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DETERMINATION OF TRACES OF URANIUM METAL BY DECOMPOSITION OF THE HYDRIDE

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A. S. Meyer, Jr., B. L. McDowell, J. C. White

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ANALYTICAL CHEMISTRY DIVISION

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ABSTRACT

Two methods were developed for the determination of uranium metal in UF_3 and mixtures of UF_3 with other fluoride compounds. A simplified method of determination which has a relatively high degree of precision (coefficient of variation 2 per cent) is carried out by decomposing the hydride in an atmosphere of carbon dioxide and subsequently measuring the hydrogen over an aqueous solution of potassium hydroxide. The ignition of the hydride in an atmosphere of oxygen and volumetric measurement of the water at reduced pressures provide a more sensitive method of determination. The coefficient of variation of the latter procedure is 7 per cent. The yield of gas from the reaction of the hydride with ammonia and gaseous hydrogen chloride was found to be neither stoichiometric nor reproducible.

DETERMINATION OF TRACES OF URANIUM METAL BY DECOMPOSITION OF THE HYDRIDE

INTRODUCTION

This study was carried out to develop a method for the determination of small concentrations of uranium metal in UF_3 and in mixtures of UF_3 with other fluoride compounds. The uranium metal in such samples is present as a result of disproportionation of UF_3 or as excess metal which remains after the reduction of UF_4 with metallic uranium. This investigation was limited to the study of analytical procedures based upon the measurement of the quantity of hydrogen combined with the uranium metal after hydrogenation of the sample.

The composition of the uranium hydride has been reported to correspond closely to UH_3[1,2]. By measuring the water obtained by the combustion of large samples of uranium hydride, Warf and Johnson[3] showed that the hydride corresponded to the formula $UH_{2.96}$. This deviation from an integral ratio of uranium to hydrogen has been attributed to the presence of carbides, oxides, or other impurities in the uranium metal[4].

The hydride corresponding to the formula $UH_{2.96}$ was prepared by heating uranium metal in an atmosphere of hydrogen at 250°C. With metal turnings, the temperature for optimum conversion was reported to be 250°C, the reaction rate decreasing considerably above 300°C and becoming extremely slow above 380°C[3]. More detailed studies by Albrecht and Mallett[5] confirm the above temperature range.

Warf and Johnson[3] decomposed samples of uranium hydride in a vacuum (approximately 0.1 mm Hg) at 256°C for 60 minutes. They reported that 6- to 7-g samples were approximately 50 per cent decomposed after one hour. The decomposition curves for the UH_3 show a rather slow increase in decomposition

rate with temperature[6]. The thermal decomposition of the UH_3 in an evacuated system was not applied to the analysis of these samples because of the inherent experimental difficulties associated with the transfer and measurement of small quantities of slowly liberated hydrogen. A modification of the Dumas technique in which the hydrogen is transferred by a readily separable gas appeared to be feasible.

It has been reported[2] that aqueous solutions of various oxidizing agents dissolve UH_3 with the liberation of hydrogen and oxidation of the uranium to the tetravalent or hexavalent state. The most satisfactory reagents for this reaction are the silver salts. Since it appeared highly probable that trivalent uranium, which is present in the samples, would also react with these solutions to produce hydrogen, this method for the determination of the hydrogen in the UH_3 was not tested.

Katz and Rabinowitch give equations for the reactions of UH_3 with certain gases. These equations, which are listed below, offer three possible approaches to the determination of the hydrogen which is present in UH_3.

$$8UH_3 + 14NH_3 \longrightarrow 8UN_{1.75} + 33H_2 \quad [7] \qquad (1)$$

$$UH_3 + 3HCl \longrightarrow UCl_3 + 3/2\ H_2 \quad [8] \qquad (2)$$

$$2UH_3 + 7/2\ O_2 \longrightarrow 2UO_2 + 3H_2O \quad [9] \qquad (3)$$

Initial observation of the three equations indicate that decomposition of the UH_3 in an atmosphere of either ammonia or hydrogen chloride offers a possible volumetric method for the determination of the hydrogen, and decomposition in an atmosphere of oxygen, a possible gravimetric method. The amount of data available on the reactions of UF_3 with ammonia, hydrogen chloride, and oxygen is not sufficient to justify the choice of any one reagent.

EXPERIMENTAL AND RESULTS

Preparation of Uranium Hydride

Uranium metal in the form of turnings of approximately 20-mil thickness were used as metal samples throughout this work. The oxide coating was removed from these samples with HNO_3 (1:3). The samples were rinsed with water and acetone, and then dried immediately before weighing. The samples were placed in a platinum boat in a quartz combustion tube. The combustion tube was flushed with hydrogen for about 15 minutes and then heated to 230 to 250° C. Hydrogen, which was obtained from the reaction of zinc with dilute hydrochloric acid, was purified by passing it through Ascarite and anhydrous magnesium perchlorate. The hydrogenation was continued for 30 minutes after the sample had disintegrated. The turnings were thus converted to a black powder after about 15 minutes of exposure to hydrogen at 250° C. The reacted sample was then cooled to room temperature in an atmosphere of hydrogen.

Samples of UF_3 and UF_3 which had been fused with other fluoride compounds were heated for a period of 30 minutes to one hour in an atmosphere of hydrogen in order to convert any uranium metal in the samples to UH_3. There was no noticeable evidence of change taking place in the sample during hydrogenation.

Decomposition of UH_3 in an Atmosphere of Carbon Dioxide

Uranium hydride reacts with carbon dioxide to produce UO_2. The UO_2 is an impure product containing some uranium carbide[9].

Essentially the same apparatus was used for the experimental work on the decomposition of UH_3 in atmospheres of carbon dioxide, gaseous hydrogen chloride, and ammonia. Hydrogenation of the sample (previous section) and subsequent decomposition of the UH_3 were carried out in a 13- x 300-mm quartz combustion tube which was heated with a Fisher micro-combustion furnace.

The hydrogen and carbon dioxide (hydrogen chloride or ammonia) were passed into the combustion tube through a three-way stopcock so that the gases could be interchanged without contamination by atmospheric oxygen or water. The exit end of the combustion tube was connected to a three-way stopcock by means of which the effluent gases from the furnace could be passed either through a bubble counter or into a 25-ml azotometer filled with 1:1 potassium hydroxide solution. When traces of uranium metal were determined a 5-ml azotometer was used. A Dewar flask filled with dry ice and sealed with a Hershberg[10] valve was used as a carbon dioxide generator. The appearance of micro bubbles of approximately 0.1 mm in diameter when the gas was passed into the potassium hydroxide was used as a satisfactory criterion of purity of the carbon dioxide.

Three samples of uranium on which calculations indicated a yield of 10 to 15 ml of hydrogen were converted to UH_3. The first of these samples had been cleaned about three weeks prior to hydrogenation and was covered with a yellowish-brown oxide. The other two samples were cleaned just prior to weighing. After the hydrogenation of a sample was completed, the combustion tube was cooled to room temperature and then flushed with carbon dioxide until micro bubbles were obtained when the gas was passed into the azotometer. The azotometer was filled to the zero mark while the flow of carbon dioxide was adjusted to 2 or 3 bubbles per second. The combustion tube was then heated to 400° C and held at this temperature until the rate of evolution of gases, insoluble in 1:1 KOH, became insignificant. The volume of gas was measured repeatedly after successive increments of temperature rise. The volumes of gas were corrected for temperature and pressure; following which the yield of gas was calculated in terms of moles of gas per mole of uranium metal. The values which were obtained at selected temperatures are recorded in Table 1.

Table 1

Volume of Gas Produced by the Reaction of UH_3 with Carbon Dioxide

Gases Collected Over 1:1 Potassium Hydroxide

Sample Number	Uranium, mg	Ignition Temperature, °C	Corrected Gas Volume, ml	Moles of Gas per Mole of U
1	66.3[a]	750	8.81	1.41
2	94.5	430	26.0	2.93
		850	28.1	3.16
3	73.7	380	20.0	2.88
		820	22.1	3.19

[a] Sample coated with oxide. This sample could not be completely disintegrated after heating for 4 hours in an atmosphere of hydrogen at 250° C.

The much smaller volume of gas obtained from the first sample indicates that the oxide coating interferes with the hydrogenation reaction or with the reaction upon ignition. This assumption is also supported by the extended period of heating which was required to complete the disintegration of the metal by hydrogenation.

The volumes of gas which were obtained for the second and third samples are equal to approximately twice that which corresponds to the stoichiometry of the hydride (1.5 moles of hydrogen per mole of uranium). On ignition in an atmosphere of carbon dioxide, UH_3 is reported to be converted to impure uranium oxide[9]. The following reactions may be postulated:

$$2UH_3 + 2xCO_2 \longrightarrow 2UO_x + 3H_2 + 2xCO \quad (4)$$

$$2UH_3 + xCO_2 \longrightarrow 2UO_x + 3H_2 + xC \quad (5)$$

The gas yield noted for the samples may be explained by equation 4, since hydrogen and carbon monoxide are not distinguishable when measured over an alkaline solution. The volume of mixed gases appeared to be reproducible;

therefore, the procedure was believed to be applicable to the determination of uranium metal in these samples provided that carbon dioxide was not also reduced by trivalent uranium.

The volumes of gas evolved at temperatures between 400 and 600° C permit the postulation of the formation of U_2O_3 in equation 4. Since this oxide has not been reported, an additional sample was converted to the hydride and ignited under an atmosphere of carbon dioxide at 480° C. The residual oxide was examined by X-ray diffraction analysis. This analysis indicated that the sample consisted of greater than 90 per cent UO_2.

In order to determine whether a gas insoluble in 1:1 KOH was produced by the reaction of UF_3 with the carbon dioxide, samples of very pure UF_3 were ignited in an atmosphere of carbon dioxide. These samples were weighed in a platinum boat and placed in the combustion tube. Carbon dioxide was passed through the apparatus until microbubbles were obtained in the azotometer. The combustion tube was then heated to 400° C and held at this temperature until the rate of evolution of gas became negligible. The volume of insoluble gas was then recorded. During the experiment, the temperature was increased by successive increments up to 800° C. The volumes of gas produced at certain temperatures are recorded in Table 2.

Table 2

Volumes of Gas Produced by the Reaction of UF_3 with Carbon Dioxide

Collected over 1:1 Potassium Hydroxide

UF_3, mg	Ignition Temperature, °C	Corrected Gas Volume, ml	Moles of Gas per Mole of U
97.0	435	2.58	0.34
	490	3.18	.43
	800	3.48	.47
126.1	440	4.41	.46
	500	4.55[a]	.48

[a] This run was discontinued when the azotometer inlet plugged.

Since the samples for which this method was intended contain traces of uranium metal in the presence of large amounts of trivalent uranium, the yield of gas indicated in Table 2 cannot be tolerated. The gas volumes correspond to oxidation of trivalent uranium to tetravalent uranium with consequent reduction of an equivalent amount of carbon dioxide to carbon monoxide. X-ray diffraction patterns of the ignited residue indicated that the material was composed principally of UO_2 and UF_4 with traces of UF_3.

Since the volume of carbon monoxide formed by the oxidation of trivalent uranium to tetravalent uranium by carbon dioxide could not be tolerated, attempts were made to eliminate the carbon monoxide from the effluent gases. The apparatus was altered by placing appropriate gas scrubbers between the furnace and the three-way stopcock to the azotometer. To avoid excessive increase in the holdup of the system, the choice of reagents was limited to those which were sufficiently active to eliminate the carbon monoxide when used in a single scrubber of low volume. Several mixtures of reactants for the oxidation of carbon monoxide were investigated. Solutions of cuprous salts[11], "Hopcalite" - an activated mixture of CuO and MnO_2[12], "Hoolamite" - a mixture of I_2O_5 and fuming sulfuric acid on pumice[13], and a mixture of I_2O_5 and pumice[14] were all considered. Only the "Hoolamite" and I_2O_5-pumice mixture appeared feasible.

A 15- x 200-mm gas scrubbing tower with a helical baffle was incorporated in the gas train for the removal of carbon monoxide. The scrubber was filled with a suspension of 5 g of pulverized I_2O_5 (iodic acid dehydrated at 235° C for one hour) in 15 ml of fuming sulfuric acid. The effluent gases from the ignition of a sample of very pure UF_3 were passed through the scrubber. The ignition was discontinued when it became evident that a significant fraction

of the carbon monoxide was unreacted. Approximately 2 g of powdered pumice was then added to the scrubbing tower to produce a thick slurry, and then the gas which was evolved by a second sample of UF_3 was measured. The results of these tests are recorded in Table 3.

The oxidation of carbon monoxide to carbon dioxide by I_2O_5 at elevated temperatures has been reported[14]. A temperature range of 120 to 150° C is recommended. The scrubbing tower was replaced by a 10-mm combustion tube which was packed to a length of 10 cm with I_2O_5. The tube was then heated to 150° C and a sample of UF_3 was ignited in the combustion tube. The 10-mm combustion tube was repacked with a mixture which was prepared by grinding I_2O_5 with one-half its volume of powdered pumice. The volume of gas derived from a sample of UF_3 with this reagent is shown in Table 3.

Table 3

Tests of Reagents for the Oxidation of Carbon Monoxide to Carbon Dioxide

Oxidation Reagent	UF_3, mg	Ignition Temp., °C	Corrected Gas Volume, ml	Mole Ratio Gas/U
$H_2SO_4 \cdot SO_3$ + I_2O_5	287	650	3.1	0.14
$H_2SO_4 \cdot SO_3$ + I_2O_5 + pumice	266	750	1.6	0.08
I_2O_5 at 150° C	285	750	1.9	0.08
I_2O_5 + pumice at 150° C	297	700	0.27	0.012

Since the results obtained with the last reagent appeared to be satisfactory, the proposed experimental procedure was repeated with a sample of uranium metal with the I_2O_5-pumice tube at 150° C being used in the system. These results are tabulated in Table 4.

Table 4

Determination of Uranium Metal in Uranium Turnings

All samples except as noted were ignited at 400° C

Sample Weight, mg	Corrected Volume, ml	Moles Hydrogen Per Mole Uranium	Uranium Metal, Per Cent
92.7 (375° C)	12.23	1.40	-
(400° C)	12.54	1.44	96.0
(550° C)	12.56	1.44	96.0
94.6	12.88	1.45	96.5
86.9	12.23	1.50	99.5
42.2	2.97	0.75	50.0
46.6	6.13	1.40	89.2
41.0	5.95	1.55	102.6
107	14.45	1.43	95.6
		Average	96.9
		Coefficient of Variation	2 per cent

From the data, presented in Table 3, it can be seen that the carbon monoxide, formed when the UF_3 or UH_3 is ignited in an atmosphere of Carbon dioxide, is removed almost quantitatively by the passage of the effluent gases over a mixture of I_2O_5 and powdered pumice heated to a temperature of 150° C.

The data for several samples of uranium metal, presented in Table 4, appeared to be sufficiently precise and accurate for the method to be applied to the determination of uranium metal in UF_3 and in mixtures of UF_3 with other fluoride compounds. The low average uranium recovery may be explained by the assumption that the uranium metal may have contained small amounts of impurities such as oxygen and carbon. The spectrographic analysis of the uranium metal indicated that the combined metallic impurities were less than 500 ppm.

Two of the samples which had been converted to the hydride were allowed to stand overnight before ignition in an atmosphere of carbon dioxide. The results (50 and 89 per cent) of these two determinations are obviously in gross error.

On the basis of these results it is recommended that samples be ignited as soon as possible after conversion to the hydride. The conditions of the I_2O_5-pumice tube is a very critical factor in the determination. Each time a new I_2O_5-pumice tube is placed in the gas train a thorough flushing is necessary to remove all gases insoluble in 1:1 KOH. The other result (103 per cent), excluded from the statistical calculations, was obtained immediately after the introduction of a freshly filled I_2O_5-pumice tube.

The method was then tested with two samples of UF_3. Samples were weighed into the platinum boat. After the train was flushed with hydrogen, the samples were ignited in an atmosphere of hydrogen at 250° C for 30 minutes to convert any metal present to UH_3. The decomposition of the UF_3 was carried out according to the procedure which was used for the uranium metal. The data for the samples of UF_3 are presented in Table 5.

Further evaluation of the method was made with some samples of fused potassium fluoride containing UF_3. These samples were treated in exactly the same manner as UF_3 samples. The evolution of gas from these samples was much more rapid than from the UF_3 samples previously mentioned. In most cases the hydrogen was completely evolved after 30 minutes; nevertheless, all samples were ignited for one hour. The test results of these samples are presented in Table 5.

Table 5

Determination of Uranium Metal in Samples Which Contain Trivalent Uranium

Sample heated in an atmosphere of hydrogen at 250° C for 30 minutes
Decomposition of UH_3 at 400° C in an atmosphere of carbon dioxide

Sample Identification	Sample Weight, mg	Corrected Gas Volume, ml	Uranium Metal, Per Cent
UF_3-1	157	0.11	0.31
UF_3-2	276	0.33	0.88
	332	0.43	0.92
$KF \cdot UF_3$-1	396	6.71	10.50
	464	6.70	9.40
$KF \cdot UF_3$-2	354	0.13	0.27
	916	0.30	0.23
$KF \cdot UF_3$-3	405	2.17	3.80
	210	1.18	3.97
$KF \cdot UF_3$-4	194	0.09	0.31
	270	0.10	0.26
$KF \cdot UF_3$-5	489	0.10	0.14
	776	0.17	0.15

The results, presented in Table 5, seem to indicate good agreement between duplicate samples. The method also appears to be applicable to mixed fluoride samples. When the uranium metal content is very low, a large sample is necessary to yield a measurable quantity of hydrogen. The small volumes of gas which were obtained for these samples indicate that the concentration limit of this procedure is approximately 0.1 per cent uranium when the hydrogen is measured at atmospheric pressure in a micro-azotometer.

The procedure was next applied to UF_3 which had been produced by the reduction of UF_4 with metallic uranium. The samples were analyzed in exactly the same manner as the previous UF_3 samples. It was necessary, however, to

heat the samples in an atmosphere of carbon dioxide for a period of 8 to 20 hours depending upon the sample size. The data for these samples are tabulated in the following table.

Table 6

Determination of Uranium Metal in UF_3 Produced by the Reduction of UF_4 with Uranium Metal

Sample Identification	Sample Weight, mg	Corrected Gas Volume, ml	Uranium Metal, Per Cent
UF-2	820	3.92	3.40
	901	4.93	3.88
UF-3	476	>5 [a]	-
	161	4.09	17.98
	1151	7.69	4.74
	1271	1.99	1.10
	517	1.03	1.41
UF-4	1057	1.64	1.10
	791	2.11	1.88

[a] A 5-ml azotometer was used. The volume of gas was greater than 5 ml; therefore uranium metal could not be calculated.

The results obtained for these UF_3 samples are very erratic. Due to the length of time necessary to decompose the hydride, the I_2O_5 tubes may have become inactive thus allowing some carbon monoxide to be measured in the azotometer. A possible explanation for the lengthy decomposition periods would be that the uranium metal is imbedded in the particles of UF_3 and is not readily accessible to the carbon dioxide. Obviously the decomposition of the hydride in an atmosphere of carbon dioxide is not a satisfactory method for the determination of the uranium in such samples; accordingly, the decomposition of the hydride in other gases was studied.

Decomposition of UH_3 in an Atmosphere of Ammonia

An intermediate nitride, of approximate composition, $UN_{1.75}$, is reported[7] to be formed by the reaction of UH_3 and ammonia at elevated temperatures and ordinary pressures. Under carefully controlled conditions it was believed that the composition of the nitride and the consequent yield of hydrogen might be reproducible. The reaction between ammonia and uranium metal, according to Katz and Rabinowitch[7], begins at 400° C. This reaction at ordinary pressures also produces a nitride of approximate composition, $UN_{1.75}$.

Certain modifications of the apparatus were necessary before the ammonia could be used. A Dewar flask, which was filled with liquid ammonia, was substituted for the carbon dioxide generator. The I_2O_5-pumice tube was removed. The azotometer was filled with a 1:2 solution of sulfuric acid. A small iron wire, sealed in glass, and moved about by a horseshoe magnet, was incorporated in the azotometer in order to detach bubbles of insoluble gases from the surface of the mercury and the azotometer walls.

Ammonia was passed through the combustion tube before heating until micro bubbles appeared. The furnace was heated to 400° C and then held at this temperature for 20 minutes while ammonia was passed through the furnace at the usual rate. The total insoluble gas volume at STP was found to be 0.05 ml. With the platinum boat in place, ammonia was then passed through the unheated furnace until micro bubbles appeared. The furnace was then heated to 600° C. Occasional gas bubbles were noted over the temperature range of 400 to 600° C. At 600° C more rapid gas evolution was noted.

The ammonia was then allowed to flow for 20 minutes with the furnace at 600° C, during which time a total volume of 0.12 ml of insoluble gas was obtained. This indicated that a blank for the ammonia flow was obviously much higher than the 0.02 ml per hour for the carbon dioxide at 400° C.

Three samples of uranium metal were carried through the usual experimental procedure. The results of these tests are presented in Table 7. In order to determine whether any insoluble gases were formed by the reaction of ammonia with UF_3, a sample of UF_3 was ignited in an atmosphere of ammonia without previous hydrogenation. These results are also shown in Table 7.

Table 7

Volume of Hydrogen Evolved When UH_3 was Decomposed in an Atmosphere of Ammonia

Material	Sample Weight, mg	Temperature, °C	Time, hr	Volume of Gas at STP, ml	Moles of Gas per Mole of Uranium
Uranium Metal	102.0	400	1.0	42.4	4.43
	38.0	400	5.0	4.9	1.37
	42.9	400	2.0	9.5	2.08
		460	4.5	12.5	2.70
		460	19.5	16.1	3.48
UF_3	141.0	400	2.0	1.6	0.15

The volumes of insoluble gases derived from the ignition of samples of UH_3 in an atmosphere of ammonia did not correspond to the expected stoichiometry. On the basis of two reactions postulated by Katz and Rabinowitch[7]

the expected yield of hydrogen was 3.75 to 4.125 moles of hydrogen per mole of uranium at 250° C. These two reactions may be represented by the equations below.

$$2UH_3 + 3NH_3 \longrightarrow 2UN_{1.5} + 7.5\ H_2 \quad (6)$$

$$8UH_3 + 14NH_3 \longrightarrow 8UN_{1.75} + 33\ H_2. \quad (7)$$

This method for the determination of uranium metal was considered unsatisfactory, because a reproducible quantity of hydrogen per mole of uranium was not obtained. A possible explanation for the continuous evolution of insoluble gases is that the decomposition of ammonia may be catalyzed by one of the reaction products. This is supported by the fact that uranium nitride has been reported to be an effective catalyst for the synthesis of ammonia[15].

Decomposition of UH_3 in an Atmosphere of Gaseous Hydrogen Chloride

The reaction of UH_3 with gaseous hydrogen chloride at 250 to 300° C. has been reported to proceed smoothly according to the equation:

$$UH_3 + 3HCl \longrightarrow UCl_3 + 3H_2 \quad (8)$$

[16]

This reported procedure for the production of UCl_3 by the passage of dry hydrogen chloride through an upright Pyrex tube containing UH_3 was modified to adapt it to the existing apparatus.

Dry hydrogen chloride was generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid. The evolved hydrogen chloride was then passed through a drying tube. Samples of both UH_3 and UF_3 were ignited in an atmosphere of hydrogen chloride. The sample of UF_3 was not hydrogenated prior to heating under hydrogen chloride. All samples were heated at 250 to 300° C until no further evolution of insoluble gas was apparent. The hydrogen was collected over a 30 per cent solution of potassium hydroxide. It was

necessary to use the more dilute solution of potassium hydroxide, because a 50 per cent solution was rapidly saturated with potassium chloride.

A sample of UH_3 and one of UF_3 were examined by X-ray analysis after ignition in an atmosphere of hydrogen chloride. The X-ray pattern for the UF_3 sample corresponded to 60 to 90 per cent UF_4, 10 to 30 per cent UF_3, and 2 to 10 per cent $UOCl_2$. The pattern for the UH_3 sample was 10 to 40 per cent UH_3, 10 to 40 per cent UCl_3, and 10 to 40 per cent $UOCl_2$. A probable explanation of the presence of $UOCl_2$ is that it is due to the oxidation of UCl_3 by air when the sample was transferred from the combustion boat to the sample vial. The data for all samples ignited in an atmosphere of hydrogen chloride are presented in Table 8.

Table 8

Determination of Uranium Metal by Decomposition of UH_3 in an Atmosphere of Gaseous Hydrogen Chloride

Sample Identification	Sample Weight, mg	Moles of Hydrogen per Mole of Uranium
Uranium Metal	52.9	2.05
	26.8	1.36
	61.5	2.25
	49.8	2.48
	59.1	0.62[a]
	50.7	2.39
UF_3	92.0	0.22

[a] Powdered sea sand was placed under this sample in an attempt to give a greater area of contact for the UH_3 and hydrogen chloride.

The reaction between UH_3 and dry hydrogen chloride was obviously not complete under the conditions tested even though gas evolution had ceased. The theoretical ratio of three moles of hydrogen per mole of uranium was not attained. Furthermore, the X-ray analysis showed that some unreacted UF_3 and UH_3 remained in both samples which were subjected to X-ray analysis.

Decomposition of UH_3 in an Atmosphere of Oxygen at Reduced Pressure

The composition of the uranium hydride was originally determined by Warf and Johnson by oxidizing the hydride with oxygen and weighing the water formed[3]. Since the gravimetric procedure would not be sufficiently sensitive for the measurement of the small quantities of water derived from these samples, a microvolumetric method was developed.

A completely new apparatus was necessary for the measurement of the water vapor which was formed by the ignition of UH_3 in an atmosphere of oxygen.

The apparatus was adapted from that of Naughton and Frodyma[17] for the microdetermination of carbon and hydrogen. In this procedure the sample is ignited in an atmosphere of oxygen at 30-mm pressure. The gaseous reaction products are transferred at reduced pressures to a liquid nitrogen cold trap where the water is condensed. After the evacuation of noncondensable gases, the water is allowed to expand into a calibrated vessel and its pressure is measured with an oil-mercury manometer. The apparatus consists mainly of three parts: the oxygen and hydrogen purification system, the combustion apparatus, and the pressure-measuring system. A drawing of the apparatus is shown in Figure 1.

The manometer which was used to measure the pressure of the water vapor was patterned after one designed by Naughton and Frodyma[17]. A drawing of this manometer is shown in Figure 2. A detailed description of the procedure for assemblying and filling the manometer is given in the appendix. Calibration of the manometer with a closed-end manometer revealed that a linear relationship between the oil displacement and pressure exists. The apparatus was calibrated by using $BaCl_2 \cdot 2H_2O$ and uranium hydride as standards. The calibration with $BaCl_2 \cdot 2H_2O$ was performed by trapping the water which is liberated

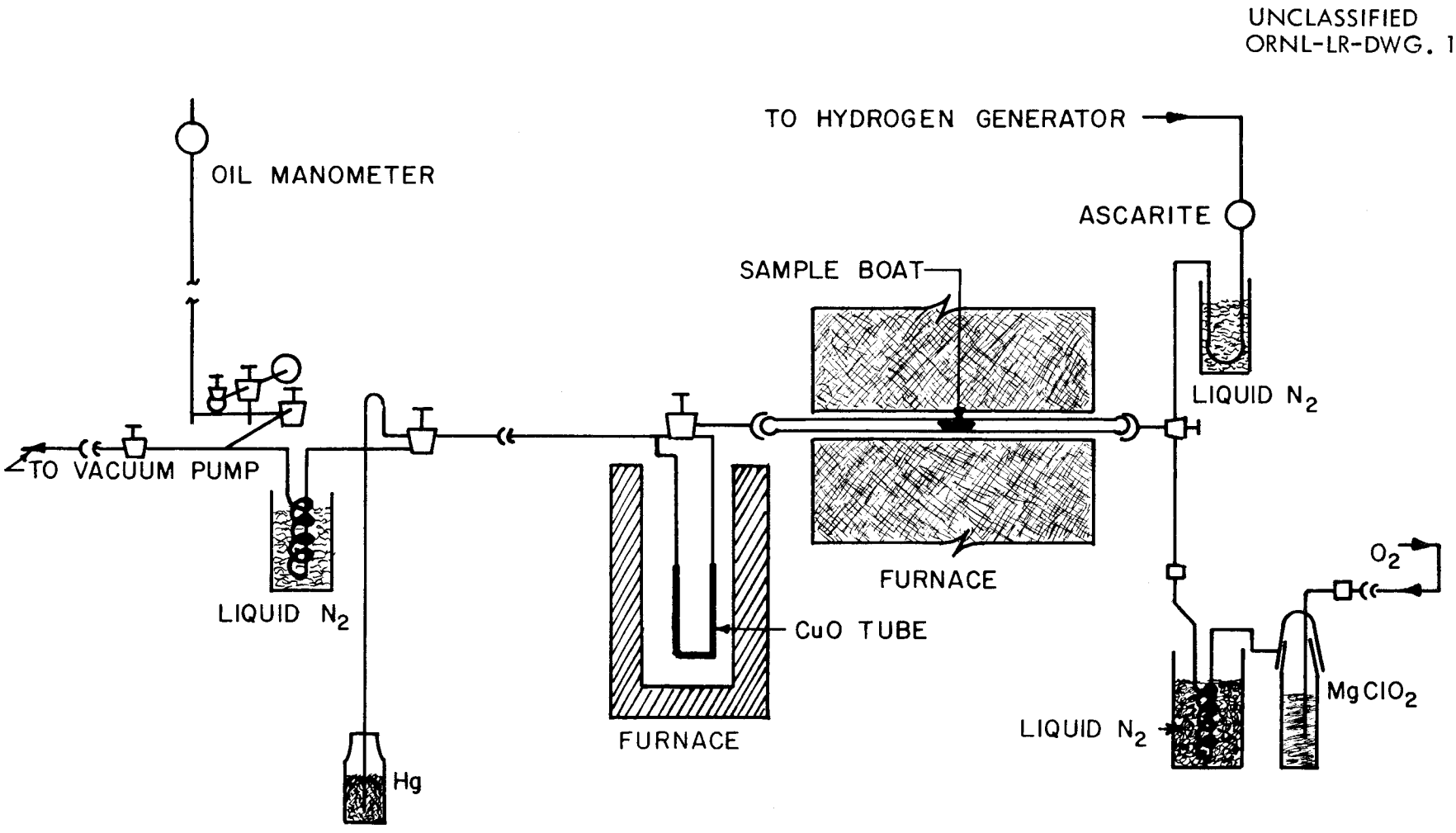

FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS FOR THE DETERMINATION OF URANIUM METAL

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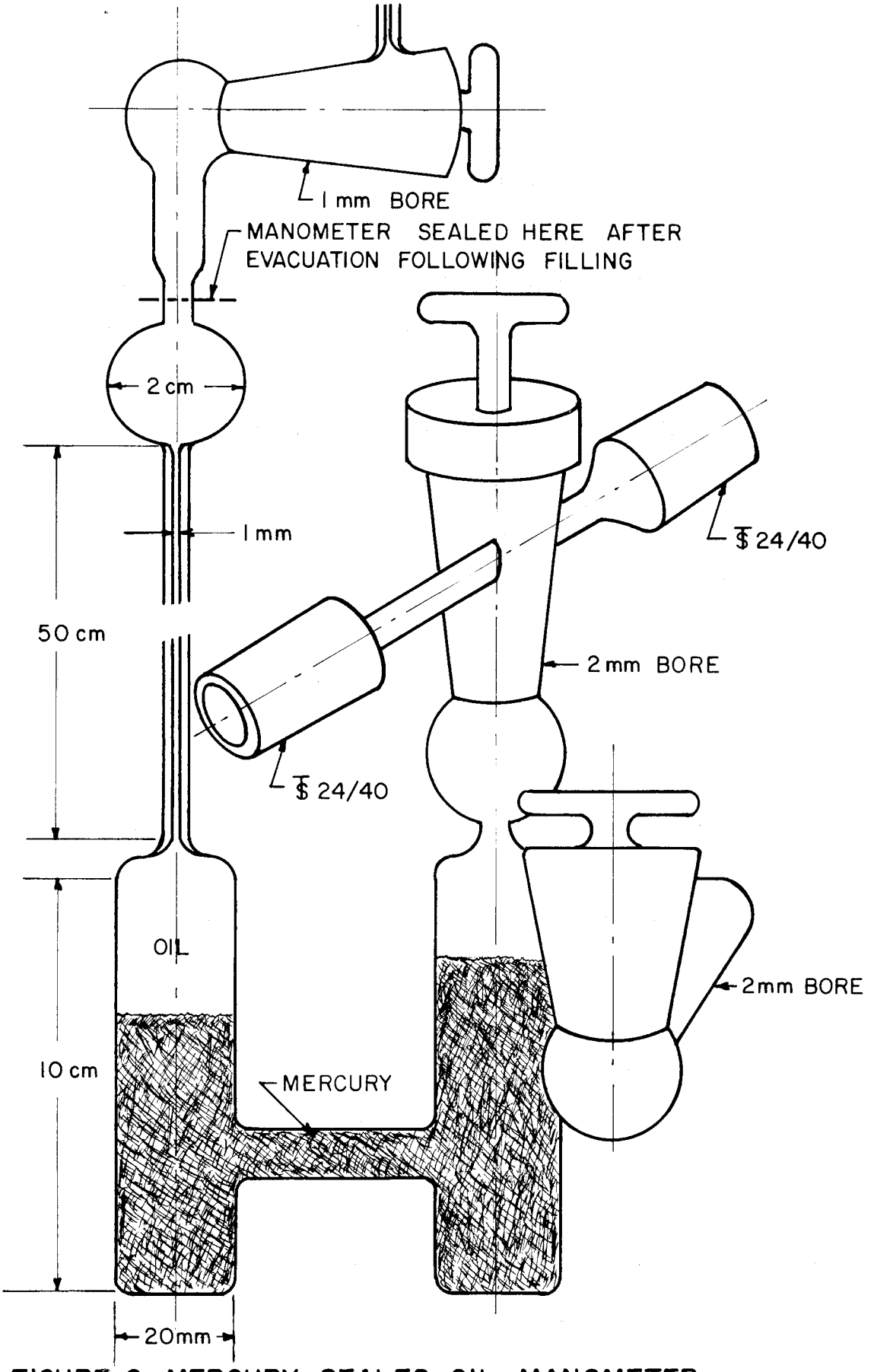

FIGURE 2. MERCURY-SEALED OIL MANOMETER

on heating the hydrated salt at 250° C for 30 minutes and allowing the water vapor to expand into a certain volume. The calibration with $BaCl_2 \cdot 2H_2O$ gave a value of 3.85 mg of water vapor per cm of oil displacement. The data for the calibration with both the closed-end manometer and $BaCl_2 \cdot 2H_2O$ are given in Appendix I, page 34.

The calibration of the apparatus with uranium metal necessitated the purification of both hydrogen and oxygen before they were admitted to the combustion tube which contained the sample of uranium metal.

Commercially available oxygen was used as the source of oxygen for all operations. The oxygen was freed of carbon dioxide by passing it through an Ascarite-filled tube, following which the gas was then passed through a tower filled with magnesium perchlorate to remove water. As a final added purification step, both gases were passed through a cold trap in a cooling bath of liquid nitrogen. The purified oxygen was then passed into the combustion tube through a three-way stopcock. Hydrogen, which was produced from the reaction of zinc with dilute hydrochloric acid and purified by passage over ascarite and magnesium perchlorate and then through the cold trap, was admitted to the combustion tube through the same three-way stopcock as the oxygen. Dual combustion tubes were used in the apparatus to reduce the overall time required for each determination.

Samples of thoroughly cleaned uranium metal turnings were used to calibrate the apparatus in terms of milligrams of uranium metal per cm of oil displacement. The samples were converted to UH_3 by heating in an atmosphere of hydrogen at 250° C for 30 minutes after the sample disintegrated. The UH_3 was then cooled in an atmosphere of hydrogen by packing dry ice around the combustion tube for 10 minutes. After the sample was thoroughly cooled, the entire apparatus was evacuated to less than 50 μ.

The sample of UH_3 was oxidized by heating for 20 minutes at 400° C in an atmosphere of oxygen at 30 mm of pressure. As an added assurance of complete oxidation of the hydrogen, a copper oxide tube, heated to 500° C, was included in the gas train following the combustion tubes. The water vapor was collected in a glass-coil cold trap which was cooled by a liquid nitrogen bath. After the UH_3 was completely oxidized, the cold trap and manometer were evacuated to less than 25 μ; the measuring system was isolated; and the water vapor allowed to expand. The pressure was determined by means of the oil-mercury manometer.

The data which was obtained for the calibration of the manometer with uranium metal are presented in Table 9 and Figure 3.

Table 9

Calibration of Oil-Mercury Manometer with Uranium Metal

Uranium, mg	Corrected Oil Pressure, cm	mg of U per cm of Oil Pressure
19.9	4.88	4.08
37.3	9.94	3.75
23.5	6.00	3.92
65.5	18.41	3.56
14.5	4.68	3.10
32.2	8.56	3.76
48.8	13.78	3.54
9.7	2.50	3.88
20.4	6.25	3.26
42.6	11.42	3.73
36.4	9.82	3.71
24.6	7.21	3.41
62.0	14.78	4.19
49.3	13.18	3.74
50.1	14.11	3.55
28.8	7.87	3.66
59.6	17.62	3.38
12.2	3.44	3.55
43.7	12.86	3.40
6.1	1.49	4.09
59.8	16.34	3.66
38.6	11.69	3.30
24.8	6.82	3.63
65.5	18.41	3.56
14.5	4.68	3.10
32.2	8.56	3.76
48.8	13.78	3.54
9.7	2.50	3.88
20.4	6.25	3.26
42.6	11.42	3.73
	Average	3.64
	Coefficient of Variation	7 per cent

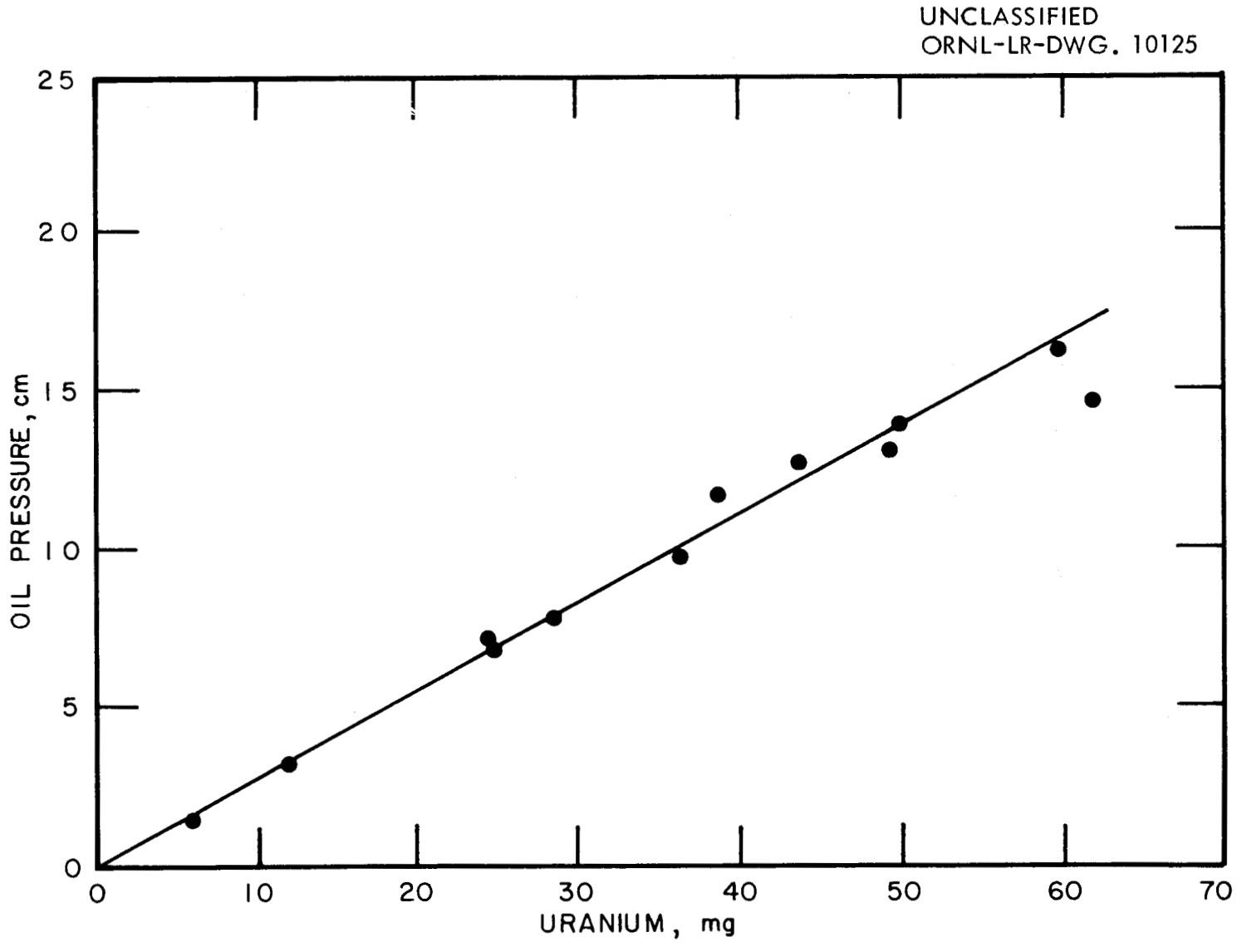

FIGURE 3. CALIBRATION OF OIL-MERCURY MANOMETER WITH URANIUM METAL

From this calibration of the manometer, it was found that one cm of oil displacement represents 3.64 mg of uranium metal in the sample. The coefficient of variation of 7 per cent may be due in part to the non-homogeneity of the metal turnings. Samples heavier than 65 mg were not used, because for this or larger sample size, the pressure in the manometer approaches the vapor pressure of water and the relationship between oil displacement and weight of uranium is no longer constant.

Several samples of UF_3, which had been produced by the reduction of UF_4 with uranium metal, were analyzed for the metal which might remain after the reduction, or, which might result from the disproportionation of the UF_3. Prior to the determination of uranium metal in these UF_3 samples, a sample of very pure UF_3 was analyzed for metal content. The scale reading for this sample was 0.01 cm. This very small scale reading corresponds to a value of 0.003 per cent uranium metal. It is evident that no condensable gases are formed by the reaction of UF_3 and oxygen under the conditions used in this test.

Since it had been noted that the hydrogen was evolved very slowly from certain UF_3 samples (p.12) it appeared likely that grinding these samples of UF_3 might render the uranium metal somewhat more accessible for reaction. In order to avoid the possibility of any air oxidation of the uranium metal, all of the samples were ground extensively in an atmosphere of hydrogen. A sealed plastic bag filled with hydrogen was used as a dry container for the grinding operation. The ground samples were stored in wax-sealed, hydrogen-filled vials until such time as they were placed in the combustion tube.

The treated samples were heated in an atmosphere of hydrogen for 1 hour at 250° C to convert uranium metal to UH_3. The sample was then cooled in the atmosphere of hydrogen. The oxidation of the UF_3 samples and the determination of the water vapor were carried out in exactly the same manner as the analyses of samples of uranium metal. The samples were observed to ignite suddenly when the temperature was raised to 300° C. The reaction was so rapid that the samples became incandescent. The data for the UF_3 samples are given in Table 10.

Table 10

Reproducibility of the Determination of Uranium Metal in Samples of UF_3

Sample Number	Weight, g	Corrected Oil Pressure, cm	Uranium Metal, per cent
16-A	2.79	4.80	0.62
-B	1.79	2.79	0.56
17-A	1.56	0.82	0.19
-B	1.92	1.06	0.20
18-A	1.36	3.27	0.86[a]
-B	2.03	0.97	0.17
19-A	1.76	1.10	0.23
-B	2.33	1.59	0.25
20-A	1.91	2.91	0.55
-B	2.15	3.14	0.53
21-A	2.73	1.38	0.18
-B	3.18	1.95	0.22
22-A	1.03	0.81	0.28
-B	1.97	0.91	0.17
-C	2.00	0.88	0.16
23-A	2.32	1.86	0.29
-B	1.80	1.41	0.28

(Table 10 concluded on page 26)

Table 10 (continued)

Reproducibility of the Determination of Uranium Metal in Samples of UF_3

Sample Number	Weight, g	Corrected Oil Pressure, cm	Uranium Metal, per cent
24-A	2.08	1.01	0.18
-B	1.39	0.79	0.20
25-A	1.87	2.36	0.45
-B	1.55	2.03	0.47
26-A	2.06	0.93	0.16
-B	2.07	1.11	0.19
27-A	2.04	0.88	0.16
-B	1.04	0.47	0.16
28-A	1.95	1.65	0.30
-B	1.40	1.35	0.35
29-A	2.26	2.00	0.32
-B	2.05	1.61	0.28
30-A	1.74	1.34	0.28
-B	2.14	1.92	0.32
33-A	2.02	1.14	0.21
-B	2.02	2.10	0.38
34-A	2.22	0.53	0.09
-B	1.57	0.31	0.07
35-A	2.28	0.24	0.04
-B	0.85	0.14	0.05
36-A	3.78	9.72	0.94
-B	1.56	3.17	0.74
37-A	1.50	2.60	0.63
-B	1.81	3.77	0.76
		Coefficient of Variation	6 per cent

[a] New Ascarite tube in the gas purification train.

The coefficient of variation based on duplicate determinations of 6 per cent is comparable with that of 7 per cent obtained with the calibration of

the apparatus with metal turnings. Positive errors are probably a result of leaks during the oxidation period; negative errors might be introduced by improper handling of the samples which results in oxidation of the uranium metal.

The sensitivity of the method could be increased by confining the water to a smaller volume during the pressure measurement. A smaller expansion vessel was incorporated in the apparatus, but it has not been calibrated or used for samples at this time because of the lack of a suitable standard.

DISCUSSION AND CONCLUSIONS

It has been demonstrated that the measurement of the hydrogen that can be combined with uranium metal as UH_3 provides a practical and sensitive method for the determination of uranium metal in fluoride samples which contain trivalent uranium. Two procedures which are satisfactory for the measurement of the combined hydrogen have been developed. These procedures are based on the reaction of hydrogenated samples with carbon dioxide or oxygen. The reaction of the UH_3 with HCl or ammonia was not quantitative under the conditions tested. It would appear that other reagents which have been reported to react with UH_3, e.g., HBr, HI, $COCl_2$, would be equally unsuitable for the quantitative measurement of the hydrogen.

The method which is based on the reaction of UH_3 with carbon dioxide is the most precise and can be carried out with a simple apparatus. The procedure is, however, lengthy and subject to gross positive errors because of uncertainties in the activity of the I_2O_5 catalyst. When one-gram samples are analyzed, the method is applicable only to samples which contain uranium metal in excess of 0.1 per cent.

The procedure which is based on the reaction of the UH_3 with oxygen is much more rapid and sensitive but less precise. A complex apparatus is necessary, and extensive calibrations must be carried out before any analyses can be performed. It must also be noted that a much higher degree of operational skill is required.

Accordingly, the procedure for the decomposition of the UH_3 in an atmosphere of carbon dioxide is recommended when the analysis of only a limited number of samples is required, while the decomposition in an atmosphere of oxygen is the more preferable for a more extensive program of analysis.

This study has indicated that the pretreatment of the sample is of paramount importance. The sample should be thoroughly pulverized and contact with atmospheric gases must be avoided.

APPENDIX

THE OIL-MERCURY MANOMETER

At room temperature, water vapor conforms approximately to the ideal gas laws only at pressures below 20 mm of mercury. The precision of pressure measurements over this region can be improved by the use of a manometer filled with a liquid of low density. Naughton and Frodyma[17] recommended a closed-end manometer which contains a low pressure oil confined to the closed arm by a mercury U-seal to prevent absorption of the water vapor by the oil. Since the cross section of the mercury-filled U-tube is much larger than the oil meniscus, see Figure 2, the displacement of the mercury interfaces is negligible with respect to that of the level of the oil in the capillary tube. Thus, the response of the oil-mercury system approaches that of a simple oil-filled manometer.

In the original design[17] the closed arm of the manometer is connected to the vacuum system through a stopcock. After evacuation, the oil is transferred to the closed arm by distillation from a small flask that is sealed to a side arm above the capillary. This arrangement has the disadvantage that the pressure on the mercury must be limited to less than 50 mm so long as the closed arm is evacuated. If this pressure is exceeded, mercury and oil are forced through the capillary and the manometer must be cleaned and refilled. Since this pressure limit could easily be exceeded during the determination of uranium metal, the modified design shown in Figure 2 was adopted. As an additional modification, the three-way vacuum stopcock was mounted on the open arm of the manometer, so that the sensitivity of the system could be easily altered to correspond to the sample size. With the stopcock in the

closed position, the water vapor is confined to the volume comprised of the open arm of the manometer and the cold trap. When large quantities of water are to be measured,the expansion volume can be increased by opening the stopcock to vessels attached to the standard taper joints on the side arms. During this investigation most of the measurements were carried out with a 300-ml flask coupled to the manometer.

While the modified manometer is stable over a larger pressure range than that of Naughton and Frodyma[17], a more involved procedure for filling the manometer must be followed. A detailed description of the filling procedure is given below. It has also been observed that when the evacuated side arm is sealed off, small quantities of non-condensable gases are liberated, perhaps as a result of thermal decomposition of traces of oil on the glass surfaces. If the seal is made at the top of the capillary, the response of the manometer to pressure is not linear and its sensitivity is materially reduced. When the void space above the oil is increased by the volume of a bulb of 1-cm radius, see Figure 2 ,the response of the manometer is linear within the experimental error of calibration as indicated in Figure 3.

Assembling and Filling the Manometer

The manometer, together withits auxillary glassware, was washed with a detergent and then with chromic acid cleaning solution. The inner walls were treated with Desicote,following which the apparatus was dried overnight at a temperature of 120° C. All permanent joints were sealed with Apiezon W. Temporary joints and stopcocks were lubricated with a high-vacuum grade of Silicone stopcock grease. The system was evacuated with a two-stage, mechanical vacuum pump. Both the capillary and pressure leg were connected

to the vacuum system to equalize the pressure on the liquid columns.

After the pressure had been reduced to 15 microns, the manometer was filled with dry air. A separatory funnel was connected to the three-way stopcock by replacing the stopcock bore with a 24/40 male joint. The manometer was again evacuated to 15 microns after which mercury was added from the separatory funnel at this reduced pressure. Sufficient mercury was added to fill the U-tube to approximately 3 cm above the connecting arm. Dried air was then admitted slowly to both legs of the manometer.

When atmospheric pressure was reached, the ground-glass joint at the top of the capillary was removed, and a low-pressure oil was added with a medicine dropper. Dibutyl phthalate, which had been refluxed under vacuum overnight to remove any volatile components, was used as the low-pressure oil. A sufficient quantity of oil was added to maintain the level approximately 0.5 cm below the capillary. With extreme care, the vacuum was applied simultaneously to the top of the capillary and the pressure leg. If the pressure is reduced too rapidly, the mercury seal will fail and oil will enter the pressure leg. When the pressure was reduced to 10 microns and all bubbles of absorbed gases were removed, the closed arm was sealed off above the 2-cm bulb (Figure 2). Mercury was added to the pressure leg until the oil meniscus stood approximately 1 cm above the bottom of the capillary when the pressure leg was evacuated.

In order to determine whether the pressure response of the oil-mercury manometer was linear, a closed-end manometer was attached to one of the ground glass joints on the three-way stopcock. Successively larger amounts of air were admitted to the evacuated oil-mercury manometer. After each addition of air the pressure reading and the oil displacement were recorded. The data for this calibration are presented in Table 12 and Figure 4.

Table 11

The Calibration of the Oil-Mercury Manometer

Pressure Registered on Closed-End Manometer, mm	Scale Reading, cm of Oil
2.1	4.00
3.5	5.65
5.2	7.68
6.2	9.73
8.5	11.65
9.5	13.71
12.9	17.72
14.5	19.75
16.2	21.78
18.0	23.68
19.5	25.61
21.0	27.50
24.0	31.11
27.0	35.08
29.0	37.70
31.0	39.20
32.5	41.00
34.0	43.02
35.0	45.00
37.0	48.90

The oil-mercury manometer was calibrated in terms of milligrams of hydrogen per centimeter of oil displacement. A stepwise procedure for this calibration operation is given below:

1. The weighed $BaCl_2 \cdot 2H_2O$ sample was placed in a platinum boat in the combustion tube, following which the entire system was evacuated to a pressure of 50 microns.

2. Purified oxygen was allowed to enter the system until a pressure of approximately 30 mm, as measured by the manometer, was attained. The entire apparatus was swept for five minutes with a flow of oxygen.

3. The cold trap for freezing the water was cooled with liquid nitrogen and the furnace was heated at 250° C for 15 minutes.

4. After complete transfer of the water to the cold trap, the pressure in the cold trap and manometer was reduced to 25 microns.

5. The water was allowed to expand into the manometer, and then the oil displacement was measured on a scale attached to the capillary tube of the manometer.

6. Blanks were determined by following the same procedure.

The data for the calibration of the manometer with $BaCl_2 \cdot 2H_2O$ are given in Table 13 and Figure 5.

Table 12

Calibration of the Oil-Mercury Manometer with $BaCl_2 \cdot 2H_2O$

Weight of $BaCl_2 \cdot 2H_2O$, mg	Weight of Hydrogen, mg	Corrected Scale Reading, cm	Hydrogen, mg per cm of Scale Reading
6.2	0.102	2.50	0.408
10.9	.178	4.28	.416
16.6	.272	6.45	.422
16.7	.273	6.50	.420
27.3	.447	10.2	.438
39.9	.653	15.0	.435
49.3	.807	18.2	.444
55.6	.910	20.0	.455[a]
60.7	.994	19.9	.499
		Coefficient of Variation	4 per cent

[a] At this point, the pressure exceeds the vapor pressure of water and this value marks the bending of the curve.

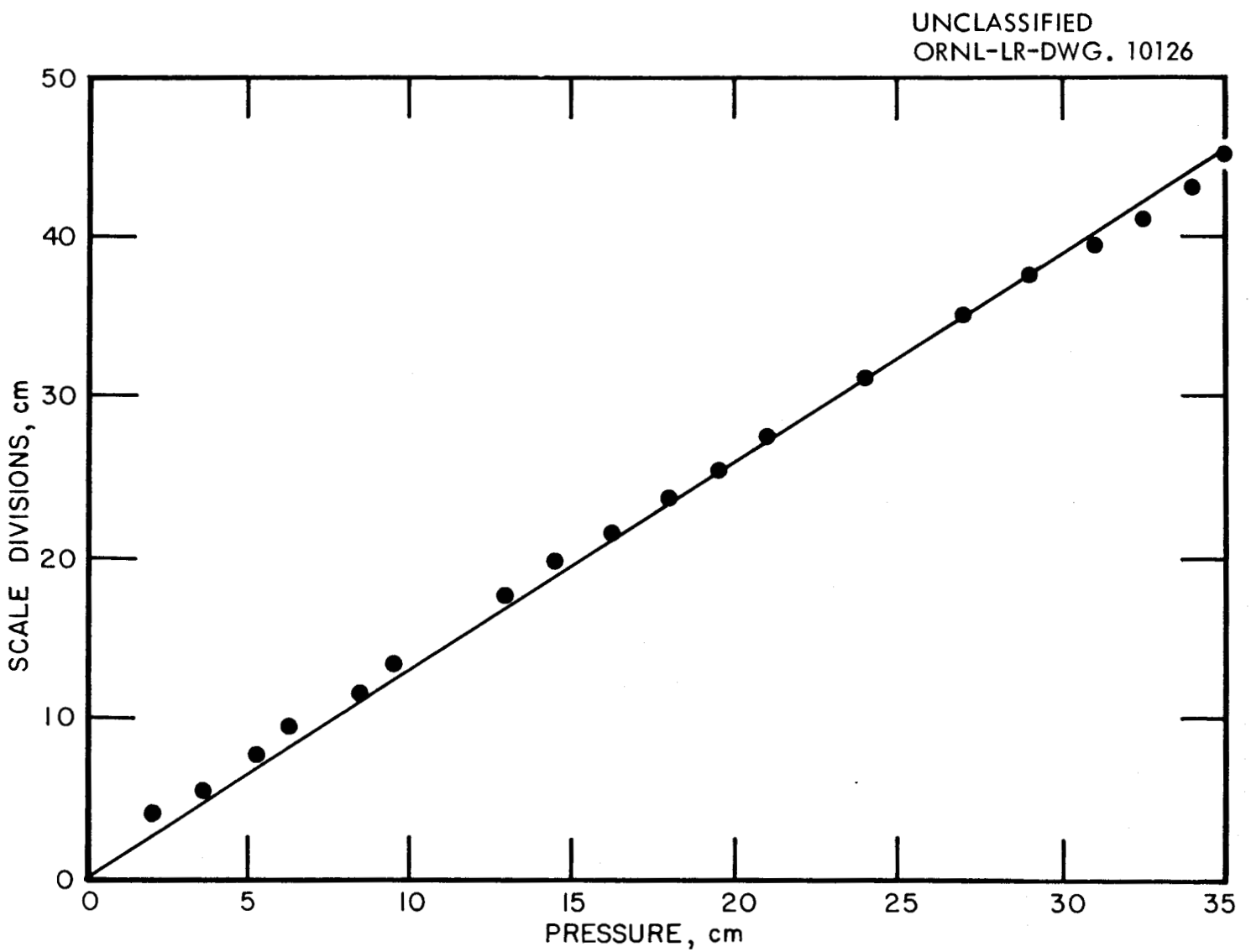

FIGURE 4. CALIBRATION OF OIL-MERCURY MANOMETER WITH A CLOSED-END MANOMETER

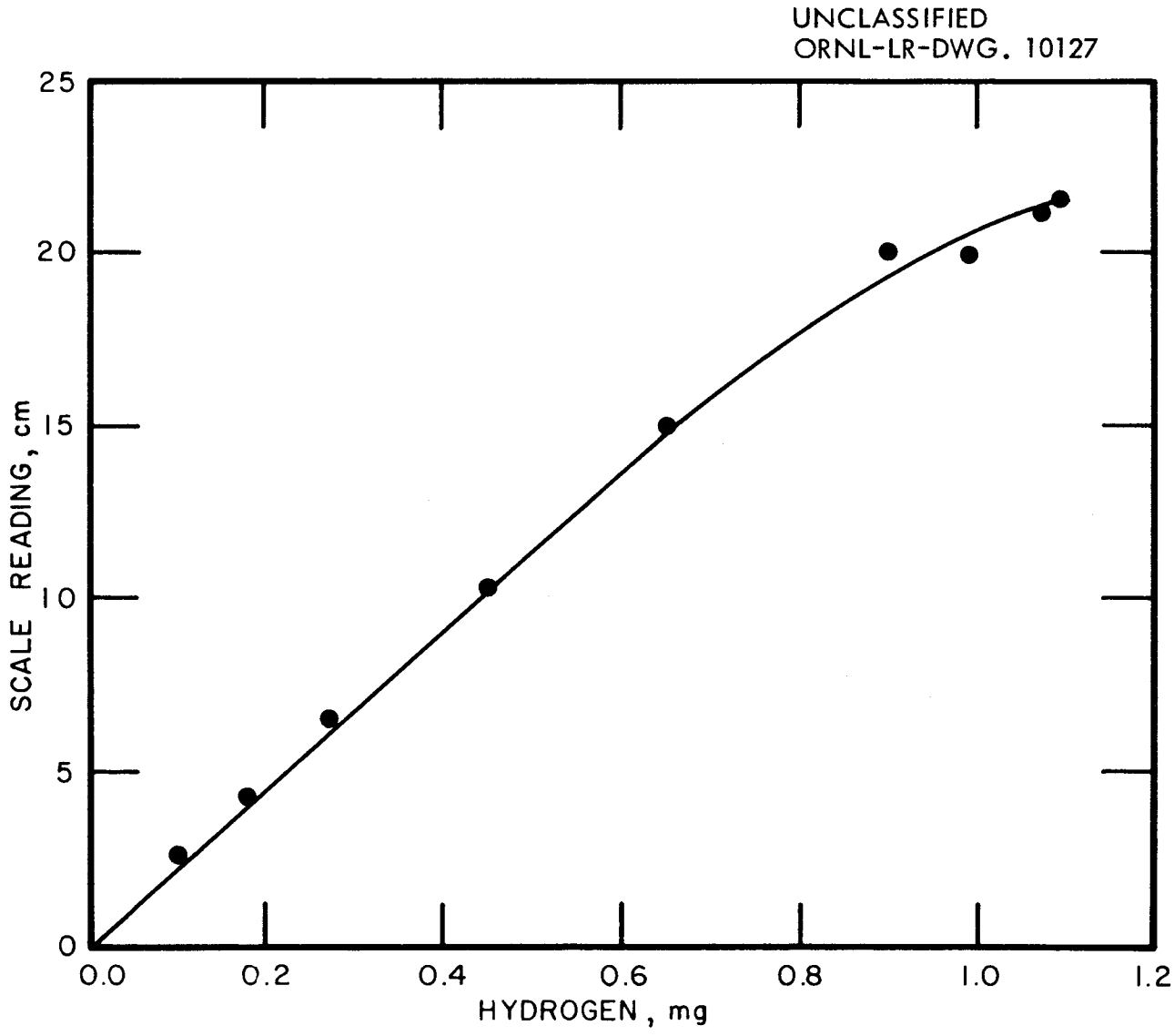

FIGURE 5. CALIBRATION OF OIL-MERCURY MANOMETER WITH $BaCl_2 \cdot 2H_2O$

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