

Technetium

Qinhong Hu

The University of Texas at Arlington, Arlington, TX, USA

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1 SUMMARY

Technetium is an artificial radioactive element of interest because of the environmental concern related to its production in nuclear operations and its utility as a diagnostic medicine. This article provides a review of its basic chemistry, occurrence and speciation in the environment, separation and analytical techniques, as well as the fate and transport behavior of technetium species in the subsurface. ^{99}Tc in the environment is dominated by its releases from the nuclear fuel cycle, with most of the isotope (>90%) discharged from reprocessing plants in Europe. It has been recognized that ^{99}Tc is a very important dose contributor in risk assessment, because of its high abundance, long half-lives, and presumably high mobility. Redox-sensitive technetium primarily exists in two (+7 and +4) stable oxidation states in the environment. Tc(VII) is mobile because of its minimal interactions with mineral surfaces across a wide range of environmentally relevant pH values. In contrast, Tc(IV) is sparingly soluble and strongly retarded in the subsurface. Probably mediated by microorganisms, conversion between Tc(VII) and Tc(IV) strongly affects the biogeochemical cycling of ^{99}Tc . Coupled with a set of separation and concentration techniques, the analysis of ^{99}Tc by ICP-MS has proven a versatile method to study the distribution as well as the fate and transport of ^{99}Tc in the environment. Rhenium has been commonly used as a nonradioactive surrogate for technetium in its biogeochemical studies and chemical analyses.

2 OCCURRENCE

The existence of technetium was predicted on the basis of a gap in the early arrangement of elements in the periodic table. Being the first element to be produced artificially, technetium was discovered by Pirrier and Segre in Italy in 1937 from a sample, sent by Ernest Lawrence, of molybdenum bombarded by deuterons in the Berkeley cyclotron.¹ The origin of the name comes from the Greek word *technetos* meaning *artificial*. Element 43 was erroneously reported as having been discovered in 1925 by Noddak and Tacke. The concentration of technetium in nature produced by spontaneous or neutron-induced fission of uranium is several orders of magnitude too low to be detected by emission of characteristic X-rays of element 43, as had been claimed in the report by Noddak and Tacke.^{2,3}

Technetium is the lightest element with no stable isotope and is, therefore, extremely rare on the Earth. Since its discovery, there have been many searches in terrestrial materials for its natural sources. It was reported by Kenna and Kuroda, in 1961 and 1964,⁴ that ^{99}Tc was isolated and identified in an African pitchblende sample with very small quantities (about 2×10^{-10} g of ^{99}Tc per kg ore) as a spontaneous fission product of ^{238}U (see *Uranium*).⁵ Essentially all the technetium on the Earth has been created by human activities involving fissionable materials (see *Anthropogenic Radioactivity*). Technetium is commercially available to permit holders of Oak Ridge National Laboratory in Tennessee, USA.

Forty-three isotopes and isomers of technetium, with atomic mass ranging from 86 to 113, are known.⁶ Most of them have half-lives that are less than an hour, and a total of 10 major isotopes with half-lives longer than 1 h are listed in Table 1. The shorter-lived isotopes $^{101-107}\text{Tc}$ are also produced during reactor operation at yields ranging from 0.2 to 5.6%.⁷ Among 11 metastates of technetium, $^{97\text{m}}\text{Tc}$ is the most stable, with a half-life of 90.1 days (0.097 MeV of γ -ray). This is followed by $^{95\text{m}}\text{Tc}$ (half-life: 61 days, 0.038 MeV) and $^{99\text{m}}\text{Tc}$ (half-life: 6.01 h, 0.143 MeV). While $^{95\text{m}}\text{Tc}$ is commonly employed in radioactive tracer studies, $^{99\text{m}}\text{Tc}$ is used in nuclear medicine for a wide variety of diagnostic tests because of its short half-life, the low γ -ray energy it emits, and its ability to chemically bind to many active biomolecules.

Among three technetium isotopes (^{97}Tc , ^{98}Tc , and ^{99}Tc ; Table 1) having half-lives sufficiently long to warrant concern over time, ^{99}Tc is produced in sufficient quantities as a byproduct from the fission of uranium in nuclear operations, typically in a nuclear reactor. With a high-abundance (6%) fission yield, it is estimated that 25–30 tons of ^{99}Tc have been produced worldwide up to the mid-1980s, with approximately 1% of that amount (150–200 TBq) released to the environment.⁸ After a burn-up of 35 000 MW days per ton of uranium with an initial enrichment of 3% ^{235}U , the spent fuel contains about 1 kg ^{99}Tc per ton.¹ Along with ^{129}I and ^{237}Np , ^{99}Tc is of particular importance to the environment and risk assessment, because of their long half-lives and presumably high mobility.^{9–11}

High activities of ^{99}Tc are present in underground nuclear test, fuel reprocessing, and spent reactor fuel (Table 2). Nuclear fuel reprocessing facilities constitute the major (>90%) source of ^{99}Tc released to the environment, especially from the discharge of ^{99}Tc from Sellafield in England, with the reported value of Bellona¹² higher than the 150–200 TBq worldwide release estimated by Dowdall *et al.*^{8,12} In the 3-year period from 1978 to 1980, Sellafield discharged almost 300 TBq of ^{99}Tc . From an average of 4–6 TBq per year throughout

the entire 1980s, the discharges of ^{99}Tc increased to 190 TBq in 1995. In the 5-year period 1994–1998, a staggering 530 TBq of ^{99}Tc was discharged from Sellafield. Such increased discharges of ^{99}Tc are result of the reprocessing of Magnox fuel. At a rate of about 90 TBq per year, current and future discharge of ^{99}Tc contributes a significant portion of the total released radioactivity.¹³ Today, it is the large release of the radioactive ^{99}Tc from Sellafield that is mainly responsible for the pollution of the Norwegian coast and the Barents Sea (*see Atlantic Ocean; Civilian Nuclear Accidents*).

To a less extent, the La Hague fuel reprocessing facility in France has also been discharging ^{99}Tc , which increased slowly from ~ 0.4 TBq per year in 1970 to a peak of ~ 25 TBq year in 1985. By 1991 the discharge had fallen to ~ 0.9 TBq year and have since remained relatively stable at <1 TBq year.¹⁴ From above reports about ^{99}Tc release from both Sellafield and La Hague, it is estimated that about 1900 TBq (equivalent to 3030 kg) of ^{99}Tc has been released into the environment. Activities conducted at these European nuclear reprocessing facilities have led to the increased radioactivity in the Arctic marine environment. For example, increased discharge of ^{99}Tc from Sellafield beginning in 1994 has yielded an average ^{99}Tc level of $1.3 \pm 0.3 \text{ Bq m}^{-3}$ in seawater and $320 \pm 70 \text{ Bq m}^{-3}$ in seaweed.⁸

Because of its long half-life (2.13×10^5 years) and presumed mobile behavior in the environment, ^{99}Tc is an important dose contributor to the calculated health risk for many US Department of Energy (DOE) nuclear facilities, including the Hanford Site, Nevada Test Site, Savannah River Site, and Idaho National Laboratory.^{11,15–21}

The Hanford Site in south-central Washington State produced plutonium for the US DOE weapons program from 1943 to 1989 (*see Plutonium*).²² It has been estimated that at the Hanford Site, a total of 1990 kg of ^{99}Tc was produced in the various operational reactors.⁷ Of this original ^{99}Tc inventory, 510 ± 210 kg was shipped off-site or coextracted during fuel element reprocessing into uranium oxide product, and 80 ± 10 kg (1387 ± 173 Ci or 51 ± 6.4 TBq) was released to the environment. The remaining 1310 ± 220 kg is estimated to be contained within the Hanford Site tanks, which corresponds to a ^{99}Tc tank inventory of $22\,720 \pm 3820$ Ci or 841 ± 141 TBq.⁷

Table 1 Nuclear properties of technetium isotopes with a half-life more than 1 h^(a)

| Isotope | Half-life | Decay mode |
|--------------------------|--------------------------|----------------|
| ^{93}Tc | 2.73 h | EC + β^+ |
| ^{94}Tc | 4.88 h | EC + β^+ |
| ^{95}Tc | 20.0 h | EC, β^+ |
| $^{95\text{m}}\text{Tc}$ | 61 days | IT, β^+ |
| ^{96}Tc | 4.3 days | EC + β^+ |
| ^{97}Tc | 2.6×10^6 years | EC |
| $^{97\text{m}}\text{Tc}$ | 91 days | IT |
| ^{98}Tc | 4.2×10^6 years | β^- |
| ^{99}Tc | 1.57×10^7 years | β^- |
| $^{99\text{m}}\text{Tc}$ | 6.01 h | IT, β^- |

EC, electron capture; β^+ , positron emission; β^- : β -emission; IT, isomeric transition.

^(a) From Baum *et al.*⁵

Table 2 Major source terms of ^{99}Tc in the environment

| Source | kg | TBq |
|---|----------------|---------------|
| Storage within Hanford Site tanks ⁷ | 1310 ± 220 | 841 ± 141 |
| Release at Hanford Site ¹¹ | 80 ± 10 | 51 ± 6.4 |
| Storage at <i>Potential</i> Yucca mountain repository ¹¹ | 63 700 | 40 000 |
| Release from NTS underground nuclear testing ^{11,15} | 33.6 | 21.1 |
| Release from spent fuel reprocessing (Europe) ^{12–14} | ~ 3030 | ~ 1900 |

Nuclear wastes from Hanford's processing for the separation of plutonium were stored in massive (24 m in diameter and 14 m in height), buried, single-shell tanks in 18 tank farms (see **Plutonium**).²³ These tank wastes were initially thermally hot because of radioactive decay, and many exhibited extreme chemical character in terms of pH, salinity, and radionuclide concentration. At present, 67 of the 149 single-shell tanks are suspected to have released over 1.9 million liters of tank waste to the vadose zone, with most leak events occurring between 1950 and 1975. The total volume of tank waste loss is difficult to determine but ranges between 1.9 and 3.8 million l, containing about 1 million curies (37 000 TBq) of radioactivity.²³ In the S and SX (particularly) tank farms, where highly radioactive and chemically hazardous aqueous fluids of high ionic strength have leaked into the vadose zone, about 30 Ci (1.1 TBq) of ⁹⁹Tc has lost into the vadose zone around six tanks in these tank farms.²⁴ The SX-108 tank spill released a total of 44 363 Ci of ¹³⁷Cs (see **Cesium**) and 13.1 Ci of ⁹⁹Tc, while T-106 tank released more than 21 000 Ci of ¹³⁷Cs, 21 600 Ci of ⁹⁰Sr (see **Strontium**), 32.5 Ci of Pu, and 60 Ci of ⁹⁹Tc.²³ According to Darab and Smith, mean ⁹⁹Tc concentrations in the waste streams range from 0.08 to 0.36 $\mu\text{Ci ml}^{-1}$ (0.05–0.21 mmol L^{-1}).⁷ The average amounts of ⁹⁹Tc, ¹³⁷Cs, and ⁹⁰Sr in four of the Hanford double-shell tanks (106-AN, 101-AW, 105-AP, and 103-AN) were determined to be 0.102, 384, and 3.43 $\mu\text{Ci ml}^{-1}$, respectively. This corresponds to ⁹⁹Tc, ¹³⁷Cs, and ⁹⁰Sr concentrations of 60.2, 32.3, and 0.262 $\mu\text{mol l}^{-1}$, respectively.

3 CHEMISTRY

The chemistry of Tc is reported to be similar to rhenium.¹ Technetium is a silvery-gray metal, with an appearance similar to platinum, that tarnishes slowly in moist air. Technetium dissolves in nitric acid, aqua regia, and concentrated sulfuric acid, but is not soluble in hydrochloric acid of any concentration.

The basic chemistry of technetium is presented in Table 3. Technetium is one of the most powerful known preventatives of rust and is also a valuable source of β -rays. Ammonium pertechnetate ($\text{NH}_4[\text{TcO}_4]$) is a specialized corrosion preventer for steel. A concentration of $\text{K}[\text{TcO}_4]$ at 5 mg l^{-1} in aerated distilled water protects mild carbon steel at temperatures up to 250 °C. However, this protection is limited to closed systems because of the radioactive nature of technetium.

The common oxidation states of technetium include 0, +2, +4, +5, +6, and +7. Depending upon the redox conditions, technetium primarily exists in two (+7 and +4) stable oxidation states in the subsurface. Under oxidizing conditions, technetium (VII) will exist as the pertechnetate ion (TcO_4^-) in aqueous solution or as volatile Tc_2O_7 in

Table 3 Chemical properties of technetium

| Atomic number | 43 |
|------------------------------|--------------------------------------|
| Naturally occurring isotopes | None |
| Atomic mass | 98.9063 |
| Electronic configuration | $[\text{Kr}]5d^24d^5$ |
| Electronegativity | 1.9 (Pauling scale) |
| Color | Silvery-gray metallic |
| Melting point | 2157 °C |
| Boiling point | 4265 °C |
| Atomic radius | 135.8 pm |
| van der Waals's radius | 275 pm |
| Molar volume | $8.63 \text{ cm}^3 \text{ mol}^{-1}$ |
| Ionization energy | 702 kJ mol^{-1} |
| Density | 11.5 kg m^{-3} |

the absence of water.³ Under reducing conditions at redox potential (Eh) values below about 220 mV with respect to standard hydrogen electrode in neutral pH conditions, reduced Tc(IV) is the most stable oxidation state, which strongly hydrolyzes in aqueous solutions and is very stable as TcO_2 in the absence of water (Figure 1). Relatively stable complexes of Tc(V) are formed in the presence of complexing agents, and fluorination leads to the volatile TcF_6 .³ In general, technetium species with oxidation states less than +4 are rapidly oxidized to Tc(IV) and ultimately to Tc(VII) and those with oxidation states between +4 and +7 usually disproportionate to corresponding mixtures of Tc(IV) and Tc(VII).⁷

Because of its weak interaction with mineral surfaces across a wide range of environmentally relevant pH values,

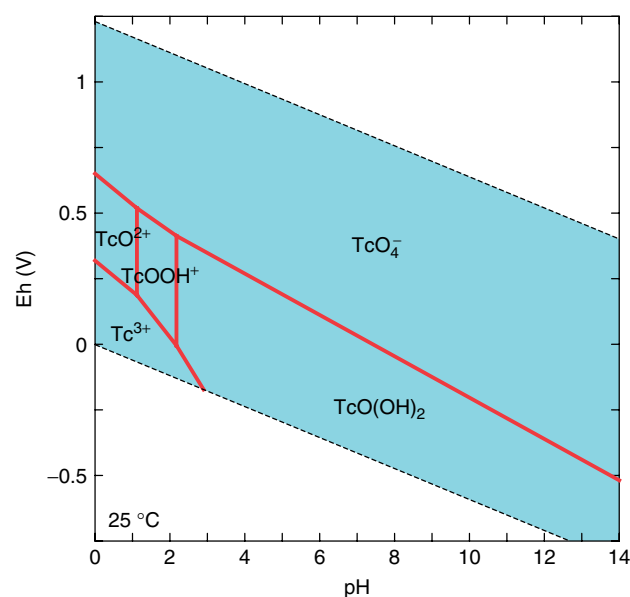


Figure 1 Eh-pH diagram drawn at 25 °C and an equilibrium activity of 10^{-11} for technetium; stability fields are shown only for the aqueous species. Diagram was produced using the “thermo” database in the Geochemist’s Workbench (version 6.0); modified from Hu *et al.*²⁵

TcO_4^- is considered one of the most mobile radionuclides in the environment. In contrast, transport of Tc(IV) species ($\text{TcO}_2 \cdot n\text{H}_2\text{O}$) are expected to be strongly retarded because of sorption at low concentrations and/or precipitation at high ones; the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}(\text{s})$ in carbonate-containing groundwater was reported to be only about 10^{-8} M.²⁶ Similarly, chemical equilibrium modeling of groundwater at Yucca mountain indicated a maximum technetium solubility of 4×10^{-9} M under reducing conditions.²⁷ Experiments conducted on sediment-groundwater samples in Germany showed significantly different distribution coefficients (K_d) for technetium among aerobic and anaerobic conditions.²⁸ By varying the redox potential, Lieser and Bauscher observed a change in the distribution coefficient value of about three orders of magnitude over a small range of Eh at 170 ± 60 mV and a pH of 7 ± 0.5 .²⁸

4 SPECIATION

At higher Eh, technetium occurs as TcO_4^- . Because of its weak interaction with mineral surfaces, TcO_4^- is considered as one of the most mobile radionuclides in the environment. In contrast, transport of Tc(IV) species ($\text{TcO}_2 \cdot n\text{H}_2\text{O}$) is expected to be strongly retarded because of sorption and/or precipitation. Tc(IV) species become associated with solid phases through either hydrolysis or the formation of strong surface complexes with aluminum and iron oxides and clays.²⁹

The presence of reductants in the aquifer matrix (e.g., Fe(II) and S^{2-} as in pyrite) can contribute to the reduction of Tc(VII) to Tc(IV). Fe(II) minerals in igneous rocks can reduce TcO_4^- and lead to sorption on mineral surfaces.¹⁰ Under reducing conditions, Cui and Eriksen reported that TcO_4^- was reduced to sparingly soluble $\text{TcO}_2 \cdot n\text{H}_2\text{O}(\text{s})$ by the Fe(II)-containing fracture-filling material and that $\text{Tc(IV)}_{\text{aq}}$ was rapidly sorbed by the material.^{30,31} Reduction of Tc(VII) to Tc(IV) occurs with Fe(II)-containing solid phases but not by aqueous Fe(II) species. Cui and Eriksen suggested that although the reduction of Tc(VII) by soluble Fe(II) is thermodynamically feasible, it is kinetically hindered and highly improbable.³² Peretyazhko *et al.* recently demonstrated that mineral-associated Fe(II) can be an effective heterogeneous reductant of Tc(VII) under anoxic conditions, yielding insoluble Tc(IV) precipitates, coprecipitates, and/or surface complexes that may significantly retard technetium migration.³³ The experimental results of Peretyazhko *et al.* suggested the following affinity series for heterogeneous Tc(VII) reduction by Fe(II): Fe(II) adsorbed on Fe(III) oxides \gg structural Fe(II) in phyllosilicates \gg adsorbed Fe(II) in phyllosilicates (ion-exchangeable and some edge-complexed Fe(II)) \sim aqueous Fe(II).

During the CHESHIRE migration experiment at NTS, ^{99}Tc activity was observed to decrease significantly

for groundwater samples with high iron content, while ^{36}Cl was not affected.³⁴ The reduction of Tc(VII) to Tc(IV) and the formation of insoluble precipitates are the most likely mechanisms for the reduced mobility of ^{99}Tc .³⁵

At the Hanford Site, four large ^{99}Tc groundwater plumes exist and new ones form as ^{99}Tc released to cribs and leaked from single-shell high-level waste tanks migrates through the vadose zone. Areas of ^{99}Tc contamination, above the US Environmental Protection Agency (EPA) drinking water standard of 900 pCi l^{-1} (33 Bq l^{-1} or $0.05 \mu\text{g l}^{-1}$), are found to be 2.4 km^2 . Monitoring data from a new well installed in early 2005 east of Waste Management Area T showed a ^{99}Tc concentration as high as $182\,000 \text{ pCi l}^{-1}$ at ~ 10 m below the water table.^{36,37} Over 40 Ci of TcO_4^- was forecast to discharge to the Columbia River in future years.¹⁷

Most polyvalent contaminants with intermediate redox potentials (e.g., Tc) released to the Hanford vadose zone in near-neutral or poorly buffered wastewaters, in consequence, remain in the fully oxidized state because the surfaces of potential mineral reductants (e.g., illmenite and magnetite) are passivated by reaction with oxygen or by physical coating with secondary mineral phases such as calcite or Fe(III) oxides.²³ However, one important consequence of the dissolution–precipitation reactions that are promoted by alkaline tank wastes is the release of redox-reactive, structural Fe(II) that is present in primary mineral phases such as biotite and chlorite. $^{99}\text{Tc(VII)}$ is reduced by Fe(II) liberated by base-induced mineral dissolution, yielding an insoluble Tc(IV) precipitate.¹⁷ This reduced form, however, apparently reoxidizes rapidly when oxidizing conditions return.²³

Using X-ray absorption spectroscopy, Begg *et al.* studied Tc association with reduced Dounreay soils in England.³⁸ In microcosm tests, technetium was found to be removed from solution on exposure to the reduced soils and was present on solids as hydrous Tc(IV) O_2 -like phases. Begg *et al.* also investigated the long-term stability and remobilization of solid-phase-associated technetium in reduced soils and found that the extent of remobilization of technetium to solution was dependent upon the oxidant used.³⁸ After oxidation with air for 60 days, $42 \pm 6\%$ of the initial soil-bound technetium was resolubilized. On the contrary, in the presence of 25 or 100 mmol l^{-1} nitrate, which is commonly present at high levels as a cocontaminant at nuclear fuel cycle sites, as an oxidant, negligible reoxidation or remobilization occurred.

Bioreduction of technetium has been reported in aquifers and sediments.^{39–42} Ishii *et al.* found that the formation of insoluble Tc was inhibited by the addition of the antibiotic chloramphenicol.⁴³ In addition, the reduction of soluble TcO_4^- to low-valence oxide was not observed in the filtered (i.e., bacteria-removed) microcosm samples, although reducing conditions were present. These results indicated that bacteria were involved in the formation of insoluble technetium.

At the Hanford site, $^{99}\text{TcO}_4^-$ is essentially nonadsorptive at circumneutral and basic pH values. It was generally assumed that technetium is released to and presented in the vadose zone and groundwater at the Hanford Site as oxidized Tc(VII). However, recent studies of waste samples from certain underground storage tanks indicate that a significant fraction of the technetium in the waste is present in the +4 oxidation state.⁴⁴ Conceptual models for the release of technetium from the Hanford underground storage tanks will need to consider the potential mobility of Tc(IV) in the near-field, vadose sediments and potential interactions of organics present in the tanks with respect to complexing and stabilizing Tc(IV) and possibly other intermediate valence states of dissolved Tc.⁴⁵

When studying radionuclide transport in the field, a distribution coefficient (K_d) approach has been commonly employed in transport codes to quantify the extent of radionuclide–solid–water interactions. The K_d data are commonly determined from laboratory batch and column experiments under oxidizing conditions. Values of K_d for a number of radionuclides were reported for representative geologic media, including alluvium, carbonate rock, and volcanic tuffs (devitrified, vitric, and zeolitic), encountered at the NTS and proposed Yucca mountain repository.^{46,47} The K_d values of ^{99}Tc are 0 in all volcanic tuffs and $0.27\text{--}0.63\text{ ml g}^{-1}$ (weakly sorbing) in alluvium.⁴⁷ These values are based on the assumption that technetium exists as mobile anionic species of pertechnetate (TcO_4^-) in the groundwaters of these sites and during experimental measurements of K_d values under oxidizing conditions.

At the NTS, The speciation and migration behavior of ^{99}Tc is controlled by the redox conditions within the underground nuclear test cavity (initial distribution) and the surrounding groundwater flow system (subsequent migration). The chemical environment of a nuclear test cavity is inferred to have a reduced nature immediately following a detonation. Reducing conditions may persist for decades in underground test cavities if the system remains isolated from the surrounding groundwater flow system.³⁵ Furthermore, geochemical measurements at wells across the NTS and close to Yucca mountain indicated that groundwaters are not uniformly oxidizing, as previously believed. Natural redox barriers associated with zones of reduction (e.g., pyrite-bearing horizons) within an aquifer would tend to inhibit the mobility of redox-sensitive radionuclides in the groundwater from the underground nuclear tests or breached nuclear fuel waste package to contribute to the enhanced performance of a potential geological repository at Yucca mountain.

Laboratory batch sorption experiments were used to investigate variations in the retardation behavior of redox-sensitive radionuclides.²⁵ Experimental redox conditions were controlled by varying the oxygen content inside an enclosed glove box and by adding reductants into the testing solutions. Under atmospheric (oxidizing) conditions, radionuclide distribution coefficients varied with the mineralogic composition

of the sorbent and the water chemistry. Under reducing conditions, distribution coefficients showed marked increases for ^{99}Tc (from 1.22 at oxidizing to 378 ml g^{-1} at mildly reducing conditions) and ^{237}Np (an increase from 4.6 to 930 ml g^{-1}) in devitrified tuff, but much smaller variations in alluvium, carbonate rock, and zeolitic tuff (see *Neptunium*). This effect was particularly important for ^{99}Tc , which tends to be mobile under oxidizing conditions.

Field-scale migration of radionuclides, including ^{99}Tc , can be assessed in natural reactors.⁴⁸ In 1972, it was found that uranium in ore deposits at Oklo, Gabon, contains significantly smaller (<0.5%) concentrations of ^{235}U than other natural uranium deposits (0.72%). At Gabon deposits, the isotopic composition of other elements is also different from the mean composition in nature. At the age of about 1.7 billion years, the natural reactors at Oklo have been in operation for about 1 million years, probably with intermissions that are dependent upon the presence of water.³ About 6 tons of ^{235}U have been consumed and about 1 ton of ^{239}Pu produced, which decayed into ^{235}U . Analysis of natural reactors at Oklo provide valuable information about the migration behavior of fission products and actinides in the geosphere. It was reported that 85–100% of the lanthanides, 75–90% of the ruthenium, and 60–85% of the technetium were retained within the reactor zones; another indication of nonconservative migration of ^{99}Tc in the natural geosphere.³ Small amounts of uranium, lanthanides, ruthenium, and technetium moved with the water over a distance of up to 20–50 m. Not surprisingly, plutonium produced at Oklo did not move during its lifetime from the site of its formation.

5 SEPARATION TECHNIQUES

Because of generally low environmental concentrations of ^{99}Tc , separation and concentration techniques are usually needed for ^{99}Tc analyses by radiometric and mass spectrometric methods. A separation procedure designed for inductively coupled plasma-mass spectrometry (ICP-MS) needs to focus on the removal of molybdenum and ruthenium.⁴⁹ Zhao *et al.* developed a methodology to analyze ^{99}Tc in both groundwater and solid samples using a modified isotope dilution ICP-MS method.⁵⁰ For groundwater samples, TEVA resin columns were used to enrich and separate ^{99}Tc from the interfering elements. Depending on the ^{99}Tc concentration, sample volumes of 10 ml–2 l were used. For solid samples, a fusion method was used, wherein a powdered sample was reacted with sodium peroxide and low carbonate sodium hydroxide at 700°C for 30 min. This method is effective in fusing all rock-forming minerals while minimizing ^{99}Tc volatilization (and hence potential loss) during the digestion process. Stable rhenium was spiked in each sample (both groundwater and solid) as a tracer to monitor rhenium and, by analogy, ^{99}Tc recovery.

Rhenium has been recognized as the technetium analog, because of their chemical similarity and since Re is not radioactive.^{7,51–53} The use of rhenium as an analog for technetium is justified based on their similar structural chemistry, electronic configuration, and thermodynamic data. Both anions of TcO_4^- and ReO_4^- have the same charge and virtually the same size, with ionic radii of 0.37 and 0.38 Å for Tc(VII) and Re(VII), respectively, and M–O distances of 1.69 Å for both TcO_4^- and ReO_4^- .⁷ The Eh–pH diagrams for Tc and Re show that similar Eh–pH fields are occupied by aqueous species (TcO_4^- and ReO_4^-) and by solids of technetium and rhenium. However, it has been cautioned that they are not identical elements.⁵³ The main difference between rhenium and technetium is in their respective oxidation potentials; the reduction of rhenium is more difficult than that of technetium.^{54,55}

5.1 Ion-Exchange Resin

To analyze aqueous samples with low ^{99}Tc concentration, Zhao *et al.* weighed 1–2 l of water sample in a suitable-sized beaker and spiked the solution with an appropriate amount of stable rhenium solution (approximately 0.5–1 µg Re in total).⁵⁰ A volume of 10 ml (for every 1 l sample solution) of 30% hydrogen peroxide was added and the sample subboiled on a hotplate for 1 h to oxidize all Tc to dissolved Tc(VII) form and to decompose organic matter (if present) as well as excess hydrogen peroxide.⁵⁶ After the sample had cooled down to room temperature, the liquid was separated from its sediments by either filtration (filter pore size 0.2 µm) or centrifugation (at 4000 rpm for 10 min) method.

Using a Bio-Rad polyprep column, a 0.8-ml TEVA resin bed was prepared and preconditioned with 5 ml of 0.1 M HNO_3 . The sample was passed through the column, which was washed with 30–50 ml of 0.01 M HNO_3 . ^{99}Tc and rhenium were now separated and cleaned from other potential ICP-MS interferences (Mo and Ru) existed in the sample matrix. Both Tc and Re were then eluted from the TEVA column using 5 ml of 12 M HNO_3 , and the effluent collected in a 6-ml preweighed Teflon beaker. The Teflon beaker was placed on a hotplate to dry the sample to the last drop of acid. It is important that the temperature in the acid sample is maintained below 90 °C at all time to avoid potentially significant loss of both technetium and rhenium due to their volatilities at higher temperatures. When the sample cooled down, the sample and the beaker weight were recorded, and 3 ml of 2% HNO_3 was added that contained ICP-MS internal standards for analyses.

For groundwater samples with a moderate (>1 pCi l⁻¹) amount of ^{99}Tc , the above-mentioned concentration and purification procedure is not necessary; the groundwater sample can be directly analyzed after acidified with 2% HNO_3 and ICP-MS internal standards. In this case, a separate standard of molybdenum and ruthenium was also analyzed to obtain

mass bias in order to correct for their potential interference to the ^{99}Tc analyses.

5.2 Alkali Fusion of Solid Samples

Alkali fusion method was published for ^{99}Tc analyses in solid samples.^{50,57,58} The solid samples were first ground into fine powder form, and 0.1–1 g of each ground sample weighed into a precleaned 20-ml zirconium crucible.⁵⁰ An appropriate amount of stable rhenium solution (~ 10 ng Re total) was spiked, and the sample dried under a heat lamp. The flux chemicals, comprising of low carbonate NaOH and Na_2O_2 that were equivalent to 2 and 6 times of sample weight, respectively, were mixed with solid sample in the zirconium crucible using a wooden stick to ensure that the sample was in good contact with the flux. The mixture was fused in a muffle furnace at 700 °C for 25–30 min to fully liberate ^{99}Tc from the rock matrix, and the sample cooled to room temperature. A total of 5–10 ml of either Milli-Q water or 1 M HNO_3 was then added to dissolve the fusion cake; the fusion cakes dissolved slowly in the water, and the addition of 1–2 ml of 1 M HNO_3 at a time could accelerate the dissolution. The dissolved fusion cake and its hydroxide precipitates were then quantitatively transferred into a 50-ml centrifuge tube; the total sample volume was kept at no more than 30 ml. Using concentrated HNO_3 , the sample solution pH was adjusted to 1–2. Afterward, the sample was centrifuged at 4000 rpm for 10 min to separate any precipitate from the liquid, with the liquid transferred into a new clean centrifuge tube. The precipitates were washed with 5 ml of Milli-Q water three times, and then the solution was centrifuged again and all the supernatants were combined for purification with a TEVA column.

After sample fusion, the zirconium crucible can be cleaned by fusing the fluxing chemicals alone (no solid sample), followed by leaching in 12 M HNO_3 over night for reuse. Although zirconium crucibles have been widely used in fusion under extreme oxidizing alkaline conditions, in some cases, the fusion cakes have shown a green color, indicating that some transition metals such as nickel, cobalt, and even zirconium were dissolved from the crucible during high-temperature fusion. This was confirmed from the ICP-MS analyses. However, both technetium and rhenium exhibited very low background so that the partial surface dissolution of the crucible during the fusion process did not cause a serious background problem. This was evidenced in the blank treatment with only fluxing chemicals in a crucible undergoing the same treatment as the solid samples.

6 ANALYTICAL CHARACTERIZATION TECHNIQUES

Hou and Roos have recently summarized the measurement techniques of various radionuclides, including

Table 4 Comparison of measurement methods for the determination of ^{99}Tc .^(a) (Reproduced from Ref. 49. © Elsevier, 2008)

| Sample | Detection method | Target preparation | Detection limit | Separation time | Count time |
|----------------------|---------------------------------|--|------------------------|-----------------|------------|
| Environmental sample | GM detector | Tc on disk | 1.5 mBq | 1–2 days/7 days | 3–4 h |
| Environmental sample | LSC | Tc solution | 17 mBq | 1–2 days/7 days | 2 h |
| Geological sample | RIMS | TcO ₂ | 20 μBq | 1–2 days | 30–60 min |
| Water | AMS | Tc in Al ₂ O ₃ or Nb ₂ O ₅ | 6–10 μBq | 1 day | 20–40 min |
| Sediment, seawater | ICP-SFMS | Tc solution | 0.16–0.29 mBq | 1–2 days | 10–20 min |
| Seawater | ICP-MS with ETV | Tc solution | 0.18 mBq | 1–2 days | 20–40 min |
| Environmental sample | ICP-QMS | Tc solution | 10 mBq | 1–2 days | 20–40 min |
| Environmental sample | ICP-SFMS on-line ^(b) | Tc solution | 0.05 mBq ml or 0.2 mBq | 1 h/4–5 h | 10–20 min |

GM, Geiger–Müller; LSC, liquid scintillation counting; RIMS, resonance ionization mass spectrometry; AMS, accelerator mass spectrometry; ICP-SFMS, inductively coupled plasma-sector field mass spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; ETV, electrothermal vaporization; ICP-QMS, inductively coupled plasma-quadrupole mass spectrometry.

^(a) The on-line method takes about 4–5 h for sample separation and 1 h for on-line separation procedure.

^{99}Tc , in various environmental samples.⁴⁹ The analytical approaches for ^{99}Tc measurements include β -counting, resonance ionization mass spectrometry (RIMS), neutron activation analyses (NAA), ICP-MS, and accelerator mass spectrometry (AMS); Table 4 compiles and compares different analytical methods for ^{99}Tc .

Being a pure and weak β -emitter, decay of ^{99}Tc has a maximum β -energy of 294 keV. Radiometric methods using β -counting by gas flow Geiger–Müller counters or liquid scintillation are the main techniques for the determination of ^{99}Tc .⁴⁹ Because of the difficulties of spectrometric identification for β -emitters, a thorough chemical separation of ^{99}Tc from the matrix and other radionuclides is required. ^{99}Tc was separated from water samples using TEVA resin column before liquid scintillation counting. After concentration of the TcO_4^- on a TEVA resin column, the ^{99}Tc -containing resin was directly transferred into liquid scintillation cocktail for counting. As a β -emitter, ^{99}Tc can be measured within a counting window from 26 to 290 KeV. Zhao *et al.* added the same amount of TEVA resin to a series of ^{99}Tc standard solutions to construct a matrix-specific calibration curve, from which the activities of ^{99}Tc in the samples were calculated. The detection limit for the method is 1 pCi l⁻¹ (37 mBq l⁻¹).⁵⁰

As a convenient and sensitive mass spectrometric technique, ICP-MS has been widely used for the determination of ^{99}Tc .^{15,50,59–65} For ^{99}Tc analyses, the major interferences are those arising from ruthenium (^{99}Ru , natural abundance 12.6%) and molybdenum ($^{98}\text{Mo}^1\text{H}$, 24% and ^{100}Mo , 9.6%) isotopes present in the analyzed solution. For Re that serves as the chemical yield tracer, the possible interference is from the isobar generation by forming hydrides with tungsten isotopes at masses 185 and 187. With a quadrupole ICP-MS, Zhao *et al.* used 10 $\mu\text{g l}^{-1}$ solutions of molybdenum, ruthenium, and tungsten to evaluate the possible interference.⁵⁰ The method checked for this interference potential by monitoring masses 92, 95, 96, and 98 (Mo), 100, 101 and 102 (Ru), as

well as 182 and 184 (W). The instrumental mass bias was determined with a linear correction algorithm with respect to the atomic mass. Typical mass-bias factors throughout this study were about 3% per mass unit at mass ranges of 92–98 (obtained from 10 $\mu\text{g l}^{-1}$ standard Mo solution) or and 0.4% per mass unit at a higher mass ranges of 182–184 (from $\mu\text{g l}^{-1}$ of W solution). This mass bias value and the natural abundance information were used to correct for ^{99}Tc results. The 10 $\mu\text{g l}^{-1}$ ruthenium solution was used to verify the mass correction and instrumental performance; the difference between the measured and the expected signal at mass of 99 (from Ru), from the mass of 101, was consistently about $\pm 5\%$. Hydride formation for $^{98}\text{Mo}^1\text{H}$, $^{184}\text{W}^1\text{H}$, and $^{186}\text{W}^1\text{H}$ under the instrumental condition was not significant, at the level of $<10^{-5}$ per $\mu\text{g l}^{-1}$ of Mo or W.

AMS is very sensitive to ^{99}Tc in environmental samples. However, there are only two main AMS facilities around the world that have demonstrated the analyses of ^{99}Tc : 10 MV Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory in California and the 14 MV Australian National University in Canberra.^{66–70}

Hot-well water samples at the Nevada Test Site (NTS) were first analyzed for ^{99}Tc by radiochemical counting.⁷¹ A small number of NTS samples were later analyzed for ^{99}Tc by AMS, which provides much greater sensitivity and precision than conventional radiochemical counting.⁶⁷ Because AMS facilities capable of running ^{99}Tc are few in number and not widely available for routine applications, Zhao *et al.* recently developed a routine and robust method to concentrate, purify, and use a quadrupole ICP-MS to analyze ^{99}Tc in NTS groundwaters.⁵⁰ Using Re to track extraction efficiency, the ^{99}Tc concentration in U-19ad PS1A groundwater (Chancellor test) was measured to be $1.70 \pm 0.01 \text{ Bq l}^{-1}$. This value was confirmed by an independent set of standard addition measurements. Using a TEVA column for preconcentration and purification of 1-l water samples, ICP-MS can provide a ^{99}Tc method detection

limit (MDL) of 0.13 mBq l^{-1} . This is only about one order of magnitude higher than that achieved by AMS, which has a reported MDL of 0.01 mBq or 1×10^8 atoms with 15–25% error for a 1-l sample volume.⁶⁷

7 POTENTIAL HUMAN EXPOSURE

^{99}Tc is a health hazard only if it is ingested into the body, and it does not pose an external hazard because it decays by emitting a relatively low-energy β -particle with no γ -radiation. The main concern is cancer induction from the β -particles associated with its radioactive decay. Technetium can concentrate in several organs depending on its chemical form, so there is no primary organ of concern. This is one reason the short-lived isotope $^{99\text{m}}\text{Tc}$ has such wide usage in nuclear medicine as a diagnostic tool. The low energy of the β -particle, the lack of significant γ - or X-rays, and the rapid excretion of ^{99}Tc from the body limit the potential for health effects.⁷²

Lifetime cancer mortality risk coefficients have been calculated for nearly all radionuclides, including ^{99}Tc . While the coefficients for ingestion are slightly lower than that for inhalation, ingestion is generally the most common means of entry into the body. Similar to other radionuclides, the risk coefficients for tap water are about 70% of those for dietary ingestion.⁷²

Although TcO_4^- itself is not considered an ingestion hazard in vivo because it is excreted quickly from the body through the bladder, many organisms such as clams, algae, and fish bioaccumulate TcO_4^- , metabolizing it into forms that are not eliminated very readily from humans.⁷³ It is also reported that the uptake of TcO_4^- into the food chain is analogous to sulfate.³⁹

Pertechnetate (TcO_4^-) is readily taken up from the intestines and lungs following ingestion or inhalation, with about 50–80% of the amount ingested being transferred to the bloodstream.⁷² Because of its similar ionic radius (0.240 nm) to iodide (0.215 nm), TcO_4^- can be preferentially absorbed into the thyroid gland of humans and animals. After reaching the blood, about 4% of the TcO_4^- deposits in the thyroid where it is retained with a biological half-life of 0.5 days; the other two organs to which this isotope preferentially distributes are the stomach wall (10%) and liver (3%). The rest of what enters the blood is uniformly distributed throughout all other organs and tissues with a short residence time. Of the amount that reaches body tissues, half is excreted in urine and half is excreted in feces. For the technetium that is distributed to organs other than the thyroid, about 75% leaves the body with a biological half-life of 1.6 days, 20% clears with a half-life of 3.7 days, and 5% clears with a half-life of 22 days.⁷²

Anthropogenic ^{99}Tc has been found in sites related to nuclear fuel reprocessing, uranium processing facilities, and nuclear testing.^{8,12,14,23,35,37} Tc-99 contamination at these sites

is a concern if individuals are exposed to ^{99}Tc through drinking contaminated water and ingesting contaminated plants. US EPA has established a maximum contaminant level (MCL) of 4 mrem per year for β -particle and photon radioactivity from man-made radionuclides in drinking water; ^{99}Tc would be covered under this MCL. The average concentration of ^{99}Tc , which is assumed to yield 4 mrem year, is 900 pCi l^{-1} . If other radionuclides that emit β -particles and photon radioactivity are present in addition to ^{99}Tc , the sum of the annual dose from all the radionuclides shall not exceed 4 mrem per year.

8 CONCLUSIONS

This article summarizes the basic chemistry, occurrence, detection methods, speciation, and geochemical behavior of technetium (^{99}Tc in particular because of its high abundance and long half-life). The following conclusions can be made regarding the current understanding of technetium in the environment.

- ^{99}Tc originates from the nuclear fuel cycle, mostly (>90%) from nuclear reprocessing plants in Europe. ^{99}Tc has been recognized as an important dose contributor in risk assessment, because of its high abundance, long half-lives, and presumably high mobility.
- Redox-sensitive technetium primarily exists in two (+7 and +4) stable oxidation states in the environment. Tc(VII) is mobile due to its minimal interactions with mineral surfaces across a wide range of environmentally relevant pH values. On the contrary, Tc(IV) is sparingly soluble and strongly retarded in the subsurface.
- Probably mediated by microorganisms, conversion between Tc(VII) and Tc(IV) strongly affects the biogeochemical cycling of ^{99}Tc .
- Coupled with a set of separation and concentration techniques, the analysis of ^{99}Tc by ICP-MS has proven a versatile method to study the distribution, as well as the fate and transport, of ^{99}Tc in the environment.
- Rhenium has been commonly used as a nonradioactive surrogate for technetium in its biogeochemical studies and chemical analyses.

9 RELATED ARTICLES

Anthropogenic Radioactivity; Rhenium.

10 ABBREVIATIONS AND ACRONYMS

AMS = accelerator mass spectrometry; DOE = Department of Energy; EPA = Environmental Protection

Agency; ICP-MS = inductively coupled plasma-mass spectrometry; MCL = maximum contaminant level; MDL = method detection limit; NAA = neutron activation analyses; NTS = Nevada Test Site; RIMS = resonance ionization mass spectrometry.

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