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THE DETERMINATION OF THORIA  
IN TUNGSTEN ELECTRODES

BY

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## ABSTRACT OF THESIS

Two methods of analysis to determine thoria (thorium oxide,  $\text{ThO}_2$ ) content of thoriated tungsten electrodes are investigated.

Chlorination methods are shown to leave thoria residues contaminated with tungstic oxide which may not be removed by extended chlorination. Ignition of the sample in air before chlorination increases contamination. A correction for the tungstic oxide in the residue is obtained colorimetrically.

The classical hydrofluoric-nitric mixed acid method is modified and shown to be equally as accurate, less exposed to operator's error, and more rapid than chlorination methods. Thin-walled polyethylene beakers are preferable to platinum ware for dissolving the sample, and quartz crucibles may replace platinum for ignitions. Tungstic oxide contamination of the thoria residue is much less than with chlorination methods.

When purity of the thoria is questioned, thorium is isolated from the common elements by precipitation as the fluoride in preference to the oxalate, and from the rare earths and uranium by precipitation with benzoic acid.

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CHAPTER 1  
INTRODUCTION

Historical Survey

Tungsten electrodes are employed in inert gas shielded arc welding when non-consumable electrodes are required. A more stable arc is obtained when 0.1 to 3.0% of powdered thoria (thorium oxide,  $\text{ThO}_2$ ) is mixed with tungsten powder before the sintering and swaging.<sup>1</sup> Longer electrode life and various other improvements in welding properties are also claimed. Alternately, thoria may be applied to the surface of pure tungsten electrodes.<sup>2</sup> Although this is a comparatively new discovery tungsten filaments containing small amounts of thoria have long been in service.

There has been question concerning the state of thorium in filaments made from sintering tungsten metal and thoria. As early as 1922 one investigator (B. Vedekind,)<sup>3</sup> reported that tungsten filaments made from 2 parts thoria and 98 parts tungsten leave a residue amounting to 2% of the total weight of filament after treatment with HF and  $\text{HNO}_3$ . His conclusion is that the thoria is present in the finished filament substantially as such and that no detectable quantity of metallic thorium results during the sintering in a reducing atmosphere. It is further suggested that the thoria is in the form of a solid solution with tungsten in the filament. Other investigators have concluded that some metallic thorium is present in filaments after long periods of service.

In the same year (1922) the research staff of the General Electric Company (London, England)<sup>4</sup> investigated the reduction of thoria by metallic tungsten. Tungsten filaments containing 0.7% thoria were burned for different periods at various temperatures. They determined that thoria is reduced to thorium at about 2700°K, and that the thoria content of tungsten filaments diminishes when the temperature and the time of burning is increased. They also found that a large part of the thoria remains in the filament as thorium, and that some of the tungstic oxide formed combines with unchanged thoria to form a compound of the form  $\text{Th}(\text{WO}_3)_n$  where  $n$  may be from about 3 to 10.

The same investigators contend that thorium is soluble in a mixture of boiling HF and  $\text{HNO}_3$  whereas thoria remains as a white residue when the tungsten dissolves. They also report that the total thorium is recovered as the oxide when the tungsten is volatilized by heating in a current of chloroform and air. Presumably the thorium content may be calculated from the differences in the weight of thoria obtained by the two procedures.

In another publication<sup>5</sup> the same group reported that thoriated tungsten filaments reduced with phosphorus vapor leaves no residue of oxide on dissolving with a mixture of HF and  $\text{HNO}_3$  in a platinum dish, whereas thorium can be detected by the usual methods. The specific procedures used for the

detection of the thorium and actual values for thorium content found in these reduced filaments are not given in these articles.

In 1926 a further contribution was made by W. Singleton,<sup>6</sup> another member of the General Electric Research Laboratories. Mr. Singleton repeats the above contention, namely, that both thoria and thorium are likely to be present in thoriated tungsten filaments, and that thorium metal dissolves in HF and HNO<sub>3</sub> mixtures whereas the oxide remains as a residue. He likewise asserts that total thorium is left behind after tungsten removal by chlorination with air and chloroform vapor. As in the preceding articles no evidence is presented in terms of actual values of thoria and thorium obtained in any sample.

In the determination of thoria content by wet methods, the tungsten filament is usually dissolved in a mixture of HF and HNO<sub>3</sub> and the residue is cleansed from residual tungsten by various separations. Typical of these procedures is one published in 1943 by W. Böhm<sup>7</sup> which consists of digesting the thoriated tungsten wire with HF and HNO<sub>3</sub>, precipitating Th(OH)<sub>4</sub> by treatment with NaOH (which at the same time dissolves residual NO<sub>3</sub>), dissolving the washed Th(OH)<sub>4</sub> in HCl, (fusing any undissolved Th(OH)<sub>4</sub> with KHSO<sub>4</sub>), precipitating thorium as the oxalate Th(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> and igniting to ThO<sub>2</sub>.

Such methods are tedious and quantitative recovery of the thoria after several precipitations is questionable, especially

when an oxalate separation is included. Some investigators have found the oxalate method for thoria satisfactory;<sup>8</sup> however, a recent study by H. L. Hall and L. Gordon<sup>9</sup> led to the conclusion that the precipitation of thorium as oxalate should be avoided whenever possible.

Attempts to establish a more rapid determination of thoria in tungsten filaments which could be applied to small samples led to chlorination methods. A critical study of these procedures by D. H. Brophy and C. Van Brunt of the General Electric Company, Schenectady, New York, appeared in 1927.<sup>10</sup>

An early attempt to establish a more rapid determination consisted of moderate heating of the wire in a current of chlorine gas, driving off the tungsten as the chloride, and weighing the white residue as thoria; however, this method was abandoned owing to the danger of losing thoria as the chloride. An attempt to remedy this loss by addition of oxygen to the chlorine resulted in widely varying results, except when the sample was first burned in oxygen followed by several hours of volatilization. Chlorination with pure HCl after oxidation was found to occasionally produce low values.

Addition of an equal part of oxygen to the HCl gas prevents the loss of thoria. Nevertheless some residues from tungsten filaments showed decided loss in weight on extended

chlorination when the first weighing was made as soon as the sample was white; however this loss is attributed to small amounts of  $WO_3$ .

An explanation of the prevention of thoria loss by the presence of oxygen is offered by the above investigators in the following equation, with the comment that the reaction is apparently complete from left to right with a very moderate concentration of oxygen:  $ThCl_4 + O_2 = ThO_2 + 2Cl_2$

The following analytical procedure was subsequently adopted by Brophy and Van Brunt:

Short pieces of filament are added to a small quartz tube 30 mm. long and 5 to 6 mm. O.D. with the ends slightly choked by fusion. The tube (which weighs about 0.5 grams) is weighed before and after to 0.01 mg. It is placed in a small quartz boat and introduced into the larger quartz combustion tube. The special electric heater is so constructed that the sample may be inspected at any time by simply raising a cover. The temperature is set at  $700^{\circ}C$ .

The sample is first ignited in oxygen, usually overnight, then dry HCl gas is added to the oxygen in about equal proportions. The tungsten is volatilized as the oxychloride in about 2 hours. The residue is reported as thoria.

Chloroform vapor was substituted for HCl with equally good results.



No gas flows or filament sample weights used in these experiments are recorded in the literature.

Chlorinating the sample directly with mixed gases (without pre-ignition in oxygen) was considered by the above investigators; however, they foresaw little advantage and also a danger of possible loss of thoria by direct chlorination. Consequently this possibility was not further investigated.

A few other methods of determining thoria in thoriated tungsten wires have been studied.

Spectrographic methods for total thorium in tungsten wires have been successful<sup>11</sup> and are useful for control purposes. Quantitative values for total thorium may be obtained but determinations by other methods must be accepted in establishing standards.

Radioactivity tests<sup>12</sup> by means of a Geiger-Müller counter have been recently studied and found to give relative values of thorium but comparison with samples standardized by other methods may be expected to have limitations owing to the variation of activity with time.

No satisfactory colorimetric procedures for thoria in the 1 - 2% range have been developed for tungsten wire although the possibility of applying a recently published method for

microgram amounts of thorium<sup>13</sup> should not be dismissed.

The use of hydrofluoric and oxalic acids in separating thorium and the rare earths from the common elements is well known.<sup>14</sup> Thorium in turn may be separated from the rare earths by precipitation with benzoic acid.<sup>15</sup> A combination of these separations should provide a satisfactory method for isolating thorium.

Small amounts of tungsten may be accurately determined colorimetrically and the method has been applied to the determination of tungsten in cast iron.<sup>16</sup> The application to residual tungsten in thoria residues seems possible.

### Discussion

Because of the growing importance of inert gas shielded arc welding an accurate and rapid method of thoria determination in tungsten electrodes is in demand.

Existing wet methods are tedious because they involve various chemical separations and long digestions which are quantitative only under carefully controlled conditions.

The more rapid chlorination methods wherein tungsten is separated from thoria by volatilization as the oxychloride are currently in use; however they have not been fully investigated. It is generally assumed that the white residue obtained by chlorination is pure thoria when constant weight is reached, but no evidence for this assumption has been offered.

The writer believes that a definite contribution to the field of analytical chemistry will be made by a systematic approach to the study of chlorination methods. This investigation will be carried out in view of determining the most desirable chlorinating mixtures, flow rates and reaction temperatures for rapid removal of tungsten without loss of thoria, and in view of determining the purity of the constant weight residues.

The hydrofluoric-nitric mixed-acid method of separating thoria and tungsten will also be investigated in the hope of establishing an acceptable procedure involving no special equipment such as that needed in chlorination methods.

The drawback of existing wet methods making use of the hydrofluoric-nitric separation is the time consumed in attempting to purify the residue. The writer believes that this method may be rendered competitive to chlorination methods if this disadvantage is overcome by correcting for residual tungstic oxide instead of attempting purification.

### Investigation Procedure

The following investigations are carried out to achieve the information essential to the establishment of the desired analytical methods:

Halogenation methods. The rate of volatility of tungsten and tungstic oxide powders and of thoria in various gaseous mixtures and at different temperatures are first in-

vestigated. Mixtures which prove satisfactory for tungsten and thoria separately are tested with homogeneous mixtures of thoria and tungsten powders.

The relative properties of quartz, alumina and porcelain combustion boats are determined.

The reaction of metallic thorium in the selected gaseous mixtures is ascertained to determine if any reduced thoria would be lost during chlorination.

The purity of the tungsten, thoria and thorium used in these investigations is determined chemically.

The chlorinating mixtures are titrated after passage through the combustion tube to determine the chemical reactions taking place between the gases as they pass through the hot zone, and to determine the possible influence of the reaction products.

The application of the thiocyanate-stannous chloride colorimetric method for the determination of small amounts of tungsten, recently studied by W. Westwood and A. Mayer,<sup>15</sup> is investigated for determining tungstic oxide in thoria residues.

Two large samples of 2% grade thoriated tungsten electrodes (about 50 grams of each heat) are prepared by crushing in a steel mortar and passing through a 50-mesh sieve. Thoria values obtained by the developed procedures

are compared.

Wet method. The solubility of tungsten, tungstic oxide, thoria, thorium and thorium nitrate in mixtures of hydrofluoric and nitric acids is determined, and the respective importance of these findings is discussed.

The possibility of substituting polyethylene beakers and quartz crucibles for platinum ware is considered, and thoria values of the two prepared samples are obtained using both polyethylene and platinum containers in dissolving the samples, and quartz and platinum crucibles for ignition.

The colorimetric tungsten method is applied to determine tungstic oxide in the ignited residue.

The precipitation of thorium as oxalate and as fluoride are compared, and the benzoic acid separation from rare earths is investigated. The possibility of separating uranium from thorium by this latter method is also tested. These separations are employed in determining the purity of thorium nitrate and metallic thorium employed in the course of this study, and in isolating thoria from residues obtained from the prepared thoriated tungsten samples.

## CHAPTER 2

### INVESTIGATION OF HALOGENATION METHODS

#### Volatility Tests for Tungsten and Tungstic Oxide

The following experiments were carried out to determine the rate of volatility of tungsten metal powder and of tungstic oxide in various halogenating mixtures and at different flow rates and temperatures.

The tungsten powder employed was -325 mesh particle size. Chemical analysis (A.S.T.M.) revealed W (total) = 99.14%. Colorimetric analysis of the residue insoluble in HF-HNO<sub>3</sub> showed WO<sub>3</sub> = 1.90%; thus W metallic = 97.63%.

The equipment employed is shown in Figure 1. A detailed description of the apparatus will be found in the appendix.

A gas dispersion bottle and only one gas line for the oxygen is used for tests with chloroform.

The apparatus of Figure 1 is for use with gaseous mixtures. Not shown in the photograph are the supports on which the combustion tube is first placed outside of the furnace. The boat containing the sample is positioned in the centre of the tube, and the apparatus assembled as in Figure 1 after the gas flow is established.

To establish the flow oxygen is passed through the flowmeter, into sulphuric acid in one of the bubbling tubes, thence to the Y-connection and into the combustion tube. When the desired oxygen flow is established, the line at-

tached to the flowmeter is disconnected (if only one flowmeter is available) and connected to the tubing which leads to the second test-tube. The flowmeter is then connected to the HCl line and the desired HCl flow is then obtained. The gases meet at the Y-connection and are mixed by convection before entering the combustion tube. The exit gases pass through a small bottle wherein most of the tungsten oxychloride which has escaped condensation in the cool end of the combustion tube is trapped. The gas stream then passes through the pyrex glass wool filter to remove the remaining particles and then through the titrating solution; the residual gases are directed up the fume cupboard. When titrations are not carried out the gases may pass directly up the fume cupboard from the small bottle trap.

With the furnace at the fixed temperature as determined by the Variac setting the combustion tube is then positioned in the furnace and the furnace is closed over the tube. The sample is examined occasionally by raising the upper section of the furnace and the state of halogenation is ascertained visually. When tungsten removal is complete as shown by the empty boat the tube is removed from the furnace to its external supports and purged with oxygen. The combustion boat is then removed. In the case of thoriated electrodes the tube is removed five minutes after the residue in the boat appears pure white.

Glazed quartz combustion boats were used exclusively in the tungsten volatility determinations.

### Observations

Results of this investigation are shown in Table 1. No titrations of exit gases were made for this series.

Furnace temperatures are recorded from the centre of the hot zone of the combustion tube; the temperature is about  $100^{\circ}\text{C}$ . lower three inches from the centre.

One gram samples of tungsten powder are employed. Samples whose time of volatilization is followed by an asterisk were preignited by burning in air at  $800^{\circ}\text{C}$ . overnight.

Visual observations are recorded below.

Oxygen dispersed through chloroform. After 2 minutes the tungsten metal powder sample in the quartz boat begins to glow at the end facing the incoming gases, and the glowing slowly moves towards the opposite end. A yellow deposit forms on the walls of the combustion tube but clears in five minutes. The entire sample soon swells in the formation of the brown oxide, then slowly disappears beginning at the incoming gas end.

Most of the products condense outside of the furnace zone of the combustion tube. The color of the deposit changes from brown just at the exit to orange, green, yellow and finally white about three inches from the exit. Swirling



white clouds are visible outside the furnace zone. After some time tiny droplets of liquid appear at the end of the combustion tube. On cooling the various colors mostly change to greenish yellow.

At  $600^{\circ}\text{C}$ . the reaction was sluggish and after  $2\frac{1}{2}$  hours when the sample was finally volatilized there was still a brown deposit on the boat walls.

Similar observations were made with oxygen dispersed through carbon tetrachloride.

Dichloro-methane forms explosive mixtures with oxygen hence was not included in these tests.

With pre-oxidized samples observations were similar with the exception that no glowing takes place, and that no further increase in the sample volume occurs. In this case the glowing and swelling takes place as the sample is burned in air to the brown oxide.

Oxygen-hydrogen chloride mixtures. Observations were similar to those with oxygen-chloroform mixtures, with the exception that with mixtures of 4:1, 3:1, 2:1 and 1:1  $\text{HCl}:\text{O}_2$  there is no glowing with metallic tungsten; there is no swelling of the sample by oxidation. With the 1:2  $\text{HCl}:\text{O}_2$  mixture we again meet with glowing and swelling of the sample.

At  $600^{\circ}\text{C}$ . chlorination required several hours in all instances.

### Volatility Tests for Thoria

Only halogenating mixtures which provide rapid volatilization of tungsten (i.e. not over 1 hour) are employed in these tests. Freon 12 ( $\text{CF}_2\text{Cl}_2$ ) is rejected because of serious etching of the Vycor combustion tube and of the quartz combustion boat.

A flow rate of 100 mls. per minute was selected for most of the runs as being a satisfactory brisk flow with no danger of mechanical loss.

Flow periods of 2 hrs. were considered sufficient, as this is well beyond the period of satisfactory halogenation of a 1-gram sample.

Samples were tested in pairs using two quartz combustion boats end to end for each test. Thoria obtained from chlorinated tungsten electrodes was transferred to pre-ignited weighed boats, ignited at  $800^\circ\text{C}$ . in air for 5 minutes, allowed to cool in a dessicator for 30 minutes and rapidly weighed. These precautions were necessary because of the slight hygroscopicity of the honeycombed thoria from the electrodes. Weights of thoria thus determined agree with absolute weights obtained by igniting and weighing in covered platinum crucibles.

### Observations

There were no visible observations during these tests other than a faint white deposit on the cool zone of the combustion tube with samples which revealed loss of thoria.

No change in weight was observed with the gases recorded in Table 2, using flow rates of 100 - 300 mls./minute for periods of 2 hours at 800°C. As there was no loss of thoria at this temperature and as tungsten volatility was found to be generally sluggish below 800°C., no tests were made at lower temperatures.

Chlorinating mixtures which caused loss of thoria are recorded in Table 3. Samples identified as (1) are either single samples or the first of a pair; samples identified as (2) are second of a pair. When there is loss of thoria in the first sample the products of reaction must pass over the second sample.

### Volatility of Thoria with Tungsten

The chlorinating gases of Table 2 are those which rapidly volatilize tungsten and which do not react with thoria separately. To determine if these mixtures of gases are satisfactory with tungsten and thoria together, weighed samples of thoria were mixed with 1.00 grams tungsten powder and treated in the same manner as the samples recorded in

Tables 2 and 3. Results are recorded in Table 4.

Moist Chlorine and chlorine-oxygen 1:1 completely volatilized thoria with tungsten when the sample was not preignited. Chlorination of preignited samples with these gases was too sluggish to be competitive with the other mixtures.

Hydrogen chloride-oxygen mixtures showed no loss of thoria with and without preoxidation. Moist hydrogen chloride showed no loss on preoxidized samples.

Oxygen dispersed through chloroform showed losses of not more than 0.3 mg.  $\text{ThO}_2$  with and without preoxidation when samples were removed five minutes after chlorination was complete.

Tungstic oxide corrections made on above residues ranged from 0.1 to 2.0 mg.

#### Selected Chlorinating Mixtures

On the basis of rapid volatility of tungsten without loss of thoria, the chlorinating mixtures and conditions shown in Table 5 appear to be ideal.

Chloroform is included because no cylinder gas other than oxygen is required; however chloroform is the least desirable and the possibility of obtaining slightly low thoria values will always be present.

Comparative Properties of Quartz, Porcelain and Alumina  
Combustion Boats, Quartz and Platinum Crucibles

All three types of boats were employed at various temperatures with diverse chlorinating mixtures. Alumina boats increased slightly in weight after the first chlorination, but showed no further change in weight after two additional chlorinations. Both porcelain and quartz showed no change in weight after many determinations. Results are recorded in Table 7.

Quartz boats have the advantage of being transparent, making it possible to view the sample from beneath. This is important when chloroform is employed, as extended chlorination causes loss of thoria. But quartz boats have the disadvantage of being extremely sensitive to static electricity, which increases the risk of mechanical loss during transportation and transferring of the residue.

There is little choice between Coors porcelain and Morganite alumina boats. Both are much less sensitive to static electricity than quartz, and both are nearly as resistant to thermal shock. The gain in weight of the Morganite boats after the first chlorination was probably owing to absorption or adsorption of the chlorinated tungsten, and does not appear to be of moment since the boats are permanently stabilized.

Platinum crucibles have the advantage of rapid cooling and insensitivity to static charges. Quartz crucibles are

satisfactory but require about one half hour to cool to room temperature. They are extremely sensitive to static electricity, hence must not be rubbed or brushed. Presumably porcelain crucibles may be used although they are somewhat more attacked by bisulfate fusions. Platinum definitely has preference as only 0.2 mg. are lost during a short bisulfate fusion; if properly cared for they are also more economical, as they retain their monetary value and are unbreakable.

#### Volatility Tests for Metallic Thorium

In view of the possibility of the presence of metallic thorium in tungsten electrodes, an investigation was carried out to determine the reaction of metallic thorium in the selected chlorinating mixtures of Table 5.

The thorium powder employed in these tests was analyzed and found to be substantially metallic thorium. The method of analysis is found in the appendix.

Weighed amounts of thoria, thorium and tungsten powders were transferred to quartz boats, thoroughly mixed, and chlorinated directly at 800°C. Metallic thorium was quantitatively recovered as the oxide. A slightly low value was obtained with chloroform. Results are recorded in Table 6.

#### Colorimetric Correction for Tungstic Oxide Contamination

In order to quantitatively determine tungstic oxide in thoria residues, the following adaptation of the Westwood-

Mayer version of the thiocyanate-stannous chloride method<sup>15</sup> was established.

Solutions:

Sodium Thiocyanate: 50.0 grams dissolved in H<sub>2</sub>O diluted to 100.0 mls.

Stannous Chloride: 70.0 grams SnCl<sub>2</sub>·2H<sub>2</sub>O dissolved in 1 liter of concentrated HCl (freshly prepared.)

Tartaric Acid: 50.0 grams dissolved in H<sub>2</sub>O diluted to 100.0 mls.

Standard Tungsten Solution: 0.0457 grams pure WO<sub>3</sub> was dissolved fusing with 1.00 grams NaHSO<sub>4</sub> in a platinum crucible. On cooling 10 mls. H<sub>2</sub>O and 5 mls. tartaric acid solution were added and the crucible warmed to dissolve the fusion. The cloudy solution was washed into a 250-ml. volumetric flask, cleared by adding 10 mls. concentrated NH<sub>4</sub>OH, cooled to room temperature and diluted to the mark. The solution was thoroughly mixed.

$$1 \text{ ml.} = 1.83 \times 10^{-4} \text{ grams WO}_3$$

Procedure:

The procedure used in determining tungstic oxide in thoria residues is precisely the same as used in the "blank" determination of the following series from which the graph of Figure 3 was established.

Five samples of stock thoria weighing approximately 0.02 gram were each fused with 1.00 gram NaHSO<sub>4</sub> in platinum crucibles. On cooling, 1, 3, 5 and 10 mls. of the standard tungsten solution were pipetted into four of the crucibles, the fifth being taken as a blank. Water was added to make a total volume of 10 mls. 2 mls. of con-

centrated HCl are added to each, and the crucibles are cautiously warmed over a low flame until the fusion completely dissolves.

The solutions are transferred to 50 ml. volumetric flasks using 5 mls.  $H_2O$  (between 4 and 6 mls.) 5 mls. of tartaric acid and 1.5 mls. of sodium thiocyanate solution are added, and the flask is swirled and set aside for 2 minutes or longer. Stannous chloride is then added to the 50 ml. line, and the 50 mls. are immediately transferred to a 125 ml. dry Erlenmeyer flask and quickly cooled to  $27 \pm 2^\circ C$ .

Absorbance readings at a wavelength of 420 millimicrons were taken at 3-minute intervals using a Beckman Model B Spectrophotometer and 1 square centimeter pyrex cells. The results are recorded Figure 2.

Three additional 10 ml. portions of the standard tungsten solution were repeated without thoria or sodium bisulfate and were found to agree closely with the original 10 ml. reading after 20 minutes, showing that neither thoria nor sodium bisulfate interferes with color formation. A blank determination without thoria or bisulfate also agreed with the blank obtained above.

Figure 3 demonstrates the graph obtained by taking the readings at 20 to 30 minutes after the stannous chloride addition, deducting the "blank" reading at 20 minutes.



Beer's law is seen to hold up to at least 1.8 mg. (36 P.P.M.) The graph was confirmed using N.B.S #50 b Tungsten Steel (W = 18.05%).

Tungstic oxide corrections in subsequent thoria residues were obtained using Figure 3, taking the readings in from 20 to 30 minutes.

A few samples were found to reach a peak in 10 minutes, others in 30 minutes; however the readings between 20 and 30 were always close to peak readings.

Residues containing over 2.0 mgs.  $WO_3$  will not completely clear after warming the sodium bisulfate fusion with 10 mls.  $H_2O$  and 2 mls.  $HCl$ . In this case ammonium hydroxide should be added dropwise following tartaric acid addition until the solution is perfectly clear. It is then cooled and a 10-ml. aliquot is taken after dilution to a suitable volume (usually 50 or 100 mls.)

#### Analysis of Thoriated Electrodes by Chlorination Methods

In the preparation of samples for analysis 50-mesh was selected as being the smallest screen size for manual preparation in a reasonably short period.

A steel mortar and pestle were employed in preparing two 50-gram, 50-mesh samples from different lots of thoriated tungsten electrodes (2% thoria grade.) Small particles of metallic iron from the mortar were removed by repeated passage

of a bar magnet through the samples. About 50 minutes are required to prepare a 50-gram sample.

Several Thoria determinations with sample (1) were made at 700° and 900°C., which may be considered the minimum and maximum chlorination temperatures. Values are recorded in Table 9.

Preignited samples were ignited in air overnight at 800 - 850 °C. before chlorination.

Most of the chlorinations with sample (2) were made at the ideal temperature 800°C. Values are recorded in Table 10.

Table 11 records values obtained with extended chlorination periods. Chlorination by means of chloroform gave decidedly low ThO<sub>2</sub> values.

#### Purity of the Employed Thorium Metal Powder

The thorium metal used in both chlorination tests and the hydrofluoric-nitric method is in the form of a very fine powder. Attempts to dissolve it in various acid mixtures, including aqua regia, were not very successful; the thorium refused to completely dissolve over periods of several hours. It was necessary to ignite the thorium to the oxide before analysis.

The thorium powder ignited in air at a brilliant white heat and weighing before and after ignition gave results lower than expected. Results of two samples ignited in quartz crucibles are recorded in Table 8.

To reduce the possibility of loss by volatilization of thoria at white heat, two additional samples of thorium were mixed with water and ashless paper pulp and filtered on #42 Whatman 11-cm. filter papers; they were ignited in weighed quartz crucibles at  $450^{\circ}\text{C}$ . in a small muffle furnace having little ventilation. The furnace door was kept closed overnight to assure slow oxidation of thorium. The following day the samples (which appeared completely oxidized) were ignited in air at  $850^{\circ}\text{C}$ . for 15 minutes, covered, cooled to room temperature in a dessicator and weighed.

Two grams of fused  $\text{NaHSO}_4$  are added to each crucible and thoroughly mixed with the residues by spatula; the crucibles gently heated over a low flame until complete solution of the contents.

After cooling, the fusions are dissolved in hot water, transferred to 400 ml. beakers, and diluted to 200 mls. Five grams of  $\text{NH}_4\text{Cl}$  are added to each solution and  $\text{NH}_4\text{OH}$  is added dropwise until the bromcresol purple indicator turns blue, then 2 drops in excess. The solutions are boiled for 30 seconds, a little ashless paper pulp added, and filtered using gentle suction on #42 Whatman 11-cm. filter papers. The beaker is polished and washed with hot 1%  $\text{NH}_4\text{Cl}$  containing 4 drops of  $\text{NH}_4\text{OH}$  per liter; the residues are washed several times with the same solution and returned to the respective beakers.

To one of the precipitates is added 10 drops of conc. HCl; the precipitate is then broken up thoroughly with a glass rod. 200 mls. of hot water are added and the contents heated to boiling. 10 grams of pure oxalic acid crystals are added with vigorous stirring, and the beaker is placed on a hot plate and held at 60°C overnight. The solution is cooled to below room temperature and after one hour is filtered on a #42 Whatman 11-cm. filter paper and washed thoroughly with cold 2% oxalic acid. It is transferred to a platinum crucible (weighed with cover), ignited at 450°C until white, finally at 850°C for 15 minutes, covered, cooled in a dessicator, and weighed.

To the other precipitate is added 10 mls. HCl and 90 mls. hot water and the paper is completely broken up with a glass rod. 10 grams  $\text{NH}_4\text{Cl}$  are added and the solution is taken to a pH of 2.2-2.6 with  $\text{NH}_4\text{OH}$ , using pHydrion indicator papers. It is then heated to boiling.

To the boiling solution is added 100 mls. of boiling hot 2% benzoic acid solution, and boiling is continued for 10 minutes. The precipitate is allowed to settle, filtered on a #42 Whatman 11-cm. paper, washed with hot 0.25% benzoic acid, and ignited in a platinum crucible (weighed with cover) at 450°C. until white, finally at 850°C. for 15 minutes, cooled with cover in a dessicator, and weighed.

The above benzoic acid procedure is essentially that of Venkataramaniah, Rao and Rao.<sup>15</sup>

Results are recorded in Table 8.

Under the conditions of the above precipitations, thorium and rare earths are precipitated as oxalates; thorium is also precipitated with benzoic acid, whereas rare earths are not, although a few other elements such as aluminum or zirconium would be precipitated if present.

The purity of the thorium metal is sufficient for the purpose of this investigation. Total thorium content is about 97.7%.

We shall endeavour to prove under 'Relative insolubility of thorium oxalate and fluoride', page 36, that quantitative precipitation of thoria may not be expected with oxalic acid in dilute HCl. It is probable that this accounts for the low ignited thorium oxalate value.

### CHAPTER 3

#### INVESTIGATION OF THE HYDROFLUORIC-NITRIC ACID METHOD

##### Solubility of Tungsten Metal, Tungstic Oxide, Thoria, Thorium Metal and Thorium Nitrate in HF-HNO<sub>3</sub> Mixtures

A small amount of thorium metal powder was boiled in various proportions of HF and HNO<sub>3</sub> in a platinum dish for about 3 hours, with no apparent solution of the sample.

Following the above preliminary test, four 1.000 gram samples of Sample (2) were transferred to small polyethylene bottles. Tungstic oxide, thorium and thorium nitrate were added in the amounts shown in Table 12. The beakers were covered with polyethylene covers containing 1/8 inch diameter circular openings for dropwise acid addition.

To beakers 1 and 4 were added 5 mls. HF and 2 mls. HNO<sub>3</sub> (dropwise). To beakers 2 and 3 were added 5 mls. HNO<sub>3</sub> and 3 mls. HF (dropwise). Beakers 2, 3 and 4 were heated in water baths and occasionally agitated for 15 minutes after the samples were dissolved. The samples in beakers 1 and 4 dissolved readily; those in beakers 2 and 3 dissolved with difficulty.

To two additional beakers 5 and 6 were added weighed amounts of thorium nitrate and treated similar to the above samples. The calculated ThO<sub>2</sub> content of the reagent Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O was obtained using the experimental value of 97.0% purity (see Table 13).

The above six samples were filtered, ignited and weighed in the manner described under "Analytical Procedure for Thoriated Tungsten." Results of these tests are recorded in Table 12.

The first four residues were yellowish in appearance in contrast with the pure white chlorination residues.

The actual weights of thorium and thorium nitrate added to beaker #2 were 0.0011 and 0.0019 gram respectively, and are converted to the oxide equivalent by multiplying by their respective conversion factors, i.e. 1.138 and 0.479 X 0.97. Similarly for beaker #4 the actual respective weights are 0.0009 gram and 0.0010 gram. The thorium nitrate added to #5 and #6 is 0.1123 and 0.0279 gram respectively.

From Table 12 we learn that  $\text{ThO}_2$  recovered in the residue is equal to the  $\text{ThO}_2$  value of the combined thoria, thorium and thorium nitrate, proving that all thorium, dissolved or otherwise, is recovered in the residue as  $\text{ThO}_2$ . We also learn that tungsten metal is completely soluble, and tungstic oxide is quantitatively insoluble. This holds true when either HF or  $\text{HNO}_3$  is in excess.

#### Analytical Procedure for Thoriated Tungsten

The following procedure was employed in obtaining the values of Thoria reported in Table 14.

**Apparatus and Reagents:**

- (a) Small polyethylene beakers with covers having small openings for dropwise acid addition. (Platinum may be used).
- (b) Platinum or quartz crucibles with cover.
- (c) A polyethylene funnel with platinum cone and SS#23 cloth supports.
- (d) Whatman #42 - 11 cm. filter papers.
- (e) Ashless paper-pulp suspension prepared from Whatman ashless tablets.
- (f) Concentrated nitric and hydrofluoric acids.
- (g) Graduates and polyethylene dropping bottles.
- (h) Muffle Furnaces (or burners), dessicator and analytical balance.

**Procedure:**

1.000 or 2.000 gram of 50-mesh thoriated electrode (or small pieces of electrode) is transferred to a polyethylene beaker and 5 mls. HF (47%) is added. The polyethylene cover is tightly positioned and  $\text{HNO}_3$  is added through the small opening 5 or 6 drops at 1 minute intervals until solution is complete. (If small pieces instead of 50-mesh sample is used, 2 mls. of  $\text{HNO}_3$  may be added at once). 5 or 6 drops excess  $\text{HNO}_3$  is added when no dark particles remain, and the contents digested 5 minutes or longer. About 15 minutes for a 1.00 gram or 25 minutes for a 2.00 gram sample is required for solution. Only 5 or 10 minutes is required for the solution of small pieces with the initial addition of excess  $\text{HNO}_3$ .



An 11-cm. #42 Whatman filter paper is folded and positioned in the polyethylene funnel supported with the platinum cone and cloth; the filter paper is then half-filled with a creamy suspension of Whatman ashless pulp in water. The contents of the beaker are transferred to the funnel using a fine stream of cold water while applying gentle suction to the filter (as a precaution the beaker is polished). The paper and residue is washed 30 times with cold water, suction dried, and transferred to a platinum or quartz crucible weighed with cover.

A small muffle furnace set at  $450^{\circ}\text{C}$ . is excellent for charring and burning the paper although a low flame is satisfactory. The crucible is then taken to a bright red heat (about  $850^{\circ}\text{C}$ .) for at least 5 minutes, transferred to a dessicator, covered, cooled and weighed.

Correction for  $\text{WO}_3$  is made in the same manner as described in chapter 2, under "Colorimetric Correction for Tungstic Oxide Contamination." The corrected residue is taken as thoria content. Multiplying by 100 gives per cent thoria for a 1.000 gram sample.

Several samples should not be placed in the same dessicator, particularly when quartz crucibles are used. Large weighing errors will be introduced if the crucibles are slightly warm; generally at least 30 minutes in the dessicator for quartz and 15 minutes for platinum crucibles are required for cooling to room temperature.

Table 14 records thoria determinations by the above procedure on portions of the original 50-mesh samples (1) and (2), with the exception of the last four values which were obtained from small pieces of electrodes of the same lot as sample (2).

Neither the above procedure nor chlorination methods isolate thoria from other elements; theoretically the residue could contain alumina, zirconia, rare earth oxides or others. If the purity or even the presence of thoria is in question, thoria should be isolated by the fluoride-benzoate procedure described under "Purity of Thoria Employed in Tungsten Electrodes." In this case no  $\text{WO}_3$  correction is required.

Investigation of the Benzoic Acid Method of Separating Thorium from Lanthanum, Uranium and the Rare Earths

Two samples of pure  $\text{ThO}_2$  (purified by hydrofluoric and benzoic acid separations) and weighing 0.0168 and 0.0170 grams respectively, are contained in platinum crucibles. Weighed amounts of cerium oxide are added and the residues cautiously fused with 2.00 gram  $\text{NaHSO}_4$ . The fusions are dissolved in water, transferred to 400 ml. pyrex beakers, and diluted to 200 mls. Uranium acetate and lanthanum nitrate are added and dissolved by stirring.

The weights of the additions are recorded in Table 15.

0.0150 and 0.0156 gram  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2) \cdot 2\text{H}_2\text{O}$  are recorded in the Table as 0.0099 and 0.0103 gram  $\text{U}_3\text{O}_8$  (conversion factor 0.661); 0.0160 and 0.0110 gram  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  are likewise recorded as 0.0059 and 0.0040 gram  $\text{La}_2\text{O}_3$  respectively (conversion factor 0.368).

To each beaker is added 5 gram  $\text{NH}_4\text{Cl}$ , and  $\text{NH}_4\text{OH}$  is added dropwise while stirring until the solution is just blue to bromcresol purple indicator, then 2 drops in excess. The  $\text{NH}_4\text{OH}$  precipitation followed by the benzoic acid separation are carried out as described under "Purity of the Employed Thorium Metal Powder."

The process of fusion followed by  $\text{NH}_4\text{OH}$  and benzoic acid separations is repeated, as it is evident from the weights of the residues that a single separation is not quite quantitative.

The initial investigation of the benzoic acid separation was made by precipitation in the presence of sodium bisulfate. Because of slightly high values, presumably by co-precipitation of sodium bisulfate, it was considered necessary to make the preliminary  $\text{NH}_4\text{OH}$  precipitation to remove sodium salts.

Co-precipitation of ammonium salts is not of moment as the salts are completely volatilized during ignition.

From Table 15 it is apparent that a double benzoate

separation is necessary for the isolation of thoria from uranium, lathanum and the rare earths (cerium is considered as representative of the latter).

#### Purity of Thoria Employed in Tungsten Electrodes

Four 1.000 gram portions of sample (2) are dissolved with HF-HNO<sub>3</sub> in polyethylene beakers, filtered and ignited as described under "Analytical Procedure for Thoriated Tungsten." The residues are then fused with 1.0 gram NaHSO<sub>4</sub> and two are precipitated with NH<sub>4</sub>OH in the manner detailed in "Purity of Employed Thorium Metal Powder," with the exception that 9-cm. filter papers are employed.

One of the NH<sub>4</sub>OH residues is transferred to a 250 ml. beaker and precipitated with oxalic acid; the other is transferred to a 400 ml. beaker and precipitated with benzoic acid. Details of precipitation are found under "Purity of Employed Thorium Metal Powder," with the exception that only half the volume and half the reagents are used for the oxalic acid procedure.

The two other fusions are dissolved in 10 mls. H<sub>2</sub>O; 5 mls. conc. HF are added, and the fluoride precipitated and ignited as described under "Purity of Employed Thorium Nitrate Tetrahydrate." The ignited residues are then fused with 1.00 gram NaHSO<sub>4</sub>, precipitated with NH<sub>4</sub>OH, and finally with benzoic acid, washed, ignited and weighed in the same manner as the second residue above.

Results of the four tests are recorded in Table 16.

The ammonium hydroxide-oxalic acid precipitations separate thorium from residual  $WO_3$  and the common elements; the ammonium hydroxide-benzoic acid precipitations separate thorium from residual  $WO_3$  and the rare earths.

The hydrofluoric-ammonium hydroxide-benzoic acid precipitations isolate thorium from all other elements, with the possible exceptions of Scandium, Yttrium, Actinium and Indium. From Table 55 of "Outlines of Methods of Chemical Analysis" by Lundell and Hoffman,<sup>14</sup> we see that the above enumerated elements, along with uranium, thorium, lanthanum and the rare earths (Elements 58-71) are precipitated with hydrofluoric acid. We have already demonstrated the separation of thorium from lanthanum, uranium and cerium (one of the rare earths) under "Investigation of the Benzoic Acid Method of Separating Thorium from Lanthanum, the Rare Earths and Uranium." However, the above enumerated elements are precipitated with  $NH_4OH$ , and have not been investigated with benzoic acid; consequently they remain as the only possible contaminants.

#### Purity of Employed Thorium Nitrate Tetrahydrate

Thorium nitrate reagent, labelled  $Th(NO_3)_4 \cdot 4H_2O$ , is examined for purity in the same manner as thorium metal, with the exception that the water soluble nitrate requires no fusion.

In addition to oxalate and benzoate separations ignited fluoride precipitates are also recorded. The fluoride precipitation is carried out as follows:

Weighed samples of the hydrated thorium nitrate are dissolved in a platinum crucible with 10 mls.  $H_2O$ . 5 mls of conc. HF are added and the contents of the crucible are heated just below the boiling point for 2 or 3 minutes. After 5 minutes the sample is poured into a #42 Whatman 11 cm. filter paper half filled with a creamy suspension of ashless pulp; the latter is supported by a platinum cone and SS#23 cloth support in a polyethylene funnel.

After filtration using gentle suction, the residue is thoroughly washed with cold water, transferred to a platinum crucible weighed with cover, ignited at  $450^{\circ}C$ . until white, finally at  $850^{\circ}F$ . for 15 minutes, transferred to a dessicator, covered, and weighed at room temperature.

Results of these tests are recorded in Table 13.

The oxalate and fluoride ignited residues include total rare earth oxides and thoria; the benzoate ignited residue excludes rare earth oxides but includes thoria. As results are in close agreement, it is evident that no measurable amounts of rare earths are present, and that the thorium nitrate tetrahydrate crystals are close to 97.0% pure. Judging from the fact that crystals were stuck to the walls of the reagent bottle, it is likely that the remaining 3.0% is additional moisture.

### Relative Insolubility of Thorium Oxalate and Fluoride

Both hydrofluoric and oxalic acids have long been used in separating thorium and rare earths from the common elements; but only oxalic acid is used when an ignition and weighing as oxides is required.<sup>14</sup>

From Tables 8 and 13 it is apparent that ignited oxalate residues yield slightly lower values for thoria content than ignited benzoate precipitates. From theoretical considerations this discrepancy could be owing to impurities such as alumina or zirconia which are precipitated with benzoic acid but not with oxalic acid; however we have additional evidence that the oxalate precipitation of thoria is not quite quantitative.

A study of Table 16 reveals that thoria from the tungsten electrodes is pure, for the preliminary fluoride separation would remove common elements, and the final benzoate separation would remove rare earths; yet the final residues of pure  $\text{ThO}_2$  agree closely with our established value of 1.71% for sample (2) (see Table 17). However, the ignited oxalate residue is the equivalent of only 1.66%.

For further confirmation, two samples of chemically pure stock thoria weighing 0.0247 and 0.0342 gram were fused, precipitated with  $\text{NH}_4\text{OH}$ , and then precipitated with oxalic and benzoic acids respectively. The ignited residues

weighed 0.0242 and 0.0343 gram, showing quantitative recovery by the benzoate method but a loss of 0.5 mg. using oxalic acid.

Table 16 also reveals that total thoria is recovered with benzoic acid following precipitation and ignition of the fluoride; consequently the precipitation of thoria with hydrofluoric acid must be quantitative.

Thorium fluoride precipitates are never weighed after ignition, and are employed only as separations;<sup>14</sup> however, the ignited fluoride residues recorded in Table 13 are in close agreement with ignited benzoate residues. The writer suggests that the conversion of the fluoride to the oxide may be quantitative by following the method of ignition used in this investigation. The conversion is explained by the following equation:

$$\begin{aligned} \text{ThF}_4 \cdot 4\text{H}_2\text{O} &= \text{ThF}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O} \\ \text{ThF}_4 \cdot 2\text{H}_2\text{O} &= \text{ThO}_2 + 4\text{HF} \end{aligned}$$

Precipitation as the fluoride has the further advantage of being quantitative in 10 minutes, whereas the oxalate is not quite quantitative after several hours.



## CHAPTER 4

### CONCLUSIONS

#### Halogenation Methods

1. Of the various halogenation mixtures tested, the following are considered the most satisfactory on the basis of rapid removal of tungsten without loss of thoria. They are listed in order of preference: (See Tables 1 to 5)

(a) HCl and O<sub>2</sub> mixtures in ratios 1:1 to 5:1, at 800°C. and total flow rates from 100 to 300 mls./minute, with oxidized or metallic samples.

(b) HCl (moist), at 800°C. and flow rates of at least 100 mls./minute (the highest flow tested), with oxidized samples only.

(c) O<sub>2</sub> dispersed through CHCl<sub>3</sub> and H<sub>2</sub>O, at 800°C. and flow rates of at least 100 mls./minute (the highest flow tested), with oxidized or metallic samples. Samples must not be chlorinated for more than five minutes after apparent completion.

2. Quartz, porcelain or alumina combustion boats may be employed. (See Table 7)

3. With all chlorination mixtures WO<sub>3</sub> contamination of the residue may not be ignored nor may it be removed by extended chlorination. This contamination is considerably higher with preoxidized samples than with metallic samples, and is highest with low temperature chlorinations. (See Tables 9, 10, 11)

4. Accurate corrections for WO<sub>3</sub> in the weighed residues may be obtained in 30 minutes by the stannous chloride-thiocyanite colorimetric method, eliminating the necessity of

tedious purification separations.  $\text{ThO}_2$  does not interfere.

5. Dry gases should be avoided since the presence of moisture prevents loss of thoria (see Appendix). In the case of gases containing oxygen moisture may be absent as oxygen also prevents thoria loss; nevertheless the addition of moisture requires no extra effort and appears to be a reasonable precaution against thoria loss.

6. Metallic thorium if present will be quantitatively retained in the residue as the oxide  $\text{ThO}_2$ , as seen in Table 6.

7. Unless thoria has been isolated by chemical methods, it is merely an assumption to consider residues corrected for  $\text{WO}_3$  as thoria.

#### The HF-HNO<sub>3</sub> Method

1. Tungsten rapidly dissolves in HF-HNO<sub>3</sub> mixtures whereas thoria remains insoluble and may be quantitatively recovered on filtering, washing with water and igniting. (Table 12)

2. Thin-walled polyethylene beakers are preferable to platinum for dissolving, as the sample may be examined without raising the cover.

3. Contamination of the residue by  $\text{WO}_3$  is much lower than with chlorination methods, in spite of the yellowish appearance as contrasted with the white chlorination residues.

4. As with residues from chlorination, accurate and rapid colorimetric corrections for  $WO_3$  eliminates further purification. This correction is negligible for the two samples employed in this investigation, as shown in Table 14.
5. Metallic thorium if present will be quantitatively recovered in the residue as  $ThO_2$ , for either thorium remains as the metal and is converted to  $ThO_2$  on ignition, or thorium dissolves and is precipitated as the hydrated fluoride which converts to  $ThO_2$  on ignition. (See Table 12)
6. Tungstic oxide and thoria are insoluble in  $HF-HNO_3$  mixtures, as demonstrated in Table 12.
7. Values of thoria in Samples (1) and (2) are in close agreement with values obtained by chlorination methods, as disclosed in Table 17.
8. Thoria employed in the tested electrodes is uncontaminated with rare earths or other impurities; the Sample (2) residue 1.70% (Table 17) is shown in Table 16 to be pure  $ThO_2$ .
9. As with residues from chlorination, chemical methods must be employed to indentify thoria. A combination of hydrofluoric and benzoic acid separations is excellent for this purpose. The use of oxalic acid should be avoided.
10. Chemical reagents employed in this investigation are correctly labelled and of satisfactory purity as determined by chemical analysis. (See Tables 8 and 13).

## CHAPTER 5

### RECOMMENDATIONS

#### Selection of an Analytical Procedure

Accuracy and speed are of fundamental concern in selecting a method of analysis; available space and equipment are also important items; the possibility of operator's error should not be overlooked. A consideration of all factors favors the nitric-hydrofluoric method.

Chlorination methods for thoria determinations require the equipment shown in Figure 1 (with the exclusion of the titration apparatus), and in addition fume-cupboard space. In small laboratories where the equipment or space are not readily available the HF-HNO<sub>3</sub> method at once offers preference.

A glance at Table 17 reveals that both methods of analysis possess accuracy; however, Table 17 does not reveal that much greater care on the part of the operator is essential to obtain accuracy by chlorination methods.

The first thoria value recorded in Table 10 is well below the average value of 1.71% ThO<sub>2</sub> for sample (2). In spite of the care taken in all of these determinations, 0.7 mg. ThO<sub>2</sub> was lost in the course of this analysis.

Transferring the thoria from boat to crucible requires the greatest care. Brushes must not be used as static

charges cause thoria to cling to the hair; transferring must be accomplished by spatula and moistened filter paper. Even with these precautions thoria tends to crawl over the wall of the boat. If quartz crucibles are used they must not be brushed before weighing, and static charges must be removed from one's body before touching the crucible by hand or by tongs.

A study of Table 14 suggests that tungstic oxide may be ignored in residues obtained by the HF-HNO<sub>3</sub> method except in the most accurate work; thus it is possible to obtain an accurate thoria value by the HF-HNO<sub>3</sub> method in 35 - 45 minutes on broken pieces of electrode with a minimum of operator's error. On the other hand, Tables 9 and 10 show conclusively that tungstic oxide in the chlorination residues must not be ignored; consequently at least 2 hours (including  $\frac{1}{2}$  hour for colorimetric WO<sub>3</sub> correction) is required for an accurate thoria determination by chlorination methods with a relatively high possibility of operator's error.

We have shown that the solubility of thorium oxalate in dilute HCl is appreciable and agree with H. L. Hall and E. Gordon<sup>9</sup> that it is well to avoid the use of oxalic acid for precipitating thoria. The hydrofluoric-benzoic acid method described under "Purity of Thoria Employed in Tungsten Electrodes" was found to be quite satisfactory for isolating thoria from the common elements, and from lan-

thanum, uranium and the rare earths, and is recommended in place of a tungstic oxide correction when the purity or even the presence of thoria is in question.

Suggestions for Differentiating Thoria and Thorium in Thoriated Tungsten

It has been demonstrated from results recorded in Tables 6 and 12 that if thoria and thorium are present in the tungsten electrode, both will be recovered and weighed as thoria. Thus it is not possible by the procedures developed to distinguish one from the other, or to prove the absence of the latter.

If thorium should form during the sintering of the electrode in a reducing atmosphere, then an oxide of tungsten would also be formed in the reaction. It seems possible that both thorium and tungstic oxide would escape from the electrode and be vaporized at the extremely high sintering temperature; however if tungstic oxide should remain, such as by combination with thoria, it seems likely that it would remain behind in the residue following an HF-HNO<sub>3</sub> treatment. If such be the case, then the WO<sub>3</sub> correction may be a function of the thorium content, making it possible to establish a relationship between the two; however, there is also the possibility that the WO<sub>3</sub> correction is an indication of good or bad sintering during the electrode manufacture, and not of

thorium content.

A second suggestion is directed towards the thorium rather than the tungstic oxide. If thorium is present and we suppose it dissolves, it will be precipitated as the fluoride. The precipitate could be centrifuged in a polyethylene centrifuge tube, washed, and re-centrifuged several times to remove tungsten. The residue could then be transferred to a platinum dish and dried below  $200^{\circ}\text{C}.$ ; under these conditions the thorium fluoride from the thorium would be in the form  $\text{ThF}_4 \cdot 2\text{H}_2\text{O}$ . Fusion of the residue with  $\text{Na}_2\text{CO}_3$  would convert the fluoride to water soluble sodium fluoride. It may be possible to determine this fluoride colorimetrically such as by extinction of the titanium-peroxide complex. From the fluoride determination the original thorium could be calculated.

The above method would depend on two factors; first, that thorium will dissolve in  $\text{HF-HNO}_3$  -- and our investigation has shed doubt on this possibility; and secondly, that no thoria will be converted to fluoride during the solution of the tungsten. Judging from our tests with finely powdered thorium metal it is more likely that thorium would remain in the residue as such and could be qualitatively determined and roughly estimated by a microscopic examination of the centrifuged or decanted residue; or more accurately determined by X-ray diffraction methods.

## APPENDIX

### Detailed Chlorination Apparatus

The chlorination equipment is shown in Figure 3. A gas dispersion bottle and only one gas line (for oxygen) is used for tests with chloroform. The titration apparatus is employed in this investigation for identifying gaseous products, and is not required for determining thoria.

The following is a detailed description of the apparatus:

- (a) A Multiple Unit type 70 Hevi Duty combustion furnace.
- (b) An oxygen cylinder with regulator.
- (c) A hydrogen chloride cylinder with needle valve.
- (d) A vycor combustion tube 19 X 25 X 600 mm. with transite adaptors.
- (e) Glazed silica combustion boats 75 X 15 X 10 mm.  
Coors porcelain combustion boats 97 X 16 X 11 mm.  
Morganite recrystallized alumina combustion boats 90 X 17 X 12 mm. (all outside dimensions).
- (f) A Variac type V10 voltage regulator.
- (g) A portable pyrometer.
- (h) Clamps and supports.
- (i) Two pyrex test tubes  $\frac{3}{4}$  X 6 inches fitted with 2-holed rubber stoppers containing inlet and outlet glass tubing (used for  $H_2SO_4$  bubbling bottles).
- (j) Two size 3 one-hole rubber stoppers containing a short length of 10 mm. O.D. pyrex tubing with ends flame-drawn to receive tygon plastic tubing.
- (k) A T-connection for combining  $O_2$  and  $HCl$  gases before entrance to the combustion tube.



- (l) Tygon tubing 1/8, 1/4 and 3/8 inch I.D.
- (m) A small bottle (150 mls.) with a 2-holed rubber stopper containing 10 mm. O.D. pyrex tubing (which serves to trap condensed tungsten oxychloride particles).
- (n) A small funnel fitted with a one-hole rubber stopper containing pyrex glass wool (which filters out most of the remaining particles).
- (o) A 150-ml. cylindrical bottle fitted with a 3-holed rubber stopper fitted with a fritted-glass gas disperser, a 25-ml. burette, and a 10 mm. pyrex tubing outlet.
- (p) A 3-foot length of 10 mm O.D. pyrex tubing leading up into the fume cupboard. It is connected to the titrating bottle exit or to the bottle at the furnace exit when the titrating apparatus is not used.
- (q) A calibrated flowmeter.
- (r) A gas dispersing bottle for use with chloroform and water.

#### Reagents

- (a) 1% HCl (in distilled water)
- (b) Sodium Thiosulfate O.I.N.
- (c) Starch-iodide indicator - 5.0gs. starch and 8.0gs. KI in 500 mls. H<sub>2</sub>O.
- (d) Sodium hydroxide O.I.N.
- (e) Phenolphthalein indicator 0.1% in ethanol.
- (f) Tungsten metal powder.

#### The Reaction of ThO<sub>2</sub> with Dry and Moist HCl and Cl<sub>2</sub>

The volatility of thoria in dry HCl gas is explained by the equation:  $\text{ThO}_2 + 4\text{HCl} = \text{ThCl}_4 + 2\text{H}_2\text{O}(l)$

Addition of moisture causes the reaction to go to the left. This explains the partial loss of thoria in dry HCl at 800°C, and the quantitative retention of thoria in

moist HCl under the same conditions of flow rate and temperature.

From the last section of Table 3 it is evident that the loss of thoria in the boat facing the incoming gases is considerably more than in the second boat; two check runs were made to confirm this finding. The explanation offered is that the small amount of  $\text{ThCl}_4$  and  $\text{H}_2\text{O}$  from the first boat causes the reaction of equation (1) to reverse more in the second boat.

The volatility of  $\text{ThO}_2$  in dry  $\text{Cl}_2$  at  $800^\circ\text{C}$  is explained by a similar equation:  $\text{ThO}_2 + 2\text{Cl}_2 = \text{ThCl}_4 + \text{O}_2(2)$

There is no loss of thoria in moist  $\text{Cl}_2$  gas under the same conditions. Although moisture is not a product of equation (2), the presence of  $\text{H}_2\text{O}$  may prevent the loss of thorium tetrachloride as shown in equation (1). At the same time oxygen is actually added to the system by reaction with chlorine according to the equation  $2\text{Cl}_2 + 2\text{H}_2\text{O} = 4\text{HCl} + \text{O}_2(3)$

#### The Oxidation of HCl with $\text{O}_2$

The addition of oxygen to the system of equation (1) has a similar dual affect. Oxygen will react with hydrogen chloride to produce  $\text{H}_2\text{O}$  according to the reverse of equation (3); thus the moisture prevents loss of thoria by reversing equation (1), and the oxygen prevents loss of thoria by reversing equation (2).

To determine the extent of the formation of chlorine, the gases leaving the combustion tube were titrated with 0.1N sodium thiosulphate using starch-iodine indicator. Titrations were made at different temperatures with and without samples in the tube, using 2 : 1 HCl : O<sub>2</sub>.

The amount of HCl entering over a fixed period was obtained from the approximate flow rate, ignoring slight corrections for temperature and pressure, and taking 22.4 liters HCl = 36.46 grams.

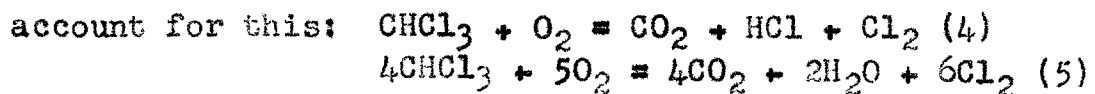
The amount of Cl<sub>2</sub> formed was determined from the titration; 1 ml. 0.1N sodium thiosulfate =  $3.546 \times 10^{-3}$  grams chlorine.

Results are recorded in Table 18. Alumina combustion boats appear to have a higher catalytic action than quartz in the formation of chlorine.

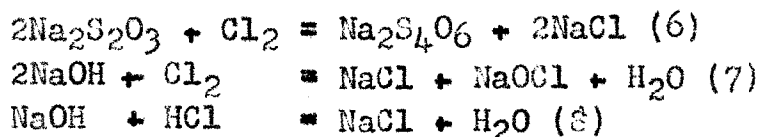
#### The Oxidation of CHCl<sub>3</sub> with O<sub>2</sub>

Titrations were also made after passing mixtures of oxygen and chloroform through the heated combustion tube. The first titrations were made using 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with starch-iodine indicator; the second titrations were made with 0.1N NaOH using phenolphthalein indicator. The indicator was added frequently as it was continually destroyed by the NaOCl formed. Results are recorded in Table 19.

The titration with sodium thiosulfate shows that chloroform is oxidized to chlorine. There are two equations which could

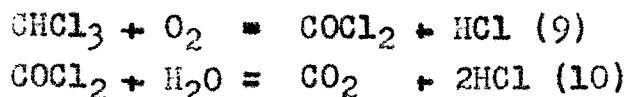


If equation (5) is correct, then the titration of 20 mls. 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  would require the same time as the titration of 20 mls. 0.1N NaOH; from Table 19 we see that such is not the case. If equation (4) is correct, then the titration of 20 mls. 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  would require three-halves of the time required to titrate 20 mls. 0.1N NaOH. This is evident from the following equations:



From Table 19 it is evident that equation (4) does not explain why the NaOH titration requires so much less time than the  $\text{Na}_2\text{S}_2\text{O}_3$  titration.

The same amount of 0.1N NaOH as of 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  is required to titrate  $\text{Cl}_2$ ; thus it is evident that much more HCl than  $\text{Cl}_2$  is formed during the oxidation of  $\text{CHCl}_3$ . This may be explained by the formation of phosgene, which reacts with water to liberate HCl:



The formation of carbonyl chloride (phosgene) is not unexpected, as it is known that chloroform may be transformed to phosgene by oxidizing agents.<sup>17</sup>

We conclude that in the oxidation of chloroform by oxygen at 800°C the reactions may be represented by equations (9) combined with one or both of equations (4) and (5).

By experiment it was found that with our dispersion bottle 25 mls. of chloroform (37.5 grams) are carried over by a flow of 100 mls. O<sub>2</sub>/minute in 220 minutes. Thus in 1 minute we carry over  $\frac{37.5}{220}$  gram CHCl<sub>3</sub> = 0.17 gram CHCl<sub>3</sub>.

From Table 19, taking average values, we see that in 1 minute we titrate 4.5 mls. 0.1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and 25.7 mls. 0.1N NaOH. This corresponds to  $4.5 \times 3.546 \times 10^{-3}$  grams Cl<sub>2</sub> and  $25.7 \times 3.647 \times 10^{-3}$  grams HCl. i.e.:

0.016 gram Cl<sub>2</sub>  
and 0.091 gram Cl as HCl  
total 0.107 gram Cl from 0.17 gram CHCl<sub>3</sub>.

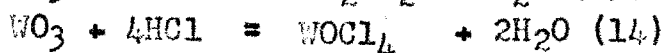
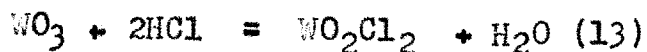
From these values it is apparent that most of the chloroform is oxidized by oxygen at 800°C. There is no explosion, not because it does not burn, but because the heat of combustion is low (89.2 kg. calories, Handbook of Chemistry and Physics), and because in the bulk of the reaction represented by equation (9) there is no change in volume.

#### The Volatilization of Tungsten and Tungstic Oxide

The reactions with tungsten may be explained by the following equations:  $W + 4HCl + O_2 = WCl_4 + 2H_2O$  (11)  
 $2W + 4HCl + 3O_2 = 2WO_2Cl_2 + 2H_2O$  (12)

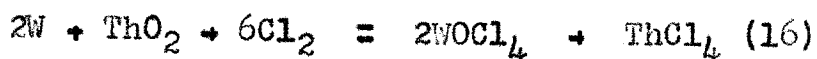
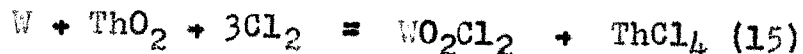
Various other reactions probably take place (judging from the various colors of the sublimate) such as the formation of  $WCl_2$ ,  $WCl_6$  or other chlorides with chlorine.

With tungstic oxide and HCl we have:



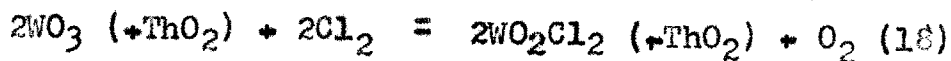
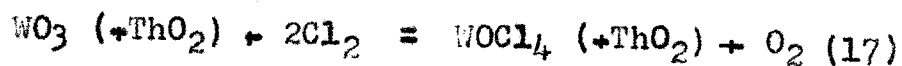
Loss of  $ThO_2$  with Tungsten and Chlorine, and with Chloroform

The complete loss of thoria in chlorine gas with metallic tungsten present may be explained in the following manner:

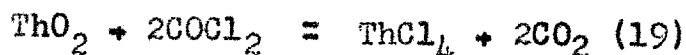


Even the presence of equal parts of oxygen to chlorine does not prevent this reaction, for we found total loss of thoria in both cases.

When the tungsten is first oxidized by burning in air, there is no loss of thoria with moist chlorine:



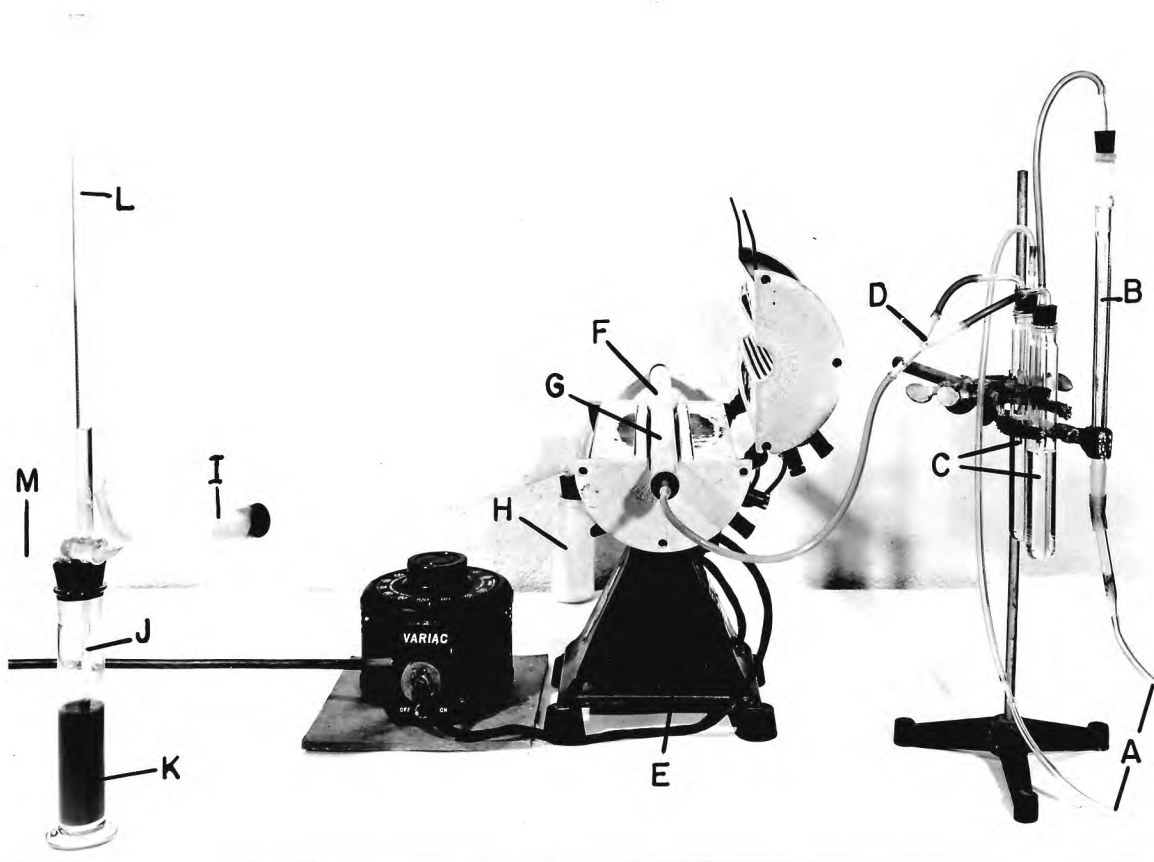
The slight loss of thoria by heating in chloroform-oxygen mixtures may be explained by reaction with phosgene:



The presence of  $O_2$  and  $H_2O$  formed by reaction with HCl and  $O_2$  tend to reduce this tendency. Bubbling the  $O_2$  through a layer of  $H_2O$  on the  $CHCl_3$  does not eliminate this loss, but

appears to be a reasonable precaution to take, considering that no extra work is involved.

FIGURE I.



## CHLORINATION APPARATUS

- |                                    |                               |
|------------------------------------|-------------------------------|
| A. GAS LEADS FROM CYLINDER         | G. COMBUSTION BOAT AND SAMPLE |
| B. CALIBRATED FLOWMETER            | H. PARTICLE TRAP BOTTLE       |
| C. SULPHURIC ACID BUBBLING BOTTLES | I. GLASS WOOL PARTICLE FILTER |
| D. Y - CONNECTION                  | J. GAS DISPERSION TUBE        |
| E. COMBUSTION FURNACE              | K. TITRATING CYLINDER         |
| F. VYCOR COMBUSTION TUBE           | L. 25-ML. BURETTE             |
|                                    | M. GAS EXIT TUBE              |



FIGURE 2. ABSORBANCE OF TUNGSTEN THIOCYANATE COMPLEX VERSUS TIME.

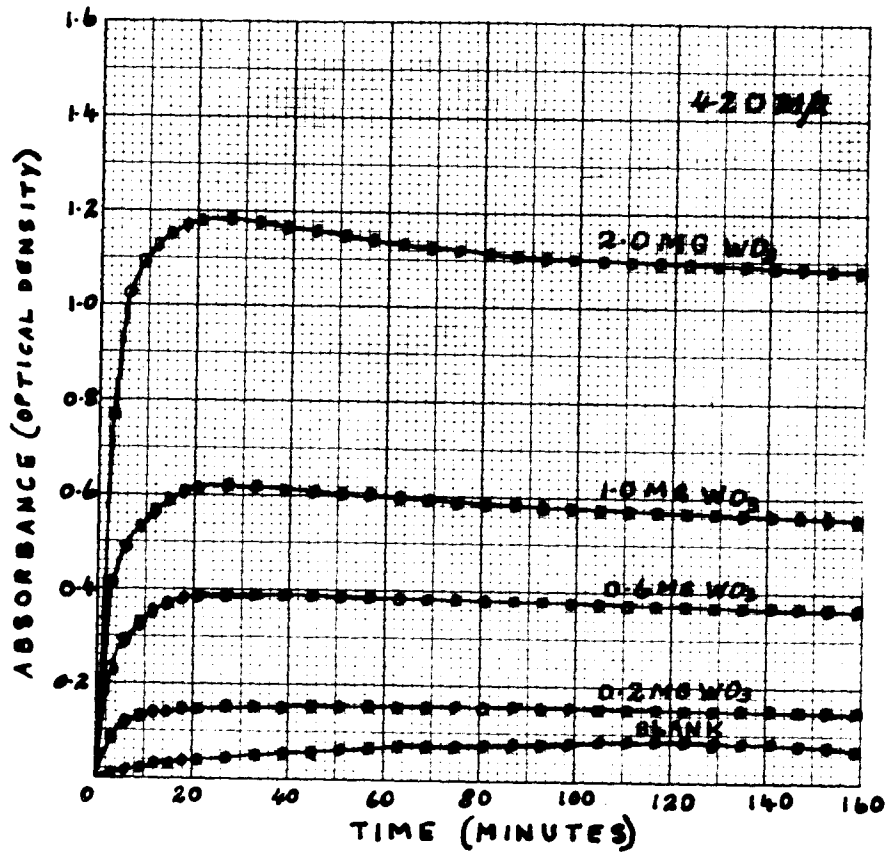


FIGURE 3. TUNGSTIC OXIDE CALIBRATION  
CURVE — ABSORBANCE VERSUS  
CONCENTRATION.

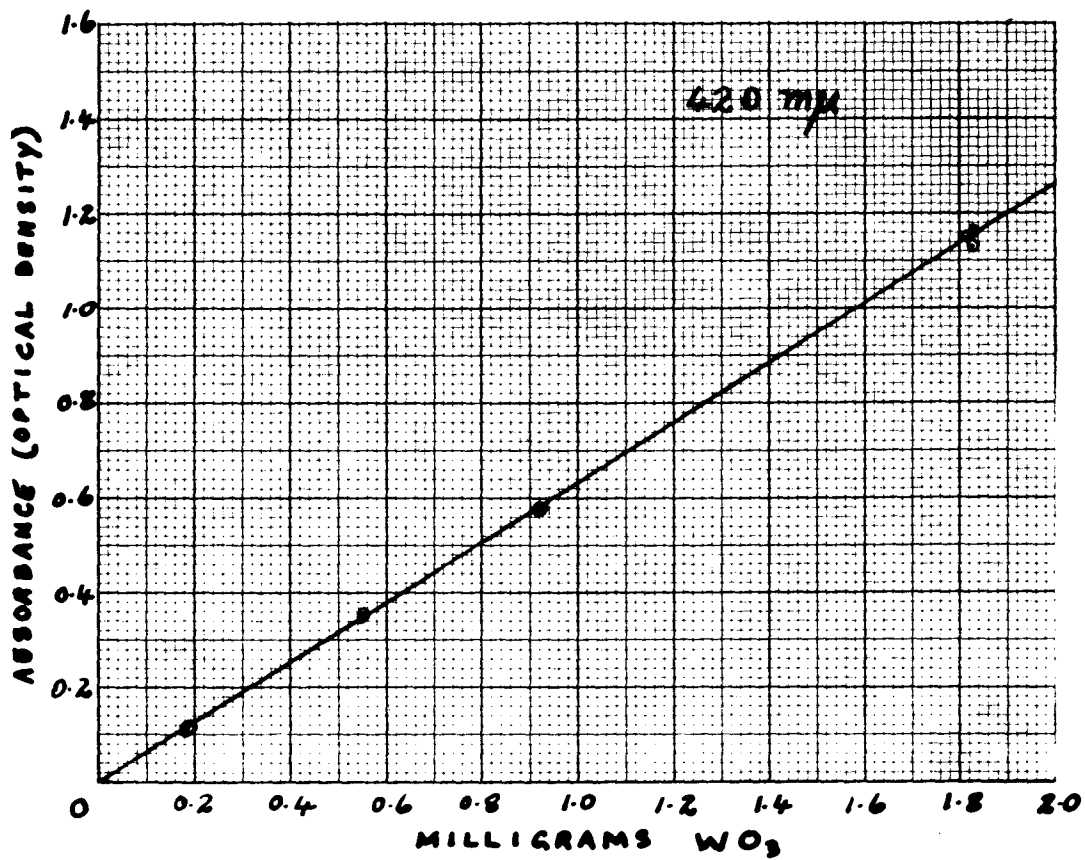


TABLE 1

## VOLATILITY OF 1.00 GRAM TUNGSTEN IN HALOGENATING MIXTURES

Gas Mixture and Flow Rate MLS/MINUTE	Temp. °C.	Time HOUR	Gas Mixture and Flow Rate MLS/MINUTE	Temp °C.	Time HOUR
HYDROGEN CHLORIDE-OXYGEN MIXTURES					
300HCl : 750 <sub>2</sub>	800	0.8 *	150HCl : 750 <sub>2</sub>	900	0.7
300HCl : 750 <sub>2</sub>	800	0.4	150HCl : 750 <sub>2</sub>	1000	0.3
300HCl : 1000 <sub>2</sub>	800	0.5	200HCl : 1000 <sub>2</sub>	800	0.5
150HCl : 500 <sub>2</sub>	600	5.0	200HCl : 1000 <sub>2</sub>	800	0.5*
150HCl : 500 <sub>2</sub>	800	1.0	50HCl : 500 <sub>2</sub>	600	8.0
150HCl : 500 <sub>2</sub>	900	0.8	50HCl : 500 <sub>2</sub>	800	2.0
150HCl : 750 <sub>2</sub>	700	1.5	100HCl : 1000 <sub>2</sub>	700	3.0*
150HCl : 750 <sub>2</sub>	700	1.2*	100HCl : 1000 <sub>2</sub>	800	0.9*
150HCl : 750 <sub>2</sub>	800	0.7	100HCl : 1000 <sub>2</sub>	900	0.8*
150HCl : 750 <sub>2</sub>	900	0.5	50HCl : 1000 <sub>2</sub>	800	5.0*
OXYGEN DISPERSED THROUGH CHLOROFORM					
100 O <sub>2</sub>	600	2.5	100 O <sub>2</sub>	800	0.8 *
100 O <sub>2</sub>	800	0.8	300 O <sub>2</sub>	800	1.0 *
300 O <sub>2</sub>	800	0.7			
MISCELLANEOUS MIXTURES					
100HCl (dry)	800	no reaction	50Cl <sub>2</sub> : 500 <sub>2</sub>	800	11.5 *
100HCl (moist)	800	no reaction	1000 <sub>2</sub> -HBR (48%)	800	oxidizes only
100HCl (moist)	700	2.0 *	1000 <sub>2</sub> -BR <sub>2</sub>	800	oxidizes only
100HCl (moist)	900	0.8 *	100N <sub>2</sub> -BR <sub>2</sub>	800	5.0
100Cl <sub>2</sub> (dry)	600	8.0	1000 <sub>2</sub> -HI (47%)	800	oxidizes only
100Cl <sub>2</sub> (dry)	800	0.3	1000 <sub>2</sub> -HCl (37%)	800	16.0
100Cl <sub>2</sub> (moist)	800	2.0	100 CF <sub>2</sub> Cl <sub>2</sub>	800	no reaction
100Cl <sub>2</sub> (moist)	800	2.5 *	100 CF <sub>2</sub> Cl <sub>2</sub>	800	0.3 *
50Cl <sub>2</sub> : 500 <sub>2</sub>	800	0.3	1000 <sub>2</sub> - CCl <sub>4</sub>	800	1.0

\* samples first oxidized in air at 800°C overnight

TABLE 2

CHLORINATING GASES CAUSING NO LOSS OF  $\text{ThO}_2$  AT  $800^\circ\text{C}$ .

Gas Mixture and Flow Rate	Time of Flow	Sample Number	$\text{ThO}_2$ Before	$\text{ThO}_2$ After	$\text{ThO}_2$ Loss
MLS/MINUTE	HOOR		GRAM	GRAM	GRAM
HYDROGEN CHLORIDE-OXYGEN MIXTURES					
100HCl : 200 <sub>2</sub>	2.0	(1)	0.0297	0.0296	0.0001
		(2)	0.0348	0.0349	-0.0001
80HCl : 200 <sub>2</sub>	2.0	(1)	0.0297	0.0297	0.0000
		(2)	0.0348	0.0349	-0.0001
150HCl : 500 <sub>2</sub>	2.0	(1)	0.1113	0.1113	0.0000
200HCl : 1000 <sub>2</sub>	2.0	(1)	0.0170	0.0170	0.0000
		(2)	0.0180	0.0180	0.0000
100HCl : 1000 <sub>2</sub>	2.0	(1)	0.0170	0.0170	0.0000
		(2)	0.0184	0.0184	0.0000
HYDROGEN CHLORIDE (MOIST)					
100HCl	2.0	(1)	0.0296	0.0295	0.0001
		(2)	0.0349	0.0348	0.0001
CHLORINE-OXYGEN					
50Cl <sub>2</sub> : 500 <sub>2</sub>	2.0	(1)	0.0677	0.0678	-0.0001
CHLORINE (MOIST)					
100Cl <sub>2</sub>	2.0	(1)	0.0676	0.0677	-0.0001
		(2)	0.0401	0.0402	-0.0001

TABLE 3

CHLORINATING GASES CAUSING LOSS OF  $\text{ThO}_2$  AT  $800^\circ\text{C}$ 

Gas Mixture and Flow Rate	Time of Flow	Sample Number	$\text{ThO}_2$ Before	$\text{ThO}_2$ After	$\text{ThO}_2$ Loss
MLS/MINUTE	HOURS		GRAM	GRAM	GRAM
OXYGEN DISPERSED THROUGH CHLOROFORM (DRY)					
100 $\text{O}_2$	2	(1)	0.0345	0.0337	0.0008
		(2)	0.0356	0.0352	0.0004
		(1)	0.0107	0.0107	0.0000
		(1)	0.0107	0.0106	0.0001
		(1)	0.0106	0.0104	0.0002
OXYGEN DISPERSED THROUGH CHLOROFORM (MOIST)					
100 $\text{O}_2$	4	(1)	0.0104	0.0100	0.0004
	2	(1)	0.0171	0.0164	0.0007
	2	(1)	0.0171	0.0160	0.0011
OXYGEN DISPERSED THROUGH CARBON TETRACHLORIDE					
100 $\text{O}_2$	2	(1)	0.0289	0.0248	0.0041
	2	(2)	0.0304	0.0271	0.0033
CHLORINE (DRY)					
100 $\text{Cl}_2$	2	(1)	0.0691	0.0676	0.0015
	2	(2)	0.0413	0.0401	0.0012
HYDROGEN CHLORIDE (DRY)					
100HCl (DRY)	2	(1)	0.0348	0.0304	0.0044
		(2)	0.0295	0.0289	0.0006
	1	(1)	0.0463	0.0395	0.0068
		(2)	0.0602	0.0583	0.0019
	1	(1)	0.0583	0.0475	0.0108
		(2)	0.0395	0.0371	0.0024

TABLE 4  
 CHLORINATION OF ThO<sub>2</sub> MIXED WITH  
 1.00 GRAM TUNGSTEN AT 800°C.

Gas Mixture and Flow Rate	Time of Flow	ThO <sub>2</sub> Before	ThO <sub>2</sub> After **	ThO <sub>2</sub> Loss
MLS/MINUTE	HR	GRAM	GRAM	GRAM
150HCl : 75O <sub>2</sub>	1.0	0.0288	0.0288	0.0000
	1.0	0.0190	0.0190	0.0000
50Cl <sub>2</sub> : 50O <sub>2</sub>	0.2	0.0402	0.0002	0.0400
100O <sub>2</sub> : CCl <sub>4</sub>	1.0	0.0180	0.0007	0.0173
100HCl (moist)	1.0 *	0.0100	0.0099	0.0001
100O <sub>2</sub> -CHCl <sub>3</sub> (moist)	1.0 *	0.0072	0.0069	0.0003
100O <sub>2</sub> -CHCl <sub>3</sub> (moist)	1.0	0.0163	0.0163	0.0000

\* samples first oxidized in air at 800°C. overnight

\*\* ThO<sub>2</sub> weights corrected for WO<sub>3</sub> contamination

TABLE 5  
 SELECTED GAS MIXTURES AND CONDITIONS FOR  
 RAPID CHLORINATION OF TUNGSTEN WITHOUT LOSS OF ThO<sub>2</sub>

Gas Mixture and Ratio	Flow Rate MLS/MINUTE	State of Sample	Temp °C.
HCl : O <sub>2</sub> 4 : 1	100 - 300	Metallic or oxidized	800
HCl : O <sub>2</sub> 3 : 1	100 - 300	Metallic or oxidized	800
HCl : O <sub>2</sub> 2 : 1	100 - 300	Metallic or oxidized	800
HCl : O <sub>2</sub> 1 : 1	100 - 300	Metallic or oxidized	800
HCl (moist)	100	oxidized	800
O <sub>2</sub> dispersed through CHCl <sub>3</sub> and H <sub>2</sub> O	100	Metallic or oxidized	800

TABLE 6

CHLORINATION OF METALLIC THORIUM MIXED WITH  $\text{ThO}_2$   
AND WUNGSTEN AT  $800^\circ\text{C}$ .

Sample Number	Gas Mixture and Flow Rate	Contents of Boat	Residue	Residue Corrected for $\text{WO}_3$	$\text{ThO}_2$ From Thorium
	MLS./MIN.	GRAM	GRAM	GRAM	GRAM
1	150 HCl 75 $\text{O}_2$	$\text{ThO}_2 = 0.0285$ Th = 0.0190 (AS $\text{ThO}_2 = 0.0216$ ) W = 1.00	0.0512	0.0502	0.0217
2	150 HCl 75 $\text{O}_2$	$\text{ThO}_2 = 0.0191$ Th = 0.0009 (AS $\text{ThO}_2 = 0.0010$ ) W = 1.00	0.0203	0.0201	0.0010
3	100 $\text{O}_2$ Through $\text{CHCl}_3$ and $\text{H}_2\text{O}$	$\text{ThO}_2 = 0.0116$ Th = 0.0235 (AS $\text{ThO}_2 = 0.0267$ ) W = 1.00	0.0394	0.0378	0.0262



TABLE 7

CHANGE IN WEIGHT OF COMBUSTION BOATS ON  
CHLORINATION OF TUNGSTEN

Boat Number	Boat Material	Initial Weight	Weight After First Chlorination	Weight After Third Chlorination
		GRAM	GRAM	GRAM
1	Alumina	13.7045	13.7052	13.7049
2	Alumina	16.2272	16.2280	16.2279
3	Alumina	16.4704	16.4711	16.4713
4	Porcelain	9.0537	9.0539	9.0537
5	Quartz	7.3711	7.3713	7.3714
6	Quartz	8.9649	8.9649	8.9650

TABLE 8

## PURITY OF EMPLOYED THORIUM METAL POWDER

Weight of Thorium Powder	Calculated Weight of ThO <sub>2</sub> (Thx 1.138)	Weight of Ignited Sample	Weight of Ignited Oxalate	Weight of Ignited Benzoate	Recovery of Calculated ThO <sub>2</sub> per cent
GRAM	GRAM	GRAM	GRAM	GRAM	
INITIAL SAMPLES IGNITED IN AIR ONLY					
0.1952	0.2220	0.2169			97.7
0.1818	0.2069	0.2022			97.7
CONTROLLED IGNITIONS - RESIDUES ANALYZED					
0.0881	0.1003	0.0982	0.0967		96.4
0.1002	0.1140	0.1110		0.1115	97.8

TABLE 9

## THORIA CONTENT OF SAMPLE (1) BY CHLORINATION

Gas Mixture and Flow Rate MLS/MINUTE	Temp °C	Weight of Sample GRAM	Weight of Residue GRAM	Correction for W O <sub>3</sub> GRAM	Thoria Per Cent
MOIST HCl -- OXIDIZED SAMPLE					
100 HCl	700	1.000	0.0193	0.0012	1.81
100 HCl	900	1.000	0.0190	0.0011	1.79
HCl : O <sub>2</sub> -- OXIDIZED SAMPLE					
100HCl : 1000 <sub>2</sub>	700	1.000	0.0283	0.0103	1.80
100HCl : 1000 <sub>2</sub>	900	1.000	0.0195	0.0013	1.82
150HCl : 750 <sub>2</sub>	700	1.000	0.0202	0.0018	1.84
HCl : O <sub>2</sub> -- METALLIC SAMPLE					
150HCl : 750 <sub>2</sub>	700	1.000	0.0185	0.0006	1.79
150HCl : 750 <sub>2</sub>	800	1.000	0.0187	0.0005	1.82
150HCl : 750 <sub>2</sub>	900	1.000	0.0184	0.0003	1.81
HCl : O <sub>2</sub> -- METALLIC SAMPLE					
150HCl : 750 <sub>2</sub>	1000	1.000	0.0180	0.0004	1.76
O <sub>2</sub> : CHCl <sub>3</sub> : H <sub>2</sub> O -- OXIDIZED SAMPLE					
1000 <sub>2</sub>	800	1.000	0.0191	0.0010	1.81

TABLE 10

## THORIA CONTENT OF SAMPLE (2) BY CHLORINATION

Gas Mixture and Flow Rate	Temp  °C	Weight of Sample  GRAM	Weight of Residue  GRAM	Correction for WO <sub>3</sub>  GRAM	Thoria  Per Cent
HCl : O <sub>2</sub> -- OXIDIZED SAMPLE					
100HCl : 1000 <sub>2</sub>	800	1.000	0.0182	0.0018	1.64
200HCl : 1000 <sub>2</sub>	800	1.000	0.0186	0.0016	1.70
200HCl : 1000 <sub>2</sub>	800	1.000	0.0186	0.0016	1.70
300HCl : 750 <sub>2</sub>	800	1.000	0.0188	0.0017	1.71
HCl : O <sub>2</sub> -- METALLIC SAMPLE					
200HCl : 1000 <sub>2</sub>	800	1.000	0.0174	0.0004	1.70
200HCl : 1000 <sub>2</sub>	800	2.000	0.0359	0.0015	1.72
300HCl : 750 <sub>2</sub>	800	1.000	0.0176	0.0005	1.71
300HCl : 750 <sub>2</sub>	800	2.000	0.0356	0.0012	1.72
O <sub>2</sub> : CHCl <sub>3</sub> : H <sub>2</sub> O -- OXIDIZED SAMPLE					
100 O <sub>2</sub>	800	1.000	0.0184	0.0014	1.70
100 O <sub>2</sub>	800	1.000	0.0181	0.0014	1.67
100 O <sub>2</sub>	800	1.000	0.0186	0.0014	1.72
O <sub>2</sub> : CHCl <sub>3</sub> : H <sub>2</sub> O -- METALLIC SAMPLE					
100 O <sub>2</sub>	800	1.000	0.0180	0.0010	1.70
100 O <sub>2</sub>	800	1.000	0.0176	0.0007	1.69
300 O <sub>2</sub>	800	1.000	0.0179	0.0008	1.71

TABLE 11

THORIA AND TUNGSTIC OXIDE CONTENT OF RESIDUES  
FROM SAMPLES (1) AND (2) ON EXTENDED CHLORINATION

Gas Mixture and Flow Rate	Weight of Sample	Temp.  °C	Extended Period  HOUR	Weight of Residue  GRAM	Correction for UO <sub>3</sub>  GRAM	Thoria  GRAM
HCl : O <sub>2</sub> -- SAMPLE (2) OXIDIZED						
200HCl : 100O <sub>2</sub>	1.000	800	2	0.0186	0.0016	0.0170
100HCl : 100O <sub>2</sub>	1.000	800	2	0.0185	0.0015	0.0170
HCl : O <sub>2</sub> -- SAMPLE (1) METALLIC						
150HCl : 75O <sub>2</sub>	1.000	900	1	0.0181	0.0004	0.0177
O <sub>2</sub> : CHCl <sub>3</sub> : H <sub>2</sub> O -- SAMPLE (2) OXIDIZED						
100O <sub>2</sub>	1.000	800	2	0.0170	0.0006	0.0164
O <sub>2</sub> : CHCl <sub>3</sub> (DRY) -- SAMPLE (2) OXIDIZED						
100O <sub>2</sub>	1.000	800	2	0.0165	0.0003	0.0160

TABLE 12

SOLUBILITY OF W, WO<sub>3</sub>, Th, Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O AND ThO<sub>2</sub> IN HF-HNO<sub>3</sub> MIXTURES

Beaker Number	Dissolving Acid Mixture	ThO <sub>2</sub> in 1.000 Gram Sample (2)	Th Calculated as ThO <sub>2</sub>	Th(NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O Calculated as ThO <sub>2</sub>	WO <sub>3</sub>	Weight of Ignited Residue	WO <sub>3</sub> in Ignited Residue	Total Thorium Addition as ThO <sub>2</sub>	ThO <sub>2</sub> in Ignited Residue
	MLS.	GRAM	GRAM	GRAM	GRAM	GRAM	GRAM	GRAM	GRAM
1	5HF 2HNO <sub>3</sub>	0.0171				0.0173	0.0001	0.0171	0.0172
2	5HNO <sub>3</sub> 2HF	0.0171	0.0013	0.0009	0.0013	0.0206	0.0014	0.0193	0.0192
3	5HNO <sub>3</sub> 2HF	0.0171				0.0170	0.0001	0.0171	0.0169
4	5HF 2HNO <sub>3</sub>	0.0171	0.0011	0.0005	0.0032	0.0220	0.0033	0.0187	0.0187
5	5HF 2HNO <sub>3</sub>			0.0521		0.0522		0.0521	0.0522
6	5HNO <sub>3</sub> 2HF			0.0129		0.0129		0.0129	0.0129

TABLE 13

## PURITY OF EMPLOYED THORIUM NITRATE TETRAHYDRATE

Weight of Sample	Calculated Weight of Oxide ( $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ $\times 0.479$ )	Weight of Ignited Oxalate	Weight of Ignited Benzoate	Weight of Ignited Fluoride	Purity
GRAM	GRAM	GRAM	GRAM	GRAM	Per Cent
0.1508	0.0722	0.0698			96.6
0.3339	0.1599	0.1542			96.6
0.1150	0.0551		0.0537		97.5
0.2000	0.0958		0.0930		97.1
0.1182	0.0566			0.0550	97.2
0.1022	0.0490			0.0474	96.9

TABLE 14

THORIA CONTENT OF SAMPLES (1) AND (2) BY THE HF-HNO<sub>3</sub> METHOD

Dissolving Container Material	Ignition Crucible Material	Sample Weight GRAM	Residue Weight GRAM	WO <sub>3</sub> Correction GRAM	Thoria Per Cent
ANALYSIS OF SAMPLE (1)					
Polyethylene	Quartz	1.000	0.0178	0.0001	1.77
"	"	2.000	0.0361	0.0004	1.79
Platinum	Platinum	1.000	0.0180	0.0002	1.78
"	"	1.000	0.0181	0.0002	1.79
ANALYSIS OF SAMPLE (2)					
Polyethylene	Platinum	1.000	0.0173	0.0001	1.72
"	"	1.000	0.0173	0.0001	1.72
"	"	2.000	0.0344	0.0002	1.71
ANALYSIS OF SMALL PIECES FROM LOT (2)					
Polyethylene	Platinum	1.000	0.0173	0.0002	1.71
"	"	1.000	0.0171	0.0002	1.69
"	"	1.000	0.0172	0.0002	1.70
"	"	1.000	0.0170	0.0001	1.69



TABLE 15

SEPARATION OF THORIUM FROM URANIUM, LANTHANUM  
AND RARE EARTHS BY THE BENZOIC ACID METHOD

Sample Number	Weight of ThO <sub>2</sub>	Weight of CeO <sub>2</sub>	Weight of U <sub>3</sub> O <sub>8</sub>	Weight of La <sub>2</sub> O <sub>3</sub>	Weight of Residue Single Separation	Weight of Residue Double Separation
	GRAM	GRAM	GRAM	GRAM	GRAM	GRAM

PRECIPITATION IN PRESENCE OF NaHSO<sub>4</sub>

1	0.0081				0.0084	
2	0.0198				0.0206	
3	0.0073	0.0062		0.0051	0.0100	0.0078

SODIUM SALTS REMOVED BY NH<sub>4</sub>OH SEPARATION

4	0.0342				0.0343	
5	0.0168	0.0358	0.0099	0.0059	0.0187	0.0166
6	0.0170	0.0416	0.0103	0.0040	0.0198	0.0168

TABLE 16

PURITY OF  $\text{ThO}_2$  EMPLOYED IN TUNGSTEN ELECTRODES

Sample Number	Weight of Sample (2)	Ignited Oxalate Residue	Ignited Benzoate Residue	Ignited Benzoate Residue Following Preliminary Fluoride Separation
	GRAM	GRAM	GRAM	GRAM
1	1.000	0.0166		
2	1.000		0.0171	
3	1.000			0.0168
4	1.000			0.0170

TABLE 17

COMPARISON OF  $\text{ThO}_2$  DETERMINATIONS OF SAMPLES (1) and (2)  
BY CHLORINATION AND WET METHODS

METHOD OF ANALYSIS	SAMPLE IDENTITY	NUMBER OF DETERMINATIONS	AVERAGE $\text{ThO}_2$ Per Cent
RESIDUES CORRECTED FOR $\text{WO}_3$			
Chlorination of Oxidized Sample	Sample (1)	6	1.81
	Sample (2)	6	1.70
Chlorination of Metallic Sample	Sample (1)	3	1.81
	Sample (2)	7	1.71
HF- $\text{HNO}_3$	Sample (1)	4	1.78
	Sample (2)	7	1.71
$\text{ThO}_2$ SEPARATED CHEMICALLY FROM $\text{WO}_3$ AND RARE EARTHS			
HF- $\text{HNO}_3$ , Followed by $\text{NaHSO}_4$ Fusion, Ammonium Hydroxide and Benzoic Acid Precipitations	Sample (2)	1	1.71
$\text{ThO}_2$ ISOLATED CHEMICALLY FROM OTHER ELEMENTS			
HF- $\text{HNO}_3$ , Followed by $\text{NaHSO}_4$ Fusion, HF Precipitation, $\text{NaHSO}_4$ Fusion, Ammonium Hydroxide and Benzoic Acid Precipitations	Sample (2)	2	1.69

TABLE 13

THE OXIDATION OF HCl WITH O<sub>2</sub>

Gas Mixture and Flow Rate	Boat Material	0.1N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Time	Amount of Cl <sub>2</sub> Formed	Amount of HCl Employed	Conversion to Cl <sub>2</sub>
MLS/MIN		MLS	MIN	GRAM	GRAM	PER CENT
TITRATION DURING CHLORINATION OF W AT 800°C						
100HCl 50O <sub>2</sub>	Quartz	35.0	71	0.124	11.2	1.11
100HCl 50O <sub>2</sub>	Alumina	10.0	11	0.0355	1.79	1.98
TITRATION AFTER CHLORINATION OF W AT 800°C						
100HCl 50O <sub>2</sub>	Quartz	11.0	20	0.0390	3.26	1.20
100HCl 50O <sub>2</sub>	Alumina	10.0	11	0.0355	1.79	1.98

TABLE 19

THE OXIDATION OF  $\text{CHCl}_3$  WITH  $\text{O}_2$ 

Gas Mixture and Flow Rate	0.1N $\text{Na}_2\text{S}_2\text{O}_3$	0.1N NaOH	Time
MLS/MINUTE	MLS	MLS	Seconds
GAS DISPERSED THROUGH EMPTY TUBE AT $800^\circ\text{C}$			
100 $\text{O}_2$ dispersed through dry $\text{CHCl}_3$	20.0		285
	20.0		255
100 $\text{O}_2$ dispersed through dry $\text{CHCl}_3$		30.0	65
		30.0	75

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