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Risø National Laboratory, DK-4000 Roskilde, Denmark
October 1987

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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 CCl_4, cyclohexanone, and 5% tri-isooctylamine (TIOA)/xylene. A method for analyzing ^{99}Tc in environmental samples has been developed by solvent extraction in which the valences of technetium and ruthenium are controlled with H_2O_2 and NaClO. Technetium and ruthenium which are oxidized to TcO_4^- and RuO_4^- by NaClO are separated by extraction with CCl_4 at pH=4. The RuO_4^- is reduced to low valence and technetium is kept in the TcO_4^- state with H_2O_2. Technetium, ruthenium, and other nuclides are subsequently separated by solvent extraction with cyclohexanone and 5% TIOA/xylene. The decontamination of the procedure is 1.35×10^5 for ^{103}Ru and 1.66×10^5 for ^{110m}Ag. The chemical yield of technetium-99 is 55%.

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INTRODUCTION

Technetium-99 ($T_{1/2}$ = 2.1 × 10^5 year) is the daughter product of ^{99}Mo, which is formed by fission of ^{239}Pu and ^{235}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[1] by carbon tetrachloride from aqueous solution at pH=4. S. Foti et al.[2] determined technetium in environmental samples with cyclohexanone extraction. N.W. Golchert et al.[3] determined technetium-99 in fresh water with 5% TIOA/xylene extraction for decontamination. E. Holm et al.[4] 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 $^{99m}Tc^{+4}$ by $Fe(OH)_2$-$Fe(OH)_3$ scavenging

Add 20 ml solution which contains 2 mg/ml $K_2S_2O_5$ and 0.16 mg/ml $FeSO_4 \cdot 7H_2O$. Acidify to pH=2. Add ^{99m}Tc tracer. Shake. Let stand for 30 min. Add NH_4OH to the solution until pH=9 to get $Fe(OH)_2$ precipitate. Let stand for 2 hours. Filter, γ-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}Tc, ^{103}Ru by volatilization at 100°C for different times

To the measuring tube add 20 ml solution which contains ^{99m}Tc, ^{103}Ru tracer, 2 drops ruthenium carrier, 1 ml 5% NaClO and 1 ml 20 mg/ml NaCl. γ-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}Tc by examining the electrodeposition at different times

The solution of ^{99m}Tc tracer is weighed on the disc which is covered with thin film. Add 20 ml 2 N NaOH solution to the electrodeposition cell and add ^{99m}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}Tc, ^{103}Ru for CCl_4 in 5% NaClO at pH=4

Add 0.5 ml 5 mg $RuCl_3$/ml, 1 ml 5 N NaOH, 2 ml 5% NaClO, ^{99m}Tc and ^{103}Ru tracer to beaker. Dilute to 10 ml. Heat 10 min. to allow isotopic exchange to be completed. Add 3 N H_2SO_4 one drop at a time with swirling until the greenish mixture suddenly turns yellow, indicating the formation of ruthenium tetroxide (RuO_4) from perruthenate. This will occur at pH=4. Extract with 10 ml CCl_4. Shake 10 seconds. The data are shown in table 4 (See appendix 1).

The extraction rate of RuO_4 depends on the purification of CCl_4, appropriate carrier of Ru and extraction shaking time. Because the RuO_4 is reduced by an impurity organic agent, the longer the shaking time, the more RuO_4 is reduced. The greater the impurity organic agent in the CCl_4, the more RuO_4 is reduced. The less the amount of carrier of Ru, the higher the per cent of RuO_4 that is reduced.

5. Determination of distribution coefficient of ^{99m}Tc for cyclohexanone extraction in different H_2SO_4 concentrations

Add ^{99m}Tc and 3 drops 5% NaClO to the beaker to get TcO_4^-. Dilute to 10 ml with different concentrations of H_2SO_4. Extract with 10 ml cyclohexanone. Shake 1 min. γ-count the organic and aqueous phases. The data are shown in table 5. (See appendix 1).

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

Add ^{99m}Tc tracer and a few drops 30% H_2O_2 to 5 ml solution to get 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}Tc and ^{103}Ru with 5% TIOA/xylene and cyclohexanone in 2 N H_2SO_4-$K_2S_2O_5$

Add 10 ml solution to the separation funnel which contains about 2 mg/ml $K_2S_2O_5$ and ^{99m}Tc tracer. At pH=2, let stand for 20 min. to get Tc^{+4}: Extract with 5% TIOA/xylene and cyclohexanone. $V_{org.}$: $V_{aqu.}$ = 10 : 10 ml. Shake for 1 min. γ-measure the organic and aqueous phases. The data are shown in table 7. (See appendix 1).

8. Determination of the distribution coefficient of ^{99m}Tc and ^{103}Ru in 1 N H_2SO_4-H_2O_2 with 5% TIOA/xylene and cyclohexanone

Add 1 ml 5 N NaOH, ^{99m}Tc, ^{103}Ru tracer and 2 ml 5% NaClO to the beaker. Heat for 10 min. Technetium and ruthenium are oxidized to TcO_4^-, RuO_4^-. Then add 1 ml 30% H_2O_2 to the solution. The RuO_4 is reduced to low valence. Technetium is kept in TcO_4^- state. Dilute to 10 ml. Acidify the solution to 1 N H_2SO_4. Exract 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}Tc and ^{103}Ru in 2 N H_2SO_4-5% NaClO extraction with 5% TIOA/xylene and cyclohexanone

Add 1 ml 5 N NaOH, 1 ml 5% NaClO, ^{99m}Tc, ^{103}Ru tracer and ruthenium carrier to beaker. Heat 10 min. to allow isotopic exchange to be completed. Acidify to 2 N H_2SO_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}Tc from cyclohexanone with H_2O and 0.5 N NaOH

Add 10 ml cyclohexanone into which ^{99m}Tc is extracted and 10 ml cyclohexanone to a separator funnel. Back-extract with 10 ml H_2O 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}Tc from 5% TIOA/ xylene with 2 N NaOH

Add 10 ml 5% TIOA/xylene into which the ^{99m}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 $^{99m}Tc^{+4}$ is shown in table 1 by $Fe(OH)_2$-$Fe(OH)_3$. The $Fe(OH)_2$-$Fe(OH)_3$ is dissolved in H_2SO_4. Add 5% NaClO to get TcO_4^- and RuO_4^-. Heat the solution. The RuO_4^- is volatilized and the 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 RuO_4^- and TcO_4^- with 5% NaClO. At pH=4, the RuO_4 is extracted by CCl_4. The 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 RuO_4 to a low valence state and maintenance of technetium at the TcO_4^- state with 30% H_2O_2. The 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 TcO_4^- and leaving the ruthenium in 1 N H_2SO_4 - 30% H_2O_2 by 5% TIOA/xylene extraction. Scavenging $Fe(OH)_3$ and AgCl precipitate are used for decontamination.

The procedure follows in detail:

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

1. Acidify the 50 L sea water to pH=2-2.5 with concentrated HCl.

2. Add ^{99m}Tc, ^{110m}Ag, ^{103}Ru, 1 ml 5 mg/ml ruthenium carrier to 50 L sea water.

3. Add 100 g $K_2S_2O_5$ mix. Leave for 20-30 min. to get the Tc^{+4} state.

4. Add 7.4 g $FeSO_4 \cdot 7\ H_2O$ mix. Leave for 5 min.

5. Add NH_4OH (about 140 ml concentrated NH_4OH) to the sea water till a precipitate is observed. Stand overnight. Centrifuge.

6. Dissolve the $Fe(OH)_2$ with 10 ml 10 N H_2SO_4. Heat 5 min. to dissolve $Fe(OH)_2$. Dilute to 150 ml. Add 10 ml 15% NaClO. Heat 10 min. to get TcO_4^- and RuO_4^-. Add NaOH (about 26 ml 5 N NaOH) to get $Fe(OH)_3$ pH=12. Heat the solution to a large precipitate. The RuO_4^- is volatilized. Centrifuge. Filter. Add 10 ml 10 N H_2SO_4 to dissolve the $Fe(OH)_3$. Heat for 5 min. Add 5 ml 15% NaClO. Dilute to 150 ml. Heat for 10 min. Add 26 ml 5 N NaOH to pH=12 to get $Fe(OH)_3$. Heat the solution. Centrifuge. Filter. Combine these solutions. Discard the $Fe(OH)_3$.

7. Add 2 ml 5% NaClO. Evaporate to 80 ml. Add 2 ml 5% NaClO. Heat for 10 min. Acidify to pH=4 to get a yellow colour with 3 N H_2SO_4.

8. Extract with 40 ml CCl_4 (two times). Discard the CCl_4.

9. Add 2 ml 1 N NaOH, 2 ml 5% NaClO and Ru carrier 0.5 ml 5 mg/ml $RuCl_3$. Heat for 10 min. Stir. Acidify to pH=4 with H_2SO_4. Extract two times with CCl_4. Shake for 15 seconds. The RuO_4 is extracted into CCl_4. TcO_4^- is left in an aqueous solution.

10. Acidify the aqueous solution to 1 N HCl and 1 N H_2SO_4. (80 ml). Add 1 ml 30% H_2O_2. 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_2SO_4 containing a few drops 30% H_2O_2. Discard the aqueous phase.

12. Add 80 ml cyclohexane and 30 ml H_2O. Back-extract three times, each time with 30 ml H_2O.

13. Add 1 ml 10 mg/ml $AgNO_3$. 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_2SO_4. Evaporate to 30 ml. Add 1 ml 30% H_2O_2. Heat for 10 min.

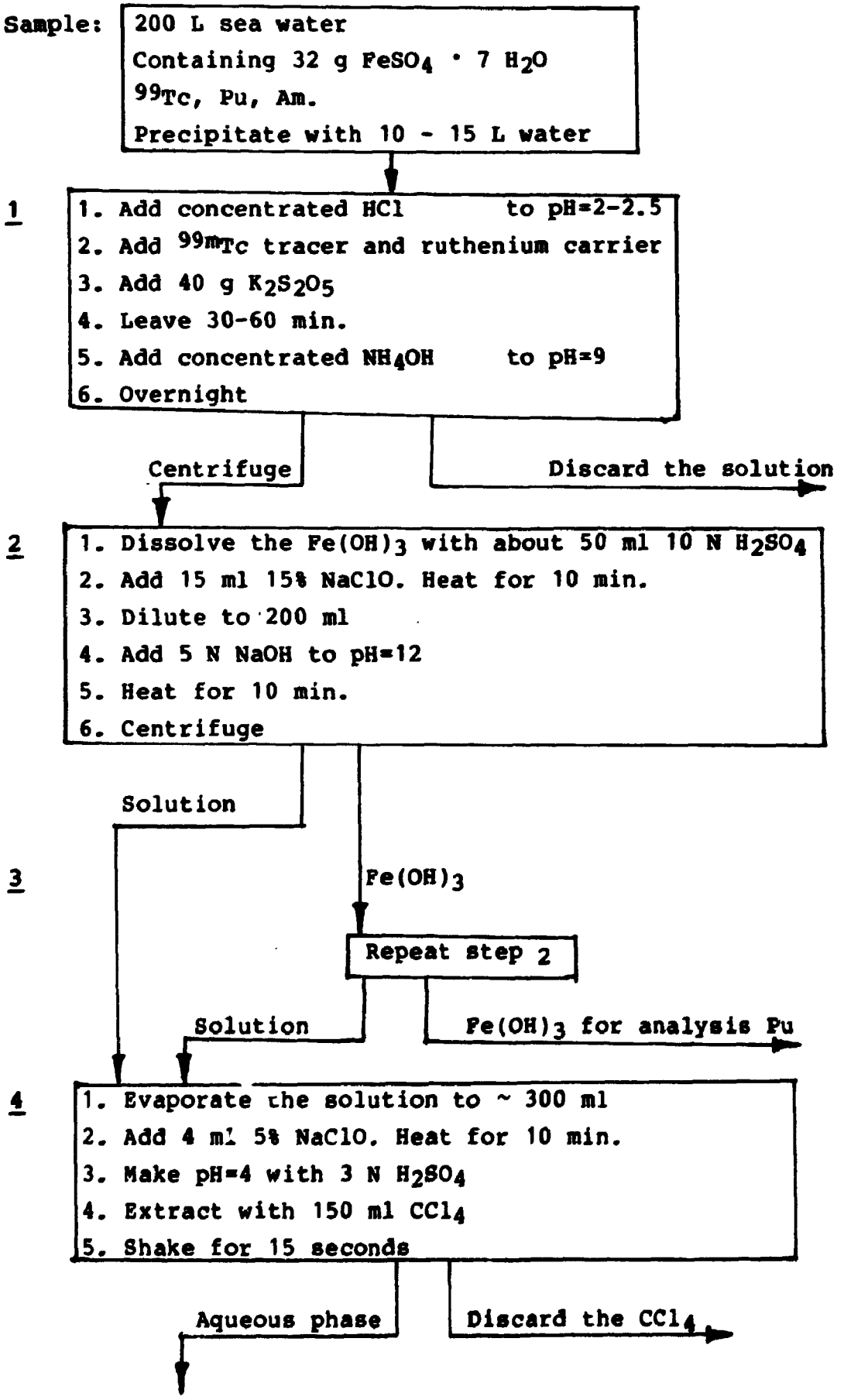
16. Extract with 25 ml 5% TIOA/xylene. Shake for 2 min. Wash with 25 ml 1 N H_2SO_4 containing a few drops 30% H_2O_2. Shake for 2 min.

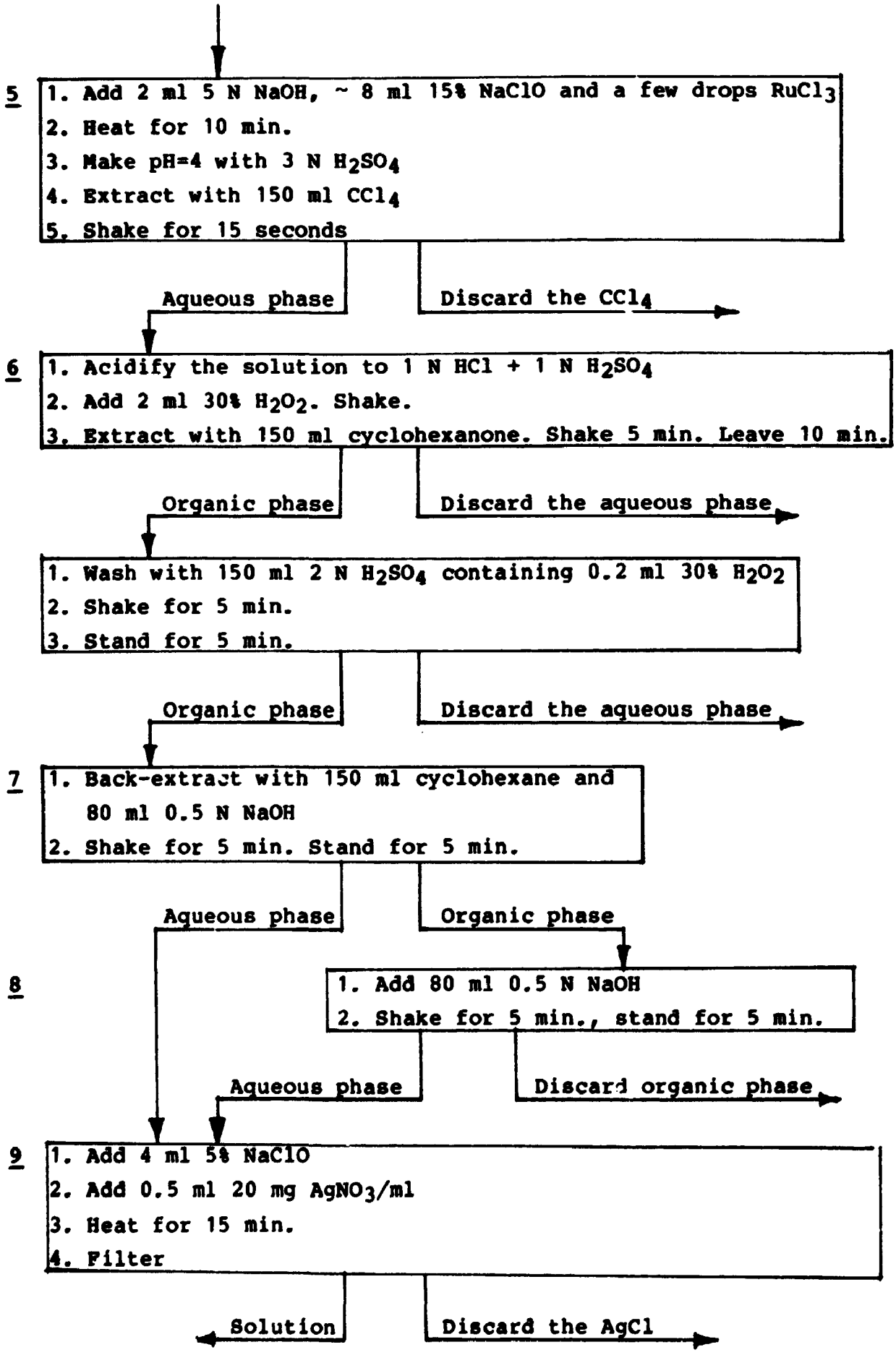
17. Back-extract two times, each time with 20 ml 1 N NaOH.

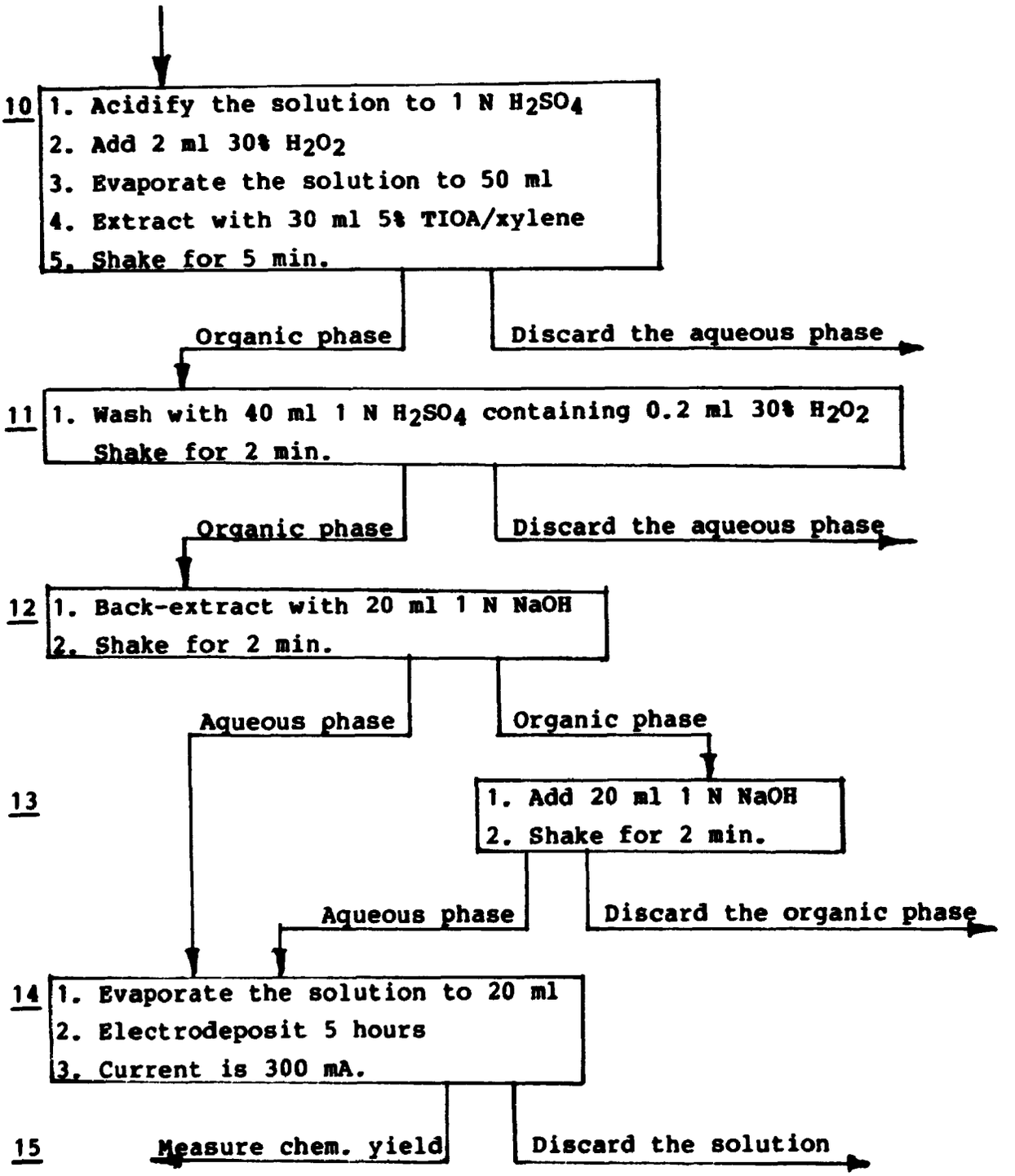
18. Evaporate to 20 ml for electrodeposition. The current is 300 mA. The time is 3 to 5 hours.

19. The results are shown in table 12.

Flow sheet


Sample:
200 L sea water
Containing 32 g $FeSO_4 \cdot 7 H_2O$
^{99}Tc, Pu, Am.
Precipitate with 10 - 15 L water
1
1. Add concentrated HCl to pH=2-2.5
2. Add ^{99m}Tc tracer and ruthenium carrier
3. Add 40 g $K_2S_2O_5$
4. Leave 30-60 min.
5. Add concentrated NH_4OH to pH=9
6. Overnight
Centrifuge
Discard the solution
2
1. Dissolve the $Fe(OH)_3$ with about 50 ml 10 N H_2SO_4
2. Add 15 ml 15% NaClO. Heat for 10 min.
3. Dilute to 200 ml
4. Add 5 N NaOH to pH=12
5. Heat for 10 min.
6. Centrifuge
Solution
3
$Fe(OH)_3$
Repeat step 2
Solution
$Fe(OH)_3$ for analysis Pu
4
1. Evaporate the solution to ~ 300 ml
2. Add 4 ml 5% NaClO. Heat for 10 min.
3. Make pH=4 with 3 N H_2SO_4
4. Extract with 150 ml CCl_4
5. Shake for 15 seconds
Aqueous phase
Discard the CCl_4


5
1. Add 2 ml 5 N NaOH, ~ 8 ml 15% NaClO and a few drops $RuCl_3$
2. Heat for 10 min.
3. Make pH=4 with 3 N H_2SO_4
4. Extract with 150 ml CCl_4
5. Shake for 15 seconds
Aqueous phase
Discard the CCl_4
6
1. Acidify the solution to 1 N HCl + 1 N H_2SO_4
2. Add 2 ml 30% H_2O_2. Shake.
3. Extract with 150 ml cyclohexanone. Shake 5 min. Leave 10 min.
Organic phase
Discard the aqueous phase
1. Wash with 150 ml 2 N H_2SO_4 containing 0.2 ml 30% H_2O_2
2. Shake for 5 min.
3. Stand for 5 min.
Organic phase
Discard the aqueous phase
7
1. Back-extract with 150 ml cyclohexane and 80 ml 0.5 N NaOH
2. Shake for 5 min. Stand for 5 min.
Aqueous phase
Organic phase
8
1. Add 80 ml 0.5 N NaOH
2. Shake for 5 min., stand for 5 min.
Aqueous phase
Discard organic phase
9
1. Add 4 ml 5% NaClO
2. Add 0.5 ml 20 mg $AgNO_3$/ml
3. Heat for 15 min.
4. Filter
Solution
Discard the AgCl


10
1. Acidify the solution to 1 N H_2SO_4
2. Add 2 ml 30% H_2O_2
3. Evaporate the solution to 50 ml
4. Extract with 30 ml 5% TIOA/xylene
5. Shake for 5 min.
Organic phase
Discard the aqueous phase
11
1. Wash with 40 ml 1 N H_2SO_4 containing 0.2 ml 30% H_2O_2
Shake for 2 min.
Organic phase
Discard the aqueous phase
12
1. Back-extract with 20 ml 1 N NaOH
2. Shake for 2 min.
Aqueous phase
Organic phase
13
1. Add 20 ml 1 N NaOH
2. Shake for 2 min.
Aqueous phase
Discard the organic phase
14
1. Evaporate the solution to 20 ml
2. Electrodeposit 5 hours
3. Current is 300 mA.
15
Measure chem. yield
Discard the solution

RESULTS AND DISCUSSION

The volatilization rates of RuO_4^- and TcO_4^- are determined by 100°C in 1 N H_2SO_4- NaClO solution; 99% of RuO_4^- is volatilized in 30 minutes, while TcO_4^- is left in the solution. No volatilisation of TcO_4^- was found by heating for 4 hours at 100°C.

The method of 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 RuO_4 and TcO_4^- are shown in table 4. The RuO_4 is extracted by CCl_4 at pH=4 in NaClO solution, and the TcO_4^- is left in solution. The distribution coefficient of ^{99m}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 H_2SO_4 to 4 N H_2SO_4.

In the solution containing the reducing agent

In the $K_2S_2O_5$-HCl solution at pH=2, technetium is reduced to Tc^{+4}, and ruthenium to a low valence state. Acidify to 2 N H_2SO_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 RuO_4^- and TcO_4^- in a strong oxidizing agent. The extraction rate of ^{99m}Tc and ^{103}Ru are obtained in 2 N H_2SO_4-NaClO with cyclohexanone, 5% TIOA/xylene, as shown table 9. If technetium and ruthenium are held in a TcO_4^-/RuO_4^- state, the technetium and ruthenium cannot be separated by extraction with cyclohexanone and 5% TIOA/xylene in 2 N H_2SO_4-NaClO.

In solution containing gentle oxidizing agent H_2O_2

The technetium is oxidized to TcO_4^-, 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_2SO_4- H_2O_2.

The different valence states of technetium and ruthenium are controlled with H_2O_2 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_2SO_4-NaClO	110
CCl_4 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 3.5×10^9. But the large volume sea water is more complicated, as it contains many elements. Add the low count of ^{103}Ru for the decontamination test, so that the decontamination of the procedure is only 1.35×10^5 for ^{103}Ru and 1.66×10^5 for ^{110m}Ag.

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

Step	Loss rate of ^{99m}Tc %
Loss in $Fe(OH)_2$ carried	~5
CCl_4 extraction	~5
$Fe(OH)_3$ 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 H_2SO_4-NaClO at 100°C.

2. Ruthenium and technetium can be separated to permit the extraction of RuO_4, and the TcO_4^- is kept in solution at pH=4 containing NaClO with CCl_4.

3. Both the RuO_4^- and TcO_4^- are extracted by cyclohexanone and 5% TIOA/xylene in 1 N H_2SO_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 TcO_4^- state at a controlled valence with H_2O_2. This permits separation of the ruthenium and technetium.

5. $Fe(OH)_3$ scavenging, extraction of cyclohexanone and 5% TIOA/xylene are used for decontamination of ruthenium and other nuclides. The 1.35×10^5 of ruthenium-103 and 1.66×10^5 ^{110m}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%.

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APPENDIX 1

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

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}Tc, ^{103}Ru by volatilization for different times at 100°

Composition of solution	No.	Nuclides	Time (min.)	5	10	20	30	60	90	120	240
1 ml H_2SO_4, 1 ml	1	^{99m}Tc	Loss %	-	0.6	2.6	1.8		7.1		
5% NaClO, 1 ml		^{103}Ru		72	90.2	95.5	99.2		99.4		
20 mg/ml NaCl	2	^{99m}Tc		2.9	4.9	3.6	3.1		4.6		
2 drops Ru carrier,		^{103}Ru		59.6	89.1	95.5	99.1		99.4		
7 ml H_2O											
1 N H_2SO_4	1	^{99m}Tc						0		2.5	0
(10 ml)	2	^{99m}Tc						0		2.3	0
10 ml 1 N H_2SO_4	1	^{99m}Tc						0		2.1	0
2 mg/ml NaCl	2	^{99m}Tc						0		1.0	0
10 ml 1N H_2SO_4	1	^{99m}Tc						0		0	0
2 mg/ml NaCl	2	^{99m}Tc						0		0	0
0.5% NaClO											

Table 3. Chemical yield of ^{99m}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}Tc, ^{103}Ru with CCl_4 from NaClO solution at pH=4

Nuclides	No.	Org.phase C.P.S.	Aqu.phase C.P.S.	Distribution coefficient	Extraction rate %
^{99m}Tc	1	2.79	825.3	3.4×10^{-3}	0.34
^{99m}Tc	2	0.69	876.1	7.9×10^{-4}	0.08
^{103}Ru	1	245.2	3.35	73.3	98.7
^{103}Ru	2	364.0	5.42	67.2	98.5
^{103}Ru	3	167.2	2.06	81.3	98.8
^{103}Ru	4	169.7	1.54	110.4	99.1
				83.0 ± 19 (average)	

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

Concentration of H_2SO_4	Org.phase C.P.S.	Aqu.phase C.P.S.	Distribution coefficient	Extraction rate %
0.2 N H_2SO_4	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}Tc dependence on sulphuric acid in 5% TIOA/xylene

Concentration of H_2SO_4	Org.phase C.P.S.	Aqu.phase C.P.S.	Distribution coefficient	Extraction rate %
0.2 N H_2SO_4	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}Tc and ^{103}Ru for 2 N H_2SO_4-$K_2S_2O_5$ 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 H_2SO_4 - $K_2S_2O_5$					
^{99m}Tc	1	2018.9	192.5	10.5	91.3
^{99m}Tc	2	1883.8	152.6	12.3	92.5
^{103}Ru	1	2.62	388.75	6.7×10^{-3}	0.67
^{103}Ru	2	1.82	280.55	6.5×10^{-3}	0.64
b) Cyclohexanone - 2 N H_2SO_4 - $K_2S_2O_5$					
^{99m}Tc	1	1119.35	138.27	8.1	89.0
^{99m}Tc	2	1225.28	127.70	9.6	90.6
^{103}Ru	1	8.197	319.45	2.6×10^{-2}	2.5
^{103}Ru	2	8.347	293.89	2.8×10^{-2}	2.76

Table 8. Distribution coefficient of ^{99m}Tc, ^{103}Ru for 1 N H_2SO_4 -H_2O_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 - H_2O_2 - 1 N H_2SO_4					
^{99m}Tc	1	5024.91	16.44	305.7	99.7
^{99m}Tc	2	4666.31	11.87	393.7	99.7
^{103}Ru	1	0.147	288.87	5.0×10^{-4}	0.05
^{103}Ru	2	2.762	442.36	6.2×10^{-3}	0.62
^{103}Ru	3	1.327	320.25	4.1×10^{-3}	0.41
^{103}Ru	4	2.027	327.65	6.2×10^{-3}	0.62
b) 5% TIOA/xylene - 1 N H_2SO_4 - H_2O_2					
^{99m}Tc	1	2500	0.94	2659	99.96
^{99m}Tc	2	3288.7	1.33	2472.7	99.96
^{103}Ru	1	0.547	315.37	1.73×10^{-3}	0.17
^{103}Ru	2	0.962	142.80	6.74×10^{-3}	0.67
^{103}Ru	3	0.987	308.80	3.2×10^{-3}	0.32

Table 9. Distribution ccefficient of ^{99m}Tc and ^{103}Ru for 2 N H_2SO_4 - 5% 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 H_2SO_4 - 5% NaClO					
^{99m}Tc	1	5411.12	50.13	107.9	99.08
^{99m}Tc	2	381.84	6.06	63	98.49
^{99m}Tc	3	441.08	1.09	404	99.80
^{99m}Tc	4	3271.95	65.65	49.8	98.0
^{103}Ru	1	236.63	10.30	22.98	95.82
^{103}Ru	2	260.45	7.25	35.9	97.3
b) 5% TIOA/xylene - 2 N H_2SO_4 - 5% NaClO					
^{99m}Tc	1	3996.46	40.18	99.5	99.0
^{99m}Tc	2	3769.63	43.92	85.8	98.8
^{103}Ru	1	240.12	79.09	3.04	75.2
^{103}Ru	2	232.69	79.11	2.94	74.6
^{103}Ru	3	247.16	81.55	3.03	75.2

Table 10. Determination of back-extraction rate ^{99m}Tc from cyclohexanone with H_2O 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}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}Ru, ^{110m}Ag and chemical yield of ^{99m}Tc of the procedure

Nucl.	Before the procedure count C.P.S.	After the proc. count C.P.S.	Chem. yield	Decontam. factor
^{99m}Tc	471.83	216.18	55.4%	
^{103}Ru	215.5	0.0016		1.35×10^5
^{110m}Ag	13.90	8.38×10^{-5}		1.66×10^5

APPENDIX 2

Purification of the ^{99}Tc from electrodeposition plate

1. Put the plate (which is deposited on the ^{99}Tc) to a 25 ml beaker. Add 0.2 ml 1 N H_2SO_4 to the plate. Add 1 ml 5% NaClO. The plate is covered by the solution. Stand 10 min. Add 1 ml 1 N H_2SO_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 H_2SO_4 to the plate. Stand a few min. Add a few drops 30% H_2O_2 or 5% NaClO to dissolve. Dilute the solution with water).

3. Add 0.5 ml 5 mg/ml $RuCl_3$ carrier and 5 ml 5% NaClO. Add 1 ml $AgNO_3$ 10 mg/ml. Heat 10 min. Add NaOH to pH=12. Heat the solution to get large precipitate. Filter. Wash the precipitate with water.

4. Add 1 ml 10 mg/ml $AgNO_3$. Heat the solution to get large precipitate. Filter. Wash the precipitate with water.

5. Add 1 ml 5 N NaOH to basic. Add 2 ml 5% NaClO. Heat 10 min. Acidify to pH=4 with H_2SO_4. Extract two times, each time with 20 ml CCl_4. Discard the CCl_4.

6. Add 1 ml 5 N NaOH and 2 ml 5% NaClO. Heat 10 min. Acidify to pH=4 with H_2SO_4. Extract two times, each time with 20 ml CCl_4. Discard the CCl_4.

7. Add 0.5 ml 30% H_2O_2. Acidify the solution to 1 N H_2SO_4. Extract with 20 ml 5% TIOA/xylene. Wash with 20 ml 1 N H_2SO_4 containing af few drops 30% H_2O_2. 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
^{99m}Tc	1	130.69	78.62	60.2%	
^{99m}Tc	2	89.88	55.86	62.1%	
^{103}Ru	1	74.74	2.62×10^{-3}		2.9×10^4
^{103}Ru	2	53.18	2.13×10^{-3}		2.5×10^4
^{110m}Ag	1	12.29	2.29×10^{-3}		5.4×10^3
^{110m}Ag	2	9.01	1.68×10^{-3}		5.4×10^3

11. Determination of the dissolution of ^{99m}Tc from electroposition 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

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Title and author(s)

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

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Abstract (Max. 2000 char.)

Distribution coefficients of technetium and ruthenium are determined under different conditions with CCl_4, cyclohexanone, and 5% tri-iso-octylamine TIOA/xylene. A method for analyzing ^{99}Tc in environmental samples has been developed by solvent extraction in which the valences of technetium and ruthenium are controlled with H_2O_2 and NaClO. Technetium and ruthenium which are oxidized to TcO_4^- and RuO_4^- by NaClO are separated by extraction with CCl_4 at pH=4. The RuO_4^- is reduced to low valence and technetium is kept in the TcO_4^- state with H_2O_2. Technetium, ruthenium, and other nuclides are subsequently separated by solvent extraction with cyclohexanone and 5% TIOA/xylene. The decontamination of the procedure is 1.35×10^5 for ^{103}Ru and 1.66×10^5 for ^{110m}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

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