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CHEMISTRY

UNITED STATES ATOMIC ENERGY COMMISSION

DETERMINATION OF OXYGEN IN URANIUM AND
URANIUM HYDRIDE BY REACTION WITH
BROMINE TRIFLUORIDE

By
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ABSTRACT

A convenient procedure for the direct determination of the combined oxygen and nitrogen content of uranium and uranium hydride is described. The uranium or uranium hydride is reacted with bromine trifluoride at $\sim 80^{\circ}\text{C}$ to evolve oxygen and nitrogen, which are measured tensimetrically. Using a sample of approximately one gram, the precision is $\pm 0.01\%$ for uranium and $\pm 0.03\%$ for uranium hydride.

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The purity of uranium hydride powders may also be evaluated by degassing and hot-pressing to the massive metal and determining the density of the uranium produced. This procedure does not differentiate between the various impurities which may be present, and is therefore of limited value as an analytical tool. The method is cumbersome and time-consuming for routine analyses.

and introduces any additional variables which may be present in the hot-pressing technique itself. The data of Table I show that while there is reasonably good correlation between density and oxygen content of uranium prepared by hot-pressing uranium hydride, it is not possible to deduce accurately the oxygen content from the density of the uranium, due, presumably, to the unknown and variable content of other impurities.

TABLE 1

OXYGEN CONTENT AND DENSITY OF HOT-PRESSED URANIUM PELLETS

$\% O^*$	ρ actual	ρ theoretical**
0.07	18.92	18.97
0.09	18.83	18.94
0.12	18.81	18.91
0.22	18.78	18.80
0.29	18.56	18.72
0.29	18.43	18.72
0.32	18.41	18.69
0.33	18.54	18.68
0.33	18.40	18.68
0.34	18.56	18.67
0.39	18.26	18.61
0.52	18.13	18.48
0.66	17.39	18.33

* Noncondensable gas calculated as oxygen

** Assuming oxygen as only impurity (See NYO-3797 for method of calculation)

DISCUSSION

The use of bromine trifluoride to quantitatively displace oxygen was first suggested by Emeleus and Woolf⁽²⁾ in 1950, when they reported the complete displacement of oxygen from the following compounds: B_2O_3 , SiO_2 , CuO , GeO_2 , As_2O_3 , SeO_2 , Sb_2O_3 , I_2O_5 , Tl_2O_3 , $BiOCl$, and UO_3 . Under the conditions of the experiments, oxygen was not completely displaced from sixteen other metallic oxides. The fact that these experiments were carried out in a quartz system limited the usefulness and applicability of the system for truly quantitative measurements of oxygen evolution. The samples could not be subjected to pro-

longed treatment with bromine trifluoride, and, even under the mild conditions employed, the quartz reaction vessel suffered small weight losses⁽³⁾.

Hoekstra and Katz have modified the procedure of Emeleus so that the materials of construction of those parts of the apparatus which come in contact with bromine trifluoride and reactive fluoride compounds are oxygen-free and inert. One of the authors has visited Drs. Hoekstra and Katz to observe personally their analytical procedure and to ascertain the feasibility of utilizing the method for the determination of oxygen as an impurity in uranium or uranium hydride. Several analyses were performed on the apparatus of Hoekstra and Katz, and while the results were not regarded as completely satisfactory, they were in qualitative agreement with the approximately known purities of the various samples, and were deemed to establish definitely the feasibility of applying the method to the determination of oxide impurities. Since that time, two high vacuum lines have been constructed at Metal Hydrides Incorporated for the direct determination of oxygen by the bromine trifluoride method. Since the determinations are for oxide impurities in uranium and in uranium hydride powders, rather than for the oxygen content of the relatively inert metallic oxides for which the method has heretofore been applied, several modifications have been made in the procedure described by Hoekstra and Katz. Some difficulty was encountered initially in getting satisfactory analytical values by this method, and it is hoped that by making known the experiences encountered in developing this method for handling these materials, particularly the pyrophoric uranium hydride powders, this valuable analytical tool will be more readily available to other workers in the field. For this reason, because of the modifications introduced to the established procedure, and because of its great potential usefulness to the over-all atomic energy research effort, the method, apparatus, and procedure are described in some detail.

Uranium, uranium hydride, and uranium dioxide all react with bromine trifluoride. The reactions are represented by equations (1), (2) and (3), respectively.

Oxygen evolved from a sample of uranium or uranium hydride on treatment with bromine trifluoride is a quantitative measure of the oxygen impurity content of the material. Nitrogen present in the sample is liberated simultaneously. Individual analytical values for oxygen and nitrogen may be obtained by measuring

tensimetrically the total amount of gas evolved, chemically removing the oxygen, and measuring the residual nitrogen. The nitrogen content of uranium and uranium hydride is, however, relatively unimportant, and it may be assayed by standard analytical procedures. It has been the practice, therefore, to calculate the analytical value as "% oxygen", assuming that all noncondensable gases are oxygen, and to correct this value for the nitrogen content if this is known and it is desired to do so.

Carbides have been reported to react with bromine trifluoride to give primarily CF, a nonvolatile polymer, and some carbon tetrafluoride, CF₄. The vapor pressure of carbon tetrafluoride is less than one-half millimeter at liquid nitrogen bath temperatures, but quite possibly it would be completely removed from the trap system by the Toepler pump, thus interfering with the oxygen analysis. However, a sample of uranium monocarbide* gave an amount of noncondensable gas which calculated as 0.19% oxygen. As this substance is known to be reactive in air, this value probably represents the oxygen and/or nitrogen content of the material, rather than interference by carbon. Hoekstra and Katz propose⁽¹⁾ to investigate the reaction of bromine trifluoride with carbides, nitrides, and borides.

Handling and Purification of Bromine Trifluoride

Bromine trifluoride is an extremely reactive compound which must be handled with extreme caution. It may be purchased commercially in cylinders. Transferring the bromine trifluoride from the cylinder to the nickel reservoir for the high vacuum line can be hazardous, and the operation should be executed in a well ventilated hood behind safety shields. Personnel should wear face shields and goatskin gloves and jackets. The method used at Metal Hydrides is shown schematically in Figure 1. The bromine trifluoride is forced from the cylinder to the reservoir by means of an inert gas pressure. As soon as fumes appear above the reservoir the three-way stopcock is closed and the bromine trifluoride allowed to siphon over until the liquid level is visible in the reservoir. The three-way stopcock is immediately turned to the vacuum outlet to draw the excess bromine trifluoride back into the cylinder. The reservoir is then positioned on the high vacuum apparatus (Figure 2). Bromine trifluoride may be partially degassed in the reservoir, but to insure complete degassing it has been necessary to subject each individual increment of bromine trifluoride introduced into the reaction tube-trap system to alternate vaporizations and condensations while under vacuum. Once the bromine trifluoride is contained within the high vacuum apparatus, standard laboratory precautions are adequate.

* Supplied by Dr. H. H. Hausner, Sylvania Electric Bayside Laboratories

FIGURE 1

APPARATUS FOR INTRODUCING BROMINE TRIFLUORIDE TO RESERVOIR

- BR Bromine trifluoride reservoir for vacuum line
- SL Dry soda lime
- NT Nickel tubing
- NF Nickel fitting
- BC Commercial bromine trifluoride cylinder
- IG Inert gas inlet
- VAC Vacuum outlet
- TS Teflon sheet

The disposal of small quantities of bromine trifluoride can be accomplished by pouring it on dry soda lime behind a shield in a well ventilated hood. Large quantities are best disposed of out of doors by tipping the container on a bed of soda lime by means of a remote-control wire, from a safe distance.

FIGURE 2

HIGH VACUUM APPARATUS FOR OXYGEN ANALYSIS

DP	Mercury diffusion pump
MG	McLeod gauge
ST	Nickel trap for soda lime
PT	Pyrex traps
BR	Bromine trifluoride reservoir
FT	Kel-F trap (polychlorotrifluoroethylene)
RT	Nickel reaction tube
V	Inconel diaphragm valves
TP	Automatic Toepler pump
DM	Differential manometer
S	Vacuum stopcocks
DT	Drying tube for helium (CaSO_4 , KOH , P_2O_5 , CaH_2)
M	Manometer

Principal impurities which may be present in the commercial product are bromine, bromine monofluoride, bromine pentafluoride, hydrogen fluoride, and metallic fluorides. While these materials may be removed by trap to trap fractionation in the high vacuum apparatus, it is unnecessary to do so, as all of these materials are completely condensed at the temperature of liquid nitrogen. The commercial product also contains considerable quantities of dissolved gases, presumably oxygen and/or nitrogen, which must be removed. This is conveniently done by successive vaporizations and condensations from trap to trap on the high vacuum apparatus. The bromine trifluoride is considered to be completely degassed when no measurable quantity of gas can be collected by means of the Toepler pump as the bromine trifluoride is allowed to vaporize from the reaction tube to the traps, which are partially immersed in liquid nitrogen.

The chemical and physical properties of bromine trifluoride are described elsewhere. Hoekstra and Katz⁽¹⁾ list references to the original literature along with an excellent although somewhat cursory review of those properties pertinent to the application of bromine trifluoride to oxygen analyses.

APPARATUS

The apparatus for the direct determination of oxygen in uranium and uranium hydride is shown in Figures 2, 3, and 4. Figure 2 illustrates the apparatus in its entirety, while Figures 3 and 4 show detail of the reaction tube-trap system and the Toepler pump-calibrated volume section, respectively. The apparatus is essentially that described by Hoekstra and Katz⁽¹⁾. It may be considered to consist of two portions--a glass portion and a fluoride inert metal and plastic portion.

The glass portion is made up of standard high vacuum equipment. It includes a mercury diffusion pump, McLeod gauge, dry helium inlet, Toepler pump for collecting the noncondensable gases, calibrated volume with differential mercury manometer, standard vacuum mercury manometer, and Pyrex traps at either end of the fluoride inert portion of the apparatus.

That portion of the apparatus which comes in actual contact with bromine trifluoride or other reactive fluorine compounds consists of the reaction tube-trap system, a nickel reservoir for bromine trifluoride, and a nickel soda lime trap. The reaction tube is made of nickel* rather than the fluoride inert

* To conserve liquid nitrogen, a nickel liner in a Kel-F tube may be used.

FIGURE 3

DETAIL OF REACTION TUBE-TRAP SYSTEM

- ST Nickel trap for soda lime
- V Inconel diaphragm valves
- RF Nickel reaction tube fitting
- TG Teflon gasket to fit between RT and RF
- TD Grooved teflon disk for vacuum tight seal on top of RF
- MD Metal disk to apply uniform pressure to TD
- HN Hexagonal nut to receive MD and TD for top of reaction tube fitting. The top (inverted in photograph) is threaded to receive a bolt which is tightened to insure uniform pressure on sealing surfaces between RF and TD.
- N 3/4 inch SAE flare nut
- FF Kel-F tube fitting
- FT₂ Kel-F trap completely assembled

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FIGURE 4

DETAIL OF TOEPLER PUMP-CALIBRATED VOLUME SYSTEM

- V Inconel diaphragm valve
- PT Pyrex trap
- S Vacuum stopcock
- TP Automatic Toepler pump
- C Calibrated volume marks
- DM Differential manometer
- T Tubing to 3-way solenoid valve (air-vacuum service for Toepler pump)
- M Manometer

plastic Kel-F (polychlorotrifluoroethylene), because the vigor of the reaction is such that use of the plastic is deemed hazardous. This is not only because the heat of reaction may be sufficient to soften the plastic, but also because it has been reported(4) that uranium hexafluoride is soluble in and will weaken the structure of Kel-F tubes if bromine trifluoride is present as a contacting agent. While no evidence of this phenomenon has been observed in this laboratory (the Kel-F trap tubes have not gained weight), this is perhaps because the reaction products are always removed from the Kel-F tubes as soon as practicable. Three Kel-F traps are included in the system to insure removal of all condensable material when the evolved oxygen is passed through the traps.

The valves are Inconel diaphragm-type packless valves (Hoke Inc., Englewood, N. J.) with the nickel or Monel tubing brazed with a special grade of silver solder, "Silvaloy #355" (American Platinum Works, Newark, N. J.). These are satisfactorily inert to bromine trifluoride and its impurities. Kovar seals were used to grade from the metal to glass line.

"Halocarbon" (polychlorotrifluoroethylene) stopcock lubricant (Halocarbon Products Corp., North Bergen, N. J.), Standard Grade, was used throughout the glass portion of the line, with the Hi-Temperature Grade used to grease the Teflon gaskets on the nickel-nickel fittings and on the Kel-F traps.

PROCEDURE

Helium pressure is used to force bromine trifluoride into the evacuated nickel tubing between V_6 and V_7 (~ 8 ml.). This measured quantity is then admitted to FT_1 and degassed as previously described. The bromine trifluoride is condensed in the reaction tube and dry helium admitted to a pressure of ~ 800 mm. The sample (0.7 to 1.2 grams) is introduced as described below and the system evacuated. V_1 and V_2 are closed and the reaction tube heated* to $\sim 80^\circ\text{C}$ for 45 minutes in the case of uranium hydride, or 90 minutes for uranium chips.

After the reaction is complete, the reaction tube is allowed to cool to room temperature and liquid nitrogen baths are placed about the Kel-F traps. S_2 is closed, V_2 is opened and any oxygen and/or nitrogen is Toeplizerized into the calibrated volume (~ 18 c.c.), where it is measured by noting the pressure on the differential manometer.

In order to introduce an uranium chip, it is weighed into a gold foil capsule when ready for analysis. At that time the screw

* An adjustable hair dryer is satisfactory for this.

cap of the reaction tube fitting is removed. The slow stream of dry helium sweeping from the head of the tube prevents water vapor or other oxygen containing compounds from entering. This also serves as an inert atmosphere blanket during introduction of the sample. However, these precautions have been found to be inadequate when handling reactive powders such as uranium hydride. To insure freedom from contamination while introducing a powder sample, the material is weighed out in an inert atmosphere box into a capsule formed from gold foil (~ 0.0005 inch thick) by double-crimping the sealing edges. This is then placed in a closed-end 10-mm.-bore vacuum stopcock (Figure 5) and removed from the inert atmosphere box. Upon removal of the screw cap from the reaction tube fitting, the open end of the introduction stopcock is positioned on the fitting so that the capsule will fall freely into the reaction tube when the stopcock is opened. The small hole in the open-end side of the stopcock tubing close to the plug permits the slow stream of helium emerging from the head of the reaction tube to completely flush out this section so that an inert atmosphere is maintained about the sample at all times.

V₁ and V₅ are never opened without first cooling PT₁, RT, and FT₁, PT₂, and FT₃, respectively, with liquid nitrogen baths. The Pyrex traps prevent diffusion of mercury vapor into the fluoride-inert portion of the system, while the Kel-F traps prevent volatile fluorides entering the glass portion.

Small quantities of bromine trifluoride are sometimes entrained and carried through two Kel-F traps, and should it condense in the Pyrex trap, it would cause a slow reaction with the glass to liberate oxygen. This reaction has been confirmed in the following way: A flat vacuum was obtained in the reaction tube-trap system, the bromine trifluoride being retained by liquid nitrogen baths. A small amount of bromine trifluoride was then allowed to distil into the Pyrex trap PT₂, which was chilled with a liquid nitrogen bath, and a slow reaction ensued, as evidenced by the evolution of a noncondensable gas which was collected by means of the Toepler pump. Replacement of the Pyrex trap containing the bromine trifluoride by a clean trap caused cessation of the gas evolution. Thus a measurable reaction was occurring between the active fluoride compounds and the glass. This further emphasizes the necessity for complete removal of these compounds in the Kel-F trap system when analyzing for trace quantities of oxygen.

It has been found advantageous to warm the screw cap of the reaction tube with the hair dryer, prior to opening, to prevent moisture condensation and to prevent excessive cooling and consequent stiffening of the Halocarbon grease. In addition, the need for frequent regreasing of the reaction tube gasket to maintain a vacuum connection is avoided by allowing air to blow

FIGURE 5

INTRODUCTION TUBE FOR PYROPHORIC SAMPLE

on the flare nut while the reaction tube is being heated.

Blank runs following in every detail the procedures outlined, except that no sample is placed in the gold foil, give no detectable quantity of noncondensable gas.

RESULTS

Using 0.7 - 1.2 gram samples, the precision obtained by this method is $\pm 0.01\%$ for massive uranium samples and $\pm 0.03\%$ for uranium hydride powder samples. The accuracy of the method is less certain, as there is little basis for comparison with other methods.

A sample of uranium which analyzed* 5480 p.p.m. oxygen and 650 p.p.m. nitrogen by vacuum fusion (equivalent to 0.62% noncondensable gas calculated as oxygen) analyzed 0.66% noncondensable gas calculated as oxygen by bromine trifluoride.

Representative duplicate analyses are shown in Table 2 to indicate the precision which has been attained.

TABLE 2

PRECISION OF DUPLICATE ANALYSES

<u>U r a n i u m</u>	<u>H y d r i d e</u>	<u>P o w d e r</u>
<u>Sample No.</u>	<u>Analytical</u>	<u>Results</u>
1	0.12	0.16
2	0.15	0.17
3	0.17	0.22
4	0.20	0.21
5	0.21	0.24
6	0.21	0.28
7	0.24	0.28
8	0.25	0.32
9	0.29	0.30
10	0.28	0.32
11	0.29	0.32
12	0.27	0.34
13	0.32	0.37
14	0.44	0.50
15	0.50	0.54
16	0.50	0.55
17	0.53	0.54
18	0.59	0.63

* Analysis by Sylvania Electric Bayside Laboratories

TABLE 2 (Continued)

<u>U r a n i u m</u>	<u>M e t a l</u>	<u>C h i p s</u>
<u>Sample No.</u>	<u>Analytical</u>	<u>Results</u>
19	0.02	0.03
20	0.03	0.06
21	0.05	0.06
22	0.09	0.09

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