



## Determination of Technetium-99 in Environmental Samples by Solvent Extraction at Controlled Valence

Chen, Q.J.; Aarkrog, A.; Dick, H.; Mandrup, K.

*Publication date:*  
1987

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*

Chen, Q. J., Aarkrog, A., Dick, H., & Mandrup, K. (1987). *Determination of Technetium-99 in Environmental Samples by Solvent Extraction at Controlled Valence*. Risø National Laboratory. Risø-M No. 2671

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

**Determination of Technetium-99  
in Environmental Samples by Solvent  
Extraction at Controlled Valence**

**Qingjiang Chen, A. Aarkrog, Helle Dick, Karen Mandrup**

RISØ-M-2671

DETERMINATION OF TECHNETIUM-99 IN ENVIRONMENTAL SAMPLES  
BY SOLVENT EXTRACTION AT CONTROLLED VALENCE

Qingjiang Chen, A. aarkrog, Helle Dick, Karen Mandrup

**Abstract.** Distribution coefficients of technetium and ruthenium are determined under different conditions with  $\text{CCl}_4$ , cyclohexanone, and 5% tri-isooctylamine (TIOA)/xylene. A method for analyzing  $^{99}\text{Tc}$  in environmental samples has been developed by solvent extraction in which the valences of technetium and ruthenium are controlled with  $\text{H}_2\text{O}_2$  and  $\text{NaClO}$ . Technetium and ruthenium which are oxidized to  $\text{TcO}_4^-$  and  $\text{RuO}_4^-$  by  $\text{NaClO}$  are separated by extraction with  $\text{CCl}_4$  at  $\text{pH}=4$ . The  $\text{RuO}_4^-$  is reduced to low valence and technetium is kept in the  $\text{TcO}_4^-$  state with  $\text{H}_2\text{O}_2$ . Technetium, ruthenium, and other nuclides are subsequently separated by solvent extraction with cyclohexanone and 5% TIOA/xylene. The decontamination of the procedure is  $1.35 \times 10^5$  for  $^{103}\text{Ru}$  and  $1.66 \times 10^5$  for  $^{110\text{m}}\text{Ag}$ . The chemical yield of technetium-99 is 55%.

October, 1987

Risø National Laboratory, DK-4000 Roskilde, Denmark

**ISBN 87-550-1368-6**

**ISSN 0418-6435**

**Grafisk Service Risø 1987**

**CONTENTS**

	<b>Page</b>
<b>INTRODUCTION.....</b>	<b>5</b>
<b>EXPERIMENTAL.....</b>	<b>6</b>
<b>PROCEDURE.....</b>	<b>9</b>
<b>Principle.....</b>	<b>9</b>
<b>Determination of <sup>99</sup>Tc in 50 l sea water.....</b>	<b>10</b>
<b>RESULTS AND DISCUSSION.....</b>	<b>15</b>
<b>In the solution containing the reducing agent.....</b>	<b>15</b>
<b>In the solution containing the strong oxidizing agent</b>	<b>15</b>
<b>In solution containing gentle oxidizing agent H<sub>2</sub>O<sub>2</sub>...</b>	<b>16</b>
<b>CONCLUSION.....</b>	<b>17</b>
<b>REFERENCES.....</b>	<b>18</b>
<b>APPENDIX 1.....</b>	<b>19</b>
<b>APPENDIX 2.....</b>	<b>28</b>

## INTRODUCTION

Technetium-99 ( $T_{1/2} = 2.1 \times 10^5$  year) is the daughter product of  $^{99}\text{Mo}$ , which is formed by fission of  $^{239}\text{Pu}$  and  $^{235}\text{U}$ . Technetium-99 is released to the environment from nuclear power plants, nuclear fuel reprocessing plants, nuclear weapons testing and nuclear medicine. Technetium-99 is expected to be an element important for the collective long-term dose.

Many works have demonstrated that ruthenium tetroxide is quantitatively extracted<sup>1</sup> by carbon tetrachloride from aqueous solution at pH=4. S. Foti et al.<sup>2</sup> determined technetium in environmental samples with cyclohexanone extraction. N.W. Golchert et al.<sup>3</sup> determined technetium-99 in fresh water with 5% TIOA/xylene extraction for decontamination. E. Holm et al.<sup>4</sup> determined technetium-99 in environmental samples with tributylphosphate.

After the Chernobyl accident contaminations with ruthenium-103, 106 were found in technetium counting samples of Baltic sea water analysed by tributylphosphate extraction. It was important to develop a new method for ruthenium decontamination from the technetium sample, which can be applied to different types of environmental samples.

## EXPERIMENTAL

### 1. Determination of the yield of $^{99m}\text{Tc}^{+4}$ by $\text{Fe}(\text{OH})_2$ - $\text{Fe}(\text{OH})_3$ scavenging

Add 20 ml solution which contains 2 mg/ml  $\text{K}_2\text{S}_2\text{O}_5$  and 0.16 mg/ml  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Acidify to pH=2. Add  $^{99m}\text{Tc}$  tracer. Shake. Let stand for 30 min. Add  $\text{NH}_4\text{OH}$  to the solution until pH=9 to get  $\text{Fe}(\text{OH})_2$  precipitate. Let stand for 2 hours. Filter,  $\gamma$ -count on the precipitate and solution to get the yield. The data are shown in table 1. (See appendix 1).

### 2. Determination of the loss of $^{99m}\text{Tc}$ , $^{103}\text{Ru}$ by volatilization at 100°C for different times

To the measuring tube add 20 ml solution which contains  $^{99m}\text{Tc}$ ,  $^{103}\text{Ru}$  tracer, 2 drops ruthenium carrier, 1 ml 5%  $\text{NaClO}$  and 1 ml 20 mg/ml  $\text{NaCl}$ .  $\gamma$ -count on original. Then heat the solution in the water bath at 100°C. Measure the count at different times. The data are shown in table 2. (See appendix 1).

### 3. Determination of the chemical yield of $^{99m}\text{Tc}$ by examining the electrodeposition at different times

The solution of  $^{99m}\text{Tc}$  tracer is weighed on the disc which is covered with thin film. Add 20 ml 2 N  $\text{NaOH}$  solution to the electrodeposition cell and add  $^{99m}\text{Tc}$  tracer solution which has been weighed. The current is 300 mA. The chemical yields are obtained for different times of electrolysis. The data are shown in table 3. (See appendix 1).

4. Determination of distribution coefficients of  $^{99m}\text{Tc}$ ,  $^{103}\text{Ru}$  for  $\text{CCl}_4$  in 5%  $\text{NaClO}$  at  $\text{pH}=4$

Add 0.5 ml 5 mg  $\text{RuCl}_3/\text{ml}$ , 1 ml 5 N  $\text{NaOH}$ , 2 ml 5%  $\text{NaClO}$ ,  $^{99m}\text{Tc}$  and  $^{103}\text{Ru}$  tracer to beaker. Dilute to 10 ml. Heat 10 min. to allow isotopic exchange to be completed. Add 3 N  $\text{H}_2\text{SO}_4$  one drop at a time with swirling until the greenish mixture suddenly turns yellow, indicating the formation of ruthenium tetroxide ( $\text{RuO}_4$ ) from perruthenate. This will occur at  $\text{pH}=4$ . Extract with 10 ml  $\text{CCl}_4$ . Shake 10 seconds. The data are shown in table 4 (See appendix 1).

The extraction rate of  $\text{RuO}_4$  depends on the purification of  $\text{CCl}_4$ , appropriate carrier of  $\text{Ru}$  and extraction shaking time. Because the  $\text{RuO}_4$  is reduced by an impurity organic agent, the longer the shaking time, the more  $\text{RuO}_4$  is reduced. The greater the impurity organic agent in the  $\text{CCl}_4$ , the more  $\text{RuO}_4$  is reduced. The less the amount of carrier of  $\text{Ru}$ , the higher the per cent of  $\text{RuO}_4$  that is reduced.

5. Determination of distribution coefficient of  $^{99m}\text{Tc}$  for cyclohexanone extraction in different  $\text{H}_2\text{SO}_4$  concentrations

Add  $^{99m}\text{Tc}$  and 3 drops 5%  $\text{NaClO}$  to the beaker to get  $\text{TcO}_4^-$ . Dilute to 10 ml with different concentrations of  $\text{H}_2\text{SO}_4$ . Extract with 10 ml cyclohexanone. Shake 1 min.  $\gamma$ -count the organic and aqueous phases. The data are shown in table 5. (See appendix 1).

6. Determination of the distribution coefficient of  $^{99m}\text{Tc}$  for different concentrations of sulphuric acid with 5% TIOA/xylene

Add  $^{99m}\text{Tc}$  tracer and a few drops 30%  $\text{H}_2\text{O}_2$  to 5 ml solution to get  $\text{TcO}_4^-$ . Extract with 5 ml 5% TIOA/xylene in different concentrations of sulphuric acid. Shake 1 min. The data are shown in table 6. (See appendix 1).



7. Determination of the distribution coefficient of  $^{99m}\text{Tc}$  and  $^{103}\text{Ru}$  with 5% TIOA/xylene and cyclohexanone in 2 N  $\text{H}_2\text{SO}_4$ - $\text{K}_2\text{S}_2\text{O}_5$

Add 10 ml solution to the separation funnel which contains about 2 mg/ml  $\text{K}_2\text{S}_2\text{O}_5$  and  $^{99m}\text{Tc}$  tracer. At pH=2, let stand for 20 min. to get  $\text{Tc}^{+4}$ : Extract with 5% TIOA/xylene and cyclohexanone. Vorg.: Vaqu. = 10 : 10 ml. Shake for 1 min.  $\gamma$ -measure the organic and aqueous phases. The data are shown in table 7. (See appendix 1).

8. Determination of the distribution coefficient of  $^{99m}\text{Tc}$  and  $^{103}\text{Ru}$  in 1 N  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}_2$  with 5% TIOA/xylene and cyclohexanone

Add 1 ml 5 N NaOH,  $^{99m}\text{Tc}$ ,  $^{103}\text{Ru}$  tracer and 2 ml 5% NaClO to the beaker. Heat for 10 min. Technetium and ruthenium are oxidized to  $\text{TcO}_4^-$ ,  $\text{RuO}_4^-$ . Then add 1 ml 30%  $\text{H}_2\text{O}_2$  to the solution. The  $\text{RuO}_4^-$  is reduced to low valence. Technetium is kept in  $\text{TcO}_4^-$  state. Dilute to 10 ml. Acidify the solution to 1 N  $\text{H}_2\text{SO}_4$ . Extract with 10 ml 5% TIOA/xylene and cyclohexanone. The data are shown in table 8. (See appendix 1).

9. Determination of the distribution coefficient of  $^{99m}\text{Tc}$  and  $^{103}\text{Ru}$  in 2 N  $\text{H}_2\text{SO}_4$ -5% NaClO extraction with 5% TIOA/xylene and cyclohexanone

Add 1 ml 5 N NaOH, 1 ml 5% NaClO,  $^{99m}\text{Tc}$ ,  $^{103}\text{Ru}$  tracer and ruthenium carrier to beaker. Heat 10 min. to allow isotopic exchange to be completed. Acidify to 2 N  $\text{H}_2\text{SO}_4$  and dilute to 10 ml. Extract with 10 ml cyclohexanone and 5% TIOA/xylene. The data are shown in table 9. (See appendix 1).

10. Determination of back-extraction rate of  $^{99m}\text{Tc}$  from cyclohexanone with  $\text{H}_2\text{O}$  and 0.5 N NaOH

Add 10 ml cyclohexanone into which  $^{99m}\text{Tc}$  is extracted and 10 ml cyclohexanone to a separator funnel. Back-extract with 10 ml  $\text{H}_2\text{O}$  and 0.5 N NaOH, respectively. Compare the back-extraction rate shown in table 10. (See appendix 1).

11. Determination of back-extraction rate of  $^{99m}\text{Tc}$  from  
5% TIOA/ xylene with 2 N NaOH

Add 10 ml 5% TIOA/xylene into which the  $^{99m}\text{Tc}$  is extracted and 10 ml 2 N NaOH. Shake 2 min. Measure the count of organic and aqueous phases. The data are shown in table 11.

(See appendix 1).

**PROCEDURE**

Principle

The high scavenging rate of  $^{99m}\text{Tc}^{+4}$  is shown in table 1 by  $\text{Fe}(\text{OH})_2\text{-Fe}(\text{OH})_3$ . The  $\text{Fe}(\text{OH})_2\text{-Fe}(\text{OH})_3$  is dissolved in  $\text{H}_2\text{SO}_4$ . Add 5%  $\text{NaClO}$  to get  $\text{TcO}_4^-$  and  $\text{RuO}_4^-$ . Heat the solution. The  $\text{RuO}_4^-$  is volatilized and the  $\text{TcO}_4^-$  left in solution, as shown in table 2. This is the first step for separating the technetium and ruthenium.

The second step is oxidation of the technetium and ruthenium to  $\text{RuO}_4^-$  and  $\text{TcO}_4^-$  with 5%  $\text{NaClO}$ . At  $\text{pH}=4$ , the  $\text{RuO}_4^-$  is extracted by  $\text{CCl}_4$ . The  $\text{TcO}_4^-$  is left in the solution, as shown in table 4.

The third step for decontaminating ruthenium and other nuclides is reduction of the  $\text{RuO}_4^-$  to a low valence state and maintenance of technetium at the  $\text{TcO}_4^-$  state with 30%  $\text{H}_2\text{O}_2$ . The  $\text{TcO}_4^-$  is extracted with cyclohexanone, and ruthenium is left in the solution, as shown in table 8.

The fourth step decontaminating ruthenium and other nuclides is extraction of the  $\text{TcO}_4^-$  and leaving the ruthenium in 1 N  $\text{H}_2\text{SO}_4$  - 30%  $\text{H}_2\text{O}_2$  by 5% TIOA/xylene extraction. Scavenging  $\text{Fe}(\text{OH})_3$  and  $\text{AgCl}$  precipitate are used for decontamination.

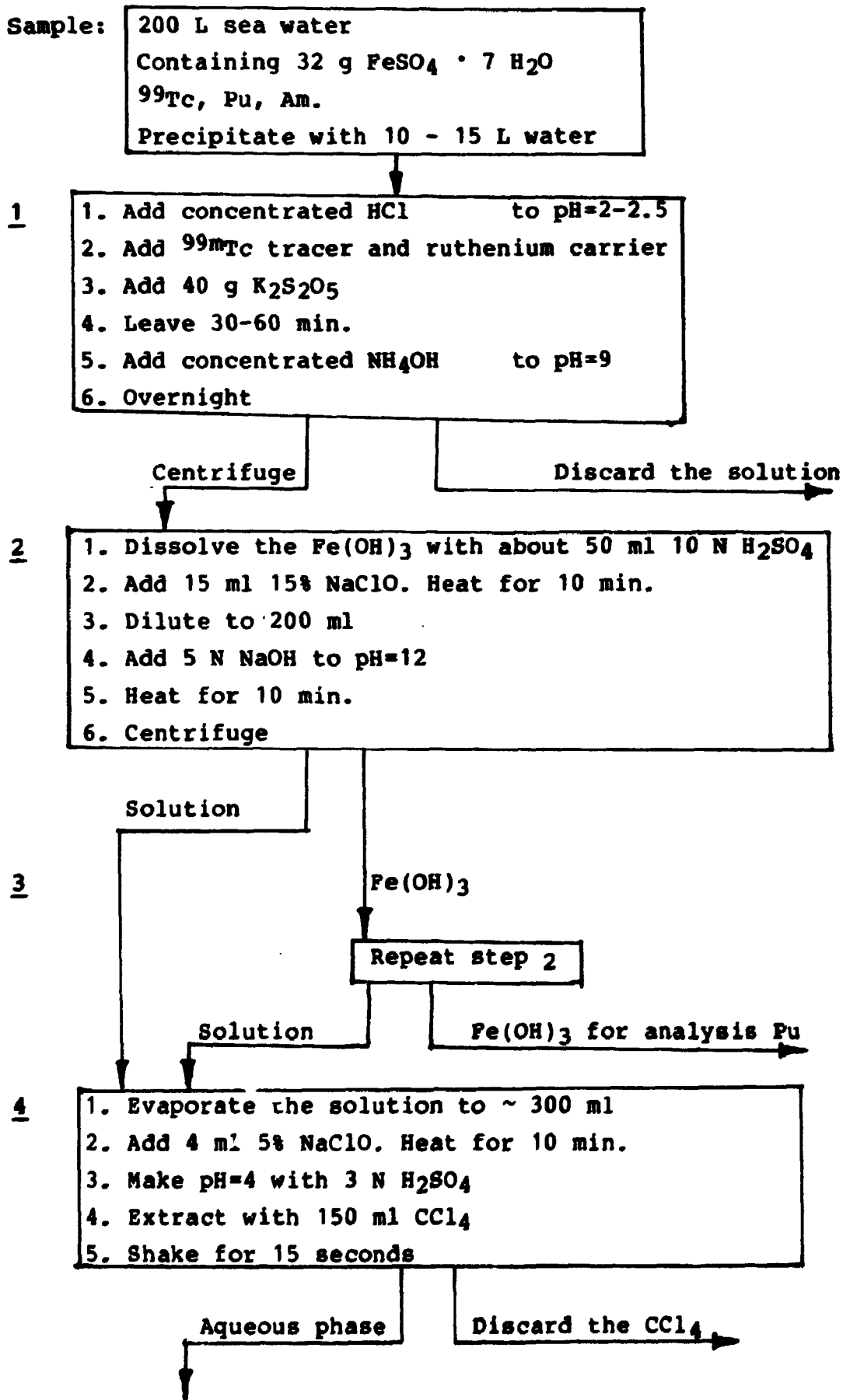
The procedure follows in detail:

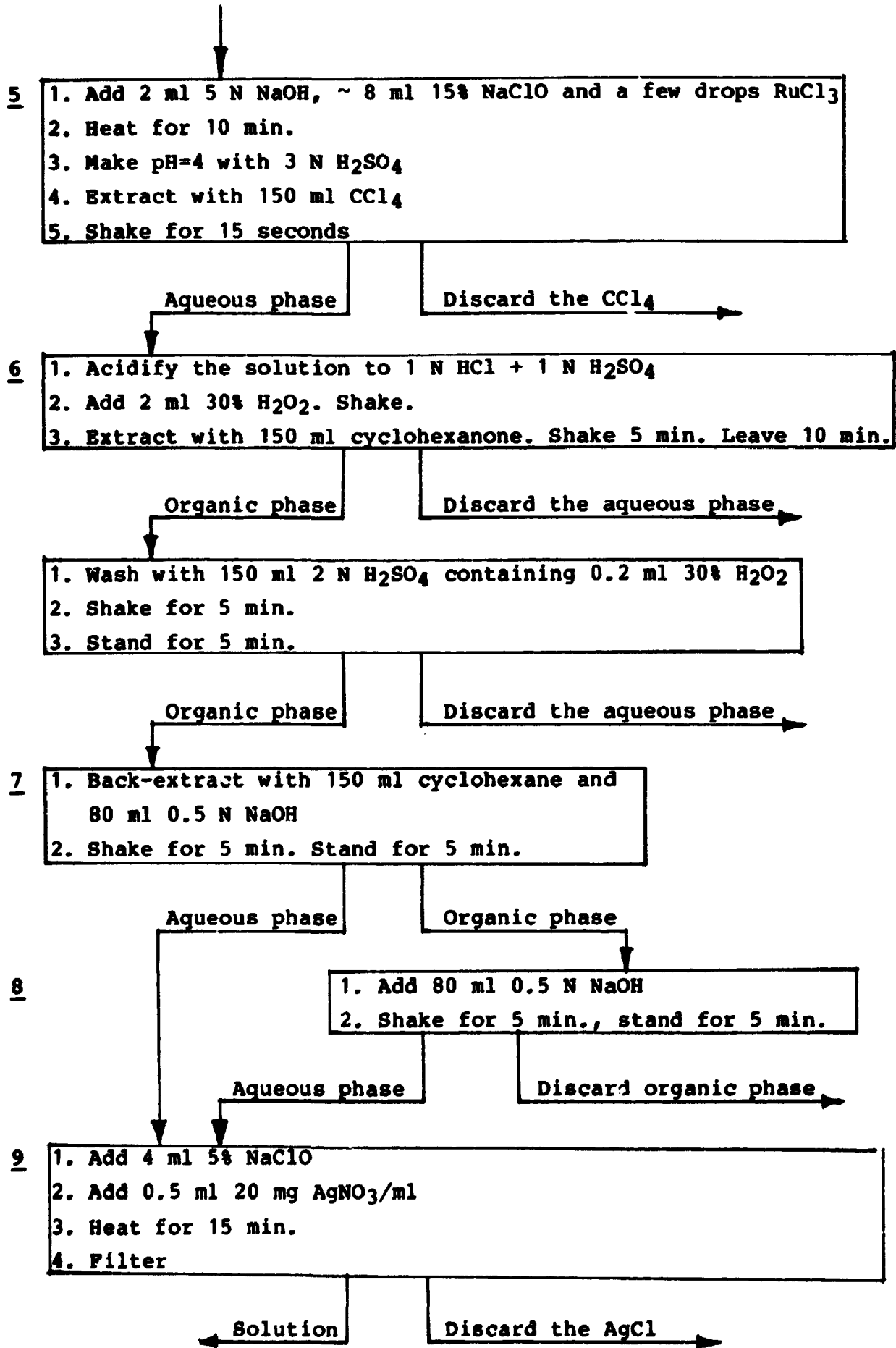
Determination of  $^{99}\text{Tc}$  in 50 L sea water

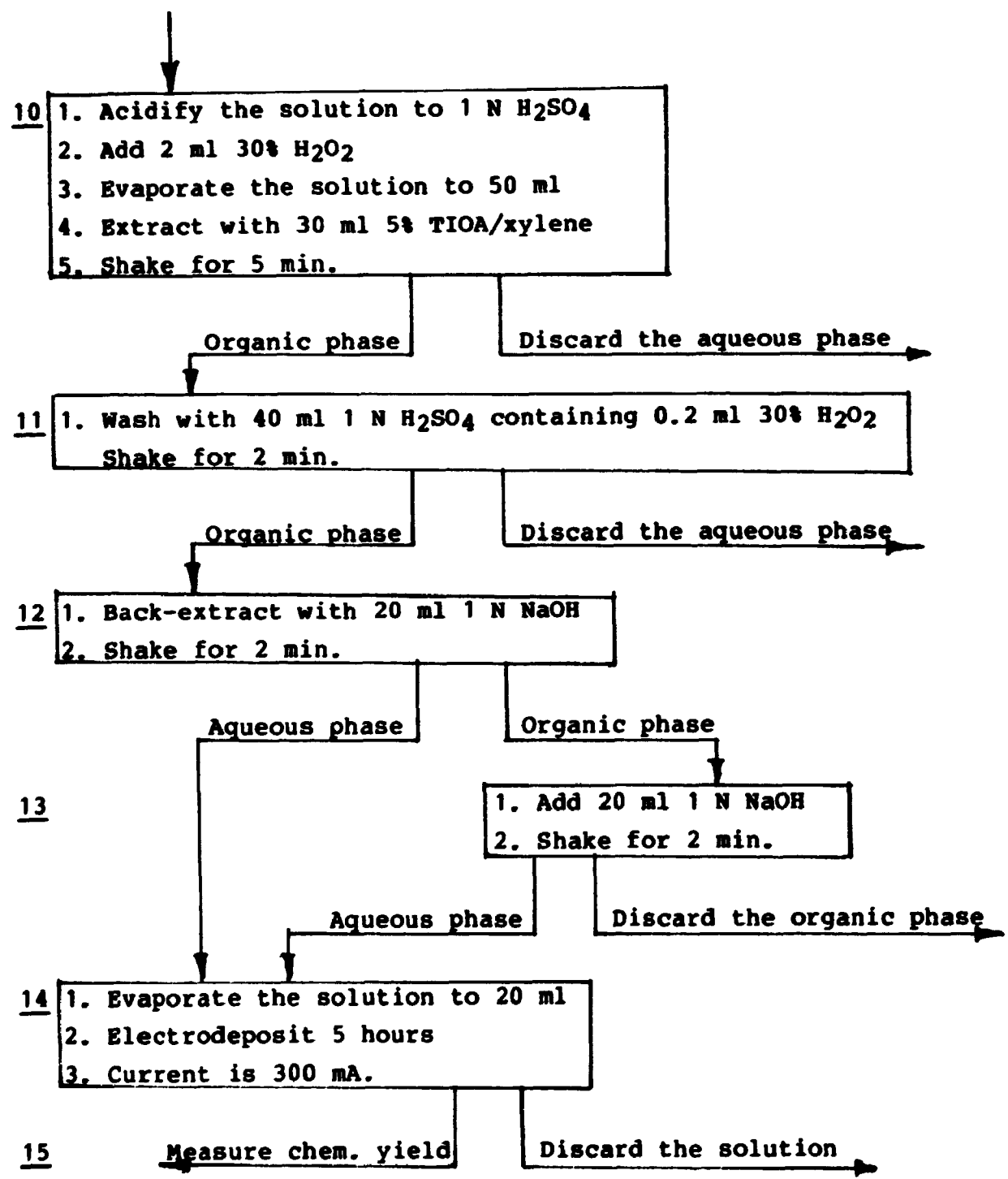
1. Acidify the 50 L sea water to pH=2-2.5 with concentrated HCl.
2. Add  $^{99\text{m}}\text{Tc}$ ,  $^{110\text{m}}\text{Ag}$ ,  $^{103}\text{Ru}$ , 1 ml 5 mg/ml ruthenium carrier to 50 L sea water.
3. Add 100 g  $\text{K}_2\text{S}_2\text{O}_5$  mix. Leave for 20-30 min. to get the  $\text{Tc}^{+4}$  state.
4. Add 7.4 g  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  mix. Leave for 5 min.
5. Add  $\text{NH}_4\text{OH}$  (about 140 ml concentrated  $\text{NH}_4\text{OH}$ ) to the sea water till a precipitate is observed. Stand overnight.  
Centrifuge.
6. Dissolve the  $\text{Fe}(\text{OH})_2$  with 10 ml 10 N  $\text{H}_2\text{SO}_4$ . Heat 5 min. to dissolve  $\text{Fe}(\text{OH})_2$ . Dilute to 150 ml. Add 10 ml 15%  $\text{NaClO}$ . Heat 10 min. to get  $\text{TcO}_4^-$  and  $\text{RuO}_4^-$ . Add  $\text{NaOH}$  (about 26 ml 5 N  $\text{NaOH}$ ) to get  $\text{Fe}(\text{OH})_3$  pH=12. Heat the solution to a large precipitate. The  $\text{RuO}_4^-$  is volatilized. Centrifuge. Filter. Add 10 ml 10 N  $\text{H}_2\text{SO}_4$  to dissolve the  $\text{Fe}(\text{OH})_3$ . Heat for 5 min. Add 5 ml 15%  $\text{NaClO}$ . Dilute to 150 ml. Heat for 10 min. Add 26 ml 5 N  $\text{NaOH}$  to pH=12 to get  $\text{Fe}(\text{OH})_3$ . Heat the solution. Centrifuge. Filter. Combine these solutions. Discard the  $\text{Fe}(\text{OH})_3$ .
7. Add 2 ml 5%  $\text{NaClO}$ . Evaporate to 80 ml. Add 2 ml 5%  $\text{NaClO}$ . Heat for 10 min. Acidify to pH=4 to get a yellow colour with 3 N  $\text{H}_2\text{SO}_4$ .
8. Extract with 40 ml  $\text{CCl}_4$  (two times). Discard the  $\text{CCl}_4$ .

9. Add 2 ml 1 N NaOH, 2 ml 5% NaClO and Ru carrier 0.5 ml 5 mg/ml RuCl<sub>3</sub>. Heat for 10 min. Stir. Acidify to pH=4 with H<sub>2</sub>SO<sub>4</sub>. Extract two times with CCl<sub>4</sub>. Shake for 15 seconds. The RuO<sub>4</sub> is extracted into CCl<sub>4</sub>. TcO<sub>4</sub><sup>-</sup> is left in an aqueous solution.
10. Acidify the aqueous solution to 1 N HCl and 1 N H<sub>2</sub>SO<sub>4</sub>. (80 ml). Add 1 ml 30% H<sub>2</sub>O<sub>2</sub>. Heat for 10 min.
11. Add 60 ml cyclohexanone and the solution to separator funnel. Shake for 5 min. Stand for 5 min. Wash with 60 ml 2 N H<sub>2</sub>SO<sub>4</sub> containing a few drops 30% H<sub>2</sub>O<sub>2</sub>. Discard the aqueous phase.
12. Add 80 ml cyclohexane and 30 ml H<sub>2</sub>O. Back-extract three times, each time with 30 ml H<sub>2</sub>O.
13. Add 1 ml 10 mg/ml AgNO<sub>3</sub>. Heat for 10 min. Add 2 ml 5% NaClO and 2 ml NaCl 20 mg/ml to get a precipitate. Heat for 20 min. Filter.
14. Repeat step 13.
15. Acidify to 1 N H<sub>2</sub>SO<sub>4</sub>. Evaporate to 30 ml. Add 1 ml 30% H<sub>2</sub>O<sub>2</sub>. Heat for 10 min.
16. Extract with 25 ml 5% TIOA/xylene. Shake for 2 min. Wash with 25 ml 1 N H<sub>2</sub>SO<sub>4</sub> containing a few drops 30% H<sub>2</sub>O<sub>2</sub>. Shake for 2 min.
17. Back-extract two times, each time with 20 ml 1 N NaOH.
18. Evaporate to 20 ml for electrodeposition. The current is 300 mA. The time is 3 to 5 hours.
19. The results are shown in table 12.

Flow sheet







## RESULTS AND DISCUSSION

The volatilization rates of  $\text{RuO}_4^-$  and  $\text{TcO}_4^-$  are determined by  $100^\circ\text{C}$  in 1 N  $\text{H}_2\text{SO}_4$ -NaClO solution; 99% of  $\text{RuO}_4^-$  is volatilized in 30 minutes, while  $\text{TcO}_4^-$  is left in the solution. No volatilisation of  $\text{TcO}_4^-$  was found by heating for 4 hours at  $100^\circ\text{C}$ .

The method of  $\text{CCl}_4$  solvent extraction is applied in the determination of ruthenium. It is applied in the present work for ruthenium decontamination. The extraction rates of  $\text{RuO}_4^-$  and  $\text{TcO}_4^-$  are shown in table 4. The  $\text{RuO}_4^-$  is extracted by  $\text{CCl}_4$  at pH=4 in NaClO solution, and the  $\text{TcO}_4^-$  is left in solution. The distribution coefficient of  $^{99\text{m}}\text{Tc}$  depends on the concentration of sulphuric acid in 5% TIOA/xylene and cyclohexanone. The extraction rate is more than 99% from 0.2 N  $\text{H}_2\text{SO}_4$  to 4 N  $\text{H}_2\text{SO}_4$ .

### In the solution containing the reducing agent

In the  $\text{K}_2\text{S}_2\text{O}_5$ -HCl solution at pH=2, technetium is reduced to  $\text{Tc}^{+4}$ , and ruthenium to a low valence state. Acidify to 2 N  $\text{H}_2\text{SO}_4$ . The extraction rates of technetium and ruthenium are obtained by cyclohexanone and 5% TIOA/xylene, as shown in table 7.

### In the solution containing the strong oxidizing agent

Technetium and ruthenium are oxidized to  $\text{RuO}_4^-$  and  $\text{TcO}_4^-$  in a strong oxidizing agent. The extraction rate of  $^{99\text{m}}\text{Tc}$  and  $^{103}\text{Ru}$  are obtained in 2 N  $\text{H}_2\text{SO}_4$ -NaClO with cyclohexanone, 5% TIOA/xylene, as shown table 9. If technetium and ruthenium are held in a  $\text{TcO}_4^-/\text{RuO}_4^-$  state, the technetium and ruthenium cannot be separated by extraction with cyclohexanone and 5% TIOA/xylene in 2 N  $\text{H}_2\text{SO}_4$ -NaClO.



In solution containing gentle oxidizing agent H<sub>2</sub>O<sub>2</sub>

The technetium is oxidized to TcO<sub>4</sub><sup>-</sup>, and ruthenium is kept in a low valence state. The extraction rates are shown in table 8. The ruthenium and technetium can be separated by extraction with cyclohexanone and 5% TIOA/xylene in 1 N H<sub>2</sub>SO<sub>4</sub>- H<sub>2</sub>O<sub>2</sub>.

The different valence states of technetium and ruthenium are controlled with H<sub>2</sub>O<sub>2</sub> and NaClO in different steps in the procedure to get a higher ruthenium decontamination. The decontamination factors of ruthenium for each step in the procedure are shown as follows:

Step	Decontamination factor of ruthenium
Heating at 100°C	
1 N H <sub>2</sub> SO <sub>4</sub> -NaClO	110
CCl <sub>4</sub> extraction	600
Cyclohexanone extraction	230
5% TIOA/xylene extraction	250

According to the step-by-step decontamination of the procedure, the decontamination factor for ruthenium should be  $3.5 \times 10^9$ . But the large volume sea water is more complicated, as it contains many elements. Add the low count of <sup>103</sup>Ru for the decontamination test, so that the decontamination of the procedure is only  $1.35 \times 10^5$  for <sup>103</sup>Ru and  $1.66 \times 10^5$  for <sup>110m</sup>Ag.

Technetium is lost in each step of the procedure as follows:

Step	Loss rate of <sup>99m</sup> Tc %
Loss in Fe(OH) <sub>2</sub> carried	~5
CCl <sub>4</sub> extraction	~5
Fe(OH) <sub>3</sub> scavenging	~10
AgCl precipitate	~10
Cyclohexanone extraction	~5
5%TIOA/xylene extraction	~5
Electrodeposition	~5

The chemical yield of the procedure is about 55 percent.

## CONCLUSION

1. Ruthenium is volatilized; however, no volatilization of technetium was found in 1 N  $\text{H}_2\text{SO}_4$ -NaClO at 100°C.
2. Ruthenium and technetium can be separated to permit the extraction of  $\text{RuO}_4$ , and the  $\text{TcO}_4^-$  is kept in solution at pH=4 containing NaClO with  $\text{CCl}_4$ .
3. Both the  $\text{RuO}_4^-$  and  $\text{TcO}_4^-$  are extracted by cyclohexanone and 5% TIOA/xylene in 1 N  $\text{H}_2\text{SO}_4$  solution in which the valences are controlled with NaClO. Therefore, the ruthenium and technetium cannot be separated in this way.
4. Ruthenium cannot be extracted but technetium can be by cyclohexanone and 5% TIOA/xylene in which the ruthenium is reduced to low valence and the technetium is kept in  $\text{TcO}_4^-$  state at a controlled valence with  $\text{H}_2\text{O}_2$ . This permits separation of the ruthenium and technetium.
5.  $\text{Fe}(\text{OH})_3$  scavenging, extraction of cyclohexanone and 5% TIOA/xylene are used for decontamination of ruthenium and other nuclides. The  $1.35 \times 10^5$  of ruthenium-103 and  $1.66 \times 10^5$   $^{110m}\text{Ag}$  decontamination factor are obtained.
7. The procedure can be applied to different types of environmental samples, and the average chemical yield for Tc is about 60%.

**REFERENCES**

1. Jesse W.T. Meadows et al. *Anal. Chem.*, 22, 1277 (1950).
2. S. Foti et al. *Anal. Chim. Acta*, 60, 269 (1972).
3. N.W. Golchert et al. *Anal. Chem.*, 41, 669 (1969).
4. E. Holm et al. *Nuclear Instrument and Methods in Physics Research* 223 (1984) 204-207.

APPENDIX 1

Table 1. Yield of  $^{99m}\text{Tc}$  by  $\text{Fe}(\text{OH})_2\text{-Fe}(\text{OH})_3$

No.	Precipitate Count C.P.S.	Solution Count C.P.S.	Yield %
1	2632.2	90.2	96.7
2	2500.2	107.6	95.9
3	2506.1	101.0	96.1

**Table 2.** Determination of the loss of  $^{99m}\text{Tc}$ ,  $^{103}\text{Ru}$  by volatilization for different times at  $100^\circ$

Composition of solution	No.	Nuclides	Time (min.)	Time							
				5	10	20	30	60	90	120	240
1 ml $\text{H}_2\text{SO}_4$ , 1 ml 5% $\text{NaClO}$ , 1 ml	1	$^{99m}\text{Tc}$	Loss %	-	0.6	2.6	1.8		7.1		
		$^{103}\text{Ru}$		72	90.2	95.5	99.2		99.4		
20 mg/ml $\text{NaCl}$ 2 drops $\text{Ru}$ carrier, 7 ml $\text{H}_2\text{O}$	2	$^{99m}\text{Tc}$		2.9	4.9	3.6	3.1		4.6		
		$^{103}\text{Ru}$		59.6	89.1	95.5	99.1		99.4		
<hr/>											
1 N $\text{H}_2\text{SO}_4$ (10 ml)	1	$^{99m}\text{Tc}$						0		2.5	0
	2	$^{99m}\text{Tc}$						0		2.3	0
<hr/>											
10 ml 1 N $\text{H}_2\text{SO}_4$ 2 mg/ml $\text{NaCl}$	1	$^{99m}\text{Tc}$						0		2.1	0
	2	$^{99m}\text{Tc}$						0		1.0	0
<hr/>											
10 ml 1N $\text{H}_2\text{SO}_4$ 2 mg/ml $\text{NaCl}$ 0.5% $\text{NaClO}$	1	$^{99m}\text{Tc}$						0		0	0
	2	$^{99m}\text{Tc}$						0		0	0

**Table 3.** Chemical yield of  $^{99m}\text{Tc}$  electrodeposition for different times

Time (min.)	33	66	96	180	240	300
Chem. yield %	38.3	65.8	85.3	92.5	93.4	95.3

**Table 4.** Distribution coefficients for extraction of  $^{99m}\text{Tc}$ ,  $^{103}\text{Ru}$  with  $\text{CCl}_4$  from  $\text{NaClO}$  solution at  $\text{pH}=4$

Nuclides	No.	Org.phase C.P.S.	Aqu.phase C.P.S.	Distribution coefficient	Extraction rate %
$^{99m}\text{Tc}$	1	2.79	825.3	$3.4 \times 10^{-3}$	0.34
$^{99m}\text{Tc}$	2	0.69	876.1	$7.9 \times 10^{-4}$	0.08
<hr/>					
$^{103}\text{Ru}$	1	245.2	3.35	73.3	98.7
$^{103}\text{Ru}$	2	364.0	5.42	67.2	98.5
$^{103}\text{Ru}$	3	167.2	2.06	81.3	98.8
$^{103}\text{Ru}$	4	169.7	1.54	110.4	99.1

83.0<sup>+19</sup><sub>-</sub>  
(average)

**Table 5.** Distribution coefficient of  $^{99m}\text{Tc}$  related to sulphuric acid concentration in cyclohexanone

<u>Concentration of H<sub>2</sub>SO<sub>4</sub></u>	<u>Org.phase C.P.S.</u>	<u>Aqu.phase C.P.S.</u>	<u>Distribution coefficient</u>	<u>Extraction rate %</u>
0.2 N H <sub>2</sub> SO <sub>4</sub>	3562.9	43.6	81.8	98.79
0.5	5210.6	44.5	117.1	99.15
1.0	4988.2	43.9	113.6	99.13
2.0	4682.7	31.2	149.9	99.34
3.0	4687.4	25.4	184.6	99.46
4.0	4392.9	22.0	199.1	99.50

**Table 6.** Distribution coefficient of  $^{99m}\text{Tc}$  dependence on sulphuric acid in 5% TIOA/xylene

<u>Concentration of H<sub>2</sub>SO<sub>4</sub></u>	<u>Org.phase C.P.S.</u>	<u>Aqu.phase C.P.S.</u>	<u>Distribution coefficient</u>	<u>Extraction rate %</u>
0.2 N H <sub>2</sub> SO <sub>4</sub>	3668.5	5.77	635.8	99.84
0.5	4669.3	1.00	4667	99.98
1.0	4374.0	1.33	3288.7	99.97
2.0	2500.0	0.84	2659	99.96
3.0	3782.8	1.36	2781	99.96
4.0	4036	2.53	1595	99.93

**Table 7.** Determination of distribution coefficient of  $^{99m}\text{Tc}$  and  $^{103}\text{Ru}$  for 2 N  $\text{H}_2\text{SO}_4$ - $\text{K}_2\text{S}_2\text{O}_5$  with either a) TIOA/xylene or b) Cyclohexanone

Nuclides	No.	Org.phase C.P.S.	Aqu.phase C.P.S.	Distribution coefficient	Extraction rate %
----------	-----	---------------------	---------------------	-----------------------------	----------------------

**a) 5% TIOA/xylene - 1 N  $\text{H}_2\text{SO}_4$  -  $\text{K}_2\text{S}_2\text{O}_5$**

$^{99m}\text{Tc}$	1	2018.9	192.5	10.5	91.3
$^{99m}\text{Tc}$	2	1883.8	152.6	12.3	92.5

---

$^{103}\text{Ru}$	1	2.62	388.75	$6.7 \times 10^{-3}$	0.67
$^{103}\text{Ru}$	2	1.82	280.55	$6.5 \times 10^{-3}$	0.64

**b) Cyclohexanone - 2 N  $\text{H}_2\text{SO}_4$  -  $\text{K}_2\text{S}_2\text{O}_5$**

$^{99m}\text{Tc}$	1	1119.35	138.27	8.1	89.0
$^{99m}\text{Tc}$	2	1225.28	127.70	9.6	90.6

---

$^{103}\text{Ru}$	1	8.197	319.45	$2.6 \times 10^{-2}$	2.5
$^{103}\text{Ru}$	2	8.347	293.89	$2.8 \times 10^{-2}$	2.76



**Table 8.** Distribution coefficient of  $^{99m}\text{Tc}$ ,  $^{103}\text{Ru}$  for 1 N  $\text{H}_2\text{SO}_4$  -  $\text{H}_2\text{O}_2$  with 5% TIOA/xylene and cyclohexanone

Nuclides	No.	Org.phase C.P.S	Aqu.phase C.P.S.	Distribution coefficient	Extraction rate %
----------	-----	--------------------	---------------------	-----------------------------	----------------------

**a) Cyclohexanone -  $\text{H}_2\text{O}_2$  - 1 N  $\text{H}_2\text{SO}_4$**

$^{99m}\text{Tc}$	1	5024.91	16.44	305.7	99.7
$^{99m}\text{Tc}$	2	4666.31	11.87	393.7	99.7

---

$^{103}\text{Ru}$	1	0.147	288.87	$5.0 \times 10^{-4}$	0.05
$^{103}\text{Ru}$	2	2.762	442.36	$6.2 \times 10^{-3}$	0.62
$^{103}\text{Ru}$	3	1.327	320.25	$4.1 \times 10^{-3}$	0.41
$^{103}\text{Ru}$	4	2.027	327.65	$6.2 \times 10^{-3}$	0.62

**b) 5% TIOA/xylene - 1 N  $\text{H}_2\text{SO}_4$  -  $\text{H}_2\text{O}_2$**

$^{99m}\text{Tc}$	1	2500	0.94	2659	99.96
$^{99m}\text{Tc}$	2	3288.7	1.33	2472.7	99.96

---

$^{103}\text{Ru}$	1	0.547	315.37	$1.73 \times 10^{-3}$	0.17
$^{103}\text{Ru}$	2	0.962	142.80	$6.74 \times 10^{-3}$	0.67
$^{103}\text{Ru}$	3	0.987	308.80	$3.2 \times 10^{-3}$	0.32

**Table 9.** Distribution coefficient of  $^{99m}\text{Tc}$  and  $^{103}\text{Ru}$  for 2 N  $\text{H}_2\text{SO}_4$  - 5%  $\text{NaClO}$  extraction with a) Cyclohexanone and b) 5% TIOA/xylene

Nuclides	No.	Org.phase C.P.S.	Aqu.phase C.P.S.	Distribution coefficient	Extraction rate %
----------	-----	---------------------	---------------------	-----------------------------	----------------------

**a) Cyclohexanone - 2 N  $\text{H}_2\text{SO}_4$  - 5%  $\text{NaClO}$**

$^{99m}\text{Tc}$	1	5411.12	50.13	107.9	99.08
$^{99m}\text{Tc}$	2	381.84	6.06	63	98.49
$^{99m}\text{Tc}$	3	441.08	1.09	404	99.80
$^{99m}\text{Tc}$	4	3271.95	65.65	49.8	98.0

---

$^{103}\text{Ru}$	1	236.63	10.30	22.98	95.82
$^{103}\text{Ru}$	2	260.45	7.25	35.9	97.3

**b) 5% TIOA/xylene - 2 N  $\text{H}_2\text{SO}_4$  - 5%  $\text{NaClO}$**

$^{99m}\text{Tc}$	1	3996.46	40.18	99.5	99.0
$^{99m}\text{Tc}$	2	3769.63	43.92	85.8	98.8

---

$^{103}\text{Ru}$	1	240.12	79.09	3.04	75.2
$^{103}\text{Ru}$	2	232.69	79.11	2.94	74.6
$^{103}\text{Ru}$	3	247.16	81.55	3.03	75.2

**Table 10.** Determination of back-extraction rate  $^{99m}\text{Tc}$  from cyclohexanone with  $\text{H}_2\text{O}$  and 0.5 N NaOH

Shaking time	No.	Org.phase C.P.S.	Aqu.phase C.P.S.	Back-extraction rate %
--------------	-----	---------------------	---------------------	---------------------------

**a) With water from cyclohexanone**

2 min.	1	2486	1878	43.0
2 min.	2	1335	1919	59.0

5 min.	1	250.2	3664	93.6
5 min.	2	91.1	3121	97.2

**b) With 0.5 N NaOH from cyclohexanone**

2 min.	1	2.63	121.5	97.9
2 min.	2	1.87	119.5	98.5

5 min.	1	0.89	83.0	98.9
5 min.	2	2.95	111.1	97.4

**Table 11.** Determination of back-extraction rate of  $^{99m}\text{Tc}$  from 5% TIOA/xylene with 2 N NaOH

No.	Org.phase C.P.S.	Aqu.phase C.P.S.	Back-extraction rate %
-----	---------------------	---------------------	---------------------------

1	5.83	4077.2	99.86
2	4.29	3680.5	99.88

**Table 12.** Decontamination of  $^{103}\text{Ru}$ ,  $^{110}\text{mAg}$  and chemical yield of  $^{99\text{mTc}}$  of the procedure

<b>Nucl.</b>	<b>Before the procedure</b>	<b>After the proc.</b>	<b>Chem.</b>	<b>Decontam.</b>
	<b>count C.P.S.</b>	<b>count C.P.S.</b>	<b>yield</b>	<b>factor</b>
$^{99\text{mTc}}$	471.83	216.18	55.4%	
$^{103}\text{Ru}$	215.5	0.0016		$1.35 \times 10^5$
$^{110\text{mAg}}$	13.90	$8.38 \times 10^{-5}$		$1.66 \times 10^5$

## APPENDIX 2

### Purification of the $^{99}\text{Tc}$ from electrodeposition plate

1. Put the plate (which is deposited on the  $^{99}\text{Tc}$ ) to a 25 ml beaker. Add 0.2 ml 1 N  $\text{H}_2\text{SO}_4$  to the plate. Add 1 ml 5%  $\text{NaClO}$ . The plate is covered by the solution. Stand 10 min. Add 1 ml 1 N  $\text{H}_2\text{SO}_4$ . Heat 5 min. Wash it with water.
2. Transfer the plate to another 25 ml beaker. Repeat step 1. Wash the plate three times with water. Combine these solutions.

(The following steps are required if more than several months have passed since the radioactivity was electrodeposited onto the plate. Add a few drops of concentrated  $\text{H}_2\text{SO}_4$  to the plate. Stand a few min. Add a few drops 30%  $\text{H}_2\text{O}_2$  or 5%  $\text{NaClO}$  to dissolve. Dilute the solution with water).

3. Add 0.5 ml 5 mg/ml  $\text{RuCl}_3$  carrier and 5 ml 5%  $\text{NaClO}$ . Add 1 ml  $\text{AgNO}_3$  10 mg/ml. Heat 10 min. Add  $\text{NaOH}$  to  $\text{pH}=12$ . Heat the solution to get large precipitate. Filter. Wash the precipitate with water.
4. Add 1 ml 10 mg/ml  $\text{AgNO}_3$ . Heat the solution to get large precipitate. Filter. Wash the precipitate with water.
5. Add 1 ml 5 N  $\text{NaOH}$  to basic. Add 2 ml 5%  $\text{NaClO}$ . Heat 10 min. Acidify to  $\text{pH}=4$  with  $\text{H}_2\text{SO}_4$ . Extract two times, each time with 20 ml  $\text{CCl}_4$ . Discard the  $\text{CCl}_4$ .
6. Add 1 ml 5 N  $\text{NaOH}$  and 2 ml 5%  $\text{NaClO}$ . Heat 10 min. Acidify to  $\text{pH}=4$  with  $\text{H}_2\text{SO}_4$ . Extract two times, each time with 20 ml  $\text{CCl}_4$ . Discard the  $\text{CCl}_4$ .

7. Add 0.5 ml 30% H<sub>2</sub>O<sub>2</sub>. Acidify the solution to 1 N H<sub>2</sub>SO<sub>4</sub>. Extract with 20 ml 5% TIOA/xylene. Wash with 20 ml 1 N H<sub>2</sub>SO<sub>4</sub> containing a few drops 30% H<sub>2</sub>O<sub>2</sub>. Shake 1 min.
8. Back-extract two times, each time with 20 ml 1 N NaOH. Shake 1 min.
9. Evaporate to 20 ml 2 N NaOH for electrodeposition. The current is 300 mA. The time is 3 to 5 hours.
10. The decontamination and chemical yield of the procedure are shown as follows:

Table 13.

Nucl. No.	Before procedure count C.P.S.	After procedure count C.P.S.	Chem. yield	Decontam. factor
<sup>99m</sup> Tc 1	130.69	78.62	60.2%	
<sup>99m</sup> Tc 2	89.88	55.86	62.1%	
<sup>103</sup> Ru 1	74.74	2.62 × 10 <sup>-3</sup>		2.9 × 10 <sup>4</sup>
<sup>103</sup> Ru 2	53.18	2.13 × 10 <sup>-3</sup>		2.5 × 10 <sup>4</sup>
<sup>110m</sup> Ag 1	12.29	2.29 × 10 <sup>-3</sup>		5.4 × 10 <sup>3</sup>
<sup>110m</sup> Ag 2	9.01	1.68 × 10 <sup>-3</sup>		5.4 × 10 <sup>3</sup>

11. Determination of the dissolution of <sup>99m</sup>Tc from electro-position plate. Compare the count between before and after the dissolved as follows:

No.	Before the dissolution count C.P.S.	After the dissol. count C.P.S.	Left on the plate %
1	546.40	0.617	0.11
2	256.76	0.342	0.13
3	742.53	1.428	0.19
4	470.11	1.181	0.25

<b>Title and author(s)</b> <b>DETERMINATION OF TECHNETIUM-99 IN ENVIRONMENTAL SAMPLES BY SOLVENT EXTRACTION AT CONTROLLED VALENCE</b>  Qingjiang Chen, A. Aarkrog, Helle Dick, Karen Mandrup	<b>Date</b> October 1987
	<b>Department or group</b> Health Physics
	<b>Groups own registration number(s)</b>
	<b>Project/contract no.</b>
<b>Pages</b> 31 <b>Tables</b> 13 <b>Illustrations</b> <b>References</b> 4	<b>ISBN</b> 87-550-1368-6

**Abstract (Max. 2000 char.)**

Distribution coefficients of technetium and ruthenium are determined under different conditions with  $\text{CCl}_4$ , cyclohexanone, and 5% tri-isooctylamine TIOA/xylene. A method for analyzing  $^{99}\text{Tc}$  in environmental samples has been developed by solvent extraction in which the valences of technetium and ruthenium are controlled with  $\text{H}_2\text{O}_2$  and  $\text{NaClO}$ . Technetium and ruthenium which are oxidized to  $\text{TcO}_4^-$  and  $\text{RuO}_4^-$  by  $\text{NaClO}$  are separated by extraction with  $\text{CCl}_4$  at  $\text{pH}=4$ . The  $\text{RuO}_4^-$  is reduced to low valence and technetium is kept in the  $\text{TcO}_4^-$  state with  $\text{H}_2\text{O}_2$ . Technetium, ruthenium, and other nuclides are subsequently separated by solvent extraction with cyclohexanone and 5% TIOA/xylene. The decontamination of the procedure is  $1.35 \times 10^5$  for  $^{103}\text{Ru}$  and  $1.66 \times 10^5$  for  $^{110\text{m}}\text{Ag}$ . The chemical yield of technetium-99 is 55%

**Descriptors - INIS**

CARBON TETRACHLORIDE; DECONTAMINATION; HYDROGEN PEROXIDE; OXIDATION; RUTHENIUM COMPOUNDS; RUTHENIUM 103; SEAWATER; SOLVENT EXTRACTION; TECHNETATES; TECHNETIUM 99; TOA

**Available on request from.  
Riss Library,  
Riss National Laboratory, P. O. Box 49,  
DK-4000 Roskilde, Denmark  
Phone (02) 37 12 12 ext.2262**

**ISBN 87-550-1368-6  
ISSN 0418-6435**