedure for the determination of any significant amounts of radium present are also given (steps D8.30 and D8.31 to D8.32 respectively).

The procedures that follow assume a laboratory built apparatus from glass parts. Use of modern automatically opening and resealing cock-joints can eliminate many cocks but the flow directions remain unchanged.

Step	Procedure	Notes
	To simplify calculations, blank runs must exactly duplicate the timing of the corresponding analytical runs. Ensure that the counting times are optimized so that whilst blank run and analytical run times are the same, they are long enough for sufficient accuracy for each count.	
	For a check list of readings required see Section D9.3.	
	Radon Extraction Closed Cycle System	
D8.1	Assemble the apparatus shown in Fig. 1, without the sample bottle. Ensure that all joints are tight, but that those to the charcoal trap and absorber tube are readily disconnectable. (Note (a)).	(a) Leaks are the commonest cause of error in the method

Step	Procedure	Notes
	Recharge the dessicant-carbon dioxide absorber tube freshly before each run (note (b)). Check the charcoal trap alpha count periodically. The count should be at or very close to background. If not, change the charcoal prior to use, ensure that there are no blockages and activate with a transfer cycle as detailed below.	(b) Partially used dessicant and carbon dioxide absorbent can cause low results. Water and Carbon Dioxide can damage the scintillation counting cell. Caking and subsequent blocking of the desiccant and absorbent can ruin the analysis.
D8.2	Ensure that cocks 1 and 2, valves 4 and 12 are closed, and cocks (or valves) 3, 5, 6, 7, 8, 9, 10, 11, 15 and 16 are open.	
D8.3	Slowly evacuate the system as completely as possible (to a pressure of c 0.1 Torr) by opening valve 4.	
D8.4	Fill the dewar flask which surrounds the carbon trap with dry ice-propanol mixture and put into place (note (c)).	(c) Top up with dry ice and propanol as necessary. Other preparations may be used giving the same temperature.
D8.5	Allow the carbon trap to cool down under vacuum for at least 10 minutes.	
D8.6	Connect up the sample bottle with bubbler, having first ensured that the bottle closure is leak tight and that cocks 13 and 14 are closed.	
D8.7	Open cocks 1 and 2 and evacuate the connecting lines to the sample bottle.	
D8.8	When the pressure is back to the original evacuated pressure, close the vacuum valve 4 and slowly fill the system with helium (if not available see D5.8) to atmospheric pressure through valve 12. Then close valve 12.	
D8.9	Open the sample container cocks 14 and 13 and close the by-pass cock 3 in that order. (The sample bottle outlet is opened first).	
D8.10	Start the circulator pump and slowly close by-pass valve 5 to set a gas circulation rate of 1-2 l min^{-1} on the flowmeter. Maintain this circulation for 90 ± 5 mins (note (d)).	(d) Do not close cocks 15 and 16 when the pump is running
D8.11	Carefully stop the gas circulation, being careful to avoid any blow back of sample water through cocks 2 or 13. This is achieved by slowly opening cock 3, then opening valve 5 and finally stopping the pump. (Note (d)).	
D8.12	Close cocks 13, 14, 1, 2 in that order and remove the sample bottle. (If either a radium analysis or a correction for radon formed in the interval between sampling and analysis due to radium present in the sample, or both are also required, see steps D8.31 and/or D8.32 and (note (e)).	(e) If previously degassed samples are to be stored it is recommended that any liquid in the safety bulb be drained back into the sample bottle immediately the bottle is disconnected and that any evaporation loss be made good by addition of pure water (D5.1) to fill the bottle to the taps (but not over) using funnel D6.2.1.

Step	Procedure	Notes
D8.13	Close cocks 6, 7, 15 and 16, (pump by-pass valve 5 open) and evacuate the charcoal trap through valve 4 for 1–2 minutes (note (f)). Close valve 4.	(f) If the flow meter will not allow a reversed flow without damage it too should have a by-pass which should be opened for this operation and closed again before the next step.
D8.14	Close cocks 8, 9, 10 and 11 and remove the charcoal trap from the system and from the dry ice—propanol cooling bath (note (g)). Allow the charcoal trap to warm up to room temperature (note (h)).	(g) Do not touch subzero glass or metal with bare skin, nor allow the dry ice–propanol to come in contact with skin. (h) Stand the charcoal trap in a bowl of water or preferably hold it under a running tap.
D8.15	Return the apparatus to the state of steps D8.1 and D8.2, but only replace the fresh drier-absorber tube and carbon trap just prior to the next analysis.	
	Radon Transfer	
D8.16	Assemble the apparatus shown in Fig. 2 without the charcoal trap (note (i)). Close cocks 17 and 18.	(i) Ensure that the gas filter is clean and check the counting cell background (see also note (r) below).
D8.17	Set cock 19 to straight through with cell line closed, set cock 20 to vacuum (helium off), evacuate the lines. Then carefully and slowly set cock 19 to cell line open to vacuum and evacuate the counting cell.	
D8.18	Connect the carbon trap to the system, but with the oven drawn clear of the trap.	
D8.19	Evacuate the carbon trap by opening cocks 10 and 18 in that order, with 20 open to vacuum, then open cocks 9 and 17. (Note (j)).	(j) The trap should still be under vacuum from step D8.13. This is a safeguard. It also evacuates the filter (F in Fig. 2).
D8.20	Close cocks 9 and 10. Set cock 20 to helium straight through (towards cock 18), and using the metering valve bring the gauge and the line as far as cock 18 almost but not quite to atmospheric pressure (note (k)). Turn off the helium.	(k) If helium is not available see D5.8.
D8.21	Bring the oven around the carbon trap and heat to 450–470°C.	
D8.22	Set cock 19 for flow from the carbon trap to cell, (with vacuum side closed). Then wait 5 mins ± 10 secs.	
D8.23	Check that cocks 17 and 18 are open, cock 20 is set for helium to carbon trap and cock 19 is set for a flow from the carbon trap to cell. Carefully open cocks 9 and 10. Then, regulating the flow by the metering valve, over 4 ± 1 min slowly bring the system up to atmospheric pressure with helium. (Note (l)).	(l) All gases must be dry. If necessary put a drying tube in the supply line after the lute.
D8.24	Then turn off the helium, and remove the counting cell for counting. Stopper the cell mouth with suitable ground glass stopper (note (m)). Alternatively, if the cell is fitted with a cock close this cock (21 in Fig. 2).	(m) Radon is appreciably heavier than air but helium is lighter. Cells can be obtained with automatically closing connectors.

Step	Procedure	Notes
D8.25	Set cocks 19 and 20 to vacuum and evacuate the carbon trap, keeping it in the oven for 5–10 mins.	
D8.26	Remove the oven, close cocks 18, 10, 9 and 17 and remove the carbon trap. Do not reuse a trap until its alpha activity has returned to an acceptable level relative to the natural background, (See Section D10). Return the apparatus to the state in D8.16. A clean counting cell should be used for the next analysis.	
	Counting Procedure	
D8.27	Place the cell in the counter, which must be a light-tight assembly (notes (n) and (s)).	(n) The counting assembly will be ruined if light enters the photo cell during operation.
D8.28	Allow the assembly to stand for two hours (note (o)). Then count for a sufficient interval of time to give an accurate result (note (p)). Note the times at which counting started and ended (note (q)).	(o) This increases the sensitivity by allowing radon to come to equilibrium with its more important alpha emitting daughters (^{218}Po and ^{214}Po). (p) The duration of count is dependent on the amount of radon present. (q) For calculation of the decay since the sample was taken.
D8.29	Recount cells once or twice at intervals typically of 24 hours to confirm the half life by following the decay which is a first order reaction (notes (q) and (r)). See also Section D9.	(r) Used cells may be recounted later provided correction is made for the decay which has since taken place. Cells should not be reused until their count has returned to background.
	Blank Value	
D8.30	Using water free of radium and radon (D5.1), carry out the whole analytical procedure, using a charcoal trap with charcoal from the same batch and previous history as that used for the analytical sample, (note (s)). Record the count obtained.	(s) The counting cells should be identical in type and history to that used for the analytical sample. As there will be a slight difference in counts between cells this should be noted prior to filling with gas and radon, and the cell residual count deducted in each case. This variation may not be significant depending on the level of radioactivity of the sample, but backgrounds and blanks are best determined in advance of use of cells.
	Determination of Radium 226 and Supported Radon 222 (Note) (t)).	(t) Radon-220 will be found among the products of the decay of thorium-232, which is fairly common in rocks and has a long half-life. However, the comparative shortness of its own half-life and of its immediate precursors makes the detection of radon-220 and radium-224 unlikely by these methods. However, radon-220 was the first radon isotope to be discovered. The geology and geochemistry of the source and catchment will suggest whether sufficiently high concentrations of thorium are likely to be present, and knowledge of local industries and geology will indicate whether thorium or radon-220 containing effluents are likely to occur. If there is doubt, consult experts for gamma ray spectrometry and other methods
D8.31	After a suitable lapse of time, not less than ten days, but for samples with low levels of initial activity at least 27 days, to allow the radium, radon, decay series to approach equilibrium (note (u)), repeat the analysis (steps D8.1–D8.30) with the exact replication of the technique used previously, noting in addition the time which has elapsed since the initial analysis	

Step	Procedure	Notes
		or the booklet to follow in this series. Due to the scarcity of its more stable precursors and its short half-life radon 219 is even less likely to be encountered unless one of its precursors with long half life is present in high concentration.
	Standardization and Analytical Quality Control	
D8.32	The method must be standardized and quality control charts kept by regularly analysing for the radon contained in standard radium solutions of known strength using steps D8.1 to D8.30. Use apparatus of the same size as for samples, especially the degassing bottle (II in Fig. 1). A standard amount of radium solution is placed in the bottle, which is then filled to the cocks with water. Once filled with a standard this bottle and its bubbler system should be kept for reuse when required, thus minimizing the risks of error and contamination. Care must be taken not to accidentally lose radon from such solutions by accidental aeration, degassing, shaking, warming, freezing, absorption or extraction. Care must also be taken firstly to keep a record of when the solutions were last analysed or stripped of radon so that the amount of radon ingrowth can be found from the tables (refs 56 and 57) or calculated and secondly to allow sufficient time to elapse for the desired concentration of radon to have formed before reuse of a solution.	(u) The return to equilibrium is a complex summation of eight first order reactions but the total activity is in excess of 90% of the maximum by this time.
	Alternative Degassing Procedure. Single Pass System	
D8.33	The apparatus is set up as in Fig. 3. The cell should be as large as practicable (250 ml or more). Cocks 1 and 2 are closed, 3, 4, 5 and 6 are open. Open cock 7 and evacuate the system and make leak tight. Close cock 7 and open cocks 1 and 2 slowly as in step D8.23, admit helium, argon or nitrogen through cock 1, controlling the flow by a metering valve and flowmeter (note (v)) on the gas cylinder so that the cell takes 5–10 minutes to fill and the contents of the sample bottle are well mixed in the process. Turn off the gas supply, close all numbered cocks, remove the counting cell and proceed as in steps D8.27 to D8.29. The blank and correction steps D8.30 and D8.31 should also be carried out, but using the procedure in this step.	(v) not shown in Fig. 3.

D9 Calculation of the Radon and Radium Content

D9.1 Basis of the Calculation for Radon Determination

The radon in the sample at the time of sampling is determined from the radon in the counter at the time of the counting, with a positive correction for the radon which has decayed in the interval between the time of sampling and the time of counting and a negative correction for the radon which has formed during the same interval of time from any radium in the sample.

Radioactive decays have pure first order reaction rates. The simplest calculation is derived by considering the radon present initially at the time of sampling to be made up of two parts, that due to radium in equilibrium with the radon from its own decay and that due to unsupported radon from the surroundings. If the alpha measurement (Method A) indicates that all the radon is unsupported with none from dissolved radium, the radium correction can be omitted and the calculation simplified. However, the sensitivity achieved in the gross alpha determination must be given due consideration in taking such a decision. All counts need to be corrected for background. This background is made up of two components; that due to natural background radiation in the vicinity of the laboratory and that due to the counter and electronics, which latter should be minimal. If this is not so, a correction must be made, see section D8 note (r). As the counter will not be perfect, the apparatus must be standardized against radon from known solutions of radium. Such solutions are commercially available. If used frequently, these standards may not have attained equilibrium, but with thorough record keeping the amount of radon present, formed since the last outgassing can be calculated.

D9.2 Basis of the Calculation for Radium

The ingrowing time used for correcting for the radon formed during sample storage and analysis from dissolved radium in the sample is often not sufficient for an accurate radium analysis and a separate determination is made. The calculation, however, is similar. If the time between the last and the present outgassings is identical for both the radium standard and the sample, the calculation becomes considerably simplified as all time dependent terms cancel out.

D9.3 Measurements required from Sampling and Analytical Procedures for Calculations

Volume of sample V1.
Activity of the radium standard solution made up ready for use A_RBq
Time of taking the initial sample
Time of last use (or of assembly) of the radium standard
Time of end of first degassing (D8.11)
Time of start of count (D8.28) } FOR SAMPLE, STANDARD AND BLANK
Time of end of count (D8.28)
Time to the end of the second degassing of sample (for record purposes only)
Time of start of second degassing of sample } FOR SAMPLE ONLY
Time of end of second degassing of sample
Count after first degassing for sample C_{S1}, standard C_{RO}, and blank C_B
Count after second degassing for sample only C_{S2}
Cell count (if not virtually background) C_C

D9.3.1 Hence drive

Time between last use of standard and the end of standard degassing t_{RO}
Time between the end of degassing and the midpoint of the corresponding count for the standard t_{R1}, the sample first and second degassings t_{S1} and t_{S2} and the blank t_B.
Time elapsed between the taking of the original sample and the first degassing t_{SO}

D9.4 Basis of Calculation

The procedure is as follows:

(1) the total radon is determined (steps D8.1 to D8.28) and the activity corrected back to the time outgassing ceased;
(2) the supported radon is determined by a second outgassing following an ingrowth period (step D8.32).
(3) the unsupported radon is obtained by difference and corrected for decay since the time the sample was taken

For the standard, as the activity of the total bottleful is known from its preparation details, and as the only activity is supported radon, which is volatile, and an equivalent amount of radium, which is not volatile, only an initial outgassing is required, followed by correction back to the time when that outgassing ceased.

D9.4.1 First derive the efficiency of the counting system for radon plus daughters.

$$\text{Radium activity } A_R = \frac{C_R}{E \, . \, f} \text{ Bq.}$$

where A_R is the certified value for the activity in the diluted standard in the bottle II fig. 1.

C_R is the counts per second from the standard corrected for blanks and background (and also cell residual count if needed).

$C_R = C_{RO} - (C_B + C_C)$

E is the counting efficiency in counts per second per Becquerel.

f is the radon ingrowth factor $(1 - e^{-\lambda t_{RO}})$,

where λ is the disintegration constant for radon and t_{RO} is the time elapsed since the last outgassing of the standard.

Note that λ and t_{RO} must be in the same units.

D9.4.2 So activity of the total radon (supported and unsupported) in the sample at the midpoint of the count is

$$A_T = \frac{C_{S1} - (C_B + C_C)}{E.V} \text{Bq.l}^{-1}$$

where C_{S1} is the first count after the first outgassing of the sample and V is the sample volume in litres.

D9.4.3 Correct the gross radon for decay since the end of the outgassing by dividing by $e^{-\lambda t_{S1}}$ where λ is as above and t_{S1} is the time which has elapsed between the outgassing and the midpoint of the count, so that gross radon at the time of sampling is

$$\frac{A_T}{e^{-\lambda t_{S1}}} \text{ Bq.l}^{-1}$$

But unsupported radon has decayed since the original sampling, while supported radon has not diminished having remained in equilibrium with ^{226}Ra.

In order to do this, the split between unsupported and supported radon has to be determined. Both ^{226}Ra and supported ^{222}Rn present are determined at the same time by reference to the second degassing after a period of ingrowth.

$$A_S = \frac{C_{S2} - (C_B + C_C)}{E.V} \text{ Bq.l}^{-1}$$

where C_{S2} is the count from the second degassing of the sample and A_S is the supported radon activity at the midpoint of the second count.

This too needs correcting for the decay of radon since the outgassing by division by $e^{-\lambda t_{S2}}$ where t_{S2} is the time elapsed between the second outgassing and the midpoint of the count, so that supported radon at time of sampling is

$$\frac{A_S}{e^{-\lambda t_{S2}}} \text{ Bq.l}^{-1}$$

D9.4.4 The activity of the unsupported radon A_U is therefore

$$A_U = \frac{A_T}{e^{-\lambda t_{S1}}} - \frac{A_S}{e^{-\lambda t_{S2}}} \text{ Bq.l}^{-1}$$

This must also be corrected for decay back to the time of initial sampling, so that the unsupported radon at the time of sampling is

$$\frac{A_U}{e^{-\lambda t_{SO}}} \text{ Bq.l}^{-1}$$

where t_{SO} is the time elapsed between the initial sampling (D7) and the end of the first outgassing.

D9.5 Additional Information Required

Decay constant for Radon-222 in hours	$\lambda = 0.007555\text{h}^{-1}$
Decay constant for radon-222 in days	$\lambda = 0.18131\text{d}^{-1}$

In the calculations below, use λ in days for times likely to exceed one day; if however, the total times associated with λ are less than one day, use the hour value instead; from the nature of the activities involved this is most unlikely.

Whatever value is used, both λ and t must be in the same units.

In these calculations e is the base for 'natural' or Naperian logarithms e = 2.7182818.

D9.6 Calculation of Radon Content at time of Initial Sampling

By substituting back in the above equations to the derived times of D9.3.1 and the counts etc of D9.3, the following are obtained:

$$\text{Supported radon} = \frac{(C_{S2} - (C_B + C_C))\,(A_R(1 - e^{-\lambda t_{RO}}))}{e^{-\lambda t_{S2}}.V(C_{RO} - (C_B + C_C))}$$

$$\text{Unsupported radon} = \frac{A_R(1 - e^{-\lambda t_{RO}})}{e^{-\lambda t_{SO}}.V(C_{RO} - (C_B + C_C))} \left\{ \frac{C_{S1} - (C_B + C_C)}{e^{-\lambda t_{S1}}} - \frac{C_{S2} - (C_B + C_C)}{e^{-\lambda t_{S2}}} \right\}$$

Total Radon at the time of initial sampling is the sum of the two equations above.

If the initial total Radon count should be less than the count after the second degassing this must mean that, either due to natural causes such as a waterfall, or by aeration in a waterworks, the sample was considerably outgassed prior to sampling. In such a case, because radon will grow back to the equilibrium value with the radium content, the analyst is recommended to report the radium value and the equilibrium radon value together with a statement that the sample as received had been at least partially degassed prior to sampling. Usually it is easy to determine what has happened from the source of the sample.

D9.7 Total Radium Content at time of Initial Sampling is then the same as the Supported Radon above

D10 Apparatus cleaning

Due to the short half-lives of radon, polonium and all the daughter isotopes to lead, having sufficient sets of apparatus to avoid reuse of carbon absorption trap and Lucas-type counting cells for at least six months, coupled with checks on their activity and the keeping of records for each cell and tube eliminates risk of contamination.

Drying—carbon dioxide absorption columns should be changed after each analysis. The carbon absorption traps can likewise be changed if either their residual activity becomes too high, or the carbon deteriorates giving too much dust in the filter. Gas filters should be cleared regularly.

Lucas counting cells are difficult to clean without damage (see references 51).

D11 Excess of Radon over Radium

Radon emanating from radium trapped in mineral lattices, regardless of decay series, being a gas, will often escape from rock through pores or fissures leaving the radium and other elements still locked in the rock. On the other hand, radium is a readily leached element having a soluble bicarbonate, chloride and nitrate (though the sulphate, is highly insoluble) and so radium can occur in solution. Radon in solution due to the decay of dissolved radium is said to be 'supported', because it is being regenerated in the sample even after taking it. Radon liberated from the rocks without leaching of radium is likewise said to be 'unsupported' because its activity slowly decays away without regeneration once the sample has been taken. Conversely, aeration in water falls may degas waters and so lower the radon content. Samples may therefore contain more or less radon than would naturally be in equilibrium with their radium content.

D12. Units of Measurement

Concentrations of radionuclides are usually given in terms of their activity in Becquerels (formerly in pico curies. See the section on units at the front of this booklet). Mass/volume concentration units (as given in Section D1.4) are rarely used except for high levels of less active elements such as uranium and thorium.

D13. Radon in Air

Radon in air is rarely a hazard except in places where it is evolved from water or rocks and can become trapped in an enclosed space. The apparatus and method described in steps D8.1 to D8.29 is capable of adaptation for the measurement of Radon in Air.

D13.1 Remove the sample bottle at the disconnects at cocks 1 and 2 in Figure 1. Fit a gas meter calibrated for air to the disconnect at cock 1 and leave the tube end open at cock 2, but, if necessary, add extra drier and carbon dioxide removal tubes at this point. Fill the dry ice-propanol bath and cool the carbon trap. (Note that the gas meter must not be on the air inlet side of the apparatus in case it absorbs radon).

D13.2 Then with cocks 3, 4, 5 and 12 closed, and cocks 1, 2, 6, 7, 8, 9, 10, 11, 15 and 16 open (cocks 13 and 14 are now out of the system), slowly pump air through the carbon trap noting the volume of air passed through the gas meter. Keep the air pressure as indicated by the gauge as close to atmospheric as possible.

D13.3 When sufficient air has passed to give good counter readings (the exact volume is dependent on previous experience of the radon concentration expected), stop pumping.

D13.4 Close cocks 1, 2, 15 and 16, open cocks 3, 5 and 4 and evacuate the system.

D13.5 Close cock 4 and slowly fill the system to atmospheric pressure with helium or other inert gas via cock 12.

D13.6 Repeat the evacuation and repressuring steps using cocks 4 and 12 to remove all oxygen which may subsequently damage the carbon in the trap. Finally reevacuate the trap with cock 4.

D13.7 Then proceed with steps D8.14 and D8.16 to D8.29 inclusive.

D13.8 Calculate as in D9 but use the volume of air passed instead of the volume of water sample. Volumes of air are usually expressed in meters cubed.

D13.9 Depending on the radon levels to be expected, other methods are also possible. For advice consult National Radiological Protection Board, Radiological Measurements Department, Harwell, Didcot, OX11. 0RQ.

Determination of Uranium

Introduction

The chemical toxicity of natural uranium is greater than its radiotoxicity. The intensity of the radiation from uranium is isotope dependent and therefore dependent on the source of the uranium. Hence non-radiometric methods are outlined below. Many colorimetric methods are given in the literature but tend to be prone to interference especially by iron. For a potentiometric method suitable for the very low concentrations found in most natural waters, see Ref 41. The simplest interference free method uses X-ray fluorescence (Ref 42). Such equipment though rare in the water industry is often available through other laboratories, hence a procedure is given below. Direct fluorescence measurement of the dioxouranium VI (uranyl) ion which is relatively interference free is also simple and is also outlined. A radio-analytical method is given in Ref 18A. Inductively coupled plasma–mass spectrometry can be used for determining low concentrations.

U X-Ray Fluorescence Measurement

U1 Principle

The sample is preconcentrated by quantitative evaporation, and a small aliquot pipetted onto a disc of filter paper cut to fit the sample holder of an X-ray fluorescence spectrometer (some instruments use a silica disc instead of a filter paper). For greater precision an internal standard, usually yttrium (as nitrate) is added. The disc is put into the apparatus and made to emit the characteristic X-ray spectra by irradiating with a suitable target X-ray tube; the disc is usually rotated during measurement. The intensities of the uranium and/or yttrium lines are measured. A series of standard samples containing known amounts of uranium and the internal standard are prepared and analysed in like manner. A working curve for uranium concentration against the ratio of uranium intensity to internal standard intensity is constructed, from which the concentration of uranium in the concentrated solution can be calculated and the uranium concentration obtained knowing the volume of sample originally evaporated. Other elements may also be quantified at the same time, see Section U7. Solid samples may also be analysed both for uranium and for other elements, see Section U8.

U2 Interferences

Provided due care is taken, none are likely. Only rarely does a combination of interferences cause problems by blocking all usable lines in X-ray analysis. From the tables of X-ray spectra by element and by wavelength given in simplified form in Table 6 and in more detail in Ref 32 it is apparent that for instruments with good resolution no strongly emitted X-ray line of any element overlaps the uranium Lα line and only curium may overlap the yttrium Kα line. Overlaps due to weak lines (such as bromine Kβ_2 with uranium and rubidium Kβ_1 with yttrium) may occur but these would only cause problems at very high interferent to uranium ratios. If internal standards other than yttrium must be used see Ref 32 for wavelengths.

U2.1 When using the method for qualitative or quantitative analysis for other elements always check whether weak lines of another element, especially a major one, are being confused with trace concentrations signals of a strong line by looking for the existence or non existence of the interfering element using one of its strong lines. Ref 64 illustrates the problems that can arise. Very faint lines are not listed in Table 6, see Ref 32. If possible, check using alternative lines.

U3 Performance Characteristics

(Information from Philips-Pye Unicam, Health and Safety Executive, the Water Research Centre, Laboratory of the Government Chemist and AERE Harwell).

U3.1	Relative Standard Deviation	The relative standard deviation decreases steadily from about 50% at twice the limit of detection to 10% when over thrice the limit of detection. Above this, the relative standard deviation can be improved by increasing the counting time logarithmically. The main criterion in deciding precision is the time available for analysis. See manufacturer's instructions. The main cause of lack of precision is variation in sample and standard preparation.
U3.2	Limit of Detection	The limit is dependent on instrument type and instrumental parameters chosen. Typically using a 3 cm diameter paper, 0.1 ml of preconcentrated sample and 200 s counting time, the limit of detection for a wavelength dispersive type instrument is about

$0.05/\mu g/cm^2$ (or 0.03 to 0.07 μg/0.1 ml of preconcentrate). This limit will be higher for saline samples.

U4 Reagents

U4.1 **Water.** Use distilled water.

U4.2 **Uranium standard solution.** Weigh out 1.179 g of triuranium octoxide (previously dried) (if there is a doubt as to the oxidation state ignite in air at 900°C for 1h), dissolve in the minimum of 4 M nitric acid and make up to 1 litre with water in a calibrated flask.

U4.3 **Yttrium standard solution.** Pure Yttrium oxide (Y_20_3) is available. Dry at 105°C to constant weight. To obtain a standard solution containing 1 g of yttrium weigh out 1.270 g of Y_20_3, dissolve in a little dilute nitric acid and make up to 1 litre with water in a calibrated flask.

U4.4 **Filter papers** of suitable size, 3 or 4.7 cm diameter for the sample holder in the X-ray Fluorescence Spectrometer. Very absorbent low ash papers (such as Whatman 540, 541 or 542) should be used.

U4.4.1 Some X-ray Fluorescence Spectrometers use silica discs instead of filter papers. These are supplied with the instrument.

U5 Apparatus

U5.1 **A circular support for drying filter papers or discs.** A beaker may be used but for filter paper discs inert three point suspension is preferred such as a glass ring with small raised points. This reduces the risk of loss of sample to the drying support.

U5.2 **A precision 0.1 or 0.2 ml pipette** (do not pipette by mouth).

U5.3 **An X-ray Fluorescence Spectrometer** The primary X-ray tube should preferably have either a rhodium, molybdenum or silver target but gold, tungsten, chromium or scandium can be used with reduced sensitivity.

Two types of X-ray Fluorescence Spectrometer have been used. The more common variety uses a rotating impregnated filter paper sample, the fluorescent radiation is diffracted with a lithium fluoride crystal cut either with the (200) or the (220) plane parallel to the surface, a fine collimator and either a scintillation or sealed proportional detector. The (200) plane (formerly called the (100) plane) gives the more intense signal and is therefore more commonly used, but the (220) plane (formerly called the (110) plane) gives the better resolution. Other crystals than lithium fluoride are used occasionally. A vacuum path is preferred, but is not absolutely essential. Alternatively a grazing incidence total reflectance geometry may be used with energy dispersive differentiation of the fluorescent spectrum. Such instruments usually use sample evaporated on to silica discs, and are often capable of detecting much lower concentrations of elements.

Note that modern computing instruments may be programmed to identify lines tentatively by element.

Ensure that for a set of determinations the same primary x-ray tube is always used and that for wave length dispersive instruments the same diffracting crystal face is used. If a non-computing instrument is used, the relation between wavelength and the angle of diffraction (2Θ) is given by $n\ \lambda = 2d \sin \Theta$, where n is an integer and almost always unity, the crystal plane dimension 2d will be given by the makers, and note that while the diffraction is 2Θ the equation is for Θ.

U6 Procedure

Hazard Uranium compounds are toxic. X-radiation is harmful. Ensure that screening is effective.

Note: If analysing solid samples and not impregnated discs, see also Section U8.

Initial Qualitative Analysis

U6.1 To prevent error it is necessary to use as internal standard a substance not present in the sample. Natural waters, and other samples sometimes contain strontium, but very rarely yttrium. It is also necessary to establish the correct amount of preconcentration required. Hence a preliminary qualitative analysis is advisable.

U6.1.1 If previous experience gives an indication of the amount of preconcentration that will be necessary to give satisfactory spectra, quantitatively preconcentrate by this amount, as detailed in Section U6.8, except that no internal standard addition is made. If the amount of preconcentration likely to be needed is unknown, prepare a series of preconcentrated samples (start with an unconcentrated sample), each successive sample in the series being twice the concentration of the one preceding it in the series. Make each sample slightly acid by dropwise addition of hydrochloric acid (d_{20} 1.18) prior to evaporation. Use this series of samples in Step U6.2. See also Step U6.3.

U6.2 Take a filter paper disc, mount it on the drying apparatus and slowly pipette 0.1 or 0.2 ml of sample into the centre of the paper and allow it to spread out across the paper. Do not allow liquid to drop or run off the paper during impregnation and drying. Allow the paper to dry by evaporation in a dust free room (or box). Do not use an infra red lamp as this can cause migration to the edge of the paper.

U6.2.1 For silica target instruments, prepare a silica target in a similar manner.

U.6.3 Mount this filter paper in the sample holder of the X-ray fluorescence spectrometer, hold the paper down with a retaining ring, and, following the maker's instructions, scan the spectrum, especially for uranium and yttrium. If yttrium is present, decide which alternative internal standard to use, other possible internal standards are rubidium (as anhydrous chloride or nitrate) or niobium (choice of compound depends on the soluble compounds available). Care is needed in interpreting spectra to discriminate weak lines and higher order lines (lines where n is an integer greater than one (see U5.3). These are not given in either Table 6 or 6A. Weak lines are listed in the more extensive compendia, Ref 32 gives some. If rubidium has to be used as a standard, the only suitable line pair is ULβl and RbKβ. If, as is probable, the uranium signal is undetectable, preconcentrate a series of samples in regular stages until the uranium line is visible or solid deposition is evident (see U6.1.1). Repeat steps U6.2 and U6.3 on this series of samples.

U.6.4 Note whether any substances interfering with the desired internal standard K alpha line and the uranium L alpha lines are present. To confirm possible interferences see Table 6 or Ref 32 and check other wavelengths of the suspected interferent. See also maker's instructions for information relating primary excitation X-ray source with fluorescent lines excitable. See also U7 below.

Note suitable positions between lines for the measurement of fluorescent spectral background close to the analytical lines used.

Preparations of Standard Samples

U.6.5 Using the uranium standard solution (U4.2) and the yttrium standard solution (U4.3) or other standard if necessary (see step U6.3) and water, prepare a series of solutions which when impregnated on to filter papers as in step U6.2 above will give a series of suitable standards such as 0.00, 0.01, 0.05, 0.10, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20, 50, 100, 200, 500 and 1000 μg.ml^{-1} of uranium and a constant amount (such as 200 μg.ml^{-1}) of the internal standard element (usually yttrium).

U.6.6 Prepare a series of filter papers using these solutions as sample in step U6.2.

U.6.7 Using the dry filter paper standards from steps U6.5 and U6.6 prepare a plot of the ratio between uranium Lα intensity and internal standard Kα intensity and the uranium content of the papers, correcting for background intensities (see step U6.11).

Analysis of Samples

U.6.8 Take a volume of sample which, it is hoped, will, after accurate evaporation, give a uranium concentration well into the accurate range of the working curve (step, U6.7). Evaporate quantitatively, to give about 5 ml of concentrate rinsing with distilled water if transferred to smaller vessels. Add the requisite amount of internal standard solution to give the same concentration of standard in 10 ml as was used for preparing the working curve samples (usually 2 mg of yttrium). Make up to 10 ml with water in a calibrated flask and prepare a filter paper as in step U6.2. If in doubt use a series of volumes.

U6.9 Analyse the paper or papers as before, following the maker's instructions.

Blanks

U6.10 Carry several distilled water blank samples through the analytical procedure.

Calculation

U6.11 Using the line intensities obtained in step U6.7

Calculate $\dfrac{\text{UL}\alpha - \text{Background UL}\alpha}{\text{YK}\alpha - \text{Background YK}\alpha}$

(or other internal standard line if not YKα), and plot this ratio against the uranium content per cm^2. If the concentrated sample and standard volumes used to prepare papers are the same and target papers are the same size, plots of signal ratio versus uranium in $\mu\text{g.ml}^{-1}$ can be made.

U6.12 Using the line intensities from step U6.9 calculate the ratio given in step U6.11. Then from this data and the graph obtained in U6.11 calculate the uranium concentration of the concentrate and knowing the volume concentrated down to give the 10 ml (from which the target 0.1 ml were taken), calculate the initial sample concentration.

U7 Quantification of Other Elements

Note: if using a solid sample instead of impregnated discs see also Section U8.1.

U7.1 Identification of peaks in the XRF spectra obtained in steps U6.3 or U6.4 using Table 6, Ref 32 or similar tables can provide a qualitative analysis for the presence or absence of many elements, especially from sodium upwards in atomic number. See U2.1 if trace amounts are being sought.

U7.2 Standard samples of these other elements identified in steps U6.3 and U6.4, prepared in a similar manner to the standard samples in Section U6 of this method can be used to quantify this qualitative analysis. Other internal standards than yttrium may be necessary, but the procedure is the same. Interference may also be checked by examining spectra for suspect elements.

U8 Analysis of solid samples (WRC-British Rail information).

Solid samples such as sludges, soils or minerals may be brought into solution and analysed by the foregoing procedure. (See Ref 58 for details of solution techniques). Alternatively briquettes may be made to fit the sample holder in the X-ray fluorescence spectrometer. Preparation of standards may be a problem. One procedure is, after a qualitative analysis as in steps U6.3 and U6.4, to incorporate a known concentration of an internal standard substance into the sample by thorough mixing, prior to briquetting. Analyses are made by standard additions, incorporated in the same way. Another alternative is to prepare fused beads using standard amounts of lithium metaborate as flux, instead of briquetting.

Calculations are made in a similar manner to that given in Ref 59.

Table 6

Wavelengths of the Strongest Fluorescent X-ray Lines of Elements Arranged in Wavelength Order

Note there are slight variations in values for the wavelengths reported in the literature, furthermore, interelement and matrix effects are known which cause slight shifts in peak wavelengths.

As some instruments with wavelength dispersive spectrometers are calibrated by the 2Θ angles for the various fluorescent lines produced, the 2Θ angles for a lithium fluoride 200 plane crystal are given in Table 6A, which follows the main table.

As the angstrom is an obsolescent unit, wavelengths have been given in picometres (1A° = 100 pm). Weak lines and lines due to higher orders (see U6.3 and U5.3) are not listed. If in doubt seek to confirm by looking for other lines due to the suspected elements. If necessary consult more detailed tables. (Such as Ref 32).

Table 6

λ pm	Kα	Kβ	Lα	λ pm	Kα	Kβ	Lα
9.7		Cf		33.3	Nd		
9.8		Bk		34.1		Ba	
10.1		Cm		34.6	Pr		
10.3		Am		35.4		Cs	
10.6		Pu		35.9	Ce		
10.9		Np		36.9		Xe	
11.0	Cf			37.2	La		
11.1		U		38.4		I	
11.3	Bk			38.7	Ba		
11.4		Pa		40.0		Te	
11.6	Cm			40.2	Cs		
11.7		Th		41.7		Sb	
11.9	Am			41.8	Xe		
12.1		Ac		43.5	I		
12.2	Pu			45.3	Te		
12.4		Ra		45.5		In	
12.5	Np			47.2	Sb		
12.7		Fr		47.5		Cd	
12.8	U			49.2	Sn		
13.1	Pa	Rn		49.7		Ag	
13.4		At		51.4	In		
13.5	Th			52.1		Pd	
13.8	Ac	Po		53.7	Cd		
14.2	Ra	Bi		54.6		Rh	
14.6	Fr	Pb		56.1	Ag		
15.0	Rn	Tl		57.3		Ru	
15.4	At			58.7	Pd		
15.5		Hg		60.1		Tc	
15.8	Po			61.5	Rh		
15.9		Au		63.2		Mo	
16.2	Bi			64.5	Ru		
16.4		Pt		66.6		Nb	
16.7	Pb			67.7	Tc		
16.9		Ir		70.2		Zr	
17.2	Tl			71.1	Mo		
17.4		Os		74.1		Y	
17.7	Hg			74.8	Nb		
17.9		Re		78.3		Sr	
18.2	Au			78.7	Zr		
18.4		W		79.2			Cf
18.7	Pt			81.0			Bk
19.0		Ta		82.9		Rb	Cm
19.3	Ir			83.0	Y		
19.6		Hf		84.8			Am
19.8	Os			86.8			Pu
20.2		Lu		87.7	Sr		
20.4	Re			87.9		Kr	
20.9		Yb		88.9			Np
21.1	W			91.1			U
21.6		Tm		92.7	Rb		
21.7	Ta			93.3		Br	Pa
22.3		Er		95.6			Th
22.4	Hf			98.0			Ac
23.0		Ho		98.1	Kr		
23.1	Lu			99.2		Se	
23.8	Yb	Dy		100.5			Ra
24.6	Tm	Tb		103.1			Fr
25.4	Er			104.1	Br		
25.5		Gd		105.7		As	Rn
26.2	Ho			108.5			At
26.4		Eu		110.6	Se		
27.1	Dy			111.4			Po
27.3		Sm		112.9		Ge	
28.0	Tb			114.4			Bi
28.3		Pm		117.5			Pb
29.0	Gd			117.7	As		
29.3		Nd		120.7			Tl
30.0	Eu			120.8		Ga	
30.4		Pr		124.1			Hg
31.1	Sm			125.5	Ge		
31.6		Ce		127.6			Au
32.2	Pm			129.5		Zn	
32.8		La		131.3			Pt

Table 6 *continued*

λ pm	Kα	Kβ	Lα
134.2	Ga		
135			Ir
139.1			Os
139.2		Cu	
143.2			Re
143.6	Zn		
147.6			W
150.0		Ni	
152.2			Ta
154.2	Cu		
157.0			Hf
162.0			Lu
162.1		Co	
165.9	Ni		
167.2			Yb
172.7			Tm
175.7		Fe	
178.4			Er
179.0	Co		
184.5			Ho
190.9			Dy
191.0		Mn	
193.7	Fe		
197.7			Tb
207.7			Gd
208.5		Cr	
210.3	Mn		
212.1			Eu
220.0			Sm
228.2			Pm
228.4		V	
229.1	Cr		
237.0			Nd
246.3			Pr
250.5	V		
251.4		Ti	
256.2			Ce
266.6			La
275.0	Ti		
277.6			Ba
278.0		Sc	
289.2			Cs
302			Xe
303	Sc		
309		Ca	
315			I
329			Te
336	Ca		
344			Sb
345		K	
360			Sn
374	K		
377			In
389		Ar	
396			Cd
415			Ag
419	Ar		
437			Pd
440		Cl	
460			Rh
473	Cl		
485			Ru
503		S	
511			Tc
537	S		
541			Mo
572			Nb
580		P	
607			Zr
616	P		
645			Y
677		Si	
687			Sr
713	Si		
732			Rb
782			Kr
798		Al	
834	Al		
837			Br
899			Se
956		Mg	
967			As
989	Mg		
1044			Ge
1129			Ga
1162		Na	
1191	Na		
1225			Zn
1334			Cu
1446		Ne	
1456			Ni
1462	Ne		
1587			Co
1759			Fe
1831		F	
1945			Mn
2164			Cr
2371		O	
2742			Ti
3135			Sc
3160		N	
3633			Ca

Table 6A

X-ray lines (first order (n = 1)) arranged in 2Θ angle order for a wavelength dispersive spectrometer with a Lithium Fluoride Crystal in the (200) plane

2Θ	line	2Θ	line
8.66	Pr Kβ	27.43	Bi Lβ_2
9.00	Ce Kβ	27.46	Th Lα_1
9.34	La Kβ	27.52	Pt Lγ_1
9.71	Ba Kβ	27.81	Th Lα_2
9.86	Pr Kα	27.84	Pb Lβ_3
10.23	Ce Kα	28.08	Bi Lβ_4
10.11	Cs Kβ	28.17	Kr Kα
10.28	Xe Kβ	28.2	Ac Lα_1
10.63	La Kα	28.25	Pb Lβ_1 & $_2$
10.94	I Kβ	28.49	Ir Lγ_1
11.03	Ba Kα	28.52	Se Kβ
11.40	Te Kβ	28.55	Bi Lβ_6
11.46	Cs Kα	28.6	Ac Lα_2
11.89	Sb Kβ	28.78	Tl Lβ_3
11.91	Xe Kα	28.9	Ra Lα_1
12.40	I Kα, Sn Kβ	28.99	Pb Lβ_4
12.92	Te Kα	29.05	Tl Lβ_2
12.97	In Kβ	29.19	Tl Lβ_1
13.46	Sb Kα	29.37	Pb Lβ_6
13.55	Cd Kβ	29.4	Ra Lα_2
14.03	Sn Kα	29.49	Os Lγ_1
14.18	Ag Kβ	29.69	Hg Lβ_3
14.66	In Kα	29.7	Fr Lα_1
14.84	Pd Kβ	29.90	Tc Lβ_4
15.30	Cd Kα	29.93	Hg Lβ_2
15.53	Rh Kβ	29.96	Br Kα
16.01	Ag Kα	30.1	Fr Lα_2
16.33	Ru Kβ	30.19	Hg Lβ_1, Tc Lβ_6
16.76	Pd Kα	30.43	As Kβ
17.1	Tc Kβ	30.5	Rn Lα_1
17.54	Rh Kα	30.55	Re Lγ_1
17.57	U Lγ_1	30.75	Au Lβ_3
18.03	Mo Kβ	30.81	Au Lβ_2
18.11	Pa Lγ_1	30.84	Hg Lβ_4
18.37	Ru Kα	31.0	Rn Lα_2
18.63	Th Lγ_1	31.08	Hg Lβ_6
18.98	Nb Kβ	31.20	Au Lβ_1
19.3	Tc Kα	31.3	At Lα_1
20.05	Zr Kβ	31.64	W Lγ_1
20.31	U Lβ_3 Mo Kα	31.7	At Lα_2
20.60	U Lβ_1	31.76	Pt Lβ_2
20.94	Pa Lβ_3	31.82	Pt Lβ_3
21.17	Y Kβ	31.88	Au Lβ_4, Se Kα
21.23	Pa Lβ_1	32.02	Au Lβ_6
21.41	U Lγ_1, Nb Kα	32.2	Po Lα_1
21.61	U Lβ_2, Th Lβ_3	32.29	Pt Lβ_1
21.93	Th Lβ_1	32.56	Ge Kβ
22.04	Pa Lβ_4	32.6	Po Lα_2
22.16	Pa Lβ_2	32.74	Ir Lβ
22.42	Sr Kβ	32.82	Ta Lγ_1
22.57	Zr Kα	32.88	Ir Lβ_3
22.59	U Lβ_6	32.94	Pt Lβ_4
22.74	Th Lβ_2 & $_4$	32.97	Bi Lα_1, Pt Lβ_6
23.15	Pa Lβ_6	33.33	Bi Lα_2
23.29	Bi Lγ_1	33.39	Ir Lβ_1
23.73	Th Lβ_6	33.80	Os Lβ_2
23.76	Rb Kβ	33.92	Pb Lα_1
23.81	Y Kα	33.98	Ir L β_6, As Kα
24.08	Pb Lγ_1	34.04	Ir L β_4, Os L β_3, Hf Lγ_1
24.89	Tl Lγ_1	34.25	Pb Lα_2
25.15	Kr Lβ Sr Kα	34.58	Os Lβ_1
25.74	Hg Lγ_1	34.85	Re Lβ_2
26.15	U Lα_1	34.88	Tl Lα_1, Ga Kβ
26.50	U Lα_2	35.06	Os Lβ_6
26.61	Au Lγ_1, Rb Kα	35.21	Tl Lα_2, Os Lβ_4
26.79	Pa Lα_1, Br Kβ	35.26	Re Lβ_3
27.02	Bi Lβ_3	35.32	Lu Lγ_1
27.14	Pa Kβ	35.80	Re Lβ_1
27.34	Bi Lβ_1	35.89	Hg Lα_1

Table 6A *continued*

2Θ	line	2Θ	line
35.98	W Lβ_2	49.02	Yb Lα_1
36.16	Re Lβ_6	49.34	Dy Lβ_3 and $_6$
36.25	Hg Lα_2	49.37	Yb Lα_2, Tb Lβ_2
36.34	Ge Kα	50.25	Dy Lβ_1
36.43	Re Lβ_4	50.38	Gd Lβ_2
36.55	W Lβ_3	50.56	Dy Lβ_4
36.70	Yb Lγ_1	50.75	Tm Lα_1, Sm Lγ_1
36.97	Au Lα_1	51.10	Tm Lα_2
37.12	W Lβ_1	51.25	Tb Lβ_6
37.21	Ta Lβ_2	51.41	Tb Lβ_3
37.30	Au Lα_2	51.73	Fe Kβ
37.36	WL β_6	52.36	Tb L β_1
37.51	Zn Kβ	52.58	Er Lα_1
37.72	W Lβ_4	52.62	Tb Lβ_4
37.87	Ta Lβ_3	52.81	Co Kα
38.05	Pt Lα_1	52.93	Er Lα
38.14	Tm Lα_1	53.31	Gd Lβ_6
38.41	Pt Lα_2	53.47	Eu Lβ_2
38.44	Hf Lβ_2	53.57	Gd Lβ_3
38.47	Ta Lβ_1	54.53	Ho Lα_1
38.59	Ta Lβ_6	54.56	Gd Lβ_1
38.90	Ga Kα	54.78	Gd Lβ_4
39.05	Ta Lβ_4	54.88	Ho Lα_2
39.20	Ir Lα_1	55.49	Eu Lβ_6
39.26	Hf Lβ^3	55.59	Nd Lγ_1
39.56	Ir Lα_2	55.72	Sm Lβ_2
39.62	Er Lγ_1	55.88	Eu Lβ_3
39.77	Lu Lβ_2	56.59	Dy Lα_1
39.89	Hf Lβ_1 & $_6$	56.62	Mn Kβ
40.44	Os Lα_1, Hf Lβ_4, Cu Kβ	56.94	Dy Lα_2, Eu Lβ_1
40.71	Lu Lβ_3	57.14	Eu Lβ_4
40.74	Os Lα_2	57.49	Fe Kα
41.17	Yb Lβ_2	57.78	Sm Lβ_6
41.20	Lu Lβ_6, Ho Lγ_1	58.27	Pr Lγ_1
41.41	Lu Lβ_1	58.31	Sm Lβ_3
41.68	Re Lα_1	58.73	Tb Lα_1
41.81	Zn Kα	59.09	Tb Lα_2
41.91	Lu Lβ_4	59.48	Sm Lβ_1
42.02	Re Lα_2	59.55	Sm Lβ_4
42.26	Yb Lβ_3	60.70	Nd Lβ_2
42.60	Tm Lβ_2	61.06	Gd Lα_1
42.78	Yb Lβ_6	61.13	Ce Lγ_1
42.90	Dy Lγ_1	61.42	Gd Lα_2
42.97	Yb Lβ_1	62.32	Cr Kβ
43.00	W Lα_1	62.95	Mn Kα Nd L β_6
43.33	W Lα_2	63.49	Pr L β_2
43.46	Yb Lβ_4	63.52	Eu Lα_1
43.73	Ni Kβ	63.72	Nd Lβ_3
43.88	Tm Lβ_3	63.89	Eu Lα_2
44.16	Er Lβ_2	64.22	La Lγ_1
44.19	Tm Lβ_6	65.07	Nd L β_1 and $_4$
44.41	Ta Lα_1	65.88	Pr L β_6
44.65	Tm Lβ_1, Tb Lγ_1	66.18	Sm Lα_1
44.74	Ta Lα_2	66.49	Ce Lβ_2
45.02	Cu Kα	66.56	Sm Lα_2
45.08	Tm Lβ_4	66.76	Pr Lβ_3
45.61	Er Lβ_3	67.62	Ba Lγ_1
45.79	Ho L β_1, Er Lβ_6	68.10	Pr Lβ_4
45.85	Hf Lα_1	68.23	Pr Lβ_1
46.19	Hf Lα_2	69.0	Pm Lα_1
46.38	Er Lβ_1	69.03	Ce Lβ_6
46.57	Gd Lγ_1	69.13	V Kβ
46.78	Er Lβ_4	69.34	Cr Kα
47.37	Lu Lα_1	69.4	Pm Lα_2
47.40	Ho L β_3	69.75	La Lβ_2
47.43	Co Kβ	70.03	Ce Lβ_3
47.50	Ho Lβ_6	71.32	Cs Lγ_1
47.53	Dy Lβ_2	71.36	Ce Lβ_4
47.71	Lu Lα_2	71.60	Ce L β_1
48.24	Ho Lβ_1	72.09	Nd Lα_1
48.59	Eu Lγ_1	72.41	La Lβ_6
48.62	Ho Lβ_4	72.48	Nd Lα_2
48.65	Ni Kα	73.29	Ba Lβ_2

Table 6A *continued*

2Θ	line	2Θ	line
73.51	La Lβ_3	110.34	Sn Lβ_3
74.90	La Lβ_4	111.79	Cd Lγ_1
75.22	La Lβ_1	111.95	In Lβ_2
75.40	Pr Lα_1	112.20	Sn Lβ_4
75.76	Pr Lα_2	113.07	Ca Kα
76.09	Ba Lβ_6	114.37	Sn Lβ_1
76.92	V Kα	117.05	In Lβ_6
77.14	Cs Lβ_2	117.27	Sb Lα_1
77.25	Ti Kβ	117.76	Sb Lα_2
77.32	Ba Lβ_3	118.04	K Kβ
78.75	Ba Lβ_4	121.03	In L β_4
78.97	Ce Lα_1	121.44	Cd Lβ_2
79.19	Ba L β_1	121.96	Ag Lγ_1
79.30	Ce Lα_2	123.93	In Lβ_1
79.78	I Lγ_1	126.65	Sn Lα_1
80.15	Cs Lβ_6	127.61	Cd Lβ_6
81.46	Cs Lβ_3	128.07	Sn Lα_2
82.86	La Lα_1	129.51	Cd Lβ_3
82.89	Cs Lβ_4	132.11	Cd Lβ_4
83.20	La Lα_2	133.53	Ag Lβ_2
83.54	Cs Lβ_1	136.28	Cd Lβ_1
84.65	Te Lγ_1	137.74	K Kα
86.08	Ti Kα	138.96	In Lα_1
86.16	I L β_2	139.61	In Lα_2
87.14	Ba Lα_1	141.90	Ag Lβ_6
87.30	Sc Kβ	144.14	Ag Lβ_3
87.49	Ba Lα_2	147.73	Ag Lβ_4
89.56	I Lβ_6	155.38	Ag Lβ_1
90.12	Sb Lγ_1	158.36	Cd Lα_1
91.05	I L β_3	159.61	Cd Lβ_2
91.38	Te L β_2		
91.79	Cs Lα_1		
92.20	CS Lα_2		
92.61	I L β_4		
93.64	I L β_1		
95.02	Te L β_6		
96.34	Sn Lγ_1		
96.59	Te L β_3		
97.28	Sb Lβ_2		
97.67	Sc Kα		
98.27	Te L β_4		
99.59	Te Lβ_1		
100.16	Ca Kβ		
101.28	Sb Lβ_6		
102.82	I L$\alpha_1$1		
102.95	Sb Lβ_3		
103.23	I Lα_2		
103.41	In Lγ_1		
104.01	Sn Lβ_2		
104.75	Sb Lβ_4		
106.40	Sb Lβ_1		
108.51	Sn Lβ_6		
109.49	Te Lα_1		
109.94	Te Lα_2		

F UV-visible Fluorescence Measurement

F1 Principle

If the dioxouranium ion is illuminated with ultra violet light (a nitrogen laser source at 337 nm is suitable) it will fluoresce at 494, 516 and 540 nm. There is interference from some organic compounds which give a band emission in the 400 nm region (see Ref 43 for a typical method).

F2 Limit of Detection

About 0.1 $ng.l^{-1}U$.

F3 Essentials of the method

F3.1 The uranium must be in the hexavalent state. In ref 43 this is stabilized by addition of sodium pyrophosphate, and triphosphate.

F3.2 Either organic matter should be absent, removed by oxidation, a filter used, or a plot made of the fluorescence and the peak heights measured against any background from the band.

F3.3 Organic matter can be removed and uranium oxidized to the hexavalent state by the procedure given in Ref 58.

F3.4 Analyses are made by comparing the fluorescence from the sample with the fluorescence from standard concentrations of uranium VI treated in like manner. For information on standard uranium VI solutions, see the preceding procedure.

The Determination of Tritium

Tritium occurs most commonly in water as water itself (HTO). Except for radiological monitoring purposes, the main reason for determining tritium in water is to assess whether the supply is being replenished by rainfall or not. As mentioned earlier, tritiated organic compounds, usually insoluble are used commercially mainly in luminous equipment or in medicine and research. Such material may eventually end in tip leachates, effluents and incinerator gases.

Tritium is a weak beta emitter, hence some form of concentration and special counting techniques are required, which will be dependent on the form in which the tritium is suspected of being present. In the most usual method for water samples, chlorine, if present, and radioiodine are removed by thiosulphate and acidity neutralized with sodium carbonate, solutes are removed by distillation to give a relatively pure water. Tritium in organic compounds is usually determined by first oxidizing the substance to give tritiated water. For most wastes it is necessary to concentrate the tritium electrolytically, for details see Refs 61 and 62. A scintillating substance is added and the sample counted for several successive intervals of time using a liquid scintillation counter. The counts are quantified by comparison with tritium standards, allowance being made for decay and statistical errors. The US Environmental Protection Agency have published a method—see reference 18A. Laboratories with a need for tritium analysis can obtain assistance from the Atomic Energy Research Establishment, Harwell, the Laboratory of the Government Chemist, London, the National Radiological Protection Board, Didcot, and a few other specialist laboratories.

The International Standards Organisation (ISO) has a draft standard method in preparation for the determination of Tritium in Water.

Analysis of Saline and Other Mineralized Waters

The methods given for radon and for radium by radon emission (Methods C and D) are capable of use with almost any water. Method D is used for marine analysis.

The methods for alpha and beta activity and for uranium by X-ray fluorescence are capable of simple adaptation to the analysis of saline or mineralized waters but the performance data given here will not apply. To adapt these methods, the standard samples must contain added salts to match the salts present in the sample. The main effect of these salts on the methods will be to increase the sample thickness during counting, absorbing some of the radiation and to reduce the precision of sample preparation with consequent reduction in the overall precision and limit of detection.

Screening of Sludges, Sediments and Similar Solids for Alpha and Beta Radioactivity

1. Purpose

The screening procedures which follow are intended for the monitoring of significant changes in the levels of radionuclides in sewage and waterworks sludges, sediments and similar solids. As is the case with all so called 'gross' alpha or beta determinations the results are expressed in terms of one arbitrary radionuclide standard which generally leads to an unspecifiable bias according to the relative energies, and hence relative counting efficiencies, of the emissions from radionuclides in the sample and the emissions from the standard radionuclide.

In making comparisons with previous determinations the influence of natural radioactive decay series elements and their decay or growth should be considered. Comparison is best made with results obtained with a similar delay after collection.

Whether radioiodine (^{131}I) beta emitter is included in part or completely, in the beta result will depend on the chemical form (oxidation state) of the iodine and whether consequently it is volatile under the test procedure conditions. The minimum precaution, of ensuring the medium is alkaline, is taken.

2. Hazards

Sludges, especially sewage sludges, contain pathogens in addition to any suspected radioactivity. Great care is necessary not to scatter dust which may be inhaled or ingested by the technician or others. Rubber or similar impermeable gloves should be worn to prevent skin contact.

3. Reagents and Apparatus

As for methods A and B (omitting sulphuric acid), Method 1 in Ref 65 and pH in Ref 66.

3.1 Extra Reagents and Apparatus

Sodium Hydroxide any convenient strength.

4. Analytical Procedure

Step	Procedure	Notes
4.1	Determine the percentage solids content of the samples using the first method in Ref 65 (note (a)). Calculate the amount of sample required to prepare a source in step 4.6. Let the percentage solids be D% w/w.	(a) See Hazard section above.
4.2	Determine the pH of the sample using the method for solids given in Ref 66 (note (b)).	(b) A spare portion of sample may be used, remainder being treated proportionately and the pH then checked.
4.3	Adjust the pH from 7.5 to 8.0 by careful addition, with stirring of a small amount of any convenient sodium hydroxide solution, rechecking the pH as necessary (note (b)).	
4.4	Dry the pH adjusted sample at 105° ±2°C to constant weight in a prepared shallow dish (note (a)).	

Step	Procedure	Notes
	Top heat from an infra red lamp is convenient, for initial drying but care is essential to prevent charring. Finish in an oven.	(c) It is essential to produce a fine, evenly spread, homogeneous powder.
4.5	Grind or macerate to produce a fine dry powder. Some sludges are fibrous and will not grind.	
4.6	For each measurement, weigh out 10A mg (± 1%) of the solid onto a counting tray where A cm^2 is the area of the counting tray, (notes (c) and (d)).	(d) Because, for alpha particle counting, efficiency is seriously affected by source thickness, it follows that standard sources (step 4.8) of the same mass loading are required for calibration of the detection system.
4.7	Disperse the sample evenly over the planchette by slurrying with a few drops of methanol and allow to dry (note (e)). Make a note of the time and date of source preparation. Check weight if necessary.	(e) Other volatile organic solvents can be used, e.g. acetone. Because alpha particle counting efficiency is seriously affected by source thickness, it is essential to produce evenly spread counting sources.

Alpha Counting

This must be started as soon as possible after source preparation.

(For Beta Counting see steps 4.10–4.12)

Step	Procedure	Notes
4.7	Set up the counter in accordance with the manufacturer's instructions.	
4.7.1	Immediately after drying the source commence measurement of the activity on the planchette by counting for an appropriate time (note (f)). Let the measured count rate be S.sec^{-1}. Note the time, duration of count, and date.	(f) The duration of count depends on the sample and background count rates and the precision required; see section A8. 1000 minutes is the longest time normally used.
4.7.2	Measure the background activity using an identical clean planchette. Let the measured count rate be B.sec^{-1}.	
4.7.3	Repeat the counting procedures in 4.7.1 and 4.7.2 periodically over a period of 1 month (notes (g) and (h)).	(g) Recounting over a period of one month may reveal ingrowth of daughter radionuclides from radium isotopes. The interpretation of such data can be complicated depending on whether uranium and/or thorium series radionuclides are present in admixture, singly or whether one predominates. At normal environmental levels it is rare for these phenomena to be apparent, particularly when long count durations have been employed. However, over a period of 1 month sources from samples which are naturally high in ^{226}Ra may show an increase of about four times the initial count. Some samples show a substantial reduction in emission rate over the month due to the decay of significant amounts of ^{224}Ra.
4.8	**Preparation of the standard for alpha activity measurement.** **Warning** This procedure requires the preparation of a dry powder spiked with alpha emitting radionuclides. Accidental ingestion of radioactive particulates must be avoided and the use of a simple closed cabinet glove box is recommended for the preparation of the spiked sources. Alternatively a laboratory fume cupboard may be used provided the extract draught is not excessive and liable to disturb or carry fine powder particles into the air. (Note (h)).	(h) See also the Hazards Section warning on pathogens.
4.8.1	Accurately weight approximately 2.5 g of calcium sulphate into a 150 ml beaker. Carefully add 10 ml (± 1%) of hot nitric acid d$_{20}$ 1.42, stir and add hot water (up to 100 mls) to dissolve.	

Step	Procedure	Notes
4.8.2	To the solution, add an accurately known amount of standard [37 Bq of ^{241}Am is suitable].	
4.8.3	Transfer the solution to a 200 ml silica or porcelain dish, weighed to ±0.0001 g and take the solution to dryness under an Infra Red Lamp.	
4.8.4	Dry the residue in an oven at 105° ± 2°C for 1 hour.	
4.8.5	Calculate the specific activity ($Sp\alpha$) of the $CaSO_4$ using the weight of the dried residue and the amount of activity added, $Bq.g^{-1}$ as ^{241}Am.	
4.8.6	(See note (i)). Crush and grind the solid (with a pestle if necessary) to produce a fine powder in a manner similar to that used for the preparation of the sample.	(i) Possible hazard. See Warnings in 4.8 and the Hazards Section.
4.8.7	Prepare planchette sources (10 A mg on each planchette) in the manner prescribed for samples. Section 4.5 and 4.6.	
4.8.8	Measure the alpha response of the detector system to these standard sources. Let the mean of the measured count rates be $K.sec^{-1}$.	
4.9	Calculate the alpha activity C per kilogram of the sample from the equation $C = \frac{(S-B)}{(K-B)} \times Sp\alpha \times \frac{1000\ D}{A}$ Where S = observed sample count rate, sec^{-1} (see 4.7.1) B = background planchette count rate, sec^{-1} (see 4.7.2) K = observed standard count rate, sec^{-1} (see 4.8.8) A = area of planchette, cm^2 [10 A = mass of standard solids, mg, on planchette (see 4.8.7)] $Sp\alpha$ = specific activity of the standard solids, $Bq.g.^{-1}$ (see 4.8.5) D = percent solids w/w content of original sample (see 4.1 above)	
	Beta Counting *(For Alpha Counting see steps 4.7–4.9)*	
4.10	Set up the Geiger counting assembly according to the manufacturer's instructions.	

Step	Procedure	Notes
4.10.1	Measure the activity on the planchette by counting an appropriate length of time. (Note (j)). Let the measured count rate be S sec^{-1}. (Note (k)).	(j) The length of count depends on the sample and background count rates and the precision required: see section B8. 1000 minutes is the longest time normally used.
4.10.2	Measure the background activity using an identical clean tray. Let this measured count rate be B sec^{-1}.	(k) Periodic recounting of sample sources (daily) may reveal decay or less commonly ingrowth. Recounting should be carried out in the event of an unexpected result when compared with earlier experience.
4.11	Using potassium chloride instead of sample carry out steps 4.5, 4.6 and 4.10 to 4.10.2 inclusive. Let the measured count rate be K sec^{-1}.	
4.12	Calculate the beta activity C per kilogram of the sample from the equation: $C = \frac{(S-B)}{(K-B)} \times 14.4 \times \frac{1000\,D}{A}$ (note 1) Where C = beta activity in becquerels per kilogram.	(l) The β-activity of ^{40}K in natural potassium is 27.4 Bq.g^{-1} and in potassium chloride is 14.4 Bq.g^{-1}.
4.13	Report the result, together with the date of counting, and the thickness of source in mg cm^{-2}. For Example 0.42 ± 0.04 Bq. Kg^{-1} (^{241}Am equivalent) 2.0 ± 0.5 Bq. Kg^{-1} (^{40}K equivalent) The confidence level (2σ) quoted is due to counting errors alone. Counting date : February 1982 Source thickness: 10 mg cm^{-2}	

5. Precision of Counting

The standard deviation, σ, associated with the activity of the sample corrected for background is

$$\sigma_{(S-B)} = \sqrt{\left(\frac{S}{T_S} + \frac{B}{T_B}\right)}$$

where T_S and T_B are the respective durations of the count of the sample and background. It is usual to ensure that the standard deviation associated with the counting of the standard alpha source is insignificant compared with that of counting the sample, and to quote the result with a standard deviation 'due to counting errors alone'.

Increasing the counting time will lower the limit of detection, limited only by the effects of daughter isotopes. 1000 minutes is the longest time normally used.

6. Sources of Error

6.1 Contamination

It is desirable to carry out the analysis in an area where radio-tracers are not used. Contamination of reagents should be checked by evaporating appropriate volumes of the reagents on separate planchettes and measuring the activities, which should be negligible compared with that of the sample. Contamination of the whole system can be checked by processing 1 litre ± 10 ml of distilled water to which 10A ± 1 mg of chromatographic reagent grade silica gel has been added and measuring the activity. This can be compared with the activity of a direct slurry of 10A ± 1 mg of the silica gel onto a counting planchette. Again the activity should be negligible compared with that of the sample.

^{60}Co may be countered as a contaminant in stainless-steel and may therefore affect the beta background count but not necessarily the sample.

The specification for some ion-exchange resins indicate that beta emitting ^{90}Sr may be present in the resin (and can be eluted). If deionized water is used all new supplies should be checked before use.

7.2 Losses of Activity

It is obvious that some radionuclides will be lost or not measured by this method. For example ^{3}H, and possibly ^{14}C and some ^{35}S will be lost on drying; β-emitters of low energy would not be measured (or would be measured with very low efficiency) with 10 mg.cm^{-2} self absorption and 7 mg.cm^{-2} external absorption. Of the radionuclides in the uranium series, ^{222}Rn would be lost during processing but with its α and β-emitting daughters it would subsequently grow back into the counting source from any ^{226}Ra present. A similar effect occurs with radionuclides from the ^{232}Th series. See also Section 1, last paragraph.

Some alpha emitting polonium isotopes which occur naturally as members of the uranium and thorium decay series may comprise a significant proportion of the gross alpha activity. The element and some of its compounds, particularly the halides which sublime at relatively low temperatures, (Ref 33) may be volatilized. If this is suspected to be significant, an accurate polonium determination should be considered.

7.3 Variation in response of the system

The unavoidable effect of absorption will result in a variation of counting efficiency depending on the composition of the sample. If necessary the response of the system to radionuclides which might be encountered can be determined by spiking silica or other blank materials with known quantities of standard solutions of these radionuclides. After careful drying and homogenization, sources 10 A mg.cm^{-2} thick can be prepared and counted. The response of the counter in count-rate per unit of activity (counts.s^{-1}.Bq^{-1}) can then be calculated.

8. Quality Control

Apart from the manufacturer's suggestions for instrumental quality control, standards prepared from an alpha emitter and silica, calcium carbonate or other convenient stable absorbent and from potassium chloride for beta standards as well as background planchettes should be counted with each batch of samples and suitable quality control graphs prepared (Refs 35, 36 and 37).

9. Regulations Governing the Use of Radioactive Materials

Regulations governing the use of radioactive materials and the disposal of radioactive wastes in the UK are set out in another booklet of this series Ref 30.

Safeguards Legislation

The acquisition of standard materials described in A4.1, except Americium isotopes, *however small the amount may be*, will bring the purchaser within the scope of the Euratom Treaty on the non-proliferation of nuclear weapons. EEC countries, as signatories to the Commission Regulation No 3227/76 of 19 October 1976, have to account for the acquisition transfer the usage of 'source materials' (uranium and thorium in all forms) and 'special fissile materials' (plutonium and enriched uranium at the present time)*.

The application of the legislation within individual nations should be ascertained before embarking on the purchase of any of the listed materials.

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* Note that although certain specified small-scale exemptions exist as for possession of gas mantles, they are not applicable to materials used in this method.

The responsible body for the UK

Safeguards Office
Department of Energy
Atomic Energy Division
Thames House South
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London
SW1P 4QJ

10. Action in the Event of a significant increase in activity

Consult Her Majesty's Radiochemical Inspectorate. See Introduction section 3.1 for addresses.

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