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END OF SYMPOSIUM

Thiocyanate Spectrophotometric Determination of Technetium

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▶ Technetium(VII), when carefully reduced in the presence of thiocyanate in an acid medium, forms a red complex with a maximum absorbance at 513 mμ and a molar absorbance index of 52,200 ± 500 at the maximum. A yellow thiocyanate complex also forms with a lower valence state of technetium. The maximum molar absorbance index of the yellow complex was approximately one half that of the red species.

RECENT literature (*4, 7, 10, 12*) has revealed the unusual complexity of the chemistry of rhenium in solution. Far less has been published on the chemistry of technetium in solution, but all indications are that its behavior is similar to that of rhenium.

Thiocyanate was first applied to rhenium analysis by Geilmann, Wrigge, and Weibke (*3*). Melaven and Whetsel (*8*), Malouf and White (*6*), Beeston and Lewis (*1*), and Hoffman and Lundell (*5*) also studied this method. Tribalat (*10*) first noted evidence for the mixed valent character of the orange-thiocyanate complex which is usually used for analytical work. The existence of two thiocyanate complexes, a yellow rhenium(V) complex, and a mixed-valent orange rhenium(IV,V) complex, was indicated by the spectrophotometric data. Literature on technetium-thiocyanate complexes appears to be nonexistent, except for brief statements (*11*) that technetium behaves like rhenium in its reactions with thiocyanate. Technetium-99 is produced as a fission product at approximately peak yield in present-day reactor fuels. The irradiation of natural molybdenum—23.8% molybdenum-98—will yield significant quantities of technetium-99 by a (n, γ) reaction. The unfavorable counting characteristics of the low-energy beta activity of technetium-99 also create added interest in other sensitive analytical methods. The reduction of technetium(VII) in the presence of thiocyanate ions produced several intensely colored complexes. The maximum molar absorbance index of the most intensely colored complex of technetium was 52,200 ± 500 at 513 mμ in an ether solution. The maximum molar absorbance index of the most intensely colored thiocyanate complex of rhenium was 45,300 ± 500 at 430 mμ. No colored complex ion formation was observed for manganese(VII) when reduced in a thiocyanate medium.

REAGENTS

Preparation and handling of the thiocyanate-acetone medium have been discussed (*2*).

Rhenium oxide, obtained from A. D. Mackay, Inc., was found by the emission spectrograph to contain less than a total of 0.2% of 26 metal components analyzed and was estimated to be better than 99.5%. Stock solutions were prepared by dissolving weighed quantities of pure, dried potassium perrhenate crystals, prepared by titrating rhenium oxide dissolved in distilled water with a stoichiometric quantity of potassium hydroxide. The white crystals were washed twice with absolute methanol and dried in a vacuum desiccator at 100° C. for several hours.

A potassium pertechnetate–aqueous solution was obtained from the Oak Ridge National Laboratory. To part of the solution was added cesium chloride, and the resulting white crystalline cesium pertechnetate was filtered on a fine sintered-glass disk and washed with absolute methanol. The precipitate was dried at 105° C. and weighed. This precipitate was completely soluble in 25 ml. of distilled water (checked by reweighing the dried sintered-glass disk), to give a standard solution of cesium pertechnetate with a concentration of 2.68×10^{-3} mole per liter. The concentration of the original potassium pertechnetate solution checked with no detectable bias when analyzed with the thiocyanate-spectrophotometric procedure.

APPARATUS

Beckman Model DU spectrophotometer and a Cary Model 11 recording spectrophotometer were both used. One-centimeter quartz cells were used throughout.

A Beckman Model G potentiometer was employed in the potentiometric titrations.

TECHNETIUM STANDARD PROCEDURE

Technetium(V) Thiocyanate Complex. The following procedure is based on a final volume of 10 ml. Adjust the technetium(VII) to 3.5 to 4.0-*M* sulfuric acid solution. Hydrochloric, nitric, and other volatile acids may be volatilized below approximately 100° C. without loss of technetium(VII). Limit the volume of the reduction medium to 4.0 ml. and the volume of concentrated sulfuric acid to less than 1 ml. to prevent possible phase separation of the final acetone solution.

The reduction is accomplished by the thiocyanate ion. Add 0.5 ml. of 4.0*M* aqueous ammonium thiocyanate to the 3.5 to 4.0*M* sulfuric acid solution of technetium(VII). This is enough thiocyanate for both complete reduction and complex formation. Allow the reduction to proceed for 30 to 45 seconds after addition of the thiocyanate. A bright red color can be observed easily with a technetium(VII) concentration of 0.1 γ per ml. Add 6 ml. of acetone, mix, and adjust the volume of the solution to 10 ml. with distilled water.

At this point, the color has generally developed to less than 50% of the final intensity. Fill quartz 1-cm. glass-stoppered cells with the technetium solution and place in a 20° C. water-cooled spectrophotometer. The absorbance will approach a maximum intensity in 1 to 3 hours. The maximum absorbance occurred at 510 mμ with a molar absorbance index and standard deviation of 47,500 ± 500 in the 60 volume % acetone-aqueous medium.

An additional check on the analysis may be obtained after complete color development in 60 volume % acetone by extracting the red thiocyanate complex with 5 ml. of ether. The resulting medium is a mixed acetone-ether medium in which the molar absorbance index and standard deviation is 52,200 ± 500 at the 513-mμ maximum. Acetone solutions of technetium in which only 80% of the color is developed gave correct absorbance values when extracted with ether. The correct absorbance is that obtained by extracting samples at the time of maximum color development in acetone-thiocyanate medium. Two extractions with ether are made, and any tendency toward the formation of hazy water-organic emulsions is removed by the addition of small volumes of acetone.

In analyzing for technetium, the solutions are scanned from 350 to 675 mμ. The width of the 510-mμ absorbance peak at half maximum is noted. This serves as an additional check on the presence of any interfering absorbance. In 60 volume % acetone-aqueous medium, the width at half maximum is 82 mμ, and in the mixed ether-acetone medium, it is approximately the same. The resolution is not sensitive to the ether-acetone ratio of the medium.

DISCUSSION

In 3 to 5*M* sulfuric or hydrochloric acid medium, thiocyanate reduces technetium(VII) to a red technetium(V)-thiocyanate complex, and to some extent, a yellow technetium(IV)-thiocyanate complex. Rhenium(VII) was also reduced to the yellow rhenium(V)-thiocyanate complex by the thiocyanate ion, but the rate of reduction was much slower in 3 to 5*M* acid solutions, requiring over 24 hours to go to completion. Manganese(VII) is reduced very rapidly by thiocyanate in acid solution to manganese(II) with no visible intermediate color formation.

The rate of formation of the thiocyanate complex species from rhenium(VII) was investigated. The addition of between 2 and 2.5 equivalents of stannous chloride to rhenium(VII) in 4*M* hydrochloric acid, and dilute thiocyanate under an inert atmosphere, gave at equilibrium a family of curves at various times similar to those in Figure 1. These stoichiometric reactions required 2 to 3 hours to reach equilibrium and were stable for more than 10 hours. The curves shown in Figure 1 were obtained by reduction of rhenium(VII) in aqueous medium with a 25-fold excess of stannous sulfate and reached equilibrium in shorter time. The times indicated on the curves in Figure 1 were measured from the addition of tin(II) sulfate to the time of addition of the acetone to adjust the medium to 60 volume % acetone. The effect of adding acetone was to stop the reduction beyond rhenium(V) and thus the formation of the mixed valent complex. The formation of the rhenium(V)-thiocyanate complex was quantitative and rapid, when the reduction with tin(II) sulfate was done in the 60 volume % acetone medium.

Figure 2 shows the rate of reduction of technetium(VII) with thiocyanate by the standard procedure. The reduction of technetium(VII) was also attempted in the presence of rhenium(VII) at over ten times the technetium concentration. The relatively small absorbance due to technetium(V) complex at 360 mμ was subtracted from the total to obtain the absorbance of rhenium(V) complex plotted in Figure 2. There was no interfering rhenium-thiocyanate absorbance at the 510-mμ technetium(V) peak. Technetium(VII) in the presence of rhenium was

95% reduced to the pentavalent complex in 3 hours. Rhenium(VII) was approximately 5% reduced to the pentavalent complex in the same time. The technetium, however, reached only 95% of the known maximum absorbance for a pure standard, and showed greater instability in the presence of rhenium.

Molybdenum(VI) was also slowly reduced to the five valence state with the technetium, to produce the characteristic molybdenum(V)-thiocyanate complex with an absorbance maximum at 460 mμ. This interferes with the 510-mμ technetium(V)-thiocyanate absorbance peak. At the end of 3 hours, known to be required for technetium(VII) to develop the correct absorbance alone, the mixed solution of molybdenum and technetium, Mo/Tc molar ratio of 4, is only 3% as high. At this point, the 510-mμ technetium peak showed only a slight dissymmetry due to the 460-mμ molybdenum peak. The known molar absorptance indices of both molybdenum(V) and technetium(V) at 460 mμ and 510 mμ, show that both elements were quantitatively reduced to the five valence state in 30 hours.

The nonaqueous medium favors the formation of the red species. Ether extraction of the yellow aqueous complex transfers a part of the technetium as the red species into the ether solution. However, these extractions of the yellow complex generally fail to transfer the technetium quantitatively into the organic phase in one equilibration. The yellow species showed little or no solubility in a wide variety of organic solvents, while the red complex is very soluble in a variety of alcohols, ethers, and ketones. The red species was associated with pentavalent technetium. The yellow species has been associated with quadrivalent technetium.

Micropotentiometric titrations of technetium(VII) were made with a calibrated microburet of 115-μl. total capacity. Standard solutions of titanium(III) and tin(II) were prepared by titration with a gravimetric iron(III) standard. Oxygen-free carbon dioxide was used to blanket the standard solutions in the storage and titration vessels. Potentiometric titrations of the gravimetrically standardized technetium(VII) solution with standard titanium(III) in $12M$ sulfuric acid gave a typical curve shown in Figure 3. Two hundred microliters of $2.68 \times 10^{-3}M$ cesium pertechnetate was introduced into a titration vessel containing 4.0 ml. of $12M$ sulfuric acid under a carbon dioxide blanket.

The initial potential reading of the platinum and calomel electrodes was always very low, starting at approximately 250 mv. and rising in about 60 minutes to a stable value. Addition of very slight amounts of titanium(III) solution did not hasten the process. When the titration with standard titanium(III) sulfate was begun, a rapid rise in potential occurred with each addition of titanium(III) sulfate, followed by a fairly rapid drop. This is shown in Figure 3 by the shaded area between the maximum and minimum values observed. The values dropped from the maximum to stable values in 3 to 4 minutes, the solid curve giving the final equilibrium values obtained. Equation 1 represents the probable initial reaction:

$$2\,\text{Tc(VII)} \rightarrow 2\,\text{Tc(VI)} \begin{array}{l} \nearrow \text{Tc(V)} \\ \searrow \text{Tc(VII)} \end{array} \qquad (1)$$

Unlike rhenium(V), in strong sulfuric or hydrochloric acids (greater than

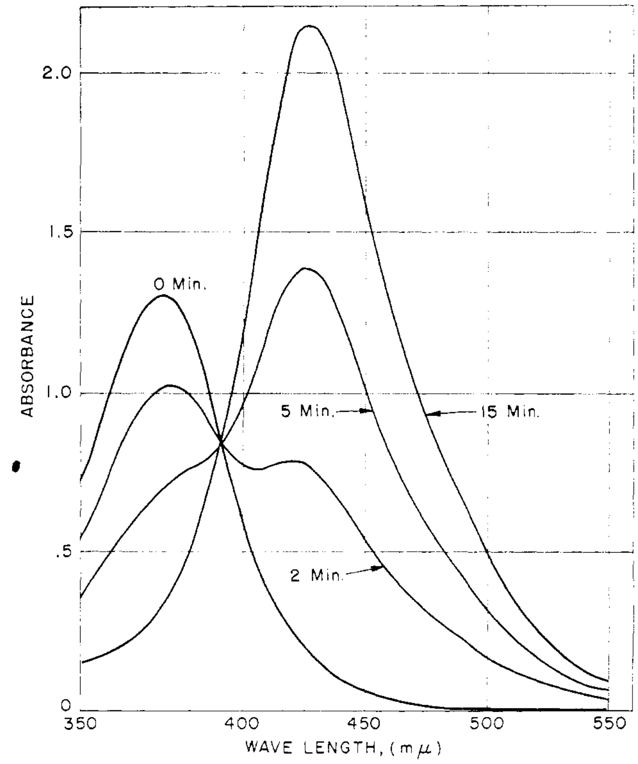

Figure 1. Time of reduction of $5.25 \times 10^{-5}M$ rhenium solutions in $3M$ sulfuric acid medium, with stannous sulfate and ammonium thiocyanate

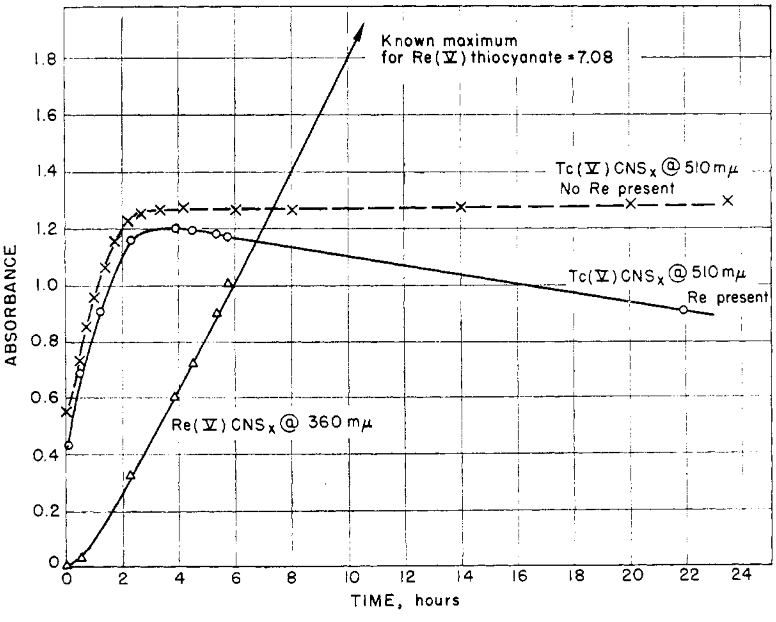

Figure 2. Reduction of technetium(VII), 2.68×10^{-5} mole per liter, with rhenium(VII), 2.84×10^{-5} mole per liter, in thiocyanate

4.0M) the technetium(V) apparently disproportionates at a measurable rate. If the titration is carried out rapidly to the calculated technetium(V) stoichiometric end point, a break will occur, as shown in Figure 3. If the titration is continued as rapidly as possible, a second potential break will occur at the calculated technetium(IV) stoichiometric end point, and the potentials will then be stable. In experiments where the titration was stopped after the technetium(V) stoichiometric end point, approximately 1 hour was required for the low potential values to reach a maximum. Equation 2 apparently represents the reaction taking place:

$$3\ \mathrm{Tc(V)} \rightarrow 2\ \mathrm{Tc(VII)} + \mathrm{Tc(IV)} \quad (2)$$

Subsequent additions of aliquots of titanium(III) always produced an immediate drop in potential. Apparently technetium(IV) reacts rapidly with technetium(VI) to produce technetium(V). However, technetium(VII) does not appear to react with technetium(IV). Stable potential readings with technetium could not be obtained in 2M sulfuric acid saturated with ammonium sulfate. However, an interesting color phenomenon was noted in these solutions when they were titrated with standard titanium(III). At the calculated stoichiometric technetium(V) end point, a distinct red color was noted in the solutions. The red absorbance maximum is at 500 mμ, compared to 510 mμ for the thiocyanate complex. A similar result was obtained for 2M hydrochloric acid saturated with ammonium chloride. No red complex was visible in 10 to 12M sulfuric or hydrochloric acid medium. The red color changed to yellow as the titration was continued to form technetium(IV).

The thiocyanate failed to develop the red complex quantitatively on solutions reduced below the pentavalent state. Solutions reduced to average valencies higher than 5 developed the known maximum absorbance at 510 mμ more slowly in thiocyanate solutions. The absorbance of a red complex species was at a maximum value with the addition of two equivalents of reducing agent in hydrochloric acid–ammonium chloride, sulfuric acid–ammonium sulfate, and dilute acid-thiocyanate solutions. The data in the latter solutions were complicated by the fact that thiocyanate reduced technetium(VII) slowly in dilute acid, and more rapidly in approximately 3 to 4M strong acid solutions.

Figure 4 shows the slow development of the red technetium(V)-thiocyanate complex obtained by adding the acetone immediately after the thiocyanate and with a relatively low thiocyanate concentration. The shape of the initial absorbance curves indicates the formation of the red species is preceded by unstable intermediate-complex species formation. The initial color of the solutions is orange, and this gradually becomes bright red. All attempts to develop the intermediate orange species in preference to the red were unsuccessful.

The molar absorbance index of the yellow technetium(IV)-thiocyanate complex is approximately half that of the red species. The yellow species is relatively sensitive to the acidity of the solution, and shows a sharp decrease in absorbance at lower acidities. Both manganese(IV) and rhenium(IV) show a marked tendency toward colloidal formation.

The thiocyanate complexes of technetium appear to be inert (*9*). The red complex was diluted by a factor of 1 to 50, with a solution of 60 volume % acetone and 40 volume % water. Thiocyanate concentration varied from 0.18M to 0.0036M, with no measurable bleaching of the red color. Attempted oxidation of the red solutions with excess bromine and cerium(IV) sulfate at room temperature in 3 to 6M sulfuric acid medium occurred only very slowly. Ether solutions of the red technetium(V)-thiocyanate complex were equilibrated with distilled water several times to remove excess thiocyanate and acid. No back extraction or bleaching of the technetium color was observed. Equilibration of the ether solutions with 4M sulfuric

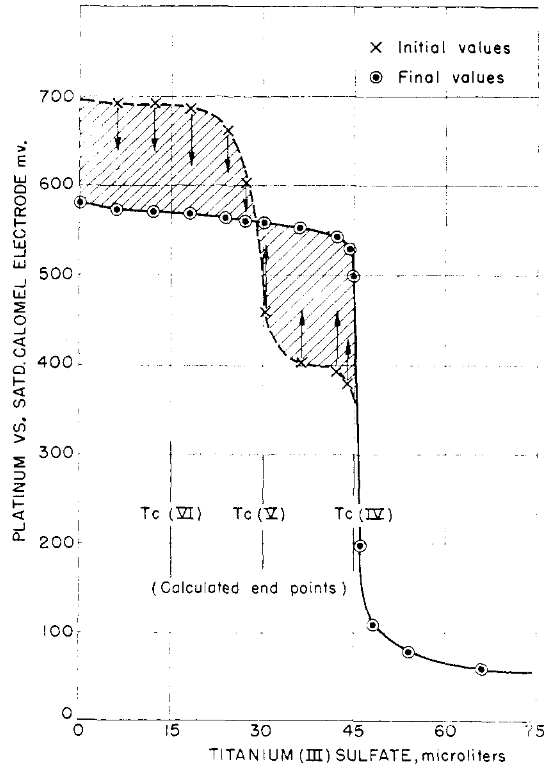

Figure 3. Potentiometric titration of technetium(VII) with titanium(III) in 12M sulfuric acid

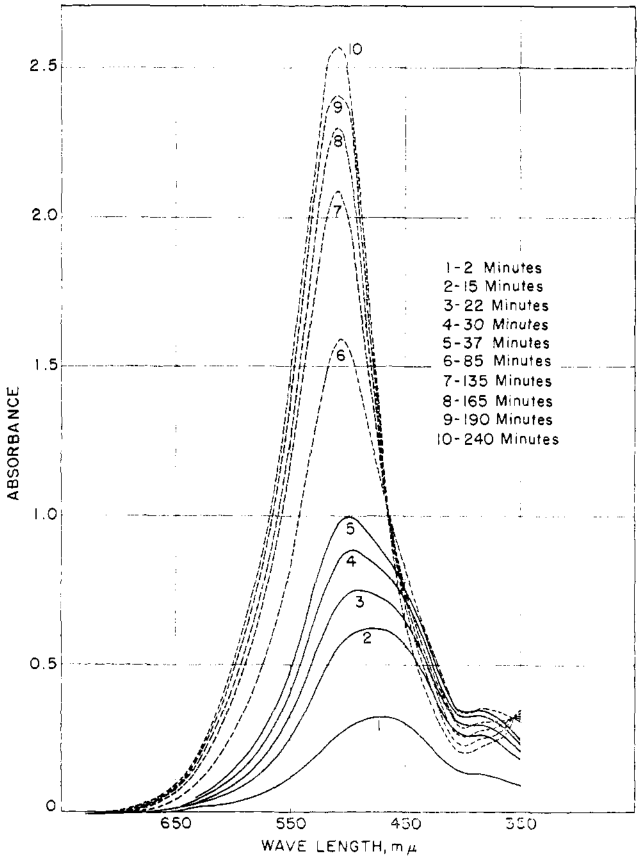

Figure 4. Development of technetium(V)-thiocyanate complex, 5.36 × $10^{-5}M$

acid saturated with cerium(IV) sulfate did not result in appreciable bleaching or back extraction of the red complex. The red complex is rather easily reduced with excess tin(II) sulfate. The yellow complex also shows no bleaching of the color on dilution by 60 volume % acetone-aqueous solution.

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Precision of the Pyrohydrolytic Determination of Fluoride and Uranium in Uranyl Fluoride and Uranium Tetrafluoride

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▶ Although much has been published on use of the pyrohydrolysis technique, to date no study demonstrates the accuracy and precision obtainable by this method in the determination of fluoride. The pyrohydrolysis of uranyl fluoride and uranium tetrafluoride was studied and the results were analyzed statistically. The maximum limits of error, at the 95% confidence level, for the fluoride and uranium were ±0.44 and ±0.17%, respectively.

Table I. Pyrohydrolysis of Uranyl Fluoride

Sample No.	No. of Detns.	%F[a]	Av. Dev., %	%U[b]	Av. Dev., %	F/U[c]
1	3	12.23	0.2	77.27	0.03	1.995
2	3	12.26	0.2	77.00	0.11	1.996
3	3	12.27	0.2	77.03	0.05	1.996
4	3	12.31	0.1	76.93	0.09	2.004
5	3	12.24	0.1	76.94	0.03	1.993
6	9	12.27	0.2	77.02	0.10	1.997
7	3	12.28	0.3	77.03	0.11	1.998
8	3	12.30	0.1	77.06	0.03	2.001
9	3	12.29	0.1	77.07	0.01	1.999
10	3	12.30	0.1	77.05	0.03	2.001
11	3	12.31	0.1	77.03	0.03	2.002
12	3	12.30	0.1	77.08	0.01	2.000
13	3	12.31	0.1	77.12	0.02	2.000
14	3	12.32	0.2	77.15	0.02	2.001
15	3	12.32	0.1	77.18	0.03	2.000
16	3	12.32	0.1	77.15	0.01	2.002
17	3	12.32	0.1	77.17	0.02	2.001
18	3	12.33	0.3	77.24	0.02	2.000
	Av.	12.29	0.15	77.08	0.04	2.000

[a] Theoretical value 12.33%.
[b] Theoretical value 77.27%.
[c] Theoretical value 2.000.

A CONCISE REVIEW of early pyrohydrolytic experiments and later industrial and quantitative applications has been published by Warf, Cline, and Tevebaugh (*5*). These authors divided the fluorides into rapidly and slowly hydrolyzable salts. Those rapidly hydrolyzed are: aluminum, bismuth, cerium, dysprosium, gadolinium, lanthanum, neodymium, samarium, and thorium fluorides, uranium tetrafluoride, uranyl fluoride, vanadium trifluoride, magnesium fluoride, zinc fluoride, and zirconyl fluoride. Fluorides of the alkali and alkaline earth metals (except magnesium) are only slowly hydrolyzed.

The technique is valuable for some fluoride determinations, particularly to workers in the field of atomic energy (*3–5*), but is rarely used by workers in the industrial field, perhaps because of lack of knowledge of the reliability of the results that may be obtained. Because no comprehensive study to date has demonstrated the accuracy and precision obtainable by this method, the following data are presented and critically analyzed. The data have been taken from the original project literature (*2*).

The pyrohydrolysis method consists essentially of passing superheated steam over the metallic halide (usually between 400° and 1000° C.), and condensing and titrating the volatile acid. Although pyrohydrolysis is usually performed in a platinum reaction tube, nickel has been used very successfully (*1, 3*).

The reactions for the two salts investigated can be represented as:

$$3\ UO_2F_2 + 3\ H_2O \rightarrow U_3O_8 + 6\ HF + {}^1/_2\ O_2 \quad (1)$$

$$3\ UF_4 + 6\ H_2O + O_2 \rightarrow 12\ HF + U_3O_8 \quad (2)$$

The oxide remaining in the reaction tube is weighed, either without further treatment, or after a short period of ignition, depending upon the salt used. As indicated by Reaction 2, a considerable amount of oxygen is necessary for the conversion of uranium tetrafluoride to uranium oxide (U_3O_8); consequently,

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