RADIOCHEMICAL STUDIES OF ^{99}Tc AND ^{14}C IN ENVIRONMENTAL SAMPLES

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A thesis submitted to the University of Glasgow in partial
fulfilment of the requirements for the degree of
Doctor of Philosophy

Scottish Universities Research and Reactor Centre

May 1991

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ACKNOWLEDGEMENTS

My sincere thanks goes to my supervisor, Dr Brian William East, for his constant help, advice and encouragement throughout this work. I am very grateful to Prof Murdoch Baxter (now in Monaco) for his valuable guidance.

My thanks go to all the academic staff, technicians, research assistants and students, without whose help this work would not have been completed so readily. I am indebted to Dr R D Scott, A B MacKenzie, G T Cook, Dr H Banford, Dr T Preston and Dr J Whitley, whom I could contact for advice and help whenever I needed. Special thanks go to Dr P MacDonald (for help in collecting the samples), Mr K McKay (for providing ICP-MS facility and valuable suggestions) and Mr R Anderson (for advice and suggestions in using liquid scintillation counting). I will always remember the smiling faces of Walter, Alex, Bob, Michael, Jim and John whose assistance came in too many varied forms to detail here. I would also like to thank all my collegues Yousuf, Nouri, Daud, Andy, Peter, and Kate for contributing to the good environment in which I have been fortunate enough to do this work. I always be grateful to Margaret and Maurreen for help in using the computer and printing the manuscript.

I would like to thank my parents, who have helped me to complete this study in so many ways which cannot be explained in words. I wish to acknowlege the moral support of my wife's parents. Finally, I will be always grateful to my family Yasmin, Annie, Asad and Fahad.

I am also grateful to the Ministry of Science and Technology, Pakistan and the Pakistan Atomic Energy Commission for a scholarship and leave of absence respectively, which made this work possible.

PUBLICATIONS

Two papers have been presented in the 2nd International Conference on Plasma Source Mass Spectrometry, 24-28 September 1990, University of Durham, UK and are due for publication in "Applications in ICP-MS", The Royal Society of Chemistry, UK.
The papers are:

1. A procedure for the determinations of ^{99}Tc in environmental samples by ICP-MS. Ihsanullah; East, B.W. (in press).

2. The determination of ^{99}Tc by ICP-MS in samples collected near nuclear installations. Ihsanullah; East, B.W. (in press).

ABSTRACT

^{99}Tc, the most crucial technetium isotope enviromentally, is a pure, weak β-emitter with maximum energy 0.292 Mev and specific activity of 630 kBq mg^{-1}. ^{99}Tc is mainly released to the environment as waste discharge from nuclear reprocessing facilities and from previous nuclear atmospheric detonation tests and nuclear accidents. Because of its long half-life and current interest in the collective long-term dose, it is necessary to establish a knowledge of the behaviour of ^{99}Tc in the environment for complete assessment of the impact of nuclear industry.

Effort has been made to develop a radiochemical method which can be applied to environmental samples in order to gain information by obtaining more accurate and precise data to assess the impact of Tc releases on man. Attention has been focussed for this purpose on inductively coupled plasma-mass spectrometry (ICP-MS), a new powerful technique for elemental and isotopic analysis which combines the remarkable characteristics of the ICP for atomizing and ionizing injected samples with the sensitivity and selectivity of mass spectrometry. Hence, with the advent of ICP-MS as a highly sensitive method of detection of long-lived radionuclides, this has been investigated and successfully applied to ^{99}Tc analysis.

Technetium from large volume water samples was concentrated by anion exchange (Dowex 1-X8) resin and recovered by elution with 12M HNO_3. Biological (algae) samples were dissolved in 9M HNO_3 by refluxing, followed by filtration, and, as with the water sample eluate, evaporated and redissolved in 2M H_2SO_4. Soil (silt) and sediment samples were ashed at 600°C, treated with 2M H_2SO_4 containing 2 cm^3 H_2O_2 added to the ash, and finally the solution was filtered to provide a clear solution.

Since ICP-MS is based on the measurement of the mass of an element, isobaric interferences at mass 99 must be eliminated as far as possible. For ^{99}Tc, ^{99}Mo is not a problem as this radionuclide decays with a half life of 67 hrs and after few days will have gone. The other isobaric nuclide is ^{99}Ru. ^{99}Ru is stable and 12.7% abundant in natural ruthenium which occurs in the environment and is a key problem. Two methods were used for the decontamination from Ru. The first method consisted of a series of steps, involving valency control with H_2O_2 and NaClO, boiling from H_2SO_4 solution and solvent extractions with CCl_4, cyclohexanone and triisooctylamine(TIOA)-xylene. The second method included: the boiling of H_2SO_4 media, NaOH elution and TIOA-xylene extraction.

After treatment to remove Ru, the resulting solution was adjusted to pH 7 and passed through Dowex 1-X8 resin in order to get a clear solution in 2% HNO_3 with a salt concentration of <0.1%. ^{99m}Tc and ^{95m}Tc tracers were used to determine radiochemical yields; ^{99}Tc for method calibration, Ru standard solution to check decontamination and Rh for monitoring the response of the ICP-MS instrument. Two reference materials i.e. IAEA marine algae and BNFL seaweed (Fucus vesiculosus) were analysed for intercomparison studies.The % chemical yield for water samples was found to be 65 ± 15, for biological material (algae) 70 ± 11 and for soil (silt) samples 65 ± 15. The limit of detection of ^{99}Tc by ICP-MS was 0.004 ppb.

Various types of samples were analysed in order to verify the new ICP-MS procedures and to determine environmental ^{99}Tc levels as follows: in order to check the liquid discharges and dilution of ^{99}Tc from the Sellafield Reprocessing Plant, Fucus vesiculosus was collected from many relevant coastal sites as it is a well known bioindicator for various radionuclides including Tc; the Ascophyllum/Fucus ratio values were measured and were in good agreement with the literature values; the levels of ^{99}Tc in Porphyra and water samples were below the detection limit; moss and lichen samples were collected from an undisturbed area 1 km east of the Chernobyl site, but the ^{99}Tc concentrations were below the limit of detection.

Another problem addressed in the present work was the measurement of environmental ^{14}C contamination in the air from a low power (300 kW) training reactor namely, that at the Scottish Universities Research and Reactor Centre, East Kilbride near Glasgow. For analysis, air from the reactor stack, the reactor hall and two sites in the immediate vicinity (downwind on the east side of the reactor stack) was passed through 0.1M barium carbonate to collect CO_2 as precipitated barium carbonate and the carbon converted to benzene. ^{14}C was measured in this form by liquid scintillation counting using a Tricarb 2260XL instrument (Packard Instrument Company). All the four sites showed enhancement when the reactor was running. The reactor stack and the reactor hall showed some enhanced activity even when the reactor was shut down. The ^{14}C released from the reactor corresponded to $\approx$ 12 MBq y^{-1}.

CHAPTER 1

INTRODUCTION

Since 1945, thousands of kilograms of ^{99}Tc have been produced artificially as a result of worldwide nuclear weapons and nuclear power programmes. Because of the continuation of these programmes and its long radioactive half-life of 2.1×10^5 years an increasing presence of ^{99}Tc in the environment is foreseen, and its contribution has therefore to be taken into account in calculations of the future long-term collective dose to the population.

Because of its importance, it is necessary to establish an ongoing knowledge of the behaviour of technetium in the environment to enable detailed assessment of the impact of the nuclear industry. Due to various analytical difficulties however, data on the behaviour of technetium in the environment are limited. There are many methods in the literature for radiochemical analysis of technetium, but most of them are not designed to deal with the low levels of activity likely to be found in environmental samples.

The work described in this thesis has been directed towards the development of an accurate and precise technique for environmental samples, and with the advent of inductively coupled plasma-mass spectrometry (ICP-MS) as a highly sensitive method of detection, this has been investigated and successfully applied to ^{99}Tc analysis.

1.1 THE ELEMENT TECHNETIUM.

The existence of a missing element with an atomic number 43 was first predicted by Mendeleev in 1869. The element was called eka-manganese from its position in the periodic table. In 1937 the Italian physicists Perrier and Segre first obtained trace amounts of the element ($\approx$0.1 ng) by bombarding molybdenum with deutrons from the University of California cyclotron via the reaction:

$$^{96}\text{Mo (d,n) }^{97}\text{Tc}$$

Isotope	**Half-life**	**Type ofdecay**	**Means of production**	**%yield**
^{90}Tc	49.2 s	$\beta^+, \gamma(0.948, 1.054)$	^{92}Mo(p, 3n)	
^{90}Tc	8.3 s	$\beta^+(7.9, 7.0)$, γ (0.948)	^{92}Mo(p, 3n)	
^{91}Tc	3.14 m	$\beta^+(5.2)$ + EC, γ	^{92}Mo(p, 2n)	
^{91}Tc	3.3 m	β^+ + EC, γ	^{92}Mo(p, 2n)	
^{92}Tc	4.4 m	β^+ + EC, γ	^{92}Mo(d, 2n)	
^{93}Tc	2.75 h	EC, β^+, γ	^{92}Mo(d, n)	
^{93m}Tc	43.5 m	IT, EC, γ, e^-	^{92}Mo(d, n)	
^{94}Tc	293 m	EC, β^+, γ	^{93}Nb(α, 3n)	
^{94m}Tc	52 m	β^+, EC, no IT, γ	^{93}Nb(α, 3n)	
^{95}Tc	20 h	EC, γ	^{95}Mo(p, n)	
^{95m}Tc	61 d	EC, β^+, IT, γ,e^-	^{95}Mo(p, n)	
^{96}Tc	4.28 d	EC, γ, e^-	^{93}Nb(α, n)	
^{96m}Tc	51.5 m	IT, EC, β^+, γ, e^-	^{93}Nb(α, n)	
^{97}Tc	$2.6\text{x}10^6$y	EC	daughter^{97}Ru	
^{97m}Tc	90.5 d	IT, $\gamma(0.096)$, e^-	^{96}Mo(d, n)	
^{98}Tc	$4.2\text{x}10^6$ y	$\beta^-(0.397)$, $\gamma(0.652)$	^{98}Mo(p, n)	
^{99}Tc	$2.13\text{x}10^5$y	$\beta^-(0.292)$	fission	6.06
^{99m}Tc	6.0 h	IT, $\gamma(0.141)$, e^-	daughter^{99}Mo	
^{100}Tc	15.8 s	β^-, γ	^{99}Tc(n, γ)	
^{101}Tc	14.2 m	β^-, γ	daughter^{101}Mo	5.6
^{102}Tc	5.28 s	β^-, γ	daughter^{102}Mo	4.3
^{102m}Tc	4.35 m	β^-, IT?, γ	^{102}Ru(n, p), fission	
^{103}Tc	54.2 s	β^-, γ	fission	3.0
^{104}Tc	18.3 m	β^-, γ	fission	1.8
^{105}Tc	7.7 m	β^-, γ	fission	0.9
^{106}Tc	36 s	β^-, γ	fission	
^{107}Tc	21.2 s	β^-, γ	fission	0.19
^{108}Tc	5.17 s	β^-, γ	fission	
^{109}Tc	1.4 s	β^-	fission	
^{110}Tc	830 m	β^-, γ	fission	

TABLE 1.1: Technetium isotopes.

The element was the first artificially created by man and was given the name technetium (from the Greek word, technetos) meaning artificial (Perrier & Segre 1937 & 1947). The name "technetium" was officially confirmed at a convention of chemists held on September 2-5, 1949, in Amsterdam (Lavrukhina & Pozdnyako, 1970).

Technetium has no stable isotopes. Twenty-one radioactive isotopes, along with seven isomers are known (Rioseco, 1987 and Long & Sparkes, 1988) and are listed in Table 1.1. There are three long-lived isotopes: ^{97}Tc($t_{1/2}$ = 2.6 x 10^6 y), ^{98}Tc($t_{1/2}$ = 4.2 x 10^6 y) and ^{99}Tc($t_{1/2}$ = 2.1 x 10^5 y). Of these only ^{99}Tc is a fission product.

1.2 PHYSICAL PROPERTIES OF TECHNETIUM.

Technetium is a silver-grey metal that tarnishes in moist air (CRC Handbook, 1983). It crystallizes in a hexagonal state similar to rhenium which is its closest analogue (Long & Sparkes, 1988). Various physical properties of Tc and its comparisons with Mn and Re are listed in Table 1.2 (Kotego et al., 1968).

Physical property	**Mn**	**Tc**	**Re**
Atomic number	25	43	75
Atomic weight	54.938	98.913	186.31
Atomic radius, °A	1.306	1.358	1.373
Crystal lattice	a = 8.896	a = 2.735	a = 2.755
parameters, °A	(α-Mn)	c = 4.391	c = 4.449
Density, (g cm^{-3})	7.30	11.487	21.02
Melting point, °C	1244	2200 ± 50	3170
Boiling point, °C	2120	4700	5870
Neutron capture cross section, barns:			
(n,γ) reaction	10.7	20 ± 5	48.7
(n,n') reaction	-	0.009	-

TABLE 1.2: Physical properties of Mn, Tc and Re (A° = 10 nm).

1.3 CHEMICAL PROPERTIES OF TECHNETIUM.

Jones and Davison (1982) reviewed many papers on technetium chemistry and found that it is still poorly developed in comparison with that of its neighbours, Mo, Mn,Ru and Re. Technetium occurs in group VII of the periodic classification lying between Mo and Ru in the second transition series, and possessing diverse chemistry. There are two expected configurations for the electronic ground state (Robb, 1983) which are:

i) Kr $4s^2$ $4p^6$ $4d^6$ $5s^1$
ii) Kr $4s^2$ $4p^6$ $4d^5$ $5s^2$

The chemistry of technetium has developed sporadically over the last 30 years. An important review on the radiochemistry of technetium, concerning investigations prior to 1960, has been undertaken by Anders. Technetium is an analogue of Mn in its analytical behaviour. Tc(VII) has an ionic radius of 5 nm, Which is similar to that of Re, but significantly greater than that of Mn (4.6 nm). Re and Tc, both form stable XO^-_4 anions that give insoluble salts with large cations. They also form volatile heptoxides and acid-insoluble heptasulphides. The differences are that the vapour pressure of Tc_2O_7 is much higher than that of Re_2O_7 at low temperature i.e 10^{-1} mm at 100°C, compared to 3×10^{-5}mm. In contrast to Re, Tc(VII) is therefore easily lost upon evaporation conducted at a low temperature (Keller, 1988).

As a result of its electronic configuration Tc exhibits different oxidation states ranging from -I to +VII. The most stable and characteristic oxidation state of Tc is +VII, arising from direct oxidation by oxygen and other oxidants. Another but less stable form than +VII, is +IV. The remaining oxidation states are found in the form of various complex compounds. Compounds with oxidation state less than IV oxidize readily to IV and VII, whereas compounds of +V and +VI have a tendency to disproportionate, as follows (Kotego et al., 1968):

$$3\text{Tc}(+\text{V}) \rightarrow 2\text{Tc}(+\text{IV}) + \text{Tc}(+\text{VII})$$
$$3\text{Tc}(+\text{VI}) \rightarrow \text{Tc}(+\text{IV}) + 2\text{Tc}(+\text{VII})$$

Technetium forms a stable pertechnetate (TcO^-_4) ion in aqueous solutions, which is equivalent to the ions MnO^-_4 and ReO^-_4. The best known compounds of Tc(+VII) are the oxide Tc_2O_7 and its salts from which the free acid $HTcO_4$ may be prepared. Pertechnetates generally have low solubility, the most common being NH_4TcO_4, a white compound which is soluble in water.

Examples of Tc(VI) compounds are golden yellow technetium hexafluoride, blue technetium oxide tetrachloride, and green coloured hexachloride. TcF_6(VI) and TcO_3F(VII) are volatile compounds and are particularly important in the nuclear fuel cycle because they result in Tc becoming associated with recovered uranium in the fluoride enrichment process. The largest source of production of Tc from recovered U is its separation in the UF_6 gas stream with solid MgF_2. It is eluted from MgF_2 with HNO_3 (Till, 1986).

As mentioned above Tc exhibits a variety of valence states and compounds of ^{99m}Tc in one or other of these states are produced by simple reduction of Tc(VII) as TcO^-_4. $^{99m}TcO^-_4$ is extensively used for brain scanning and thyroid imaging. Other Tc radiopharmaceuticals include $^{99m}TcO_2.SnO_2$ (for liver scanning), ^{99m}Tc-diethylenetriaminepentaacetate (for kidney scanning), ^{99m}Tc-diethylacetanilidoiminodiacetate (for gall bladder imaging) and ^{99m}Tc-phosphates for bone investigations (Keller, 1988).

The increasing use of the element as ^{99m}Tc in nuclear medicine has resulted in many gaps in Tc chemistry being filled. Clearly, hitherto there was no means of obtaining this information as Tc was not readily available since it has no stable isotopes.

In many respects Tc can also be assumed to behave like iodine. For example, ^{99}Tc and ^{129}I exist primarily as soluble anions in aerobic solutions (TcO^-_4, I^- and IO^-_3), and are mobile in surface soils and readily available for uptake by plants (Wildung et al., 1977). ^{99m}Tc and ^{131}I are used in the preparation of radiopharmaceuticals and according to Attrep et al. (1971) and Ehrhardt & Attrep (1978), pertechnetate will concentrate and behave in the thyroid glands of mammals in a similar way to iodide. ^{99}Tc and ^{129}I are both fission products and are present principally as a result of nuclear weapons testing and fuel reprocessing. Recent laboratory studies have however shown marked differences in the behaviour of these elements in plant systems (Ehrhardt & Attrep, 1978).

1.4 SOURCES OF ^{99}Tc.

^{99}Tc, the most important technetium isotope environmentally, is a pure, weak beta emitter with maximum energy 0.292 MeV and specific activity 630 kBq mg^{-1} (Long & Sparkes, 1988). ^{99}Tc is the daughter product of ^{99}Mo, which is formed by fission of ^{239}Pu and ^{235}U and also by neutron capture in ^{98}Mo which has a natural abundance of 23.78% (Holm et al., 1984). The capture cross section for this reaction is 0.13 barn. ^{99}Tc is also formed in high abundance from the fission of ^{233}U(fission yield,4.8%), ^{235}U(6.06%), ^{238}U(6.3%), ^{239}Pu(5.9%) and ^{232}Th(2.7%) (Till, 1986).

1.4.1 NATURAL SOURCES OF ^{99}Tc.

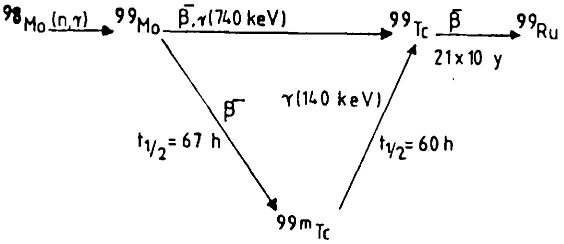
In 1952, Merrill first observed the emission spectrum of Tc in the light emitted by stars, demonstrating the fact that

Tc existed outside the earth. ^{99}Tc occurs naturally in the earth's crust primarily from spontaneous fission of ^{238}U and the slow neutron-induced fission of ^{235}U (Kenna & Kuroda 1964). Low concentrations of the radionuclide have been detected from the spontaneous fission of ^{238}U in natural ores and from the neutron capture in Mo ores of cosmic-ray neutrons (Rioseco, 1987).

1.4.2 MAN-MADE SOURCES OF ^{99}Tc.

^{99}Tc is produced from nuclear detonation tests,nuclear fuel reprocessing plants, nuclear power plants and by the use of ^{99m}Tc in the nuclear medicine.

^{99m}Tc is formed from the decay of ^{99}Mo($t_{1/2}$ = 67 h), which is produced as a fission product from ^{235}U or ^{239}Pu or by neutron capture in ^{98}Mo. Stainless steel material often contains Mo isotopes including ^{98}Mo (Holm et al., 1981) and so can give rise to ^{99m}Tc in the reactor environment. ^{99m}Tc is chiefly used as a body organ imaging agent in medical diagnosis. A typical dose per investigation is 370 MBq. ^{99m}Tc is an ideal radionuclide for diagnostic purposes as it has a short half-life (6h), is a pure gamma-emitter (140 keV), is convenient for clinical use and commercially available in the form of ^{99}Mo-generators in activities up to 2 x 10^{10} Bq (Luykx, 1986). A high proportion (85%) of the ^{99}Mo decays via the metastable nuclide ^{99m}Tc and then to the ground state ^{99}Tc:



The γ-radiation from ^{99m}Tc is poorly absorbed by tissue, minimising the radiation dose to the patient on the one hand while providing a high external detection efficiency by scintillation counting. The 140 keV gamma energy is close to optimum for thin NaI(Tl) crystals giving good resolution when NaI crystals of suitable dimensions are used (Keller, 1988).

Discharges of Tc from the nuclear fuel cycle.

Technetium discharges occur during the following steps of the nuclear fuel cycle:

- reactor operation
- nuclear fuel reprocessing
- conversion of recycled uranium into UF_6
- enrichment of recycled uranium
- fuel fabrication
- waste treatment

Luykx (1986) found that the major discharge of ^{99}Tc to the environment in the nuclear fuel cycle arises from reprocessing nuclear fuel. The normalised ^{99}Tc discharge rate for the years 1981 to 1983 at Sellafield was measured as 0.44 TBq $GW(th)^{-1}$ y^{-1} whereas the theoretical value was about 6 TBq $GW(th)^{-1}$ y^{-1}, this indicates that about 7 % of the ^{99}Tc produced in the fuel is discharged with liquid effluents.

At Karlsruhe (FRG) the quantity of ^{99}Tc over a six month sampling period (September 1983-March 1984) in the distillate discharged from the evaporator (which receives the liquid effluents from the reprocessing plant at Karlsruhe, FRG) was 2.5 x 10^5 Bq. In the reprocessing off-gas, concentrations of up to 0.3 Bq m^{-3} have been detected (Luykx, 1986).

Small amounts of Tc (≈ 0.1%) are released to the environment during the conversion of U_3O_8 to volatile UF_6 enriched from 0.7% of the fissile ^{235}U found in natural ores to 3-4% required for the reactor by a gaseous diffusion process. Till (1986) expected that the main release of ^{99}Tc was in the enrichment step, being annually, 0.4 TBq and 10 GBq to water and air respectively. About 7.4 GBq out of 44.4 GBq ^{99}Tc is lost during the fuel fabrication process).

The main route of ^{99}Tc to the environment is the disposal of aqueous waste from nuclear facilities or during separation and recovery of spent nuclear fuels. From the Diablo Caynon Power Station, Calif, USA, 37% of the total annual liquid waste activity expected to be released in the condenser cooling water is attributed to ^{99}Mo, the parent nuclide of ^{99}Tc, although the expected release of 97.68 GBq y^{-1} of ^{99}Mo would represent only about 3.52 kBq y^{-1} of ^{99}Tc. (Wilding et al., 1979).

Kotegov et al. (1968) estimated that the world inventory of ^{99}Tc by the year 1980 was exceeding 1 x 10^4 kg. It was estimated the US inventory of ^{99}Tc by the year 2000 will be 1.69 x 10^5 kg or 1.06 x 10^5 TBq (Wilding et al., 1979). Luykx (1986) estimated that electricity generated by nuclear power stations at the end of 1983 over the world would be 762 GW(e)y (or 2500 GW(th)y) corresponding to the production of 1.5 x 10^4 TBq (2.4 x 10^4 kg) ^{99}Tc. He also estimated the global release to the environment from the nuclear fuel cycle to be 1 x 10^3 TBq. From the ^{137}Cs fission yield (5.57%) it was estimated that the global activity of ^{99}Tc released into the stratosphere up until 1980 was 140 TBq. Stratospheric fall-out accounted for the dominant world-wide contamination (from nuclear weapons testing, releases from the nuclear fuel cycle and by the use of ^{99m}Tc). If local fall-out is included then a total of 180 TBq of ^{99}Tc was released during 1945 to 1980 (Luykx, 1986 and Rioseco, 1987).

1.5 THE SIGNIFICANCE OF CHEMICAL SPECIATION IN RELATION TO ENVIRONMENTAL BEHAVIOUR.

The behaviour and effects of Tc in the environment are largely controlled by its source, its chemistry in soil, sediment and water, and its biological interactions. The fate of a radionuclide in environmental systems is frequently dependent on a variable combination of factors, such as chemical, physiochemical and biological effects (pH, redox conditions, sediment compositions, complexing agents, microflora etc.). For the present purpose, the definition of chemical speciation is taken to be: the inorganic form of the element; the oxidation state of the element; complexation with both inorganic and organic ligands; and the formation of distinct organometallic moieties where the element is fixed into an organic molecule, primarily by carbon-metal bonding (Wildung et al., 1979 and Sparkes & Long, 1988).

1.5.1 THE ENVIRONMENTAL CHEMISTRY OF TECHNETIUM.

Studies of the chemistry of Tc show that this element can exist in the valency states (0), (II), (III), (IV), (V), (VI) and (VII) in aqueous solutions. Of these only Tc(II) is stable in the form of a complex (Guppy et al., 1989). Under oxidising conditions, Tc(VII) is the dominant oxidation state existing as pertechnetate, TcO^{-}_{4}, in the absence of complexing agents. TcO^{-}_{4} is considered to be the most stable chemical form of Tc in the environment over a wide range of both pH and Eh (Figure 1.1).

As Eh decreases, reduced species can be formed which could include TcO_2. Tc(IV) is not considered to be stable under most of the conditions encountered in the environment, although species such as $TcO(OH)_2$ and $TcCl^{-2}_{6}$ would be present (Anders, 1960). Some of the reducing conditions, e.g. oxygen depleted sediments or waterlogged

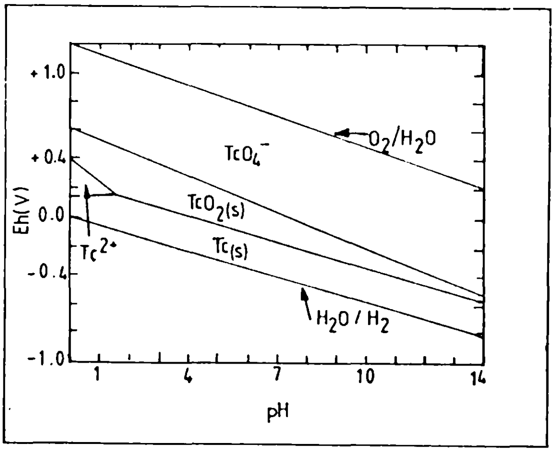


Figure 1.1: Technetium stability diagram under various conditions of Eh and pH (Beasley & Lorz, 1986).

soils may be sufficient to promote the reduction of Tc(VII) to Tc(IV). Tc(IV) can readily complex with amine, carboxyl, hydroxyl and sulphur containing groups found in soil organic matter. This may result in the immobilisation of Tc in such environments because of complexation with substances such as humic acid. As a result, Tc may be less biologically available. However, these environments may represent sinks with the potential for remobilisation of this element should subsequent environmental conditions alter. No evidence is available to indicate the presence of metallic Tc in the environment (Beasley & Lorz, 1986; and Guppy et al., 1989).

Very little is known about the speciation of Tc in freshwater. The oxidation state of Tc in this environment is usually predicted by its chemistry and the redox conditions of the system (Sparkes & Long, 1988). More information is called for by Vandecasteele et al. (1989) to account for the effects of Tc chemical form modifications on the transfer of this nuclide from source to man.

1.5.2 BEHAVIOUR AND PRESENCE OF Tc IN AIR AND RAIN.

At the processing plant, Tc is predominantly converted to volatile pertechnic acid ($HTcO_4$) during the dissolution phase. A portion of the Tc follows uranyl nitrate through the solvent extraction process and is converted to another volatile form, technetium heptaoxide (Tc_2O_7). Releases from reactors, however, are expected to be small with respect to other fuel cycle facilities because essentially all of the ^{99}Tc formed will be contained in the fuel elements. Routine releases are 0.84 kg of ^{99}Tc per metric ton of U fuel. ^{99}Tc is released to the environment by the use of ^{99m}Tc in the nuclear medicine in negligible quantities (Till et al., 1979 and Wildung et al., 1979).

Garcia-Leon et al. (1984) measured ^{99}Tc in atmospheric filters taken during 1965-1967 on a monthly or bimonthly basis, and found a maximum below 3 mBq 1000 m^{-3}. As in the Seville area (place of study) there were no nuclear facilities yielding ^{99}Tc, the presence of ^{99}Tc was assumed to be of fall-out origin. Attrep (1962), Attrep et al. (1971) and Ehrhardt and Attrep (1978) observed ^{99}Tc concentration in rain samples in the range of 66.7 μBq l^{-1}-1.3 mBq l^{-1}. The authors suggested that atmospheric ^{99}Tc had two origins: from the nuclear devices; and influx into the nuclear fuel reprocessing plants.

1.5.3 TECHNETIUM IN FRESHWATER ENVIRONMENTS.

Many facilities which release ^{99}Tc are located on freshwater streams into which effluents are discharged. Of the total amount of ^{99}Tc that is disposed of by these facilities, more than 90% may enter the liquid pathway. Information on the behaviour of Tc in freshwater aquatic ecosystems is however, limited.

Blaylock et al. (1986) have observed that ^{99}Tc added to an experimental pond as TcO^-_4 had a low affinity for particulate matter and sediments with the majority of the activity remaining associated with the water body. Tc was accumulated rapidly from the water by periphyton, zooplankton and algae. In contrast, snails and mosquitofish accumulated Tc slowly but eventually attained some of the highest whole-body concentrations.

1.5.4 TECHNETIUM IN GROUNDWATERS.

Technetium speciation in groundwaters has been studied in investigations into the disposal of radioactive waste. Groundwater samples collected from the Cheshire, Bilby, Nash, Bourbon, Cambric and Faultless event sites showed concentrations of ^{99}Tc below the MPC_w (maximum permissible concentration in water) of 11.5 Bq cm^3. The results indicated that the Tc was present primarily in solution rather than sorbed on colloial material (Silva et al., 1988).

Evidence is available that at least a portion of the Tc released to the environment remains as a soluble species. Tc was detected in ground waters beneath deep sediments underlying the Hanford nuclear waste storage facilities suggesting that Tc is mobile in soil. This may result from the presence of Tc as the soluble pertechnetate ion or as a soluble complexed species. Evidence supporting TcO^-_4 as the soluble species includes Tc solubility in alkaline wastes at Hanford, the stability of the TcO^-_4 ion in solution, and the low organic C content and likely absence of microbial activity in the deep sediments (Wildung et al., 1979).

1.5.5 TECHNETIUM IN THE MARINE ENVIRONMENT.

Mackenzie and Scott (1984) have reviewed the quantities and composition of low level liquid radioactive waste discharged to the marine environment around the UK. ^{99}Tc levels in filtered samples of coastal waters of the Central Irish sea ranged between 0.015 to 0.074 Bq l^{-1} (Riley & Siddiqui, 1982). Matsuoka et al. (1990) found ^{99}Tc at the average of 9.7±3.5 x 10^{-5} Bq l^{-1} in seawater collected at Wakasa Bay and 9.9±2.4 x 10^{-5} Bq l^{-1} in seawater collected at the coast of Kyushu Island. Because of Tc's low specific activity, data for the distribution and dynamics of Tc in aquatic ecosystems are limited.

1.5.6 TECHNETIUM IN THE MARINE ECOSYSTEM.

The biological behaviour of Tc in marine organisms.

Biota play a considerable role in characterizing the distribution and chemical forms of the minor constituents of seawater. The presence of biota affects, directly or indirectly, all oceanographic processes. Organisms remove chemical species from solution, convert them into various compounds, excrete them and after death decompose, thus adding decomposition products and skeletal remains (organic detritus in the case of planktonic seaweeds) to the seawater. There is a close interrelationship between the oceanic organisms. Bacteria and protozoa, for example, carry out the first stage of processing of simple, soluble salts into more complicated compounds available for feeding other organisms.

The capacity of marine organisms to concentrate radioactive substances is characterized by an accumulation coefficient, K_{ac}; (Sometimes called an enrichment or concentration coefficient). This is defined by Gromov (1976) as the ratio of the concentration of the radioisotope in the organism (C_1) to that in solution (C_2):

$$K_{ac} = C_1/C_2$$

Marine plankton and algae.

In an early study on the uptake of ^{99}Tc by plankton, Gromov (1976) indicated that significant uptake occured in these organisms. The accumulation of Tc to a significant extent by certain marine macroalgae is widely recognised, and the largest accumulation of this element is found in the species of brown seaweed (Jeanmaire et al., 1981 and Sparkes & Long 1988). Topcuoglu and Fowler (1984) found that uptake of Tc by brown seaweeds exposed to Tc occured in both the Tc(IV) and Tc(VII) states with the process appearing to be under metabolic control rather than a process of passive absorption of the element. The most rapidly growing parts of the plant appeared to show the greatest affinity for Tc. Uptake and distribution of Tc was studied by Bonotto et al. (1985) in several green and brown marine algae. ^{95m}Tc as TcO^-_4 was supplied to the algae in these experiments. The authors suggested that the element was present both in association with proteins and as ionic technetium, some of which was believed to be complexed with small molecules. It was also suggested that the Tc as TcO^-_4 was present in these plants.

In contrast to phytoplankton, certain marine macroalgae (brown algae) do concentrate Tc (C.F. between 250 and 2500) to a significant degree (Beasley & Lorz, 1986). The brown alga Fucus spiralis (Fucales) grows along the Belgian coast. The algae were collected at four different places from March 1985 to Febeuary 1986. ^{99}Tc was analysed in apical, middle and basal parts and in whole plants (Hurtgen et al. 1988).

Marine organisms.

All crustaceans concentrate Tc in the hepatopancreas and viscereal organs (Swift, 1985 and Beasley & Lorz, 1986). The uptake and retention of Tc from seawater by Juvenile lobsters, and the effects of moulting on these processes, have been studied by Swift (1985) who found that uptake was highest in the digestive glands. The whole body equilibrium concentration factor for the direct accumulation of ^{95m}Tc from seawater by the edible winkle was 45 with a biological half-time of 115 days. Winkle shells accumulate ^{95m}Tc by adsorption only, there being no evidence for metabolic accumulation. About 98% of the ^{95m}Tc in the whole animal was in the flesh. Fowler et al. (1983) found that the uptake of Tc by amphipods was dependent upon the speciation of Tc.

Geochemical behaviour of Tc in marine systems.

Most of the experimental studies have employed the classical approach of determining a distribution coefficient, K_D (K_D = activity g^{-1} solid phase ÷ activity g^{-1} solution). As expected from its behaviour with $Fe(OH)_3$ in alkaline media, TcO^-_4 is not strongly sorbed to the mixed mineral components of marine sediments low in organic matter (Beasley & Lorz, 1986 and Handoll, 1989). Fowler et al. (1983) developed K_D values for TcO^-_4 which rarely exceeded 1-4. In contrast, values of K_D for TcO^-_4 on sediments high in organic matter can be appreciable. Masson et al. (1981) recorded K_D values as high as 1500 in sediments containing 7% organic matter, following 50 days equilibrium in seawater.

1.5.7 TECHNETIUM IN THE TERRESTRIAL ENVIRONMENT.

One of the most important factors used in assessing the impact of Tc releases to the environment is the mobility of the Tc in the soils and waters and availibility for uptake into plants. Technetium is assumed to be present as TcO^-_4 in most of the studies.

The behaviour of Tc in terrestrial and aquatic environs was presented in a symposium held 5-10 May 1986 in Seattle to summarize the latest results in these areas. These results are published in a special issue of Health Physics Vol 57(2), 1989.

Technetium in the soil.

From the studies of a number of workers it is clear that the rate of sorption of Tc is very dependent upon the type of soil/rock examined. The complexation with organic molecules may increase the mobility of Tc within the soil as in the case of low molecular weight ligands, or reduce availability for transfer and root uptake, as in the case regarding complextion with humic acid (Cataldo & Wildung, 1983). Sheppard and Sheppard (1986) have shown that reducing conditions restrict the mobility of Tc in soil, with the soils typical of such conditions (peaty/water logged soils) showing little transfer of Tc away from spiked locations. Balogh and Grigal (1980) commented that when TcO^-_4 entered a reducing environment, the Tc could be readily transformed to a less soluble form.

The uptake of technetium by plants.

The distribution of Tc in plants can be divided into two components. The first is the uptake of the element (primarily from soil) and the second is the transport of Tc within the plant and any biochemical effects such as the toxicity to the plant or the incorporation of the element into chemical forms more available for uptake by animals.

From the observed concentrations of ^{99}Tc in plants and their associated soils, soil to plant concentration factors can be calculated for each data set. The soil-to-plant concentration factor (B_v) is given by:

$$\frac{\text{Concentration of } {}^{99}\text{Tc in plant, wet weight}(\text{Bq.g}^{-1})}{\text{Concentration of } {}^{99}\text{Tc in soil, dry weight}(\text{Bq.g}^{-1})}$$

These notations are used by Clooth and Aumann (1990). TF_{sp}(soil-plant transfer factor) and TF_g(soil-plant surface deposition factor) are applied and discussed in detail by

Mascanzoni (1989).

Technetium present as the TcO^-_4 is rapidly taken up by plants in comparison to other nutrient elements. In soil experiments, up to 70% of the added TcO^-_4 was absorbed by the plant with virtually complete uptake of Tc by plants (Landa et al., 1977). Sheppard et al. (1983) compared the uptake of Tc from soils having high and low organic material and observed that the uptake was high from soils low in organic material.

Cataldo (1979) have shown that 20-30% and 33-41% uptake of ^{99}Tc from surface soil was observed for cheatgrass and tumblewed respectively while in sub-surface soil it was 4-14% and 7-16% for the same plants. Considering the transport of Tc in plants, TcO^-_4 is the species that is present in the plant sap. Investigations of the chemical form of Tc in the plant storage organs show that a large proportion remains in soluble forms with 50-70% associated with molecules of molecular weight between 500 and 50000 Daltons (1 Dalton = 1 a.m.u.) (Cataldo et al., 1986).

The uptake of technetium by animals.

The main route by which Tc is most likely to enter an animal is through the food. Many workers comment that TcO^-_4 is likely to be highly soluble in the gastrointestinal tract, with plant-incorporated Tc appearing to be less available for uptake (Cataldo & Wildung, 1983). Garten et al. (1986), in a study of uptake of Tc by rats, found that Tc incorporated into corn showed a much lower availibility for uptake relative to inorganic TcO^-_4. ^{99}Tc(1 μg labelled with ^{95m}Tc) was injected into sheep as inorganic TcO^-_4 or fed bound to the brown alga Fucus vesiculosus by Van Bruwaene et al. (1986). Faeces and urine were assayed for radioactivity up to 93 days after administration, and animals were sacrificed at different times after application. Absorption of Tc from the intestine was small, and urinary excretion amounted to only about 1% of the dose with the majority of the Tc introduced being excreted in the faeces within four days. The uptake of Tc by quail was studied. In the egg, less than 1% of the Tc was associated with the shell, 8% in the yolk and 20% in the albumin.

The goat milk transfer coefficients of ^{99m}Tc, ^{95m}Tc and ^{99}Tc, administered as TcO^-_4 by Ennis et al. (1989) were 1.5×10^{-4}, 8.5×10^{-4} and 1.1×10^{-2} d l^{-1}, respectively. The rapid appearance of Tc in blood and milk of goats after oral doses of TcO^-_4 suggests that Tc might be absorbed directly from the rumen. Gut absorption of ^{99m}Tc administered in reduced form is only about one-tenth that of ^{99m}Tc administered as TcO^-_4 (Ennis et al., 1989). Gerber et al. (1989) note that the absorption, metabolism and retention of Tc in animals are modified during passage through the gastrointestinal tract.

The uptake of technetium by microorganisms.

The role of microorganisms in the reduction and fixation of Tc in soils and sediments has been extensively studied and several experiments have shown that microbial flora are capable of accumulating Tc. Mania et al. (1986) found that TcO^-_4 was readily absorbed by a range of microorganisms with the subsequent binding of the Tc to organic molecules in the cells. This accumulation and organic speciation may critically determine the availability of the element for uptake by higher organisms.

The uptake of technetium by man.

Kirchmann et al. (1985) carried out experimental studies on Tc transfer to man, via the animal food chain , following contamination of the soil surface. About 1.7% of the ^{99}Tc investigated was transferred to the body of the sheep and progressively eliminated afterwards.

Of the terrestrial pathways, Hoffman et al. (1984) suggested ingestion of vegetables to be dominant one, with the possible addition of eggs. The effective dose equivalent (resulting from a ^{99}Tc concentration of 37 mBq m^{-1} in surface ground) for all pathways was 0.34 μSv y^{-1}, of which 0.21 μSv y^{-1} was contributed by vegetables. For aquatic pathways the effective dose equivalent (resulting from a ^{99}Tc concentration of 37 mBq l^{-1} in fresh water) from all pathways was 220 μSv y^{-1}, of which 120 μBq y^{-1} arose from drinking water and 52 μSv y^{-1} was contributed by aquatic organisms. However, Hoffman et al. emphasised great uncertainty about the water aquatic organism-human pathway.

Biological retention in all tissues is described by the multicompartment exponential model of Beasley et al. (1966). A fractional uptake of 95% from the small intestine to blood is assumed with only 5% of the initial GI tract contents of Tc reaching the critical lower large intestine. Kazem et al. (1967) have indicated a rapid initial pertechnetate uptake of approximately 2% to the thyroid from blood, with some estimates as high as 8-10% in euthyroid while Harper et al. (1964) noted 6-30% in hyperthyroid individuals. A fractional uptake of 80% is assumed from the small intestine to blood (Hays and Wesselossky (1973).

All investigators agree that thyroid accumulation and retention (biological half-life) are much less than that of iodine (Palms et al. 1977). Tc competes with iodine in thyroid uptake and is therefore dependent on the level of dietary iodine (Coughtrey & Thorne, 1983). Since Tc can not be utilised in the production of thyroid hormones, it will be lost rapidly from the thyroid.

1.6 THE LONG TERM RADIATION DOSE IMPLICATIONS OF ^{99}Tc.

Technetium is thought to be a significant long-term risk resulting from the use of nuclear energy due to its high fission yield, its long half-life and its ability to spread more readily in the environment than many other radionuclides with long half-lives (Till, 1986 and Gerber et al., 1989).

1.6.1 THE BASIC UNITS.

It is now well established that the biological effects produced by the action of ionizing radiation on living cells depend both on the type and quantity of the radiation. Also it has been established that equal energy absorption of different radiation may not produce equal biological effects. To account for these concepts the following terms and units are used:

Absorbed dose.

The absorbed dose is defined as the amount of energy imparted to matter by ionizing particles per unit mass of irradiated material at the place of interest. The unit of absorbed dose is the Gray denoted by Gy (1 Gy = 1 J kg^{-1}).

Dose equivalent.

To measure the biological damage, a further unit of "dose" is used called the dose equivalent. It is defined as the absorbed dose multiplied by a quality factor (Q) which is determined by experiment for various types of radiation (Q for α and $n_f = 20$ and for X, γ and $\beta = 1$). If the absorbed dose is measured in Gy, the dose equivalent is expressed in Sievert (Sv).

Dose equivalent = Absorbed dose x Quality factor

To account for non-uniform distribution in the case of internally deposited radionuclides, a distribution factor

(N) can also be used. Thus the dose equivalent (H) in Sv is given as:

$$H = DQN$$

1.6.2 OCCUPATIONAL WORKERS AND THE GENERAL PUBLIC.

For purposes of radiation safety, the International Commission on Radiological Protection (ICRP) recognizes two categories:

1. Occupational exposure: Persons, who are exposed to ionizing radiation in the course of their work, in this context called radiation workers.
2. Exposure of the general public: ICRP (International Commission on Radiological Units and Measurements) limits (levels) for individual members of public are given in Table 1.3.

Source of exposure	**Dose limit or level**
1. Routine exposure excluding medical and natural sources	1 mSv y^{-1} for lifetime exposures and 5 mSv y^{-1} for short periods
2. Natural radiation	No numerical recommendation
3. Accidents-control of foodstuffs	Range 5-50 mSv in the first year

TABLE 1.3: ICRP limits and referenc levels for individual members of the public (Camplin & Aakrog, 1989).

1.6.3 THE INTERNAL RADIATION HAZARD.

Radioisotopes within the body are exceptionally dangerous since, i) they are present 24 hours per day and not just during working hours, ii) their radiations are in intimate contact with the living cells in the body and there is no "distance protection" compared with sources outside the body and iii) there is a tendency in most isotopes to concentrate in certain organs, or structures in the body. Technetium is assumed to be uniformly distributed throughout all organs and tissues of the body other than the thyroid, stomach wall and liver. ^{99}Tc is classified into toxicity group III by the IAEA (International Atomic Energy Agency).

Annual limit of intake (ALI).

The ALI of a radioisotpoe is that activity which taken alone would irradiate a person (represented by Reference Man) to the limit set by ICRP for each year of occupational exposure. ALI for a given radioisotope depends on the physical and chemical properties, half-life, the metabolism and excretion rate and the route of entry of radionuclide.

The derived air concentration (DAC) is analogous to the old concept of MPC_{air} and is obtained by dividing ALI by the air breathed (Faires & Boswell, 1981):

$$DAC = ALI/2.4 \times 10^3 \text{ Bq m}^{-3}$$

The ICRP Task Group on Lung Dynamics assigned oxides, hydroxides, halides and nitrates of Tc to inhalation class W and all other compounds of the element to inhalation class D. The ALI (Bq) and the DAC (Bq m^{-3}) for ^{99}Tc are given as follows:

	Inhalation	
	Class D	Class W
ALI	2×10^8	2×10^7
DAC	8×10^4	1×10^4

1.6.4 PATHWAYS OF ^{99}Tc TO MAN.

The major pathways by which Tc can be taken in by man are via drinking water, fish, food crops, egg, milk and meat and air (inhalation). For ^{99}Tc, the external irradiation mechanisms are not generally considered significant since they lead to a negligible dose because of the low energy β emission.

1.6.5 LONG TERM WASTE DISPOSAL OF ^{99}Tc FROM THE NUCLEAR FUEL CYCLE.

Kirchner (1990) has recently developed a new hazard index, on the basis of a discussion of the advantages and limitations of hazard calculations of nuclear waste. It is clear that ^{99}Tc will be a most significant component of high-level radioactive waste at the 10^5 year post-disposal time point (Figure 1.2).

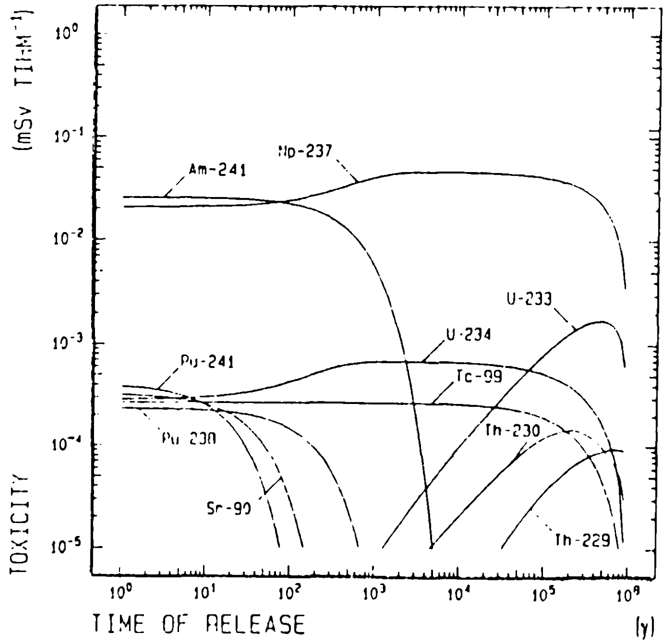


Figure 1.2: Nuclide toxicities as a function of release time (Kirchner, 1990).

1.6.6 RADIATION DOSES DUE TO ^{99}Tc.

Holm and Rioseco (1987), studied ^{99}Tc in the sub-arctic food chain lichen-reindeer-man and found the average dose rate from ^{99}Tc for reindeer (1966-1981) to be about 0.02 μGy y^{-1} in liver, 0.06 μGy y^{-1} in bone and 0.006 μGy y^{-1} in flesh. This was insignificant when compared to the dose rate from ^{210}Po (0.7 mGy y^{-1} for reindeer liver and 5 mGy y^{-1} for bone). According to the authors the dose rate in tissues with a concentration of 1 Bq kg^{-1} of ^{99}Tc was 0.5 μGy y^{-1}. The annual dietary intake of ^{99}Tc in reindeer meat by Lapps was estimated to be 1.4 Bq. This produced ^{99}Tc activity concentrations of 0.65 mBq kg^{-1} in liver, 0.19 mBq kg^{-1} in flesh and 3.5 mBq kg^{-1} in bone. The highest committed dose equivalent is delivered to the thyroid and stomach walls (1.6×10^{-9} and 3.4×10^{-9} Sv Bq^{-1}) from oral intake, but however Holme and Rioseco found these figures to be insignificant.

For GI-LLI (gastrointestine-lower large intestine) as critical organ, a 50 y accummulated individual dose of 2.6 mSv was calculated from a ^{99}Tc release rate of 3.33 TBq y^{-1} over a period of 2.5×10^{2} year (Koplik et al., 1979). The committed effective dose equivalent rate was 6.6×10^{2} Sv y^{-1} (from 1983 to 1986) as a result of ^{99}Tc discharge of 1.2×10^{13} Bq y^{-1} to a local critical group near Cap de La Hague. A routine liquid discharge of 4.54×10^{10} Bq y^{-1} ^{99}Tc will lead to 5 μSv y^{-1} to individuals (Camplin & Aakrog, 1989).

1.7 REVIEW OF THE ANALITICAL TECHNIQUES FOR THE DETERMINITION OF TECHNITIUM.

Various physical and chemical properties of technetium such as its β-radioactitivity; complex formation; absorption bands of X-rays and UV and IR light; mass to charge ratio etc, can be used for its qualitative, as well as its quantitative analysis. In the literature, classical and chemical methods are described in early work on Tc for its determination while more recently physical and instrumental techniques have become available and have proved suitable for the analysis of Tc. Clearly the selection of a method for the determination of Tc is mainly dependent on the concentration in the samples, the type and number of samples, the location of the samples, the availability and cost of facilities and the type of information required.

In general, the different techniques can be arranged in the following order of sensitivity:

Method	**Mass of Tc measurable(g)**
1. X-rays fluorescence	10^{-5}
2. Gravimetry/classical	10^{-6}
3. Infra-red spectrometry	10^{-6}
4. Spectrophotometry	10^{-6}-10^{-7}
5. Emmission spectrometry	10^{-8}
6. Polarography	10^{-8}-10^{-9}
7. Atomic absorption	10^{-8}-10^{-9}
8. Radiometry (β-counting)	10^{-9}
9. Mass spectrometry	10^{-10}-10^{-11}
10. Response multiphoton ionisation MS	10^{-11}-10^{-12}
11. Neutron activation	$10^{-11}10^{-12}$
12. ICP-MS	10^{-12}

1.7.1 CLASSICAL TECHNIQUES

The classical method mainly involves the precipitation (gravimetric) of a stable, insoluble or very slightly soluble form of the element under study. The gravimetric methods available involve the formation of insoluble Tc compounds such as Tc_2S_7 and TcO_2 or the formation of an insoluble compound from the reaction between TcO^-_4 and a large organic molecule, for example, formation of tetraphenylarsonium pertechnetate $(C_6H_5)_4AsTcO_4$, and formation of nitron(4,5 dihydro-1, 4-diphenyl-3, 5-phenylamino-1,2,4, triazole) pertechnetate.

1.7.2 RADIOMETRIC ANALYSIS

Technetium has no stable isotopes and therefore most methods for the determination of ^{95m}Tc, ^{97}Tc, ^{99m}Tc and ^{99}Tc have been based on radiometric measurements. The analysis of the last two is most commonly encountered. The various methods used for ^{99}Tc are liquid scintillation counting, G.M. counters, proportional counters and others all based on β-counting. Detection limits for radiometric analyses are of the order 10^{-9} to 10^{-10}g of ^{99}Tc.

Beta counting of ^{99}Tc is difficult due to the low energy of the emitted β-particles (E_{max} = 0.29 Mev), and also a relatively low specific activity of 629 MBq g^{-1}. As in all β-counting, rigorous sample preparation procedures must be followed due to significant self absorption, back scattering and geometric effects. When Tc is determined by radiometry, radioactive impurities must first be removed from the sample.

Muenze and Grossmann (1984) used Bremmstrahlung measurements for the determination of ^{99}Tc for routine sample analysis by placing the sample in a well-type γ-ray [NaI(Tl)] scintillation detector. The counting efficiency was very low compared with liquid scintillation counting, but the method was very fast, did not require sophisticated instrumentation and avoided problems of incorporation of the sample into liquid scintillation mixtures etc. The methodology has been applied to a wide range of sample types a knowledge of which is useful in the selection of particular methods for ^{99}Tc environmental analysis.

Holm et al (1981) used surface barrier detectors for the determination of ^{99}Tc by β-spectrometry. Dutton and Ibbett (1973), Riley and Siddique (1982) and Patti et al (1981) have determined Tc in seawater and marine biological samples using β-counting. Golchert and Sedlet (1969), Malcolme-Laws et al. (1982) and Robb et al. (1985) used GM counters for environmental waters while Holm and Rioseco (1987) and Kaye et al (1982) used GM β-counting for water, vegetation and soil samples. The GM gas flow counter has been used by many workers for environmental samples (Holm et al., 1984; Rioseco, 1987 and Chen et al., 1990). Garcia-Leon et al. (1984) and Martinez-Lobo et al. (1986) used proportional counters for environmental samples. A limitation of β-spectrometry for ^{99}Tc has been the lack of a stable isotope tracer for determination of chemical yield. The short-lived γ-emitting isotopes e.g. ^{95m}Tc, ^{97m}Tc and ^{99m}Tc can be used as internal tracers and can be measured using NaI(Tl) detectors.

Liquid scintillation counting (LSC) has been applied to the determination of ^{99}Tc by many workers (Walker et al., 1980; Luxenberger & Schuttlekopf, 1984; Koide & Goldberg 1985 and Cattarin et al. 1985).

1.7.3 NEUTRON ACTIVATION ANALYSIS

Neutron activation is a very sensitive technique for the determination of ^{99}Tc. Irradiation of ^{99}Tc with slow neutron produces ^{100}Tc by the (n,γ) reaction which has the relatively high neutron capture cross section (20 barns), for thermal neutrons. ^{100}Tc decays (with a half-life of 15.8 seconds) by two gamma ray emissions i.e 539.6 keV (6.95 %) and 590.8 (5.70 %). The limit of detection for neutron activation is 10^{-11} to $^{-12}10$ g. According to Foti et al. (1972), it should be possible to determine ^{99}Tc up to 4 x 10^{-12} with a neutron flux of 5 x 10^{13} n cm^{-2} sec^{-1}. The (n,γ) method was used by Foti et al. (1972) for environmental samples.

The main disadvantage of the (n,γ) method is the very short half-life of ^{100}Tc, requiring accurate timing of irradiation within the neutron source and accurate counting. A rapid sample transportation and measurement system is needed, as well as access to a suitable neutron source.

Another possible reaction is ^{99}Tc (n,p) ^{99}Mo $\xrightarrow{\beta}$ ^{99m}Tc. Ikeda et al. (1988) tried fast neutron activation of ^{99}Tc, and found that appreciable activity of ^{99m}Tc was formed by the ^{99}Tc(n,n$'$)^{99m}Tc reaction, while only negligible ^{99}Mo activity resulted. The possibility of determining ^{99}Tc by the ^{99}Tc (γ,γ') ^{99m}Tc reaction using bremsstrahlung irradiation has been studied and shown to have a detection limit of 10^{-9} g under optimum irradiation conditions (Sekine et al., 1989).

1.7.4 X-RAY FLUORESCENCE ANALYSIS.

Characteristic X-ray fluorescence (XRF) processes are induced when a specimen is irradiated with a beam of sufficiently short wavelength X-radiation. The emitted radiation can be determined in an XRF spectrometer. The detection limit for this method has been shown to be 32 μg for ^{99}Tc in nuclear fuel reprocessing waste (Willard et al., 1981; and Robb 1983).

1.7.5 SPECTROPHOTOMETRIC METHODS

Several spectrophometric methods have been used, based on the absorption of pertechnetate ion or complexes formed with various colorimetric reagents i.e, thiocyanate, potassium ferrocyanide, rubeanic acid and hydrocloric acid.

UV/Visible Spectra.

The pertechnetate ion has been measured in the UV range at 287 nm. Tc(VII) can be reduced to Tc(IV) by heating in concentrated hydrochloric acid to form the $TcCl_6^{2-}$complex ion, which exhibits absorption maxima at 240 nm and 338 nm in the presence of rhenium and molybdenum. Tc can be identified by spectrofluorimetry at 411nm (Kenna, 1961, and Long & Sparkes, 1988).

IR Spectroscopy.

Infra-red (IR) spectroscopy, with a sensitivity of 5 mg, is used for the determination of Tc. Tetraphenylarsonium pertechnetate has an intense IR absorption band at 11.1 μm (Tc-ostretch). The interfering species especially are perrhenate and permanganate ions. (Lavrukhina & Pozdnyakov, 1970 and Handoll, 1989).

Spot Tests.

Technetium in aqueous solution lends itself to a number of spot tests. These tests have been primarily developed for qualitative analysis but at higher concentrations of Tc some tests have been used for quantitative analysis e.g. thiocynate complexes (Robb, 1983).

1.7.6 ELETROCHEMICAL TECHNIQUES.

Several electrochemical methods have been developed for the determination of Tc. Since Tc exists in a number of oxidation states, its electrochemical behaviour is dependent on oxidation state and this has been used for the study of oxidation state equilibria.

Polarography.

The polarography method of analysis is based on the current voltage relationships arising at a microelectrodes when diffusion is the rate determining step in the electrochemical reaction. Polarography is described in many papers but the method may be best suited for on-stream monitoring in purge gaseous diffusion plants. The sensitivity of the method is 10^{-7}M Tc in the absence of significance interferences. Differential pulse polarography is used for the simultaneous determination of U and Tc (Lavrukhina & Pozdnyakov, 1970; and Handoll, 1989).

Coulometry.

The coulometry method measures the quantity of electricity, that is, the number of coloumbs, required to carry out a chemical reaction. In a controlled potential coulometry, Tc(VII) in a solution of sodium tripolyphosphate buffered to pH 4.7 with acetate, is titrated at a potential of -0.70 V vs. SCE (Saturated calomel electrode) to produce Tc(III). Mazzocchin et al. (1974) used different types of electrochemical detection for the volumetric titration of Tc(IV) solution with Ce(IV) (Willard et al., 1981; and Long & Sparkes, 1988).

Adsorption Stripping Voltammetry.

Friedrich and Ruf (1986) used adsorption stripping Voltametry at the HMDE (Hanging mercury drop electrode) electrode operated in the differential pulse height mode for low concentrations in acidic media in the presence of thiocyanate.

1.7.7 MASS SPECTROMETRY

In mass spectrometry (MS) charged particles consisting of the parent ion and ionic fragments of the original molecule are produced and passed through magnetic and electric fields, where they are separated according to their mass/charge ratio. A mass spectrum can be detected after separation and provides a record of the number of different ions characteristic of individual elements or compounds. Examples of the application of MS to the determination of Tc are given by many workers (Lavrukhina & Pozdnyakov, 1970; Willard et al., 1981; and Long & Sparkes 1988).

1.7.8 ATOMIC SPECTROSCOPY

Astrophysicists have long used atomic emission spectroscopy (AES) in the search for Tc in stars (Moore, 1951 and Merrill, 1952). A detection limit of 6 x 10^{-11} g is quoted for the analysis of Tc using graphite furnace atomic absorption spectrometry by Kaye and Ballou (1978). Meggers, 1951, presented tables of wavelengths and relative intensities for Tc.

Brown and Pickford (1984) found that inductively coupled plasma optical emmission spectrometry (ICP-OES) could be applied to the determination of Tc in aqueous solution down to 4 ppb (4 ng ml^{-1}). The determination of Tc was investigated by Karnowski (1981) in an assessment of the ICP for nuclear fuel analysis and a detection limit of 20 ppb was achieved (Long & Sparkes, 1988). Long et al. (1987) used the relatively new technique of ICP-MS for the determination of Tc in environmental samples. A detection limit of 10-20 ppt (10-20pg ml^{-1}) was quoted (Long & Sparkes 1988). ICP-MS was used along with ICP-OES, ion exchange/liquid scintillation counting (IEX/LSC) and graphite furnace atomic absorption spectrometry (GFAAS) for direct measurement of ^{99}Tc in aqueous samples. ICP-MS is considered the most sensitive of these four techniques, having the potential to detect Tc below 0.1 ppb (Brown et al., 1985). Kim et al. (1989) applied ICP-MS to the determination of ^{99}Tc in soil samples, without using decontamination steps to remove the interference (^{99}Ru). A detection limit of 3.2 ppt (3.2 pg ml^{-1}) was reported.

Nicholson et al. (1990) used ICP-MS for soil samples with a detection limit of 0.01 ppb, while Bullivant et al. (1990) used ICP-MS for the determination of ^{99}Tc in Springfields effluent. The authors also found slight traces of Ru (< 1 ng ml^{-1}). To remove ^{99}Ru interference, a simple correction was applied by monitoring the ^{102}Ru. A detection limit of 0.006 ppb was obtained. The Springfields effluent arose from two sources. Firstly, the disposal of washings from the decommissioning of the gaseous diffusion plant at Capenhurst and secondly, the handling of reprocessed uranium from the Sellafield plant.

In the present research work based on many aspects reported in the literature, a comprehensive radiochemical method has been developed for ^{99}Tc which can be applied to all types of samples as a preparation for ICP-MS analysis.

1.8 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY(ICP-MS).

1.8.1 INTRODUCTION

The original concept of inductively coupled plasma-mass spectrometry (ICP-MS) developed from a requirement, expressed in 1970, for the next generation of multielement instrument systems to follow the rapidly developing technique of inductively coupled plasma-atomic emission spectrometry (ICP-AES). After a survey of available and emerging techniques (section 1.7), the conclusion made by Date and Gray (1989) was that atomic mass spectrometry was the only basic spectrometric technique that had the potential for the wide element coverage, element specificity and relatively uniform sensitivity for almost all the elements of the periodic table to provide a good successor to the powerful tool that ICP-AES was promising to become. Gray and Date (1983) compared ICP-MS, ICP-AES and FAAS (flame atomic-absorption spectrometry) for detection limits and concluded that ICP-MS has very low detection limits for most of the elements.

1.8.2 ORIGINS AND PRINCIPLES OF ICP-MS.

Inorganic samples, in the form of simple molecules, require complete vaporization and dissociation before their constituent atoms can be ionized for mass analysis. Relatively large amounts of energy are thus required to bring inorganic samples into a suitable state of ionization. The most difficult part of the process is the initial volatilization and dissociation of the sample, after which ionization is easy. A clue to the solution to this problem was presented during a seminar in Manchester at which ion extraction from flames and plasmas, at gas pressures up to atmospheric, was described. "It was realized that although a chemical flame, at a gas temperature of up to 3000°K, was probably not hot enough for most material, and constituted an undesirably reactive environment, the atmospheric pressure arcs and plasmas then being explored as atomic emission sources were almost certainly much more suitable" (Date & Gray, 1989). In plasmas operating at atmospheric pressure, gas temperatures of 5000°K or more were achieved and, because of the relatively long dwell time of a few milliseconds, energy transfer to the sample was very efficient as it attained equilibrium with the plasma gas (Alkemade, 1973).

The use of an atmospheric pressure plasma as an ion source for atomic mass spectrometry is an attractive concept, not least because of the ease and rapidity of sample introduction and exchange, normally a difficult and restricting aspect of inorganic mass analysis. When an ICP is used as the plasma it offers the additional possibility of high sensitivity and freedom from matrix and inter-elemental effects, making the ICP a useful source for AES.

ICP-MS consists of two techniques, an ICP for ion generation and a quadrupole mass analyser for the separation and detection of these ions. "Samples are introduced into the central channel of the plasma as a finely dispersed mist, which is rapidly desolvated and vaporised. Dissociation is virtually complete during transit through the plasma core and elements with a first ionisation energy of less than 10 eV, are fully ionised. Ions are extracted from the central channel of the plasma through a sampling aperture into the quadrupole mass analyser, where they are separated on the basis of their mass-to-charge ratio prior to detection by an electron multiplier. These pulses are amplified, accumulated in a high capacity multi-channel analyser and then subsequently processed by a powerful microcomputer" (VG Isotopes, 1987).

1.8.3 DESCRIPTION OF THE ICP-MS INSTALLED AT SURRC.

The measurements of long-lived ^{99}Tc were carried out on a VG Element ICP-Mass Spectrometer (PlasmaQuad PQ1) installed at Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow in 1988. Figure 1.3 shows the schematic diagram of the VG PlasmaQuad used for the determination of ^{99}Tc. It can be divided into the following four sections:

(i) Sample introduction.
(ii) The inductively coupled plasma (ICP).
(iii) Plasma sampling interface.
(iv) Ion focussing, mass analysis and detection

1.8.4 OPERATING CHARACTERISTICS OF THE ICP-MS.

Considerable improvements in the ^{99}Tc detection limits, removal of interferences and instrument stability have been made during present studies.

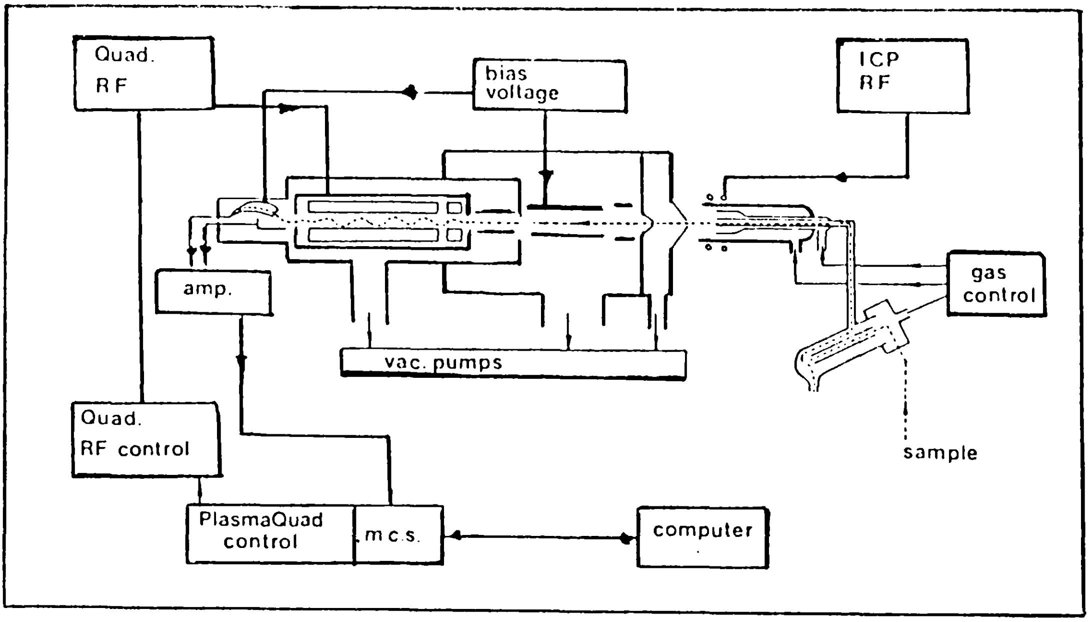


Figure 1.3: Schematic diagram of the ICP-MS system at SURRC.

Plasma ion populations and system response.

The properties of Ar, H and O will clearly control the plasma equilibria. However, the dominance of the plasma by Ar, H and O ions means that the ionization conditions for the analyte elements are disturbed very little by matrix concentrations up to 1%. The count rate (cps) obtained at the detector after mass analysis for a monoisotopic, fully ionized element of mass about 100 m/z, from the plasma population of 10^{10} ions per cm^3 is between 10^5 and 10^7(0.1-10 MHz), depending on system parameters and setting up.

Spectra.

The most dominant feature of ICP-MS, especially for an analyte, is the extreme simplicity of the spectra obtained, even for complex matrices. The background peaks may usually be subtracted using the data handling system, leaving a simpler spectrum from which unknown elements may be identified.

Detection limits.

Detection limits are the most useful figures of merit for the selection of a method. Detection limits can be calculated from the sample counts. For each isotope (in the element menu) the counts displayed are obtained from the integrated raw counts for that isotope and are corrected for Area Counts Per Second (ACP's) and for any internal standards used.

$$\text{Sample Counts}=\text{Counts} * \text{ACPS Factor} * \frac{\text{(Original Int Std Counts)}}{\text{(Sample Int Std Counts)}}$$

To correct for sample blanks:

Corrected Sample Counts = Sample Counts - Blank Counts

For multiple runs (commonly, Runs = 3) on a sample the mean and standard deviation are calculated as:

$$\text{Mean Counts} = \Sigma\text{(Sample Counts)/Runs,}$$

$$\text{Std Dev} = \sqrt{\Sigma\text{(Sample Counts - Mean Counts)}^2\text{/(Runs - 1)}}$$

Error for a given standard is noted as: $\text{Std Dev}/\sqrt{\text{Runs}}$

For a blank subtracted standard:

$$^{\text{Er}}\text{Error} = \sqrt{\text{(Blank Error)}^2 + \text{(Sample Error)}^2}$$

Now Limit Of Detection (L.O.D.) = $3 * \sqrt{\text{Error}}$

Interferences-oxides and doubly charged ions.

Oxide response is expressed as a ratio of the oxide to metal peak size MO^+/M^+, taken as a percentage. The correct ratio is $MO^+/(MO^+ + M^+)$, and values normally rarely exceed 5%. Doubly charged ions are produced for those elements whose second ionization energy lies below the first ionization energy of Ar (15.76 eV) which dominates the equilibrium. The formation of these species may cause isobaric interferences if they are formed from the analyte. The density of the monocharged analyte ions is reduced and hence the counts are suppressed (Houk et al., 1980)

The response of doubly charged and hydroxide species is similar to but lower than that of oxides, and instrument settings are slightly different. In any case, the setting of the instrumental parameters to give a maximum response for singly charged ions and minimum response for the interferences is complex and usually results in a compromise (Hursthouse, 1990).

Interferences-polyatomic ions.

The plasma consists of matrix species which are as much as 10^8 those of a trace analyte present in the sample solution at a level of 1 $\mu g\ cm^{-3}$. Analyte and matrix ions can undergo reactions with the plasma ions and form relatively complex polyatomic species. Of the polyatomic ions resulting from matrix elements, the most serious are MO^+ from elements that form refractory oxides, particularly the light rare earths, W, Mo etc. Operating conditions can be found that minimize these interferences. Another polyatomic ion of concern is ArM^+, which should ideally be $<10^{-5}$ of M^+, but sometimes is still large enough to cause problems (Houk & Thompson, 1988 and Date & Gray, 1989).

Interferences-isobaric overlap.

Coincident isobaric interferences between neighbouring elements may cause serious interferences even in the absence of oxide, doubly charged ion and polyatomic interferences and common spectral interferences. Commercial instruments include isotopic abundance tables in their computer programmes to correct any potential interferences.

Interferences- matrix suppression (non-spectroscopic).

Matrix interferences are observed from a shift in the plasma equilibria caused by the addition of easily ionizable elements such as Na, K, Cs, Ca etc., in concentrations which are large enough to produce a significant increase in the electron population from their ionization. These easily ionizable elements contribute most to matrix suppression and in extreme cases, even the ionization of Ar can be suppressed (Olivares & Houk, 1986; and Houk & Thompson, 1988). Most ratios at 1% will cause substantial signal suppression; 0.1% is safer for most of the elements; heavy elements that are easily ionized can produce suppression even at 0.1% or less. Although the phenomenon is not clear, it may be due to blockage of the apertures in the skimmer and cones. To decrease the effect of the matrix, the samples may be diluted to reduce salt loading of the plasma or the technique of isotope dilution can be used. Other non-spectroscopic interferences may result from memory effects due to traces of solution remaining trapped in part of the system or as oxides deposited on sample and skimmer cones (Hursthouse, 1990).

Interferences-physical effects.

Two types of physical effects are observed. One is the memory effect. This can often be observed when the sample solution is replaced by a blank in the normal sequence of sample throughput. Care is required in the run sequence to ensure that the concentrations of the standards introduced before the samples, are not high. Also it is advisable to use clean glassware for samples.

The interference unique to ICP-MS arises from the flow of the extracted plasma gas into the extraction aperture of the cooled cone. The cooled area forms a site for the condensation of vaporized analyte in the plasma, which forms a coating of fine powder around the lip of the aperture. The growth rate of this deposit depends on the total dissolved solids content of the sample solution and on the nature and volatility of the analyte matrix. With any matrix, if apertures of 1 mm diameter or more are used, little trouble is experienced at solids contents of 0.1% and less (Date & Gray, 1989).

1.8.5 VG PLASMAQUAD-ELECTROTHERMAL VOLATILIZATION (ETV).

The most exciting feature of the ETV-ICP-MS combination is that multielement analysis can be carried out. ETV is a very convenient alternative method of introducing small samples to the plasma. The principle of operation is that 10-100 μl sample solutions are injected into the graphite furnace. The furnace is then sealed with a carbon rod and is resistively heated in three steps as follows:

a) 75°C for 2 min to evaporate water from the sample
b) 350°C for 1 min to ash organics in the sample
c) and then to 2850°C in 5 seconds to vaporize the residual trace elements.

The vaporized trace elements are rapidly transported from the furnace to the plasma where they are atomised, ionized and detected by the mass spectrometer. Because the furnace allows volatile matrices to be evaporated and ashed from the sample, this can help to overcome isobaric molecular interferences and improve limits of detection. In general a 100 times improvement in L.O.D is achieved by ETV over nebulization (VG Isotope, 1990).

1.9 OBJECTIVES AND SELECTION OF SAMPLES SITES.

Monitoring radioactivity for safe operation of nuclear facilities involves measurement of many radionuclides especially those which are long-lived. The fate of long-lived radionuclides released from nuclear installations is of radiological interest because of the possibility of eventual intake by man long after discharges may have ceased. The measurement of environmental samples provides essential information for radiological assessments as to quantity and the behaviour of the radionuclide in question.

In general, very sensitive analytical techniques are required for comprehensive investigations because of low environmental concentrations. The analytical procedures should ideally have features such as; the ability to utilise available apparatus; require only straight-forward manipulations; have adequately low limits of detection for environmental samples; have adequate chemical recovery; include the analysis of a variety of samples; and have high decontamination factors for interferences.

Once the procedure is optimised, the second requirement is the selection of suitable sites to give the requisite information about the concentration of ^{99}Tc near the source and to see dilution at distant locations. The levels of ^{99}Tc in many materials in the natural environment around the Sellafield nuclear fuel reprocessing plant are sufficient for analysis. The authorised discharged to the Irish sea of artificial radionuclides including ^{99}Tc, in low level wastes from the BNFL Sellafield site provides a unique opportunity to study the behaviour of ^{99}Tc in the marine environment. Because of the significance of the Chernobyl accident as a source of environmental radioactive pollution, and the opportunity of obtaining samples, material from the

Chernobyl area was also selected for sampling.

CHAPTER 2

DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF ^{99}Tc.

In this chapter, the details of each experiment performed are described, followed by the results and a discussion of achievements. Where possible and relevant a review of the literature section is given at the beginning of each section.

In relation to all practical work the following criteria were applied throughout:

1. All the reagents used were at least of Analar Grade or better.
2. All the glassware used was routinely washed with 5% Decon 90 (Decon Laboratories Limited, England) followed by dilute 2% HNO_3 and rinsed with deionized/distilled water in order to maintain a high standard of cleanliness and minimise cross contamination.
3. All work involving leaching/ashing, solvent extraction, evaporation and elution was performed in the fume-hood according to Laboratory Rules and COSHH (UK) regulations.
4. As a general rule, after each sample run, a blank sample was measured to check the background. Although there was automatic washing of the system after each sample, this principle was adopted to monitor possible memory effects, especially when samples of high Tc concentration were run.
5. In order to obtain the desired sensitivity for ^{99}Tc, the analyses were carried out in a clean (low level) laboratory.

2.1 DEVELOPMENT OF A RADIOCHEMICAL METHOD FOR THE DETERMINATION OF ^{99}Tc IN ENVIRONMENTAL SAMPLES.

When using ICP-MS, a key problem is the elimination of ^{99}Ru. Adequate decontamination of the Ru interference can be achieved by a combination of simultaneous procedures. Two methods have been developed and either of them can be used to remove Ru. This work is described in detail in this chapter but to begin with methods of treatment of various types of environmental sample are outlined.

2.1.1 SAMPLE TREATMENT.

Due to low specific radioactivity, the Tc from environmental water samples was concentrated on anion exchange resin from bulk water samples. In order to obtain Tc in solution, biota samples and soil samples were subjected to leaching and ashing respectively.

Biota samples

Between 1-30 g of oven dried material was weighed into a conical flask and approximately 20 Bq of ^{95m}Tc added as radiochemical yield tracer. For 1-6 g of dried algae, 200 cm^3 of 9M HNO_3 was added and for each further 6 grammes, a further 200 cm^3. After fitting a reflux condenser, the mixture was warmed on a hot plate with magnetic stirring. Refluxing was continued until brown fumes ceased to be evolved and all the organic tissues had dissolved. The solution was cooled and filtered. The filtrate, containing the technetium, was evaporated to dryness on a hot plate and the residue redissolved in 50-100 cm^3 2M H_2SO_4 and 2 cm^3 of H_2O_2 added. The mixture was heated for 10 min to ensure solution and cooled prior to processing for Tc separation.

Soils and sediments

About 20 Bq of ^{95m}Tc was added to 10-20 g of weighed sample in a nickel crucible. The sample was ashed at 600°C in a furnace overnight (about 24 hrs). The ash was transferred to a 250 cm^3 beaker and 50-100 cm^3 2M H_2SO_4 containing 2 cm^3 of H_2O_2 added and the mixture set aside for approximately 20 hours before filtering through Whatman filter paper no. 1 to remove any residue, which was discarded. The filtered solution was then treated for Tc separation.

Water samples

Approximately 20 Bq of ^{95m}Tc was added to 5-30 dm^3 of filtered (0.2 μm filter paper) sea water or filtered rain water. The solution was concentrated by anion exchange onto 5 cm^3 of resin (Dowex 1-X8,50-100 mesh). The anion exchange column is shown in Figure 2.2. The resin was eluted with 40-50 cm^3 12M HNO_3 with a flow rate of 0.2-0.3 cm^3min^{-1}. The eluate was evaporated to dryness on a hot plate and 50-100 cm^3 2M H_2SO_4 containing 2cm^3 of H_2O_2 added. The mixture was heated for 10 min, cooled and taken for processing for the removal of interfering substances.

2.1.2 TECHNETIUM SEPARATION FROM INTERFERING REAGENTS

Two methods to separate Tc from other elements and in particular from the Ru were developed as follows:

METHOD I

Solutions obtained as described in section 2.1.1 are taken and the following steps applied to separate Tc from other elements, especially Ru:

STEP 1. Add 2M NaOH until pH=12 to precipitate $Fe(OH)_3$. Heat the solution for 10 min, cool and filter. Then make 2M H_2SO_4 with 6M H_2SO_4, add 1-2 cm^3 sodium hypochlorite (NaOCl) and boil for 30 min.

STEP 2. Add 1-2 cm^3 5% NaOCl and acidify to pH=4 with 10M H_2SO_4. Extract with 50 cm^3 CCl_4 (twice). Discard the organic layer.

STEP 3. Make the aqueous phase 1M in HCl and 2M in H_2SO_4 and add 1-2 cm^3 30% H_2O_2. Add 50 cm^3 cyclohexanone and stir for 10 min using a magnetic stirring bar. Separate the phases in a separating funnel. Wash the organic layer with 50 cm^3 4M H_2SO_4 (containing 0.1 cm^3 30% H_2O_2). Add 50 cm^3 cyclohexanone and back extract twice with 40 cm^3 0.5M NaOH.

STEP 4. Add 1 cm^3 $AgNO_3$ (10 mg cm^{-3}) and 2 cm^3 5% NaOCl to the aqueous phase and heat the precipitate for 15 min, cool and filter through Whatman No 1.

STEP 5. Acidify the filtrate until 2M in H_2SO_4 and evaporate to approximately 40 cm^3. Add 2 cm^3 30% H_2O_2 and heat for 10 min. Shake the cooled solution in a beaker with 40 cm^3 5% tri-iso-octylamine (TIOA) in xylene for 10 min. Wash the organic portion with 40 cm^3 2M H_2SO_4 containing a few drops of 30% H_2O_2 by shaking for 5 min. Back-extract the organic phase twice with 20 cm^3 of 2M NaOH.

METHOD II

The method consists of the following steps:

STEP 1. Heat the solution from section 2.1.1 for 15 min after the addition of 1-2 cm^3 5% NaOCl.

STEP 2. Stir the cooled solution with 40 and 35 cm^3 5% TIOA in xylene in a 250 cm^3 beaker for 10 min using a magnetic stirring bar. Transfer to a separating funnel and drain off the aqueous phase. Wash the organic portion with 40 cm^3 2M H_2SO_4 containing few drops 30% H_2O_2 by shaking for 5 min. Back-extract the organic phase twice with 20 cm^3 1M NaOH.

STEP 3. Neutralize the above aqueous solution and then pass through a column of 5 cm^3 Dowex 1-X8 anion exchange resin. Wash the column with cold and hot deionized water.

STEP 4. Pass 100 cm^3 1M NaOH through the column to remove retained elements from the anion exchange resin. Wash the column with hot and cold water.

The necessity and function of steps used in method I and II are given below:

1. NaOCl was added to obtain TcO^-_4 and RuO^-_4. The RuO^-_4 is volatilized from 2M H_2SO_4-NaOCl solution by heating to 100°C while the TcO^-_4 is left in the solution. Heating was carried in most steps to ensure the mixing of various reagents and to obtained the desired oxidized/reduced states.
2. At pH 4, the RuO^-_4 was extracted twice with 50 cm^3 CCl_4. The TcO^-_4 was left in the solution.
3. Another step for decontaminating Ru and other nuclides was reduction of the Ru to a low valence state and maintenance of Tc at the TcO^-_4 with 1-2 cm^3 30% H_2O_2. The TcO^-_4 was extracted with cyclohexanone, and Ru in low valence state was left in 2M H_2SO_4-1M HCl-H_2O_2 solution.
4. A further step for Ru removal was the extraction of the TcO^-_4 leaving Ru in 2M H_2SO_4-H_2O_2 by 5% TIOA-xylene extraction.
5. AgCl precipitation was used for general decontamination.
6. Fe (if present in samples) was precipitated with NaOH.
7. NaOH washing step was used to get rid of Ru prior to Tc elution.
8. The eluent of the anion exchange column was evaporated to decrease HNO_3 strength. Ruthenium was also evaporated during this step.

For complete elimination of Ru, a series of different steps are required e.g method I & II. Further sets can be obtained by the combination of different steps of the two methods or of other methods (given in detailed in section 2.3.3) for complete decontamination from Ru.

2.1.3 ELUTION OF Tc AND SAMPLE PREPARATION FOR ICP-MS/ETV.

Method

Adjust the pH of the aqueous phase to 7 and pass through a

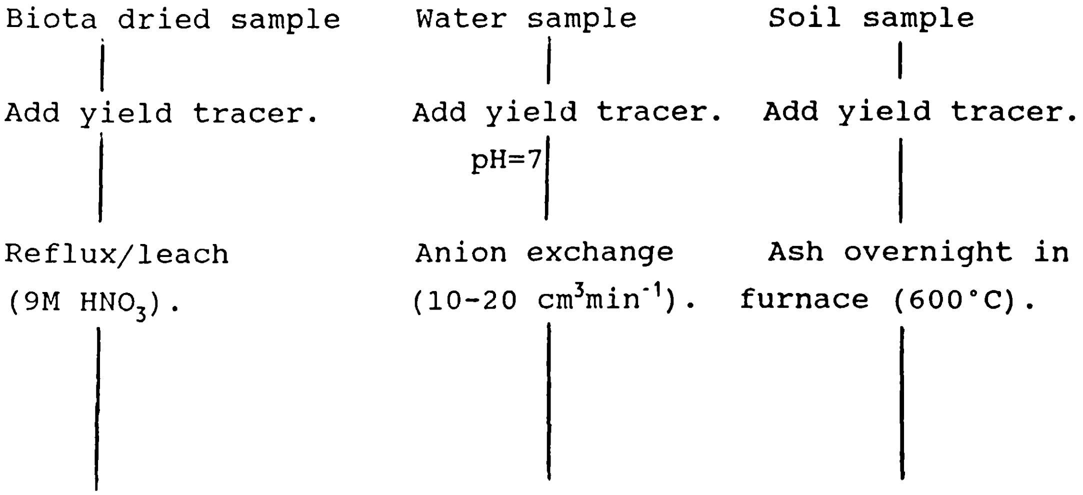
Dowex 1-X8 anion exchange resin column (5 cm^3 of preconditioned NO^-_3 form). Wash the column with 100 cm^3 hot and 100 cm^3 cold deionzed water. The technetium is eluted with 40-50 cm^3 12M HNO_3 with a flow rate of 0.2-0.3 cm^3 min^{-1} into a selected container and counted in reproducible geometry with a 4cm x 4cm NaI detector. After counting, the eluate is evaporated to dryness and dissolved in 10 cm^3 2% HNO_3 (filter if necessary) for ICP-MS analysis. When measuring by the ETV method, the residue is dissolved in the minimum quantity (<0.5 cm^3) of 2% HNO_3.

Discussion

A suitable form of solution is required for ICP-MS analysis. A final solution, which should be less than 2% in HNO_3 , should have a salt concentration of less than 0.1% and be clear, can be prepared by passing the sample extract, after elimination of interferences, through an ion exchange column. The column is washed thoroughly with cold and then hot distilled water to remove salts and Tc is stripped with 12M HNO_3. The eluate is evaporated, the residue redissolved in 2% HNO_3 and filtered if necessary.

FLOW SHEET OF THE PROCEDURE.

A. Initial sample treatment to isolate technetium.



Filtrate

Evaporate to dryness at <100°C.

Analysis by ICP-MS Determine ^{99}Tc by elimination of ^{99}Ru on the basis of $^{99}Ru/^{101}Ru$ ratio (May not be feasible for biota samples due to salt concentration)

Elute Tc with 12M HNO_3 (0.2-0.3 $cm^3 min^{-1}$).

Add 2M H_2SO_4 (50-100cm^3) +2 cm^3 (30% H_2O_2), heat for 10 min and cool.

Continue with decontamination steps to remove Ru.

B. Ruthenium decontamination steps.

METHOD I

Add 2M NaOH solution to ppt. $Fe(OH)_3$ at pH=12.Heat for 10 min, cool and filter Make 2M H_2SO_4-NaOCl, boil for 30 min and cool.

Add 1-2 cm^3 5% NaOCl, ext. with 2 x 50 cm^3 CCl_4.

Discard CCl_4 phases

Acidify to 2M H_2SO_4-1M HCl (1-2 cm^3 30% H_2O_2). Extract with 50 cm^3 cyclohexanone. Wash organic layer with 50 cm^3 4M H_2SO_4 (0.1 cm^3 H_2O_2).

METHOD II

Heat solution from A for 15 min after the addition 5% NaOCl.

Extract with 40 & 35 cm^3 of 5% TIOA-xylene. Then wash organic layer with 40 cm^3 2M H_2SO_4+few drops of H_2O_2.

Discard aqueous and wash phase

Discard aqueous
and wash phases

Add 50 cm^3 cyclohexane and back extract twice with 40 cm^3 0.5M NaOH.

Discard the
organic layer

Mix with 1 cm^3 $AgNO_3$ (10 mg cm^{-3}) and 2 cm^3 NaOCl. Heat for 15 min and cool. Filter.

Discard
the solid
residue

Make 2M w.r.t. H_2SO_4 and add 1 cm^3 30% H_2O_2. Extract with 40 cm^3 5% TIOA-xylene and wash the organic phase with 40 cm^3 2M H_2SO_4 in the presence of few drops of H_2O_2.

Discard the aqueous
and wash phases

Back extract the organic phase with 2 x 20 cm^3 1M NaOH.

Discard the
organic phase
continue to C.

Back extract the organic phase with 20 cm^3 1M NaOH. Repeat with a further 20 cm^3 1M NaOH.

Discard
organic layer

Adjust the pH to 7 with 8M HNO_3 and pass through a 5 cm^3 anion exch. column.

Discard the filtrate

After passing 100 cm^3 1M NaOH.Continue to the washing column step in C.

C. Final preparation of technetium.

Adjust pH (of solution from B) to 7

then pass through 5 cm^3 slurry of Dowex 1-X8 (50-100 mesh) with a flow rate of 10-20 cm^3 min^{-1}.

Discard filtrate

Wash the column with 100 cm^3 cold and 100 cm^3 hot distilled/deionized water.

Elute Tc with 40-45 cm^3 12M HNO_3 at a flow rate of 0.2-0.3 cm^3 min^{-1}.

Determine tracer yield by γ-counting.

Evaporate the eluate to dryness.

Add 5 or 10 cm^3 of 2% HNO_3 and analyse ^{99}Tc by ICP-MS.

2.1.4 DISCUSSION OF THE TECHNETIUM METHODOLOGY DEVELOPED.

The new technique of ICP-MS offers significant advances and advantages over previous methods for the measurement of this radionuclide. The long radioactive half-life of ^{99}Tc means that its direct measurement is possible by ICP-MS because of the very high sensitivity of the technique. Thus ICP-MS measurements of ^{99}Tc are based on the direct detection of its atoms rather than the measurements of its radioactivity. As well as superior sensitivity, ICP-MS takes less time for analysis and offers potentially very low limits of detection compared with other techniques. The application of ICP-MS to ^{99}Tc determination in environmental samples, on the basis of a shorter analysis time (8 minutes for 3 complete runs including washings) and lower detection limits, appeared very advantageous for ^{99}Tc.

The overall analytical problem compromises up to five steps: (1) the definition of the problem, (2) the sampling and preliminary treatment (concentration), (3) the separation from interfering substances, (4) the measurement using efficient and available technique, and (5) analysis of the results.

The optimised procedure consists of three principal parts as follows:

1. Sample treatment

Due to the low specific activity of ^{99}Tc in the environment, large samples have to be considered for analysis. Keeping in view the need for precise and high chemical yields reflux/leaching (biota samples), ashing (soils and sediments) and anion exchange (water samples) were the methods selected.

2. Separation of Tc

Many methods are available for the decontamination from interfering elements, in partular Ru. A series of steps were chosen for complete removal of interfering substances. Two methods have been optimised for the separation of Tc. The main steps include solvent extraction, boiling and NaOH elution.

3. Final solution

In order to meet the requirements of the ICP-MS instrument, the final solution was obtained by using an anion exchange column.

In the present work, a common reagent i.e. nitric acid was used for wet oxidation for biota samples. To minimize the hazards, 9M HNO_3 is used with a corresponding increase in the time for the leaching of biota samples. Leaching of biota samples gave high % chemical yield compared to ashing because if carbon remained in samples, the radiochemical yield was lowered considerably. The disadvantage of leaching is that the conditions are less severe than in some other procedures, with the result that some types of organic material, notably those containing heterocyclic nitrogen, escape complete destruction. Hence, it is not suitable for soil samples. In the present study, it gave high chemical recovery; ashing was preferred for silt (soil) samples.

The very low level of ^{99}Tc expected to be found in water samples necessitated the use of large sample volumes. Keeping in view, the low concentration of the radionuclide and the high chemical recovery required, the anion exchange resin method was found much more feasible than other methods i.e. evaporation, direct extraction and coprecipitation. Therefore, during the development of the method in the present work, very large sample volumes could be analysed. Concentration of Tc into a volume of less than 50 cm^3 could be achieved by extracting the technetium onto an anion exchange resin and then eluting the Tc from the resin in as small a volume of eluant as possible.

Since the ICP-MS technique is based on the measurement of the mass of an element, any interferences must be eliminated as far as possible. For ^{99}Tc, two isobaric nuclides are important. ^{99}Mo is a radioactive nuclide which decays with a half-life of 67 hours and which after few days will have gone. The other isobaric nuclide is ^{99}Ru. ^{99}Ru is stable and 12.7% abundant in natural ruthenium and so will interfere. A high Ru decontamination was possible by controlling the different valence states of Tc and Ru with H_2O_2 and NaOCl in different steps in the procedure. In method II, the decontamination of interfering reagents was obtained by a series of steps e.g boiling of NaOCl-H_2SO_4, TIOA-xylene extraction and washing of the column with 1M NaOH solution.

It was found that when the same organic solvent extraction was repeated, a certain limit came when no further separation was possible. Hence, more than one organic solvent was selected for use when developing the separation schemes which enabled extraction efficiencies to be maintained (especially in method I). It was not clear why this phenomenon occured and reasons can not be given. Possible explanations may include (i) the extraction is influenced by the concentration of other ions, (ii) the concentration of Tc may influence its extraction, (iii) Tc is extracted as ion associate but if present as a complex it may not be extracted by some solvents, and (iv) Mn, Mo and Fe may interfere if present. In a similar way, the use of repetitive evaporation step was not adopted for complete removal of Ru.

In the present work, precipitation was not feasible for the following reasons:-

1. The optimized procedure had to be applicable to all types of sample and not just water samples.
2. Due to the low specific activity of ^{99}Tc, the volume of water samples was large and so it was not easy to precipitate Ru from such large volumes.
3. The use of methanol to induce precipitation tends to produce severe bumping in the boiling sample which can lead to losses by spillage.

An efficient decontamination of Ru was obtained by boiling Tc and Ru from NaOCl-H_2SO_4 solution. And also washing the column with NaOH prior to the elution of Tc with HNO_3.

Liquid-liquid extraction has long been used for the isolation of Tc from interfering elements. Solvent extraction of Tc can be performed with a wide range of organic reagents by mixing with the aqueous phase. The objective of the solvent extraction experiments was to assess the decontamination factor of Ru from Tc solutions by this method. Each experiment was repeated with and without ^{99}Tc in order to obtain Ru results.

Following the back extraction of TIOA-xylene with 1M NaOH solution, an anion exchange column was used. Thorough washing of the column with cold and hot water was used in order to get rid of salts. Then the eluate was evaporated to dryness to reduce the HNO_3 strength. The residue was redissolved in 2% HNO_3 solution and filtered if the solution was not clear.

For the purpose of optimising a method for the determination of ^{99}Tc in environmental samples, ICP-MS was applied. Radiometric (γ-spectrometry of ^{99m}Tc and ^{95m}Tc) analyses were carried out throughout the development of the method and for the radiochemical yield determination in the environmental samples. For the measurement of ^{99}Tc and ^{95m}Tc (^{99m}Tc), ICP-MS and γ-spectrometry were applied respectively.

By using the tracers i.e. ^{99}Tc and ^{95m}Tc, the chemical yields for different types of samples were measured and found to be as follows:-

1. Biota samples (alga) → Reflux/leach → removal of Ru → anion exchange column → ICP-MS

   70 ± 11 %
2. Soils and sediments → Ashing → Ru elimination → anion exchange → ICP-MS

   65 ± 15 %
3. Water samples → anion exch. → Ru elimination → anion exchange → ICP-MS

   65 ± 15 %

The yields during different steps were (see section 2.5) in good agreement with other techniques described in the literature. The values for ^{99}Tc obtained from IAEA and BNFL reference materials (seaweeds) were in good agreement with the average values. Due to the non-availability of a soil intercomparison sample, reliance had to be placed on the ^{99}Tc and ^{95m}Tc tracers used. The recovery of Tc from the Ravenglass silt sample as measured by ^{95m}Tc tracer appeared satisfactory when compared with the biota samples.

Although in the normal ICP-MS analysis Mo isotopes (having natural abundances) are not important, a consideration was that when using ETV (in future) overlapping of peaks might become significant, especially ^{98}Mo and ^{100}Mo. An ETV unit has recently been installed at SURRC and is under preliminary examination. It was not however used for the present sudy.

2.2 STANDARDS AND TRACERS

In order to standardise the analytical method and to determine the chemical yield of the radiochemical procedures the following standards and tracer were used in the determination of technetium.

2.2.1 Technetium-99

^{99}Tc was used (in blank procedures) to determine radiochmical yield. ^{99}Tc with an activity of 21.4 MBq cm^{-3} (3.4 x 10^{9} ng) as ammonium pertechnetate in aqueous solution of 0.1 M NH_4OH was obtained from Amersham International plc.

2.2.2 Ruthenium standard solution

Atomic absorption grade standard ruthenium solution of 1000 ppm as $RuCl_3$ in 20% HCl was supplied by Johnson Matthey. A

10 ppm stock solution was prepared by dilution, and 50-100 ppb solutions of Ru were used as required to determine Ru decontamination. As there is no interfering peak at mass 101, ^{101}Ru peak was chosen for calculating Ru decontamination factor. The count rates of all the Ru isotopes are proportional to their % natural abundance. Calibration curve for ^{101}Ru (at concentrations of 1, 10 and 100 ppb) is shown in Figure 2.1.

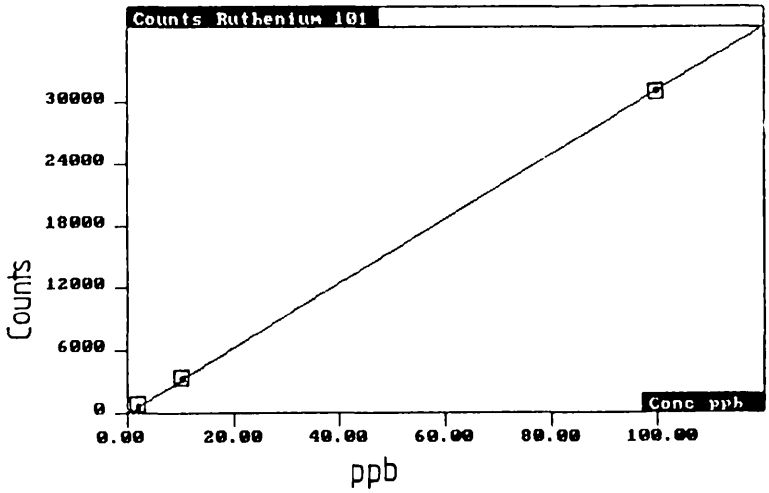


Figure 2.1: Calibration curve of ^{101}Ru using ICP-MS.

2.2.3 Rhodium-103 standard solution

Atomic absorption grade 1000 ppm rhodium solution was obtained from Johnson Matthey and a 10 ppm stock solution was prepared in a similar way to ruthenium. 50 ppb and 5 ppb solutions were taken for each ICP-MS and ETV (preliminary experiments) analysis respectively. ^{103}Rh was added in the final solution before the analysis by ICP-MS. ^{103}Rh was used as an internal standard to check any drift in the response of instrument. ^{99}Tc observations could be corrected with ^{103}Rh since at mass 103, there were no other interferring isobars.

2.2.4 Technetium-99m

The short-half-life (6hrs) γ-emitting isotope 1MBq ^{99m}Tc (as $NaTcO_4$ solution) was obtained from the Radionuclide Dispensary at the Western Infirmary, Glasgow and was used in appropriate quantities by dilution.

2.2.5 Technetium-95m

The 60 days half-life γ-emitting isotope ^{95m}Tc was preferred as internal tracer. ^{95m}Tc (6MBq) as NH_4TcO_4 in aqueous solution was supplied by the Isotope Division, Harwell, UK.

2.3 OPTIMISATION OF VARIOUS STAGES OF THE RADIOCHEMICAL PROCEDURES.

A key aspect of the development of radiochemical separation procedures for technetium was that they should be optimised to achieve maximum decontamination factors for the interfering ruthenium. Because of the strict demands of the ICP-MS method for high decontamination to remove ^{99}Ru, considerable effort had to be put into this aspect. Adjustments were made individully to each stage of the procedures and these are described in detail along with the results cited and discussed in this section.

In general, high quality glassware and teflon beakers were used. Adjustable pipettes (i.e. 0.04-.20 cm^3 and up to 1 & 5 cm^3) and volumetric flasks were used for the preparation of solutions. For vigorous shaking of aqueous and organic layers teflon-coated magnetic stirrers were used. In optimising procedures the first stage was to quantify the quantity and quality of ion exchange resin.

2.3.1 ION EXCHANGE AND THE NECESSITY FOR IT.

Ion exchange is a very efficient technique widely used for the separation and concentration of radionuclides. It is an exchange process of ions of like sign between a mobile phase and a stationary phase. Usually the mobile phase is an aqueous solution of electrolyte while the stationary phase is a highly insoluble solid body with sites capable of exchanging ions. The methods available using anion exchange for the separation of Tc are tabulated in Table 2.1.

Use of anion exchange in present work.

One of the limitations of ICP-MS is that the solution for analysis should preferably have a salt concentration of less than 0.1% in order to minimise corrosion and deposition in the spectrometer. To reduce the salt concentration and thereby minimise a large "background" of electrolyte, ion exchange can be used.

In procedures involving high temperatures Tc losses can occur due to volatilization. During precipitation technetium because of its tracer concentration, tends to be coprecipitated resulting in losses. When handling large volume samples, solvent extraction is often a difficult technique. Technetium losses and the problems of handling large volumes can be avoided by the use of anion exchange methods and procedures can be made selective and efficient for the separation of Tc.

The column dimensions adapted were 20 cm length and 12 mm diameter and the support was a sintered glass plug instead of glass wool. A diagram of the ion exchange resin support is shown in Figure 2.2. The flow rate was controlled by a Teflon tap. The column head was closed with a glass woolplug and was loaded with a glass rod.

A number of experiments were carried out to select the type and the quantity of the resin, the flow rate, the various appropriate volumes and concentration of the eluant and the sample media prior to to anion exchange step.

Reference	Anion exchange resin	Eluant
Anders (1960)	Dowex 1-X8	3M NaOH/1M $HClO_4$
Anderson & Walker (1980)	AG 1-4X	4M HNO_3
Atteberry and Boyd(1950)	Dowex-2	NH_4sulphate thiocyanate
Attrep (1962) and Attrep et al. (1971)	Dowex 1-X8	0.25M $NaClO_4$
Ballestra et al. (1987)	ion ex. column	NaCl
Chen et al. (1990)	AG 1-X4	10M HNO_3
Hall & Johns (1953)	AmberliteIRA400	0.5M NH_4SCN
Hamaguchi et al. (1964)	Dowex 1-X8	0.5M HCl+0.5M NH_4SCN
Huffman et al. (1956)	Dowex-1	4M HNO_3
Hurtgen et al. (1988)	BioRad AG 1X8	7.5M HNO_3
Ikeda et al. (1988)	MCl GEL CA 08P	HNO_3/resin bed
Kaye et al. (1982)	BioRad AG 1-X8	6M HNO_3
Kenna and Kuroda (1964)	Dowex 1	0.25M ClO^-_4
Koide and Goldberg(1985)	BioRad AG 1-X8,	12M HNO_3
Lavrukhina and Pozdnyako 1970)	AV-17	3-4M HNO_3
Luxenburger & Schuttelkopf (1984)	Dowex 1-X8	NH_4SCN,HNO_3/ $HClO_4$
Malcolm-Lawes et al.(1982)	AmberliteIRA93	1M KSCN
Matsuoka et al. (1990)	Dowex 1X8	con. HNO_3
Mincher & Baker (1990)	BioRad AG 1X8	NH_4OH/column
Muddukrishna et al.(1990)	Alumina	MEK
Niktin (1963)	AB-17	20M HF
Pirs & Magee (1961)	AmberliteIRA400	4MHNO_3
Riley and Siddiqui(1982)	Duolite A101D	4M HNO_3
Robb et al. (1985)	AmberliteIRA93	4M NaSCN
Ryabchikov & Borisova(1958)	EDE-10	2M H_3PO_4
Schulz (1980)	Amberlyst A-26	For con. waste

TABLE 2.1: Various anion exchange resin used for the separation and purification of technetium.

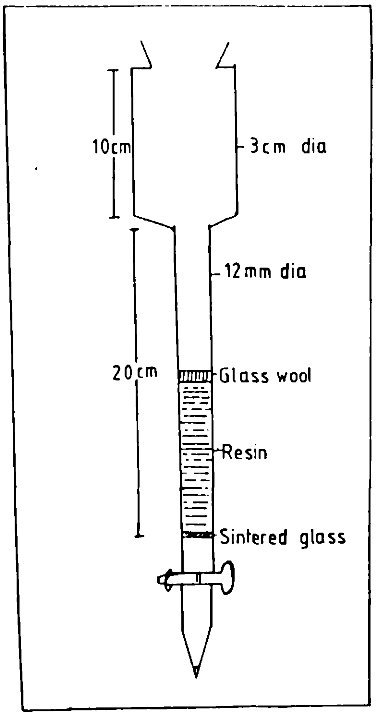


Figure 2.2: Diagram of resin column.

Ion exchange selection.

Review

The sorption of Tc carried out for anion exchangers from $NaNO_3$ solutions. The highest adsorption was observed on AV-17 with strongly alkaline quaternary ammonium groups $N^+(CH_3)_4$, a similar adsorption is characteristic of Dowex 1-X8, which contains the same active groups (Lavrukhina & Pozdnyakov, 1970). Malcolme-Laws et al. (1982) and Robb (1983) also compared different resins.

Method

Three available resins were, Dowex 1-X8(50-100 mesh); Dowex 1-X4(50-100 mesh) and Duolite 113(52-100). Before use, they were soaked in deionised water for few hours and a $5cm^3$ slurry of each of resin was placed in a column. The form, of the three resins, was converted from chloride to nitrate by washing the resin with 50 cm^3 of 8M HNO_3, followed by a rinse of distilled water to a near neutral pH. 50 cm^3 water samples which had been spiked with ^{99}Tc and made slightly acidic with HNO_3 were passed through the three resins. Finally Tc was eluted by 12M HNO_3.

Results and discussion of present work.

The anion exchange resins (Dowex 1-X8, Duolite 113 and Dowex 1-X4) in Cl^- forms, available in the laboratory were used in order to check their efficiencies for Tc recoveries. 'Dowex' is a the Registered Trade Mark of the Dow Chemical Company, Michigan, USA and 'Duolite' is the registered trade name of Diamond Shamrock (Polymers) Limited (BDH, 1981). The % ^{99}Tc recovery for the three resins using ICP-MS was calculated by the following equation:

$$\% \ ^{99}Tc \text{ recovery} = \frac{\text{eluted activity}}{\text{added activity}} \times 100$$

The % recoveries for the radionuclide are given in Table 2.2.

Resin	% Ch. recovery
Dowex 1-X8 (50-100 mesh)	98 ± 2
Dowex 1-X4 (50-100 mesh)	96 ± 2
Duolite 113 (52-100 mesh)	93 ± 3

Table 2.2: Percent chemical recoveries of ^{99}Tc for different anion exchange resins.

From the results it is clear that sorption and elution of Tc was in each instance > 90 % but the maximum recovery was obtained for Dowex 1-X8 resin and this resin was therefore adopted for further work.

Once the resin was chosen, a series of experiments were carried to find the minimum quantity of the resin and the eluant which could be used.

Choice of the quantity of resin.

Method

a) Five columns were prepared with different amounts of resin. The resins taken were slurries of 2, 4, 6, 8 and 10 cm^3 respectively. The Cl^- form was converted to NO_3^- by passing 50 cm^3 of 8M HNO_3 through the resin. Five samples each of 50 cm^3 water, spiked with ^{99}Tc and ^{99m}Tc were loaded at a flow rate of 10-20 cm^3 min^{-1} onto the anion exchange columns (Dowex 1-X8, 50-100 mesh) preconditioned by 8M HNO_3. The columns were washed with distilled water to remove thoroughly any salt remaining in the column. Technetium was eluted with five fractions of 12M HNO_3 at a flow rate of 0.2-0.3 cm^3 min^{-1}. Each fraction was of 20 cm^3. The eluates were counted by γ-spectrometry for ^{99m}Tc to determine the chemical yield. Then the eluates were evaporated on a hot plate at temperature of <100°C and redissolved in 10 cm^3 2% HNO_3 for the analysis of ^{99}Tc by ICP-MS.

b) The above experiment was repeated with ^{99}Tc and ^{95m}Tc in order to compare the recoveries of both tracers by using ICP-MS and γ-spectrometry.

Results and discussion

a) The results of the analysis of filtrate, passed through the different quantities (slurries) of the resin, are given in Table 2.3 and are plotted in Figure 2.3. The results of ^{99}Tc using ICP-MS, showed that % loss was almost acceptably low beyond 5 cm^3 of resin.

Resin (cm^3)	**2**	**4**	**5**	**6**	**8**	**10**
% ^{99}Tc rec.	1.31	0.37	0.28	0.22	0.07	0.06

TABLE 2.3: % Tc in filtrate.

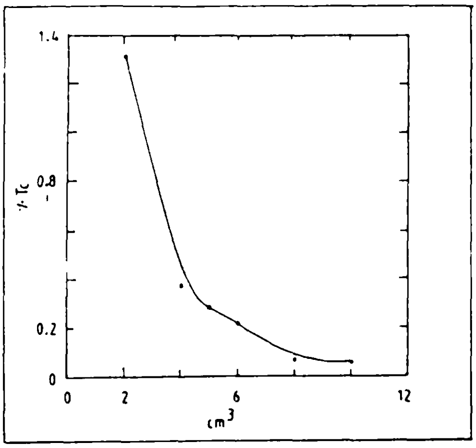


Figure 2.3: Percent Tc lost in the filtrate.

The % Tc elution recovery for different quantities of resin using ICP-MS are given in Table 2.4. Analysing the results, >90 % recovery was obtained but only after a second elution and also with low quantities of resin, loss in the filtrate was unacceptably large. Low quantities may not be feasible for large volumes/quantities of real samples. On the other hand, for resins of > 5 cm^3 , the elution becomes difficult. On the basis of these results, it was concluded that 5 cm^3 resin volume was the best to use and hence 5 cm^3 slurries of the resin were used for further work.

12M HNO$_3$ (eluate)	quantities of Dowex 1-X8 slurries					
	2 cm^3	4 cm^3	5 cm^3	6 cm^3	8 cm^3	10 cm^3
1st 20 cm^3	92.4	94.4	89.0	83.6	55.3	38.2
2nd 20 cm^3	2.4	3.0	9.6	13.8	42.1	57.7
3rd 20 cm^3	0.2	0.0	0.12	0.1	0.3	0.9
4th 20 cm^3	0.0	0.1	0.09	0.05	0.0	0.2
5th 20 cm^3	0.0	0.0	0.02	0.05	0.0	0.0

TABLE 2.4: Percent recoveries of ^{99}Tc by ICP-MS in the eluates using different quantities of Dowex 1-X8 slurries.

Resin (cm^3)	12M HNO$_3$ (eluate)	% ^{99}Tc rec. (ICP-MS)	% ^{95m}Tc rec. (γ - Spectrometry)
2	1st 20 cm^3	91.9	86.5
	2nd 20 cm^3	3.6	6.4
	3rd 20 cm^3	0.4	0.1
4	1st 20 cm^3	84.6	83.0
	2nd 20 cm^3	13.6	16.3
	3rd 20 cm^3	0.4	0.0
6	1st 20 cm^3	81.0	85.4
	2nd 20 cm^3	13.5	12.7
	3rd 20 cm^3	0.1	0.0
8	1st 20 cm^3	38.1	37.1
	2nd 20 cm^3	53.6	51.6
	3rd 20 cm^3	6.6	6.3
10	1st 20 cm^3	21.3	21.4
	2nd 20 cm^3	20.9	19.2
	3rd 20 cm^3	14.1	17.6

TABLE 2.5: Comparison of % ^{99}Tc and ^{95m}Tc recoveries.

b) The results of another experiment, in which both ^{99}Tc and ^{95m}Tc were used are given in Table 2.5 in order to compare the yields of both the tracers using different quantities of resin.

Effect of molarity of eluant on recovery.

Method

In order to determine the most favourable concentration of HNO_3 to strip the Tc from the anion exchange resin and the required volume, a series of experiments were carried out. Columns, each consisting of 5 cm^3 of resin slurry were prepared as described above using four concentrations of HNO_3. 50 cm^3 water samples, containing ^{99}Tc or ^{99m}Tc as chemical yield tracer, were allowed to flow through the resins. The columns were washed with 50 cm^3 of deionised water and the washings discarded. The technetium was eluted with various dilutions of HNO_3 i.e. 4M, 8M, 12M and 16M in 20 cm^3 fractions. Each column was eluted with 5 fractions. The flow rate for the sample and the eluant was the same as in 2.3.1(choice of the quantity of resin). Each fraction was analysed for Tc tracer. As well as the selection of quantity of the resin and the concentration of the eluant, another important factor was to check for any possible losses of Tc in the column eluate so that the quantity of resin required could be minimised. This was done by monitoring the column filtrate.

Results and discussion

Various concentrations of HNO_3 were used for elution of ^{99}Tc. The fractions of eluate were analysed by ICP-MS. The results are given in Table 2.6 and plotted in Figure 2.4. It can be seen that for the 4M acid the elution was incomplete even after 100 cm^3 had been used. Much better elution was obtained for the remaining acid concentrations above 8M. Both 12M and 16M HNO_3 gave nearly 100% yields in the first two fractions (40 cm^3) but to minimise acid concentration, 12M HNO_3 was selected for future use.

Volume of eluate (HNO_3)	**4M**	**8M**	**12M**	**16M**
1st 20 cm^3	0.3	37.0	92.0	96.0
2nd "	5.9	52.7	8.2	3.4
3rd "	21.5	8.8	0.1	0.2
4th "	32.2	0.4	0.02	0.04
5th "	25.8	0.03	0.02	0.05

TABLE 2.6: Effect of different molarities (M) of HNO_3 on %^{99}Tc recoveries using 5 cm^3 slurries of Dowex 1-X8 resin.

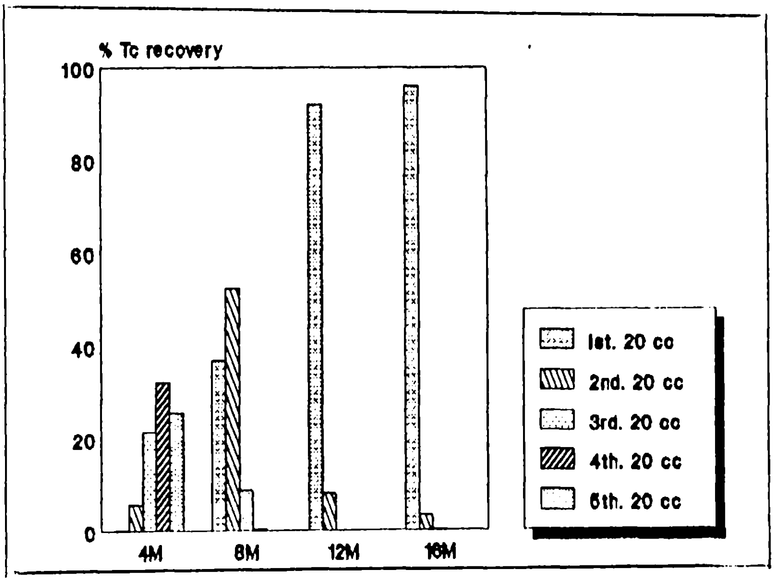


Figure 2.4: Elution of ^{99}Tc from Dowex 1-X8 at various HNO_3 concentrations.

<u>The effect of various reagents on Tc retention.</u>

The pertechnetate ion was shown (in literature) to be absorbed from slightly acid, neutral, or basic solutions at concentrations as high as 7.5M in nitrate by a variety of strong-base anion exchange resins. The purpose of this experimet was to select a feasible medium to retain maximum Tc on the resin when passed through the column.

Method

After the addition of radio-tracers aqueous solutions in three different media (i.e H_2O, 2M NaOH and HNO_3) were passed through 5 cm^3 resin(Dowex 1-X8).

Results and discussion

The results of experiments in which ^{99}Tc in different media were passed through Dowex 1-X8 resin are shown in Table 2.7. It is clear from the results that neutral solutions can give high chemical yields (≈ 100 %) while solution in acidic media show poor yield. The filtrate of the basic media could not be analysed by ICP-MS due to its large salt concentration.

Reagent (medium)	**% Tc in filtrate**	**% Tc retained on resin**
2M HNO_3 (acidic)	22.9	77.2
2M NaOH (basic)	-	92.9
dist. H_2O (neutral)	0.2	> 99.5

TABLE 2.7: Percent ^{99}Tc retained/not retained on Dowex 1- X8.

The effect of flow rate on the elution.

Review

Robb (1983) and Luxenburger and Schuttelkopf (1984) concluded from their experiments that the rate of elution should not be selected to be too high.

Method

An experiment was carried out in which the rate of elution was varied keeping the quantities of resin and the eluate constant. The different times were 15, 22, 83 and >360 minutes for 5 cm^3 resin and 40 cm^3 12M HNO_3.

Results and discussion of present work.

The results obtained from the experiment for checking flowrate effects on elution using ^{95m}Tc as tracer are given in Table 2.8. Slow elution was preferred as it gave comparatively high yield but as is normal practice, columns were never allowed to run "dry" so that air was admitted. If the flowrate is slow enough to allow this then the method is useless. A flowrate of 0.2-0.3 $cm^3\ min^{-1}$ (≈100-200 min for 40 cm^3) was adopted in further work.

40 cm^3 eluate	**recovery**
15	82.1
22	87.9
83	89.4
> 360	82.5

Table 2.8: Effect of flow rate on elution recovery.

Loss of Tc in the resin.

Method

After the elution of ^{99}Tc, columns were checked for Tc losses by NaI counting of the ^{95m}Tc tracer. 41 observations of this type were made on discarded resins.

Results and discussion

The analysis (^{95m}Tc) of the anion exchange resin after the elution with 12M HNO_3 gives the following figures:

^{95m}Tc retained in the resin = 7.5 ± 3.2 % (n = 41)

Besides other factors i.e. medium of solution, molarity of eluate etc., the main factor for large losses of Tc is the flowrate in order to avoid running the column 'dry'.

Reproducibility of the anion exchange elution step.

Method

Two different experiments were carried out to determine the reproducibility of the step. In the first experiment four columns of 5 cm^3 resin were taken. Technetium solution was passed through them and Tc eluted with two 20 cm^3 fractions of 12M HNO_3. In the second experiment the ^{95m}Tc and ^{99}Tc were eluted with two 40 cm^3 12M HNO_3 fractions.

Results and discussion

This experiment was performed using four columns, each of 5 cm^3 slurry of Dowex 1-X8. Evaporation of the eluate was done at 84-95°C. Analysis of ^{99}Tc was carried out by using ICP-MS. The results for fractions of eluate and of filtrate are given in Table 2.9. The small variation found may be explained by the factors such as evaporation temperature, sample medium prior to passing through the column and the flowrate of passing the sample and elution etc. Using 40 cm^3 of 12M HNO_3 for elution of 5 cm^3 slurry of Dowex 1-X8, the recoveries after the evaporation were as follows:

^{99}Tc = 90.5 ± 3.8 % (n = 4)
^{95m}Tc = 92.6 ± 4.3 % (n = 3)

12M HNO_3 (eluate)	Column I	Column II	Column III	Column IV
1st 20 cm^3	85.69	80.34	79.58	89.59
2nd "	13.29	16.09	16.35	7.40
3rd "	0.15	0.52	0.86	0.12
4th "	0.15	0.06	0.08	0.08
Filtrate	0.31	0.25	0.28	0.62

Table 2.9: Experiment carried out for checking the reproducibility of eluates/filtrates of the anion exchange step.

Tc and Ru in the resin blanks.

Method

A blank experiment was performed by eluting 5 cm^3 resin (preconditioned with 8M HNO_3) with 40 cm^3 12M HNO_3. The eluate was evaporated and redissolved in 2% HNO_3 for analysis on ICP-MS.

Results and discussion

Using a 5 cm^3 slurry of Dowex 1-X8 resin, elution with 2 x 50 cm^3 12M HNO_3 showed that there was no Ru contamination but only in one case 0.07 ppt Tc was observed. This might have been due to instrument high response, statistical error in the background counts or contamination, although every precaution was taken to avoid contamination. It was assumed overall, that there was no ^{99}Tc in the resin blank.

Molybdenum in the resin.

Practically, Mo does not interfere with Tc at mass 99 as the isotope ^{99}Mo decays with a half-life of 66 hours. But when dealing with very low concentrations of ^{99}Tc, ^{98}Mo and ^{100}Mo may cause interference by overlapping the ^{99}Tc peak.

However, since significant quantities of Mo were observed in the spectrum in initial runs a simple experiment was performed to establish the level of Mo present in the resin.

Method

To check for the presence of Mo, a column of 5 cm^3 slurry of Dowex 1-X8 was eluted with 2 x 50 cm^3 12M HNO_3. The experiment was repeated with 8M HNO_3. All the 4 fractions were evaporated to 10 cm^3 and were analysed by ICP-MS. The spectrum was compared with the blank (2% HNO_3) and standard ^{99}Tc (6.8 ppb) solution.

Observations and comments.

When a standard of ^{99}Tc was analysed without passing through the resin, very small background peaks were seen as shown in Figure 2.5(a). When however the standard solution was passed through the Dowex 1-X8 anion exchange resin prior to ICP-MS analysis, ^{99}Tc (added), ^{103}Rh (added) and Mo (not added), at mass nos 92, 94, 95, 96, 97, 98 and 100, peaks were more prominent as shown in Figure 2.5(b). ^{95}Mo (for Mo presence) and ^{101}Ru (for Ru presence) were selected to obtain semiqualitative/ semiquantitave analysis data, as there were no interfering isotopes at these mass numbers. Hence, it was found that the peaks observed belonged to Mo and not to Ru, as no peak was seen at mass 101.

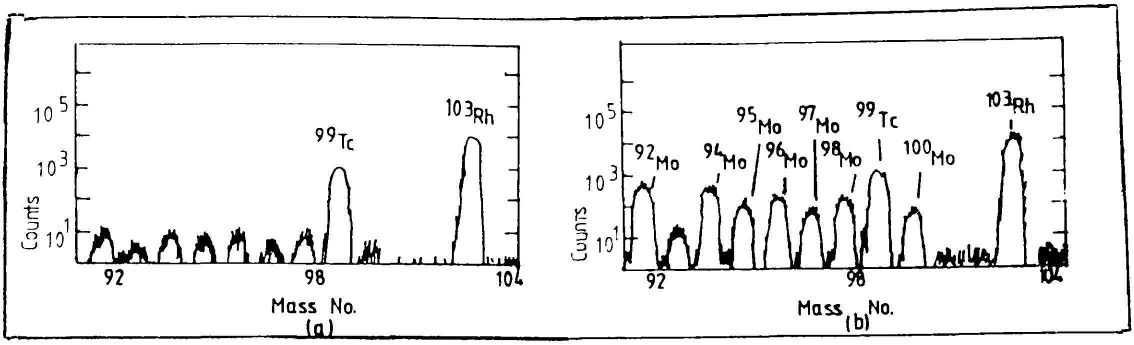


Figure 2.5: Spectra from ICP-MS, (a) blank (b) resin blank.

Although Mo peaks did not appear to affect the ^{99}Tc result when using ICP-MS, problems might arise (due to contribution of side peaks towards peak at 99, especially at mass 98 and mass 100) if ETV would be used.

Mo removal from the resin.

Review

The separation procedures applied are based on methods of chromatography, precipitation, extraction or sublimation, all of which reveal advantages and disadvantages (Anders, 1960 and Kotegov et al., 1968).

Results

Following the finding that the resin columns were contaminated with Mo, premliminary experiments were carried out to remove the element prior to using the resin for Tc analysis. Table 2.10 shows the results of these experiments.

Elution of Mo with various concentrations of HNO_3.

Method and discussions.

Four columns of 5 cm^3 slurry of Dowex 1-X8 resin were taken.

Quantity of (eluate)	4M	8M	12M	16M
1st 20 cm^3	1449	2770	2394	2916
2nd 20 cm^3	1664	1956	1665	3433
3rd 20 cm^3	1177	1328	1456	2462
4th 20 cm^3	4448	1615	1303	2618
5th 20 cm^3	758	1291	1366	2507

TABLE 2.10(a): ^{95}Mo concentrations (counts sec^{-1}, corrected with ^{103}Rh) eluted with different molarities of HNO_3 using 5 cm^3 slurries of Dowex 1-X8.

Quantity of eluate	2 cm^3	4 cm^3	6 cm^3	8 cm^3
1st 20 cm^3	300	263	210	265
2nd 20 cm^3	186	217	452	232
3rd 20 cm^3	162	-	789	537
4th 20 cm^3	186	172	189	335
5th 20 cm^3	150	121	218	438

TABLE 2.10(b): ^{95}Mo (corrected counts sec^{-1}) in the eluate for different quantities of Dowex 1-X8 slurries using 12M HNO_3 for elution.

Quantity of eluate	Column I ^{95}Mo	Column II ^{95}Mo	Column I ^{101}Ru	Column II ^{101}Ru
50 cm^3 8M HNO_3	266	292	4	10
1st50$cm^3$1M HCl	355	302	5	6
2nd50$cm^3$1M HCl	360	382	6	8
3rd50$cm^3$1M HCl	501	489	7	9
Blank	33	33	3	3

TABLE 2.10(c): ^{95}Mo and ^{101}Ru(corrected counts sec^{-1}) eluted with different quantities of 1M HCl (5 cm^3 slurry of Dowex 1-X8).

Quantity of 3M NaOH	Quant. of 12M HNO_3	^{95}Mo	^{99}Mass	^{101}Ru
50 cm^3	45 cm^3	477	17102	446
100 cm^3	45 cm^3	1144	20359	302
200 cm^3	45 cm^3	1266	20960	286
-	45 cm^3	630	20909	1326

TABLE 2.10(d) : **Concentrations (corrected counts sec^{-1}) at mass nos 95, 99 and 101 in eluate using 3M NaOH washing followed by 12M HNO_3 as eluent (5 cm^3 slurry of Dowex 1-X8). (100 ppb Ru and 20.4 ppb ^{99}Tc passed through the resin prior to NaOH elution.**

Each column was washed with HNO_3 at different concentrations. The concentrations of HNO_3 were 4, 8, 12 and 16 molar respectively. Each column was washed with 5 fractions and each fraction being 20 cm^3. The fractions were evaporated and redissolved in 2% HNO_3 for analysis by ICP-MS.

Examining the Table 2.10(a), it is clear that from 1st elution to the 5th elution the Mo concentration decreases. Also it is clear with high concentration of HNO_3 the Mo elution is high from the very begining.

Elution of Mo from different sizes of resin column.

Method and discussions.

2, 4, 6 and 8 cm^3 of Dowex 1-X8 slurry were taken in four columns and each eluted with 100 cm^3 12M HNO_3 in 5 fractions as above. The fractions were finally analysed by ICP-MS.

In Table 2.10(b), it can be seen that by increasing the quantity of the resin, the Mo concentration increases.
But counts are not in proportional with the quantities of

the resin, hence more work is required to be done.

Elution of Mo with 1M HCl.

Method and discussions.

In this experiment the column (5 cm^3 Dowex slurry) was eluted with 50 cm^3 8M HNO_3 followed by 150 cm^3 1M HCl in 3 fractions. The eluates were analysed as above.

From Table 2.10(c), it is observed that the Mo quantity increases with increasing elution but that more work is required to optimise Mo removal.

Elution of Mo with 3M NaOH.

Method and results

In this experiment the column was washed with 50, 100 and 200 cm^3 of 3M NaOH followed by elution with 40-45 cm^3 12M HNO_3. The eluate was evaporated, redissolved in 2% HNO_3 and analysed by ICP-MS.

Clearly, the quantity of Mo increases with increasing elution as shown in Table 2.10(d), but the Mo could not be entirely removed by the procedure. The reduction in Mo was however considered to be acceptable for the purposes of Tc procedure.

2.3.2 LOSSES OF Tc ON EVAPORATION AT DIFFERENT TEMPERATURES.

Review

It is well known that in any analytical scheme for Tc strong heating must be avoided because of the high vapour pressure of Tc_2O_7 and $HTcO_4$, which can lead to losses. The results of Kramer (1983) however indicated that under reflux conditions the results which could be obtained were identical to those obtained under "open-beaker" conditions. Special attention was given to the evaporation step between the anion exchange column and the solvent extraction steps at low (room) temperature to avoid volatilisation (Anderson & Walker, 1980). According to these authors, evaporation was necessary in order to reduce the volume of the solution as well as to minimise the nitrate ions. The reduced nitrate ions eliminated loss of Tc in the extraction.

Method

The following experiments were carried out in order to check the % Tc and Ru losses during evaporation. In the first experiment, 50 cm^3 in 12M HNO_3 samples containing ^{99}Tc (13.6 ppb) tracer were evaporated to dryness on a hot plate at a temperature > 100°C and redissolved in 10 cm^3 2% HNO_3 for analysis by ICP-MS. In a second experiment, ^{99}Tc (13.6 ppb) in 50 cm^3 12M HNO_3, in 1.7M HNO_3 and in 50 cm^3 H_2O were evaporated at a temperature below 100°C and redissolved in 2% HNO_3. Similarly Ru (100 ppb) was evaporated from 12M HNO_3 and H_2O and redissolved in 2% HNO_3.

In other experiments, ^{95m}Tc was added to the samples in order to check the loss of Tc by evaporation. The measurements were carried out using γ-spectrometry. An aliquot of 50 cm^3 12M HNO_3 was evaporated at a temperature < 100°C and redissolved in 50 cm^3 2M H_2SO_4 for analysis. Soil and seaweed samples were leached in 720 cm^3 9M HNO_3, the leachate was filtered and evaporated to 50 cm^3 for analysis. In another experiment, a soil sample containing ^{95m}Tc tracer was ashed at 600°C, dissolved in 100 cm^3 2M H_2SO_4 and evaporated to 50 cm^3 at a temperature < 100°C for analysis by γ-sectrometry.

Results and discussion of present work.

The evaporation step was considered to be a critical step in many procedures. The % ^{99}Tc recovery, of the 50 cm^3 12M HNO_3 aliquot which was evaporated at a temperature > 100°C and redissolved in 2% HNO_3 for analysis by ICP-MS, was found to be:-

1. 74.5 %
2. 58.7 %
3. 68.6 %
4. 81.7 %

Mean ± S.D = 70.9 ± 9.7

Another experiment was carried out for different media at temperature < 100°C. The results are given in Table 2.11.

^{99}Tc and Ru were analysed by ICP-MS while ^{95m}Tc was measured using γ-spectrometry. It could be seen from the results that at temperature > 100°C, losses of Tc were up to 50% during evaporation. On the other hand, below 100°C the losses of Tc and Ru were almost constant. Losses of Tc (at temperature < 100°C) were found < 1% for low acidic and neutral media while for Ru the losses were higher in these media.

Table 2.11(b) shows the percent losses of ^{95m}Tc at temperature < 100°C, except 2.11(b) iv (ashing at 600°C) during some procedures.

2.3.3 RUTHENIUM DECONTAMINATION.

Table 2.12 shows the isotopes of Mo, Tc and Ru and indicates the possibility of isobaric interferences. Inspection shows that Ru represents the most serious interference to the determination of ^{99}Tc as mentioned earlier. Radiochemical separations often involve carrier (Ru) or spiked (^{95m}Tc or ^{99}Tc) procedures in which trace amounts of the elements or radionuclides of interest are

a.	Element	Temp. (°C)	Medium	% rec. ± δ (no. of obs.)
	^{99}Tc	95	12M HNO_3	94.6 ± 3.1 (10)
	Ru	"	"	94.22 ± 0.95 (3)
	^{99}Tc	84	dist. H_2O	99.26 ± 0.06 (2)
	Ru	"	"	89.4 ± 8.1 (2)
	^{99}Tc	"	1.7M HNO_3	99.33 (1)

b.	Processes (^{95m}Tc)	% rec. ± δ (no. of obs.)
i.	Evaporation from 12M HNO_3 & redissolution in 50 cm^3 H_2SO_4	95.3 ± 2.2 (3)
ii.	Leaching of soil in 9M HNO_3, filtration & evap. to 50 cm^3	91.91 ± 0.48 (2)
iii.	Leaching of seaweeds in 9M HNO_3 filtration & evap. to 50 cm^3	92.4 ± 7.0 (12)
iv.	Ashing of soil at 600°C, dissol. in 100 cm^3 3M H_2SO_4 & evap. to 50 cm^3	73.8 ± 7.6 (2)

TABLE 2.11: Effect of temperature on % recoveries of Tc and Ru a) at evaporation b) during various processes.

added at the begining of the procedure. Since the amount of inactive Ru carrier or tracer (^{95m}Tc or ^{99}Tc) added is known, determination of the amount present at the end of the separation, will allow the chemical yield or decontamination of the separation to be calculated. The methods given below were considered to determine the degree of removal of Ru from samples.

In trial experiments the degree of removal of Ru can be expressed by the decontamination factor (D.F) defined as follows:

$$D.F = \frac{\text{Ru added to sample}}{\text{Ru remaining after chemical separation}}$$

Methodology for present work.

(a) The determination of ^{99}Ru by means of the ^{99}Ru/^{101}Ru ratio.

Isotope	% nat. abundance	Atomic mass	Lifetime	Modes of decay	Decay energy (MeV)	Particle energies (MeV)	Particle intensities	Thermal neutron capture cross-section	I	μ
${}_{42}\mathrm{Mo}^{95}$	15.72%	94.90584						14.4 ± 0.5b	5/2	−0.9133
${}_{42}\mathrm{Mo}^{96}$	16.53%	95.9046						1.2 ± 0.6b	0	
${}_{42}\mathrm{Mo}^{97}$	9.46%	96.9058						2.2 ± 0.7b	5/2	−0.9325
${}_{42}\mathrm{Mo}^{98}$	23.78%	97.9055						0.14 ± 0.02b	0	
${}_{42}\mathrm{Mo}^{99}$			66.69 ± 0.06h	β^-	1.37	0.26 0.45 0.86 1.19	0.3% 17% 1% 82%			
${}_{42}\mathrm{Mo}^{100}$	9.63%	99.9076						0.20 ± 0.05b	0	
${}_{42}\mathrm{Mo}^{101}$			14.6m	β^-	2.82	0.84 1.23 1.61 2.23	38% 13% 25% 10%			
${}_{42}\mathrm{Mo}^{102}$			11m	β^-	1.2	1.2				
${}_{43}\mathrm{Tc}^{95}$			20.0h	EC	1.66					
${}_{43}\mathrm{Tc}^{96m}$			52m	IT	0.0344					
${}_{43}\mathrm{Tc}^{96}$					2.9					
${}_{43}\mathrm{Tc}^{97m}$			90d	IT	0.0965					
${}_{43}\mathrm{Tc}^{97}$			2.6×10^6y	EC	~0.3					
${}_{43}\mathrm{Tc}^{98}$			1.5×10^6y	β^-	1.7	0.3				
${}_{43}\mathrm{Tc}^{99m}$			6.0h	IT	0.1427					
${}_{43}\mathrm{Tc}^{99}$			2.12×10^5y	β^-	0.292	0.292		22 ± 3b	9/2	+5.68
${}_{43}\mathrm{Tc}^{100}$			17s	β^-		2.2 2.88 3.38				
${}_{43}\mathrm{Tc}^{101}$			14m	β^-	1.63	1.07 1.32				
${}_{43}\mathrm{Tc}^{102}$			4.5m	β^-	4.4	~2				
${}_{43}\mathrm{Tc}^{102}$			5s	β^-	4.4	4.4				
${}_{44}\mathrm{Ru}^{95}$			1.7h	β^+, EC	2.03	0.7 1.01 1.33	1.3† 12 4			
${}_{44}\mathrm{Ru}^{96}$	5.51%	95.9076						0.21 ± 0.02b		
${}_{44}\mathrm{Ru}^{97}$			2.9d	EC	~1.2					
${}_{44}\mathrm{Ru}^{98}$	1.87%	97.9055						<8b		
${}_{44}\mathrm{Ru}^{99}$	12.72%	98.9061						10.6 ± 0.6b	5/2	−0.63
${}_{44}\mathrm{Ru}^{100}$	12.62%	99.9030						10.4 ± 0.7b		
${}_{44}\mathrm{Ru}^{101}$	17.07%							3.1 ± 0.9b	5/2	−0.69
${}_{44}\mathrm{Ru}^{102}$	31.61%	101.9037								

TABLE 2.12: Isobaric nuclides of Mo, Tc and Ru (CRC Handbook, 1983).

After the anion exchange concentration step for water samples, ^{99}Ru counts were calculated using the observed ratio of ^{99}Ru/^{101}Ru and subtracted from total counts at mass 99 in order to correct for Ru contamination. However this method was not reliable for solid samples due to the high concentration of salts after the leaching/ashing steps. This was overcome by using an additional anion exchange step.

(b) Decontamination of Ru by various methods.

The possible ways (i.e. precipitation, elution with NaOH and solvent extraction) for the separation of Ru from Tc are shown in Figure 2.6. and are discussed in detail here.

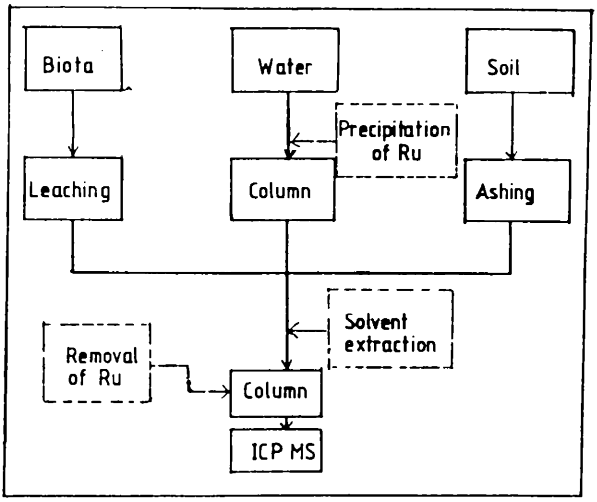


Figure 2.6. Possible methods of decontamination from Ru.

Precipitation of ruthenium.

Review of literature.

Ruthenium is known to be precipitated from aqueous solutions by alkaline hydroxide. Technetium does not appear to be coprecipitated with the Ru carrier to any appreciable extent and the amount of Ru precipitated from the sample depends upon the amount of NH_4OH or NaOH.

The literature contains several procedures which can be used for the precipitation of Ru isotopes from aqueous solution (Robb, 1983).

Precipitation of Ru using NaOH/NH_4OH and alcohol.

Method

A sample of tap water (400 cm^3) was taken and spiked with 100 ppb of a Ru(III) carrier solution. ^{99}Tc (13.6 ppb) as NH_4TcO_4 was then added to this solution. After adding 10 cm^3 of 6M NaOH and anti-bumping granules the test sample was brought to boil using a hot plate in a well ventilated fume cupboard. When boiling, a 10 cm^3 aliquot of methanol was carefully added to this solution. The reaction mixture was allowed to cool slowly to room temperture and the precipitate was filtered using GF/F glass fibre paper. The filtrate was passed through a 5 cm^3 Dowex 1-X8 anion exchange resin which had been preconditioned with 8M HNO_3. Following the elution, the column was washed with cold and hot deionzed/distilled water. The eluate was evaporated and redissolved in 10 cm^3 2% HNO_3. The ^{99}Tc and Ru levels were measured by ICP-MS.

The precipitation procedure was repeated using a 20 cm^3 aliquot of NH_4OH(0.88 s.g.) in place of the 6M NaOH.

Results and discussion

The results obtained are given in Table 2.13.

Process	$\%^{99}Tc$	D.F(Mean)
a) NaOH, methanol, precipitation, anion exchange column	88.4 69.1 90.4	345
b) NH_4OH, methanol, ppt., column	58.0	715

Table 2.13: Percent recoveries of ^{99}Tc and D.F of Ru by precipitation.

To check the removal of Ru isotopes from the sample, Ru(III) carrier was added prior to carring out the precipitation.

A D.F of Ru of 345 and 715 and % chemical recoveries of 83.0 (mean) and 58.0 were obtained from the precipitation of Ru with NaOH and NH_4OH respectively. Although the D.F with NH_4OH is almost double of that obtained from NaOH, the chemical recovery of Tc was very low. This might be explained by the severe bumping produced by the addition of alcohol which led to spillages. In addition, the alcohol tended to evaporate when it was slowly added to the sample so that it was not possible to add exactly the same amount of alcohol to each sample.

Ru elution with NaOH.

The ease with which a number of nuclides and in particular Ru could be removed from the anion exchange resin using NaOH was investigated and experiments were carried out to investigate the use of NaOH as a "clean-up" eluant.

Review

Robb (1983) used 1M NaOH for the elution of Ru prior to the elution of Tc.

Methods

^{99}Ru is likely to be present in environmental samples analysed by this method and therefore the ease with which this isotope can become absorbed onto the anion exchange resin and elution of the Ru prior to the elution of Tc was investigated.

A number of samples of 50 cm^3 deionized/distilled water were spiked with 13.6 ppb ^{99}Tc, 100 Bq ^{95m}Tc and 100 ppb Ru and were passed through a 5 cm^3 Dowex 1-X8 anion exchange resin (preconditioned with 8M HNO_3) followed by water wash.

After elution of Ru with NaOH, the columns were washed with 50 cm^3 cold and hot deionized/ distilled water. Tc was then stripped from the column with 40 cm^3 of 12M HNO_3. The eluate was measured in 50 cm^3 counting geometry for ^{95m}Tc by γ-spectrometry. The solution was eventually evaporated to dryness, redissolved in 10 cm^3 2% HNO_3 and the concentrations of ^{99}Tc and Ru determined by ICP-MS.

Results and discussion

Solutions containing ^{95m}Tc and Ru were passed through Dowex 1-X8 resin and various volumes and concentrations of NaOH were used to **elute** Ru in order to check the degree of removal which could be obtained without disturbing Tc on the column. The results obtained are tabulated in Table 2.14.

This experiment clearly showed that most of the sorbed Ru may be removed from the resin using NaOH that the maximum decontamination from Ru was achieved by 200 cm^3 3M, 50 cm^3 2M, 100 cm^3 1M and 150 cm^3 1M NaOH. To avoid high concentrations of salts, 100 cm^3 1M NaOH was prefered for the present work. The D.F and % recovery for 2M and 1M NaOH were almost the same. Also the loss of Tc was high when using 3M NaOH.

Conc. (Molarity)	Quantity (cm^3)	%^{99}Tc (recovered)	%^{101}Ru (left)	Decont. Factor
1M	10	-	37.50	3
	20	95.04	20.06	5
	40	89.70	8.83	10
	50	82.85	2.13	50
	60	93.38	0.93	110
	100	90.40	0.84	120
	150	88.76	0.63	160
2M	50	90.62	0.63	160
	100	92.50	1.87	55
3M	50	60.41	0.93	110
	100	72.54	0.62	160
	200	74.74	0.59	170
4M	100	89.46	1.90	55
6M	100	94.71	2.05	50

TABLE 2.14: Ruthenium decontamination with NaOH.

The NaOH clean-up eluate was checked by γ-spectrmetry and showed that the premature elution of Tc from the resin did not occur. It was found that only 3.0 ± 1.0 % ^{95m}Tc was eluted with 100 cm^3 1M NaOH. After Ru elution, the column was washed with cold and hot water in order to remove the salt concentration of NaOH from the column followed by Tc elution with 12M HNO_3 for analysis of ^{99}Tc and Ru (if any remained) by ICP-MS.

Solvent extraction.

Solvent extraction is a partitioning process based on the selective distribution of substances in two immiscible phases, normally organic and aqueous. The liquid-liquid extraction or solvent extraction can be achieved either by extraction of the element to be separated into the organic phase or by extraction of the interfering elements leaving the element to be separated in the aqueous phase.

Review of literature.

In view of the general advantages of extraction over other methods of isolating Tc, solvent extraction is particularly widely used. There are several extraction methods for the separation of Tc from Mo and Ru using different extraction reagents.

Technetium was readily extracted into organic solvents from aqueous solution and the efficiency of a given extraction procedure calculated using the equation:

$$E = A_o/A_i \times 100 = (A_i-A_a)/A_i \times 100 \%$$

where, E = extraction efficiency, A_i = initial aqueous activity, A_o = activity in organic phase, and A_a = activity in aqueous phase.

Different solvents used by various workers are summarised in Table 2.15.

Results

Different organic solvents were used for the decontamination of other radionuclides, especially Ru in present work. Sulphuric acid was used to dissolve the residue after the evaporation of HNO_3 filtrate (from leaching of biota samples) and anion exchange eluate for water samples. Dissolution with HCl could lead to the formation of Fe-chloro-complexes which might disturb the subsequent extraction. Nitric acid media was not a good

Solvent	Reference
1. Tri butyl phosphate (TBP)	Holm et al. (1981); Martinez-Lobo et al. (1986) & Walker et al. (1980).
2. TBP/HF	Holm et al. (1984); Garcia-Leon et al. (1984) & Rioseco (1987).
3. TBP-petroleum benzene	Luxenburger & Schuttelkopf (1984).
4. TBP-shellsol T	Sattelberger et al. (1989).
5% TIOA-xylene	Golchert & Sedlet (1969); Chen et al. (1989) & Chen et al. (1990).
5. 10% TIOA-xylene	Holm et al. (1981).
6. Carbon tetrachloride	Meadows & Matlack (1962); Chen et al. (1989) & Sattelberger et al. (1989).
7. Cyclohexanone	Foti et al. (1972); Anderson & Walker (1980); Schulz (1980); Koide & Goldberg (1985) & Chen et al. (1989).
8. Chloroform	Foti et al. (1972) & Koide & Goldberg (1985).
9. Tetraphenyl arsonium-Chloroform	Sattelberger et al. (1989).
10. di(2-ethyl)-or o-H_3PO_4 in CCl_4	Sattelberger et al. (1989).
11. Butane-2-one	Malcolme Lawes et al. (1982).
12. Methyl ethyl ketone (MEK)	Kenna & Kuroda (1961); Attrep (1962); Kramer (1983) & Matsuoka et al. (1990).
13. MEK-chloroform	Attrep et al. (1971).
14. Diethyl ether	Attrep (1962).
15. 4-methyl-2-pentanone	Anderson & Walker (1980).

TABLE 2.15: Various organic solvents used for the extraction of technetium.

medium for extraction of Tc into organic solvents. For example, distribution coefficients using TBP were 0.24 for HNO_3 and for H_2SO_4 50-100, hence, the H_2SO_4 medium was many times better than HNO_3. To be sure that Tc was oxidised completely and the of residue containing Tc fully dissolved, the H_2SO_4 solution was heated to 90°C in the presence of H_2O_2.

The distribution coefficients and % extraction for various solvents used in the present work are summarised in Table 2.16. The % recoveries of different steps of solvent extraction and decontamination factor (D.F) are tabulated in Table 2.17. The importance and results of each solvent used in this work are discussed below.

S.No.	Medium (from)	Solvent (organic)	Dist. coeff.	% Tc ext. (max.)
1.	H_2O	Cyclohexanone	1200	97
2.	2M H_2SO_4	"	100	98
3.	2M H_2SO_4-1M HCl		2000	98
4.	H_2O	Chloroform	0.003	0.3
5.	pH=4 + NaOCl	CCl_4	-	<90
6.	2M H_2SO_4-H_2O_2	5% TIOA-xylene	100	98
7.	12 HNO_3-H_2O_2	TBP	0.25	3
8.	2M H_2SO_4-H_2O_2	TBP	40	11
9.	2M H_2SO_4-H_2O_2	50% TBP in xylene	40	80

TABLE 2.16: Distribution coefficient and % Tc extraction for different solvents and media.

Solvent extraction into cyclohexanone.

Method

Various experiments were carried out using cyclohexanone with different media and quantities of extractants and media.

In the initial investigation, a 20 cm^3 aliquot of cyclohexanone was added to 20 cm^3 of distilled water containing 100 ppb Ru and 13.6 ppb ^{99}Tc in a 100 cm^3 beaker. The mixture was mixed for 5 min with magnetic stirrer. The mixture was transfered to a clean 100 cm^3 separating funnel and allowed to settle for 10 min. After separation, the aqueous layer was discarded while the organic layer was mixed with 20 cm^3 distilled water and 20 cm^3 cyclohexane and back-extracted by shaking for 5 min in a 100 cm^3 beaker and transferring to a 100 cm^3 separating funnel. Back-extraction

Media (aq)	Org. solvent	Aq. left Tc Ru	Back 1st 2nd	extrac Tc Ru Tc	D.F (max.)
H_2O	Cyclohexanone	0.02±0.04 73.9±16.9	H_2O H_2O	91.9±8.7 16.7±2.2 2.9±1.3 -	10
2M H_2SO_4	″	1.06±1.5 -	0.5M NaOH 2nd,	93.8±5.5 - 4.1±1.2 -	1000
2M H_2SO_4- 1M HCl	″	4.1±1.6 -	″		4000
H_2O	Chloroform	99.7 90.9			1
2-3M H_2SO_4	5% TIOA- xylene	5.9±6.0 -	1M NaOH 2nd	92.6±9.0 - 4.1±4.1 -	700
pH=4 with NaOH/H_2SO_4	Carbon tetra- chloride	79.7±0.05 -			700
12M HNO_3	Tri-n-butyl phosphate	80.3 95.8	- -		2600
2M H_2SO_4	TBP	1.7±0.7 -	2M NaOH 2nd	2.5±0.1 - 3.0±0.8 -	1000
2M H_2SO_4	TBP/xylene (50%)	″	2M NaOH 2nd	79.2±1.4 - 19.7±0.4	4000

TABLE 2.17: Losses and recoveries of ^{99}Tc (or ^{95m}Tc) and Ru in the different solvent extraction processes.

was repeated by adding 20 cm^3 water to the organic phase. The aqueous phases were combined and all the aqueous phases were analysed by ICP-MS for Ru and ^{99}Tc.

A second experiment was carried out by taking 30 cm^3 cyclohexanone and shaking with 50 cm^3 2M H_2SO_4(1-2 cm^3 H_2O_2) containing 100 Bq ^{95m}Tc and 100 ppb Ru. The organic layer was washed with 30 cm^3 4M H_2SO_4(H_2O_2) and the washings discarded.

Back-extraction was carried out twice with 30 cm^3 0.5M NaOH in the presence of 30 cm^3 cyclohexane. Cyclohexane was added to cyclohexanone in order to make back-extraction easy. The aqueous phases were combined, neutralized to pH 7 and passed through Dowex 1-X8 resin preconditioned with 8M HNO_3. The column was eluted with 12M HNO_3 and ^{95m}Tc was analysed by γ-spectrometry. The eluate was evaporated and redissolved in 2% HNO_3 for ICP-MS analysis.

A further experiment was made to extract Tc and Ru into 2M H_2SO_4-1M HCl in place of 4M H_2SO_4-H_2O_2.

Results and discussions.

Cyclohexanone was used as organic solvent for the separation of Tc from Ru applying different media. Viewing the Tables 2.16 & 2.17, it was found from the results that from the 2M H_2SO_4-1M HCl-H_2O_2 medium, a high decontamination factor could be achieved. Water medium was better comparatively than the rest of the media, but this medium was not feasible for dissolving the residue after evaporation. The distribution using the water-cyclohexanone system, gave a distribution coefficient of 0.35. Cyclohexane was added in order to make the back extraction easy and efficient. From the first back extraction with 30-50 cm^3 H_2O, almost the same degree of extraction (94%) was obtained as that with 0.5M NaOH and 3-4% Tc was recovered with second back extraction. However in all cases, <1% Tc was left in the aqueous phase after extraction with cyclohexanone.

Solvent extraction into chloroform.

Method

Chloroform is used for washing the aqueous phase. In this experiment a 25 cm^3 aliquot of distilled water containing

13.6 ppb ^{99}Tc and 100ppb Ru and was shaken for 4 min with 25 cm^3 chloroform and the chloroform phase was discarded. The chloroform wash step was repeated twice. The aqueous phase was analysed by ICP-MS.

Results and discussions.

The strip solution from the cyclohexanone extraction was washed with chloroform to minimize the presence of cyclohexanone/ cyclohexane traces from the solution and in order to obtain high Tc yield. The purpose of using chloroform in present work was to clarify the level of decontamination from Ru. The distribution coefficients for ^{99}Tc and ^{99}Ru were 0.0033 and 0.1 respectively. >99 % of Tc and 91 % of Ru were found in the aqueous phase after the chloroform wash.

Solvent extraction into 5% TIOA-xylene.

Method

Extraction of Tc into 5% TIOA-xylene was used by Golchert and Sedlet (1969). To assess its suitability, tri-isooctylamine (TIOA) in xylene was tried as an extractant.

A 50 cm^3 2M H_2SO_4(1 cm^3 H_2O_2) solution containing ^{95m}Tc,^{99}Tc and Ru was placed in a 250 cm^3 beaker, 40 cm^3 5% TIOA-xylene was added and mixed for 5 min with a magnetic stirrer. The mixture was transfered to a 250 cm^3 separating funnel and left to separate for 10 min. To the aqueous phase a second aliquot of 35 cm^3 of 5% TIOA-xylene was added and mixed. After separation the organic phase was washed with 50 cm^3 2M H_2SO_4 by shaking for 5 min. The organic phase was back-extracted twice with 20 cm^3 1M NaOH and shaken for 2 min. The aqueous phases were neutralized with 8M HNO_3 and passed through Dowex 1-X8 resin. The eluate was evaporated and redissolved in 2% HNO_3. ^{95m}Tc was analysed by γ-spectrometry and ^{99}Tc and Ru by ICP-MS.

Results and discussions

In the present case extraction with 5% TIOA-xylene was very variable, especially for biota/soil samples. For these samples, the loss of ^{95m}Tc was up to 15-20% but gave a high D.F of 700 from Ru. The % extraction of Tc was upto 98% and a distribution coefficent up to 100 was obtained.

Solvent extraction into carbon tetrachloride.

Method

The method of CCl_4 solvent extraction can be used for the determination of Ru. The RuO_4 is extracted by CCl_4 at pH=4 in NaOCl solution and the TcO^-_4 is left in solution.

An aliquot of 50 cm^3 of water containing 100 Bq ^{95m}Tc and 100 ppb Ru was adjusted to pH 4 with the help of $NaOH/H_2SO_4$ and extracted with 50 cm^3 CCl_4 by shaking for 1 min. The organic layer was discarded.

The extraction was repeated with a second aliquot of 50 cm^3 CCl_4. The aqueous phase(pH 7) was passed through Dowex 1-X8 resin. ^{95m}Tc was analysed by γ-spectrometry. The eluate was finally adjusted to 2% HNO_3 for ICP-MS.

Results and discussions.

Ruthenium and technetium could be separated to permit the extraction of RuO_4, and the TcO^-_4 was kept in solution at pH 4 containing NaOCl while mixed with CCl_4. The % extraction for Tc was < 90%. In order to minimize the acidity/bascity of the solution, an anion exchange column was essential. After the extraction and column steps about 80% ^{99}Tc and a D.F of 700 from Ru were achieved.

Solvent extraction into tri-n-butyl phosphate.

Method

In the initial investigations of this work, 5 cm^3 TBP was added to a 20 cm^3 aliquot of 12M HNO_3 containing 1 cm^3 H_2O_2, 13.6 ppb ^{99}Tc and 100 ppb Ru and shaken for 5 min. After separation, the aqueous phase was again extracted with a further 5 cm^3 of TBP and discarded. The organic phase was back-extracted twice by shaking for 2 min with 7 cm^3 2M NaOH. The aqueous phase was neutralized with 8M HNO_3 and passed through 5 cm^3 Dowex 1-X8 resin. The eluate was evaporated and redissolved in 2% HNO_3 for ICP-MS analysis. The above procedure was repeated by taking 2M H_2SO_4 in place of 12M HNO_3 and using ^{95m}Tc instead of ^{99}Tc.

An alternative extraction procedure was investigated with a view to improving the back-extraction efficiency obtained using 50% TBP in xylene.

Results and discussions.

Tri-n-butyl phosphate is widely used in the nuclear industry for the extraction of nuclides into an organic phase. Examining the Tables 2.16 & 2.17, the distribution coefficient for 2M H_2SO_4-TBP was 160 times higher compared to 12M HNO_3-TBP extraction. About 98% of Tc was extracted by TBP from 2M H_2SO_4. The % extraction (radiochemical yield) measured was only 11%. It was concluded that Tc was not efficiently back extracted from TBP. When TBP was diluted with an equal volume of xylene (50% in xylene), 95-98% ^{95m}Tc was obtained with 2M NaOH. To run the sample by ICP-MS, the solution was passed through an anion exchange column and a final yield of 75-85%(^{99}Tc) obtained. A D.F of 4000 from Ru was achieved. 5.5 and 99% of ^{95m}Tc was back extracted from TBP and 50% TBP-xylene respectively.

Cation exchange separation of Tc.

Review

Cation exchange resin (Dowex 50 W) was used to remove the bulk of the cations from the solution rapidly. However, cation exchange resins adsorbed Tc only to a negligible extent (Anders, 1960., Foti et al., 1972; Kotego et al., 1968 and Koide and Goldber 1985). Matsuoka et al. (1990) obtained a D.F(Ru) of 1.04 and 1.52 for anion exchange and cation exchange columns respectively.

Methods

An aliquot of 50 cm^3 1.7M HNO_3 containing ^{99}Tc was passed through AG-50WX(5cm^3) preconditioned with 1.5M HNO_3, followed by 2 x 20 cm^3 rinses of water. The filtrate and washings were evaporated to 10 cm^3 for analysis by ICP-MS.

A second experiment was carried out, in which an aliquot of 50 cm^3 distilled water containing ^{99}Tc and Ru was passed through 5 cm^3 slurry of Dowex 1-X8(NO^-_3) followed by 12M HNO_3 elution. The eluate was evaporated and redissolved in 1.7M HNO_3 and passed through cation exchange AG-50WX resin(NO^-_3). The eluate was analysed by ICP-MS.

It should be noted that the cation and anion exchange resins were washed 2 to 3 times in double their volume of deionized/distilled water prior to use. After a brief settling time, the supernatants and suspended fines were decanted to waste. The resultant resins were stored under small excesses of water and slurried for column preparation when needed. 5 cm^3 aliquots of slurry were always taken.

Results and discussion of present work.

Technetium can be separated from many cation contaminants on a cation exchange resin. Tc has a very low K_d and thus will pass through the resin essentially quantitatively. The purpose of this experiment was to check the decontamination from Ru which could be obtained.

In the first experiment, 92.6 ± 1.3% ^{99}Tc was found in the filtrate of cation exchange resin and 3.36 ± 0.34% ^{99}Tc was passed with first 20 cm^3 dist. H_2O wash while in further water washings no ^{99}Tc was detected. In the second experiment, when the eluate of anion exchange resin was dried, redissolved in 1.7M HNO_3 and passed through Dowex 50 WX resin followed by evaporation to 10 cm^3, 83-90% ^{99}Tc was recovered and a D.F (Ru) of 10 was achieved. The use of cation-type exchangers for the separation of Ru did not appear promising, perhaps because of the ease of formation of anionic type complexes. Due to this reason cation exchange was not considered useful in the present work.

Significance of removal of ^{99}Ru interference.

Masson and Moore (1982) has given the average amounts of the elements in crustal rocks in ppb levels (Ru = 10 ppb and Mo = 1500 ppb), whereas the L.O.D for ^{99}Tc is 0.004 ppb and the ^{99}Tc in most of the environmental samples is only just above the L.O.D. Hence, the potential interference from Ru is highly significant and samples have to be decontaminated from Ru before analysis.

As ^{99}Ru/^{101}Ru is not constant at low concentrations, monitoring the ^{101}Ru peak can not be used for eliminating the ^{99}Ru contribution to the ^{99}Tc peak.

Methods of determining Ru decontamination.

Method

In trial experiments, ^{95m}Tc(100 Bq), ^{99}Tc(13.6 ppb) and Ru(100 ppb) were added to solutions to be analysed. The total γ-activity from ^{95m}Tc present at each stage of the analyses was determined by γ-spectrmetry. The concentration of ^{99}Tc and Ru was finally determined by ICP-MS and the appropriate decontamination factors calculated from these data.

Results and discussion of present work.

The D.F from Ru was determined from the percent (%) yield of Ru by ICP-MS. The % yield was selected because the response of the instrument was not same all the time. Standard Ru and Tc solutions were analysed during each analysis run and from these, % yields of Tc and Ru were determined.

It was not possible to determine the D.F for every step because of the unavailability of a suitable Ru tracer. ICP-MS was used for the analyses of stable isotopes of Ru. The limitations of ICP-MS (salt conc. <0.1%; in 2% HNO_3; no organic traces; and clear solutions are required), did not allow the measurement of Ru after each step. Therefore, in many cases in addition , an anion exchange step followed by evaporation was performed. The observed D.F values calculated in this way for the many combinations of procedures which were tried are reported in Table 2.18.

The lower limit of detection obtained is 0.004 ppb (section 1.8.4) which corresponds to 10 counts (0.136 ppb corresponds to ≈ 350 counts). A decontamination factor of > 4000 is required to reduce Ru levels to the background levels at mass 99 i.e. < 10 counts. By using step-by-step decontamination procedures (Metho I or Method II, described in section 2.1.2), a D.F. of > 4000 , as required, for Ru was achieved.

S.No.	Process	% Tc rec.	D.F (Ru)
1.	NaOH washing of anion exch. column	>95	170
2.	Precipitation of Ru with NaOH and methanol	85	350
3.	Precipitation with NH_4OH & methanol	60	710
4.	2M H_2SO_4-5% TIOA-xylene extraction	95	700
5.	NaOH washing of column and 5% TIOA-xylene	7	750
6.	12M HNO_3-tri-n-butyl phosphate(TBP) extraction & anion exch. column	3	360
7.	2M H_2SO_4-TBP extraction & column	6-11	140
8.	2M H_2SO_4-50% TBP in xylene extraction & anion exch. column	95	550
9.	Cation exch. column & chloroform extraction → water	95	40
10.	NaOH washing of anion exch. column, cation exch. column & cyclohexanone extraction	75	280
11.	Water-cyclohexanone ext. → water	97	10
12.	2M H_2SO_4-cyclohexanone & anion exch. column	95	1000
13.	2M H_2SO_4-1M HCl-cyclohexanone & anion exch. column	95	4000
14.	Anion and then cation exch. column	90	10
15.	Water-chloform extraction	99.7	1
16.	Carbon tetrachloride (CCl_4) extraction & anion exch. column	75	700
17.	NaOH washing of column & CCl_4 ext.	78	24

TABLE 2.18: % Tc recoveries and decontamination factors (D.F) for Ru applying various processes.

2.4 ^{99}Tc DETERMINATION BY ICP-MS.

ICP-MS was used to measure ^{99}Tc levels in aqueous solutions throughout the development of the analytical method. The first experiments carried out were to set up a suitable "parameter group" on the ICP-MS in such a way that ^{99}Tc levels could be measured. A parameter group was chosen by taking 6.79 ppb solution of ^{99}Tc standard in 10 cm^3 2% v/v HNO_3. This standard was used in a set of acid concentrations (1-5% v/v HNO_3).

A number of operational parameters have been discussed in section 1.8 which affect the analysis of the required element. ^{103}Rh was routinely used as an internal standard to correct for instrument drift during sample runs and to optimise the operation of the instrument daily. Standard ^{99}Tc solution was aspirated in 2% high purity HNO_3. The nebulizer flow was varied between 0.6 and 0.9 $dm^3\ min^{-1}$. A typical ICP-MS spectrum including ^{99}Tc and ^{103}Rh peaks is shown in Figure 2.5.

The PQ1 instrumental parameter "menus" used during ^{99}Tc optimisation are given in Table 2.19. From Figure 2.7, it is clear that concentrations upto 5% v/v HNO_3 solution do not effect the response significantly.

Blank samples were presented in 2% v/v HNO_3, bracketting each sample. A special blank was also analysed by taking 40-45 cm^3 of eluant from 5 cm^3 of resin slurry, evaporating and redissolving in 2% high purity HNO_3. All the samples were eventually concentrated in 5 or 10 cm^3 2% HNO_3 (depending on ^{99}Tc concentrations) and measured at least in duplicate. Each analysis was based on three ICP-MS runs. 50 ppb ^{103}Rh was added to all blanks and all samples to act as an internal standard.

2.4.1 THE BACKGROUND, LIMIT OF DETECTION AND STABILITY OF THE INSTRUMENT.

The background, limit of detection (L.O.D) and the stability of the instrument were checked each time, whenever analyses were carried out. Sample blanks were also run to check the background counts in the mass region of interest. During the experiments, instrument operating parameters and standard concentrations were kept constant.

Forward power (r.f.)	1357 W
Reflected power	< 5 W
Nebuliser	V-groove (kel-F)
Spray Chamber	Double pass Scott, water-cooled
Loadcoil-sampling cone distance	10 mm
Coolant flow	14.2 l min^{-1}
Auxiliary flow	0.41 l min^{-1}
Nebuliser flow	0.71 l min^{-1}
Peak jump parameters:	
points per peak	20
dwell time	160 μs
peak jump sweeps	20
DAC steps between points	5
Mass range	92-104
Number of channels	1024
Number of scan sweeps	400
Collector type	Pulse
Points per peak	5

TABLE 2.19: Instrumental parameters and element menus for ^{99}Tc analyses on the VG PlasmaQuad PQ1 at SURRC.

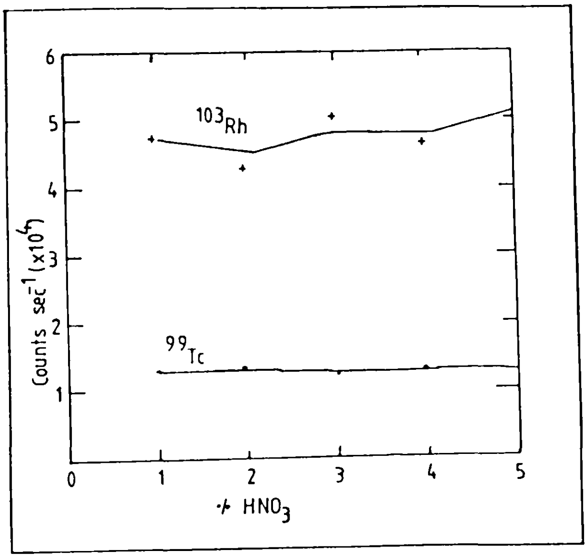


Figure 2.7: Variation of ICP-MS response for ^{99}Tc (13.6 ppb) and ^{103}Rh (50 ppb) with HNO$_3$ concentation.

Methods

Routine experiments were carried out periodically over a period of approximately one and a half years between January 1989 to June 1990 to monitor background, detection limits and stability. Analyses of blanks were regularly performed (in 2% HNO_3) to check the background peaks. Also, a ^{99}Tc standard in 2% HNO_3 was routinely analysed. In each analysis 50 ppb ^{103}Rh was added to check the instrument response.

A set of 25 samples was analysed for ^{99}Tc recoveries and after each sample a blank was run to check the instrument automatic washing procedure. Similarly, in the same experiment the ^{103}Rh response was checked.

Discussions

Figure 2.8, shows a simple background spectra for the mass region of interest. It was noticed that the background counts varied to small extent, which may have been due to nebulizer flow, contamination or statistical variations.

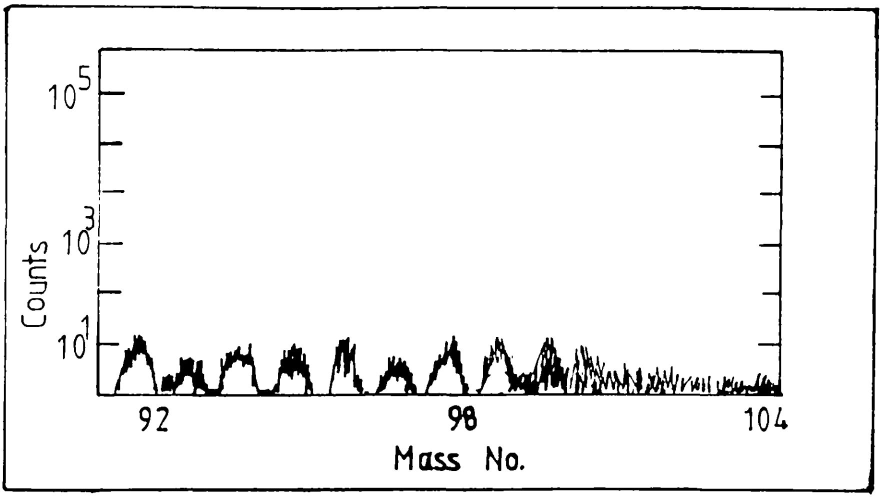


Figure 2.8: A background spectrum for the mass region of interest.

Figure 2.9, shows the variation with time in the ICP-MS response for the ratio of ^{99}Tc/^{103}Rh.

Figure 2.10 shows the response of Rh at mass 103 and Tc at mass 99 over a period of 600 days. The detection limit of the system based on a 10 count background and the 3σ background criterion is 0.004 ppb (see section 1.8.4.).

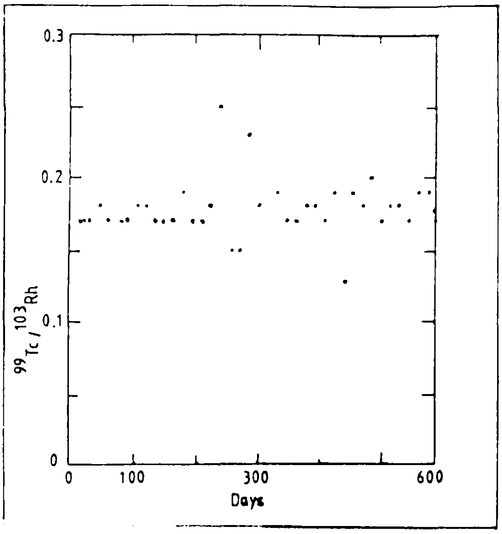
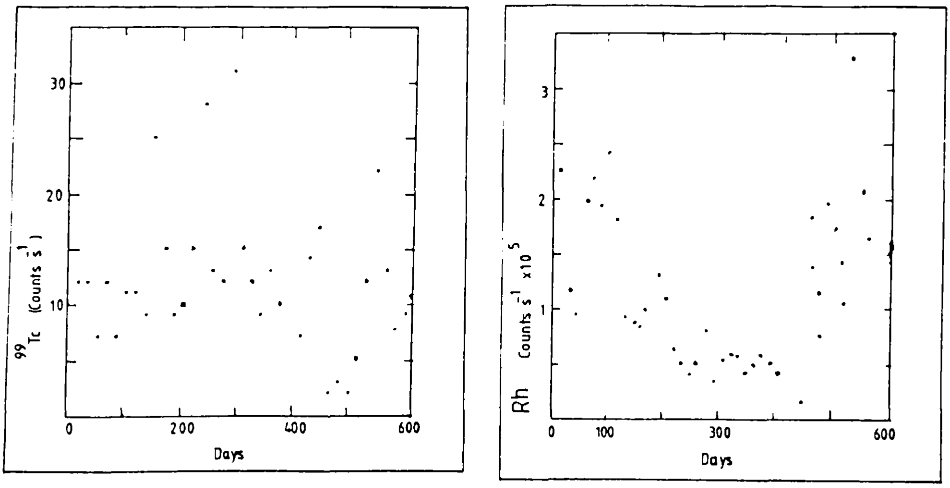


Figure 2.9: Tc/Rh variation with time.

The factors which affect both the background and the instrument stability are expected to vary daily.



(a)　(b)

Figure 2.10: Spectra over a period of 600 days, (a) at mass 99 (Background) and (b) mass 103 (50 ppb).

2.4.2 CALIBRATION

A solution of 1.36 ppm of ^{99}Tc was prepared from the stock solution based on the information supplied by Amersham. A set of further dilution standards in high purity HNO_3 was prepared (i.e. 13.6 ppb and 0.136 ppb).

Three dilution standards (0.136, 6.8 and 13.6 ppb) were selected in order to derive ICP-MS calibration curves covering the range expected in the unknown samples. The calibration curve obtained is shown in Figure 2.11. The linearity is very good over 2 or 3 orders of magnitude and the correlation coefficient is unity.

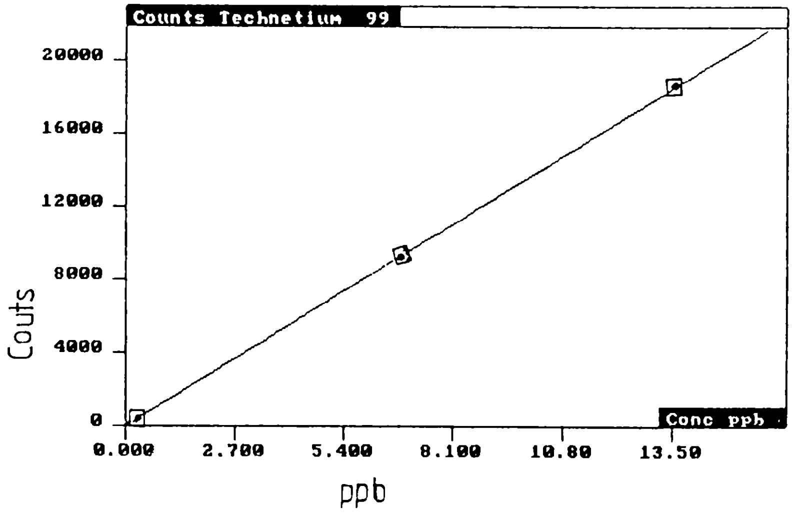


Figure 2.11: ^{99}**Tc calibration curve.**

2.4.3 DETERMINATION OF Tc CHEMICAL YIELD.

The radioactive tracer method was used to correct for the losses during chemical processing. It was assumed that after suitable mixing the added tracer behaved chemically in an identical way to the analyte. The strong, well resolved emissions at 141 keV (^{99m}Tc, $t_{1/2}$ = 6 h) and 204 keV (^{95m}Tc, $t_{1/2}$ = 60 d) could be used for yield calculations.

Method

Perhaps the commonest of all applications of radioisotopes in chemical analysis is their use as a "yield monitor". All available quantitative procedures for ^{99}Tc involve separation steps from the matrix and species and eventual concentration. To develop a method capable of highly accurate determinations, losses during various steps must be accounted for. The element to be measured can be labelled by the addition of a known amount of a suitable γ-emitting isotope, in the same chemical form, to the sample. During and after chemical separation, a comparison of the activity of the recovered material with the original activity gives the "chemical yield".

For technetium analysis, either ^{99m}Tc or ^{95m}Tc (approximately 20 Bq) were added to the sample as tracers depending on the particular procedure. Analyses of the tracers were carried out by γ-spectrometry. Calibration of the NaI detector was done with known sources of ^{137}Cs, ^{60}Co and ^{22}Na while ^{226}Ra was used for the Ge detector. When measuring liquid γ-activity levels, care was taken to ensure that sufficient volume was present in the fixed geometry vessel to maintain a satisfactory counting efficiency. The detector efficiency depended very much on the volume of liquid present because of the counting geometry. Usually three geometries were used as follows: (i) 150 cm^3 sample (ii) 50 cm^3 sample and (iii) 5 cm^3 slurry in a total of 50 cm^3.

For the measurement of ^{99m}Tc (140 keV) a 127 cc Ge detector with 4096 multichannel analysis was used from which a hard copy printoutcould be obtained. For the measurement of ^{95m}Tc, a 4 cm x 4 cm NaI(Tl) detector was used, 512 multichannel analysis was used (Canberra Series 35). Any detector can be used for both Tc isotopes. A diagram of a typical spectrometry system is given in Figure 2.12.

The radiotracers (^{99m}Tc and ^{95m}Tc) were selected on the basis of availability and an added advantage was their easy disposal because of their short half-lives.

i) ^{99m}Tc tracer: When ^{99m}Tc was used for radiochemical yield determination, a 127 cc Ge detector was used for its measurement. Clearly, ^{99m}Tc was not suitable for long procedures, because of its short half-life.

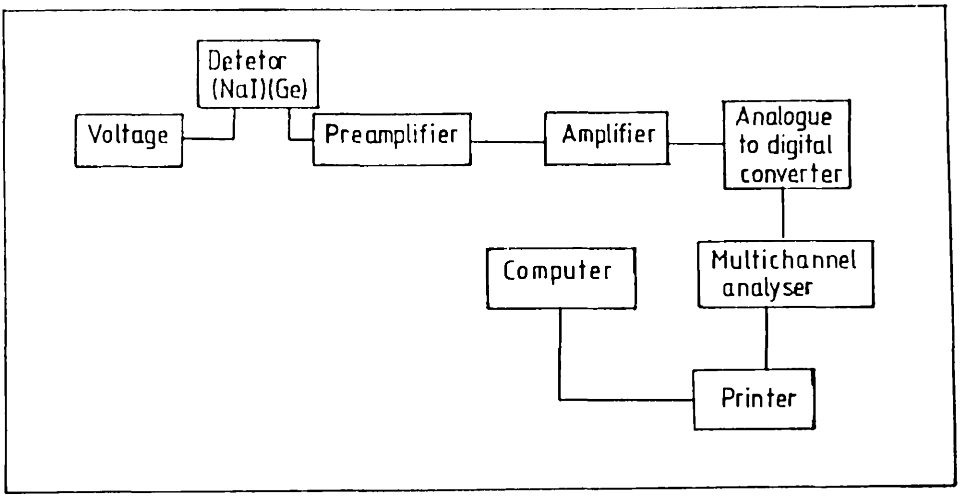


Figure 2.12: The main components of typical gamma spectroscopy systems.

ii) ^{95m}Tc tracer: A more convenient chemical yield tracer was found to be ^{95m}Tc. ^{95m}Tc was used to determine yields and to optimise procedures when examining environmental samples. In use, approximately 20 Bq of ^{95m}Tc was added to each sample and measured with a NaI detector. The radiochemical yield was calculated by comparing the γ-activity of the 204 keV photopeak in the final sample, with that in the initial spike. The result was used to correct the ^{99}Tc ICP-MS observations. The decay schemes of ^{99m}Tc and ^{95m}Tc are shown in Figure 2.13.

2.5 Tc LOSSES IN DIFFERENT STEPS OF THE PROCEDURE.

Methodology

When aqueous media with low concentrations of salts and acids were being analysed, ^{99}Tc was suitable as a tracer, but if the yield of Tc was required in other steps e.g. solvent extraction and in high concentrated acid or salt, then the γ-emitters ^{99m}Tc and ^{95m}Tc were used. ^{99}Tc was added only to blank samples (samples with no ^{99}Tc already present or to distilled water), while ^{99m}Tc or ^{95m}Tc tracers were added at the begining of each procedure. ^{95m}Tc was preferred for real samples as the radiochemical yield determinant. Tracers were used to determine the yields in steps involving anion-exchange, leaching/ashing, solvent extraction, precipitation and evaporation. During the work a number of observations were carried out.

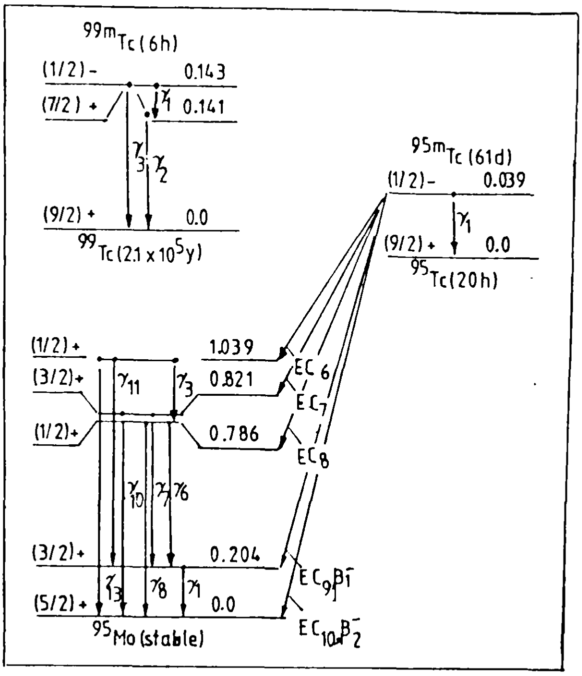


Figure 2.13: Decay schemes of ^{99m}Tc and ^{95m}Tc (ICRP, 1983).

Discussions

Individual steps are discussed in detail in earlier sections. The losses of different steps are summarised here for comparison.

Typical average losses for the various steps in the procedure are tabulated in Table 2.20. The results are reported with their standard deviation and the number of observations (n). The losses were dependent on many

Sr.No.	Process	% Tc loss ± σ (no. of obs.)
	Anion exchange resin process:	
1.	Not retained onto resin	0.36 ± 0.17 (4)
2.	Not eluted from the resin	7.5 ± 3.2 (41)
3.	In NaOH washing of column	3.0 ± 1.0 (11)
4.	Loss during evaporation from 12M HNO_3	5.4 ± 3.1 (10)
5.	Loss during whole anion exchange step	9.5 ± 3.8 (4)
	Solvent extraction process:	
6.	Not extracted with cyclohexanone from aqueous phase	4.1 ± 1.6 (5)
7.	Loss during washing of cyclohexanone	1.38 ± 0.03 (3)
8.	Not back extracted from cyclohexanone	3.36 (1)
9.	Not extracted with 5% TIOA-xylene from aqueous phase	5.9 ± 6.0 (25)
10.	Loss during TIOA-xylene washing step	3.3 ± 2.0 (16)
	Other processes:	
11.	During cation exchange washing step	4.1 ± 1.8 (3)
12.	Loss during evaporation from distilled water	0.74 ± 0.06 (2)
13.	Loss during washing (soil)	23.5 ± 3.8 (2)
14.	During leaching, filtration and then evaporation to 50 cm^3 of: i) Soil sample	8.09 ± 0.48 (2)
	ii) Seaweeds sample	5.4 ± 3.1 (12)

TABLE 2.20: % Tc losses during different processes.

factors, for example the time required for the step, the exact amount of the reagents used, the exact method used for the step (e.g. shaking by hand, magnetic stirrer or flask shaker etc). Various other parameters (e.g. pH, heating, design of glassware etc), detector efficiency, laboratory conditions and experience also contributed to losses. Clearly a knowledge of the loss in each step was very important, so that if care was taken on the basis of experience then losses could be minimized.

In summary, throughout the practical work care was taken to achieve minimum Tc losses. The results of the percentage losses of Tc obtained by measuring ^{99}Tc, ^{99m}Tc or ^{95m}Tc in various steps are in good agreement with the results of Foti et al. (1972); Anderson & Walker (1980) and Chen et al. (1989).

2.6 CHEMICAL RECOVERIES OF APPLIED PROCEDURES.

With the aim: "To determine ^{99}Tc in environmental samples" established, attention was paid to the question of the most suitable procedure or procedures to be employed for the required determinations. Faced with such a problem, it was necessary to seek guidance by consulting published procedures. The resulting literature survey lead to the compilation of a list of possible procedures. It was found that many procedures for the measurement of the ^{99}Tc were available, but as expected, almost all of them were optimised for techniques other than ICP-MS.

Methods and chemical yields of applied procedures.

Different procedures in the literature have been modified for the analyses of ^{99}Tc by ICP-MS. The details of the procedures developed along with their percentage chemical yields are given Table 2.21.

S.No.	**Procedure**	**Tracer, %ch.rec. (no. of obs.)**
1.	Water samples → anion exchange resin → CCl_4 extraction → 2M H_2SO_4-NaOCl boiling → cyclohexanone/cyclohexane extract. → AgCl precipitation → 5% TIOA-xylene extraction → anion exch. resin.	^{99}Tc, 67 ± 15 (7)
2.	Water samples → 2M H_2SO_4 → CCl_4 ext. → 2M H_2SO_4-NaOCl boiling → cyclohexanone/cyclohexane ext. → AgCl pptn. → 5% TIOA-xylene → anion exch. resin.	^{99}Tc, 78.2 ± 5.3 (3)
3.	Water samples → anion exch. resin and washing column with 1M NaOH → evapora-	^{99}Tc, 74.0 ± 8.3

	tion of eluate → 2M H_2SO_4-NaOCl boiling → CCl_4 ext. → cyclohexanone/cyclohexane ext. → anion exch. resin.	(2) ^{95m}Tc, 79.90 (1)
4.	Water samples → + 6M NaOH → boiling + methanol → cooling, then filtration → anion exch. resin.	^{99}Tc, 83 ± 12 (3)
5.	Water samples → + NH_4OH → boiling + methanol → cooling, then filtration → anion exch. resin.	^{99}Tc, 57.95 (1)
6.	Seaweeds → + HCl and overnight drying → ashing at 600°C (fresh air) → 2M H_2SO_4 → CCl_4 ext. → 2M H_2SO_4-NaOCl boiling → cyclohexanone/cyclohexane ext. → AgCl pricipitation → 5% TIOA-xylene ext. → anion exch. resin.	^{99}Tc, 16.11±0.49 (3)
7.	Seaweeds → leaching in 9M HNO_3 → filtration and evaporation → making 2M in H_2SO_4 → CCl_4 ext. → 2M H_2SO_4-NaOCl boiling → cyclohexanone/cyclohexane ext. → AgCl pricipitation → 5% TIOA-xylene ext. → anion exch. resin.	^{99}Tc, 70 ± 11 (4)
8.	Seaweeds → ashing at 600°C by fusing with Na_2O_2 → precipitation of Ni & Fe by NaOH → anion exch. resin → cation exch. resin → cyclohexanone/cyclohexane ext. → chloform extraction.	^{99}Tc, 9.6 ± 1.7 (3)
9.	Seaweeds → leaching in 9M HNO_3 → filtration and evaporation → making 2M H_2SO_4-NaOCl boiling → 5% TIOA-xylene ext. → anion exch. resin and washing the column with 1M NaOH → Tc elution.	^{95m}Tc, 76 ± 12 (13)
10.	Soil → leaching in 9M HNO_3 → filtration and evaporation → CCl_4 ext. → 2M H_2SO_4-NaOCl boiling → cyclohexanone/cyclohexane ext. →AgCl pricipitation → 5% TIOA-xylene ext. → anion exch. resin.	^{95m}Tc, 18.8 ± 1.9 (2)
11.	Soil → leaching in 9M HNO_3 → ext. → anion exch. resin and washing the column with 1M NaOH → Tc elution.	^{95m}Tc, 79.33 (1)
12.	Soil → ashing at 600°C → 3M H_2SO_4-NaOCl boiling → 5% TIOA-xylene ext. → anion exch. resin and washing the column with 1M NaOH → Tc elution.	^{95m}Tc, 66 ± 1.3 (2)

TABLE 2.21:Percent chemical recoveries for different procedures.

Discussion and comparison of different procedures.

Keeping in view, the low specific activity, Ru interferences and the instrument (ICP-MS) requirements, various methods were modified and combined. From the information surveyed, combinations and modifications of different steps were utilised for the present work. The purpose of the present work was to optimise a procedure, for high chemical yield, good precision and effective decontamination of the interfering reagents, for environmental samples. Effort was made to devise a procedure which could be applied to all types of environmental samples for analysis by ICP-MS.

The observations obtained from this exercise are mentioned here. Anion exchange, leaching and ashing were selected for initial pretreatment of water, biota and soil samples respectively. The choice and selection of these steps for the different media were made on the basis of high chemical recovery of Tc and effective preconcentration steps compared to others.

Ashing of biota samples was not feasible due to the large losses of Tc at high temperature, although the ashing was done in the presence of fresh air as well as in the presence of HCl or NH_3 as suggested by some workers. Digestion of algae samples was not good as it was expected that complete leaching might not be achieved. Fusing ashed samples with Na_2O_2 gave residues which were not easy to dissolve in HCl and this caused a significant problem. The chemical recovery from refluxed leaching of soil samples was very low, probably due to organic material in the soil media not being destroyed. In comparison, the yield from the ashing of soils was good.

Second priority was given to the separation of interfering substances. In analytical separations the object was to reduce the concentration of the interference to a level of negligible influence without significant loss of the analyte material of interest (Tc). The separation of the interfering reagents is described in section 2.3.3 which covers the decontamination from Ru. Separation from other substances (e.g. Fe, Ag etc) was also necessary for efficient and low background analysis.

In most cases, anion exchange was applied at the end of each procedure to reduce the salt concentration and give the required form for ICP-MS analysis as described earlier.

2.7 INTERCOMPARISON STUDIES.

The effectiveness and accuracy of chemical separation and concentration methods can be confirmed by the analysis of known standard materials. The absolute requirements for such standards include: (i) the concentration must be known to the required degree of accuracy; (ii) the material must be homogeneous in the smallest aliquot to be used commensurate with the accuracy desired; (iii) the material must contain similar matrices or interferences to the samples which cause difficulties or biases in the analytical method and; finally, (iv) the material must be chemically stable and physically reproducible.

In the present study two intercomparison reference materials were analysed. The first of these was a marine algal material "AG-B-1", the brown alga, Fucus vesiculosus, obtained from the International Atomic Energy Agency (IAEA), Vienna, Austria (IAEA, 1985).

The second reference material was also Fucus vesiculosus which had been harvested off the Sellafield coast in 1985 and prepared in the Bioanalytical Chemistry Laboratories of British Nuclear Fuels plc (BNFL) at the Sellafield nuclear complex (Bates, 1988).

From the IAEA algae samples 20-25 g samples were taken for analysis while from BNFL samples < 1 g samples for method I and < 0.1 g samples for method II were taken respectively.

Results of this work and comparison with published results.

By using ICP-MS, the results of ^{99}Tc obtained for both the refernce materials (for both the methods) along with the certified values of other laboratories are given in Tables 2.22 & 2.23.

IAEA Marine Alga Sample, AG-B-1: The average results of 12.5 and 12.55 mBq g^{-1} from both the methods are higher than the mean value of 11.5 mBq g^{-1} of the published results but lie within the range i.e. 11.1-14.7.

Lab Code No.	**^{99}Tc, mBq g^{-1} (no. of obs.)**
2	11.4 ± 0.5 (2)
5	11.1 ± 1.5 (5)
6	14.7 ± 0.2 (2)
27	13.3 ± 1.2
28	11.5 ± 1.5
Overall median of 2, 5 & 6 results, Md	11.5
Confidence interval ($\alpha = 0.05$)	11.1-14.7
Present work:	
Method I	12.5 ± 1.4 (5)
Method II	12.55 ± 1.5 (2)

TABLE 2.22: Intercomparison of ^{99}Tc measurements in IAEA Marine Alga Sample AG-B-I.

Lab	gms taken	method used	^{99}Tc Bq g^{-1} ± σ
1	2	Liquid scintillation spectrometry	4.54 ± 0.31
2	2	L.S. spectrometry	4.42 ± 0.20
3,A	2	β-counting	3.38 ± 0.25
B	1	Gas-flow Geiger counting	4.60 ± 0.43
4	1	β-counting	4.99 ± 0.19
5	2-3	ICP-MS	ca. 4.0
6	2-3	ICP-MS	<4.40
The overall mean (1-6 samples) =			4.64 ± 0.25
7*I	<1	ICP-MS	4.7
II	<0.1	ICP-MS	4.51 ± 0.45

* = Results of present work of Method I & II.

TABLE 2.23: Intercomparison studies of BNFL material.

BNFL intercomparison material: Only one observation was possible for method I. However, the results obtained from both the methods are in good agreement with the mean values (4.64 ± 0.25 Bq g^{-1}).

They clearly indicate that the present procedures and analyses are accurate and of high precision.

CHAPTER 3

ENVIRONMENTAL SAMPLES.

3.1 ANALYSIS OF ^{99}Tc IN ENVIRONMENTAL SAMPLES.

Having developed a successful procedure for the determination of ^{99}Tc by ICP-MS, attention was paid to the selection of appropriate sites for environmental sampling.

3.2. SOURCES OF ^{99}Tc IN THE ENVIRONMENT.

Reprocessing is the accepted chemical method for recovering U and Pu from spent fuel. The accepted industrial technique is called the Purex process and the liquid wastes generated by this contain mixed fission and activation products and transuranium nuclides. This part of the nuclear fuel cycle has given rise to the largest effluent discharges into the marine environment to date (Till, 1986 and Camplin & Aarkrog, 1989).

Several nuclear fuel reprocessing plants discharge mixed products to the sea at coastal locations in Western Europe and constitute significant sources of ^{99}Tc. The principal source of discharged fission products in the UK is the reprocessing plant at Sellafield which lies close to the town of Whitehaven in Cumbria on the eastern side of the Irish sea. Discharges from the site are made to the Irish sea via a pipeline which ends 2-4 km below the low-water mark out to sea. British Nuclear Fuels plc (BNFL), which operates the site, regularly publishes reports giving information on discharges and environmental monitoring. (Hunt, 1978-89). Figure 3.1 shows ^{99}Tc discharges in liquid effluents over the last eleven years from the Sellafield plant, UK.

Dounreay Nuclear Power Development Establishment (DNPDE) is located on the northern coast of Scotland near the town of Thurso. Low-level radioactive wastes from these operations are discharged to the Pentland Firth via a pipeline ending 600 m beyond high water mark under the authorisation of Scottish Development Department. The scale of reprocessing and other activities on the site results in levels of discharges to the sea which are considerably smaller than those from Sellafield (Camplin & Aarkrog, 1989).

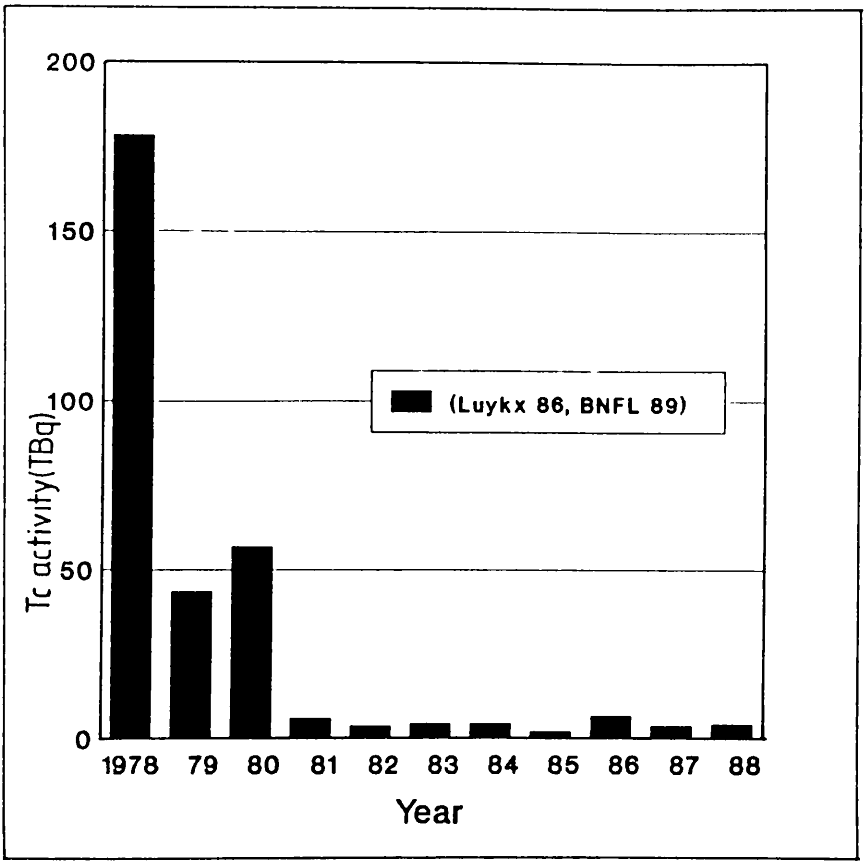


Figure 3.1: ^{99}Tc discharges in liquid effluents from Sellafield in TBq y^{-1}.

The reprocessing plant at Cap de la Hague is located on the Cherbourg peninsula of Northwestern France. Liquid effluents are discharged under authorisation from the

French Government to the English channel. The French reprocessing plant released 11.7 TBq ^{99}Tc to the sea in 1983. The plant at Marcoule in France discharges via the Rhone to the Mediterranean. The French and the German reprocessing plants were outside the remit of this study.

The releases of ^{99}Tc in liquid effluent from the enrichment plant at Capenhurst (UK) are small in comparison with reprocessing discharges. The enrichment plant at Capenhurst, has known releases of ^{99}Tc in liquid effluent for 1978 (2.6 GBq), 1979 (12.2 GBq), 1980 (11.5 GBq), 1981 (6.3 GBq), 1982 (20.4 GBq) and 1983 (3.4 GBq) (Luykx, 1986 and Camplin & Aarkrog, 1989).

From these sites technetium is released in a soluble form and the prevalent valence state of Tc in oxygenated seawater, the pertechnetate ion, TcO^-_4, represents the most likely form of this radioelement (Beasley & Lorz, 1986).

The Chernobyl Nuclear Power Station is a multi-reactor unit site. On Saturday 26 April 1986 at 01:23 local time, reactor 4 and the surrounding plant and building were destroyed by an explosion caused by a prompt critical power excursion which resulted in a massive release of active debris from the reactor core into the atmosphere. The first effect was noticed by Swedish Scientists at Forsmark on 28 April 1986. Atmospheric dispersion of fission products from the damaged core of reactor 4 caused fallout over large areas of Europe as well as in the immediate vicinity of the reactor. ^{99}Tc was among the products released.

3.3 ENVIRONMENTAL ^{99}Tc

Preliminary environmental analysis for ^{99}Tc has been carried out on samples from the marine ecosystem of the Northwest coast of England, West, North and East coast of Scotland, where excellent bioindicators (mainly the brown alga i.e

Fucus vesiculosus) exist and were collected for the determination of ^{99}Tc. The potential concentration ratio for Fucus(dry)/water of 30000-35000 (Rioseco, 1987) for radionuclides was the principal reason for choosing this material for sampling. On the South coast of Norway in 1981-2, the observed concentration ratios Fucus/water for Cs in the North Atlantic was ≈ 260 and for Tc ≈ 90000. The concentration ratio of Fucus/water in Fucus sample collected off the NE Scottish coast was 85000 and was 75000 in samples collected off the NW coast of Norway during the Swedish expedition in 1980, the ratio was 75000 (Holm et al. 1986). In the Baltic sea the ratio estimated was 44000 for lower salinity (≈8%) water. From the results of Riley and Siddique (1982) the concentration ratio for Fucus vesiculosus(dry)/water (at Cheshire, Irish sea) was approximately 4200. Holm et al. (1988) observed water concentrations of 0.108 Bq l^{-1} (Irish sea) in 1972 and Fucus vesiculosus concentration of 81.4 Bq g^{-1} (dry) at St. Bees, the ratio became very high i.e 750000. A special investigation on ^{99}Tc revealed that its concentration in Fucus samples from the Swedish East coast was very constant, 1.3 Bq kg^{-1} while on the Swedish West coast the concentration of ^{99}Tc was influenced by the inflow of water from the North sea and an increase in concentration from about 3 Bq kg^{-1} (1967-72) to 50-150 Bq kg^{-1} (1980) had been observed (IAEA, 1986).

Release of radioactive material from the Chernobyl accident led to widespread contamination in the Russia and over Europe especially Scandinavia, Italy, Greece and West Germany. Actual levels depended on a number of factors including the distance and direction from Chernobyl of the plume, rainfall during the passage of the radioactive cloud, ground deposition and local conditions such as topography. Small airborne particles are deposited on the ground by various mechanisms, but the most important is washout by rain (NRPB, 1986).

3.4 DETAILS OF ENVIRONMENTAL SAMPLES ANALYSED.

In 1989-90, seaweed samples were hand-picked from the following coastal areas: (i) the Northwest of England (off the Sellafield); (ii) the West coast of the Isle of Bute; (iii) the North of Scotland and the East of Scotland. The locations are shown in Figure 3.2. The samples were washed thoroughly in seawater and in tap water to remove detritus adhering to surfaces and then spread on trays for drying. The materials were ground by hand and finally homogenized by mixing in a food processor (Moulinex). To remove moisture, the samples were dried at 100°C for 24 hours in an oven.

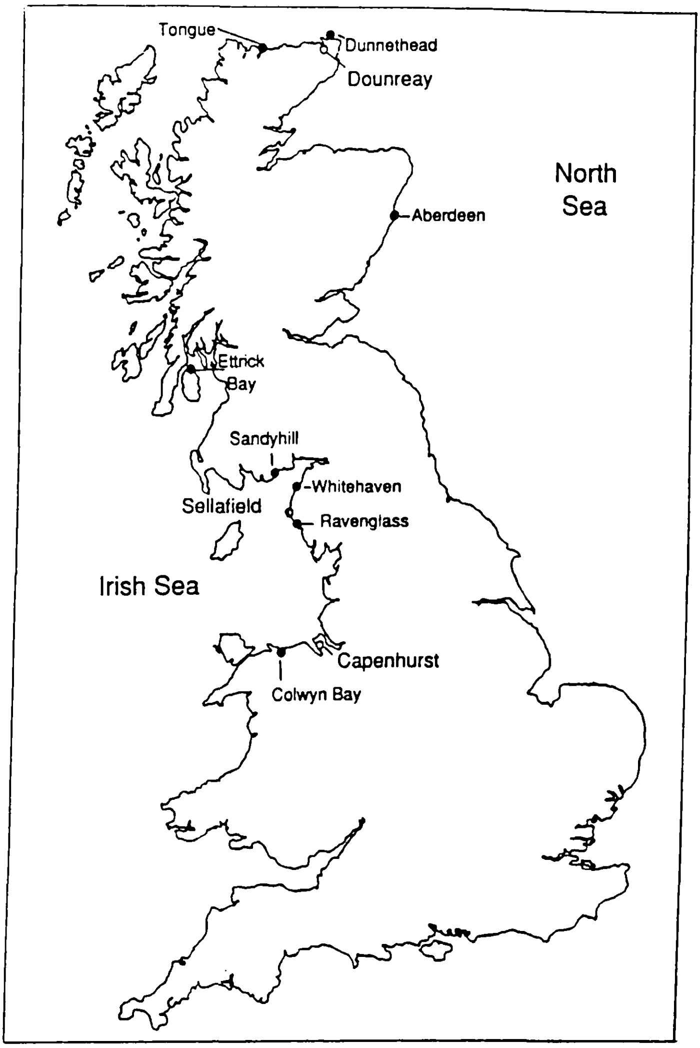


Figure 3.2: Sampling sites (UK).

A seawater sample was collected from Tongue in the North of Scotland (Figure 3.2) and pretreated by filtering through a 0.2 μm Whatman filter paper using gentle suction.

A sample of surface (0-5 cm) silt from an area approximately 40 cm x 40 cm, 10-15 m from the high-water mark from the Esk Estuary at Ravenglass (Figure 3.2) was collected by hand at low tide. This was then dried in an oven and passed through a 2 mm mesh sieve.

Environmental samples (lichen and moss) were collected from the "Forest of Miracles" (1 km East of the Chernobyl accident site) in 1989 and dried as above.

3.5 METHOD

The method used for the environmental samples is given in Chapter 2 (section 2.1).

All the samples were analysed in duplicate or triplicate and an average value taken with an accompanying error of 1σ. Each analysis was run for three times to obtain good statistics and to check the response of the instrument especially the nebuliser flow. A constant nebuliser flow was also confirmed by the use of an internal standard ^{103}Rh. Although a blank of 2% HNO_3 was always used, to ensure that there was no significant interference from ^{99}Ru from the last step of anion exchange, a special blank sample (blank passed through the resin) was also examined. This blank sample was prepared from the blank eluent. The spectrum of this blank showed no ^{99}Ru peak.

3.6 RESULTS AND DISCUSSIONS.

The results obtained for the determination of ^{99}Tc in various samples are given in Table 3.1.

Sample	Location	Date of sampling month/yr	Dry wt taken (gms)	^{99}Tc activity Bq g^{-1}(dry weight) ± S.D.
Fucus vesiculosus	Colwyn Bay	9/89	24	0.74 ± 0.05
″ ″	Ravenglass	10/89	25	10.18 ± 0.53
″ ″	Whitehaven	10/89	23	1.98 ± 0.06
″ ″	Sandyhill	10/89	24	1.78 ± 0.09
″ ″	Ettrick Bay	4/90	25	0.49 ± 0.04
″ ″	Tongue	4/90	24	0.14 ± 0.02
″ ″	Aberdeen	4/90	25	0.10 ± 0.02
Ascophyllum nodosum	Ettrick Bay	4/90	20	1.06 ± 0.31
Porphyra (Sloke)	Dounreay (Dunnethead)	7/90	5	<2.5 x 10^{-3}
Silt	Ravenglass	11/86	30	0.025 ± 0.001
Moss	Chernobyl*	10/89	1	<12.6 x 10^{-3}
Lichen	″	10/89	0.2	<63.0 x 10^{-3}
Water	Tongue	3/90	7.5**	<17 Bq l^{-1}

* Forest of Miracle
** litres

TABLE 3.1: ^{99}Tc determinations in environmental samples using ICP-MS.

3.6.1 WATER.

A sample of water was collected from Tongue in March 1990. The sample was run in duplicate (7.5 l filtered water for each run). Filtration through 0.2 μm filter paper was found to be difficult, even using suction and took a long time. On analysis, the level of activity was below the detection limit due to the low specific radioactivity and the distance (≈ 700 km) from Sellafield.

Although a definite result was not obtained, the sample was useful in providing a run on an experimental basis to check the procedure and determine the chemical yield by means of ^{95m}Tc tracer which was found to be satisfactory.

3.6.2 MIXED PORPHYRA (SLOKE).

The Porphyra was collected from Dunnethead, Dounreay in July 1990 and also gave no result for ^{99}Tc in the sample. The Porphyra species is not a good bioindicator compared to Fucus vesiculosus. From the results of Dutton and Ibbett (1973) and Hunt (1985 & 1989), the ^{99}Tc uptake ratio of Porphyra/ Fucus was found to be (1.6-2.0) x 10^{-3}. Dounreay is about 750 km away by sea from Sellafield. The liquid discharges from the Dounreay site are negligible compared to Sellafield. In summary, the low uptake of ^{99}Tc by Porphyra can probably be accounted for the distance from Sellafield and the small quantity of the material taken (≈ 5 g for each sample).

3.6.3 SILT (SOIL).

A very low but easily measurable activity of 25 mBq g^{-1} of ^{99}Tc was found in the Ravenglass silt sample collected near Sellafield in 1986 during the current study. By comparison, ^{99}Tc was also found by other workers in silt samples collected from Whitehaven (1982). The concentrations reported in the silt are 8 mBq g^{-1} (Whitehaven in 1982), 2.5 mBq g^{-1} (Hoylake, in the vicinity of Wirral, in 1986) and

5.4 mBq g^{-1} (Hoylake in 1986) (Hunt, 1982-86). According to the author, the ^{99}Tc concentrations in these areas are mainly due to Sellafield discharges. A value of 9.2 mBq g^{-1} (wet weight) for ^{99}Tc was obtained for Ravenglass silt by Pentreath et al. (1979).

The maximum activity of 7.0 ± 1.5 mBq g^{-1} ^{99}Tc in soil samples collected from Hanford Reservation (USA) was reported (Kaye et al, 1982). Although the ^{95m}Tc chemical yield for silt sample was satisfactory when compared to biota samples, but due to non-availability of standard reference materials for ^{99}Tc for soil, the exact leaching of ^{99}Tc could not be determined.

3.6.4 ASCOPHYLLUM NODOSUM.

In order to obtain a good comparison, it is desirable to use as many species as possible as bioindicators. Hence Ascophyllum nodosum and Porphyra in addition to Fucus vesiculosus were used in the present studies. The ratio of ^{99}Tc concentration of Ascophyllum nodosum to Fucus vesiculosus (2.18) is in good agreement with the value estimated (2.1 ± 0.4) by Holm et al. (1986) and a value of 2 by Rioseco (1987) while the ratio fluctuates between 1.4 to 2.4 in samples from St. Bees analysed by Hunt (1986-7). Activity ratio for Ascophyllum/water was about 50000 (Holm and Rioseco, 1987). Hence the ratio indicates the validity of the optimised procedure developed in the present work.

3.6.5 FUCUS VESICULOSUS.

Review of Fucus vesiculosus:- dilution, transit time etc.

The Irish sea in particular, due to Sellafield releases, has formed an interesting "natural laboratory" for studying radionuclide behaviour (Garcia-Leon, 1990).

^{99}Tc is in the form of pertechnetate, that is highly soluble in seawater, so it is widely and rapidly dispersed by tides and ocean currents. In contrast, the actinides are insoluble in that more than 90% of the radioactivity discharged becomes associated with particulate materials (Hetherington, 1975).

Aarkrog et al. (1986) concluded that ^{99}Tc can be used as a long distance (10^3-10^4 km) tracer for Sellafield effluents in Arctic waters with Fucus vesiculosus as the bioindicator. The transport time of 7 years from Sellafield to East Greenland was confirmed by ^{99}Tc. It was also shown by them that the levels of ^{99}Tc discharges began in about 1970 from Sellafield.

The activity concentration of ^{99}Tc in algae (Fucus vesiculosus) at different locations from Sellafield are given by Holm et al., 1986. A study of $^{239+240}$Pu and ^{241}Am/$^{239+240}$Pu in Fucus vesiculosus and Mytlus edulis as a function of distance from Sellafield along the Scottish coast was carried out by Hallstadius et al (1986). Holm et al. (1986) also plotted ^{99}Tc concentration in Fucus vesiculosus from different locations as a function of distance from Sellafield.

From the studies in seaweeds from Greenland waters, Aarkrog et al. (1986) considered the transfer factor for ^{99}Tc to be similar to ^{90}Sr, because both these nuclides are sedimented only to a very small extent and estimated the annual mean discharge rate of ^{99}Tc from Sellafield to be 0.04 PBq (1 Peta Bq = 10^{15} Bq) during the period 1970-7. The transfer factor for ^{99}Tc to Fucus in East greenland was estimated as 8-2/0.04 = 150 Bq kg^{-1} per PBq y^{-1} and in West Greenland at 3.7-2/0.04 = 40 Bq kg^{-1} per PBq y^{-1}, whereas 2 Bq ^{99}Tc kg^{-1} Fucus was the fallout background in these calculations. The results of ^{99}Tc analyses in seaweed from East Greenland have confirmed the transport times and dilution factors calculated from ^{137}Cs. Aarkrog et al. (1984) suggested that Sellafield ^{99}Tc can be traced even to West Greenland.

Holm et al. (1988) studied the transport of ^{99}Tc by water ways over a long distance of 7000 km using Fucus in temperate and arctic regions of the North Atlantic and the Baltic sea during 1981-1984. Radiocaesium transport from the Irish sea via the North sea and the Norwegian coastal current to East Greenland over 7000 km was studied by Dahlgaard et al. (1986). Kautsky (1979) has estimated the mean transport time of artificial radioisotopes from Sellafield to the Pentland Firth to be 2 years while Jefferies et al. (1982) estimate the transport time for ^{137}Cs from Sellafield to the North channel as 1 year and Livingston et al. (1982) give a transit time, from Sellafield to the North sea, of 3 years. The transit time from the Sellafield to Sardal is about 4 years (Holm et al., 1986)

From a comparison of the ratios of ^{99}Tc to ^{137}Cs in the Irish sea in November 1978, it is suggested by Pentreath et al. (1979) that the ^{99}Tc discharged remains waterborne to a greater extent than ^{137}Cs and ^{99}Tc remains available for accumulation over a greater distance than does ^{137}Cs.

Dahlgaard et al. (1986) suggested that results for ^{99}Tc in seaweed (Fucus) may give more information than that already obtained from radiocaesium, since the ratios between Sellafield discharges and fallout background are higher for ^{99}Tc compared to ^{137}Cs. ^{99}Tc has a high concentration factor in Fucus ($\approx 10^5$ Bq kg^{-1} dry per Bq l^{-1}), and this nuclide is easily measured in spite of its low discharge ratio relative to ^{137}Cs.

Holm et al. (1986) observed a maximum ^{99}Tc concentration in Fucus during winter and minimum values during summer. An explanation, given by them, for this is the higher inflow of contaminated water from the North sea during winter and the higher outflow from the Baltic sea during spring-summer.

The concentration ratio Fucus/water is enhanced for ^{137}Cs but not for ^{99}Tc in low salinity. The Tc/Cs activity ratio in the water is expected to be higher than for integrated fallout due to longer residence time in water of Tc than Cs. The variation of ^{99}Tc/^{137}Cs may be used to calculate transport times or differences in biological removal or sedimentation between Tc and Cs. The activity ratio ^{99}Tc/^{137}Cs in the Baltic sea water (surface) was (4-5) x 10^{-3} which is 20 times higher than in integrated fallout (Holm et al., 1986).

Seaweeds are considered to be a source of human nutrition, containing protein, carbohydrates, vitamins, minerals and trace elements. The use of edible seaweeds is common in Japan. As a complete diet, it is becoming more popular in the UK (McDonald et al. 1990).

Results and discussion of Fucus vesiculosus samples.

Fucus vesiculosus was selected for many sites as it is well known bioindicator for various radionuclides including technetium. The main aim was to study the Sellafield-derived ^{99}Tc activity in edible seaweeds and subsequently to comment on the behaviour of this radionuclide in the sea.

The seven results for Fucus vesiculosus can be examined as a set. They are tabulated in Table 3.1 and shown in Figure 3.3 in which their approximate distances from Sellafield are given. It can be seen that there is a correlation between ^{99}Tc concentration and distance from the plant. One of these samples is from the Colwyn Bay which is

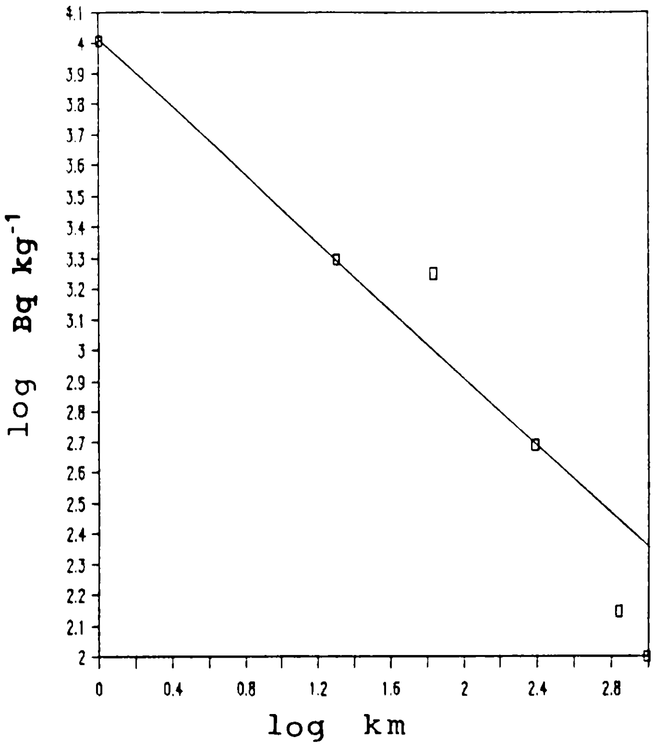


Figure 3.3: ^{99}Tc concentration in Fucus vesiculosus as a function of distance from Sellafield.

approximately 125 km to the South of Sellafield while the others are to the North. Looking the results of ^{99}Tc from present studies it is clear that the flow of water is towards northwards. Although the Colwyn Bay (south of Sellafield) site shows high activity, but it is smallar than the north sites (i.e Sandyhill, Whitehaven and Ettrick Bay) when compared with equal distance.

Sample from Colwyn Bay showing ^{99}Tc activity, may be explained by two reasons. Firstly, the Capenhurst enrichment plant may also contribute towards ^{99}Tc activity. Secondly, due to the water movement in the Irish sea, Sellafield discharges may also disperse towards south. The influence of the French reprocessing facility at Cap de la Hague may be neglected for present studies in Irish, Scottish and North sea samples. Also, ^{99}Tc values found in Fucus species collected from the coast in the vicinity of the French nuclear fuel reprocessing plant, are two orders of magnitude less than those in the Sellafield area in the

Irish sea (Jeanmaire et al., 1981). Finally, installations at Dounreay, may have a significant effect on the local environment but in comparison with Sellafield sources, the impact around Dounreay is negligible.

The activity of ^{99}Tc measured by Hunt (1989) in Fucus vesiculosus was 1.90 Bq g^{-1} (wet) or 9.50 Bq g^{-1} (dry). The sample was collected in 1988 at Sellafield. By comparing it with the activity of 10.18 Bq g^{-1} obtained from the present work in a Ravenglass sample of 1989, it can be concluded that the ^{99}Tc activity discharged to the sea during 1989 is almost the same as in 1988, although it is difficult to compare the two results directly because of the different methods of reporting, sampling locations and the methods applied.

The salinity of water in percentage at different locations is: 31.10 (Colwyn Bay), 32.36 (Ravenglass), 32.32 (Whitehaven), 30.41 (Sandyhill), 32.01 (Tongue) and 33.99 (Aberdeen) (Mcdonald et al., 1991). The concentration ratio Fucus/water for ^{99}Tc is not affected with low salinity (Holm et al., 1986).

The results of ^{137}Cs and $^{239+240}$Pu obtained by McDonald et al. (1991) for Fucus vesiculosus along with the ^{99}Tc results are given in Table 3.2. Clearly, it is observed from the comparison that the Tc values are in good agreement with the trend of Cs and Pu values. It is observed that Ascophyllum nodosum concentrates Tc twice as efficiently as Fucus vesiculosus and Porphyra is not a good bioindicator for Tc. The ^{99}Tc/^{137}Cs ratios do not change very much over a wide distance while ^{99}Tc/$^{239+240}$Pu ratios increase with distance (Table 3.3). It is concluded that Cs like Tc may be soluble and can be dispersed over a long distance while Pu may not be as readily dispersed.

The "half-distance" (i.e. the distance of transport by which the ^{99}Tc concentration has been reduced by half) from Sellafield along the English coast is ≈ 10 km while on the Scottish North-west coast (Between Ettrick Bay and Tongue) it is ≈ 225 km. The half-distance of Sellafield Pu along the Scottish west coast was estimated to be about 260 km and the corresponding removal half-life to be 8-10 months. The half-distance for Am was about 100 km with a removal half-life of 3-4 months along the same coast, i.e. a residence time of 4-6 months. The half-distance in itself is a function of dilution as well as actual removal (Hallstadius et al., 1986).

Site	^{137}**Cs** Bq kg^{-1}	$^{239+240}$**Pu** Bq kg^{-1}	^{99}**Tc** Bq kg^{-1}
Ravenglass	274 ± 5	214 ± 8	10180 ± 530
Whitehaven	131 ± 3	27.2 ± 3.8	1980 ± 60
Sandyhill	133 ± 3	38.7 ± 7.4	1780 ± 90
Tongue	4.5 ± 1.7	0.85 ± 0.01	140 ± 20
Aberdeen	3.3 ± 1.4	0.79 ± 0.19	100 ± 20
Colwyn Bay	50 ± 4	6.15 ± 0.82	740 ± 50

TABLE 3.2: Activity levels of ^{137}Cs, $^{239+240}$Pu and ^{99}Tc in Fucus vesiculosus.

Site	^{99}**Tc/**^{137}**Cs**	^{99}**Tc/**$^{239+240}$**Pu**
Ravenglass	37	48
Whitehaven	15	73
Sandyhill	13	46
Tongue	31	165
Aberdeen	30	127
Colwyn Bay	15	120

TABLE 3.3: Tc/Cs and Tc/Pu ratios in Fucus vesiculosus.

3.6.6 LICHEN AND MOSS.

Literature review.

It is well known that slowly growing lichen of the Cladonia family have the ability to retain various radionuclides from atmospheric fallout. Lichens are a food for reindeer during winter. Lapps who are engaged in reindeer breeding consume considerable amounts of reindeer meat and thus radionuclides deposited onto lichen can be transferred to both reindeer and man (Holm & Rioseco, 1987).

By measurement of ^{99}Tc in 1972 from integrated deposition, a value of 540 ± 100 mBq m^{-2} was obtained by Rioseco (1987) which was in good agreement with the value estimated from the deposition, migration and annual variation of ^{99}Tc fallout in Lichen carpet collected in Central Sweden (1961-1971) which had a value of 500 ± 50 mBq m^{-2} (Holm et al., 1988). It was found to be: 15% from the deposition in lichen, 7% in the gelatinous layer of decomposed plant material and 78% in the soil. The 15% was a representative value since the average integrated deposition from 1961 to 1975 was 80 ± 14 mBq m^{-2}, i.e. 15 ± 2.6%.

Once on the lichen plant, the highly soluble pertechnetate is readily transported to the soil. In the plant, a fraction of the TcO^-_4 is probably transformed into the less mobile and insoluble TcO_2 or related hydrated forms or actively taken up by some metabolic process (Rioseco, 1987).

A review of the literature shows that moss has not been studied in the same detail as lichen.

Results and discussion.

Two samples of lichen and moss from a place called "The

Forest of Miracles" approximately 1 km to the East of the Chernobyl site were found to be below the detection limit for ^{99}Tc. Although the samples were collected 31/2 years after the Chernobyl accident, there was the possibility that ^{99}Tc remained representative of the initial deposition. A factor which might explain the inability to observe ^{99}Tc was that only small quantities of each sample were available for analysis.

The main contribution to contamination in plants/vegetation (i.e. lichen and moss) during the dynamic transient of the Chernobyl accident was by direct deposition on exposed surfaces; and due to continuous growth and death of plants and changes in the chemical states of the radionuclide in question, ^{99}Tc might have been transported from the sample. ^{99}Tc as pertechnetate is very soluble and mobile in the soil, it might have penetrated deep by into the soil surface. There were no other data available for ^{99}Tc concentrations in the environment following the Chernobyl accident, so that it is difficult to discuss the result in greater detail.

3.7 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.

A radiochemical procedure has been optimised for the determination of ^{99}Tc using ICP-MS for analysis. By comparing it, to other procedures available in the literature, it has been found to be practical and effective. The chief features of the procedure are:

- the ability to utilise available apparatus
- the need for only straight-forward manipulation techniques
- low limits of detection for environmental samples can be achieved
- adequate chemical recoveries can be achieved
- a variety of environmental sample materials can be

handled
- high decontamination factors for interferences can be obtained
- satisfactory working of the procedure has been established from intercomparison studies

Once the procedure was optimised, the second priority was focussed on the selection of suitable sites. As the Sellafield reprocessing plant, discharges ^{99}Tc into the Irish sea, particular attention was paid to the ecosystem in its vicinity. In summary, the results of the present study represent some of the first recorded ^{99}Tc data for seaweeds and other environmental samples by ICP-MS analysis. Ascophyllum is found to concentrate technetium twice as efficiently as Fucus and Porphyra is a poor bioindicator. The results for Fucus vesiculosus are in good agreement with MAFF reports obtained by β-counting.

After the optimisation of the procedure for the determination of ^{99}Tc to meet the high purity requirements of ICP-MS, and handle the low specific radioactivity found in environmental samples, this procedure has been successfully applied to ^{99}Tc analysis. A range of sample has been examined in a limited way and the analysis of the following samples is recommended for future work:

a. Large quantity seawater samples from various locations, starting from Sellafield moving round the coasts to the North sea, to be analysed in order to get a picture of the dispersion of the radionuclide.
b. Seaweeds samples should be analysed and compared with the seawater results.
c. Fish and other organisms should be analysed.
d. The analysis of all types of samples around the reprocessing plants and around the other sources will be helpful, in assessing the importance of the collective long-term dose.

A new sample introduction system for ICP-MS the electrothermal vaporisation (ETV) furnace, will probably be extremely useful to improve the performance of the system as it could offer an increase of up to 100 times in sensitivity. Recently an ETV unit was installed at the SURRC but was not used for the determination of ^{99}Tc in the present study. Because of the improved sensitivity much lower limits down to concentrations of for example, sub ppt levels should be possible and much smaller sample volumes (50 μl) adequate for analysis.

CHAPTER 4

CARBON-14

4.1 INTRODUCTION AND AIM.

Carbon (C) plays a crucial role in all forms of life. It takes part in biological and biochemical processes on earth, appearing in the structural framework of all organic materials. The long lived radioactive isotope of carbon, namely ^{14}C, is a soft β-emitter with half-life of 5730 years (Lederer et al., 1978).

The problem addressed in the present work was the measurement of environmental ^{14}C contamination in the air from a low power training reactor namely, that at the Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow. In relation to the measurements made in this work it is relevant to review the properties, sources and behaviour of ^{14}C in the biosphere and this is done in the following sections.

4.2 PROPERTIES OF CARBON.

Only 4.1 x 10^{19} g, out of total earth carbon of 1.6 x 10^{24} g, is exchangeable throughout the atmosphere, the oceans, and the biosphere. About 95% of the exchangeable carbon with which airborne ^{14}C interacts resides in the oceans. Almost all of the C is in the form of carbon dioxide (CO_2) in the atmosphere; globally, < 1% is in the form of carbon monoxide (CO), methane, formaldehyde, and other molecules. As mentioned, carbon occurs in nature as more than one isotope and details are listed in Table 4.1 (NCRP, 1985). The nuclide mass has been defined internationally by assigning to the carbon isotope $^{12}_{6}C$ a mass of 12.00 u.

The carbon isotope of mass number 14 was first prepared in the laboratory by bombarding a graphite, enriched in ^{13}C, with low energy (3 to 4 Mev) deutrons (Ruben & Kamen, 1941) and was later identified in nature by Libby et al. (1955). ^{14}C decays to ^{14}N by emission of a β-particle with a maximum energy of 0.156 Mev (100%) and an average energy of 0.045 Mev (Lederer et al., 1978). The decay equation is:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta + \nu^{-}$$

Isotope	**Isotopic mass (^{12}C = 12.00000)**	**Decay mode**	**Maximum energy (MeV)**	**Half-life**	**Natural abundance (%)**
^{10}C	10.01700	β^+	1.9	191 s	-
^{11}C	11.01114	β^+	0.98	20.4 min	-
^{12}C	12.00000	stable	-	-	98.89
^{13}C	13.00335	stable	-	-	1.11
^{14}C	14.00324	β^-	0.156	5730 y	10^{-10}
^{15}C	15.00940	β^-, γ	9.8 5.3	2.3 s	-
^{16}C	16.00963	-		0.74 s	

TABLE 4.1: Properties of carbon isotopes.

4.3 SOURCES OF ^{14}C.

4.3.1 NATURAL SOURCES OF ^{14}C.

The formation of ^{14}C in the atmosphere was first postulated by Libby (1946) through the interaction of cosmic ray neutron with atmospheric nitrogen as ^{14}N (n,p) ^{14}C and its existance was confirmed by Anderson et al. (1947). The production rate of cosmogenic ^{14}C is dependent on the cosmic ray flux and energy spectrum. The secondary neutrons and natural ^{14}C increase with altitude and reach a maximum at a pressure altitude of between 120 to 75 millibar (15-18 km). Due to the distribution of the mass of air with height, half of the natural ^{14}C resides in the stratosphere and half in the troposphere (NCRP, 1985). After production, ^{14}C is rapidly oxidised to $^{14}CO_2$ and becomes dispersed amongst the various reservoirs of the global carbon cycle (McCartney, 1987) as shown in Figure 4.1.

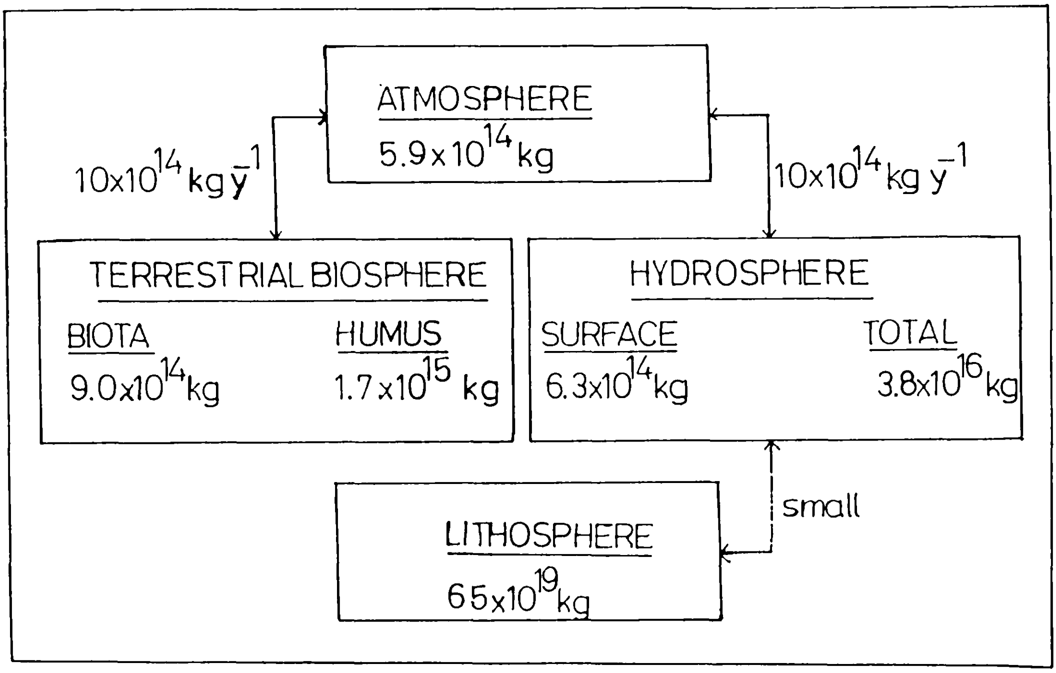


Figure 4.1: The global carbon distribution.

According to MacKay et al. (1963) the main product of cosmogenic ^{14}C oxidation is initially ^{14}CO. The appearance of ^{14}C in methane and other hydrocarbons in ground level air shows some exchange of carbon atoms among various molecules. Since CO and hydrocarbons are formed from fossil fuel combustion, the fraction of manmade pollutants can be estimated from the ^{14}C activity in the gas (Currie & Klouda, 1982).

4.3.2 ARTIFICIAL SOURCES OF ^{14}C.

Approximately 3.55 x 10^5 TBq of ^{14}C (as CO_2, the only detectable form) have been released into the atmosphere through the testing of nuclear weapons (Machta et al., 1963). ^{14}C is generated in nuclear power reactors from absorption of neutrons by C, N ,or O which may be present as fuel, moderator, coolant, core construction material or impurities. Details of neutrons-induced reactions and across sections are given in Table 4.2.

Reaction	**Natural isotopic ab.target elements (%)**	**Neutron capture cross-section (barns)**	
		Thermal neutrons	**Fast neutrons**
$^{13}C(n,\gamma)^{14}C$	1.108	1.0×10^{-3}	5.0×10^{-7}
$^{14}N(n,p)^{14}C$	99.635	1.8	1.3×10^{-2}
$^{15}N(n,d)^{14}C$	0.365	small	1.0×10^{-3}
$^{16}O(n,^{3}He)^{14}C$	99.759	small	3.0×10^{-8}
$^{17}O(n,\alpha)^{14}C$	0.037	2.4×10^{-1}	1.2×10^{-4}

TABLE 4.2: Possible reactions for producing ^{14}C.

Carbon and oxygen can occur in the coolant (H_2O and CO_2), moderator (graphite and H_2O) or in the fuel (UO_2). ^{14}N is the major contributor to ^{14}C production because of its high neutron capture cross-section and high isotope abundance in natural nitrogen. Nitrogen can be present as an impurity in the fuel or in the structural material. In the graphite-moderated reactor ^{13}C (n,γ) ^{14}C is as important as the ^{14}N (n,p) ^{14}C reaction. It is thought likely that, sometime in the future, nuclear fusion reactors will become a major energy source. A relatively high production rate of ^{14}C of $\approx$ 100 TBq y^{-1} is expected and a smaller amount of $\approx$ 1.3 TBq y^{-1} may be released to the atmosphere from such reactors (McCartney, 1987).

Clearly the production rates of different reactions depend upon:

(a) the neutron flux,

(b) the neutron capture cross-section of the atom at a particular neutron energy,

(c) the amount of the target element present in the different reactor components, and
(d) the abundance of isotopes in the target elements.

To simplify the estimation of ^{14}C releases from nuclear power plants, the different reactors can be categorized into four general types, the detail of each type is given below:

Light Water Reactors-including PWRs and BWRs.

The ^{14}C from Boiling Water Reactor (BWR) is released in the CO_2 (95%) form, CO (2.5%) and hydrocarbons (12.5) whereas from Pressurised Water Reactor (PWR), generally only 10% of the ^{14}C is in the form of CO_2, the rest being CO, methane and other hydrocarbons. In some PWR's the CO_2-bond ^{14}C activity is ≈ 30%. About 0.6 TBq $(GW(e)y)^{-1}$ ^{14}C is released from BWR fuel at the Karlsruhe reprocessing plant and only 0.12% of total emission of ^{14}C is not in the chemical form of CO_2 (Schwibach et al., 1978). A summary of the production of ^{14}C from various target materials is given in Table 4.3.

Reactor type	**Formation matrix**	**Sources of formation**	**^{14}C $TBq(GWe)^{-1}y^{-1}$**
PWR	Fuel	O_2	0.15
		N	0.59
	Cooling water	O_2	0.22
		N_2 (dissolved)	0.04-0.19
		N (added)	0.11
	Core hardware	N (impurity)	1.11-1.59)
BWR	Fuel	O_2	0.15
		N	0.59
	Cooling water	O_2	0.22
		N_2 (dissolved)	<0.04
	Core hardware	N (impurity)	1.92-2.66

TABLE 4.3: ^{14}C formation in PWR and BWR (NCRP, 1985).

The global inventory (between 1975 and 2000) of ^{14}C produced by the nuclear power industry will be 10% of that from weapons testing, and only 0.3% of the natural ^{14}C level (Hays & MacMurdo, 1977). The production rates of ^{14}C from LWRs estimated by different workers are tabulated in Table 4.4.

Ref	**PWR**		**BWR**	
	Fuel Coolant,1 moderator,2		**Fuel Coolant,1 moderator,2**	
	1	**2**	**1**	**2**
Hays & MacMurdo (1975)	0.4	0.1	1.2	0.4
Kelly et al. (1975)	0.5	0.2	0.5	0.6
Fowler et al. (1976)	0.8	0.1	0.8	0.3
United Nations (1977)	0.4	0.2	0.6	0.3
Davis (1979)	0.7	0.2	0.8	0.2
Bonka (1980)	0.5	0.3	0.4	0.2
Average	0.6	0.2	0.7	0.3

TABLE 4.4: ^{14}C production in LWRs [TBq (GW(e))$^{-1}$y^{-1})] (McCartney, 1987).

Fast Reactors-mainly LMFBRs.

Presently most fast reactors are Liquid Metal Fast Breeder Reactors (LMFBR) which utilize sodium as the coolant. The

Reference	**Fuel**	**Fuel cladding**
Davis (1979)	0.2	0.5
Bonka (1981)	0.2	0.3
Bush et al. (1983)	0.2	0.7
Average	0.2	0.5

TABLE 4.5: ^{14}C production in LMFBR [TBq (GW(e))$^{-1}$y^{-1})] (McCartney, 1987).

production of ^{14}C in a LMFBR originating from fuel and cladding is given in Table 4.5. The generation from coolant and structural materials is small.

The Cinch River Breeder Reactor (CRBR) is a specific type of LMFBR. This reactor is designed to use a mixed oxide fuel (U and Pu) and the primary structural material of the core is composed of stainless steel. The production rate of ^{14}C in CRBR is given in Table 4.6.

Location	**Source**	**Production in core** $[TBq\ (GW(e))^{-1}y^{-1}]$
Fuel	O	0.005
	N	0.226
Core hardware	N (impurity)	0.474

TABLE 4.6: ^{14}C production in LMFBR (CRBR) **(NCRP, 1985).**

Possibilities are that in the future carbide and nitride fuels will be used in LMFBRs because of their high fissile densities, improved breeding ratios and high thermal conductivities. These would give rise to ^{14}C production rates of 11.1 and 5900 TBq $(GW(e)y)^{-1}$ for carbide fuel and nitride fuel respectively (Till et al., 1976).

Graphite Moderated Reactors-primarily Gas Cooled and High Temperature Gas Cooled Reactors.

The Gas Cooled Reactor (GCR or MAGNOX) uses natural U metal canned in a Mg alloy (Magnox) and the reactor core is moderated by graphite and cooled by CO_2. This reactor type was the initial basis of the UK nuclear energy programme. The Advanced Gas Cooled Reactor (AGR) is similar to MAGNOX except that it utilises enriched UO_2 fuel and higher operating temperatures to increase the reactor's thermal efficiency. In the High Temperature Gas Cooled Reactor (HTGR), the fuel consists of highly enriched U-carbide-coated particles which can sustain higher temperatures than the AGR. The fuel is embeded in a graphite matrix which acts as a moderator, and the coolant is helium. A summary of the production of ^{14}C in these reactors is given in Table 4.7.

a)

Reference	**Fuel**			**Coolant moderator**		
	1	**2**	**3**	**1**	**2**	**3**
Kelly et al. (1975)	3.7	0.7		0.1	0.3	
Magno et al. (1975)			9.3*			
Davis (1979)			7.4*			
Bonka (1981)	4.8	0.6	3.4*	0.3	0.3	small
United Nations(1982)	3.2			0.1		
Bush et al. (1983)	3.7	0.3	5.6*	0.4	0.2	small

b)

Reference	Fuel cladding			Structural material		
	1	2	3	1	2	3
Kelly et al. (1975)	-	-		9.1	9.0	
Bonka (1981)	1.3	1.2		11.0	3.5	
United Nations(1982)				9.3		
Bush et al. (1983)	0.3	1.8		9.5	5.7	small

* (^{14}C in fuel assembly/moderator). 1 = MAGNOX, 2 = AGR and 3 = HTGR. GMR = Graphite moderated reactor

TABLE 4.7: ^{14}C production in GMR [TBq $(GW(e))^{-1}y^{-1}$] (McCartney, 1987).

Heavy Water Reactors.

In the Heavy Water Reactors (HWR), the core is cooled and moderated by heavy water (D_2O). The low neutron absorption of the D_2O allows the use of natural UO_2 fuel. Data on the formation of ^{14}C in HWRs is limited (Kelly et al., 1975). CANDU is an example of a HWR. Due to design differences (i.e. larger moderator mass of CANDU) CANDU reactors produce significantly more ^{14}C than LWRs (Stasko & Vivian, 1982). The production rates of ^{14}C ($TBq(GW(e)y)^{-1}$) are: 0.7-1.7 (fuel), 7.4-20.6 (coolant moderator, 1.3 (fuel cladding), 1.3 (for structural material they are assumed to be similar to the LWR i.e. 1.3) and 18.2 (overall) (Beninson & Gonzalez, 1981). A total production rate of ^{14}C of 21.44 TBq $(GW(e)y)^{-1}$ in a typical Pressurised Heavy Water Reactors (PHWR) is suggested by Joshi et al. (1987).

Waste disposal.

Generally, ^{14}C has not been a major waste disposal problem, largely because of its relatively liberal authorised concentration limit in air. However, because this isotope is produced in quite large quantities in reactors, it is desirable to determine the contribution of this type of source to possible local environmental contamination (Chudy and Povinec, 1982). ^{14}C wastes arising at the different reactor types (McCartney, 1987) are summarised in Table 4.8.

Reactor type	**Production TBq. $(GW(e))^{-1}y^{-1}$**	**Gaseous waste $TBq(GW(e))^{-1}y^{-1}$**		**Solid waste $TBq(GW(e))^{-1}y^{-1}$**	
		Reactor	**Reproc. plant**	**Reactor**	**Reproc. plant**
PWR	2.4	0.2	0.6	1.0	0.6
BWR	3.3	0.3	0.7	1.7	0.6
HWR	18.2	14.4	1.2	1.3	1.3
MAGNOX	14.6	0.9	3.9	9.0	0.8
AGR	8.4	0.7	0.5	5.3	1.9
HTGR	6.4	small	6.4	small	small
LMFBR	0.7	small	0.2	small	0.5

TABLE 4.8: ^{14}C waste arising from different reactors (McCartney, 1987).

Other sources.

The tracer method (labelling of compounds with radionuclides) is one of the most useful in radiochemistry, in which ^{12}C is replaced by ^{14}C in organic compounds by direct chemical synthesis, recoil labelling, exchange reactions and biochemical synthesis. Figures for the total amount of ^{14}C used for labelling in medical or biological research are unavailable. The US Department of Energy has estimated the production to be between 3.7-18.5 TBq annually (NCRP, 1985 and Keller, 1988).

4.4 CHEMICAL FORMS OF CARBON.

In reactors CO_2, CH_4, C_2H_6, C_3H_8 and C_4H_{10} containing ^{14}C have been identified in stack gas, containment air, off gas and gas in decay tanks (Kunz, 1985). The relative abundance of different chemical species including CO varies from one reactor to another.

Normal effluent release of ^{14}C is mainly CO_2 i.e. > 95% for BWRs and 75% for reprocessing plants (Palms et al., 1977). In Low and Intermediate Level Waste originating in the nuclear fuel cycle,the chemical form of ^{14}C is usually assumed as carbonates (Gruhlke et al., 1986).

4.5 DISTRIBUTION OF ^{14}C IN THE ENVIRONMENT.

The biosphere is described as the living film of the earth-that part of the earth inhabited by living things (Vallentyne, 1971). The carbon reservoirs in the biosphere include the atmosphere, the terrestrial biosphere, the ocean, the ocean sediment, and the organic shale (NCRP, 1985). Different carbon cycle models are proposed to illustrate the interaction of these reservoirs. A mathematical model of three reservoirs (atmosphere, mixed layer and deep ocean) has been developed to assess the dose levels to man from ^{14}C (Krishnamoorthy et al., 1982). The natural ^{14}C store has been distorted by two counteracting effects: (a) the burning of large quantities of fossilised C in the form of coal, natural oil and gas, which reduces the proportion of ^{14}C, and (b) atomic and hydrogen bomb explosions which increase ^{14}C (Keller, 1988). This dilution effect is called the Suess effect (Suess, 1955) and both opposing processes have to be considered together for dose evaluation.

^{14}C produced in nature is rapidly oxidised to $^{14}CO_2$ which mixes with ordinary CO_2. Through the natural processes of photosynthesis and respiration ^{14}C is incorporated into green plants, subsequent transfer through the food chain results in the radioactive labelling of all living organisms. Each mixing or exchange process (Figure 4.2) involved in nature is assumed to be rapid in comparison with the average life time of radiocarbon which is about 8000 years (Radiocarbon Dating Manual, 1981), so that of equilibrium exists in the biosphere:

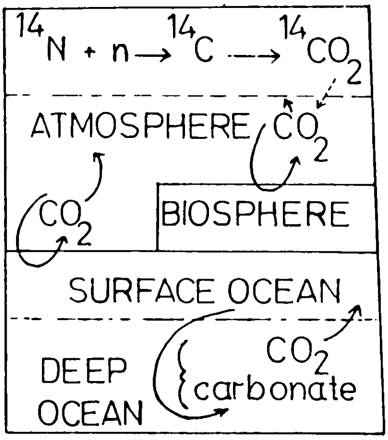


Figure 4.2: Mixing and exchange of $^{14}CO_2$.

Exchange with the oceans is presumably the principal mechanism for the removal of CO_2 from the atmosphere. In the 1950s and 1960s the dilution of atmospheric ^{14}C by "dead" CO_2 was overshadowed by nuclear bomb tests. By 1963, the ^{14}C concentration in the troposphere had approximately doubled, in the stratosphere it had increased by much larger factors, but since the moratorium on atmospheric testing it has been gradually decreasing again as a result of vertical mixing and exchange with ocean bicarbonate. It is interesting to note that future generations will certainly be confronted with complex problems in the interpretation of ^{14}C dating of 20th century objects (Friedlander et al., 1981).

4.5.1 THE ATMOSPHERE.

The rate of production of ^{14}C in nature averaged over the whole of the atmosphere is 2.4 atoms cm^{-2} sec^{-1}. This natural carbon exhibits a specific activity of 0.27 Bq g^{-1}. ^{14}C is in equilibrium and $\approx$ 90% is in the deep oceans below 100 m, $\approx$ 2% is in the atmosphere, and $\approx$ 8% is in the surface waters, sediments, and biosphere (Hays & MacMurdo, 1977 and Keller, 1988).

4.5.2 THE ATMOSPHERIC-TERRESTRIAL BIOSPHERE SYSTEM.

The terrestrial biosphere is the part of the land masses which support life. Baes et al. (1976), divide the carbon content of the terrestrial biosphere into two compartments: the living and dead compartments containing 6.8 x 10^{14} and 10.8 x 10^{14} kg C. The continental plants contain essentially all of the world's living C, 90% of it residing in the forests, but only 66% of the global net primary production. Continental animals including man and domestic livestock, contain only 0.02% of the global plant C. According to several investigators, the global fresh water system contributes little to the total exchangeable carbon or natural ^{14}C.

4.5.3 THE ATMOSPHERIC-OCEAN SYSTEM.

For modelling puposes, the ocean is divided into three compartments. The surface layer of volume 0.024 x 10^{9} km^{3}, which extends to a depth of about 75 m, is relatively well mixed and in equilibrium with atmospheric CO_2. The thermocline (0.25×10^9 km^3, extending to 100 m below surfce layer), is a relatively stagnant zone stabilized by decreasing temperature and increasing density with depth. The third compartment is the deep ocean (1.1×10^9 km^3) (Broecker, 1974).

Among the C in the ocean (as dissolved inorganic material), ≈ 89% is bicarbonate ion, ≈ 10% is carbonate ion and ≈ 1% is carbonic acid. The next most abundant form in the ocean is the dead organic matter and the concentration varies widely (NCRP, 1985).

4.6 ENVIRONMENTAL DISPERSION OF ^{14}C.

The magnitude of exposure is dependent on atmospheric dispersion and deposition processes. Elements of an airborne plume are affected by turbulent eddies in the atmosphere which diffuse the effluent material as the entire plume is being transported downwind. Generally, the combined influences of diffusion and transport are called dispersion. Certain removal mechanisms affect the effluent. For example, in the rainout process, gaseous and particulate effluents may become involved in precipitation formation processes within cloud by contact with falling precipitation. The removal of gaseous or particulate material below cloud by contact with falling precipitation is referred to as washout. In dry deposition, effluent material may be removed through gravitational settling, or through contact with the ground, vegetation, or other ground cover such as buildings. Radioactive material may decay during transport (Slinn, 1973).

A number of models have been developed to solve the equation for the ground level activity concentration in air, depending upon the simplifying assumptions made and the boundry conditions imposed. The Gaussian dispersion model is widely used for the purposes of estimating regional collective doses. The main advantage of the Gaussian dispersion model over-other models are its relative ease of calculation, and the availability of meteorological data expressed in terms of a diffusion typing scheme directly applicable to this model (Killough & Rohwer, 1978). The second basic equation used to estimate atmospheric dispersion in air is Pasquill's Equation as modified by Gifford.

4.7 PATHWAYS AND BEHAVIOUR OF ^{14}C IN BIOLOGICAL SYSTEMS.

An estimate of the total radiation exposure following an atmospheric release of radionuclides should account for several pathways, including direct atmospheric transport from the release point, contamination of the terrestrial environment by deposition from the airborn contamination, and resuspension of the deposited material and continued atmospheric transport (Horst, 1982). The major pathway to man of ^{14}C (as CO_2) is ingestion in food. The external radiation as well as that from inhalation is insignificant (Palm et al., 1977).

The inventory of ^{14}C and stable carbon in each environmental compartment can be used to evaluate the intake of ^{14}C by man. The local atmosphere was assumed to contain 330 ppm CO_2 or 162 mg C m^{-3} (McKee & Rowsell, 1984). The carbon content of an adult human is about 23%. The intake of C by reference man is 300 g d^{-1} through diet; the intake by inhalation is < 1% of the total.

The metabolism and kinetics of radiocarbon in the human body follow those of ordinary carbon. A fractionation of C introduced into the body is retained as protein, fat, carbohydrates, and other materials and is excreted unchanged or is metabolized to CO_2, urea or other metabolites. The biological half times range from a fraction of an hour to several years. The ICRP suggests a biological half time of 40 days for ^{14}C for dosimetric purposes as a conservative value (NCRP, 1985). It was concluded from a long term analysis of ^{14}C in human blood and hair samples that Bomb ^{14}C enters the human body 1.4 years after production in the atmosphere, and remains there with a mean lifetime of 10 years (Nydal et al., 1971). Stenhouse and Baxter (1977) used Bomb ^{14}C as a biological tracer for the determination of ^{14}C activities of atmospheric CO_2, dietary and human tissue samples enabling a more detailed evaluation of residence times.

4.8 RADIATION DOSES FROM ^{14}C.

The importance of the contribution of ^{14}C towards doses is due to (1) its long half-life, (2) easy access via the food chain to all key molecules of body tissue, and (3) relatively long residence times in both stratosphere and troposphere of four and eight years respectively (Stenhouse & Baxter, 1977).

As ^{14}C is a weak β-emitter, consideration of the external irradiation of man by ^{14}C can be limited to irradiation of skin. The dose equivalent rate in skin from the external irradiation of man by ^{14}C is 2.16×10^{-8} Sv y^{-1} (Bq $m^{-3})^{-1}$ (McCartney, 1987). Ingestion accounts for more than 99% of the ^{14}C dose to individuals in a uniformly contaminated exposure medium (Killough & Rohwer, 1978).

From the analysis by liquid scintillation counting of environmental saples, primarily of grass, McCartney concluded the collective dose to the population in 1984 was 15×10^{-3} man Sv, the maximum annual individual dose of 12 μSv (1% of dose limit) being delivered at 0.4 km distance to the east of Hunterston and the largest annual individual effective dose equivalents around Sellafield were 0.2 mSv in 1982. The annual dose (in the ICRP Man) per unit of specific activity will be of the order of 5.4 x 10^{-2} mSv Bq^{-1} per gram of carbon (ICRP, 1975).

The overall radiological impact from ^{14}C releases is assessed by means of the collective dose commitment resulting from the release. The dose commitment from a given release of ^{14}C (Beninson and Gonzalez, 1981) is given by:

$$D^c_Q = D^\cdot_B\ Q/B$$

where

D^c_Q = the dose commitment due to release Q;
$D^\cdot_B$ = the dose rate due to natural ^{14}C;
B = the rate of production of natural ^{14}C; and
Q = the activity of ^{14}C released into the environment.

The annual limits on intake, ALI (Bq) and derived air concentration, DAC (Bq m^{-3}) (40 h wk) for $^{14}CO_2$ are given as:

	Inhalation
ALI	8 x 10^9
DAC	3 x 10^6

Because of its long half-life,waste ^{14}C once discharged to the environment, the potential exposure times may last for many human generations, until finally the radioisotope are removed from the biosphere by physical decay or environmental processes. A new hazard index (see section 1.6.5) for long-lived radionuclides including ^{14}C (that contribute significantly to the calculated hazard) is presented in Figure 4.3.

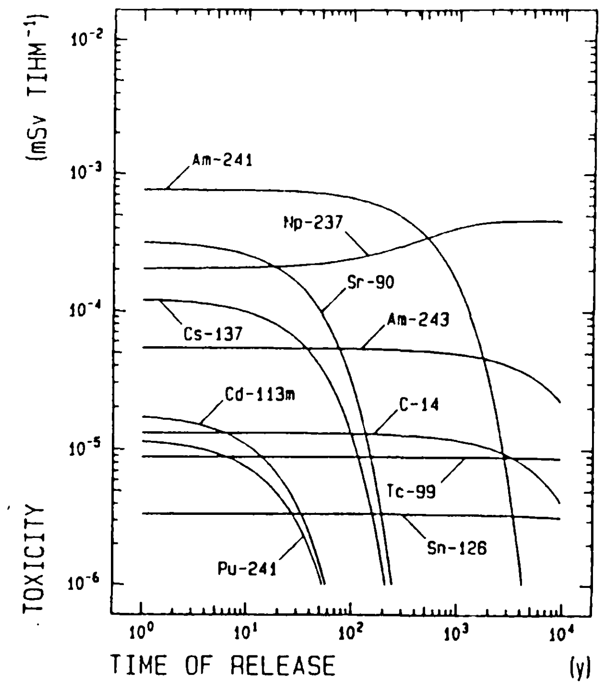


Figure 4.3: Nuclide toxicities with time of wastes (Kirchner, 1990).

4.9 REVIEW OF SAMPLING OF ^{14}C.

The separation techniques for ^{14}C reported in the literature are based on the separation and recovery of ^{14}C as $^{14}CO_2$; these techniques are: adsorption onto molecular sieves, permeation through a suitable membrane and precipitation as an insoluble carbonate salt.

The principal drawback to using a molecular sieve in an automatic, semi-continuous application is its lack of specificity. Polar compounds in the sampled gases, such as water vapour and NO_x, would also be absorbed. Water vapour decreases the adsorption efficiency of the molecular sieve for CO_2. Major interferences would be HTO, a radiochemical interference, and NO_x, which would degrade counter performance. Molecular sieve units were first developed for aircraft and balloon sampling of the upper atmosphere

(Ashenfelter et al., 1972) where the amount of water vapour is low. Winkelman et al. (1982) give a method for the collection of CO_2 using a molecular sieve which was routinely applied for air and reactor effluent assessment of $^{14}CO_2$ from German power reactors. Degassed CO_2 may be purified and counted directly as a gas, collected in $Ba(OH)_2/BaCl_2$ solution for counting as $BaCO_3$, or absorbed in a trapping solvent for liquid scintillation counting.

The main drawback of the second method is to obtain selective permeation i.e. that materials should be permeable only to CO_2. A permeation device is possible by forming the membrane into a shell and tube configuration and then using a purge gas of the proper composition. Gases, such as Kr and H_2O, used in making a proper purge gas would have no radioactive isotopes only, thereby eliminating radiochemical interferences.

The formation of solid carbonates as the form to be measured is in wide use. This is because the procedure for sample preparation is very simple and requires no particularly special equipment (Pfeiffer et al., 1981). Samples of $^{14}CO_2$ in ground-level air can be collected by exposing NaOH solutions in dishes or trays (Walton et al., 1970) for several days. The main drawback to this sampling method is the extended time period required to collect a measurable quantity of CO_2 (NCRP, 1985). To overcome this drawback, pumps are used to pass greater volumes of air ($^{14}CO_2$) through air-tight NaOH solutions. A dry, ambient temperature process using using $Ca(OH)_2$ as the sorbent to remove $^{14}CO_2$ from gaseous streams was developed by Chen et al. (1982). The well known $Ba(OH)_2$ solution method is also used to extract CO_2 from atmosphere (Saro et al., 1978).

4.10 THE LIQUID SCINTILLATION TECHNIQUE.

4.10.1 PRINCIPLE OF LIQUID SCINTILLATION COUNTING.

Liquid scintillation counting (LSC) is generally used for a wide range of β-emitting radioisotopes in many chemical forms. Low-energy β-emitters such as ^{3}H, ^{14}C and ^{35}S are commonly counted by dissolving the sample in a liquid scintillator (LS). The LS mixture consists of a solution of at least one fluorescent aromatic solute dissolved in an aromatic solvent. The basic objective of the technique is to arrange for β-particles to collide with the solvent molecules. The energy resulting from the collisions excites the solvent molecules and is passed to other molecules until it is finally transferred to a solute molecule which converts the energy to a visible light quantum. The light from the scintillators can be converted into electrons by photosensitive devices known as "photomultiplier" tubes (usually two). The electrons are accelerated through a series of dynode stages that produce between two and six electrons for each electron input. This overall multiplication may amount to a 10^{5}-fold increase over eleven stages, to form electrical pulses of sufficient strength to be detected by the counter electronics (Gibson & Lally, 1971 and Willard et al., 1981).

4.10.2 ^{14}C BACKGROUND.

The background ^{14}C level is not the same as the natural atmospheric ^{14}C level and is constantly changing because of the various natural and anthropogenic perturbations. There are many sources of background events in LSC. The contributions from common sources in LS materials, sample, vial and multiplier phototubes (MPT) and other radioactive sources are summarised by Gupta & Polach (1985).

^{14}C is produced naturally in the lower stratosphere and the upper troposphere; the atmospheric equilibrium value, between production and radioactive decay (decay mainly occurs in the ocean), amounts to 226 mBq g^{-1} carbon. This value corresponds to the "zero point" in the generally adopted $\Delta^{14}C$-scale (Stuiver & Polach, 1977). Assuming an atmospheric CO_2 concentration to be 350 ppm, then the natural atmospheric $^{14}CO_2$ activity is 42.4 mBq m^{-3} (STP air)(Levin et al., 1988).

4.11 THE MEASUREMENT OF ATMOSPHERIC ^{14}C AROUND THE SURRC UTR300 REACTOR-EXPERIMENTAL METHOD.

The Scottish Universities Research Reactor Centre (SURRC) is situated at East Kilbride, near Glasgow. It houses a reactor of the "Argonant" type, the UTR(Universities Teaching Reactor)300, which can operate at a maximum power of 300 kW (thermal). The enriched uranium fuel is contained within two tanks in a graphite reflector, which is surrounded by a biological shield approximately 2 meters thick of high density concrete. It utilises enriched uranium fuel (≈ 95% ^{235}U) and light water as moderator. The water also acts as the primary coolant. Due to urban development since it was first built, it is situated far closer to large populations than most nuclear facilities. East Kilbride itself has a population of over 65,000 and nearby Glasgow and its surrounds contain well over 800,000 people. Therefore monitoring of discharges such as $^{14}CO_2$ is an important aspect in relation the dosimetry of the local population.

4.11.1 SAMPLING SITES.

The sampling sites I and II (downwind in east side of the reactor stack), from the reactor stack and from the reactor hall are shown in Figure 4.4.

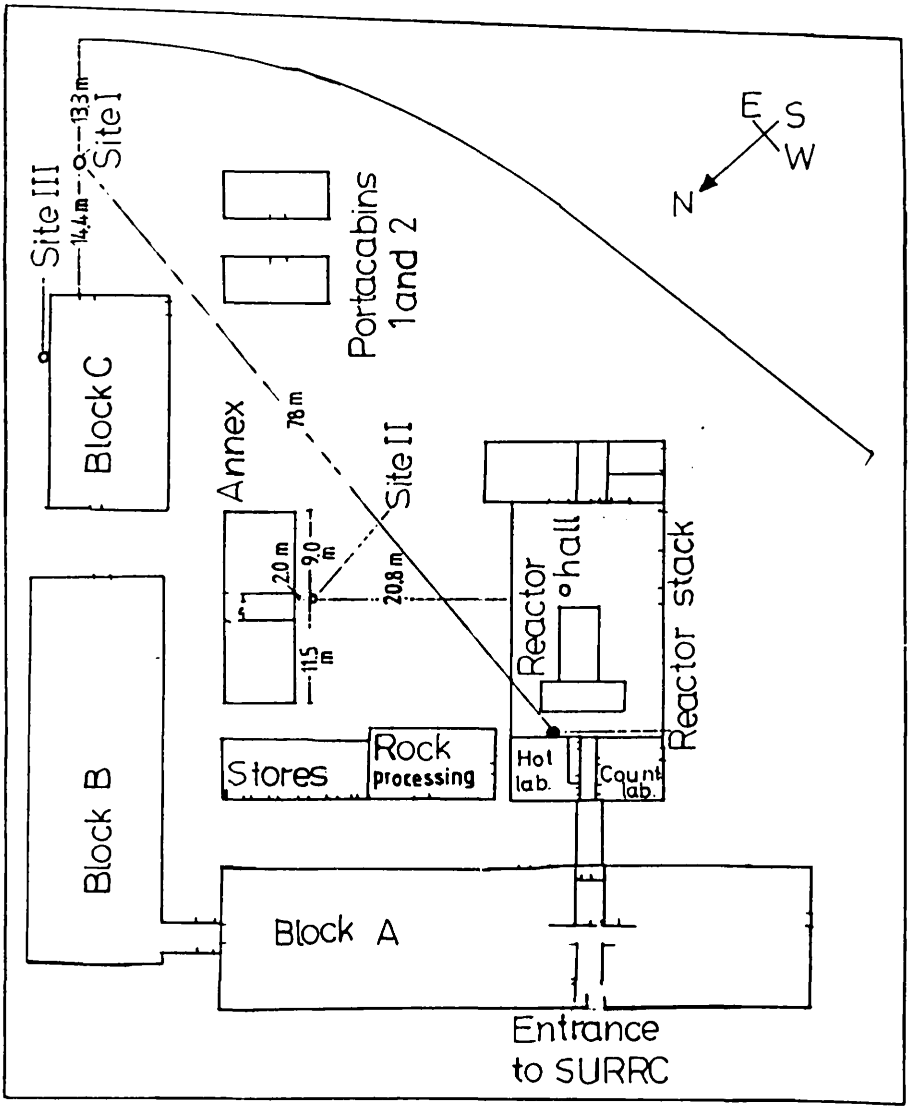


Figure 4.4: Sampling locations.

4.11.2 REAGENTS AND AIR SAMPLING APPARATUS.

All reagents used were of "AnalaR" grade. Deionised water was used for washing and preparation of the samples. All glassware and other accessories was acid-washed followed by water washing to minimise cross contamination. Separate apparatus and glassware was used when high activity was expected in the samples i.e. samples from the reactor stack.

Barium hydroxide solution: A 0.1M $Ba(OH)_2$ solution was prepared by stirring overnight under airtight conditions followed by filtration through a Whatman filter No. 42. The

$Ba(OH)_2$ solution was kept airtight before and after sampling to minimse the background absorption of CO_2.

A diagram of the air sampling system is given in Figure 4.5. A Dymax model 2A pump (Charles Auston Pumps Ltd, Surrey, England) was used to draw air at a flow rate of 1.5 l min^{-1} through $Ba(OH)_2$ solution contained in the aspirater as shown. The inlet point (through filter paper) was positioned 50 cm above the ground surface.

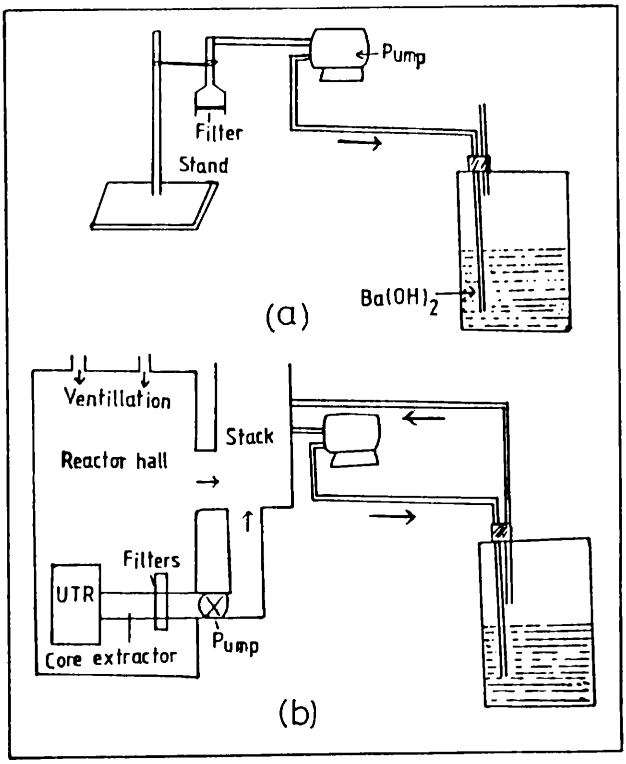


Figure 4.5: Diagram of the air sampling system for (a) all sites except the reactor stack (b) the reactor stack.

4.11.3 SAMPLING.

To analyse ^{14}C in the form of CO_2 in effluent gas, a portion of the gaseous effluent from the exhaust air of the UTR-300 was passed through 2.5 l of 0.1M barium hydroxide ($Ba(OH)_2$)

solution using Dymax-2A pump. Similarly, air from the Reactor Hall, and sites I and II was passed through $Ba(OH)_2$ solution as above. The sampling periods varied from 715 to 4184 minutes. Samples were taken both with the reactor at power (300 kW) and shut down (0 kW) at these various locations. At the end of the sampling period the precipitate of $BaCO_3$ from the resultant solution was filtered off through Whatman No. 42 filter paper and washed with distilled water. The precipitate ($BaCO_3$) was dried in a oven and weighed to obtain the chemical yield.

4.11.4 CONVERSION OF BARIUM CARBONATE TO BENZENE.

After completion of the collection procedure, the samples were available as $BaCO_3$ and needed further chemistry to convert the carbonate to a suitable form for ^{14}C measurement. The principal steps of conversion were: (i) the preparation of carbon dioxide, (ii) the production of acetylene, and (iii) the catalytic conversion to benzene. A detailed description of each of these steps is given below (Gupta & Polach, 1985):

i) The carbonate was hydrolysed by treatment with 4M HCl in excess, and the subsequent purification and recovery of CO_2 was carried out in a glass vacuum system using wet chemistry procedures developed by Rafter (1955). The chemical reaction involved was:

$$BaCO_3 + 2HCl \rightarrow CO_2 + BaCl_2 + H_2O$$

In detail, the powdered $BaCO_3$ sample was placed in a flask and wetted with demineralised water. Controlled amounts of freshly prepared dilute HCl, from a specially designed dropping funnel, were then added dropwise to the stirred sample and the partial pressure, was allowed to build up to just below atmospheric pressure. This pressure was then maintained until all the carbonate had been hydrolysed. The excess CO_2 evolved was continuously collected in liquid-N_2-cooled traps which had been evacuated at the same time as the reaction vessel. During CO_2 collection, the system was however isolated from the vacuum pumping system (i.e. a static collection without pumping was performed).

ii) The second step in sample preparation involved the conversion of the sample CO_2 to acetylene (C_2H_2). The C_2H_2 synthesis involved two steps in which sample CO_2 was reacted with molten Li metal to form lithium carbide (Li_2C_2), and the Li_2C_2 was hydrolysed with H_2O to yield C_2H_2. This reaction was first described by Barker (1953), has been further studied and refined by Polach and Stipp (1967), who have established that the reaction mechanism is the simultaneous formation of elemental carbon and Li_2C_2. The elemental carbon subsequently reacts with free Li metal to form further carbide, according to the stoichiometric equations:-

$$2CO_2 + 8Li \rightarrow 2C + 4Li_2O \qquad (1)$$

$$2C + 2Li \rightarrow Li_2C_2 \qquad (2)$$

$$(1+2) \qquad 2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O$$

Simultaneously, a second reaction generates lithium carbonate and elemental carbon:-

$$4Li + 2CO_2 \rightarrow Li_2CO_3 + Li_2O + C$$

To minimise this latter side reaction, the initial stage reaction temperature must be kept above 750°C (when the furnace temperature is 750°C in vacuum, the Li melts and forms a mirror like surface in about 10-15 min, when the evacuation is stopped and sample CO_2 is admitted) and to obtain a high yield of Li_2C_2, the final (2nd stage) temperature must be maintained at 900°C, under vacuum for about 30 min, during which excess Li reacts with elemental carbon to form carbide (equation 2).

The formation of acetylene gas was accomplished by hydrolysing Li_2C_2 at room temperature by slowly adding demineralised water from a glass reservoir to the reaction vessl after cooling. The reactions involved were:

$$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$$
$$2Li + 2H_2O \rightarrow 2\ LiOH + H_2$$

With the entire acetylene collection system under vacuum and isolated from the pump, water was allowed to drip steadily into the reaction vessel. After the pressure in the reaction vessel reached about 50 cm Hg, the generated C_2H_2, and the H_2 produced from hydrolysis of excess Li , were allowed to pass slowly through a recirculating condenser (to return LiOH), a P_2O_5 trap (to retain water vapour) and then into two traps cooled by liquid N_2 for C_2H_2 collection.

iii) Acetylene was converted to benzene by letting the frozen C_2H_2 slowly sublime on to an activated vanadium catalyst. The column was then sealed and allowed to stand overnight at room temperature. Under these conditions trimerisation took place to form benzene:-

$$3C_2H_2 \dashrightarrow C_6H_6$$

To recover the benzene, the column was heated to 110°C and the benzene collected under vacuum in a liquid N_2 cold trap. The frozen benzene was aerated, allowed to melt at room temperature, transferred to a storage vial and refrigerated (-15°C) until required for counting. A double freeze/melt and aeration sequence was essential prior to counting to obtain stable quench conditions.

4.11.5 LIQUID SCINTILLATION COUNTING OF ^{14}C.

^{14}C was measured by liquid scintillation counting using a

Tricarb 2260XL instrument (Packard Instrument Company). The Tri-carb 2260XL analyser incorporated temperature controlled refrigeration as a standard feature, and was equipped with an opaque cover to prevent room light from affecting samples on the sample changer. It also included a special slow scintillating plastic detector guard to further improve background reduction and enhance sensitivity and it was possible to observe β-spectrua directly. The performance of the Tri-Carb 2260XL analyser depended on the types of samples counted and the background environment.

4.12 RESULTS AND DISCUSSION.

$BaCO_3$ precipitation

Methods of assaying ^{14}C as CO_2 in air in effluents or in the environment have already been discussed. The formation of solid carbonates as the form to be measured is in wide use as a procedure for CO_2 sampling and has the advantages of providing a simple measurement technique. The solid carbonates as the form to be measured provide a very simple method and require no expensive equipment. At present a liquid scintillation counter, which has high sensitivity for low energy β-emitters compared to other techniques, is one of the most powerful methods and when coupled to a pulse height analyser it is possible to identify the β-emitting nuclides from their spectra easily.

Figure 4.6 shows the weight of precipitate of $BaCO_3$ (grams) verses time (hours) for the collection of CO_2 from air. It can be seen that the relationships deviates from a straight line.The following observations on the method can be made:

1. It is not amenable to an automated, continuous monitoring system, because sufficient carbonate must be generated to form a filterable precipitate and this would require a two week sampling period at least. This is a

direct result of the low concentration of CO_2 in air (0.033%).

2. The method is not entirely quantitative. The introduction of a second bubbler in series might be useful to collect CO_2, escaped from first bubbler.

3. $BaCO_3$ is slightly soluble (0.002 g dm^{-1}), so that some of the salt is lost in subsequent handling. A double filter paper was used to minimise the losses of precipitate while the temperature was controlled to keep variable solubility effects as low as possible.

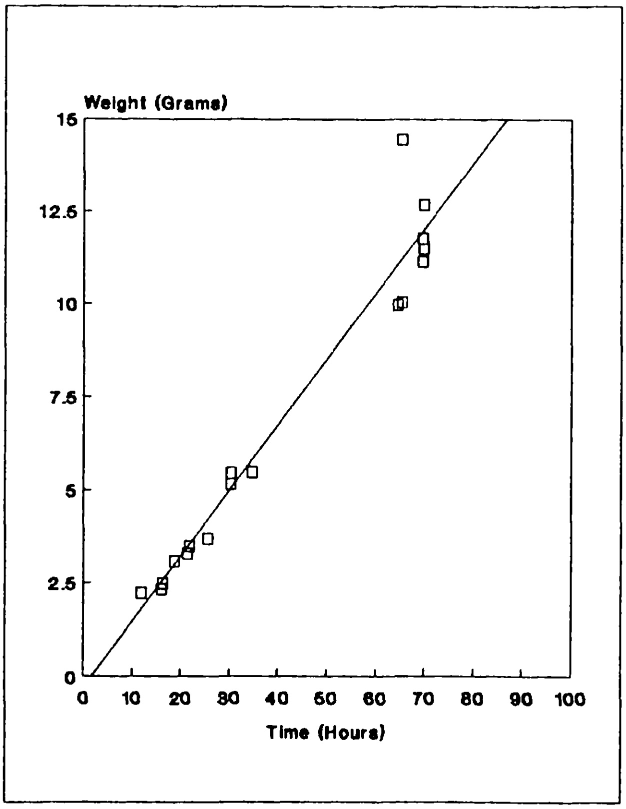


Figure 4.6: Weight of $BaCO_3$ for various sampling times.

4. It is difficult to recover all of the $BaCO_3$ because fine material tends to adhere to the walls of containment vessels.

Calculation of ^{14}C results.

The following steps were considered for calculating the results:

1. Total air passed was calculated, from the pump flow rate of 1.5 l min^{-1}.
2. Percent chemical recovery was calculated by the equation:

$$\% \text{ chemical recovery} = \frac{\text{Wt. of } BaCO_3 \text{ obtained}}{\text{Theoretical } BaCO_3 \text{ wt}} \times 100$$

The theoretical weight of barium carbonate was obtained by assuming a concentration of 0.033% in air and 100% recovery according to equation:

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

A density for air of 0.001293 g ml^{-1} was used for calculating the mass of $BaCO_3$.
3. Activity (Bq Kg^{-1} Carbon) in the precipitate was calculated from the % Modern.
4. The activity obtained was corrected for % chemical recovery and divided by the total air volume i.e. Bq l^{-1}. The average of duplicate counts was taken.
5. For the reactor stack, the total activity was calculated for the sampling time taking the core extractor flow rate to be 1400 $\text{dm}^3 \text{ min}^{-1}$. Finally the total annual output (MBq y^{-1}) was obtained by taking the integrated operating power to be of 216000 kWhrs y^{-1} (based on average power of four years i.e. from 1985-1988).

Results.

The results obtained from the present study are given in Tables 4.9. & 4.10.

Discussion

^{14}C is produced in the UTR(Universities Teaching Reactor)300 from the interaction of neutrons with C, N or O. Carbon and

Sample No.	Date of sampling	Reactor operat.	Total air passed(l)	^{14}C concentration mBq l^{-1} ± 1σ
Site I				
1.	27/3-20/4/90	ON	5645	0.0841 ± 0.0017
2.	20/4-23/4/90	OFF	5879	0.0532 ± 0.0008
3.	23/4-25/4/90	OFF	3113	0.0608 ± 0.0029
Site II				
4.	30/4-15/5/90	ON	3642	0.0737 ± 0.0028
5.	27/4-30/4/90	OFF	5798	0.0690 ± 0.0039
6.	04/5-08/5/90	OFF	5888	0.0693 ± 0.0039
Reactor hall				
7.	21/5-13/6/90	ON	4185	0.1752 ± 0.0050
8.	18/5-21/5/90	OFF	6251	0.0824 ± 0.0001
9.	25/5-28/5/90	OFF	6276	0.0945 ± 0.0011
Reactor stack				
10.	22/5-24/5/90	ON	1073	173.67 ± 0.88
11.	28/5-13/6/90	ON	2726	216.18 ± 0.98
12.	18/5-21/5/90	OFF	6263	2.44 ± 0.014
13.	25/5-28/5/90	OFF	6276	2.93 ± 0.001
14.	19/2-07/3/88	ON/OFF	36683	41.12
15.	07/02/1990	ON/OFF	458	46.04
16.	09/02/1990	ON	533	139.07
Block C				
17.	03/2-08/3/90		70956	0.0306

TABLE 4.9: ^{14}C concentrations in the samples of present study.

Sample No.	KWhrs during Sampling	MBq (total air of reactor stack, litres)	MBq per year (released)
10.	3575	0.1764 (1012261)	10.65
11.	9085	0.5579 (2572418)	13.26
14.	15125	1.4237 (34622166)	20.32*
15.	975	0.0199 (431804)	4.40*
16.	1775	0.0699 (502591)	8.50

* = when reactor was ON/OFF during sampling.

TABLE 4.10: ^{14}C activity released per year of reactor stack.

oxygen are often major constituent elements of the reactor design e.g. in the coolant and moderator (H_2O), reflector (graphite), or in the fuel (UO_2). Nitrogen is present mainly as an impurity in the fuel or in the structural material.

The main exception in this type of reactor, is the graphite-reflected reactor in which, to a first approximation, the $^{13}C(n,\gamma)^{14}C$ route is as important as the $^{13}N(n,p)^{14}C$ reaction.

^{14}C possesses a recoil energy of 40 keV, which is so large that a ^{14}C atom may be detached from its original molecule and can therefore react with surrounding molecules in many ways. At high temperatures, C reacts with many elements including O. One of the first chemical reactions of recoil carbon to be discovered was its ready reaction with oxygen to produce CO_2. The reactions occuring during production of the oxides are:

$$2C + O_2 \rightarrow 2CO$$

$$C + O_2 \rightarrow CO_2$$

The exact mechanism and the rate of reaction are still not fully understood. Another possibility is that carbon in the form of hydrocarbon (produced from reaction of C with H) and carbon monoxide react with OH radicals in the atmosphere and are converted to CO_2 (Greenwood and Earnshaw, 1986).

Sample No. 17 at site III (block C) was run in order to check the chemical yield. The sample was also analysed for ^{14}C and the activity i.e. 0.031 mBq l^{-1} was found to be very low compared to other places.

All the other four sites (i.e. Site I & II, reactor stack and reactor hall) showed enhancement when the reactor was at power. Site I showed a value of 0.084 mBq l^{-1} of ^{14}C which was greater than site II (0.074 mBq l^{-1} of ^{14}C), when the reactor was operating while the concentration was higher at site II when the reactor was shutdown. This indicates that ^{14}C might dispersed (due to speed and direction of the wind) some distance from the release point. The reactor stack and the reactor hall location showed ^{14}C activity even when the reactor was shutdown. The ^{14}C activity released from the reactor corresponds to a release of approximately 12 MBq y^{-1} (216000 kWhr y^{-1}).

The samples, when the reactor was shutdown, were collected in duplicate and the results are in good agreement. Also the samples were collected in duplicate when the reactor was at power, but because of the low weight of $BaCO_3$ collected, they were combined for analysis.

Two samples (No. 14 and 15) were collected over a period of 24455 and 305 mins both when the reactor was at power for some time and when it was shutdown but showed large difference (about a factor of 5). The large difference may be explained as follows:

i) Sample No. 14 was sampled for a long time (24455 min) compared to sample No. 15 (305 min), affecting % chemical yield due to losses of $BaCO_3$ in various steps (as described above).
ii) Differences in time and the reactor power. The reactor was operated for 15125 kWhrs (sample 14) and 975 kWhhrs (sample 15). If the power of the reactor is not considered in calculations, the ^{14}C concentrations are 41.12 and 46.04 mBq l^{-1} for sample 14 and 15 respectively and the differences are very small.
iii) ^{14}C is present even when the reactor was shutdown.
iv) the drawbacks of using precipitate methods (as explained above under drawbacks of $Ba(OH)_2$).

Due to uncertainties in the results (explained above), the average of the sample nos. 10 and 11 (12 MBq y^{-1}) was used for the assessment of the radiological impact from ^{14}C releases.
On the basis of an average reactor (power) run (in terms of $GW(th)^{-1}y^{-1}$), 12 MBq y^{-1} corresponds to 0.04 TBq $(GW(th))^{-1}y^{-1}$

at SURRC. By comparing to power stations 0.04 TBq $(GW(th))^{-1}$ y^{-1} corresponds to 0.12 TBq $(GW(e))^{-1}y^{-1}$. While taking the result of sample no. 14, 20 MBq y^{-1} (based on air sampling for 17 days, and calculating from this for one year) corresponds to 0.10 TBq $(GW(th))^{-1}y^{-1}$ or 0.30 TBq $(GW(e))^{-1}y^{-1}$. In both cases, it was assumed that all ^{14}C was released as CO_2. If ^{14}C releases from the reactor stack occur in forms other than CO_2, then the production rate of ^{14}C would however underestimated by these assumptions. Comparing these results with other reactors (Table 4.11) the production rate of ^{14}C by the UTR reactor is much less than all of them except the FBR and the HTGR types. In particlar, in comparison with the GMR the production of ^{14}C is a factor of up to 80 (sample no. 15) times less.

Reactor type	**Emission rate TBq $(GW(e))^{-1}y^{-1}$** **Reactor system**	**Reprocessing**
PWR	0.18-0.41	0.57-0.68
BWR	0.17-0.41	0.65-0.68
GMR	3.7	0.56
FBR	0	0.18
HTGR	0-3.7 x 10^{-7}	3.03-5.55
HWR(CIRUS)*	37	7.4 x 10^{-3}
Others	0.18	1.11

* (thermal to electrical efficiency taken as 1/3).

TABLE 4.11: ^{14}C emission in different reactors (Krishnamoorthy, 1982).

Although less sites are considered, they give useful information and an idea of dispersion of the radionuclide. A simple model can be made by comparing mBq $kWhr^{-1}$ for these locations when the reactor is at power. Table 4.12 shows the production (output) rate in mBq per kWhr.

By comparing the values at sites I and II, is clear that the plume line passes above site II (closer to the reactor stack) and comes down at site II. Many other locations would ideally be needed in all directions and particularly in the downwind direction to obtain a complete picture. The results of grass samples collected in 1985 at 0.05 km and 0.1 km from SURRC (McCartney, 1987) showed no enhancement of the ^{14}C levels. This may be explained by the following factors:

Site	**Total activity (mBq)**	**Total power (kWhr)**	**mBq kWhr^{-1}**	**Ratio of mBq kWhr^{-1} to R. Stack**
Site I	468	17700	0.026	4.7×10^{-7}
Site II	276	12015	0.023	4.1×10^{-7}
R. hall	734	13950	0.053	9.6×10^{-7}
R. stack	5.58×10^{8}	9085	6.14×10^{4}	
	1.76×10^{8}	3575	4.92×10^{4}	
Average, R. stack		=	5.5×10^{4}	

Table 4.12: The production rate (mBq kWhr^{-1}) at different locations.

1. These sample sites were far away from the reactor.
2. Plume line dispersion factors e.g. wind direction, temperature, etc. caused dilution to very low concentrations.
3. Weather conditions (season, rain, sunlight for absorption of CO_2 by grass).
4. Short operating period of the reactor.

Hence, again it is apparent that many more sites need to be sampled for grass concentrations over a range of times to obtain a complete data set.

Radiation dose due to ^{14}C.

The dose commitment for the ^{14}C activity released is calculated by using the following equation (section 5.8):

$$D^{c}_{Q} = D^{\cdot}_{B} Q/B$$

A value of 1.4 x 10^{-18} Sv y^{-1} is obtained for 12 MBq y^{-1}. The annual intake of ^{14}C at SURRC can be calculated from the present results by taking ICRP Reference Man, working 2000 hours per year, and breathing 0.02 m^3 air per minute. Assuming a ^{14}C air concentration of 196 μBq m^{-3}, the value for intake of the radionuclide is 4.7 x 10^{-1} Bq and at sites (0.8 μBq m^{-3}) the value becomes 1.9 x 10^{-3} Bq, which is very low compared to the Annual limit of intake (ALI) value of 8 x 10^{9} Bq.

4.13 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.

Measurements of ^{14}C in the air surrounding the UTR300 at SURRC were made for the first time and provided detailed data on the releases and dispersion of this radionuclide. Calculations of collective dose etc show that the exposure of the global population by the ^{14}C from this research reactor is completely negligible. In the wider context it should be noted that the total installed power of research reactors in the world is equal only to one large nuclear power station (Tschurlovits et al., 1982). However, monitoring is still important to give an assurance that release rates are low enough so that operating personnel and the local population cannot receive excessive exposure.

Although only a few results were obtained, the data were very informative as this was the first detailed measurement ^{14}C survey to be completed by the absorption method. The main points arising from the present study were:

1. The level of background of ^{14}C in and in the close vicinity of the reactor was measured.
2. By comparing the results when the reactor was at power

and when was shutdown, it was found that ^{14}C was enhanced by reactor operation.

3. ^{14}C continued to be released after shutdown of the reactor.
4. The releases of ^{14}C were very low, but provided data for comparison with acceptable release limits and targets.
5. The study confirmed the presence of only background levels in the laboratories in the area of study, in which low level environmental samples were routinely analysed.
6. It was concluded that analysis of other samples e.g. grass etc would be useful for the derivation of a suitable overall model.

Although significant information, concerning the releases and levels of ^{14}C from and in the vicinity of the reactor stack, was gained more detailed work would be necessary for a complete environmental picture. It is suggested that a second bubbler should be used in order to improve the chemical yield of carbon as well as to improve statistics.

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