THE DETERMINATION OF TECHNETIUM-99 
BY LIQUID SCINTILLATION COUNTING*

By

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ABSTRACT

A rapid and reliable method for analyzing technetium-99 in a wide variety of environmental samples, including waters, soils, stream sediments, and vegetation, has been developed. The procedure entails oxidizing the technetium to the hepta-valent state and dissolving it in 6 N sulfuric acid. From that medium the technetium is quantitatively and selectively extracted into tributyl phosphate. A portion of the extract is then added to a scintillation cocktail, and technetium-99 activity is measured by liquid scintillation counting. Since a relatively large sample can be handled, the method can detect as little as 0.016 pCi $^{99}$Tc/ml water, 0.1 pCi $^{99}$Tc/g soil or sediment, and 0.2 pCi $^{99}$Tc/g vegetation. The procedure has also been adapted to analyzing urine samples, in which technetium activity as low as 0.12 pCi/ml can be detected.

INTRODUCTION

To help protect the environment and to assure the health and safety of employees, many samples must be analyzed for technetium-99 at the Portsmouth Gaseous Diffusion Plant. Technetium-99, a weak beta emitter (0.292 Mev) with a long half-life (2.1 x 10$^5$ years), is a major product of nuclear fission. For uranium-235 fission, the yield of technetium-99 is about six percent. Technetium produced in this manner is not completely separated from irradiated uranium that is reprocessed to recover usable uranium-235, and since it forms volatile fluorides that accompany uranium as UF$_6$ in the gaseous diffusion process, technetium-99 contamination of gaseous diffusion plant equipment occurs. Thus, during the handling...
and decontamination of process equipment and the recovery of deposited uranium, its presence must be monitored for both environmental and industrial hygiene considerations. Samples analyzed to verify conformance to state and federal regulations for releases of and exposure to technetium–99 include aqueous effluents, stream sediments, soils, airs, and urines.

The method previously used at the Portsmouth Gaseous Diffusion Plant for analysis of technetium–99 involved the solvent extraction of technetium as its crystal violet complex and subsequent beta counting of an evaporated portion of the extract with a proportional counter. This procedure proved adequate for a large variety of samples, but interferences from nitrate limited sample sizes and resulted, in some instances, in unsatisfactory limits of detection.

When a liquid scintillation counter became available, other solvent extraction systems were considered. For this purpose, a solvent was required that would quantitatively extract the technetium from other radionuclides, produce a colorless extract, and be chemically compatible with scintillation counting. Based on the extensive work of Boyd and Larson on the solvent extraction of technetium, tributyl phosphate (TBP) was selected as the solvent. Preliminary work verified that TBP met the above criteria and that it gave an extraction efficiency of 98–99 percent. The effects of other radionuclides and chemical interferences and the elimination of emulsion problems and chemiluminescence were also studied. For these studies a reliable procedure for analyzing technetium–99 by liquid scintillation counting was developed.

PROCEDURES

Sample Preparation

Soils and Sediments

Weigh a 40-g portion of sample into a 300 ml porcelain dish and ignite at 500°C for 30 minutes to destroy organic matter. Add 75 ml of 6 N H₂SO₄ and 10 g potassium persulfate (K₂S₂O₈). Boil for 20 minutes to solubilize the technetium. Filter the cooled leachate through two Whatman #41 filter papers into a 250 ml separatory funnel. Wash the residue with sufficient 6 N H₂SO₄ to give a final volume of 225–250 ml.

Vegetation

Weigh a 15-g portion of dried and ground vegetation into a 300-ml porcelain dish and wet with 75 ml concentrated NH₄OH. Evaporate the sample to dryness and then bake it at
550°C on a hot plate until charred. Place the sample in a muffle furnace at 515°C and ignite for one hour. Add 75 ml of 6 N H$_2$SO$_4$ and 10 g K$_2$S$_2$O$_8$. Boil for 20 minutes to solubilize the technetium. Treat the leachate as described for soils samples.

**Waters**

Place 200 ml of homogenized water into a 250-ml separatory funnel. Add 40 ml concentrated H$_2$SO$_4$ and sufficient 1 percent KMnO$_4$ solution to maintain a pink color.

**Urines**

Pipette a 25-ml aliquot of urine into a 250-ml beaker. Add 50 ml 9 N H$_2$SO$_4$ and 10 g of K$_2$S$_2$O$_8$. Heat to boiling for 20 minutes and transfer to a 100-ml separatory funnel.

**Extraction of Technetium**

Allow the solution produced in any of the preparation procedures given above to cool to room temperature in the separatory funnel. (For soil or vegetation samples only, add 2 ml concentrated HF to complex silica.) Pipette 5.0 ml concentrated TBP that has been previously equilibrated with 9 N H$_2$SO$_4$ into the separatory funnel. Stopper and shake for two minutes to extract technetium. Discard the aqueous phase and wash the extract for one minute first with 25 ml 6 N H$_2$SO$_4$-2% HF and then with 25 ml 4 N HCl. Allow the phases to separate for ten minutes so that sufficient extract will be available for counting. Discard the aqueous phase and transfer the extracts to a 15-ml centrifuge tube. Centrifuge for 2-3 minutes to obtain a clear extract.

**Scintillation Counting**

With a Finnpipette, pipette 4 ml of extract into a scintillation vial, and add 12 ml of Insta-Gel scintillation cocktail. Shake vigorously to mix and wipe off exterior of vial. Place in counter and begin counting sample after one hour.

**RESULTS AND DISCUSSION**

Tributyl phosphate is an excellent solvent for extracting several radionuclides, including technetium, uranium, thorium, and some transuranics. Boyd and Larson showed that technetium could also be extracted into TBP from 1 N sulfuric acid solution. Since strong anionic complexes that are not extracted into TBP are formed between sulfate and any of the above-mentioned radionuclides except technetium, selective extraction of technetium into TBP from sulfuric acid is
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possible. Consequently, the sulfuric acid solvent medium was chosen for further investigation.

Effects of Sulfuric Acid Concentration

Preliminary extraction of $2 \times 10^4$ pCi of technetium-99 into 5 ml TBP from 1 N sulfuric acid solution gave excellent extraction efficiencies, but because the phase separation was poor, the decontamination from other nuclides entrained in the extract was not complete. When extractions from higher concentrations of sulfuric acid were tried, the phase separations improved. To evaluate the technetium extraction efficiency, raffinates from the extractions, along with solutions from the wash steps, were analyzed for technetium by a crystal violet extraction-beta counting procedure. Results of the evaluation are found in Table I.

<table>
<thead>
<tr>
<th>Normality</th>
<th>Technetium Found (pCi)</th>
<th>% Tc Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_4$</td>
<td>Raffinates</td>
<td>H$_2$SO$_4$ Wash</td>
</tr>
<tr>
<td>3</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>4.5</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>6</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>7</td>
<td>128</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>176</td>
<td>26</td>
</tr>
<tr>
<td>9</td>
<td>258</td>
<td>46</td>
</tr>
</tbody>
</table>

The raffinate and wash solutions were too turbid to perform technetium analysis.

A clear extract was obtained from acid concentrations of 6 - 9 N H$_2$SO$_4$; 6 N was selected for further studies since that concentration gave an extraction efficiency of about 99 percent.

Counting Efficiency

Aliquots of a standard solution containing $2.22 \times 10^3$ pCi of technetium-99 were extracted into 10 ml TBP from 6 - 9 N H$_2$SO$_4$ solutions. The extracts were washed with the same concentration of H$_2$SO$_4$ and then with 4 N HCl. Aliquots of 1, 2, and 3 ml of the TBP extract were added to Insta-Gel scintillation cocktail and counted in a scintillation counter. Several aliquots of the above standard were also extracted into 5 ml TBP from 6 N H$_2$SO$_4$ and, for these, 4 ml of each extract were counted. The results listed in Table II show that
varying sample volume from 2 to 4 ml extract produced no significant difference in counting efficiency. Taking 4 ml of a 5 ml TBP extract was chosen as the standard procedure since the counting of 80 percent of samples taken for analysis would improve the sensitivity of the method.

### TABLE II EFFECT OF AMOUNT OF TBP EXTRACT ON COUNTING EFFICIENCY

<table>
<thead>
<tr>
<th>Normality</th>
<th>1 ml Extract Counted</th>
<th>2 ml Extract Counted</th>
<th>3 ml Extract Counted</th>
<th>4 ml Extract Counted</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>94.2</td>
<td>89.7</td>
<td>89.3</td>
<td>90.0</td>
</tr>
<tr>
<td>7</td>
<td>92.8</td>
<td>90.4</td>
<td>88.8</td>
<td>----</td>
</tr>
<tr>
<td>8</td>
<td>94.1</td>
<td>91.4</td>
<td>90.8</td>
<td>----</td>
</tr>
<tr>
<td>9</td>
<td>90.1</td>
<td>90.9</td>
<td>90.0</td>
<td>----</td>
</tr>
</tbody>
</table>

This % efficiency represents an average of more than 20 determinations.

Elimination of Chemiluminescence

In many types of samples, technetium is found in a less soluble, reduced state; therefore, before it can be completely dissolved, it must first be oxidized to the more soluble hepta-valent state. Potassium persulfate (K₂S₂O₈) has proven to be an excellent oxidizing agent for this purpose. When K₂S₂O₈ is used as oxidant, however, peroxides are formed. These undesirable components dissolve in TBP and are not readily removed by washing with 6 N H₂SO₄; and, if left in the extract to be counted, they cause severe chemiluminescence, which gives false counting events. Since complete decay of chemiluminescence requires several hours, this phenomenon is a problem when rapid determination of low levels of technetium (<1 pCi) is necessary. Therefore, procedures for its elimination were investigated. The addition of stannous chloride in 0.1 N HCl, as reported by Newman, was investigated, and found to reduce the chemiluminescence considerably, but has the disadvantage of adding a step to the procedure. However, since technetium is also extracted into TBP from HCl solutions, 4 N HCl was tried as a wash solution for the extract, and chemiluminescence was found to be reduced to a point that even blank solutions could be counted within an hour. The effects of the 4 N HCl wash on the chemiluminescence of TBP extracts from solutions containing 10 g K₂S₂O₈ with and without technetium are shown in Figures 1 and 2. HCl reacts with peroxides to liberate chlorine, thereby reducing peroxide to free oxygen and eliminating chemilumines-
cence. Also, the apparent enhancement of the chemiluminescence in the presence of $2 \times 10^3$ pCi Tc suggests that the radioactivity of technetium-99 is causing secondary reactions between peroxides and the scintillator.

![Figure 1](image1.png)

**FIGURE 1** EFFECT OF H$_2$SO$_4$ AND HCl WASHES OF TBP EXTRACTS OF CHEMILUMINESCENCE - BACKGROUND

![Figure 2](image2.png)

**FIGURE 2** EFFECT OF H$_2$SO$_4$ AND HCl WASHES OF TBP EXTRACTS ON CHEMILUMINESCENCE - $2 \times 10^3$ pCi $^{99}$Tc

Analysis of Soil Samples

A major consideration in the analysis of soils or sediments is the valence state of technetium. Heptavalent technetium is readily soluble in dilute acids, whereas the lower valence states produce insoluble compounds within the matrix of the soil or sediment. Another consideration is the
presence of organic matter which, unless destroyed, will ex-
tract into TBP and cause both color and chemical quenching in
liquid scintillation counting. Thus, three soils were ana-
lyzed by several approaches to evaluate the effects of
ignition at 500°C and of oxidation with K₂S₂O₈ on the results.
The results, as shown in Table III, definitely show that large
quantities of soils should first be ignited to oxidize most
of the organic matter and then leached with 6 N H₂SO₄-10 g
K₂S₂O₈ to solubilize technetium prior to extraction. The H
Numbers (H#) tabulated are an indication of scintillation
counting efficiency. High H Numbers (i.e., more than 125)
indicate color or chemical quenching in the scintillation
medium.

TABLE III STUDY OF SAMPLE TREATMENT VARIABLES
IN ANALYSIS OF SOIL FOR ⁹⁹Tc

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Wt. Taken (grams)</th>
<th>Sample Treatment</th>
<th>H#</th>
<th>pCi Tc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>No oxidant in leach</td>
<td>155</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>No oxidant in leach</td>
<td>246</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>10 g K₂S₂O₈ added</td>
<td>124</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>10 g K₂S₂O₈ added</td>
<td>253</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10 g K₂S₂O₈ added</td>
<td>100</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Ignited + 10 g K₂S₂O₈</td>
<td>96</td>
<td>117</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>NH₄OH added, ignited, oxidized</td>
<td>92</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Ignited, oxidized</td>
<td>92</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>NH₄OH added, ignited, oxidized</td>
<td>88</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Ignited, oxidized</td>
<td>88</td>
<td>160</td>
</tr>
</tbody>
</table>

*All samples were leached with 6 N H₂SO₄*

Analysis of Environmental Samples

Numerous samples of soil, sediment, vegetation and
effluent water are analyzed routinely at the Portsmouth Gas-
eous Diffusion Plant for technetium. Previously, these
analyses were accomplished by complexing the technetium with
crystal violet, extracting it into chloroform, and then beta
counting an evaporated portion of the extract. Several sam-
ple that had been previously analyzed by this method and
found to contain low concentrations of technetium were chosen
for analysis by TBP extraction-liquid scintillation counting.
The results obtained by both methods and tabulated in Table
IV show the acceptability of this new procedure for low-level
technetium determinations.
**TABLE IV ANALYSIS OF ENVIRONMENTAL SAMPLES FOR TECHNETIUM-99**

<table>
<thead>
<tr>
<th>Samp. No.</th>
<th>Type</th>
<th>Crystal Violet</th>
<th>Liquid Scintillation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Soil</td>
<td>&lt;2.2 pCi/g (2)</td>
<td>0.38-0.45 pCi/g (5)</td>
</tr>
<tr>
<td>2</td>
<td>Soil</td>
<td>&lt;2.2 pCi/g (2)</td>
<td>0.45-0.52 pCi/g (5)</td>
</tr>
<tr>
<td>3</td>
<td>Soil</td>
<td>3.8-4.4 pCi/g (2)</td>
<td>4.2-4.9 pCi/g (5)</td>
</tr>
<tr>
<td>4</td>
<td>Vegetation</td>
<td>4.7-6.3 pCi/g (2)</td>
<td>5.4-6.2 pCi/g (4)</td>
</tr>
<tr>
<td>5</td>
<td>Water</td>
<td>0.31-0.36 pCi/ml (5)</td>
<td>0.31-0.32 pCi/ml (8)</td>
</tr>
</tbody>
</table>

( ) Number of determinations.

With the liquid scintillation method, technetium determination could be made on two of the soil samples that were below the crystal violet detection limit of 2.2 pCi/g Tc. The results obtained with the new procedures on the other soil, vegetation, and water samples are in excellent agreement with those obtained by the crystal violet method. They prove that TBP extraction of technetium and subsequent determination by liquid scintillation counting is at least as good as the crystal violet technique and that it can accommodate much larger sample sizes.

**Detection Limits**

Low detection limits on the order of 0.1 pCi Tc/g require large amounts of sample. In the previously used crystal violet procedure, sample sizes were limited to 5 g for soil, 2 g for vegetation, and 50-75 ml for water. In the new liquid scintillation procedure, sample sizes are increased by a factor of eight for soil and vegetation and by a factor of four for waters. The improved detection limits, along with sample size for routine analysis, are found in Table V. These limits of detection are not necessarily the lowest obtainable by this procedure. For water, a sample size of 200 ml was chosen because the technetium can be extracted easily from 250 ml solution in 250-ml separatory funnels. Further increases can be made by evaporation of the sample. Larger samples of soil and vegetation can be analyzed if an evaporation step is incorporated after the technetium is leached.

**Urine Analysis**

Our standard procedure for analyzing technetium in urine starts by screening the samples by direct liquid scintillation counting. A 2-ml aliquot of urine is added to 12 ml scintillation cocktail and the counts are measured in two channels.
The first channel is set to detect low energy emissions from technetium-99 and any other weak alpha or beta emitters and the second to determine if any high energy alpha or beta is present. For this preliminary measurement, the limit of detection is about 2 pCi $^{99}$Tc/ml urine. If a positive result of more than 7 pCi/ml above background is found, an additional aliquot of the sample is evaporated to dryness on a stainless steel planchet with NH$_4$OH present and then beta counted. If a positive result is again obtained, the residue on the planchet is fumed with perchloric acid to volatilize Tc and then recounted to confirm the presence of technetium-99.

To achieve a lower detection limit, a method involving the TBP extraction of technetium and subsequent liquid scintillation counting has been developed. The method involves the preliminary oxidation of the organic matter in the urine without loss of technetium. The urines are made 6 N in H$_2$SO$_4$, and 10 g K$_2$S$_2$O$_8$ is added to each aliquot. The samples are then boiled for 20 minutes, cooled, and extracted into 5 ml TBP. Four milliliters of extract are added to a scintillator and counted. To evaluate the method, aliquots of five urine samples were taken in duplicate and one aliquot from each sample was spiked with 12.8 pCi Tc. The results of the analyses of these aliquots are found in Table VI. The recovery of technetium ranges from 93-115% at 0.5 pCi/ml. Analysis of 50 ml urine is more difficult since two or more oxidations with K$_2$S$_2$O$_8$ are required.

CONCLUSIONS

The TBP extraction-scintillation counting method developed for the analysis of technetium-99 has proven to be successful for many types of environmental samples as well as for urines. The limits of detection are, for many samples, lower than those obtained by the crystal violet method by a factor of eight with no loss in precision or accuracy.
### TABLE VI  TECHNETIUM-99 IN URINE

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original cpm$^a$</th>
<th>Spike cpm$^a$</th>
<th>Spike pCi</th>
<th>pCi Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31.2</td>
<td>53.0</td>
<td>12.8</td>
<td>14.8</td>
</tr>
<tr>
<td>2</td>
<td>34.2</td>
<td>55.2</td>
<td>12.8</td>
<td>12.4</td>
</tr>
<tr>
<td>3</td>
<td>34.5</td>
<td>57.9</td>
<td>12.8</td>
<td>13.7</td>
</tr>
<tr>
<td>4</td>
<td>35.1</td>
<td>59.6</td>
<td>12.8</td>
<td>14.0</td>
</tr>
<tr>
<td>5</td>
<td>33.1</td>
<td>52.3</td>
<td>12.8</td>
<td>11.9</td>
</tr>
</tbody>
</table>

$^a$Count includes 33 cpm background

### REFERENCES
