

⁹⁹Tc in the Environment: Sources, Distribution and Methods

Manuel García-León*

Facultad de Física Universidad de Sevilla Apdo. 1065, 41080 Sevilla Spain

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⁹⁹Tc is a β -emitter, $E_{\max} = 294$ keV, with a very long half-life ($T_{1/2} = 2.11 \times 10^5$ y). It is mainly produced in the fission of ²³⁵U and ²³⁹Pu at a rate of about 6%. This rate together with its long half-life makes it a significant nuclide in the whole nuclear fuel cycle, from which it can be introduced into the environment at different rates depending on the cycle step. A gross estimation shows that adding all the possible sources, at least 2000 TBq had been released into the environment up to 2000 and that up to the middle of the nineties of the last century some 64000 TBq had been produced worldwide. Nuclear explosions have liberated some 160 TBq into the environment. In this work, environmental distribution of ⁹⁹Tc as well as the methods for its determination will be discussed. Emphasis is put on the environmental relevance of ⁹⁹Tc, mainly with regard to the future committed radiation dose received by the population and to the problem of nuclear waste management. Its determination at environmental levels is a challenging task. For that, special mention is made about the mass spectrometric methods for its measurement.

1. Introduction

The discovery of element 43 was announced at the beginning of the 20th century after the observation by Noddack and Tracke¹ of an unknown radioactive isotope in uranium ores. Results were not reproduced in further experiments and the scientific community did not accept this finding.

Nowadays it is fully accepted that the element Technetium ($Z = 43$) was discovered by Perrier and Segré in 1937.² It was produced by irradiating for some months a molybdenum target with deuterons at the Berkeley cyclotron.

Ten years later, Paneth³ suggested the name of technetium, after the Greek word τεχνητικός (artificial), for the new element due to the fact that it was the first chemical element artificially produced.

So far 24 isotopes of the element are known with 9 nuclear isomers. All of them are radioactive with half-lives ranging from a few milliseconds to a few million years.

From an environmental viewpoint, only ⁹⁹Tc seems to be relevant because of its high production rate in the fission of ²³⁵U and ²³⁹Pu, around 6%, similar to that of ¹³⁷Cs, and its nuclear characteristics. Indeed, it is a β emitter with $E_{\max} = 294$ keV and $T_{1/2} = 2.11 \times 10^5$ y. Such a long half-life assures its presence in nature once released from a given source. Therefore, it is considered to be an important contributor to the future collective dose to the population due to the use of nuclear energy, playing an important role in the problem of nuclear waste management.

On the other hand, due to its chemical characteristics ⁹⁹Tc can be used to trace the evolution of natural compartments. For instance, ⁹⁹Tc conservatively behaves in water. This is the reason why it is a potential tracer of marine water dynamics or other water masses movement.

In what follows a comprehensive account on the sources, distribution and behavior of ⁹⁹Tc in the environment will be given. The methodology for its measurement in environmental samples will also be reviewed.

Of course I will feel satisfied if this paper could be considered as a good complementary reading of other excellent views

on the topic of environmental ⁹⁹Tc, as for instance that presented by Prof. K. Yoshihara.⁴

2. Sources

At the beginning of Tc research, scientists did not believe that Tc was present in nature. In fact, this was an important reason why they called technetium. Nowadays, it is well known that it can be found in nature as produced by natural means.⁵ Indeed, it was 30 years after its discovery that Kenna and Kuroda⁶ were able to detect it in pitchblende samples. And on the basis of the ⁹⁹Tc/²³⁸U isotopic ratio, they concluded that ⁹⁹Tc was mainly produced by the spontaneous fission of ²³⁸U, although the neutron-induced fission of ²³⁵U could be a minor way of production. As an example, it can be said that ⁹⁹Tc/²³⁸U ratio of around 10^{-12} is found in U-mineral samples⁵ which gives an idea on the experimental difficulty for the characterization of this production way. These findings are scientifically relevant. However, the production of ⁹⁹Tc by the spontaneous fission of ²³⁸U is a negligible source of ⁹⁹Tc in the modern environment.

The most important way of ⁹⁹Tc production and, consequently, the main source in the modern environment is the nuclear fission in nuclear weapons and reactors.

Estimations by Aarkrog et al.⁷ showed that about 140–160 TBq of ⁹⁹Tc have been produced by nuclear weapon detonation. This amount, although important, is at least one order of magnitude smaller than that produced by the nuclear industry. The weapon pulse is nowadays masked by it and cannot be found in environmental samples with the probable exception of ice and, to a less extent, sediment cores.

⁹⁹Tc produced in reactors enters the nuclear fuel cycle and from the different steps of the whole cycle it is introduced into the environment. It is calculated that the inventory in PWR fuels is about 9 kg of ⁹⁹Tc per 1 GW(e) year. Thus, it is estimated that, up to 1983, around 15000 TBq of ⁹⁹Tc was produced in nuclear power stations worldwide.⁸ From that date to 1993, the production of ⁹⁹Tc is estimated to be 49000 TBq.⁴ Calculations made by F. Luykx in 1986⁸ showed that up to such date about 1000 TBq of ⁹⁹Tc had been released into the environment mainly from the nuclear fuel reprocessing, since the release from nuclear power stations is very low, roughly 4 GBq.⁹

However, according to Kershaw et al.¹⁰ only from the Sellafield

*Corresponding author. E-mail: manugar@us.es. FAX: +34-95-4460145.

plant, about 950 TBq of ^{99}Tc was released into the environment from 1978 to 1998. The radioactivity release trends have been very different at Sellafield and La Hague nuclear reprocessing plants. From 1982 to 1991, 102 TBq was discharged from La Hague, while 40.2 TBq was from Sellafield.¹¹ This tendency drastically changed after that the Enhanced Actinide Removal Plant (EARP) began its operation in 1994 (see following sections for details).

It is not easy to estimate the total ^{99}Tc radioactivity actually stored in nuclear power plants or classified as low to medium radioactive wastes, especially bearing in mind that the whole ^{99}Tc inventory related to the former Soviet Union countries is not known. With the previous data a very rough calculation shows that a lower limit could be 60000 TBq.

Inputs of ^{99}Tc from the use of nuclear medicine ^{99}Mo - $^{99\text{m}}\text{Tc}$ generators should also be taken into account although its contribution on a global scale is clearly less important than the other sources. According to Reference 9, a medium-sized Nuclear Medicine Service produces some 200 kBq/y in the average. Thus, a gross calculation would give that this source has contributed to the total inventory with a few GBq of ^{99}Tc during the last 10 years.

The major accident of Chernobyl introduced 0.75 TBq into the environment.¹²

Generally speaking, it can be concluded that the most intense source to the environment is the reprocessing of nuclear fuel and it is also apparent that the amount of stored ^{99}Tc in nuclear wastes is at least one order of magnitude greater than the amount so far introduced in to the environment.

3. Distribution and Behavior

Sea Water. Due to its chemical characteristics, ^{99}Tc is known to behave as a conservative radionuclide in marine and fresh water under oxidizing conditions.¹³ Indeed, the most probable Tc compound in water is TcO_4^- which is very stable and soluble,¹⁴ showing very low affinity to particulate matter and sediments.¹⁵

Since the main source of ^{99}Tc in the environment is associated to the release of radioactive wastes into the sea, many works have been devoted to the determination of ^{99}Tc in marine water. A pioneer work by Golchert and Sedlet,¹⁶ reported on ^{99}Tc concentration in water, of unknown origin, of about some tens of mBq per liter. I will refer later to this work, since the authors present one of the first procedures for Tc measurement in water appeared in the current literature.

More recent determination has been carried out in the vicinity of the European fuel reprocessing plant of Sellafield and La Hague. For instance, Riley and Siddiqui¹⁷ found concentration levels ranging from 15 to 75 mBq/L in water samples from the North Sea. Parallel measurement in the English Channel coasts by Patti et al.¹⁸ showed that concentrations lay between 5 and 21 mBq/L. Some 500 mBq/L has been measured by Eroglu et al.¹⁹ in water samples collected close to the location of Sellafield release area in the Irish Sea. All these results show the influence of the reprocessing plant on the close environment.

Far from the plants, it is also possible to find their fingerprints in the form of enhanced ^{99}Tc concentrations with regard to the expected fallout level. Several factors make complex the relationship between the release from a reprocessing plant and the concentration increase at a location far away from the release point. Some of them are: 1) the amount of discharge, which is not constant with time (see Figure 1), 2) the ocean conditions, which can vary with time, and 3) the existence of a certain time and space dispersion of pollutants in the sea, which arrive to the collection places as successive tides.

Taking into account these factors, a transit time from La Hague to Kattegat was calculated¹³ to be in the range from 15 to 18 months. In the case of Sellafield, the transit to Northern Norway takes about 40 months. The data have recently been

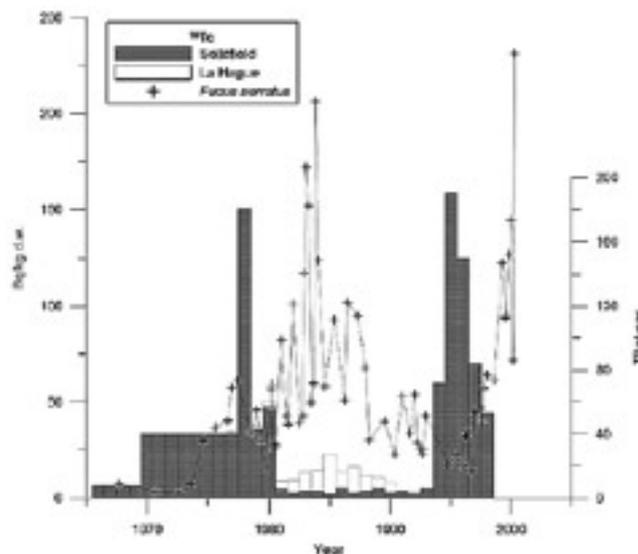


Figure 1. Taken from Reference 23. Technetium-99 activity concentration in *Fucus serratus* (primary axis) from Särda (56.76 °N, 12.63 °E) in Sweden, 1967–2000, and annual ^{99}Tc activity discharge from Sellafield (U.K.) and La Hague (France) reprocessing plants (secondary axis).

updated, as shown in Reference 20. These authors reported levels of some 1 mBq/L from 1990 to 1992 in Norwegian coastal waters. The concentration reached the value of up to 9 mBq/L for the period from 1996 to 1997, just after the Enhanced Actinide Removal Plant (EARP) at Sellafield began its operation in 1994.

The influence of EARP was also noted by Smith et al.²¹ who measured the concentration of up to 60 mBq/L in seawater from the open Irish Sea. This peak coincided with the maximum release of ^{99}Tc from Sellafield which happened around 1997. Then in 1998, the authors observed a decrease in the contamination till about 20 mBq/L.

The influence of Sellafield is also observed in the Greenland coasts and, in the North Pole environment. Many literatures are certainly relevant to these regions. As an example, I can take the Reference 22 which provides the data on the concentration of ^{99}Tc , in Eastern Greenland water with special mention on the origin of the water masses. Polar water is found to contain about 70 mBq/m³ of which the author estimates that 10 mBq/m³ are the weapon fallout contribution.

A recent long-term study on ^{99}Tc in the marine environment of the Swedish coasts²³ shows that the more important source has been the liquid discharges from the reprocessing plant of Sellafield. Levels in seawater of about 1 Bq/m³ were found. The authors also claim that ^{99}Tc is one of the best transit tracers for the water circulation in the Baltic Sea.

Better analytical procedures allowed the determination of ^{99}Tc in seawater that was not affected by intense radioactivity sources. Momoshima et al.²⁴ reported levels as low as 1 mBq/m³ in the sea water taken in 1993 at Fukuoka, Kyushu, Japan. Nevertheless, Hirano and Matsuba²⁵ were able to detect the activity concentration as high as 200 mBq/m³ in water samples collected from the Iozaki Coast, during the period from 1987 to 1990. The authors carefully analyze the data and conclude that the observed peak can be attributed to the operation of the nearby nuclear installations although the exact source could not be identified.

Seaweed. The determination of ^{99}Tc in sea water is a challenging task. For that, in many cases, the use of bioindicators has been the choice to determine ^{99}Tc in the marine environment. Brown seaweeds, mostly *Fucus vesiculosus*, *serratus* or *spiralis*, have been the most popular bioindicators for ^{99}Tc in marine systems. The mechanisms of ^{99}Tc incorporation into the seaweed are not precisely known. At the very beginning of

research, surface absorption was the suggested mechanism.

A good, although not the only, example on how good ⁹⁹Tc concentrations in brown seaweed represent those in sea water can be seen in Reference 18. The authors studied the presence of ⁹⁹Tc in the marine environment close to La Hague plant. The dependence on the distance from the plant release point is almost identical for water and seaweed. Concentration values of the order of 10⁴ L/kg were found for *Fucus spiralis*. Some authors found a concentration of 10⁵ L/kg for *Fucus vesiculosus*.⁹ Actually this figure significantly changes among different environment and cannot be taken as a fixed number. But the potential of such algae species as a ⁹⁹Tc bioindicator is obvious.

This finding can be traced back to the work by Dutton and Ibbett.²⁶ They studied the ⁹⁹Tc content in *Fucus vesiculosus* collected in the Irish Sea. After these first studies, the use of *Fucus* species as spatio-temporal indicators of the ⁹⁹Tc evolution in the marine environment became a common practice. In particular, it has permitted to evaluate the impact of Sellafield and La Hague on the North European marine environment, including Greenland and Polar surroundings. Examples can be seen in the above cited works for sea water (see Figure 1). Of course, the concentration in sea water can help to estimate the levels in algae. It could be also said that these studies had provided with a plenty of information on the water circulation in the North Atlantic area.

Almost all the studies on ⁹⁹Tc concentration in seaweed have been carried out in the North Atlantic transect due to the contaminant character of the nuclear fuel reprocessing plants at La Hague and Sellafield. However, the measurement of ⁹⁹Tc concentration in algae samples has been carried out in the other environments. For instance, levels in *Fucus vesiculosus* samples taken at Galicia, Northwestern Spain, in 1984 reached values of some 0.4 mBq/g dry weight, which were attributed to fallout background in such area.²⁷ Manjón et al.²⁸ measured ⁹⁹Tc in several seaweed species collected at the Southern Spanish coasts during 1988 and 1989. ⁹⁹Tc was detected basically in *Fucus spiralis* and *vesiculosus* and, in general terms, the concentration values of some 0.1 mBq/g were found and interpreted as general background in the absence of local sources of radioactivity. For the sake of comparison, levels up to 10⁴ mBq/g were found for *Fucus vesiculosus* taken at the Irish Sea after the beginning of EARP operation.²¹

Hirano and Matsuba²⁵ presented very interesting results of ⁹⁹Tc in *Sargassum* algae collected in Japan. The authors found concentration values of 10⁴ L/kg for this algae species.

Atmosphere. There are not so much works published on the presence of ⁹⁹Tc in the atmosphere. Attrepp et al.²⁹ and later Ehrhardt and Attrepp³⁰ communicated the data on rainwater (14 samples in total) taken at Texas from 1960 to 1970. Concentrations of the order of 10⁻² mBq/L were reported in these works. In 1993 results were published³¹ on rainwater taken at the South of Spain from 1984 to 1987. Levels ranged from 10⁻³ to 10⁻¹ mBq/L and are compatible with those found by the previous authors. The American and the Spanish groups found anomalously high ⁹⁹Tc/⁹⁰Sr and ⁹⁹Tc/¹³⁷Cs activity ratios in the samples from Texas and Spain compared to what it is expected if fission were the only source of ⁹⁹Tc in the environment, i.e. ~10⁻⁴. Furthermore, the ratio steadily increased since 1960 till 1987. Calculations showed that ⁹⁸Mo neutron activation was not a significant source of ⁹⁹Tc which could explain the deviation from the expected ratio. Some hypothesis was done on the possibility that a slightly higher residence time of ⁹⁹Tc in the stratosphere could account for the discrepancy.³¹ The answer to this problem still remains unresolved, since the influence on a global scale of gaseous emissions from nuclear reprocessing plants cannot be discarded as an additional explanation for this fact. Nevertheless, as far as I know, there is no work in the open literature supporting this possibility. The only observa-

tion related to this effect is found in Reference 32, which gave results on the environmental impact of the ⁹⁹Tc gaseous releases from the Karlsruhe nuclear reprocessing plant. The detected effects were local in any case.

The concentration of ⁹⁹Tc was also measured in samples taken after the Chernobyl accident.³¹ It was found no relevant difference between the concentration found before and after the Chernobyl accident. This is consistent with the results of Reference 12. For the same samples, it was found that the levels of ¹³⁷Cs increased some two orders of magnitude after the Chernobyl accident.

It is interesting to note that the same group³³ measured ⁹⁹Tc in atmospheric filters taken in the south of Spain during the sixties. Its maximum concentration was found to be 3 μBq/m³ in 1967. E. Holm³⁴ calculated the ⁹⁹Tc/¹³⁷Cs activity ratio with these data and found higher ratios than expected. In the same reference, the data on air filters taken at Sweden and Monaco showed also such anomaly.

Finally, the data of Holm and Rioseco³⁵ on ⁹⁹Tc in carpets of lichen and soils deserve attention since they could inform on the behavior of ⁹⁹Tc in the atmosphere.

Sediments and soils. As it was stated before, ⁹⁹Tc is very soluble and mobile in seawater. For that reason, it is not easily measured in open sea sediments. Reducing conditions in water and in the sediment, or in the sediment, facilitate its absorption on the sediment. Interesting works on the process that could lead the incorporation of ⁹⁹Tc onto the sediment are those of References 36 and 37. In these works, chemical speciation of ⁹⁹Tc was studied in real samples. The authors found that organic material appeared to be the most important binding phase for Tc(IV). Apparently, highly reducing conditions enhance the organic uptake of Tc, which, in fact, was already stated by Tagami.³⁸ Low organic matter content, on the other hand, enhances the Tc association to carbonates.

The majority of the works on the concentration of ⁹⁹Tc in marine sediments have been carried out in the surroundings of intense release sources. From this viewpoint, the North Atlantic area is fairly well studied. A very complete work can be found in Reference 39 on the ⁹⁹Tc inventory in sediments of the Irish Sea close to Sellafield. Up to 2 Bq/cm² can be found in the most contaminated samples.

A very unique work is that reported by Aarkrog et al.⁴⁰ on the presence of ⁹⁹Tc in river sediments. The authors found the maximum activity peak (780 mBq/g) at a sediment-core depth of 14–18 cm that corresponded to the year 1950. This date coincides with the maximum releases from the MAYAK plutonium production plant at the Urals. According to them some 100 PBq of low to medium liquid wastes was discharged into the Techa river from 1949–1952. The authors supposed the existence of reducing conditions to explain the presence of ⁹⁹Tc in the sediment.

For the same reason as in the case of sediments, the measurement of ⁹⁹Tc in soils is difficult due to the low concentration in them, in the absence of a direct source. In spite of this, global fallout ⁹⁹Tc distribution in Japanese soils has been determined by Tagami and Uchida.⁴¹ The values found range from 4 to 88 mBq/kg. The observed high differences were attributed by the authors to the variability of soil types. The ⁹⁹Tc/¹³⁷Cs activity ratio in the soils was reported to be one order of magnitude higher than that theoretically expected. The authors explained such fact not only on the basis of the ratio during the deposition but also to the irrigation practices and behavior in soils of the two radionuclides. The vertical distribution of ⁹⁹Tc in soil cores shows that it migrates faster than ¹³⁷Cs. Nevertheless the bulk of ⁹⁹Tc still remains within the first 20 cm of soils.

The described set of data can be compared to those obtained in the soils from the Marshall Islands by the same group.⁴² The area was presumably contaminated by nuclear tests and the

obtained results confirmed it, since levels of some 0.1 to 1.1 mBq/g were found.

Morita et al.⁴³ also presented concentration profiles of ⁹⁹Tc in a soil and compared its behavior to the other long-lived radionuclides. The authors found that ⁹⁹Tc and the other nuclides were retained also in a part of the profile which contained more organic matter.

As stated in Reference 4, it is not easy to understand the behavior of ⁹⁹Tc in soils. It depends on many variables and their combinations. What it seems clear is that under aerobic conditions ⁹⁹Tc is very mobile since it is expected to be as TcO₄⁻. In that case, its availability to plants is high.⁴⁴ At anaerobic conditions, ⁹⁹Tc is reduced at lower valence states and its mobility decreases. ⁹⁹Tc needs, therefore, the existence of reducing conditions to be absorbed in soils. If this happens, its transference to vegetal species decreases very much, which is certainly relevant to agricultural soils.³⁸ The last two cited works are the key to understand the behavior of ⁹⁹Tc in soils as well as its availability to plants.

4. Methods

In general terms, the concentrations of ⁹⁹Tc in the environment are very low. Therefore, very sensitive methods are needed for its determination. In all the cases, the chemical separation of Tc from a sample is required and the addition of a yield tracer is necessary. Once Tc is separated, radiometric or non-radiometric methods can be used for ⁹⁹Tc determination.

Radiochemistry. Broadly speaking, the chemical separation method for environmental Tc consists of three steps: sample pretreatment, Tc extraction, and final conditioning for counting. A brief discussion of the methods found in the literature is given below on the basis of these three steps.

As for the pretreatment of water samples, pioneer works were based on its evaporation to smaller volumes. Many authors claim that it has to be done at basic pH to avoid losses of Tc during the process.¹⁶ Ulterior tests showed that this condition is not totally necessary when the temperature was kept under 90 °C.³⁸ The method rapidly appeared as unpractical for large water volume. An interesting advance was represented by the use of anion exchange resins.¹⁷ The authors used such method for analyzing as much as 10 L of seawater. A similar way for the preconcentration of Tc is that presented by Holm et al.⁴⁵ They use activated carbon filters to preconcentrate Tc in situ.

Larger volume of water can be pretreated with a reduction-coprecipitation process. In this case, Tc is reduced by adding a reducing agent, FeSO₄ (Ref. 27) or K₂S₂O₅,²⁴ in to the water sample. Under these conditions, Tc precipitates with Fe(III) at basic pH. The advance is clear since the analysis of huge volume of water is substituted by some grams of precipitate.

Either the residue or the precipitate are then dissolved with HCl, HNO₃, H₂SO₄ or even aqua regia and introduced into the extraction process.

For solid samples, seaweed, sediments or soils, the calcination has been the most popular way of sample pretreatment. The temperature of 500 or 600 °C is used in the literature.^{46, 47} Distillation has been used also, but as far as I know, it is not the most widely used method.^{26, 48}

After the calcination, the ashes are dissolved and Tc is extracted according to the different methods described below.

Liquid-liquid extraction with TIOA,¹⁶ TBP^{47, 49} or C₆H₁₀O (Ref. 50) as extracting agent has been widely used. An anion exchange resin, Dowex AG1-X8, for instance, is an interesting option as well. Riley and Siddiqui¹⁷ incorporated Tc in a slightly acidic solution into the resin. Basic media were used in References 40, 50, and 51.

More recently, TEVA resins (see for instance References 52 and 53) have proven to be highly selective with regard to Mo

and ⁹⁹Ru, the main interfering isotope in mass spectrometric methods, including accelerator mass spectrometry (AMS). In this case, Tc is introduced into the resin under slightly acidic conditions.

The final step of sample conditioning for counting essentially depends on the physical method of ⁹⁹Tc measurement.

Radiometric methods, based on the counting of the β radiation from ⁹⁹Tc, usually need an electroplating process in order to prepare a thin counting sample so as to avoid the self-absorption of relatively soft radiation. The electrodeposition is carried out under basic conditions, usually a 2 M NaOH solution.⁴⁷ When liquid scintillation counting is carried out, electrodeposition is not needed and the extracting agent in a liquid-liquid extraction, TBP for instance, is dissolved directly in the scintillator.⁴⁹

In the case of mass spectrometric methods, the final source of Tc has to be in a form which depends on the method. For instance, a slightly acidic solution, 2% HNO₃, is used for ICP-MS methods.⁵⁴ Resonance ionization mass spectrometry (RIMS) uses electroplated ⁹⁹Tc sources onto Re filaments.⁵⁵ The form of the final source for AMS is somewhat different since the sample is injected into the accelerator as an oxide. It is thoroughly mixed with highly pure aluminum powder⁵⁶ which acts as the sample holder.

The yield of the chemical separation must be measured to quantify the concentration of ⁹⁹Tc. Early works used Re as a tracer.²⁹ This method is based on the chemical similarity between Tc and Re. But this practice is not common nowadays. A recent intercomparison exercise⁵² has shown that the use of Re as a yield tracer systematically overestimates the ⁹⁹Tc activity in the sample. Mas et al.⁵⁷ show, however, that the use of Re or ^{95m}Tc for the measurement of ⁹⁹Tc in seaweed is equivalent. Certainly the more comfortable possibility is the use of ^{99m}Tc (T_{1/2} = 6.01 h), because it is easily available^{58, 59} and measurable, since it practically emits only a γ ray. But ^{99m}Tc decays into ⁹⁹Tc, which provokes some prevention with its use. Nevertheless, even in very sensitive methods it is an acceptable alternative, although with some limitations.⁵⁹

^{97m}Tc (T_{1/2} = 90.5 d) is also an option which was proposed by Kaye et al.⁵¹ ^{97m}Tc has a little more complex decay scheme, emitting mostly conversion electrons, and longer half-life than ^{99m}Tc. Thus, it is less accessible than ^{99m}Tc.

^{95m}Tc (T_{1/2} = 61 d) is probably the most suitable option. Its half-life is not too long and emits γ-rays with enough intensity. As far as we know, it was first used by Thein et al.⁶⁰ Nevertheless, some authors highlight the fact that the commercial solutions of ^{95m}Tc often contain detectable ⁹⁷Tc, ⁹⁸Tc, and ⁹⁹Tc which does not advise its utilization.³⁸ The direct production of ^{95m}Tc in a cyclotron through the reaction ⁹³Nb(α,2n)^{95m}Tc is proposed by Sekine et al.⁶¹ as a cleaner alternative. This is, however, accessible to a few laboratories.

A complete method for ⁹⁹Tc extraction can be seen in Figure 2, taken from Reference 62.

Physics. Radiometric methods are based on the counting of the β-radiation emitted by ⁹⁹Tc. Since its concentration in nature is very low, techniques of low-level counting (LLC) are required. A good text on the principle and practice of LLC is that was written by P. Theodorsson.⁶³

Gas ionization detectors of Geiger-Müller or proportional types have been widely used for ⁹⁹Tc determination.^{17, 35, 51} For 24 h counting time, typical instrumental detection limits between 1 to 5 mBq can be obtained.

Holm et al.⁵⁸ use a surface barrier detector for ⁹⁹Tc determination. The spectrometric response of the detector could allow the identification of interfering β-emitters. Nevertheless, for 16 h counting time a detection limit of 10 mBq can be reached, i.e. slightly higher than those obtained with gas counter.

Scintillation counters have been an option used from the beginning.^{46, 49} Detection limits of some 40 mBq in 10 h count-

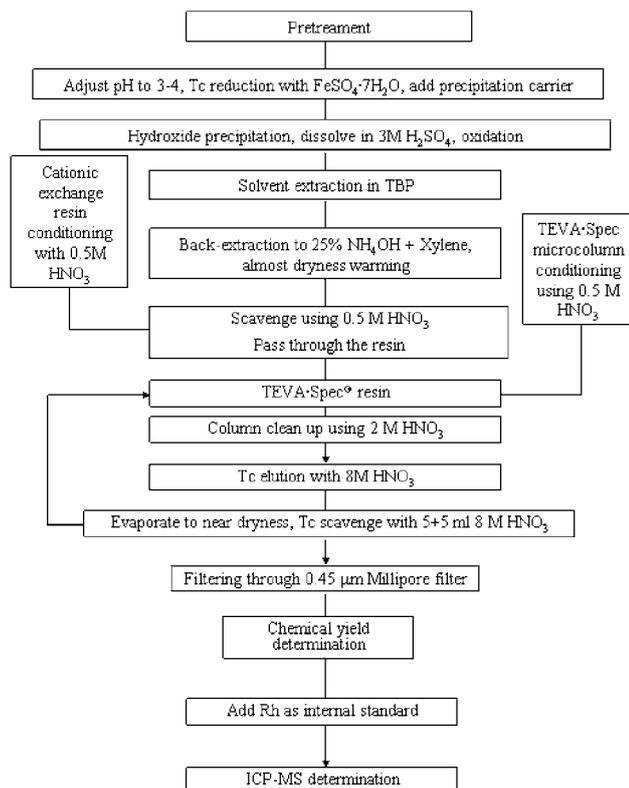


Figure 2. An example of a whole radiochemical method for ⁹⁹Tc determination in water. Taken from Reference 62.

ing time are reported by the authors.

In Figure 3, taken from Reference 64, a comparison is done on the minimum detectable activity (MDA) obtained for ⁹⁹Tc by the published radiometric methods. MDA is conventionally defined as the smallest activity in a sample that can be detected with a 5% probability of erroneously detecting radioactivity, when in fact none was present (Type I error) and also, a 5% probability of not detecting radioactivity, when in fact it is present (Type II error). Liquid scintillation method seems to give slightly smaller MDA than gas counters.

The conventional radiometric techniques have, however, limitations due to the long ⁹⁹Tc half-life. A simple inspection of the popular activity equation

$$A = \lambda N$$

shows that for a long half-life is more effective to measure directly N than A . That is the case for ⁹⁹Tc. Non-radiometric methods can help to overcome the difficulties.

Historically, they have already played their roles. In fact, very early works used neutron activation for ⁹⁹Tc determination.⁶⁵ The authors separated ⁹⁹Tc from the sample of interest and then irradiated it in a reactor to obtain ¹⁰⁰Tc ($T_{1/2} = 15.8$ s). After the separation and purification of the ¹⁰⁰Tc, they measured the radioactivity by a low-background gas counter. According to the information that the authors gave in the paper, for a thermal neutron flux of $5 \times 10^{13} \text{ ncm}^{-2}\text{s}^{-1}$, the detection limits for filter papers and vegetation samples are 5 and 9 pg of ⁹⁹Tc, which in radioactivity terms are about 3 and 6 mBq, respectively. The method is complicated taking into account the very short half-life of ¹⁰⁰Tc. An alternative is that presented by Ikeda et al.⁶⁶ The authors used reactions of the type (n, n') to obtain ^{99m}Tc which has longer half-life than ¹⁰⁰Tc and, thus, is easy to separate and measure. The ⁹⁹Tc radioactivities of some 10 Bq are reported by the authors.

A refined approach used other reactions as (γ, γ') , instead of the traditional (n, γ) activation reaction.⁶⁷ The authors also obtained ^{99m}Tc by using bremsstrahlung radiation from the

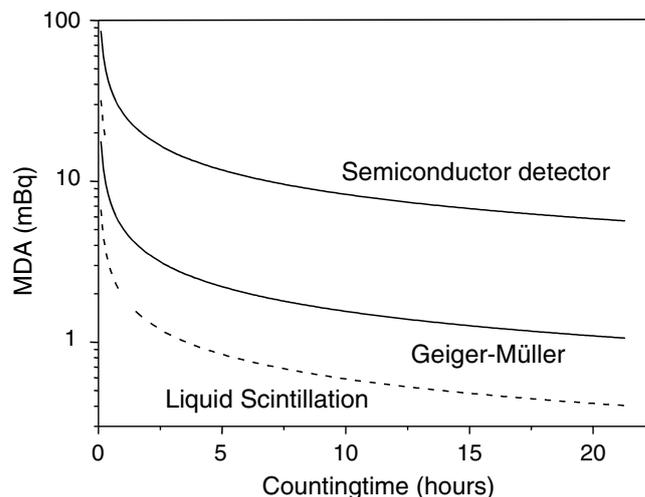


Figure 3. Taken from Reference 64. Minimum Detectable Activities for different detectors as a function of the counting time.

electron linear accelerator of Tohoku University.

Nevertheless, only mass spectrometric techniques can nowadays compete with radiation counting.

The technique that has demonstrated to be more accessible and realistic so far is ICP-MS. Many works can be found in the literature on the use of ICP-MS to detect ⁹⁹Tc in environmental samples. Examples are References 24, 50, 52, 54, 62 and 68. Detection limits of a few mBq, obtained with counting times of a few minutes, are presented by the authors, which makes ICP-MS superior to radiometric methods. A deep study on the tuning of conventional quadrupole ICP-MS for ⁹⁹Tc atom counting and of the interferences in ⁹⁹Tc determination can be found in Reference 69. When high resolution ICP-MS is used, the detection limit falls to a few μBq ,⁷⁰ the best so far obtained with ICP-MS.

The use of RIMS for ⁹⁹Tc determination was reported.^{55, 71} The authors claimed to reach sensitivities of some 10^7 atoms which means 10 fg or 10^{-2} μBq . Nevertheless, the application of RIMS to environmental determination has not been yet done.

AMS is increasingly competitive with regard to radiometric methods.^{56, 72, 73} Tc is accelerated up to 125 or 225 MeV and sensitivities from 10^6 to 10^8 atoms, i.e. from 10^{-2} to a few μBq were obtained by using about 250 mL of sea water.

5. Conclusions

⁹⁹Tc is a relevant nuclide from an environmental viewpoint. Its long half-life assures its presence in the environment once introduced in it. It behaves as a conservative element in water which serves to trace, for instance, the water current pattern in the ocean. It is also very mobile in soils and in, general terms, available to plants under aerobic conditions. A reducing environment provokes a decrease in its mobility and availability to plants. However, lack of knowledge still exists on its behavior in the environment. Intensive speciation studies have to be carried out to overcome this problem.

The use of non-radiometric methods, specially conventional or high resolution ICP-MS as well as AMS can help to overcome the difficulty of its measurement at environmental levels.

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