Four Essay Reviews on applications of Radiation Measurement in the Water Industry 1984

Methods for the Examination of Waters and Associated Materials

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This document contains 59 pages

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Methods for the Examination of Waters and Associated Materials

This booklet contains Four Reviews and Two Notes. Each is self contained in presentation.

Contents

London Her Majesty's Stationery Office

PBO

Warning to Users

The procedures reviewed in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local and National Safety Regulations must be observed and appropriate authorities consulted when necessary. 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 whether for one's self, one's colleagues in the laboratory, outsiders or subsequently for maintenance workers. Lone working, whether in the laboratory or field, should be discouraged. 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, equipment cleanliness and reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for 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.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care must be taken beyond that which should be exercised at all times when carrying out analytical procedures. 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 radio-chemical 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.

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.

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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 individual methods, 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 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 reponsible 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 analytical chemist, biologist, bacteriologist etc. 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

31 October 1983

Note on the 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 the 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 curie (Ci) which was based upon the activity of one gram of radium. 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 relationship between the new and the old units is summarized below. The same prefixes are used with these units for denoting larger and smaller multiples as are used for other SI units of measurement.

Units

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

Prefixes

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	μ
10^{-9}	nano	n
10^{-12}	pico	p

Regulations Governing the Uses of Radioactive Materials

1. Introduction and Disclaimer

Sources of radiation are nowadays widely used in medicine, research and industrial processes, and nuclear energy is used in the production of electricity. There are radioactive substances in many products and devices that are available to the public or used in general industry, for example, smoke detectors. The penetrating power of radiation is used to measure the thickness of materials and to detect liquid levels in conditions where conventional techniques are inadequate. New uses are constantly being developed. With these increasing uses of radiation and radioactivity, statutory and other controls, relating to radioactive materials and machines capable of producing ionizing radiations, have come into force.

This brief introduction to regulations covering the use, storage, transport and disposal of radioactive materials within the United Kingdom is for guidance only. It does not purport to be an exhaustive coverage of all the regulations, which may, in any case, be changed in the future, nor should it be regarded as having any legal authority. The detailed provisions of the relevant documents should be consulted and, in case of doubt, advice should be obtained from the relevant government department or other competent organisation.

2. Insurance

Before using or transporting radioactive materials, the provision of valid adequate insurance should be arranged.

3. Statutory and Other Controls

In the United Kingdom there is no single general statute concerned with radiological protection. A number of separate statutes, statutory instruments and non-statutory codes of practice (or guidance notes) involving several government departments are directed to specific aspects of the use of radioactive materials, ionizing radiations and disposal of radioactive waste. The organizations listed in 5.1–5.3 are responsible for ensuring compliance with the various regulations.

3.1 Keeping and Use of Radioactive Materials on Premises

The keeping and use of radioactive materials on premises is controlled by the Radioactive Substances Act 1960(1), which is administered by the Department of the Environment in England and by corresponding government departments in other parts of the UK.

Under Section 1 of the Act, no one in the United Kingdom may keep or use radioactive material on premises used for the purposes of an undertaking unless registered with the appropriate Secretary of State or exempted from registration. The Secretary of State may impose conditions on registration or may refuse registration, but, apart from conditions relating to the removal of material to other premises, and labelling, he shall have regard exclusively to the amount and character of the radioactive waste likely to arise from the keeping or the use of the material on the premises.

NHS hospitals, except those in Northern Ireland, are exempt from registration under Section 1, and Crown premises are exempted from all the provisions of the Act, although they notify the use of radioactive materials by letter and in practice comply with the statutory provisions. Under Section 2, UKAEA sites and premises in respect of which a nuclear site licence is in force are also exempted from registration.

Under Section 3 of the Act, persons are required to be registered in respect of mobile radioactive apparatus unless specifically exempted. (UKAEA are exempted.)

Further, under Sections 6 and 7, no one may dispose of or accumulate radioactive waste from or on premises used for the purposes of an undertaking unless authorised by the appropriate Secretary of State, or exempted by virtue of an Exemption Order made under the Act. Section 6 authorisations in respect of UKAEA and licensed sites in England are issued jointly by the Department of the Environment and the Ministry of Agriculture, Fisheries and Food and by corresponding government departments in other parts of the UK. Such sites do not require authorization under Section 7 of the Act for accumulation of radioactive waste.

A more detailed explanation of the provisions of the 1960 Act is given in "Radioactive Substances Act 1960, A guide to the administration of the Act". HMSO (1982).

3.2 Protection of Workers

3.2.1 Factories

In factories which are subject to the Factories Act (1961) (2), the use of radioactive material is governed by two sets of Regulations: The Ionizing Radiations (Unsealed Radioactive Substances) Regulations 1968 (3) and the Ionizing Radiations (Sealed Sources) Regulations 1969 (4). The corresponding legislation for Northern Ireland is the Factories Act (NI) 1965 (5) and the Ionizing Radiations (Sealed Sources) Regulations (NI) 1969 (6).

The Unsealed Radioactive Substances Regulations impose requirements for the protection of persons against ionizing radiations arising from unsealed radioactive substances and from objects contaminated with unsealed radioactive substances. The various sections detail the procedures for administration, notification, record keeping, radiological and medical supervision and the organization of work. The need to provide special facilities, personal protective equipment and monitoring apparatus is also covered. The Regulations do not apply to luminized articles, incandescent mantles and small amounts of uranium and thorium compounds intended for use as chemical reagents, except in any factory in which they are manufactured or repaired.

The Sealed Sources Regulations impose similar requirements for the protection of persons against ionizing radiations arising from sealed sources and machines producing ionizing radiations.

3.2.2 Research, Educational and Medical Establishments

The use of radioactive substances, whether sealed or unsealed, or of machines emitting ionizing radiations in research establishments should follow the terms of the Guidance Notes for the Protection of Persons Exposed to Ionizing Radiations in Research and Teaching (7), except in the case of hospital research establishments to which the Code for Medical and Dental Practice applies (8).

The Codes specify similar requirements to those in the Regulations relating to factories in terms of administrative organization, protective measures etc.

Under the provisions of the Health and Safety at Work etc. Act (1974) (9), the Health and Safety Executive inspects educational, research and medical establishments. Similar establishments in Northern Ireland are inspected by the Health and Safety Inspectorate of the Department of Economic Development under the Health and Safety at Work (NI) Order 1978 (10).

3.3 Transport

In 1979, the International Atomic Energy Agency (IAEA) published a revised edition of their model regulations for the safe transport of radioactive materials (11). In the United Kingdom conditions of carriage and regulatory requirements are based on the IAEA model.

3.3.1 Road

The carriage of radioactive substances by road is subject to The Radioactive Substances (Carriage by Road) (Great Britain) Regulations 1974 (12), the Radioactive Substances

(Road Transport Workers) (Great Britain) Regulations 1970 (13) and the Radioactive Substances (Road Transport Workers) (Great Britain) (Amendment) Regulations 1975 (14). The Carriage by Road Regulations impose packaging and handling requirements and administrative obligations on consignors, carriers and drivers. The Regulations are expressed in general terms, requiring a proper course of conduct on the part of those concerned, but do not for the most part lay down precise technical requirements. The Code of Practice for the Carriage of Radioactive Materials by Road (15) sets out in more detail the necessary technical requirements in support of the Regulations but does not purport to give legal interpretation of them. Corresponding regulations have been made in Northern Ireland entitled the Radioactive Substances (Carriage by Road) Regulations (Northern Ireland) 1983 (16).

Conditional exemption from registration under Section 1 of the Radioactive Substances Act (1) in respect of storage of radioactive substances during transit is provided in an Exemption Order (17). A separate Exemption Order (18) applies to Northern Ireland.

3.3.2 Sea

The transport of radioactive substances by sea is subject to the Merchant Shipping (Dangerous Goods) Regulations 1981 (19) and the detailed provisions of Class 7 of the Report of the Standing Advisory Committee on the Carriage of Dangerous Goods in Ships, third edition, 1978 — known as the "Blue Book" (20). The Blue Book adheres very closely to the International Maritime Dangerous Goods Code (21).

3.3.3 Rail

The carriage of radioactive substances by rail is subject to British Railways conditions of acceptance of dangerous goods (22).

3.3.4 Air

In the United Kingdom the Civil Aviation Authority licenses air carriers in accordance with the Air Navigation Order 1980 (23) as amended. Such a licence will generally specify that dangerous goods must be transported in accordance with the provisions of the International Air Transport Association Restricted Articles Regulations (24) and the International Civil Aviation Organization, Technical Instructions for the Safe Transport of Dangerous Goods by Air (25), coupled with any Carrier and Government Exceptions incorporated therein.

3.3.5 Post

Acceptance of radioactive substances for transport by post is subject to conditions set down in the Post Office Guide (26).

4. Future Legislative Changes

A Directive of the Council of the European Community (27) applies to the production, processing, handling, use, holding, storage, transport and disposal of natural and artificial radioactive substances and to any other activity that involves a hazard arising from ionizing radiation.

It is expected that new Regulations will be issued under the Health and Safety at Work etc. Act (1974) (9) to comply with the requirements of the Directive. These will replace the above-mentioned Factories Act and Road Transport Workers Regulations and will be supported by approved codes of practice which will give guidance on the practical implementation of the regulations. The Health and Safety Commission has published a consultative document which outlines the framework and content of such a structure in detail (28).

The IAEA model transport regulations have been reviewed and revised and a new edition will be published in 1985.

5. Sources of Advice

Further advice on the various Acts, Regulations and Codes of Practice can be obtained from the relevant departments listed below or the National Radiological Protection Board or the Northern Ireland Radiation Protection Service at one of the addresses shown.

(The information is correct at the time of going to press but could change in the future.)

5.1 Advice on compliance with Section 3.1

England

Department of the Environment
Radiochemical Inspectorate
Romney House
43 Marsham Street
London SW1 3PY
Tel: 01-212-8088 *or* *Emergency:* 01-212-7071
01-212-6315

Scotland

Scottish Development Department
H.M. Industrial Pollution Inspectorate for Scotland
Pentland House
47 Robbs Loan
Edinburgh EH14 1TY
Tel: 031-443-8681 *Emergency:* 031-556-8400

Wales

Welsh Office
Water and Environmental Protection Division
(Environment Protection Section)
Floor 2
Crown Building
Cathays Park
Cardiff CF1 3NQ
Tel: 0222 824158

Northern Ireland

Department of the Environment for Northern Ireland
Environmental Protection Branch
Stormont
Belfast BT4 3SS
Tel: 0232-63210

5.2 Advice on compliance with Section 3.2

United Kingdom

Health and Safety Executive
F.I. 10
25 Chapel Street
London NW1 5DT
Tel: 01-262-3277 or Local Area Office of the Health and Safety Executive (see local telephone directory)

Northern Ireland

Department of Economic Development
Health and Safety Inspectorate
Maryfield
100 Belfast Road
Holywood
Co. Down BT18 9QX
Tel: 02317-4232

5.3 Advice on compliance with Section 3.3

United Kingdom

Department of Transport
Radioactive Materials Transport Division
2 Marsham Street
London SW1P 3EB
Tel: 01-212-7247

Northern Ireland

Department of the Environment for Northern Ireland
Environmental Protection Branch
Stormont
Belfast BT4 3SS
Tel: 0232-63210

5.4 General Advice

Southern England and Wales

National Radiological Protection Board
Southern Centre
Chilton
Didcot
Oxon OX11 0RQ
Tel: Abingdon (0235) 831600

Northern England

National Radiological Protection Board
Northern Centre
Hospital Lane
Cookridge
Leeds LS16 6RW
Tel: Leeds (0532) 679041

Scotland

National Radiological Protection Board
Scottish Centre
155 Hardgate Road
Glasgow G51 4LS
Tel: 041-440-2201

Northern Ireland

Northern Ireland Radiation Protection Service
The Belvoir Park Hospital
Hospital Road
Belfast BT8 8JR
Tel: 642942 Ext 20

References

(1) The Radioactive Substances Act 1960. London, HMSO.

(2) The Factories Act (1961). London, HMSO.

(3) The Ionizing Radiations (Unsealed Radioactive Substances) Regulations 1968. (S.I. 1968 780) London, HMSO.

(4) The Ionizing Radiations (Sealed Sources) Regulations 1969. (S.I. 1969 808) London, HMSO.

(5) The Factories Act (NI) 1965. Belfast, HMSO.

(6) The Ionizing Radiations (Sealed Sources) Regulations (NI) 1969. (S.R. 1969 318) Belfast, HMSO.

(7) Guidance Notes for the Protection of Persons Exposed to Ionizing Radiations in Research and Teaching. HSE 1977, London HMSO. (Formerly Code of Practice for the Protection of Persons exposed to Ionizing Radiations in Research and Teaching).

(8) Code of Practice for the Protection of Persons against Ionizing Radiations arising from Medical and Dental Use. DHSS 1972, HMSO.

(9) The Health and Safety at Work etc. Act 1974. London, HMSO.

(10) The Health and Safety at Work (NI) Order 1978. (SI 1978 1039 (NI 9)). London, HMSO.

(11) International Atomic Energy Agency, Regulations for the Safe Transport of radioactive materials, 1973 Revised Edition (As Amended). Vienna IAEA Safety Series no. 6 (1979).

(12) The Radioactive Substances (Carriage by Road) (Great Britain) Regulations 1974. (S.I. 1974 1735) London, HMSO.

(13) The Radioactive Substances (Road Transport Workers) (Great Britain) Regulations 1970. (S.I. 1970 1827) London, HMSO.

(14) The Radioactive Substances (Road Transport Workers) (Great Britain) (Amendment) Regulations 1975. (S.I. 1975, 1522) London, HMSO.

(15) Code of Practice for the Carriage of Radioactive Materials By Road, DTP 1982. London, HMSO.

(16) The Radioactive Substances (Carriage by Road) Regulations (Northern Ireland) 1983 (SR 1983 No. 344) Belfast, HMSO.

(17) The Radioactive Substances (Storage in Transit) Exemption Order 1962. (S.I. 1962 2646) London, HMSO.

(18) The Radioactive Substances (Storage in Transit) Exemption Order (Northern Ireland) 1962. (SR 1962 246) Belfast, HMSO.

(19) The Merchant Shipping (Dangerous Goods) Regulations 1981. (S.I. 1981, 1747) London, HMSO.

(20) Report of the Standing Advisory Committee on the Carriage of Dangerous Goods in Ships 1978 (The "Blue Book") Class 7, London, HMSO.

(21) International Maritime Organization International Maritime Dangerous Goods Code, (1977 Edition as amended) Volume 4 Class 7 Radioactive Substances, London, IMO Publication Section.

(22) British Railways, Dangerous goods by freight train and by passenger train or similar service, list of dangerous goods and conditions of acceptance. London, British Railway Board, (B.R. 22426, 1977 Edition as amended).

(23) The Air Navigation Order 1980. (S.I. 1980 1965) London, HMSO.

(24) International Air Transport Association Restricted Articles Regulations Issued in a new and updated version every 12 months. Geneva IATA.

(25) International Civil Aviation Organization (ICAO) — Technical Instructions for the Safe Transport of Dangerous Goods by Air — (Annual Revision).

(26) Post Office Guide. Issued yearly, HMSO.

(27) Council Directive of 15 July 1980 amending the Directives, laying down the basic safety standards for the health protection of the general public and workers against the dangers of ionizing radiation. (80/836 Euratom). *Official Journal of the European Communities,* Vo. 23 no. L246 (17 September 1980).

(28) Consultative Document — "The Ionizing Radiations Regulations 198–". HMSO (1982).

Analytical Instrumentation Using Radioactive Sealed Sources

1. Introduction

The continuous monitoring of the performance of industrial and other processing plant has shown spectacular growth over the past few years (1). The results obtained coupled with on-line computer processing of the data has resulted in significant economies in the operation of a number of processes. The trend to greater control over the discharge of effluents has also resulted in an increase in on-line monitoring of waste streams. Radioisotope instruments for both control and monitoring purposes have been developed and in some cases are in routine use e.g. density measurement. This review describes the physical bases and application of these instruments and outlines some of the newer methods which can be expected to appear over the next few years.

Instruments utilizing sealed radioactive sources have a number of technical advantages over more conventional instrumentation which are summarized below.

(a) If penetrating radiation is used then the measurement can be carried out with no contact between the instrument and the material whose property is being measured. This allows measurements to be carried out on corrosive, abrasive, sterile and hot or cold materials where the introduction of a conventional analysis probe is likely to cause problems.

(b) Installation and servicing are facilitated. Because the instrument is totally external to the process material, installation and servicing can be carried out while the plant is on-line.

(c) The instruments are usually robust and compact and can often be operated using an internal power source. The instruments can therefore be used in restricted spaces and in isolated areas, for example for field measurements.

(d) Measurements are generally carried out non-destructively and without sampling. It is also possible, in some cases, to carry out measurements over a large cross-sectional area, for example, over a whole pipe diameter. A result is therefore integrated over this area and hence inhomogeneities in the material do not affect the instrument and an average value is obtained. Conversely the instrument can be made to detect inhomogeneities and to indicate their presence.

(e) Because of the statistical nature of the radioactive measurement the precision of the analysis can be varied by accumulating counts for different time periods, thus either an 'instantaneous' analysis can be obtained or small variations can be removed by integrating over a longer time interval.

A disadvantage in the use of instruments of this type is that the radioactive source itself is hazardous. Radioactive sources present two major hazards.

(a) Ingestion or inhalation of the radioactive material — internal radiation.

(b) External radiation to the body from the radioactive source or from a machine producing ionizing radiation.

The instruments discussed here use only sealed sources which are encapsulated so that the danger from internal radiation is negligible. The external radiation hazard may be reduced by the use of shielding so that the radiation dose at any accessible surface or boundary is reduced to or below the legal maximum. The use of radioactive sealed sources is controlled by the Radioactive Substances Act 1960 and the Ionizing Radiations (Sealed Sources) Regulation, 1969. These regulations may be amended from time to time and the latest documents should be consulted.

2. Devices Using γ - ray Sealed Sources

γ-rays are electromagnetic radiation with quantum energies generally in the range 0.01–10 MeV. The lower energy boundary with X-rays is, of course, a matter of definition and the properties of the radiation are qualitatively similar. γ-rays are produced during nucler transformations (radioactive decay etc.), or the stopping of charged particles in a medium (bremsstrahlung) or during annihilation of a particle-antiparticle pair.

On passing through matter γ-rays interact by three main processes; photoelectric absorption, Compton scattering and pair production. As a result of these processes the energy of the γ-quantum is either totally or partially transferred to the electrons of the material through which the γ-ray is passing. This process of absorption may be represented by equation 1.

$$I = I_0 \exp(-\mu\text{eff}\,\rho x) \qquad (1)$$

where I_0 is the initial radiation intensity, I the intensity of radiation at the detector, x is the pathlength of the absorber, ρ is its density and μeff is the effective mass absorption coefficient which is a composite of the individual absorption coefficients for the three processes mentioned above. The effective mass absorption coefficient μeff is constant for a given absorber and γ-ray energy.

Examination of the parameters in equation (1) indicates that the absorption of γ-rays can be used as the basis for a number of measurements.

(i) Thickness, x assuming that ρ and μ are constants.

(ii) Density, ρ in which cell absorber path length, x, is constant and usually μeff is constant.

In this case, in addition to the density measurement, the system can be used for the measurement of level (liquid or solid/gas interface) or of the position of interfaces (liquid/liquid or solid/solid or liquid/solid) where a density change exists.

(iii) Composition i.e. a measurement of μeff where ρ and x are constant. In this case the concentration of any interfering elements must also be constant (see section 2.3).

2.1 Level measurement

A simple level alarm system is provided by the system shown in figure 1. The system consists of a collimated source of γ – radiation (usually ^{60}Co or ^{137}Cs) and a γ-ray detector at the point where the alarm is required. The most usual detectors are either Geiger Muller tubes or scintillation counters. The radioactive source size is usually chosen so that no radiation reaches the detector when the denser material is between source and detector, while when gas is present the dose rate at the detector is optimally in the region 1–5 μGy/hr.* This optimal arrangement will obviously not be possible when the interface between two materials of similar density is being located.

If proportional measurement is required then this may be achieved using the system shown in figure 2 in which the collimated source is replaced with a source assembly which gives a 20° downward spread of radiation down and across the vessel. The single detector is replaced by a series of detectors which span the region of interest. As the denser material rises in the pipe it attenuates the radiation over an increasing length of the detector and the signal from the detector therefore decreases. By increasing the number of sources and detector arrays levels can be measured and controlled over heights in excess of 10 metres.

2.2 Density measurement

The configuration of a density measurement system is essentially that of the simple alarm system shown in figure 1. The source's size, γ-ray energy and path length are chosen so as to optimize the signal change for the particular density range being measured. For the highest accuracy the source and detector and sample cell should be of integral construction with a very small temperature coefficient so as to minimize path length changes. For a system of this type densities in the range 1–2 g/ml can be measured with an accuracy of 0.0002 g/cm^3 (2) with a response time of 25 seconds (1).

The measurement of the concentration of suspended solids in rivers can be measured by a γ-ray transmission device. The concentration of this material in rivers is usually in the region 0.1–50 g/l and this can be measured by preferential absorption of the 22 keV X-rays of ^{109}Cd. Using a portable instrument with a 74 MBq Cd source, an eight cm path

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* Gray is the SI unit of absorbed dose 1 Gy = Joule/Kg

length and a 15 minute measuring time, with a scintillation counting detector, an accuracy of ±20% at a sediment concentration of 0.1 g/l. and of ±10% at 0.5 g/l. was obtained (4,5). This instrument does require calibration with a sediment of known density and in the example quoted above an average density of 2.65 g/cm^3 for the suspended solid was used and distilled water was used to provide the reference reading.

2.3 Analysis by γ-absorption (2)

γ-absorption is a simple but crude analysis method. It is usually only applied at relatively high metal concentrations and is very sensitive to interferences. The equipment is, however, very rugged and can be used for continuous measurement in situations where other analytical methods would fail completely.

As was mentioned in 2.0 the effective mass absorption coefficient μeff is a composite of three different mechanisms. To a first approximation μeff can be obtained by summing the three individual mass absorption coefficients (equation 2).

$$\mu\text{eff} = \mu\text{q} + \mu\text{c} + \mu\text{p} \qquad (2)$$

where μq, μc and μp are the absorption coefficients for photo-electron production, Compton scattering and pair production respectively. It has been shown that the absorption coefficient depends on the energy of the γ-ray, the atomic number, z, of the absorber and the number of atoms per unit volume of the absorber. Thus, for photo-electron production $\mu\text{q} \propto Z^n$, with $n \simeq 4$–5 depending on the γ-ray energy. For Compton scattering and pair production $\mu\text{c} \propto Z$ and $\mu\text{p} \propto Z^2$ respectively. It can thus be seen that μeff increases rapidly as the atomic number Z increases.

This increase in μeff has been used as the basis for the analysis of solutions of heavy metals in low atomic number matrices e.g. water or hydrocarbons. The method, is of course, non-specific but it has been used for the measurement of Pb, Sn, Zn and Cu in froth flotation feeds (3). Accuracies in the order of ±5–±10% were obtained in continuous on-line measurement at metal concentrations in the range 0.5-10% w/w. The analysis depends both on the increase in μeff and of density with increasing concentration.

Preferential γ-absorption has also been used for the measurement of sulphur in crude oil. A 10 mCi ^{241}Am/Ag source is used and the 22 keV γ-rays are detected with a proportional counter. The sulphur content can be measured over the range 0–6% w/w with a precision of ±0.01 wt. % or ±1% of the indicated value. Changes in density are automatically compensated.

2.4 Transmission Tomography

Materials examination by transmission tomography is now well established especially for medical purposes but also in industry. Although γ-radiation is often used, most other forms of radiation especially X-radiation and ultrasound are suitable. The type of radiation used varies with the material to be inspected and the reason for the inspection.

Radiation is transmitted through the object and measured at several angles, the information then being reconstructed to an image by a microcomputer and TV tube read-out. Caesium gamma sources are often used. (25)

A variant of this method using the natural γ-radiation from the ground scanned from the air has been used to estimate snow cover in remote regions.

3. Neutron Methods

The neutron has a number of properties which allow it to be used as an analytical probe.

(a) It has no electrical charge; it is, therefore, very penetrating and can easily interact with the highly charged atomic nuclei. The probability of capture of a neutron by a nucleus is proportional to the time which the neutron spends near the target nucleus. This forms the basis for analysis by neutron activation and neutron absorption.

(b) Most radioisotopic neutron sources produce neutrons with a range of energies up to 11 MeV. The maximum intensity usually being between 4 and 6 MeV. Successive elastic collisions especially with light nuclei such as hydrogen, slows down these neutrons to thermal energies (<0.03 MeV). The properties of a neutron vary with the energy and "slow" neutrons can be easily differentiated from "fast" neutrons. This forms the basis for the measurement of hydrogen concentration by neutron thermalization.

The various sources of neutrons are listed in section 3.1.

3.1 Neutron Activation Analysis

The principles, practice and limitations of nuclear reactor produced neutron activation analysis are discussed in another review in this booklet. Other neutron sources, either from isotopes or generators, are available and have been used to carry out on-line neutron activation analysis.

These alternative neutron sources are of three types.

(a) **α-emitter/light element** (6) combinations such as ^{227}Ac/Be, ^{226}Ra/Be, ^{239}Pu/Be, ^{241}Am/Be, etc., produce neutrons by an (αn) reaction such as ^{9}Be (αn) ^{12}C.

The neutron yield increases with the α-energy. The neutron energy spectrum is complex except for ^{210}Po/Be sources.

(b) **Fisson sources**(6) produce neutrons during atomic fission processes of transuranic elements such as ^{252}Cf, ^{244}Cm, ^{240}Pu. The neutron yield from ^{252}Cf has made many on-line applications of Neutron Activation Analysis possible.

(c) **Neutron Generators** (7) Instruments are available which produce 14MeV neutrons at fluxes of 10^{9}n cm^{-2} sec^{-1}. The neutrons are produced by the bombardment of a tritium target with deuterons.

$$^{3}H(d,n)^{4}He$$

Recent advances in generator technology have made fluxes of 10^{12}n cm^{-2}sec^{-1} possible. The lifetime of such instruments has increased to typical values of 1000 hrs. and more when used in a pulsed mode system whereby target life is extended.

These fast neutron generators find particular application in instrumental Neutron Activation Analysis (INAA).

A summary of the various neutron sources is given in table 1.

Table 1
(see Ref 6)

Nuclide	Half Life	Available Flux	Remarks
^{227}Ac/Be	22y	4.9×10^{5} n sec^{-1} GBq^{-1}	
^{241}Am/Be	458y	7.3×10^{4} n sec^{-1} GBq^{-1}	
^{210}Pb/Be	22y	6.2×10^{4} n sec^{-1} GBq^{-1}	
^{239}Pu/Be	2.44×10^{4}y	$3.8 \times$ n sec^{-1} GBq^{-1}	
^{226}Ra/Be	1620y	3.5×10^{5} n sec^{-1} GBq^{-1}	High γ-emission
^{228}Th/Be	1.91y	6.8×10^{5} n sec^{-1} GBq^{-1}	High γ-emission
^{252}Cf	2.65y	2.6×10^{12} n sec^{-1} g^{-1}	Fission source
^{244}Cm	1.4×10^{7}y	1.0×10^{7} n sec^{-1} g^{-1}	Fission source
^{240}Pu	1.3×10^{11}y	7×10^{2} n sec^{-1} g^{-1}	Fission source
Generator	-	10^{9} - 10^{12} n cm^{-2} sec^{-1}	14 MeV neutrons 1000hr tube life

The choice of neutron source will depend upon the application.

The application of various neutron sources to NAA has been reviewed and the sensitivity of some elements calculated. (8,9)

On-line systems usually consist of an activation chamber followed by the γ-ray detectors further down-stream at a distance determined by the flow rates and the elements to be measured.

Sensitivities of on-line analysis may be improved by irradiation in a loop in which the flow of the analyte can be controlled and by discontinuous use of the neutron generator.

The use of ^{252}Cf sources for on- and off-line analysis of environmental samples is increasing. For example, a nominal 10mg ^{252}Cf source was used to determine trace elements in river water and sediments. The water samples (125g) were irradiated for one hour and counted for 20 minutes after a decay time of 30 secs. The sediment samples (7g) were irradiated for 15 minutes. The elements determined and the ranges found are shown in table 2. (10)

Table 2
(see Ref 10)

Elemental concentration ppm (w/w)

Water (14 samples)

Br	Mn	Mg	Cu	Na
0.9–6.9	0.1–0.7	10–324	0.2–4	15–30

V	K	Cl	Al	Ca
0.003–0.03	30–200	20–30	0.4–1	8–400

Sediment (10 samples)

Br	Mn	Mg	Cu	Na
30–100	250–8000	430–2200	0–180	1000–3000

V	K	Cl	Al	Ca
14–30	1500–6000	0–150	90–160	160–6000

The interference free detection limits for a number of elements has been measured using a 4 mg ^{252}Cf source. The results are shown in table 3.

Table 3
(see Ref 11)

Element	γ-ray Energy MeV	Irradiation Time (m)	Counting Time (m)	Detection Limit ppm (w/w)
Al	1.78	10	5	0.05
Sc	0.142	1	0.5	0.004
Mn	0.847	10	10	0.002
Co	0.059	10	10	0.003
Ni	0.059 (^{60m}Co)	30	10	12.2
Cu	1.039	10	10	0.07
Se	0.161	1	0.5	0.03
Rh	0.051	10	10	0.002
Ag	0.658	1	0.5	0.03
In	0.819	25	10	0.001
Dy	0.108	5	2	0.001
Hg	0.159	15	10	0.8

Other elements which possess detection limits of a few ppm in a ^{252}Cf activation system of this type are sodium, chlorine, titanium, vanadium, zinc, arsenic, bromine, molybdenum, cadium, tin, antimony and barium. (9)

The analyses of sewage sludges for Cr, Zn, Ag, Au, Na, Cu and Mn have been carried out using a 5mg ^{252}Cf source and 500ml samples. (12)

3.2 Neutron Absorption Analysis

The absorption or scatter of a neutron beam by another in its path depends on the cross section of each nuclide. Cross section, σ, is a measure of the probability that the absorption, or scatter, of neutrons of a specified energy will occur.

$R = N \phi \sigma$ where R = the reaction rate in sec^{-1}
N = the number of target nuclei present
ϕ = the neutron flux density, neutrons cm^{-2} sec^{-1}
σ = the reaction cross section cm^2

And the transmission of neutrons through a sample is given by:

$$I = I_0 \exp\left(-\sum n_i \sigma_i\right) \qquad (6)$$

where I_0 is the initial intensity of a neutron beam, I the intensity after passage through a sample, n_i is the number of atoms of the ith kind per cm^2 and σ_i is the cross section of the ith atom in cm^2.

The measurement of the attenuation of a neutron beam can be used to monitor the concentration of elements of high thermal neutron absorption or scattering cross sections. Thus high cross section elements such as Li, B, Cd and a number of the rare earths can be determined by this method provided that the matrices do not interfere. For Cd and the rare earths the neutrons are captured in a reaction of the type

$$^{113}Cd + n \rightarrow {}^{114}Cd$$

The light elements are absorbed by reactions of the type

$$^{10}B(n, \alpha)^{7}Li$$

whereas, the absorption of neutrons by hydrogen is essentially a scattering mechanism followed on a much longer time-scale by absorption by the hydrogen nucleus.

Several neutron detectors are available e.g. ^{3}He detectors, BF_3 detectors, europium activated lithium iodide scintillation detectors etc. (3) The detector response can often be tailored to the neutron energy being detected.

3.3 Moisture Determination (13)

Although neutron gauges are sold for moisture determination, they, in fact, measure hydrogen content. The method depends on the ability of hydrogen to moderate fast neutrons i.e. to remove energy from a fast neutron (c.14MeV) and to produce thermal neutrons (E_{av} = 0.025eV at room temperature) by processes of elastic and inelastic scattering.

A fast neutron source (e.g. Am/Be, $E^{neutron}$= 0–11 MeV) is exposed to the sample and the thermal neutron flux is measured using a thermal neutron detector e.g. (BF_3 or ^{3}He proportional counters). These detectors are virtually insensitive to epithermal and fast neutrons. The thermal neutron flux is proportional to the hydrogen concentration or if the assumption is made that all the hydrogen is present as water, to the moisture content of the sample. The instrument may be used both in transmission and backscatter modes (fig. 3).

The calibration of moisture gauges presents some difficulties. Static gauges are the simplest and providing that the nature of the material to be measured is constant and the moisture is reasonably evenly distributed it is possible to obtain moisture measurements, to, say ±0.5% moisture in the region 0–15% (w/w) moisture content. Portable instruments used, for example, in the measurement of the moisture content of soils are much less accurate and knowledge of the soil density and chemical composition of the soil are desirable. (14)

Most moisture gauges incorporate a γ-attenuation density device which is used to correct the moisture content for soil density. Soil composition, however, can affect result markedly resulting in errors of, for example, 0± 2%, 10± 5%, 20± 8%, 30± 10% and 40± 13% (v/v) for varying soil moisture contents for soil containing 1% w/w Cl. (15)

4. X-ray Fluorescence Analysis

If energy is supplied to an electron bound to an atom of any element it will jump to a higher quantum state provided that the supplied energy is greater than a critical value known as the absorption edge energy. The vacancy created by the supply of energy can be filled by an electron in an outer shell and this process results in energy release usually in the form of X-ray emission.

The energy required to cause X-ray fluorescence can be provided either by an X-ray tube or by a radioisotopic source.

The choice between radioisotope and X-ray tube is complicated. In situations where portability and power supply problems are important then the radioisotope source will be used. Radiosotopes sources are monochromatic but the power available from an X-ray tube plus monochromator usually outweigh any advantage of the isotope source; X-ray fluorescence spectroscopy employing the more commonly used X-ray tube is described in other method reviews in this series. (17,18)

The fluorescent X-rays produced by bombardment by photons from a suitable radioisotope source have energies which are characteristic of the element from which they were emitted. The detection and identification of the fluorescent X-ray allows the identification of the elements present in the sample. Measurements of the relative numbers of X-rays from the various elements allows their relative concentrations to be calculated.

4.1 Apparatus

The source chosen must emit photons having energy greater than the absorption edge of the elements of interest. Table 4 gives a list of commonly used sources.

Table 4

Source	Half-Life	Radiation Energy (keV)	K-X-Rays Excited	L X-Rays Excited
^{55}Fe	2.7y	5.9	Al-Cr	Br-Xe
^{238}Pu	86.4y	12–17	Mn-Y	Eu-Bi
^{109}Cd	1.27y	22	Fe-Mo	Nd-Th
^{241}Am	458y	59.6	I-Lu	
^{57}Co	0.74y	122,126	Hg-Cf	

Excitation of the L-X-rays is often preferred for elements of higher atomic number.

A typical radioisotope XRF arrangement is shown in figure 4.

Several detectors are available e.g. gas proportional, scintillation and semi-conductor. The most widely used, at present, are the scintillation type although the development of solid-state devices capable of working at room temperature and atmospheric pressure but possessing the energy resolution of existing semi-conductor devices would obviously change this.

Energy selection from the detector in order to measure specific X-rays can be carried out in two ways.

(a) Balanced Filters

Filters are designed to isolate particular X-rays of interest. Table 5 lists various filter combinations and figure 5 shows the absorption characteristics of a typical filter pair. The thickness of the filters is chosen so that transmissions above and below a well defined "pass band" are as close as possible. The energy range of the pass band coincides with the energy of the required X-rays. Thus these X-rays are transmitted by the upper filter and strongly absorbed by the lower. The difference in count rate obtained with the two filters is proportional to the number of characteristic X-rays from the sample.

(b) Pulse Height Analysis

The voltage pulses from the detector have heights proportional to the energies of the incident X-rays on the detector. The pulses may be fed to an amplifier followed by a pulse height analyser which produces a standard pulse whenever the amplitude of the input voltage pulse lies between some preselected values which include the characteristic X-ray required.

Radioisotope XRF analysers have been used in a portable form to carry out numerous field measurement of rocks, ores, steels and alloys etc., and are finding an increasing use for on line analysis particularly in the metal processing industries where the probes are immersed directly into the process streams thus removing sampling problems. In most applications radioisotopic XRF instruments are used only for analyses of elements present at levels greater than 0.01%.

Table 5

Element	Energy of X-Ray (keV)	Filter Pair
Ti	4.51	Sc/Ti
V	4.95	Si/Ti
Cr	5.41	Ti/V
Mn	5.90	V/Cr
Fe	6.4	Cr/Mn
Co	6.93	Mn/Fe
Ni	7.48	Fe/Co
Cu	8.05	Co/Ni
Zn	8.64	Ni/Cu
Mo	17.48	Y/Zr
Cd	23.17	Ru/Rh
Sn	25.27	Pd/Ag
I	28.61	In/Sn
W	59.31 (8.40L-X-ray)	Er/Tm (Ni/Cu)
Hg	70.82 (9.99L-X-ray)	W/Re (Zn/Ca)
Pb	74.96 (10.55L-X-ray)	Re/Ir (Ga/Ge)

Radioisotope XRF analysis has been used for the determination of Zn, Cu, Fe and Hg in water at levels down to 5 ppm and a standard deviation of ±4 ppm using a ^{238}Pu source (10 mCi) and a 5 minute counting time. Pb can be determined to the same level and accuracy using a ^{109}Cd source (2.5 mCi) and Cd using a ^{241}Am source. Portable instruments with an immersion probe for continuous or discrete measurements can be made.

5. Electron Capture Detectors (19)

Beta particles are electrons (negatrons) and they have the property of being able to ionise gases. Selected pure beta emitting radionuclides find application as sources of electrons in gas detection systems.

The separation of a mixture of volatilizable organic compounds is accomplished by Gas Chromatography, an effective and popular technique (26–34) used in the examination of all types of water for traces of organic pollutants.

The detection of the chromatographically separated organic species is effected in a number of ways, the commonest being Flame Ionization (FID), thermal conductivity, and electron capture (ECD). Each type has advantage for particular application but only ECD has relevance in the context of radioactive sealed sources. [Strictly speaking, within the meaning of the legislation, these detectors (ECD) are "closed" sources not sealed sources].

The parent/daughter pair, Strontium 90/Yttrium 90 is seldom used now in ECD's having been superseded by nickel-63, and tritium, (as interstitial hydrides in matrices of titanium or scandium).

$$1.\quad \begin{array}{lll} {}^{90}\text{Sr-}\beta = 0.54\ \text{Mev} & {}^{90}\text{Y-}\beta = 2.26\ \text{Mev} & {}^{90}\text{Zr} \\ \qquad\longrightarrow & \qquad\longrightarrow & \\ t_{1/2} = 28\ \text{yr} & t_{1/2} = 64\ \text{hrs} & \text{stable} \end{array}$$

$$2.\quad \begin{array}{ll} {}^{3}\text{H-}\beta = 0.018\ \text{Mev} & {}^{3}\text{He} \\ \qquad\longrightarrow & \\ t_{1/2} = 12.3\text{yr} & \text{stable} \end{array}$$

$$3.\quad \begin{array}{ll} {}^{63}\text{Ni-}\beta = 0.067\ \text{MeV} & {}^{63}\text{Cu} \\ \qquad\longrightarrow & \\ t_{1/2} = 100\text{yr} & \text{stable} \end{array}$$

Non-radioactive ECDs exist only as early prototype instruments.

ECDs are used in conjunction with an ionizable carrier gas usually nitrogen, but also Argon or Helium with a small percentage of Methane, in which the action of the electrons from the beta source produces ions, radicals and thermal electrons. The application of a voltage potential to the cell results in a detector standing current which is the carrier gas baseline and the introduction of an organic compound from the chromatograph column produces a fall in the baseline current which can be related to the amount or concentration of material present.

Functional groups which have a high affinity for electrons and hence have high sensitivity to ECDs include:—

Halogen and nitro groups, ketene and conjugated structures, and organometallic compounds.

The most valuable application is in the determination of pesticide and pesticide residues of the halogenated type in water and environmental samples.

Modern commercial detectors operate on more sophisticated electronic bases including features such as pulsed voltage cells and fixed voltage variable frequency systems.(22, 23, 24)

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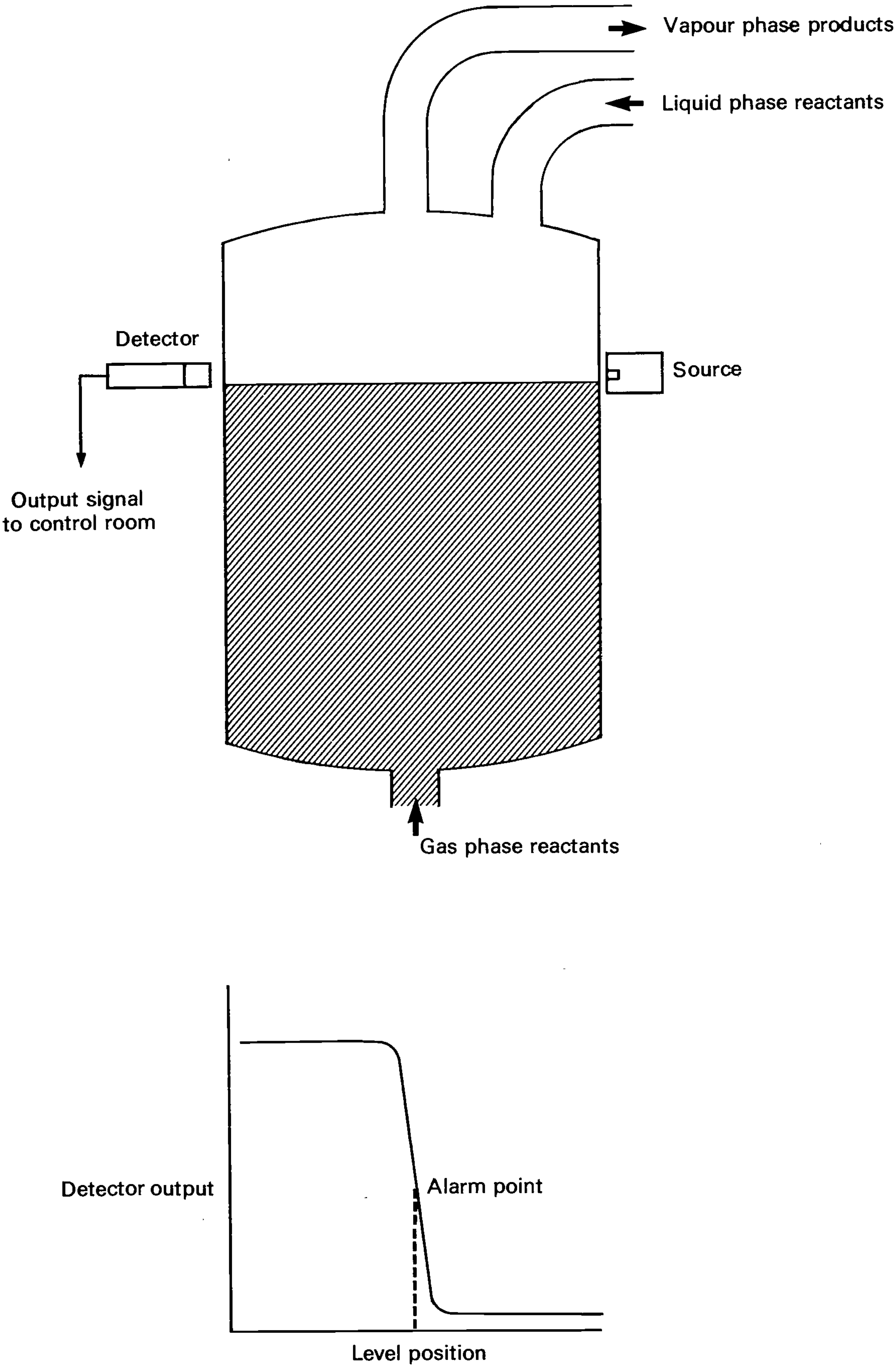


Fig. 1. High Level Alarm Base on γ Source

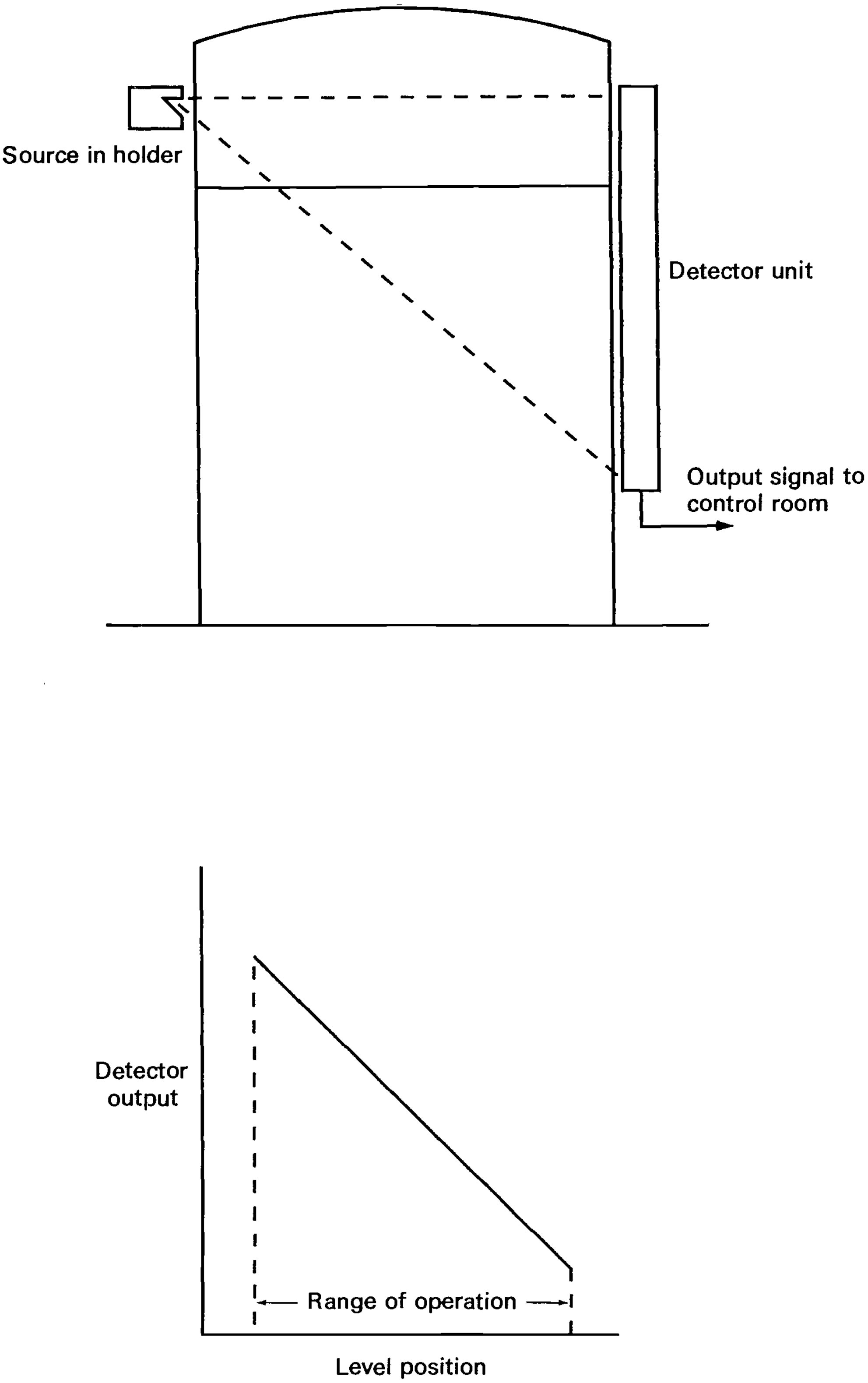
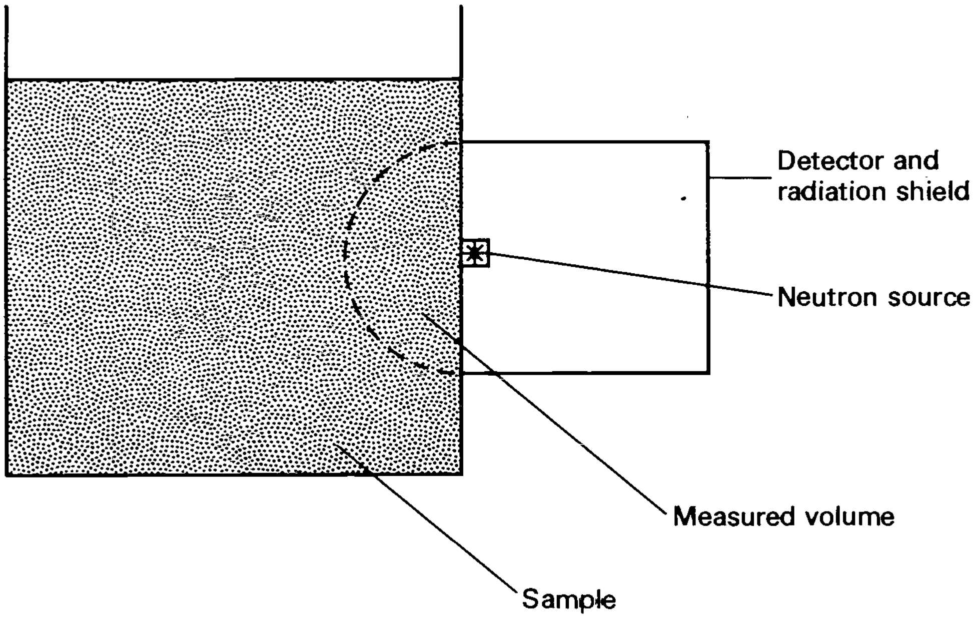


Fig. 2. Proportional Level Indication

(a) Backscatter mode



(b) Transmission mode

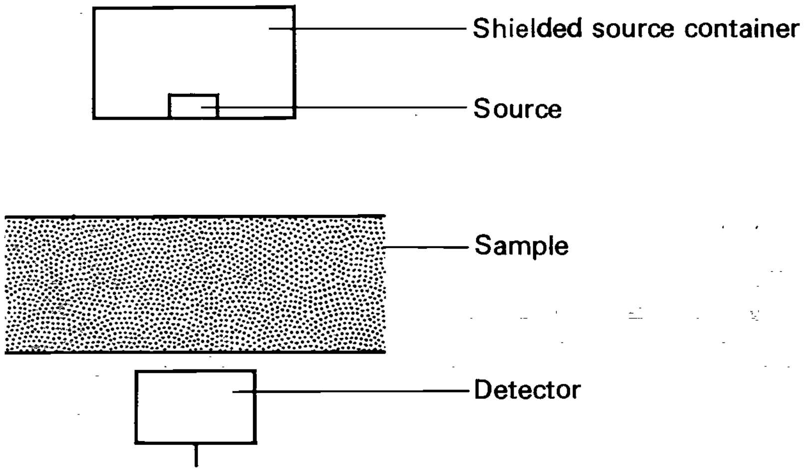


Fig. 3. Moisture Determination by Neutron Thermalization

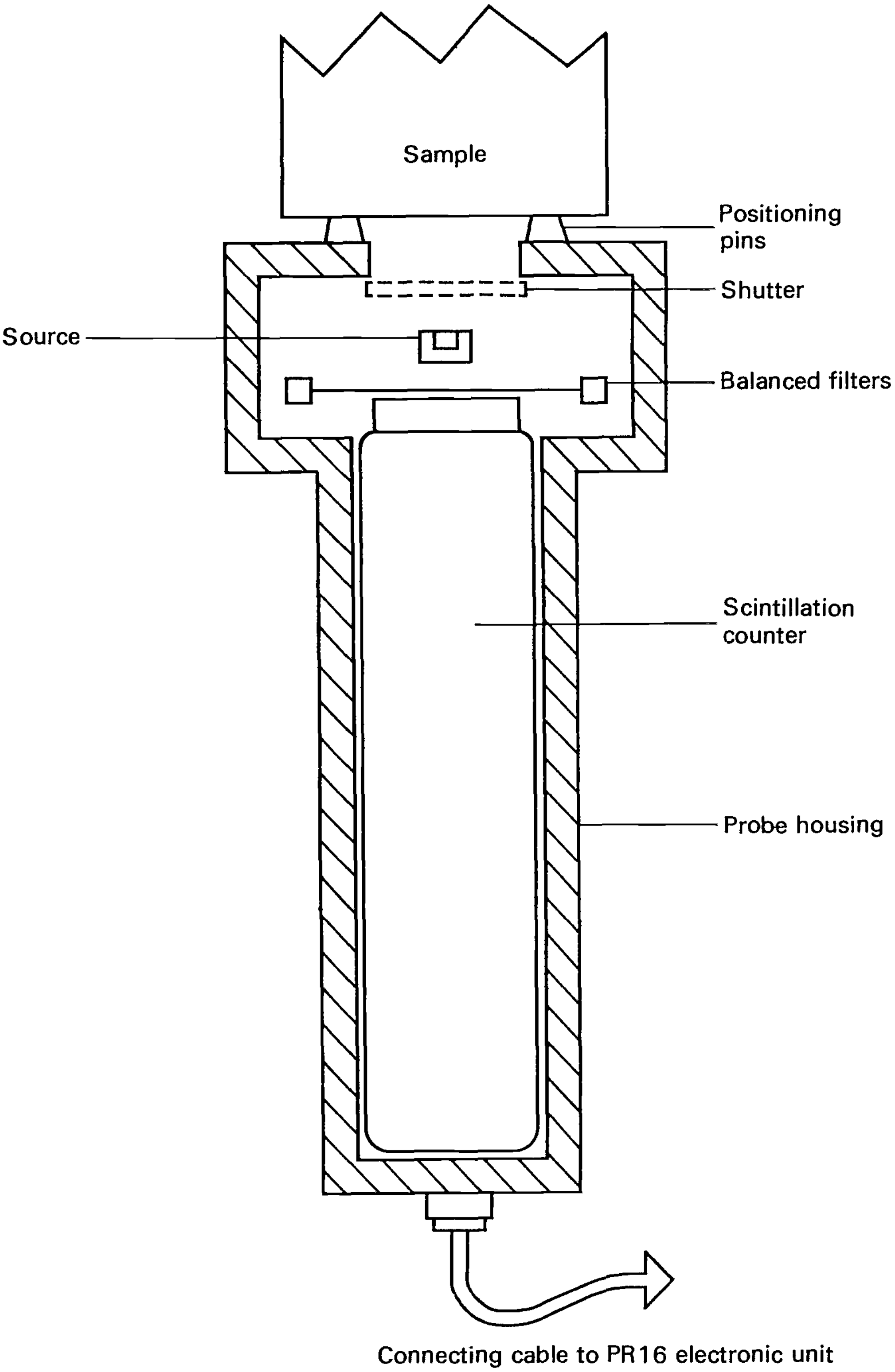


Fig. 4. The Probe Unit

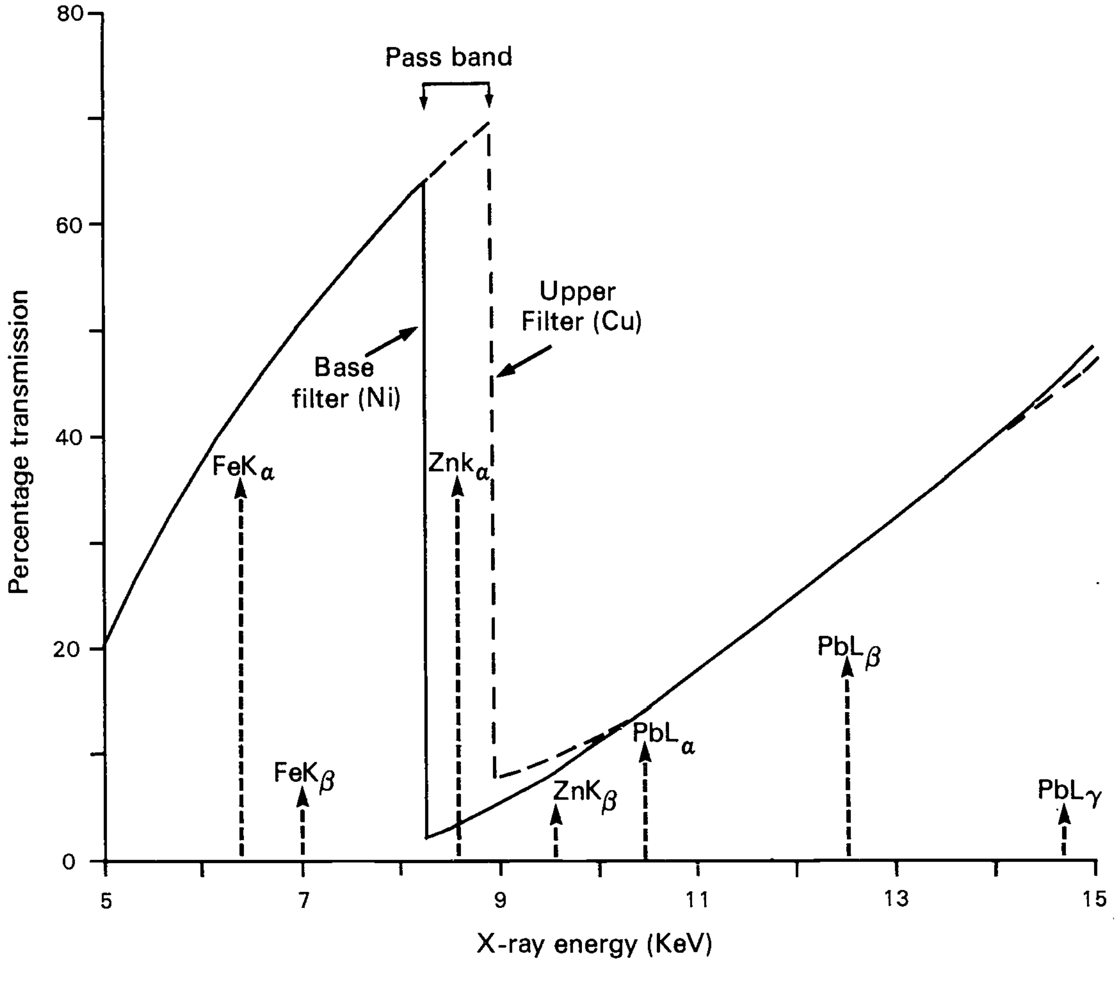


Fig. 5. Theoretical Transmission Characteristics of Balanced Ni and Cu X-ray Filters for Zn K X-rays

Activation Analysis

1. The identification and measurement of an element by converting it to a radioactive form is known as activation analysis. The method can offer very good sensitivity and specificity coupled with freedom from contamination and blank problems. Its major disadvantage is the need for a flux of atomic particles to induce the radioactivity and the high cost of such a facility with associated radiochemical laboratories: therefore a single determination may cost several hundred pounds. Nevertheless, if large numbers of specimens must be analysed for many elements the technique can be very fully automated and the cost of a single element determination may be as low as one or two pounds.

2. The atomic particles most commonly used for analysis are the thermal neutrons in a nuclear reactor and this offers the highest sensitivity for the widest range of elements. The limits of detection are dependent on the facilities available and Table 1 shows the sensitivity for 71 elements under favourable conditions using the DIDO reactor (2×10^{13} neutrons/cm^{2}sec) at Harwell.

TABLE 1 Sensitivity of Thermal Neutron Activation Analysis

Limit of detection, μg	Element
10^{-7}	Dy
10^{-6}	Eu, Au, In, Mn, Sm
10^{-5}	Sb, As, Br, Cu, Er, Ga, Hf, Ho, Ir, La, Lu, Re, Rh, Sc, Se, Na, W
10^{-4}	Ar, Cs, Co, Gd, Ge, I, Hg, Pd, K, Pr, Ru, Sr, Tb, U, V, Yb, P*, Y*
10^{-3}	Al, Ba, Cd, Ce, Cl, Mo, Nd, Ni, Os, Pt, Rb, Ta, Te, Th, Tm, Ti, Zn, Si*
10^{-2}	Bi*, Cr, Mg, Nb, Ag, Zr, S*, Tl*, Sn
10^{-1}	Ca*, Fe
1	Pb*

*Radioisotope emits only β particles and radiochemical separation is essential.

3. Neutrons readily penetrate most materials so the weight of a sample which can be irradiated may range from a fraction of a microgram up to about 100 g. Thus a small section of a single hair or a large sample of dry sludge can both be analysed with equal facility and the same absolute sensitivity. Most elements form radioisotopes which decay with characteristic half-lives and emit one or more γ-rays of characteristic energy. The radioactivity of several elements can often be resolved entirely instrumentally and by coupling a γ-spectrometer and computer some 20–30 elements may be measured in one γ-spectrum and the results can be tabulated, correlated, printed and stored by the computer. Such a system, fully automated, is an efficient way of analysing large numbers of samples for many elements.

4. If the induced activity cannot be resolved instrumentally or if the radioisotope emits only β-particles, radiochemical separations must be employed. A relatively large, known amount (10 mg) of the normal, non-radioactive form of the desired element designated as the carrier is added to carry the radioisotope through the separations. The reactions need not be quantitative because the carrier indicates the yield of the procedure. Another advantage over conventional chemical methods is that none of the reagents used contributes to the blank.

5. The normal method of calibrating activation analysis is to irradiate a dilute standard solution of the element being determined at the same time as, or under comparable

conditions to, the sample and to compare the intensity of the activities. Being an elemental method of analysis the chemical forms of the standard and the sample do not matter. In routine work at concentrations well above the limit of detection the accuracy and precision of the method are about ±3%.

6. Because the half-lives of radioactive nuclides can range from seconds to many years it is possible to determine different combinations of elements by using short or long irradiations and short or long delays ("cooling") before measuring the activity. Similarly, the time to complete an analysis may be as little as a few minutes for elements such as Al, Mg, Ti and V and could be as long as several weeks for Co, Fe and Ta. If the half-life of a desired element is very short the counting equipment must be close to, but well shielded from, the irradiating source. Fast pneumatic transfer tubes ("rabbits") are generally used to transport the samples and they are processed one at a time. If the half-life is a few hours or more, many samples (and standards) can be irradiated simultaneously and then transported considerable distances for counting at leisure.

7. Apart from nuclear reactors, neutrons can be obtained from radioisotope sources and neutron generators. The fluxes are currently at least 1000 times smaller than those of reactors and the limits of detection are correspondingly worse. Nevertheless they are finding increasing use in on-line applications. (9)

8. Charged nuclei such as protons and deuterons, obtained from accelerators and cyclotrons, will also generate radioisotopes. They will not, however, penetrate far into solids and are therefore most valuable for the analysis of surfaces or thin specimens. On the other hand, γ-photons derived from a high-energy electron linear accelerator are very penetrating and create neutron-deficient isotopes in place of the neutron-rich isotopes produced by neutrons. Thus when neutron irradiation fails to create a suitable radioisotope, γ-photon irradiation will often succeed. One of the most notable examples is in the determination of lead where γ-activation produces ^{203}Pb which has a half-life of 52 hours and emits 0.28 MeV γ-rays whereas neutron activation produces ^{209}Pb which has a half-life of 3.3 hours, emits only β-particles and must be separated for counting. The sensitivity of the technique for a large number of metallic elements using γ-photons of maximum energy of 40 MeV from the Harwell Linac under practical analytical conditions is given in Table 2. The poorer absolute sensitivity (in terms of μg) compared with neutron activation can often be compensated for in terms of concentration (e.g. ppm) by being able to use sample weights of 1 g or more.

TABLE 2 Sensitivity* of γ Photon Activation Analysis

Limit of detection μg	Element
$<10^{-2}$	Sc, Sr, Ru, Cd, In
$<10^{-1}$	Mg, Ni, Cu, Ga, Ge, Y, Zr, Nb, Mo Rh, Sb, Te, I, Cs, Ta, Au, Tl
<1	Be, Ti, Cr, Co, As, Se, Rb, Pd, Sn Ba, Hf, W, Re, As, In, Pt, Hg, Pb
<10	Ca, Mn, Fe, Zn, Br, Bi
>10	Na

*Based on 1 hour irradiation and 1 hour count after 3 hour decay

9. For an analytical laboratory situated some distance from a nuclear reactor or accelerator, activation analysis will generally prove economic for the determination of one element only when very high sensitivity is needed or for multi-element determinations in large numbers of samples. At some reactor sites, laboratory space and equipment may be hired so that visitors can process their own samples under expert supervision and minimize the financial cost of the analysis. One problem with automated multi-element analysis is that it is extremely difficult to predict before irradiation which elements will be sufficiently free from interference to be determined. Three types of interference can be distinguished:—

(a) The same nuclide may be produced by different nuclear reactions on neighbouring elements in the periodic table but this does not usually create problems in water analysis;

(b) Radiation of similar energy may be emitted by more than one nuclide but modern high resolution detectors and data processing systems have virtually eliminated this difficulty;

(c) Radiation emitted by one nuclide will suffer Compton scattering to lower energies and may mask the radiation from other nuclides.

With river waters it is usually possible to measure Ag, Br, Cl, Co, Cr, Cs, Fe, K, Mn, Na, Rb, Sb, Sc, Se and Zn; in this case the sample is evaporated to dryness and sealed in a silica ampoule. Rainwaters are routinely analysed by evaporating 100 ml of a filtered specimen onto cellulose paper. In addition to the above elements it is normally possible to measure Al, As, Au, Ca, Cd, Ce, Cu, Hg, I, In, La, Ti, Th, V and W. With such a large suite of elements it is sometimes possible to pinpoint sources of environmental pollution because of the known associations of some pollutants. If aqueous samples must be irradiated the ampoule cannot be more than one third full because of the radiolytic decomposition of the water but it is still possible to irradiate three aqueous samples each of 0.5 ml and one ampoule of standards in one "rabbit" container.

10. One of the most important roles of activation analysis is to act as a referee method and confirm the accuracy of more widely available methods. If the material to be analysed is irradiated without any kind of physical or chemical pre-treatment, the risks of contamination or loss are virtually eliminated. The radioisotope produced may remain in its original chemical form (which in natural materials may be very complex and difficult to synthesize) and then can be used as a radiotracer to study the efficiency of the traditional chemical methods. Thus it has been shown that lead is lost from bone samples ashed above 700° C. If surface contamination is suspected of inflating the analytical result, the surface can be removed after irradiation so that only the bulk content is measured.

11. The bibliography below contains sources of more detailed information on the technique and its application. Information and advice is usually available at reactor sites and assistance and the addresses of suitable contacts can be obtained through the Member Services Division, Water Research Centre, Elder Way, Stevenage, Herts, SG1 1TH, Tel. (0438) 312444. Future developments in activation analysis will no doubt take full advantage of progress in counting and computing equipment as well as in the development of new sources of radiation. The nuclear reactor is likely to remain the most intense source of neutrons and can serve the water industry with sensitive analytical methods just as well as it currently serves the medical field by providing regular supplies of isotopes for diagnostic purposes.

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The Application of Radioactive Tracers in the Water Industry

Summary

The methods used to trace water movements in most aspects of the terrestrial water cycle are outlined and the use of radionuclides as particle radiolabels demonstrated. Specialist applications in micro-biological, biological and analytical chemistry are also discussed. A selection of radionuclides for aqueous and solid labelling are tabulated and their suitability for certain applications highlighted. The main Research Establishments where work is carried out using radionuclides and where assistance or advice may be obtained, together with the areas of research that they are involved in, are listed. The paper contains a comprehensive and lengthy bibliography.

Regulations

Prior to using radioactive substances as tracers, users must familiarize themselves with the legislation and regulations governing their use. See the first Review in this booklet.

1. Introduction

Radioisotopes provide a powerful tool for the water engineer or hydrologist particularly where large water systems or high flow rates are being studied. They can be used to verify predictions based on theory or the use of physical models. With conventional equipment concentrations of tracers of 4 Bq/l (about 10^{-10} Ci/l) are readily detectable and thus up to about 10^9 m^3 of water can be labelled without incurring undue risk of excessive exposure to radiation at the dispensing stage (i.e. a single dose of 3.7 TBq (100 Ci) of a γ-emitting isotope may be applied under properly controlled operations in the field). The need to avoid undue exposure of the population to additional radiation is readily reconciliable with the quantities of radio-tracers necessary for experimental purposes by ensuring that critical contact does not occur until the tracer is effectively dispersed, or decayed away but some effort is usually required to assuage public sensitivity. All operations involving radioactive materials are subject to the specific approval of and ultimate control by the Radiochemical Inspectorate of the Department of the Environment*.

It is also necessary to alert the Water Authority and local authorities who may be affected, including both the police and fire services who will need the information in the event of an emergency in the area.

The useful properties of radio-tracers which are exploited in studying the movements of large bodies of water are:

(1) the possession of a high specific activity which means that only small quantities of irradiated material are required,

(2) the existence of a choice of radionuclides possessing half-lives ranging from a few hours to a few years and particle or energy emissions suited to facilitate detection by portable equipment,

(3) the ease with which quantitative studies of high precision may be made because of the linearity of detection of energy emission at all concentrations and because the chemical and physical state of the radionuclide does not affect its nuclear properties,

(4) the self-destructive nature of the radionuclide which can be exploited by choice of appropriate half-life to avoid contamination of biota and enable repeat studies to be made without interference from earlier releases.

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This paper describes a number of topics briefly to illustrate the types of application and gives some key references. Establishments where advice and services may be obtained are listed. Data on some of the radioisotopes used for flow measurement and tracing movements of an aqueous phase and labelling suspended matter are given in Tables 1 and 2.

2. Flow Measurements

There are three ways in which tracers can be used to determine the rate of flow of a substance in a pipeline or open channel. The first is based on the velocity-area principle, and the second and third on dilution gauging by the constant-rate injection method (1) or the integration (gulp injection) method (2). These are absolute methods which may therefore be used to calibrate structures or devices installed in the pipe or channel to give continuous indications of flow.

TABLE 1. Data on some radioisotopes suitable for aqueous-phase tracing (listed in order of half-life)

Radio-isotope (stable product)	Half-life	Main Radiations (MeV)		Remarks
		β	γ	
F-18 (O-18)	1.8 h	0.65	0.51	
I-132 (Xe-132)	2.3 h	complex	complex	Generator half-life 78 h (Te-132)
K-42 (Ca-42)	12.4 h	3.6	1.5	
Na-24 (Mg-24)	15.0 h	1.39	1.4 2.8	
Br-82 (Kr-82)	35.4 h	0.44	complex	K-42 allowed to decay before use
I-131 (Xe-131)	8.0 d	0.61	0.36	Use as iodide, not iodate carrier concs. up to 10 mg/l to avoid adsorption
Rb-86 (Sr-86)	18.7 d	1.77	1.08	Uptake by mud possible
I-125 (Te-125)	60.2 d		0.035 (0.027 X-rays)	Useful for long shelf-life
Co-56 (Fe-56	77.3 d	1.50 (β+)	0.85 to 3.5 complex	May be used as colbalticyanide
Cs-134 (Ba-134)	2.1 y	0.65	0.61, 0.80	Uptake by clay possible at high pH
Na-22 (Ne-22)	2.58 y	0.54	1.28	
Co-60 (Ni-60)	5.26 y	0.31	1.17, 1.33	(As for Co-56)
H-3	12.43 y	0.018		One of the most common waste products of power reactors
Cl-36 (Ar-36)	3.10^5 y	0.71		Laboratory — scale experiments only

TABLE 2. Data on some radioisotopes suitable for labelling suspended solids (listed in order of half-life)

Radioisotope (stable product)	Half-life	Main radiations (MeV)		Remarks
		β	γ	
In-113m (In-113)	1.73 h		0.39	Generator half-life 118 d (Sn-113)
Zn-69m (Ga-69)	13.8 h	0.91 (Zn-69)	0.44	In equilibrium with Zn-69 (half-life 55m)
Ga-72 (Ge-72)	14.1 h	0.67, 0.96 complex	0.6 to 2.5 complex	Ga-70 (half-life 21m) allowed to decay before use
Ho-166 (Er-166)	27.2 h	1.76, 1.84	weak	
La-140 (Ce-140)	40.2 h	0.83 to 2.20 complex	0.3 to 2.5 complex	
Au-198 (Hg-198)	64.8 h	0.96	0.41	
P-32 (S-32)	14.29 d	1.71		Best adsorption when carrier concs min.
Cr-51 (V-51)	27.8 d	0.32 weak		Chemical state important (Cr^{51}-EDTA used as water tracer)
Fe-59 (Co-59)	45 d	0.27, 0.46	1.1, 1.3	Fe-55 (half-life 2.7y) also produced but does not interfere with in situ detection
Sb-124 (Te-124)	60 d	0.22 to 2.31 complex	0.6 to 2.1 complex	Sb-122 (half-life 2.7d) allowed to decay before use
Sc-46 (Ti-46)	84 d	0.36	0.89, 1.12	
Ta-182 (Wa-182)	115 d	0.18 to 0.51 complex	0.066 to 1.29 complex	
Zn-65 (Cu-65)	245 d	0.33 (β+)	1.11	
Ag-110m (Cd-110)	253 d	0.087, 0.530	0.66 to 1.51 complex	(160 Ci used by WRC (Ref. 15)
Eu-152 (Gd-152)	12.4 y	0.71	0.3 to 1.4 complex	Few per cent Eu-154 (half-life 16 y) also produced

2.1 Velocity Area Method

The advantage of utilizing the velocity-area principle is that access to the fluid is only required at one point and a trivial quantity of a very rapidly decaying tracer (half-life of minutes or hours) may be used. Two detectors are placed on the pipe or channel a known distance apart to record the passage of a "spike" of tracer (no accurate knowledge of quantity required) introduced sufficiently far upstream of the first detector to give complete vertical and lateral mixing across the section so that its velocity may be taken to represent the average velocity of the fluid. Some longitudinal dispersion will take place between the detectors but this should not present any problems as the most probable velocity may be estimated directly from the output recording of the nucleonics as indicated schematically in Fig. 1(a). This method is clearly applicable to pipes where the cross-sectional area of flow is known and the advantage of "remote" direction through the wall can be used.

2.2 Dilution Method by Constant-Rate Injection

The concept of the constant-rate injection method of dilution gauging is equally straightforward (3,4) but radionuclides of longer half-life are usually required because samples have to be taken for concentration measurements. The tracer solution is injected at a precisely controlled rate of flow for a period long enough to establish a 'plateau' of equilibrium concentration at the sampling station. Injection periods of about 10 minutes may be satisfactory for turbulent flow in a pipe but 20 minutes to 1 hour might be more typical for a river. The flow is calculated by simple comparison of the concentrations of the solution injected, after successive dilutions, and the concentrations at the sampling station as shown in Fig. 1(b). Only a few samples taken when the steady state has been reached are required to determine the flow, thus minimizing analytical and numerical work but suffering the disadvantage that more tracer is required than in other methods — possibly an order of magnitude greater than is required by the "'gulp" method and two orders greater than the velocity area method.

2.3 Dilution Method by Gulp Injection

In the gulp method of dilution gauging the radiotracer is applied much more simply than in the constant-rate method but many more samples are required. The concept of the method is shown in Fig. 1(c). The injection can be a simple decanting operation lasting several minutes to lessen maximum concentrations just below the point of entry of the tracer. A continuous recording is made of the concentration with time of passage of the tracer past a fixed point and the quantitative accuracy of the curve is checked by comparison with the activity content of at least 10 samples, counted on a reference equipment, taken while the tracer cloud is passing. For reasons of tracer economy this method is preferred for use in rivers particularly at higher flow rates whereas either the 'gulp' or the constant injection method is applicable to small channels or sewers (5,6,7,8).

It is emphasized that the success of any of the dilution methods depends on complete mixing of the tracer with the entire flow in the cross-section at the sampling point. Cross-sectional sampling may therefore be necessary to establish that this condition is met. In pipes the mixing distance is about 100 pipe diameters but in rivers several kilometres may be required and various empirical formulae are available to act as guidelines (36).

3. River Surveys Using Short-Lived Radio-Tracers

When a river system is polluted by many waste discharges along its length it is often difficult to gauge the significance of a particular discharge as it mixes with polluted water originating upstream and other discharges downstream. For intensive surveys of complex systems a given effluent or an arbitrary mass of water is labelled with a radioisotope at a convenient point of access. The passage of the water is then recorded at a number of sites downstream where samples for chemical analysis are taken during the passge of the tracer. Surveys have been made over distances of up to 120 km in flows of up to 100 m^3/s (1900 m.g.d.) but these do not represent upper limits. The information which may be gathered includes

(i) dilutions at points of interest downstream,

(ii) the retention times between stations (also times of travel between accidental spill-risk points and water intakes),

(iii) the residence time of water in any works abstracting water and returning it to the river,

(iv) the flow rate of the river at each station and therefore of any tributary (or ground water) entering between stations,

(v) the dispersion features of the system,

(vi) the self-purification capacity of each reach and an insight into the chemical and biological processes acting on the pollutants.

Examples of the curves recorded on such intensive surveys are shown in Fig. 2 with times-of-travel shown in Fig. 3.

In most cases a "gulp" of a few hundred millilitres of potassium bromide (Br-82) solution is added to the river, at an activity corresponding to about 2 GBq (54 mCi) per m^3/s flow.

The half-life of 35.3 h allows measurements to be taken for a day or two but for some exercises the tracer cloud is "topped-up" when dilutions downstream are considerable — Fig. 2. The quantity of radioisotope used and the injection method will depend on the purpose of each individual exercise. In one instance bromine-82 was injected at constant rate into a highly polluted river for a period of 48 h to measure variations in flow rate during intensive sampling of the reach downsteam. Variations in retention times during this period were measured by stopping the injection for a short time occasionally, the chart recorders giving inverse concentration curves corresponding to these breaks.

The radiation detectors used are thallium-activated sodium iodide scintillation crystals, usually 75 mm thick and 75 mm in diameter, connected to photomultiplier tubes in light-proof containers. These are in water-tight submersible containers and are connected to a charge-sensitive amplifier which feeds pulses to a scaler with visual display. The pulses are integrated over a set time period and then printed onto paper tape. The detecting crystal may be placed above, on the surface of, or below the surface depending on the degree of turbulence and the depth of water. The sensitivity of detection for bromine-82 is about 4 counts per second (above a natural background rate of 30 counts per second) per kBq/m^3 with the detector just beneath the water surface. The effect of variable geometry can be eliminated by taking a sample during the passage of the tracer and counting it in a standard detection apparatus. The shape of the dispersion curves is not affected by the geometrical arrangement of the detector providing this is not altered during the exercise.

The mathematical model for one-dimensional flow under ideal conditions is:

$$\frac{\partial C}{\partial t} + V \frac{\partial C}{\partial t} = K \frac{\partial^2 C}{\partial^2 x}, \qquad (1)$$

where C is the concentration at time t (distance x) from the time of tracer injection, V is the mean velocity and K is the dispersion coefficient. The solution of this equation enables the concentration of pollutants at any given downstream point to be predicted as

$$C(x\ ,t) = Bt^{-\frac{1}{2}} \exp - \frac{(x - Vt)^2}{4Kt} \qquad (2)$$

where B is a constant incorporating the quantity of tracer injected and parameters appropriate to the type of injection. This equation yields symmetrically distributed dispersion curves having maximum values of $x = Vt$ and of standard deviations $\sigma_x = 2Kt$. In practice curves are usually skew and are concentrations/time, not concentration/distance, curves. The dispersion coefficient is usually estimated by the application of

$$K = \frac{\sigma x^2}{2t} \simeq \frac{(V\sigma t)^2}{2t} \qquad (3)$$

Equation 3 which is valid only when $xV \gg K$ (9). This condition derives from the one-dimensional model which is not applicable upstream of the point where lateral and vertical mixing of the tracer may be regarded as complete. A high value of K would therefore result if the equation $K = (V\sigma t)^2/2t$ were applied uncritically. The curves shown in Fig. 2 illustrate that the rate of longitudinal dispersion of the tracer decreases at the lower stations, in comparison with upper measuring sites. The maximum concentration for each curve will be $C_{max} = Bt^{-\frac{1}{2}}$ (from Equation 2) and if the C_{max} values found experimentally are plotted against $t^{-\frac{1}{2}}$ then the graph will be linear for that stretch of river in which mixing may be regarded as complete. Curves fulfilling this criterion may be used in conjunction with Equation 3, and Fischer (10) has shown that the dispersion coefficient can be calculated by Equation 4 where $\sigma^2 t_1$ and $\sigma^2 t_2$ are the variances of the concentration/time curves for two stations below the point of satisfactory mixing,

$$K = \frac{V^2\ (\sigma^2 t_2 - \sigma^2 t_1\ )}{2\ (\bar{t}_2 - \bar{t}_1\ )} \qquad (4)$$

and t_1 and t_2 are the mean times of passage of the tracer cloud past each station. Methods of obtaining the best estimate of $\sigma^2 t$ from a skew curve which may be incomplete have been given by Godfrey and Frederick (11) and by Yotsukura *et al.* (12).

4. Coastal Dispersion and Dilution Studies

Waste waters are often disposed of in untreated form to estuaries or shallow coastal waters. Where disposal causes nuisance or failure to conform to certain standards, for example the EEC requirements for bathing water, the waste must either be treated or transported further out to sea. Both courses of action involve high costs and it is important to be able to assess dispersion and dilution characteristics from actual or proposed outfall positions in order to plan the economic solution in each case. Radioactive tracers are used to find:—

(a) the "initial dilution" of existing outfalls i.e. the dilution resulting as the plume of waste rises to the surface of the sea

(b) the effectiveness of various designs of diffuser, fitted to the end of waste pipelines, in increasing initial dilution

(c) the rate of dilution caused by local mixing and dispersion. The apparent mortality rate of bacteria can be corrected to true mortality rates using such data

(d) the overall transport pattern and time-of-travel to the shore.

These factors will, of course, vary with the state of the tide and wind forces and it is possible to carry out repeat studies using a short-lived tracer such as Br-82 without serious background interference from previous experiments.

4.1 Tracing of Sewage Discharged to the Sea

In cases where a single experiment on the fate of the waste is required and *in situ* tracking equipment is not available tritiated water may be used by taking samples at a matrix of positions. Curies of bromine-82 may be required or tens of curies of tritium. The latter is found in nature, is of low toxicity and its dispersion in the sea cannot be followed directly because it does not emit gamma rays. Using tritium however an unlimited number of samples may be taken and analysed at leisure because of its long half-life.

To complement *in situ* tracking when Br-82 is used samples are measured in volumes of up to two litres in a re-entrant container surrounding a scintillation detector crystal of size up to 100 mm high by 100 mm in diameter, mounted in a thick lead shield to cut down natural background radiation. Because tritium emits only beta rays of very low energy, samples are counted by the liquid scintillation technique. Aliquots of up to 5 ml of samples are mixed with 10 ml of liquid scintillator in a counting vial which is lowered between a pair of photomultiplier tubes. In most instruments several hundred samples can be loaded into a continuous belt and the samples are then automatically counted for half an hour to several hours in rotation.

Where studies are being conducted on existing pipelines it is possible to inject bromine-82 to give several measurements from one injection. The radioisotope is injected at a calibrated constant rate upstream of the pumphouse at the head of the pipeline. Samples of labelled waste or sewage are taken at the pumphouse to give the flow rate by dilution. The arrival of the tracer in the sea measures the pipeline retention time and samples taken in the "boil" compared with those taken at the pumphouse give initial dilution measurements. The fate of the sewage can then be tracked.

The tracer may be tracked over many miles by towing scintillation detectors through the patch at various depths and recording depths, position and count rate information on tape for subsequent analysis by computer as described by Barrett et al (13). Clearly very much more data can be gathered in this way than by taking samples. Details of the detection and recording equipment have been given by Briggs et al (14). Sewage from submerged outfalls rises to the surface and spreads out on the surface due to its relatively low density, so that adding tracer carefully at the sea surface to assess proposed outfall sites is valid provided care is taken that the density of the radioactive solution is similar to that of partially diluted sewage.

4.2 Tracing of Solids Movement

For dispersion of solid particles, not wholly dependent on water movements, the material involved must be labelled in order to trace its fate. The dispersion and sedimentation of sludge dumped at sea is an instance where radioisotopes may be used either to ascertain whether traditional dumping grounds are satisfactory or to find new ones. Lanthanum-140 and silver-110m have been used successfully but other possibilities exist. In one case where scandium-46 was used, glass particles incorporating the natural scandium were ground to match the solids to be tracked and then irradiated in a nuclear reactor. The choice of isotope depends on the tracking period, the degree of on-site detection wanted and the convenience of labelling. Isotope cost may be important or repeated experiments.

Labelling the material, which may be mixture of crude, digested and activated sludges or natural bed sediment, involved mixing an active solution of radionuclide with the solids in suspension. Also it was realized that, as the labelling would probably be a surface effect, the smaller particles and colloidal matter would take up a disproportionately large fraction of the isotope (particle mass $\propto r^3$, surface area $\propto r^2$; hence mass labelling efficiency $\propto r^{-1}$). It was therefore decided to elutriate the sludge to replace the interstitial fluid by tap water and at the same time to remove fine particles below an arbitrary size. Sedimentation tests on labelled and unlabelled samples of sludge showed that the settling properties in sea water were not affected by the label and also that the sludge particles were labelled fairly uniformly.

4.3 Fate of Sludge Disposed of in Liverpool Bay

One study carried out in Liverpool Bay (15) illustrates the measurements made possible using radioisotopes. The aim was to assess the fate of sludge dumped about 20 km offshore in order to decide whether present practice could be extended to cope with future needs involving considerable increases in quantities of sludge for disposal. As it was hoped to follow the fate of the sludge for several months, and because reliable labelling could be provided under field conditions, silver-110m was chosen.

It was decided that labelled sludge would be injected into the sea under conditions identical to those of normal discharges, using one of the ships involved. It was estimated that at least 750 GBq (20 curies) would be required to track a single cargo of 1500 tons of sludge, and that the fate of several cargoes would be measured. As a considerable lapse of time occurred between each loading and discharge, it was shown to be impracticable, on radiological safety grounds, to label the cargo uniformly during loading, so the method of labelling part of the cargo during discharge was developed. Shortly before release of sludge to the sea, a diaphragm pump was started to circulated part of the cargo (180l/min) past the labelling apparatus to the discharge valve in the bottom of the ship. One minute after the discharge valve was fully open, the labelled particles were injected into the main body of the sludge adjacent to the outlet valve during 45 s of the period of 6 to 8 min during which sludge was discharging from the ship. This procedure, which resulted in part rather than the whole cargo being labelled, was adopted not only to avoid possible complications from the sludge field breaking into a number of parts shortly after discharge, but also to make best use of the radioisotope by ensuring high initial concentrations in the sea.

Subsequent laboratory tests on samples of sludges labelled during the exercise suggested that at least 99 per cent of the silver had been adsorbed on the particulate matter although the reactions involved in the labelling process are not fully understood. The detailed dispersion results may be found elsewhere (15) but an example of one of the patterns (Fig. 4) illustrates the size of area over which it is possible to follow dispersal of waste using only a few grams of active tracer.

4.4 Tracing an Effluent in a Divided Estuary

A second example concerns an estuary having two arms and a common sea channel typical of many in this country. The problem here was to assess the effect of a new sewerage scheme with a proposed outfall in the position shown by the arrow (Fig. 5a). Very little was known about the hydraulics of this estuary and it was uncertain to what extent an effluent, discharged at the proposed site, would clear the estuary to the sea on the ebb tide or be trapped in Arm B or remain in the common sea channel to be taken into Arm A. In order to assess such a continuous source of pollution a tracer was injected over one tidal cycle, from one low water to the next. In this example 303 GBq (8.2 Ci) of bromine-82 were used and during the low-water period the tracer pooled in the area of the injection and was then pushed upstream as the first flood tide came in. The pattern of Fig. 5(a) shows the relative concentrations of tracer at the first high water. As the ebb tide took effect, a situation developed where newly-injected tracer was added to that injected earlier, to be carried towards the sea, but only part of the total quantity of tracer injected reached the common sea channel as shown in Fig. 5(b) which gives the relative concentrations at low water when the injection had just stopped. It is immediately clear that effluent, simulated by the tracer, would not clear Arm B and that some would be trapped within the system. On the next high water the tracer was pushed further upstream than previously with a maximum relative concentration of about 50 units.

Variations in tracer concentrations were plotted continuously, day and night, in both arms of the estuary for more than six tidal cycles but it is only possible to indicate some typical patterns to show how relative dilutions with each tide are determined. Fig. 5(c) shows the relative concentrations at the third high water. By this time tracer has dispersed along both arms of the estuary and Fig. 5(d) illustrates the situation at third low water where concentrations were about one-tenth of those existing at first high water. It would appear that pollution from Arm B enters the common sea channel to be pumped into Arm A. Conversely, Arm A of the estuary could also have been pumping pollution into Arm B, but this was not as probable because Arm A drains last and fills first. From such surveys it is possible to predict, for any point in the system and for any stage of the tide, the concentration of any pollutant per gramme per second discharged continuously at the proposed outfall, from the start of any release to the equilibrium level. Results of this nature may give considerable economic return in providing guidelines for proposed new sewerage schemes and the degree of treatment facilities necessary to achieve certain standards of water quality at sensitive points in an estuary.

5. Mixing and Residence Time Studies

Knowledge of mixing patterns and residence time distributions are often required for both water supply and waste water treatment and disposal operations. For example where reservoirs are used not only for storage but to act as a preliminary dilution and purification system for pollutants it is important to know that inlet water is not taking a short-circuit to the outlet and that stagnant areas do not exist. Similar information is required about effluent lagoons or tanks used for treatment processes e.g. digesters treating sewage sludge or trade wastes (39).

Two examples will be given below but the general method is the same for most studies of this nature. The radionuclide is injected upstream of the inlet to the system, in order that it mixes in a representative way with the entire flow, over a period of time which is very short compared to the average retention time. The outlet is monitored continuously to record the quantity of tracer leaving the system in each increment of time (flow rate q x concentration C_t) to give the residence time distribution f_t where

$$f_t = \int_0^t q\ C_t\, dt\ \int_0^\propto q\ C_t\, dt.$$

This will be of exponential form for a perfectly mixed system and a steeply rising 'S' curve for a system 'plug flow'. Regular 3-dimensional surveys are made, to determine the rate of advance of the tracer front, the dispersion pathways and dilutions, using a number of portable sets of recording nucleonics. Where such studies are conducted in systems used for potable supply a short lived isotope such as sodium-24 or bromine-82 is chosen and the sensitivity of the equipment is such that even at the inlet to the system concentrations of tracer may be kept below drinking water standards for the isotope concerned. The application of radioisotope can afford great precision but where only qualitative pathway or retention time estimates are required tracer economy by several orders of magnitude may be possible. It is therefore essential to keep in mind the objectives in order that only the minimum quantities of tracer of the shortest possible half-life are used.

The first example is a study which was carried out to compare the efficiencies of mixing in two digesters, of capacity 2700 m^3, treating sewage sludge. The purpose was to give guidance on the type of circulator to be installed in a number of digesters under construction. The investigation included experiments to discover the fate of the solids as well as the mixing of the sludge liquor because it is essential that solids are well mixed and do not settle out. It was decided to use Au-198 to label solids, and tritiated water to measure the mixing of the sludge liquor. Tritium was chosen as the aqueous tracer since it would not interfere with the *in situ* tracking of solids labelled with Au-198. Laboratory tests were carried out to check that exchange of tritium atoms between tritiated water and sludge was negligible.

Injections of 16.1 GBq (435 mCi) tritiated water were made into each digester two days prior to the Au-198 injections, so that some early indications of mixing rates could be obtained before samples contained any Au-198. The Au-198 was transported to the site as irradiated gold foil. Five litres of sludge were washed to remove most of the finest suspended matter which would take up a disproportionate amount of the tracer. The prepared samples of sludge were mixed with an ammoniacal solution of gold containing 2.22 GBq (60 mCi) Au-198 and then pumped into the digester feed sludge flow over a period of 10 min, using a peristaltic pump (Fig. 6).

Scintillation detectors were lowered into the digesters at various points to assess mixing and others positioned for monitoring tracer passing through the external heat exchanger. Sampling devices which would open and seal at the required depth were used to take samples for the assay of tritium. Au-198 started to pass through both heat exchangers within 30 min of tracer injection. Vertical scans which were made about 2 h after tracer injection indicated that the solids were distributed evenly throughout both digester volumes within this period. Subsequent regular scans over a period of about one week indicated satisfactory distribution of solids throughout the bulk of the digesters. This observation was supported by the fact that neither of the detectors monitoring the heat exchangers detected 'slugs' of active sludge. However it soon became evident that the concentration of Au-198 within the bulk of one of the digesters was decreasing at a faster rate than that in the other. Subsequently more detailed vertical scans were carried out each day and it was possible to illustrate a tendency towards settlement in that digester (Fig. 7).

The tritium results showed that the mixing in both digesters was entirely satisfactory (Fig. 8). The equations of the lines of best fit of the experimental tritium data are also given (Fig. 8). By extrapolating this best fit line back to the 'y' axis a theoretical tritium concentration at time zero (C_0) can be calculated and from the quantity of tritium added (A) the mixing volume of the digester can be calculated. ie A/C_0. This may differ from the capacity of the digester and may therefore indicate stagnant zones or decreases in active volumes due to deposits. From the slopes of the lines of the best fit the retention time of the digester can also be deduced.

The study demonstrated that mixing must be sufficiently vigorous to keep suspended solids from settling even though the liquid phase may be completely mixed at a lower expenditure of mixing power. It also indicated that the use of tracer for the aqueous phase alone may be adequate for proving trials on such systems. Laboratory tests were conducted to prove that the Au-198 was still predominantly attached to sludge solids at the end of the experiment.

The second study was carried out in a raw-water reservoir of capacity 3.10^6 m^3, as part of a research programme sponsored by the Water Engineering Directorate of the Department of the Environment with the objective of determining the degree of short-circuiting and its effect on raw-water quality. This phenomenon is of importance because the possibility exists of polluted water being inadvertently taken into bankside storage reservoirs from a river. A quantity of 63 GBq (1.7 Ci) of bromine-82 was injected at a constant rate over a period of 4 h at the inlet to ensure that the concentration of tracer was below drinking-water tolerance levels. The nominal average retention time of the reservoir, as it was being operated at the time, was 90 d.

The initial dispersion of tracer along one bank was reversed as the wind veered round and subsequently a wide dispersion lobe developed along the other bank consisting of a straight wall. The pattern of tracer concentration one day after tracer addition is shown in Fig. 9 to illustrate the dispersion detail attainable. The main tracer lobe not only still exists as an identifiable body of water but has reached the region of the outlet. In this 90d system, tracer was recorded in the outlet 15 h after entering the reservoir, the maximum concentration being recorded about 15 h later. (This was one-hundredth of the maximum permissible level allowed in drinking water for continuous exposure conditions.) The dispersion pattern was determined under relatively calm conditions after winds had moderated overnight. The tracer-free water then coming in was taking the curved bank route towards the outlet, indicating a second mode of short-circuiting. Depth profiles showed that vertical mixing was reasonably uniform, and the fate of the tracer was followed for about one week. Similar investigations, including hydrodynamics and water-quality studies, have been made at a number of sites.

6. Biological and Chemical Applications

Although specific examples are described it is intended that these be taken as typical applications of radiotracers which may be carried out with only a few kBq (Ci) of tracer.

The applications described in Sections 6.1 to 6.3 are of a biological nature. Radiotracers can be used in biological studies where the amounts of reactants taking part in biological activity or the concentrations of chemical species in the system may be small, and where processing and analysing biological materials may be difficult or unreliable. The limitations of poor sensitivity of conventional analytical procedures or the problems of being able to get sufficient sample for good reproducibility are overcome. Liquid scintillation counting techniques are usually employed since the studies involve the nuclides tritium, carbon-14, phosphorus-32 and sulphur-35. Some biological materials may require special techniques of sample preparation and reference may be made to reviews (16,17), texts and the series of Proceedings of Symposia on liquid scintillation counting organized by the Society or Analytical Chemistry (18,19,20,21). The range of applications for studies in chemistry is wide and in many areas, such as chromatographic studies or solubility determinations, is outside the scope of this manual. However, a few applications are mentioned briefly in Section 6.4.

Sections 6.1 and 6.2 describe field tests using radiotracers *in-situ* whereas sections 6.3 and 6.4 involve laboratory based studies. Generally, the studies require investigating the behaviour of a particular ion or chemical species labelled with one or more radioactive tracers.

6.1 Algal Blooms

Studies on the eutrophication of lakes include the rate of primary production, i.e. the photosynthesis of cellular carbon from carbon dioxide, by, for example, planktonic algae. The simplified equation of the process is:

$$6CO_2 + 6H_2O \xrightarrow{\text{light}} C_6H_{12}O_6 + 6O_2$$

and the uptake of carbon-14 dioxide is used as a more sensitive and reliable alternative for measuring photosynthesis than either pH changes or the amount of oxygen or algae produced. In the method (22,23,24,25) a sample of lake water is taken from the required depth and transferred to clear and opaque flasks. A sample is also retained for analysis of total carbon dioxide expressed as mgC/m^3 (26). A sterile solution containing a quantity, A, of carbon-14 labelled sodium bicarbonate adjusted to pH 10.5 with sodium hydroxide (to prevent carbon dioxide loss to the atmosphere) is added to the flasks which are sealed and then lowered to the original sampling position. After several hours of incubation, for example solar midday to dusk, the flasks are recovered and the algae filtered onto membrane filters. The filters are rinsed with membrane filtered lake water, exposed to hydrochloric acid fumes to remove any carbonates produced, dissolved in methyl acetate and counted by liquid scintillation counting (27). The photosynthetic uptake of carbon-14, ΔA, is given by subtracting the uptake in the opaque flask (non-photosynthetic) from that in the clear flask (total). The quantity of carbon taken up, ΔM, is then given by

$$\Delta M = \frac{KM\ \Delta A}{A}$$

where the constant, K, is approximately 1.05 and accounts for the slightly slower photosynthesis of carbon-14 than inactive carbon. There is some doubt as to whether the method measures net or gross productivities (26), however by using a few kBq(nCi) of carbon-14 it is theoretically possible to measure productivities as low as $0.02\ mgC/m^3$.day although this value may be higher as a result of dark bottle uptake. A similar technique involving tritiated water instead of carbon-14 has also been used (26).

6.2 Sewage Fungus Slime

Biomass determinations of sewage fungus slime by classical methods, for example direct weighing, are unreliable because of uneven growth, sloughing and debris trapped in the slime. In some open channels the loss of added phosphate can be almost totally attributable to absorption by slime organisms (sewage fungus). Therefore, phosphorus-32 uptake may be used to estimate the slime biomass (28). Phosphorus-32 labelled orthophosphate solution is injected at a constant rate for about one hour at the start of the reach of interest and samples of water and slime taken regularly at downstream sites. An example of tracer flow-through curves and specific activity distributions of slime are shown in Figs. 10 and 11. The total phosphorus-32 removed between two sites is given by the difference in area under the curves at the sites and the slime biomass is then determined from the loss of phosphorus-32 and the specific activity of debris-free slime.

Samples of aquatic rooted plants and river sediments are also taken to estimate the quantity of phosphorus not removed by the slime (for example by precipitation). The phosphorus-32 is measured directly in the sampling vial by liquid scintillation counting using Cerenkov radiation which obviates the need to use a liquid scintillator.

6.3 Biodegradation

The ability of micro-organisms to biodegrade organic pollutants released to the aquatic environment may be studied using radiotracers. The method is based on the formation of carbon-14 dioxide by the biodegration of organic chemicals labelled with carbon-14 (29). The labelled chemical is mixed with stream water, nutrient and a particular micro-organism e.g. Pseudomonas Sp. in sealed flasks which are incubated in the dark to prevent any photosynthetic uptake of carbon-14 dioxide or photodegradation of the labelled chemical. The flasks are designed so that the contents can be acidified after incubation and the carbon-14 dioxide flushed with nitrogen into ethanolamine. The trapped carbon-14 dioxide and ethanolamine are then mixed with liquid scintillant and counted in a liquid scintillation spectrometer. As well as using single species of cultured micro-organisms, the method has been extended to natural microbial communities in stream waters (30). In any event, care must be taken to ensure that the tests are conducted with the organic compound at the concentration likely to be present in the environment.

6.4 Analytical Chemistry

Radiotracers can be used for studies in chemistry since the differences in the physical or chemical behaviour of the radioactive and stable isotopes of an element are small. Any differences are usually due to the percentage mass difference of the isotopes and may only affect the lightest elements. Radiotracers offer two distinct advantages over non-radioactive chemical methods. Firstly, the measurement of radiotracers is very sensitive so that the tracer can be associated with nanograms of the material and small losses will be readily detectable. Secondly, the radiotracer can be measured without interference effects either from other ions in the sample or due to matrix effects in the sample.

For the chemical analyst radiotracers provide a means whereby the performance of an analytical method can be assessed right from sample collection, through sample storage and preparation, to the final analysis (37). To study losses of a particular ion from solution onto a sample container, a known "spike" of the radioactive ion is added to the sample (38). By measuring the concentration of radiotracer subsequently in solution and comparing this to the concentration expected after dilution, any losses can be assessed. Concentrations in samples may be checked subsequently to see how sample storage effects losses and the technique can also be extended to any river sediments contained in the samples (31). When samples have to be filtered ion losses to filter papers can be measured either by comparing the activities in the solution before and after filtration or by measuring any activity on the filter paper. If separation of a determinand is required before analysis, for example pre-concentration of an organic pollutant by a resin, then recovery efficiencies may be determined using compounds labelled with carbon-14 (32).

Isotope Dilution (33,34) may be used to measure quantities of inactive material in a sample simply by adding a radioactive form of the determinand and measuring the specific activity of a recovered portion of the pure determinand. The method does not require total recoveries as in non-radioactive methods although it is inaccurate in determining very low concentrations and then the technique of substiochiometric analysis (35) may have to be employed. Inverse or Reverse Isotope Dilution, as the name suggests, is used to determine the quantity of radiotracer in solution by the addition of an inactive carrier.

Other major applications of radiotracers in analytical chemistry are normally referred to under the title Radiometric Analyses. Radiometric titrations involve the use of radiotracers, usually as end point indicators, and have the advantage of a more clearly defined instrument reading end point than a visual colour change in chemical methods. In titrations involving precipitation either the solution or the precipitate can be monitored. Thus, to titrate iodide with silver nitrate, iodine-131 (as sodium iodide solution) is added to the sample and the end point is indicated when the activity of iodine-131 in the solution or on the precipitate ceases to decrease or increase respectively. Indirect-titration or back-filtration methods require the addition of an access of radioactive titrant to a sample and a comparison of the activities of the original titrant and the supernatant of the sample after titration.

7. Establishments Using Radioactive Tracers Where Advice or Service May be Obtained

Most large hospitals and universities use small quantities of radioisotopes routinely but there are four organizations which offer a service of radioactive tracer techniques on the scale required for many investigations in the water industry.

(a) Nuclear Applications Centre, Harwell

Located in Oxfordshire, this Centre forms part of AERE Harwell, and is concerned with the industrial application of nuclear measurement techniques. A main activity is the use of radioactive tracers in field or industrial plant studies — projects range from acquifer diffusion measurements in oil reservoirs to process dynamics studies in chemical production plants. The Isotope Measurements Laboratory carries out high-accuracy measurements on low levels of radioactivity in customers' samples, especially those containing Tritium and Carbon-14.

(b) Central Electricity Generating Board, Hydraulic Calibration Centre

Located at Hams Hall, Warwickshire, the Centre comprises a comprehensive calibration facility for liquid-flow measuring installations. *In-situ* flow measurements at power stations throughout the country are carried out using radioactive tracer techniques.

The flows measured are in general cooling-water flows of between 30 000 and 60 000 m^3/h. Measurements are carried out at a frequency of approximately six per year. Other radioactive tracer applications, include leak testing, measurement of the wetness of steam and steam flow-rate measurements.

(c) Imperial Chemical Industries Limited

Flow measurements utilizing radioactive tracers are available at three ICI locations within the UK.

Mond Division at Runcorn, Cheshire, maintains a small tracer applications group which carries out two or three liquid dilution flow-rate measurements each month. These are predominantly on Mond Division sites and are concerned with effluent and process flow-rate measurements.

Petrochemicals Division's Physics and Radioisotope Services Group, based at Billingham, Cleveland, provides a tracer applications service to all divisions of ICI throughout the UK, to ICI subsidiaries at home and overseas and to other industrial companies in applications of radioactive tracers to the study of a wide variety of problems on industrial process plant. Requirements for flow measurements for flow measurements in open channels (effluent channels, chemical drains, etc) is continuous and the Group carries out approximately 120 measurements of this type in a typical year. The range of compositions of the flows which are studied is wide: aqueous, acidic organic and multi-component flows are all commonly encountered. The magnitude of the flow rates measured are in general small and rarely exceed 10 000 m^3/h — though the capability exists to measure flow rates well in excess of this should the need arise.

The Group operates a 250 kW Triga nuclear reactor for the production of suitable radioactive tracers.

A further small applications group is based at the Petrochemicals Division site at Ardeer in Southern Scotland.

(d) Water Research Centre (Medmenham Laboratory)

Located at Medmenham, Bucks, the Water Research Centre has utilized radioactive tracers for at least 25 years. Applications include flow-rate measurements in rivers and sewers, usually to calibrate flow-measuring devices, dispersion studies in reservoirs, estuaries and coastal waters, mixing and retention studies in treatment plant, environmental systems, and biological, biochemical and chemical studies.

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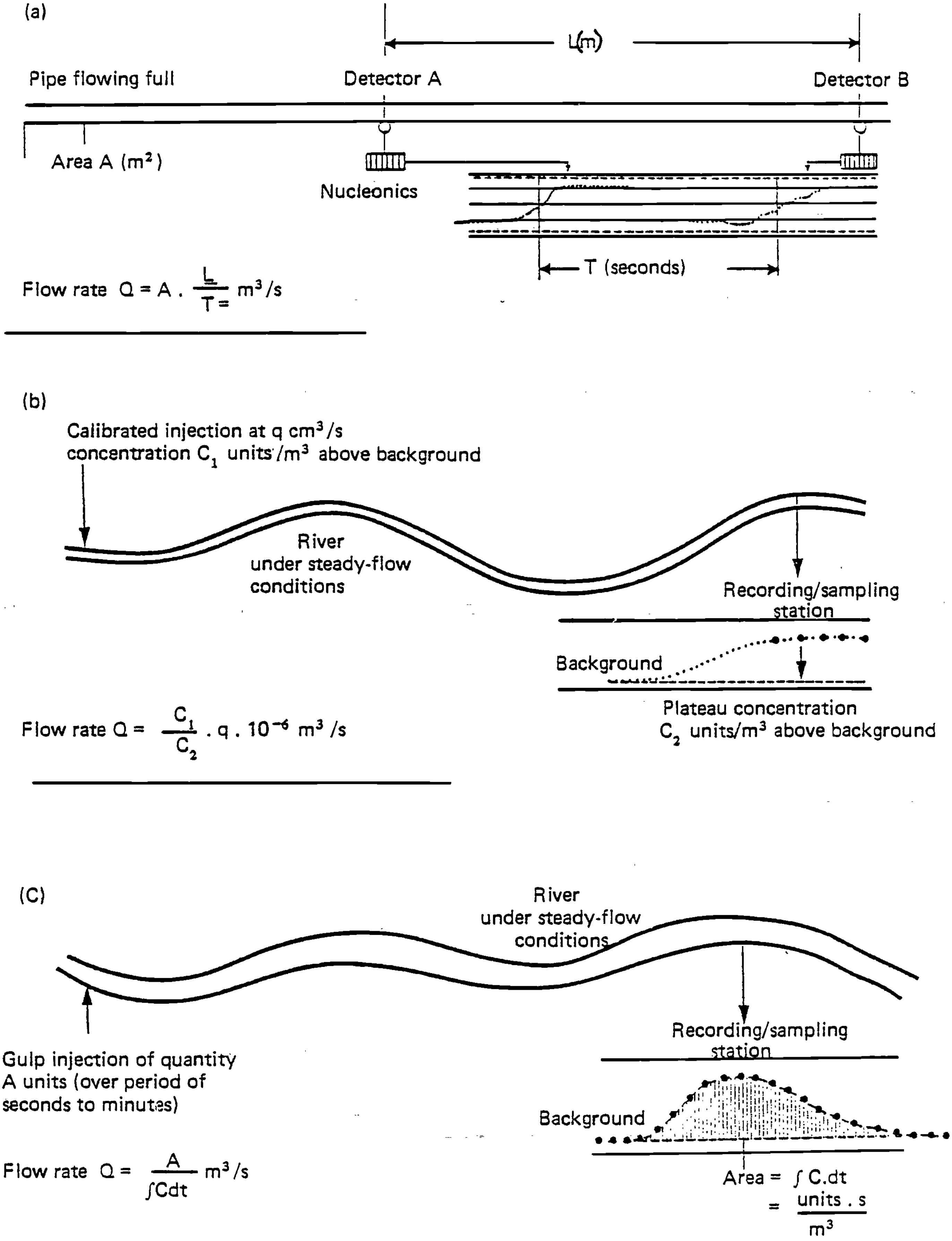

Fig. 1. Three methods of measuring flow with tracers

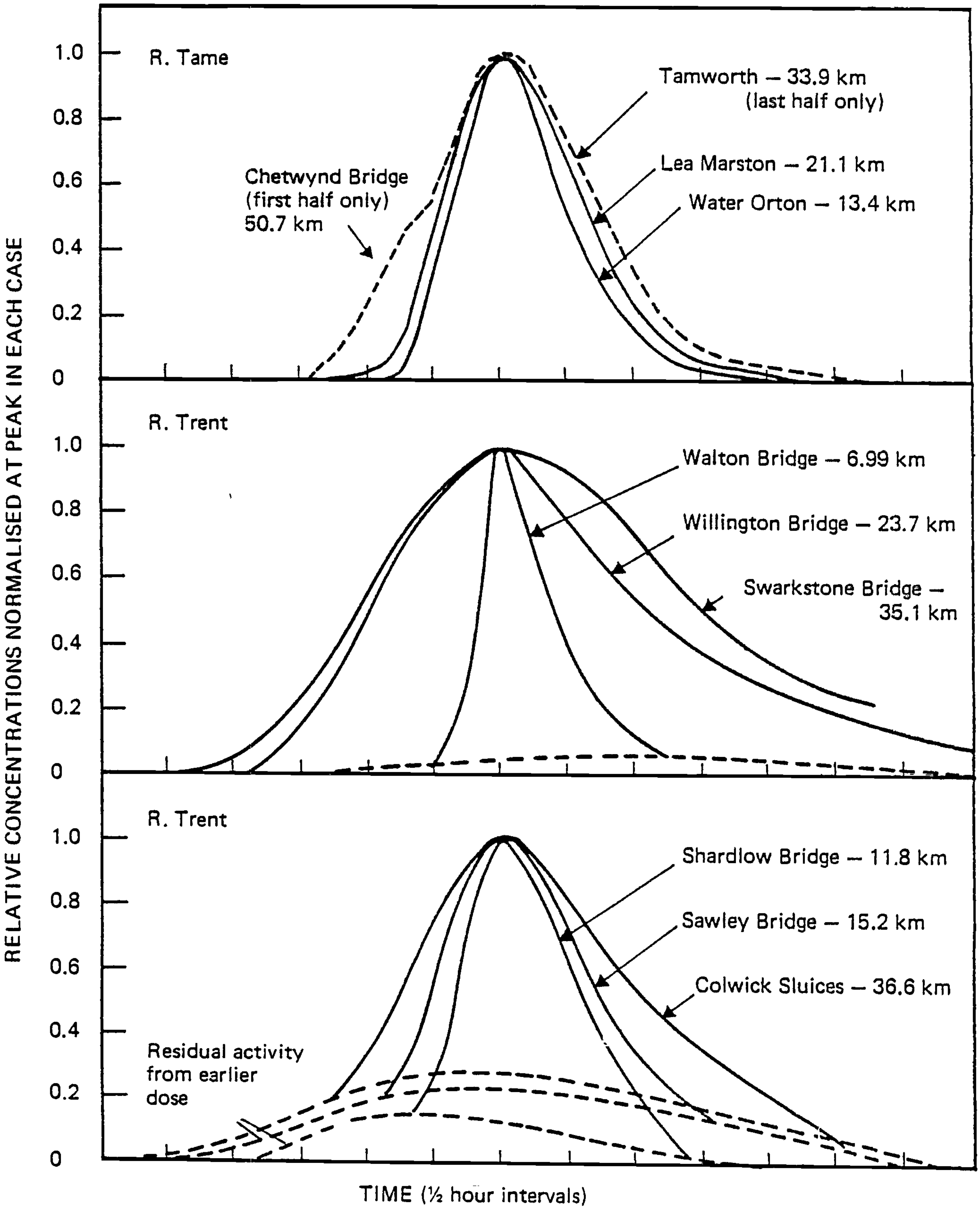

Fig. 2. Dispersion curves for 120km Tame/Trent survey using Bromine-82 with distances from Perry Bar and topping up stations at Chetwynd Bridge and Swarkstone Bridge

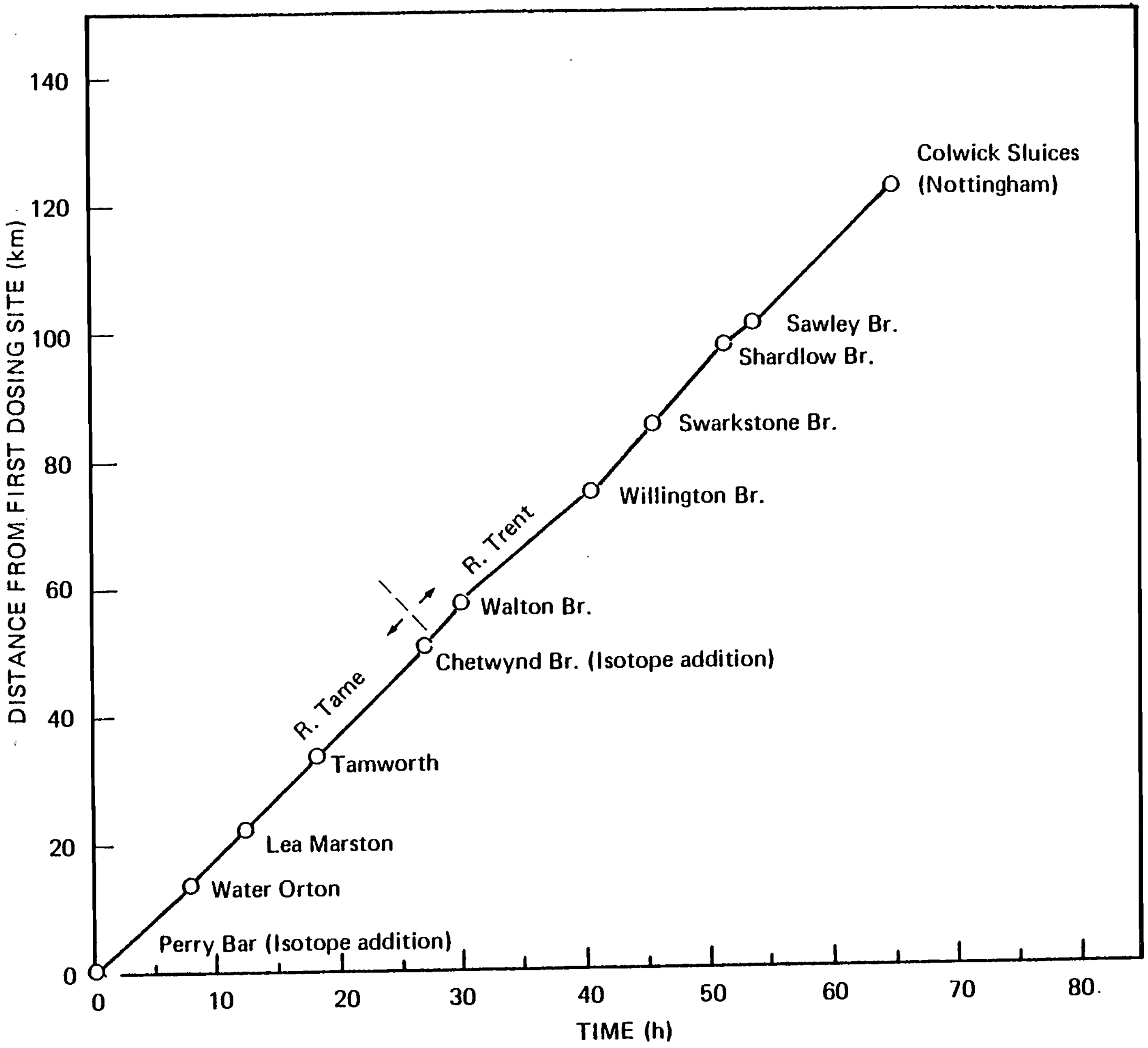

Fig. 3. Times of travel between stations at which the Bromine-82 dispersion curves of Fig. 2 were recorded

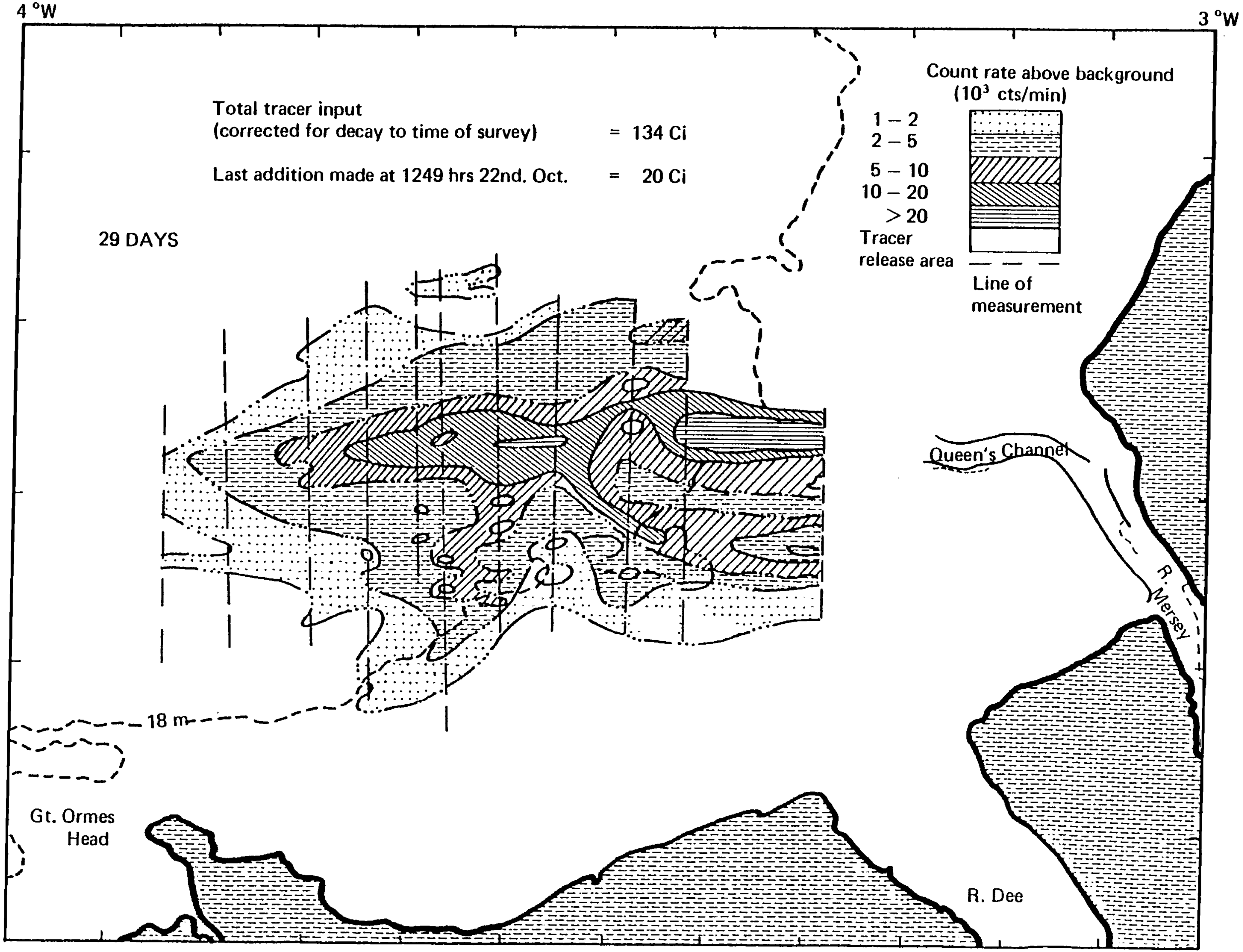

Fig. 4. Bed radiation survey — 2010 hrs — 22nd October — 0520 hrs — 24 October 1970

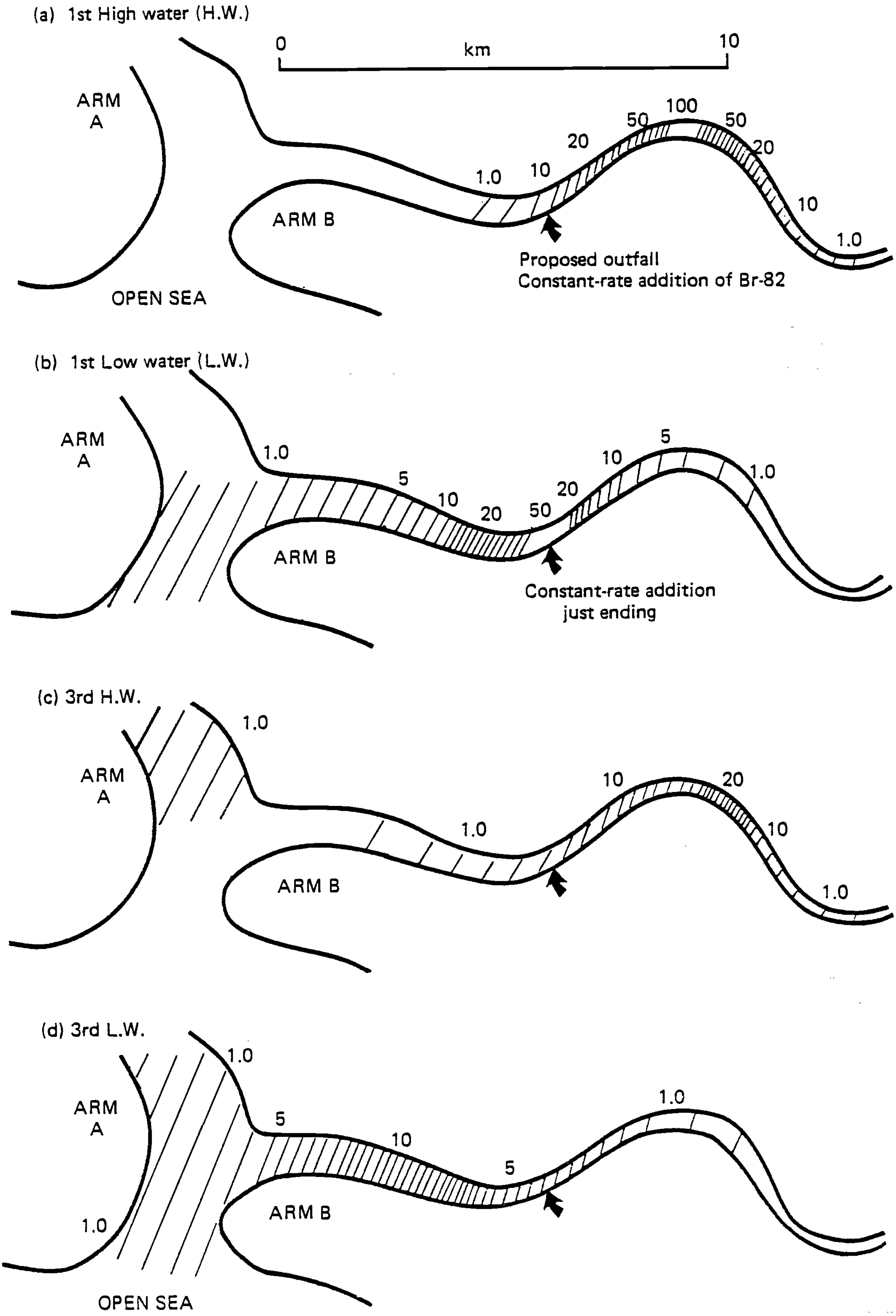

Fig. 5. Dispersion of Br.82 in estuary showing dilutions as a function of time

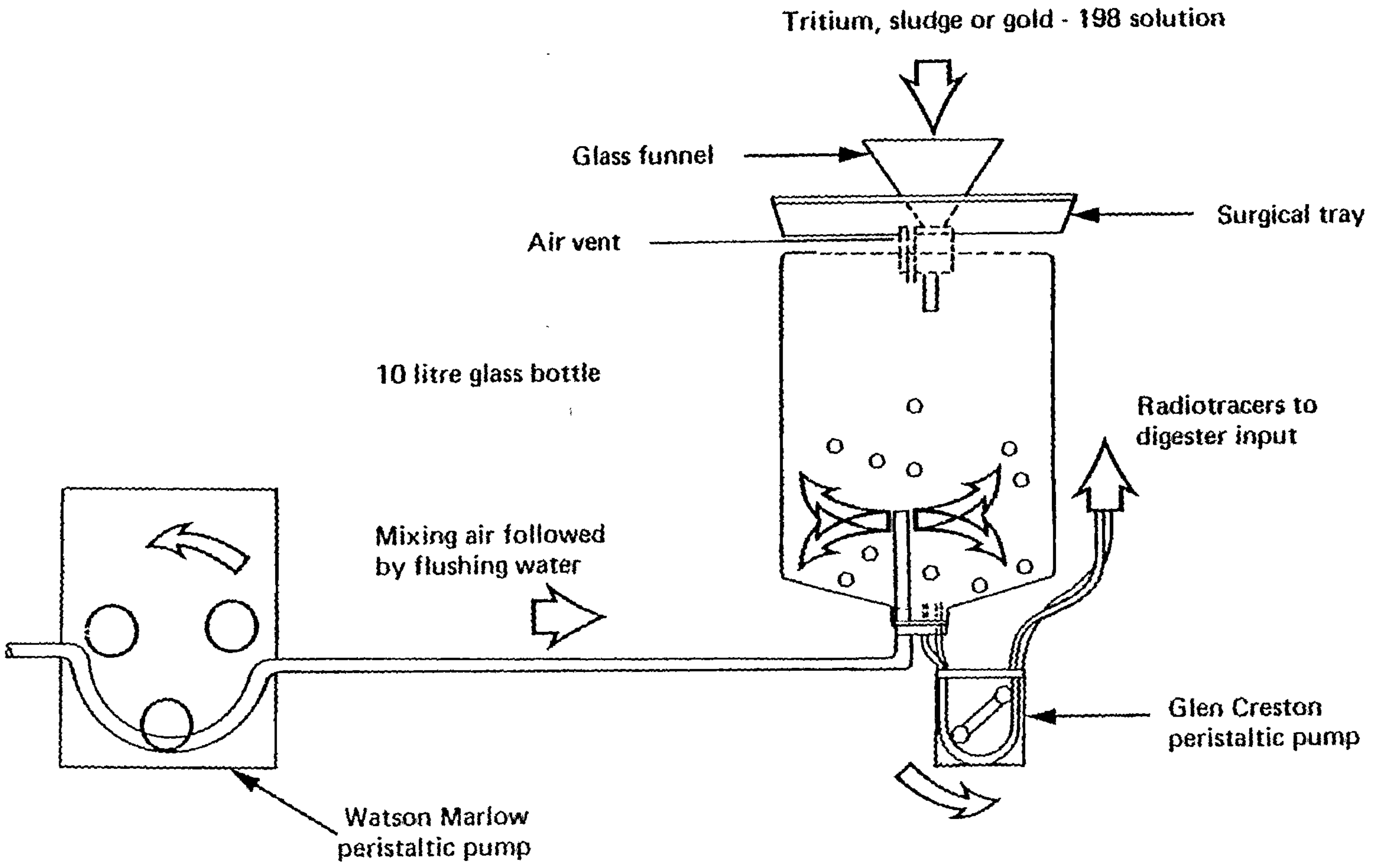

Fig. 6. Equipment for site labelling of sludge and injection of radiotracers

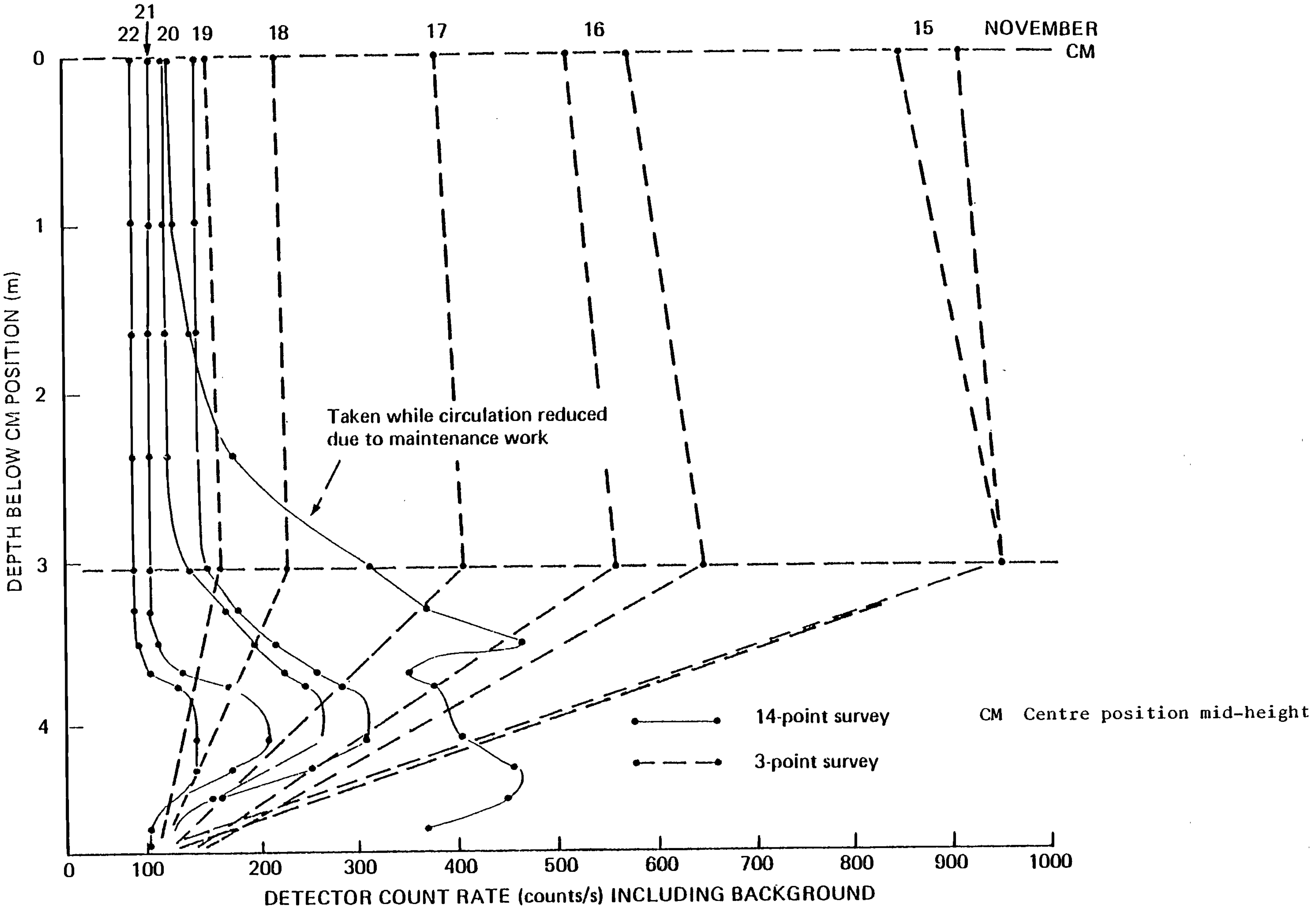

Fig. 7. Digester 2. Centre position, relative concentrations of Gold-198 below CM position

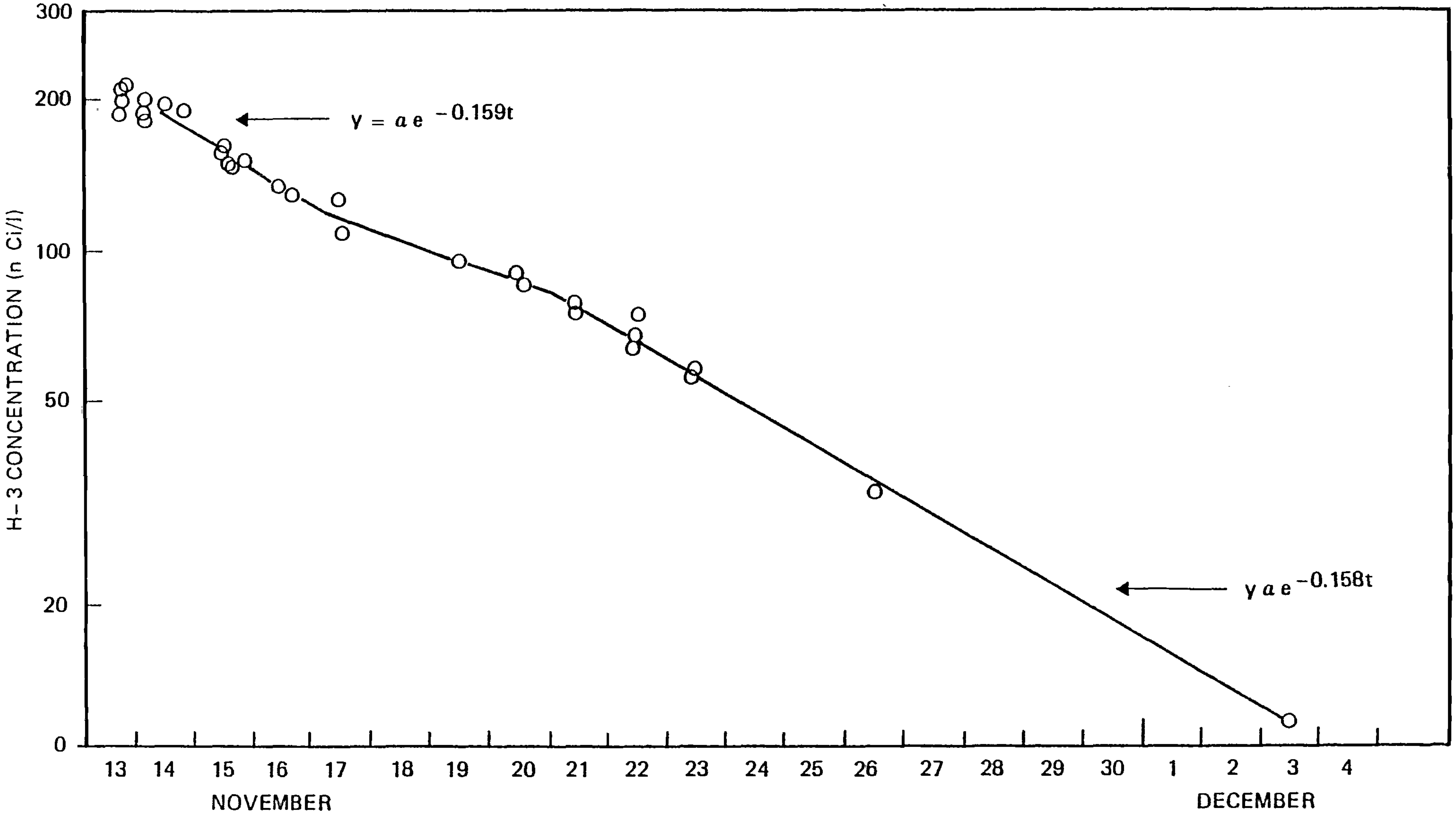

Fig. 8. Concentration of tritium in digester liquor for a period of 3 weeks following injection of tritiated water

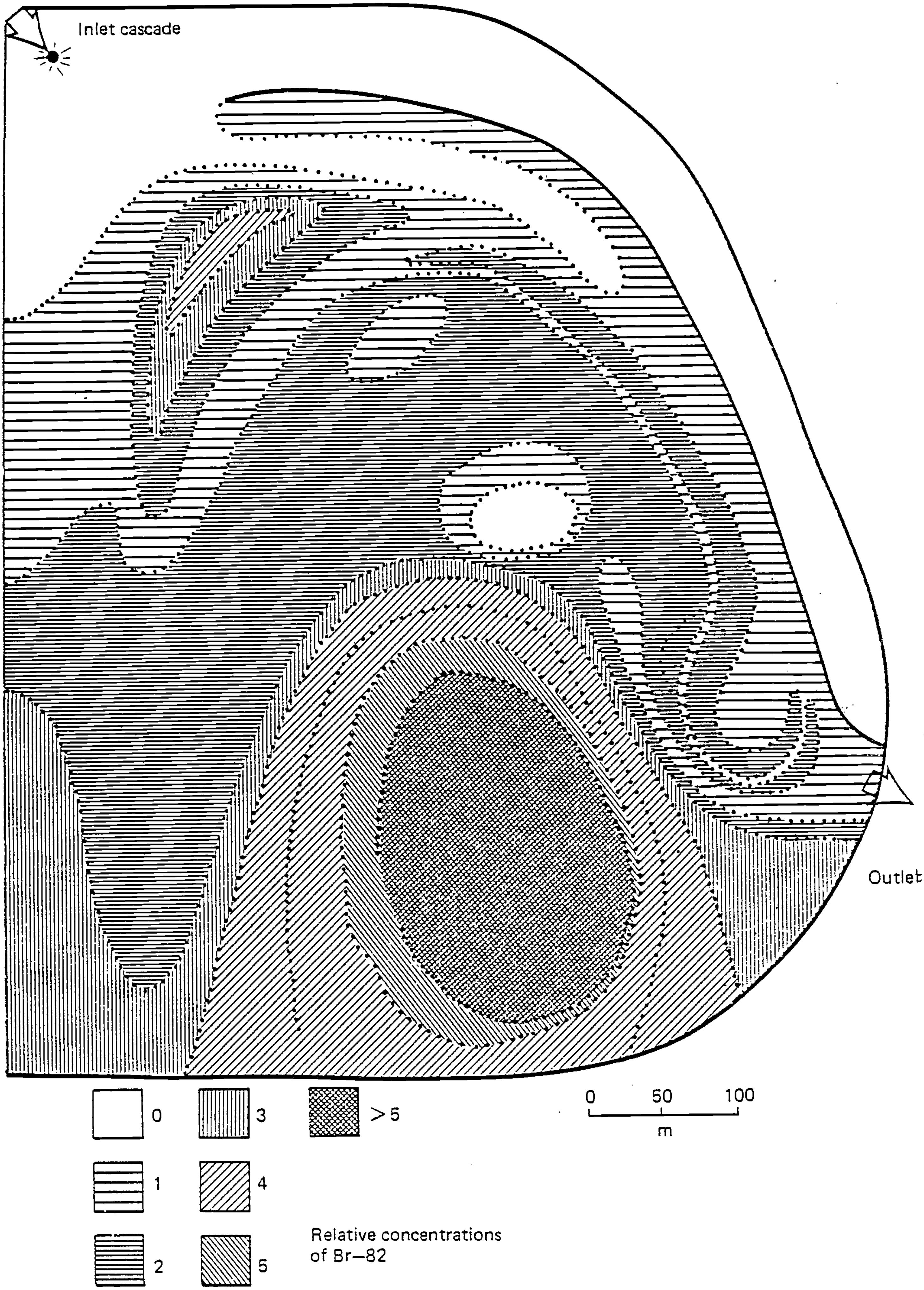

Fig. 9. Distribution of tracer in a reservoir one day after injection at the inlet

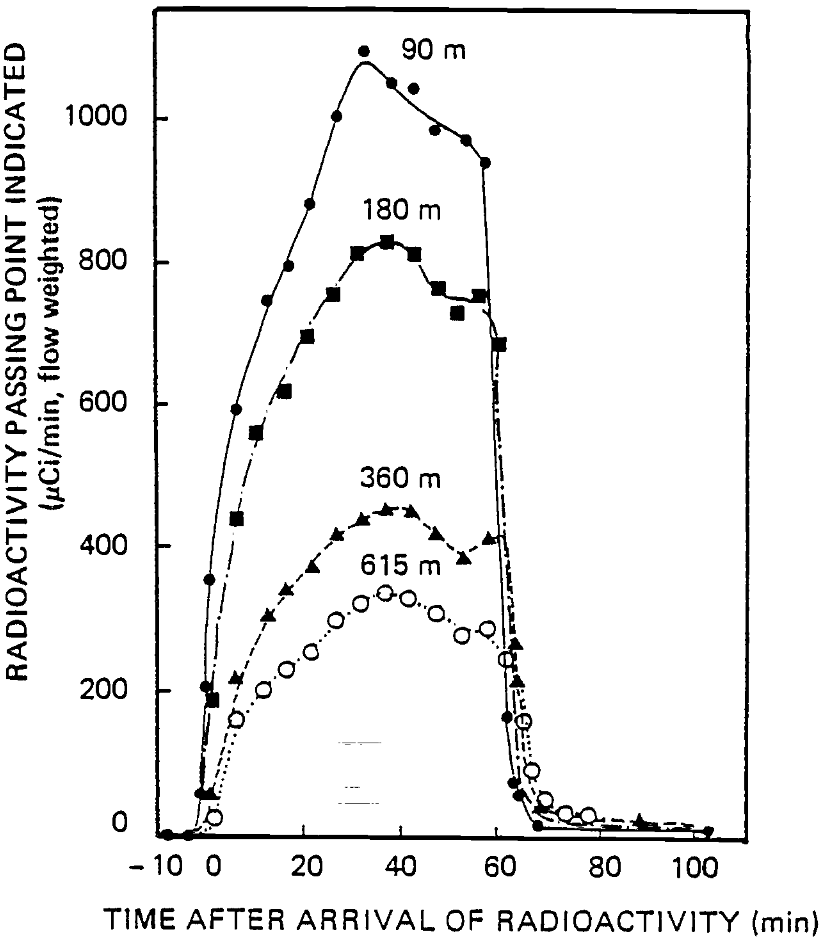

Fig. 10 Removal of P-32 from solution on passage down a slime-infested channel (Distance from point of addition shown against each curve)

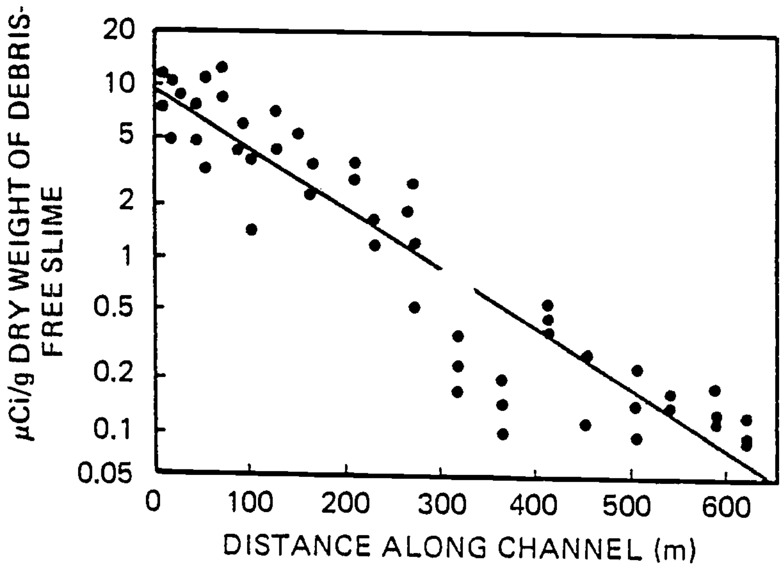

Fig. 11. Variation in specific activity of P-32 in slime with distance along effluent channel

Note on the use of stable isotopes and other parameters for water studies

Stable Isotope Studies

Several stable elements either have isotopes which can be readily separated or which vary in abundance in nature dependent on locality, which can be used in investigations. The most important of these are Hydrogen 2 (deuterium), carbon 13 and Nitrogen 15. The first two are chiefly used to label organic compounds, carbon 13 being suitable for NMR studies in the same way as Hydrogen 1 and Fluorine 19, Nitrogen 15 has been used for studies into the fate of nitrate in the soil, its rate of movement in the ground and to follow the flows of surface streams that sink into the ground in areas where there are several underground rivers, it can also be used for labelling organo nitrogen compounds. Among the elements with differences in isotope distribution significant enough to be measured are helium, boron, oxygen, sulphur and lead. The variations in oxygen isotopes are sometimes used to determine the climatic or salinity conditions under which a deposit or rock has been formed in the presence of water. The ratio of oxygen 16 to oxygen 18 incorporated into minerals has been found to vary with temperature and salinity. This ratio also varies with mineral and for water and carbon dioxide can vary between liquid water and the atmosphere, and under certain circumstances with water body location. Mass dependent fractionating effects are responsible for this differentiation, which is, however, slight. The differentiation of the stable lead isotopes is a result of the four different decay series (listed in Ref 1). Very slight differences also occur occasionally in other elements for similar reasons, notably argon, rubidium and some of the lanthanides due to other naturally occurring radioactive isotopes outside the heavy element series, all with exceedingly long half lives (see Ref 1, table 5). These latter variations are sometimes used to date the age of rocks and sediments from the last time there was the possibility of equilibriation, which may not always be the time of formation. Carbon 14 and Hydrogen 3 (Tritium) with short half lives are used similarly. For information on variations in naturally occurring isotope ratios see Ref 2.

Other Parameters

Although isotopes are very convenient, especially in studies such as those on the uptake of elements from water by plants, there are often other ways of studying the movement of water. Thus dyes, especially fluorescein and eosin have been used, though these do suffer from problems of detection at extreme dilution, the possibility of absorption or decomposition and public complaint at the resultant discoloration. Addition of an unusual easily detectable ion such as lithium has also been used. Again there is the possibility of absorption. Trace element patterns are sometimes used, but require a lot of analysis, usually multi-element spectrographic (emission, ICP or XRF), but they did, for instance, show the poor mixing at the Niger-Benue confluence and the effect of other tributaries on the pattern; this method has also been used on one or two Nile tributaries, but precipitation on mixing can cause complications, though easily detected. A combination of pH and Total Dissolved Solids analyses has been used to show that the rivers flowing to Lake Awassa must have an outlet, underground seepage to the Lake Abbaye — Lake Chamo watershed, which in turn must have an outlet, in this case via the Sagan River to Lake Chew Bahr (Stephanie), which is the ultimate terminal sink. Temperature measurements have also been used, especially to locate springs in the bed of the sea or in lakes, the spring being colder or warmer than the surrounding water; this method has also been used to study water movements in the sea. Turbidity, or suspended solids has been a useful indicator for centuries as in Lake Geneva, the Nile confluence at Khartoum and around the shores of Iceland and Britain.

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