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**The Determination of Technetium-99
in Environmental Materials**

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FOREWORD

As part of its responsibilities under various Acts of Parliament, MAFF Directorate of Fisheries Research has a duty to carry out a substantial programme of monitoring, surveillance and research in relation to the quality of the aquatic environment in and around the United Kingdom. In the course of that programme, a wide variety of methods of analysis are used for a wide variety of contaminants, both inorganic and organic, stable and radioactive. This series of publications describes the main methods used in the course of this work and parallels the existing Aquatic Environment Monitoring Report series, in which much of the resulting data is published. Regardless of whether the analytical procedure relates to a radionuclide or a non-radioactive contaminant, each report contains a step-by-step guide to analytical procedures and an explanation of the calculation of results.

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1. INTRODUCTION

The Aquatic Environment Protection Division of the Directorate of Fisheries Research (DFR), Lowestoft carries out analyses, on a routine basis, for a considerable range of radionuclides in a wide variety of environmental materials. These analyses constitute an essential part of the Ministry of Agriculture, Fisheries and Food's (MAFF's) statutory role in the authorization, monitoring and research relating to the disposal of radioactive wastes into the aquatic environment. Gamma-emitting nuclides can normally be determined with a minimum of preparative chemistry whereas alpha-emitting and pure-beta-emitting nuclides invariably require radiochemical separation for quantitative analysis. Although ^{99}Tc is a low-energy pure-beta emitter, it is expected to be one of the most significant radionuclides in relation to the long-term storage of nuclear waste (Denham *et al.*, 1973). This is chiefly due to its long half life (2.1×10^5 years) and poor sorption by oxidic soils and sediments which could lead to considerable mobility in groundwater and other aqueous systems (Bondietti and Francis, 1979). Technetium-99 is included in the list of radionuclides for which analysis is regularly carried out as part of the DFR monitoring programme. Its determination is inevitably somewhat labour-intensive and over the years the procedures used have changed to accommodate increasing demands for information on the environmental behaviour of the nuclide.

Element number 43 (sometimes seen in old text books referred to as masurium) was the first of the missing elements, in Mendeleef's periodic table, to be produced artificially. The name technetium comes from the Greek word "technetos" meaning "artificial" and credit for the discovery is usually ascribed to Perrier and Segré (1937) and (1947). They found the nuclides $^{95\text{m}}\text{Tc}$ and $^{97\text{m}}\text{Tc}$ on a molybdenum plate which had been bombarded with deuterons in a cyclotron at the University of California. Since then, 21 isotopes, along with their various isomers, have been produced, ranging in mass from 90-110 (Rioseco, 1987; Long and Sparkes, 1988). All are radioactive, with no stable isotope of technetium being known. The longest lived nuclide, ^{98}Tc , has a half life of only 4.2×10^6 years, thus the existence of primordial technetium can be discounted. Of all the nuclides, only ^{99}Tc is important in radioactive waste disposal. This is because of its high yield (about 6%) in the thermal neutron fission of both ^{235}U and ^{239}Pu and its relatively long half life. It therefore occurs naturally (albeit in very small quantities) in the earth's crust from fission of ^{235}U and also from the spontaneous fission of ^{238}U (Kenna and Kuroda, 1964), but substantial amounts have now been produced from the operation of nuclear reactors (estimated to be about 25-30 t world wide), of which some 1% (150-200 TBq) is thought to have been released to the environment (Aarkrog *et al.*, 1986; Beasley and Lorz, 1986).

Reliable analytical procedures for the radiochemical

separation and assaying of ^{99}Tc are thus important. The procedure described in this publication has been developed over a substantial period of time and has given excellent results in international intercomparison exercises.

2. ANALYTICAL TECHNIQUE

Technetium is a member of group 7A in the periodic table and is the middle member of the triad manganese, technetium, and rhenium. As a member of the second transition series, it lies between molybdenum and ruthenium, but its chemical properties most closely resemble those of rhenium.

As shown in Figure 1, both rhenium and technetium can exist in a large number of valency states but heptavalent and, to a lesser extent, tetravalent compounds are the most stable compounds. The other valencies are normally displayed only in conjunction with complexing ligands. Analytically, the ready oxidation of technetium

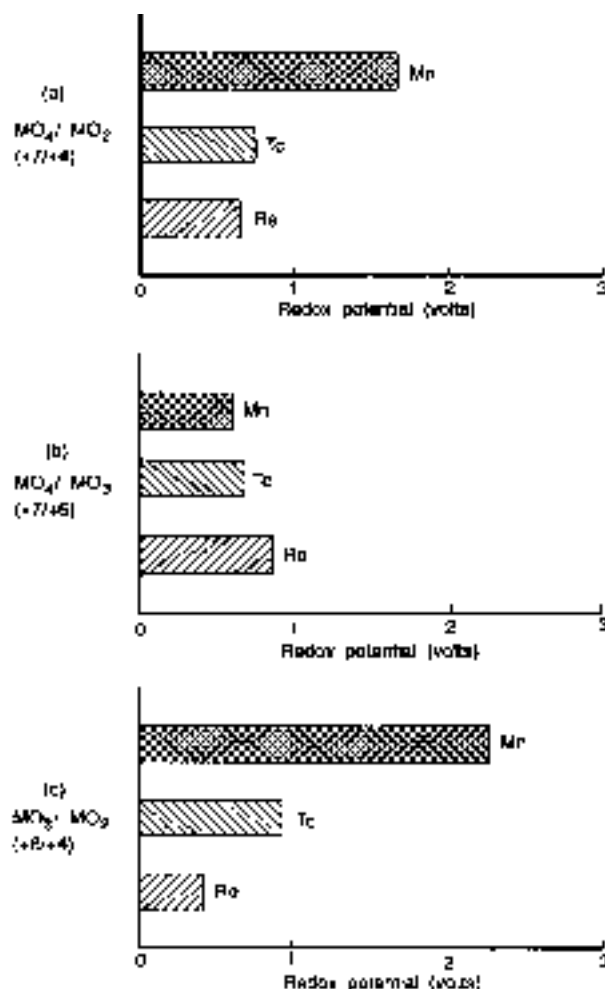


Figure 1. Comparison of redox potentials for selected reactions in aqueous solution for manganese, technetium and rhenium. (Redrawn from data given in Greenwood and Earnshaw, 1984)

to the very stable heptavalent pertechnetate ion, TcO_4^- , is of major importance. Also of importance is the volatility of the +7 state (vapour pressure of Tc_2O_7 at $100^\circ\text{C} \approx 0.1 \text{ mm Hg}$). This provides one very useful method for separating technetium from many other radionuclides and from matrix components.

Unfortunately, this volatility also means that the element can easily be lost from oxidizing acidic solutions. Dry ashing of solid environmental materials presents similar difficulties unless specific steps are taken to prevent such losses, as will be discussed later.

The pertechnetate ion is a weaker oxidizing agent than permanganate. It is reduced to the tetravalent state by such reagents as hydrochloric acid, ascorbic acid and hydroxylamine. In hydrochloric acid solution, chlorocomplexes of TcIV such as TcCl_6^{2-} (hexachlorotechnetate) are formed and these are fairly stable. In alkaline or neutral solution, complex anions of tetravalent technetium of the type $[\text{Tc}(\text{OH})_6]^{2-}$ are thought to be present (Lavrukhina and Pozdnyakov, 1970).

From a consideration of the chemistry of technetium, therefore, the isolation of ^{99}Tc from most accompanying radionuclides and from environmental matrices ought to be reasonably straightforward. To a large extent this is true, so long as precautions are taken to cope with volatility. The major difficulty in the radiochemical determination of this nuclide arises from the lack of an ideal means of measuring chemical yield in the analysis. The first method used at DFR, for the quantitative determination of ^{99}Tc in environmental materials, involved the distillation of technetium as pertechnetate from a nitric/perchloric acid mixture (Dutton and Ibbett, 1973). Because of the simplicity of this procedure and the quantitative removal of technetium from biological matrices, the technique was successfully operated without need for a yield monitor. It did, however, suffer from several drawbacks including severe restriction on sample size, an unsuitability for water samples and difficulties in trying to handle more than a very limited number of samples at any one time.

In order to cope with large samples of sea water (and incidentally overcome most of the other problems at the same time) a new procedure, based on anion-exchange separation of the technetium, by pertechnetate in alkaline solution was developed. Initially, no yield tracer was used in this procedure, but operating

conditions have now been devised in which rhenium can be used successfully as a non-isotopic yield monitor (see Section 3).

The analytical procedures can be divided into four main sections:

- 1) preliminary solubilization and addition of yield monitor;
- 2) concentration/purification of technetium by anion-exchange in mildly alkaline conditions;
- 3) isolation of technetium and rhenium as the tetraphenyl arsonium salts; and
- 4) gravimetric yield recovery measurement and radiometric assay.

Figure 2 summarises these procedures in the form of a schematic diagram.

Samples of sea water are normally filtered through $0.45 \mu\text{m}$ membrane filters to separate suspended particulate matter. In oxic waters, technetium is present almost exclusively as the TcO_4^- ion (Beasley and Lorz, 1986). This shows a very low affinity for particulate matter (typical K_d about 10). The amount of ^{99}Tc associated with the solid phase will thus normally be very little and the primary purpose of filtering such water samples is to avoid clogging the ion-exchange column in the preliminary concentration step. The rhenium yield monitor is added, after filtration, as perrhenate; no redox cycling, to equilibrate tracer and determinand, is necessary for oxic sea waters. Table 1 shows that both technetium and rhenium can be recovered quantitatively at this stage by the use of anion exchange.

The form of ^{99}Tc in other waters is less certain, particularly where organic components are present at higher concentration and the total ionic strength is low. In such cases, the safest form of treatment is evaporation to dryness in the presence of hydrochloric acid. The dried residue is then treated in the same way as sediments and biota. Treatment with oxidizing acids is not reliable and can result in the loss of both technetium and rhenium.

For sediments and biota, the sample is initially dried after the addition of ammonia solution and then ashed by raising the temperature slowly to $450 \pm 25^\circ\text{C}$ in a muffle furnace. The use of ammonia, to prevent volatilization of technetium, was first proposed by

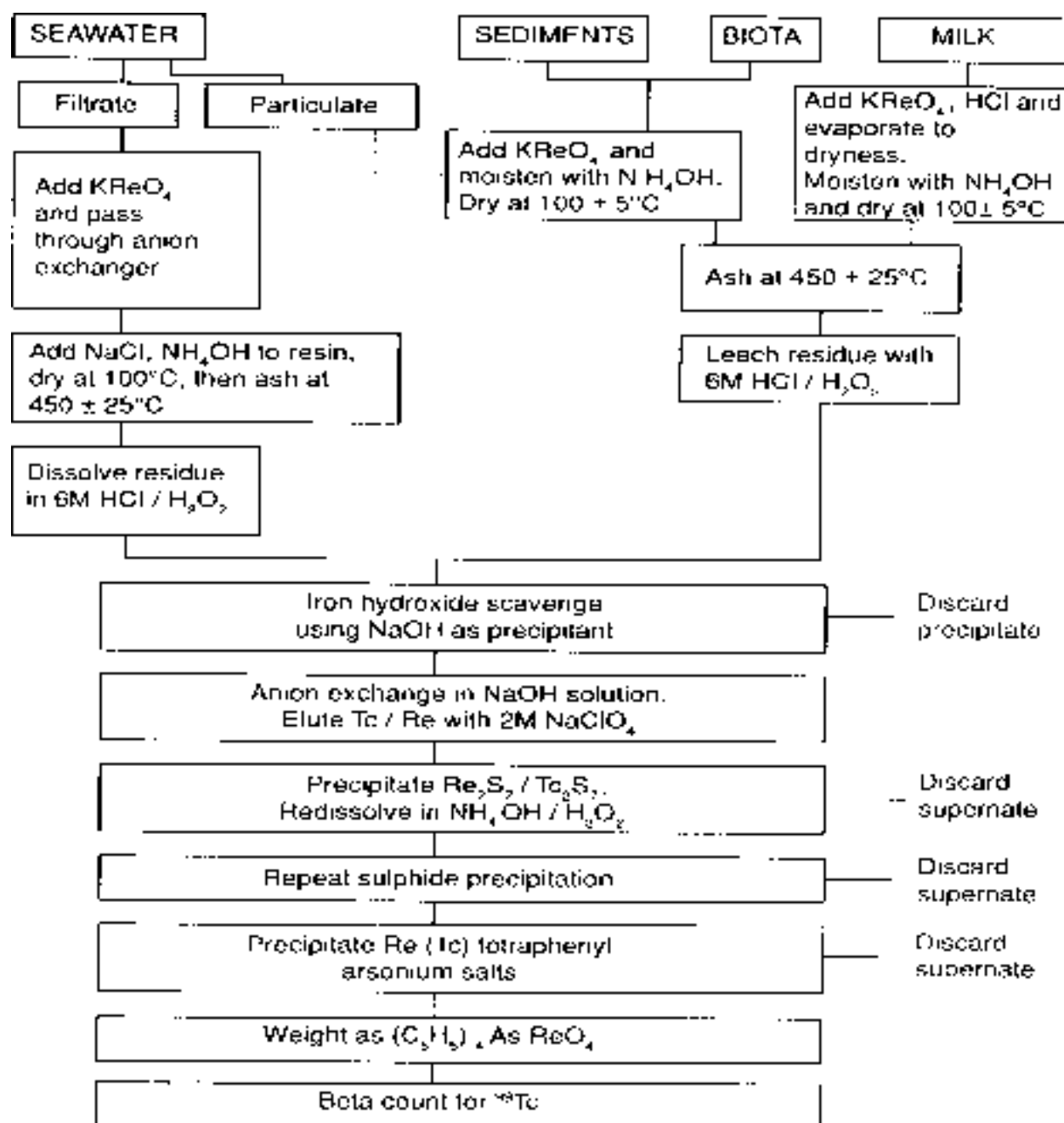


Figure 2. Simplified schematic diagram of the analytical procedures

Table 1. Uptake of technetium and rhenium from oxic sea water by BioRad AG1 x 8 (100-200 mesh) anion exchange resin (100 mm x 20 mm diameter column through which 50 l of spiked sea water was passed)

Tracer added	Amount added	Amount recovered	Percentage recovered	Number of replicates
$\text{NH}_4^{99}\text{TcO}_4$ aqueous solution	$2264 \pm 45 \text{ Bq}$	$2121 \pm 42 \text{ Bq}$	93.7 ± 2.8	3
KReO_4 aqueous solution	$9.94 \pm 0.10 \text{ mg}$	$9.59 \pm 0.49 \text{ mg}$	96.5 ± 5.2	3

Table 2. Recovery of technetium and rhenium under various conditions of drying and ashing

Drying/ashing temperature (°C)	Recovery (%)	
	Tc	Re
a) $\text{NH}_4^{99}\text{TcO}_4$ (2000 Bq) + KReO_4 (10 mg Re) alone		
100	99.8±0.5	100.5±0.6
350	99.6±0.6	100.0±0.6
450	94.3±0.8	97.0±2.0
550	44.8±2.3	83.5±1.9
b) $\text{NH}_4^{99}\text{TcO}_4$ (2000 Bq) + KReO_4 (10 mg Re) + 1 g NaCl		
100	100.6±0.5	100.5±1.6
350	99.5±0.6	100.0±0.6
450	99.0±0.9	98.2±2.1
550	97.8±0.8	96.9±1.8
c) <i>Fucus</i> seaweed + KReO_4 (10 mg Re)		
350	99.6±1.3	99.5±0.6
450	94.3±1.7	97.0±2.8
550	44.8±3.6	83.5±2.9
d) Cod muscle + $\text{NH}_4^{95\text{m}}\text{TcO}_4$ + KReO_4		
400	100.9±1.1	—
450	99.6±1.0	100.0±1.9
500	98.3±1.0	—
550	87.5±5.4	82.2±2.4

Foti *et al.* (1972), and its use is thought to ensure that all free acidic sites, on the complex organic molecules present, are neutralized, thus decreasing the opportunity for the volatile acids HTcO_4 or HReO_4 to form. Table 2 illustrates the effect of ashing materials containing technetium and rhenium under various conditions. In all cases, the samples were dried under ammoniacal conditions before ashing. Table 2(a) shows that losses of both elements begin to occur when a glass beaker containing just the heptavalent salts is heated above 400°C in a muffle furnace. However, the volatility is

reduced, as Table 2(b) shows, if sodium chloride is added to the mixture. Its presence has also been found to facilitate the ashing of ion-exchange resins containing pertechnetate and perrhenate at a temperature of $450 \pm 25^\circ\text{C}$ without significant loss of either of the two elements.

Table 2(c) demonstrates the behaviour of a sample of *Fucus* seaweed when ashed with added KReO_4 at various temperatures, and Table 2(d) the behaviour of cod muscle. After the initial ammoniacal drying, the temperature of the muffle is raised gradually to the

chosen temperature, so as to first char and then burn off the carbonaceous material slowly. In this way, the results show that such biological materials can be ashed successfully without significant loss of either the added rhenium carrier or the matrix bound technetium. After ashing, the residue is extracted with hydrochloric acid in the presence of hydrogen peroxide, to ensure that all of the technetium and rhenium are solubilized as pertechnetate and perrhenate respectively. The solution is then made alkaline with sodium hydroxide. The insoluble hydroxide precipitate, which forms at this point, is filtered off and discarded. It contains iron (including any added as a scavenging agent) and a number of other unwanted components such as alkaline and rare-earth elements and phosphates. It will also remove various corrosion and neutron activation products if they are present. The filtrate is retained for anion exchange purification.

The anion exchange step is extremely selective for pertechnetate and perrhenate under neutral or alkaline conditions. BioRad AG1x8, initially in the chloride form, is recommended and columns are prepared with about 1.5 ml of resin. The alkaline sample is then applied to the column, and contaminants are removed with up to 100 bed volumes of 2M sodium hydroxide (one of the few elements likely to persist to this point is ruthenium). Technetium and rhenium are eluted together, using dilute alkaline sodium perchlorate solution. This elution is illustrated in Figure 3, from which it can be seen that the two elution patterns are not identical, with the rhenium leaving the column ahead of the technetium. However, it is clear that, provided sufficient eluant is used, both are recovered completely.

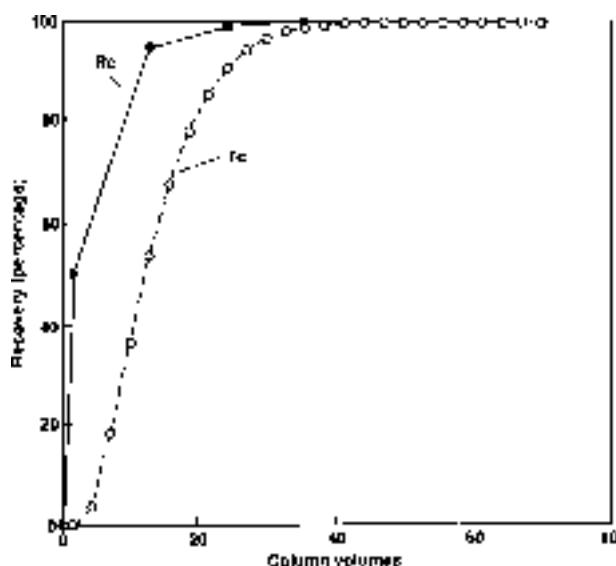


Figure 3. Elution of Tc and Re as pertechnetate and perrhenate from an anion exchange column of BioRad AG1x8 100-200 mesh with alkaline sodium perchlorate solution (50 mm long x 0.6 mm in diameter)

At the end of the anion exchange stage the sample is radiochemically pure, but needs to be prepared in a suitable form for presentation to the end window beta counter. Precipitation in the classical manner, as tetraphenyl arsonium perrhenate/pertechnetate (Willard and Smith, 1939), is selected for this purpose but, before this can be done, perchlorate must be thoroughly removed because this too forms an insoluble tetraphenyl arsonium salt. The rhenium and technetium are therefore first precipitated as sulphides, and this precipitate is washed free from perchlorate ions before redissolving in hydrochloric acid/hydrogen peroxide for the final precipitation of the mixed tetraphenyl arsonium salt. Figure 4 shows that, here again, care must be taken to ensure that complete recovery of both technetium and rhenium is achieved. With insufficient tetraphenyl arsonium chloride, the technetium will be precipitated preferentially.

Chemical yield is determined by comparing the weight of this precipitate with that which is obtained from 10 mg of rhenium precipitated directly as tetraphenyl arsonium perrhenate. In all normal circumstances, the ^{99}Tc makes no significant contribution to the source weight. The beta activity of the ^{99}Tc is subsequently measured on a thin end window gas-flow proportional counter.

Full laboratory working details are given in the Appendix, together with practical notes for the analyst.

3. YIELD TRACERS

The mass of technetium present in the majority of environmental materials is likely to be extremely small. Thus, 27 mBq (1 pCi) of ^{99}Tc has a mass of only 6×10^{-11}

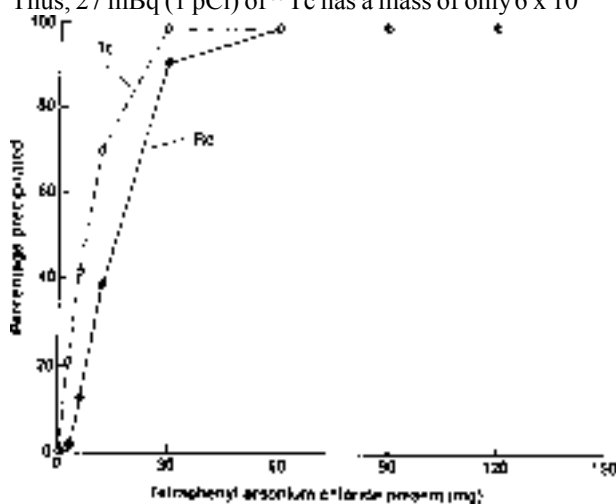
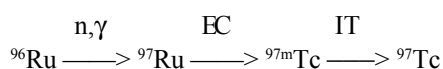


Figure 4. Co-precipitation of Re and Tc as tetraphenyl arsonium perrhenate and pertechnetate with varying amounts of tetraphenyl arsonium chloride reagent

g and no stable isotope of the element will be present to act as a carrier for the ^{99}Tc during the analytical separation. It is impossible to devise any procedure which could guarantee complete recovery of all of the ^{99}Tc from the environmental matrix, hence, some means must be found to determine the chemical yield in a way which is as reliable as possible.

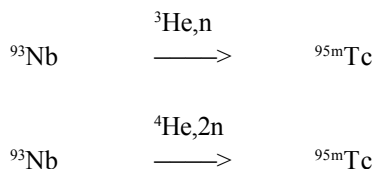
Despite the multiplicity of other technetium nuclides, none is available for use at the present time which possesses the characteristics necessary for an ideal yield monitor in this analysis (see Harvey and Lovett, 1984).

Four isotopic tracers have been described in the literature, $^{99\text{m}}\text{Tc}$ ($t_{1/2} = 6.02$ hours), ^{97}Tc ($t_{1/2} = 2.6 \times 10^6$ years), $^{97\text{m}}\text{Tc}$ ($t_{1/2} = 90$ days), and $^{95\text{m}}\text{Tc}$ ($t_{1/2} = 61$ days), but each has drawbacks. For example, the very short-lived $^{99\text{m}}\text{Tc}$ is a popular and, in many ways, very good yield tracer (Holm *et al.*, 1984). However, immediately prior to use, this has to be separated from its parent ^{99}Mo , which itself has a half-life of only 66.7 hours (Mattsson, 1978). It is thus unsuitable for pre-concentration applications in the field. Furthermore, doubts have been expressed concerning the faithfulness with which this (and other very short-lived nuclides) reacts chemically, in an identical manner to the long-lived nuclide which it is intended to monitor (Martinez-Lobo *et al.*, 1986). For these reasons, $^{99\text{m}}\text{Tc}$ has not been chosen for general use as a yield monitor at DFR. Kaye *et al.* (1982) described the use of $^{97\text{m}}\text{Tc}$ as a yield monitor, but the quantities that must be added in order to make reliable measurements of the tracer can frequently cause significant interference in the β -assay of the small amounts of ^{99}Tc present in many environmental samples. Elimination of this interference by the use of absorbers significantly reduces the counting efficiency of the ^{99}Tc . The long-lived ^{97}Tc is of course used in the isotope dilution, mass spectrometric analysis of ^{99}Tc (Anderson and Walker, 1980). In this application it is very satisfactory, and consideration has been given to its use for radiometric assay at DFR (by counting the 19.7 KeV molybdenum K X-rays emitted during its decay). Unfortunately, the only practical production process for ^{97}Tc is as follows:



Even when enriched ^{96}Ru is used as the target, a variety of other nuclides of Tc are formed and efforts to date have not resulted in the production of ^{97}Tc which is pure enough to be used as a yield monitor in this way.

$^{95\text{m}}\text{Tc}$ is probably the most satisfactory yield monitor for analysis of ^{99}Tc , provided that it can be obtained in a pure state (Chu and Feldstein, 1984). This is most easily achieved by the cyclotron bombardment of niobium with helium nuclei, thus:

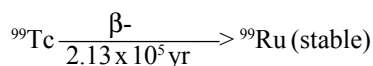


Unfortunately, the yield by this production route is rather low making the product expensive, particularly when its relatively short half-life is taken into consideration. Most $^{95\text{m}}\text{Tc}$ available commercially is produced by cyclotron bombardment of molybdenum targets and inevitably contains other technetium nuclides, most of which interfere in the beta-counting of ^{99}Tc .

Because of the foregoing difficulties in the use of isotopic tracers, the procedure currently favoured at DFR for the determination of chemical yield, makes use of stable rhenium. This non-isotopic tracer acts also as a carrier for the technetium and has much to recommend it. As with all non-isotopic yield monitors, differences in chemical behaviour between tracer and determinand exist and these must be accommodated. The important differences for the present work can be summarized as differences in volatility, differences in the ease with which reduction occurs, slight differences in anion-exchange behaviour and differences in scavenging with tetraphenyl arsonium chloride reagent. These are all discussed in Section 2, where it is shown that the conditions for each stage of the analytical procedure are chosen to ensure that both rhenium and technetium follow each other faithfully throughout the scheme.

4. RADIOMETRIC AND GRAVIMETRIC ASSAYS

^{99}Tc decays entirely by beta particle emission yielding stable ruthenium as follows:



The mean beta energy is rather low at 0.1013 MeV (β -max = 0.293 MeV), hence counting is most satisfactorily carried out by liquid scintillation spectrometry or by thin end-window gas-flow proportional counter or Geiger counter. The choice depends to some extent on availability of equipment but, for low-level samples, the low background end-window counter system is to be preferred. The performances of typical liquid scintillation and end-window proportional counters are compared in Table 3, where the better figure of merit $\frac{E^2}{b}$ of the latter with its low background is clear.

At DFR, all environmental ^{99}Tc samples are now assayed by end-window proportional counters.

Figure 5 shows a calibration of a ten detector machine (Berthold LB770-2) using ^{99}Tc standard supplied by the National Physical Laboratory, Teddington, deposited along with varying weights of rhenium as tetraphenyl arsonium pertechnetate/perrhenate over a 35 mm diameter area of a 50 mm diameter planchette (using a hydrophobic edge filter paper). For an average recovery, of say 70-80%, the uncertainty associated with the calibration is better than $\pm 2\%$ at the 90% confidence level.

In order to calculate the lower limit of detection (LOD) for this procedure, a minimum amount of activity, based on a critical count (MACC) may be defined such that, above this critical level, there is a probability $<P$ that the result is due to the net zero signal (background).

Thus:

$$\text{MACC} = F \times k \times \sqrt{2N}$$

where N is the the number of background counts recorded;

k is a factor dependent on the probability requirement for not being in error (for probability <0.05 , $k = 1.645$); and

F is a factor converting counts to activity.

Thus, for a measurement time of 500 minutes, background count-rate of 0.5 cpm, counting efficiency of

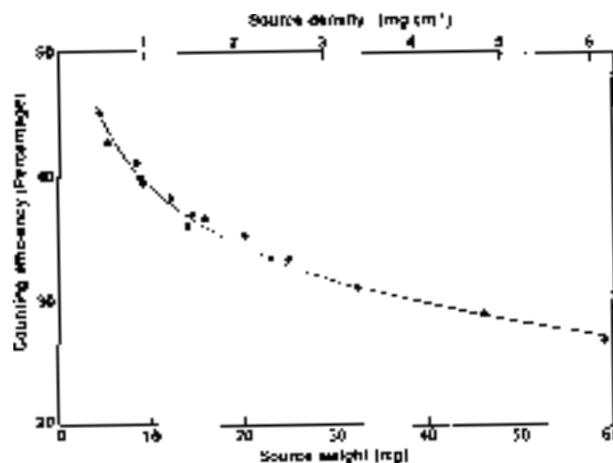


Figure 5. Efficiency versus source weight calibration of Berthold LB770-2 ten-detector, end-window, gas-flow, proportional beta counter for ^{99}Tc (window 0.4 mg cm^{-2})

32% and mean recovery of 80%

$$\text{MACC} = F \times 1.645 \times \sqrt{2 \times 500 \times 0.5} = 0.0048 \text{ Bq.}$$

Hence, by commonly accepted practice:

$$\text{LOD} = 3 \times \text{MACC} = 0.014 \text{ Bq.}$$

The radiochemical yield is determined by weighing the tetraphenyl arsonium perrhenate/pertechnetate precipitate as $(\text{C}_6\text{H}_5)_4\text{As ReO}_4$. This compound has been shown to possess excellent characteristics as a gravimetric reagent for rhenium (Willard and Smith, 1939). Figure 3 seems to indicate that the rhenium starts to precipitate before the technetium, and may indeed act as a scavenging agent for the very small mass of ^{99}Tc present.

5. METHOD PERFORMANCE

Several sources of error need to be considered in the radiochemical analyses of ^{99}Tc ; the more important ones are discussed below.

Table 3. Detection characteristics of ^{99}Tc by different counting systems

System	Background (b) (cpm)	Efficiency (E) (cpm/dpm)	$\frac{E^2}{b}$
Liquid scintillation spectrometer (LKB 1217 Rackbeta)	19	0.90	0.043
End-window proportional counter (50mm) (Berthold LB 770-2)	0.45	0.32	0.23

5.1 Volatility of Tc and Re

Possible losses of ^{99}Tc as the heptoxide Tc_2O_7 , or pertechnetetic acid HTcO_4 and ways of preventing such losses during dry ashing have been discussed in Section 2. The conditions recommended for ashing are effective but there remains an uncertainty at this stage because no effective yield tracer can be employed to cover losses.

Volatility is also possible from solutions at subsequent stages, for example, if the mixture is allowed to go dry in the presence of nitric or other oxidizing acids. Even though the rhenium yield monitor may be present in the solution, error might occur because of differential losses of tracer and determinand.

5.2 Yield monitor

Two types of error are possible in the present procedure. As with any yield monitor its function can only be performed reliably if proper equilibration between tracer and determinand is achieved at the earliest possible stage in the analysis. In the present case, the rhenium is added as an inorganic perrhenate salt and it is the responsibility of the analyst to ensure that the technetium is brought completely into this same oxidation state and that none is left as the complex organic species.

After having achieved the above equilibration, errors are still possible with a non-isotopic yield monitor if the two elements are allowed to respond differently to the chemical manipulations employed. The various opportunities for errors and their prevention have been discussed in Section 2.

5.3 Contaminants

However well designed an analytical procedure might be, it is unlikely to cope with every possible situation. In the case of a low-energy beta emitter such as ^{99}Tc , the ultimate proof of source purity is best achieved by reprocessing any sample for which doubts exist. On reprocessing, the specific activity of the ^{99}Tc relative to the rhenium yield monitor should remain constant if the source was free from beta-active contaminants. The most likely contaminants and the decontamination factors achieved by the present method are listed in Table 4.

5.4 Tetraphenyl arsonium perrhenate/pertechnetate precipitate

The errors that occur so easily at this stage are worthy of special mention. The greatest potential source of error at this point is the persistence of perchlorate ions in the sample following the sulphide precipitation. Perchlorate also forms an insoluble tetraphenyl arsonium salt and its presence increases the apparent yield achieved. This particular source of error is most easily avoided by repeating the sulphide precipitation.

6. METHOD VALIDATION

Good reproducibility has been obtained with an in-house, 'quality-control' sample as illustrated in Table 5. A sample of this 'quality control' material and a process blank are analysed as part of every batch of environmental samples.

Table 4. Decontamination factors for nuclides most likely to interfere in the analysis of ^{99}Tc

Nuclide	β -max(MeV)	Decontamination factor
^{137}Cs	0.514	$> 10^5$
^{106}Ru (^{106}Rh)	0.0396(3.54)	10^4
$^{110\text{m}}\text{Ag}$ (^{110}Ag)	0.529 (2.89)	10^5
^{125}Sb	0.300	5×10^4
^{90}Sr (^{90}Y)	0.546(2.28)	$> 10^5$

Table 5. Replicate analysis of a 'quality-control' sample, prepared from *Fucus* seaweed from the Sellafield area

Sample	Chemical recovery of Re (%)	⁹⁹ Tc concentration (Bq kg ⁻¹)
QCX 1	99.5	1967
QCX 2	97.3	1990
QCX 3	95.2	2042
QCX 4	94.0	2082
QCX 5	85.2	2007
QCX 6	88.1	1967
QCX 7	88.1	2069
QCX 8	89.3	2009
QCX 9	99.3	1951
QCX 10	92.6	2054

Mean	92.9±5.0	2014±46

The method has also been shown to perform successfully in intercomparison exercises with several different types of environmental materials, including sediments and marine biota (see for example Bates, 1988 (laboratory 3, method B)).

The reference to proprietary products in this report should not be construed as an official endorsement of these products, nor is any criticism implied of similar products which have not been mentioned.

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APPENDIX. Laboratory procedure

A1 Reagents

Analytical reagents are suitable unless otherwise stated.

Prepared reagents may be stored in polythene bottles.

A1.1 Water

Distilled or deionized water should be used throughout.

A1.2 Ion-exchange resins

BioRad AG 1x8 (100-200 mesh) is specified. Supplies are available from BioRad Laboratories Ltd. Caxton Way, Holywell Industrial Estate, Watford, Hertfordshire WD1 8RP*. Other anion exchange resins, including the basic Dowex resin from which the BioRad material is prepared, might also be suitable but would need to be checked carefully before substitution.

A1.3 Standard rhenium solution

Dry potassium perrhenate (KReO_4) at 105-110°C and cool in a desiccator. Dissolve 0.7769 g in distilled water and make up to 100 ml. The rhenium concentration of this solution is 5 mg ml⁻¹.

A1.4 Thioacetamide

Use as a solid.

A1.5 Ferric iron solution

Dissolve 96.2 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 6M HCl and make up to 1 litre. This gives a solution of 20 mg Fe⁺³ ml⁻¹.

A1.6 6M hydrochloric acid

Dilute 530 ml of hydrochloric acid (1.18 sp. gr.) to 1 litre with distilled water.

A1.7 6M sodium hydroxide

Dissolve 240 g sodium hydroxide pellets in distilled water and dilute to 1 litre. (Care is needed because the dissolution is strongly exothermic).

A1.8 Sodium perchlorate reagent (0.3M NaOH/0.15M HClO₄)

Dissolve 12 g sodium hydroxide in distilled water, add 25 ml of perchloric acid (60% w/v) and make up to 1 litre with distilled water. Check that the solution is alkaline and if necessary add additional sodium hydroxide.

A1.9 Tetraphenyl arsonium chloride reagent

Dissolve 0.55 g of tetraphenyl arsonium chloride (C_6H_5)₄ AsCl x H₂O in distilled water and make up to 100 ml.

A1.10 ⁹⁹Tc standardized solution

Standardized solutions of this nuclide are available (for example) from the National Physical Laboratory, Teddington, Middlesex* or from Amersham International plc. Little Chalfont, Buckinghamshire*.

**The reference to proprietary products in this report should not be construed as an official endorsement of these products, nor is any criticism implied of similar products which have not been mentioned.*

A.2 Hazards

In addition to observing normal standards of safety in the chemical laboratory, the regulations governing the handling of radionuclides must be observed. Reference should be made to the Ionizing Radiations Regulations 1985 (Great Britain-Parliament, 1985) before using the radioactive tracers recommended in this booklet.

Hydrogen sulphide is released when thioacetamide is added to warm acid solutions. It is very poisonous (TLU 10 ppm or 15 mg m⁻³) and the sulphide precipitation should be carried out in a fume cupboard.

Tetraphenyl arsonium chloride is also highly toxic.

A.3 Precipitation of ⁹⁹Tc standard solution

Sources for calibrating the radiometric detector are prepared from dilutions of the standardized ⁹⁹Tc solution in exactly the same manner as samples are prepared for counting (see calibration procedure in Section 4 of the main text).

A.4 Apparatus

- (1) A thin end-window beta counter designed for 50 mm diameter planchettes, and of the gas-flow proportional type or gas-flow Geiger type, is ideal for assaying ⁹⁹Tc. A scaler and timer are also required if not present as an integral part of the counter.
- (2) A centrifuge, capable of taking samples up to 1 litre in size, is most convenient for the procedure recommended below.
- (3) An analytical balance, capable of weighing the planchette and precipitate to four decimal places, is required for the determination of gravimetric yield.

A.5 Detailed practical procedure

A5.1 Preliminary treatment of sea-water samples

Step	Experimental procedure	Notes
1	Collect a 40 litre sample of sea water	
2	Filter through a 0.45 µm membrane filter to remove particulate matter.	Filtering avoids clogging of the ion exchange column. The K _d in oxic waters is very low and very little ⁹⁹ Tc is likely to be associated with the particulate phase.
3	To the filtrate, add 2 ml of the standard rhenium solution and shake to ensure mixing (10 mg Re).	
4	Pass the filtrate through a column of anion exchange resin at a rate of 2 litres hr ⁻¹ .	A convenient column is made with 40 ml of AG 1x8 (100-200 mesh) contained in a 50 ml polystyrene syringe.
5	Wash the resin from the syringe into a 250 ml Pyrex glass beaker, add 1 g NaCl and moisten thoroughly with ammonia solution (0.880 sp.gr). Dry in an oven at about 100°C.	—

Step	Experimental procedure	Notes
6	Place the beaker in a muffle furnace at 250°C and then raise the temperature by 50°C per hour to 450 ± 25°C.	—
7	When cool, add 25 ml of distilled water, 25 ml of 11.3M HCl, 1 ml of the Fe ³⁺ solution and 2 ml of 100 vol. H ₂ O ₂ . Warm on a hot-plate for about 15 minutes then dilute to 100 ml with distilled water.	—
8	Add 50 ml of 6M NaOH, 2 ml of 100 vol. H ₂ O ₂ and warm for a further 2 hours.	Ensure that the solution is alkaline.
9	Cool and then filter off the Fe (OH) ₃ precipitate.	An 18.5 cm Whatman No. 542 paper is suitable.
10	Proceed to the purification stage.	See note at A5.3 (Step 1).

A5.2 Preliminary treatment of biota and sediments

Step	Experimental procedure	Notes
1	Weigh out 10 g of the dried material into a 250 ml beaker. Add 2 ml of the standard rhenium solution, moisten thoroughly with ammonia solution and dry at about 100°C in an oven.	Samples are normally dried at 100 ± 5°C.
2	Ash the dried sample as described in A5.1 (Step 6).	—
3	To the ashed sample, add 25 ml of distilled water, 25 ml of 11.3M HCl, 1 ml of the Fe ³⁺ solution and 2 ml of 100 vol. H ₂ O ₂ . Warm on a hotplate for 15 minutes and then dilute to 100 ml with distilled water.	If insoluble carbonaceous material remains, filter off and re-ash. Then repeat the HCl/H ₂ O ₂ extraction on the re-ashed material using the first filtrate as extractant and combine the solutions before proceeding to Step 4.
4	Add 50 ml of 6M NaOH, 2 ml of 100 vol. H ₂ O ₂ and warm for a further 2 hours.	Ensure that the sample is alkaline by adding more 6M NaOH if necessary.
5	Cool and then filter off the Fe(OH) ₃ precipitate.	An 18.5 cm Whatman No. 542 paper is suitable.
6	Proceed to the purification stage.	See note at A5.3 (Step 1).

A5.3 Purification stage

Step	Experimental procedure	Notes
1	Pour the filtered sample through an anion-exchange column, formed from 1.5 ml of AG 1x8 (100-200 mesh), into a glass Pasteur pipette of internal diameter 0.6 cm containing a small plug of glass wool to support the resin.	A sample volume to resin ratio of about 100:1 is suitable. A filter funnel may be attached to the column so that the filtration operation can be combined with passing the sample through the resin.
2	Discard the effluent and wash the column with 100 ml of 2M NaOH solution. Discard the washings.	—
3	Elute Tc and Re with 150 ml of the sodium perchlorate reagent, collecting the eluate in a 250 ml glass beaker.	The reagent should be alkaline. The elution takes about 2 hours.
4	Add 2 ml of 100 vol. H_2O_2 and warm on a hotplate for 2 hours. Then add 20 ml HCl and heat to boiling. Add 2 g thioacetamide and maintain at 80-90°C in a water bath for a further 2 hours.	—
5	Filter off the Tc and Re sulphides using a small membrane filter rig. Then wash the precipitate thoroughly with deionized water.	Such as 47 mm diameter 0.45 μ m pore size.
6	Reject the filtrate and thoroughly wash out the reservoir. Reassemble the filter rig and dissolve the sulphide precipitate in 60-70 ml of a warm 4:1 mixture of 0.880 sp. gr. NH_4OH /100 volume H_2O_2 .	—
7	Suck the membrane dry and transfer the filtrate to a 250 ml glass beaker. Heat on a hotplate until the volume is reduced to 20-30 ml.	The initial brown colour of the solution is lost during volume reduction.
8	Dilute to 150 ml with deionized water. Add 15 ml of 11.3 M HCl and heat to boiling. Add 2 g of thioacetamide and maintain at 80-90°C for 2 hours. Repeat Steps 5 to 7.	—
9	Make the volume up to 50 ml with deionized water and then cool in a refrigerator overnight.	—

A5.4 Source preparation

Step	Experimental procedure	Notes
1	To the cold 50 ml sample, add 20 ml of the tetraphenyl arsonium chloride reagent, slowly and with swirling.	—
2	Filter the precipitate on to a tared filter membrane (47 mm in diameter, with 0.45 µm pore size). Wash the filter twice with a few millilitres of distilled water. Vacuum desiccate overnight.	Hydrophobic edged membranes produce a more even source for counting.
3	Weigh the membrane and precipitate to determine the chemical yield.	The precipitate is weighed as $(C_6H_5)_4AsReO_4$ MW = 633.5482. For Re, MW = 186.207.
4	Mount the membrane onto a 50 mm diameter stainless-steel planchette, using a smear of glue, and count using an end-window beta counter, suitable for low energy beta particles.	—
5	Count a standard ^{99}Tc source with each batch of samples to confirm that the detector response agrees with the calibration.	—

A.6 Calculation of results

A6.1 Chemical yield

A known amount (normally 10 mg) of Re is added to samples as potassium perrhenate solution, to act as yield monitor and carrier for the ^{99}Tc .

At the end of the separation scheme, the Re (+Tc) is precipitated and weighed as $(C_6H_5)_4AsReO_4$:

molecular weight of $(C_6H_5)_4AsReO_4$ = 633.548;

atomic weight of Re = 186.207.

Thus, the percentage recovery (R%) is given by:

$$R_{\%} = \frac{\text{weight of precipitate} \times 186.207 \times 100}{\text{weight of Re added} \times 633.548}$$

A6.2 Concentration of ^{99}Tc

The counting efficiency for ^{99}Tc in the sample is obtained by reference to a graph (prepared as in text Figure 4). The counter's background count rate should be measured regularly to give a running mean.

The ^{99}Tc content (A) of the sample (in Bq kg⁻¹) is then given by:

$$A_{^{99}Tc} = \frac{s}{t_s} - \frac{b}{t_b} \times \frac{100}{R_{\%}} \times \frac{100}{E_{\%}} \times \frac{1}{60} \times \frac{1000}{w} \text{ Bq kg}^{-1}$$

where s is the counts recorded for the sample in time (t_s) minutes;
 b is counts recorded for background in time (t_b) minutes;
 $E_{\%}$ is the percentage counting efficiency for ^{99}Tc
 i.e. $100 \times \text{counts per minute (cpm)}/\text{disintegrations per minute (dpm)}$
 at the given source weight;
 $\frac{1}{60}$ is the factor to convert dpm to becquerels; and
 w is the weight (g) of sample taken.

A6.3 Precision of the analysis

The errors associated with the analysis arise chiefly from the following two sources:

- (1) that associated with the determination of yield; and
- (2) the statistics of radioactive counting.

For the determination of chemical yield, an overall error of $\pm 4\%$ is allowed to cover the collective uncertainties of the gravimetric procedure, including calibration of the Tc standard and weighing of the filter membrane and final precipitate.

For the beta counting:

$$\% \sigma_{S-B} = \frac{100}{(S-B)} \left(\frac{S}{t_s} + \frac{B}{t_b} \right)$$

where $\% \sigma_{S-B}$ is the percentage standard deviation on the net count rate of the sample (Faires and Boswell, 1981);

S is the sample count rate (cpm);

B is the background count rate (cpm); and

t_s and t_b are as defined in A6.2

Thus the total percentage error on the analysis is given by:

$$(\%) \text{ total error} = \frac{100}{S-B} \left(\frac{S}{t_s} + \frac{B}{t_b} \right)^2 + (4)^2$$

A.7 Appendix references

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