ORNL - 2043

CHEMISTRY — GENERAL

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DETERMINATION OF TRIVALENT URANIUM IN FLUORIDE SALT MIXTURES
BY THE MODIFIED HYDROGEN EVOLUTION METHOD

J. C. White, A. S. Meyer, Jr., W. F. Vaughan,
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Price $ 0.50

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

DATE ISSUED:

FEB 28 1956

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Oak Ridge, Tennessee

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INTRODUCTION

The hydrogen evolution method for the determination of uranium trifluoride which was developed by Manning, Miller and Rowan[2] has been used for the determination of trivalent uranium in this laboratory for the past three years. The method has been applied to many different sample types; supposedly pure UF_3, mixtures of UF_3 and UF_4 and the large variety of mixtures of fluoride salts that have been investigated as possible nuclear fuels. These mixtures contained alkali metal, beryllium and zirconium fluorides.

Several modifications have been made that have substantially improved the performance and ease of operation of the method. These improvements include the use of (1) an inexpensive, long-lasting source of pure carbon dioxide, (2) vacuum to assist in purging the system of gases that are insoluble in potassium hydroxide solution, (3) deaerated acid that has an extremely low quantity of non-absorbable gases, (4) slower flow rates of purging gas, (5) a sampling technique to minimize contamination, and (6) more dilute absorber solution to reduce film error.

It is the purpose of this report to show the effect of these modifications and the applicability of the method to various sample types that contain uranium trifluoride.

The hydrogen evolution method is based on the collection and measurement of the hydrogen which is evolved from the oxidation of trivalent

uranium by the hydrogen ion as hydrochloric acid as represented by the equation[1,2]

$$H^+ + UF_3 \longrightarrow U^{+4} + 3F^- + 1/2 \, H_2. \tag{1}$$

Where fluoride salts are concerned, the reaction is accelerated by adding boric acid which facilitates the dissolution of the sample by complexing the fluoride ion.

The apparatus is assembled as shown in Figure 1 and is purged with carbon dioxide by alternately evacuating the system and filling it with carbon dioxide. Hydrochloric acid is then added to the reaction flask containing the sample which is intimately mixed with boric acid. The solution is heated until the sample is completely dissolved. The hydrogen which is evolved from reaction(1) is swept by a current of carbon dioxide into the gas buret in which potassium hydroxide solution is confined. A correction for the vapor pressure of the potassium hydroxide solution[3] and a blank correction, the magnitude of which depends primarily on the amount of carbon dioxide used to sweep the hydrogen into the buret, is applied to the measured volume of hydrogen. In this report, the term "non-absorbable gases" refers to those gases that are not soluble in potassium hydroxide solution.

MODIFICATIONS

Source of Carbon Dioxide

The carbon dioxide which is to be used for purging the system must be of the highest purity available in order to have as low a volume of gases that are not absorbable in potassium hydroxide as possible. Perhaps the purest source of carbon dioxide is calcium carbonate in the form of iceland spar, which, upon acidification, releases carbon dioxide. The volume of non-absorbable gases per 100 ml is 0.05 ml. An alternate choice is marble

chips, another form of calcium carbonate. With both these reagents, a Kipp generator is required. The main disadvantage of either of these sources is their relatively high cost and attendant waste due to the use of a Kipp generator.

Carbon dioxide gas in cylinders was also investigated as a source of purge gas. This source was unsatisfactory because of its relatively poor degree of purity. The volume of non-absorbable gases varied from as low as 0.7 to as high as 2.5 ml per 100 ml. The disadvantage caused by these high, erratic blanks far outweighed any advantages that tank CO_2 might provide.

Solid carbon dioxide (dry ice) proved to be the most completely satis- factory source of gas. A two-liter Dewar flask is charged with dry ice and fitted with a safety valve arrangement as shown in Figure 2. This device is constructed from 8-mm outside diameter glass tubing. The vertical delivery tube is about 4-inches long and extends through a tight-fitting rubber stopper into the Dewar flask containing the dry ice. The right horizontal arm, which is connected to the gasometer, is approximately two- inches long and is equipped with a stopcock. The left horizontal arm is also 2 inches in length. The safety device is located at a distance of about 2 inches from the vertical delivery tube. This device consists of a vertical U-tube manometer approximately 8-inches long and a descending arm with an opening about one-half inch in diameter at a distance four inches below the horizontal arm. This opening is covered with a paper diaphragm, which is cut from Whatman No. 42 filter paper and glued securely to the opening, so that excess gas pressure can be released. The paper is of such porosity that mercury cannot diffuse through it. The flask is allowed to

"age" overnight, a process by which the dense carbon dioxide gas displaces
the less dense gases, present as impurities, such as oxygen and nitrogen
from the system.

The pertinent information concerning carbon dioxide with respect to
cost and volume of gas unabsorbed in potassium hydroxide is summarized in
the following table.

Table I

Comparison of Cost and Amount of Unabsorbed Gases of
Various Sources of Carbon Dioxide

Source	Cost, dollars		Gas Unabsorbed in KOH, per cent V/V
	Per Pound	Per Determination	
Dry ice	0.02	0.0004	0.03 to 0.05
Cylinder	0.20	0.004	0.7 to 0.05
Marble chips	0.50	0.01	0.15 to 0.3
Iceland spar	4.50	0.09	0.03 to 0.05

The advisability of using dry ice is obvious from the standpoint of
purity and cost. Iceland spar is equally pure but over 200 times as
expensive.

Vacuum to Provide Rapid Displacement of Non-Absorbable Gases from System

The atmosphere in the system is prepared rapidly by attaching a vacuum
line to the system (see Figure 1) and alternately evacuating and filling
the system with pure carbon dioxide from the CO_2 generator. Complete dis-
placement of the air and other non-absorbable gases can be accomplished
in about two minutes as compared to approximately ten minutes which is
required by following the original procedure[2] whereby carbon dioxide was
allowed to flow through the system until any non-absorbable gases were
completely removed.

Deaerated Hydrochloric Acid

Significant volumes of non-absorbable gas have been encountered from time to time that were attributed to dissolved air in the hydrochloric acid used to dissolve the trivalent uranium salt. These volumes were often quite large of the order of 0.1 to 0.8 ml (per 100 ml of CO_2) and, more importantly, were seldom reproducible. Attempts were made to expel the dissolved air by boiling the acid prior to its addition into the system. The volume of non-absorbable gases was of the order of 0.15 ml per 100 ml after this treatment.

Further tests were made in which the acid was boiled and cooled under a blanket of carbon dioxide. The blanks which are obtained on the hydrochloric acid when it is deaerated by this technique were somewhat lower; however, they were not reproducible on different solutions of hydrochloric acid which had been treated in the same manner. The method that proved to be the most satisfactory way to deaerate the hydrochloric acid was to purge the solution thoroughly with carbon dioxide by adding dry ice chips just before the introduction of the hydrochloric acid into the reaction flask. The blanks obtained on 100 ml of carbon dioxide and the hydrochloric acid solution under these conditions were of the order 0.05 ml of non-absorbable gases.

Rate of Flow of the Carbon Dioxide into the Gas Buret

The evolved hydrogen is swept by carbon dioxide into the gas buret at a carbon dioxide flow rate of about 15 ml per minute. It has been established that under these conditions, the carbon dioxide is completely absorbed by the potassium hydroxide solution and micro-bubbles are formed. In the earlier procedure[2] a slower flow rate was used that closely conformed to the flow rate recommended for the gasometric determination of nitrogen by

the Dumas method[3]. This modification has added to the overall decrease in analysis time.

Improved Sampling Technique

Uranium trifluoride, as such, is fairly stable to air and moisture; however, in the presence of alkali metal fluorides, in which trivalent uranium can exist as a complex fluoride salt, its stability is radically lessened. For example, in the presence of rubidium fluoride, uranium trifluoride is rapidly oxidized to tetravalent uranium in a matter of minutes when exposed to the atmosphere. In order to insure a suitable sample, all handling of trivalent uranium salts is conducted in a controlled, moisture-free atmosphere. The samples are ground in a dry box, weighed on a balance which is located in a dry box and transferred to the reactor flask tube in the dry box. In this manner the contamination of the sample by moisture is maintained at a minimum.

Dilute Potassium Hydroxide Absorber Solution

No correction is made for the adhesion of the potassium hydroxide solution to the wall of the gas buret since this device was fabricated from a 5-ml buret which had been calibrated to deliver rather than to contain. There is probably a slight but negligible film error due to the difference in viscosity of water and the potassium hydroxide solution. The magnitude of this possible error has been further decreased by reducing the concentration of the KOH absorbing solution to 33 W/W per cent.

RESULTS

In Table II are listed some typical analyses of different fused fluoride salt mixtures for trivalent uranium by the modified hydrogen evolution method. The duplicate analyses in all the tests we.. obtained simultaneously by two operators on two apparatus. Under these conditions one operator can make a single determination in approximately 30 minutes exclusive of sample preparation time. In an average work-day, one operator can make 10 determinations with ease.

Table II

The Analysis of Various Sample Types for Trivalent Uranium
by the Modified Hydrogen Evolution Method

Type	Hydrogen Measured, ml	Trivalent Uranium, Per Cent	Average	Coefficient of Variation, Per Cent
UF_3-UF_4	5.54	79.4		
	4.71	78.6	79.0	
	4.52	78.9		
	8.11	80.5	79.7	
	6.47	79.3		
	4.60	80.1	79.7	
	4.72	80.0		
	4.54	80.9	79.5	0.9
LiF-BeF_2-UF_3-UF_4	5.65	25.9		
	5.33	24.9	25.4	
	2.54	11.5		
	2.62	12.3	11.9	
	0.24	1.1		
	0.25	1.1	1.1	

Table II continued

Type	Hydrogen Measured, ml	Trivalent Uranium, Per Cent	Average	Coefficient of Variation, Per Cent
LiF-BeF$_2$-UF$_3$-UF$_4$ (continued)	0.57 0.58	2.63 2.59	2.6	
	4.00 4.15	56.8 57.6	57.2	3.3
NaF-LiF-UF$_3$-UF$_4$	2.87 2.61	44.8 45.4	45.2	
	3.47 3.43	21.2 20.8	21.0	
	2.32 2.35	20.4 20.3	20.3	
	2.41 2.68	41.4 40.8	41.1	
	2.76 2.63	12.6 12.2	12.4	1.4
NaF-LiF-KF-UF$_3$-UF$_4$	0.55 0.60	2.6 2.6	2.6	
	1.03 1.18	9.2 9.0	9.1	
	0.55 0.53	2.4 2.5	2.4	
	0.30 0.32	1.4 1.5	1.4	
	0.34 0.25	1.3 1.2	1.2	5.0
NaF-ZrF$_4$-UF$_3$-UF$_4$	0.40 0.35	2.9 2.2	2.6	
	0.27 0.26	1.5 1.6	1.5	
	0.39 0.51	2.2 1.8	2.0	
	0.49 0.48	2.2 2.0	2.1	
	0.23 0.34	1.3 1.9	1.6	
	0.30 0.32	1.4 1.4	1.4	1.2

The coefficient of variation for each sample type was calculated from the difference between duplicates.

$$P = \text{number of pairs of duplicates}$$

$$V = \text{coefficient of variation}$$

$$D = \text{difference between duplicates, per cent}$$

$$V = \sqrt{\frac{\Sigma D^2}{2P}}$$

The results show that the precision of the method is affected not only by the volume of hydrogen measured, as is to be expected, but also, by the composition of the sample. The most precise results were obtained on samples of essentially pure UF_3 that had UF_4 as the major impurity. When the concentration of UF_3 was approximately 12 to 40 per cent by weight in a mixture of $NaF-LiF-UF_4$, the precision was still quite satisfactory. The addition of either KF or ZrF_4 to this mixture of fluoride salts resulted in a marked decrease in precision. This effect can also be attributed to the small volume of hydrogen collected.

The obvious solution is to take a larger sample and thereby collect a larger volume of gas. This approach has practical limitations, however. The reaction flask, which has a 25-ml capacity, is the ideal size to permit adequate sparging of residual air and hydrogen by carbon dioxide. The maximum size sample that can be handled is 1.5 g of which 1 g is boric acid, which is required in dissolving the fluoride samples. Larger samples would require a larger capacity flask. In the original investigation of this method, it was found that erratic results were obtained when 50-ml flasks were used. It was only when the smaller flask was used that satisfactory precision was realized. This phenomenon is often encountered in gasometric measurements.

The overall precision, when measuring volumes of gas less than 1 ml is, nevertheless, quite satisfactory since such important factors as sample homogeneity and contamination during sampling may easily account for significant errors when such small volumes are measured.

CONCLUSIONS

A number of modifications have been made to the hydrogen evolution method for the determination of trivalent uranium that have resulted in a significant decrease in time of analysis per sample and a more reliable and reproducible result.

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3. J. B. Niederl and V. Niederl, Micromethods of Quantitative Organic Analysis, Second Edition, p. 95, John Wiley and Sons, Inc., New York, N. Y. (1947).

APPENDIX

DETERMINATION OF TRIVALENT URANIUM IN FLUORIDE SALT MIXTURES
BY THE MODIFIED HYDROGEN EVOLUTION METHOD

Preparation of Sample

1. Place the sample, along with a mortar and pestle, in a dry-box in which a completely dry atmosphere is maintained at all times.

2. Grind the sample so that it will pass through a No. 48-mesh sieve.

3. Mix the sample thoroughly and transfer it to a dry sample bottle.

4. Transfer the sample bottle and its contents to a dry-box which contains an analytical balance.

Reagents

1. Hydrochloric acid (4:1). Prepare by adding 400 ml of concentrated hydrochloric acid to 100 ml of water. Before addition of the acid to the samples, add several chips of dry ice.

2. Boric acid, fine crystal, reagent grade.

3. Potassium hydroxide solution (approximately 33 W/W per cent). Add 450 g of reagent grade potassium hydroxide to 1000 ml of water. Allow to cool and keep tightly stoppered.

4. Dry ice (for carbon dioxide generator).

5. Mercury.

Apparatus

1. Dewar flask - 2-liter capacity.

2. Gasometer - 100-ml capacity.

3. Reaction flask - 15-ml, round-bottom flask fitted with two side arms as shown in Figure 1.

4. Acid buret - 10-ml buret.

5. Heater - Fisher-Snell "Hotspotter."

6. Gas buret - 10-ml capacity.

7. Vacuum pump.

Procedure

1. Close all stopcocks on apparatus.

2. Open stopcock No. 6 and fill gas buret to zero mark with KOH solution. Close stopcock, check to be sure no leaks occur.

3. Weigh a sample (maximum size 0.5 g) to nearest mg in a balance pan and transfer to a clean, oven-dried reaction flask. (Note: This operation must be performed in a moisture-free atmosphere (CO_2 is recommended). A convenient device consists of an analytical chainomatic keyboard-type balance, from which the front glass has been removed, placed in a plastic box equipped with portholes and rubber gloves.)

4. Add 0.5 to 1 g of boric acid crystals to the reaction flask.

5. Remove the reaction flask containing the sample from the dry-box and place on the apparatus as shown in diagram. (Note: Keep the reaction flask closed by placing a stopper in the flask during transfer to apparatus in order to exclude moist air.)

6. With reaction flask in place, open stopcocks No. 1 and 2 and fill gasometer with 100 ml of CO_2.

7. Close stopcock No. 2 and open No. 5 to vacuum line for approximately 30 seconds.

8. Close stopcock No. 5 and open No. 3 to fill system with CO_2.

9. Repeat steps 6, 7, and 8 several times.

10. Check for residual air in the system by passing 100 ml of CO_2 through the gas buret. Only micro-bubbles should be observed rising through the KOH solution in the gas buret. If the system is air-free, the volume of gas measured should be 0.3 to 0.6 ml per 100 ml. If a greater volume is recorded, steps No. 6, 7, 8, and 10 should be repeated.

11. When the system is air-free, zero the gas buret as in step No. 2.

12. With gasometer at zero level and stopcocks No. 2 and 5 closed, lower mercury bulb slightly and open stopcock No. 4. Allow 10 ml of hydrochloric acid solution to flow into the reaction vessel and then close stopcock No. 4.

13. Return gasometer to zero level and open stopcock No. 5 to the gas buret.

14. Close stopcock No. 5.

15. Apply heat to the reaction vessel with a "Hotspotter" heater. Continue gentle heating until the entire sample is in solution and the solution is green in color.

16. While solutioning is proceeding in step 15, the gasometer is again filled with CO_2 as described in step 6.

17. After solutioning is complete, open stopcock No. 3 and flush the system with 100 ml of CO_2. After the first 20 or 30 ml of gas have passed through, micro-bubbles should be observed rising in the gas buret.

18. Close all stopcocks and record the volume of hydrogen collected.

19. Note barometric pressure and room temperature at the time the analysis is made.

20. Each new batch of acid made should be checked for the absorbed gas content. This is done by following steps 1, 2, and 6 through 18 using a dry reaction vessel in place of a sample. The volume measured not only includes the volume of absorbed gases in the hydrochloric acid solution, but also the impurities in 100 ml of CO_2.
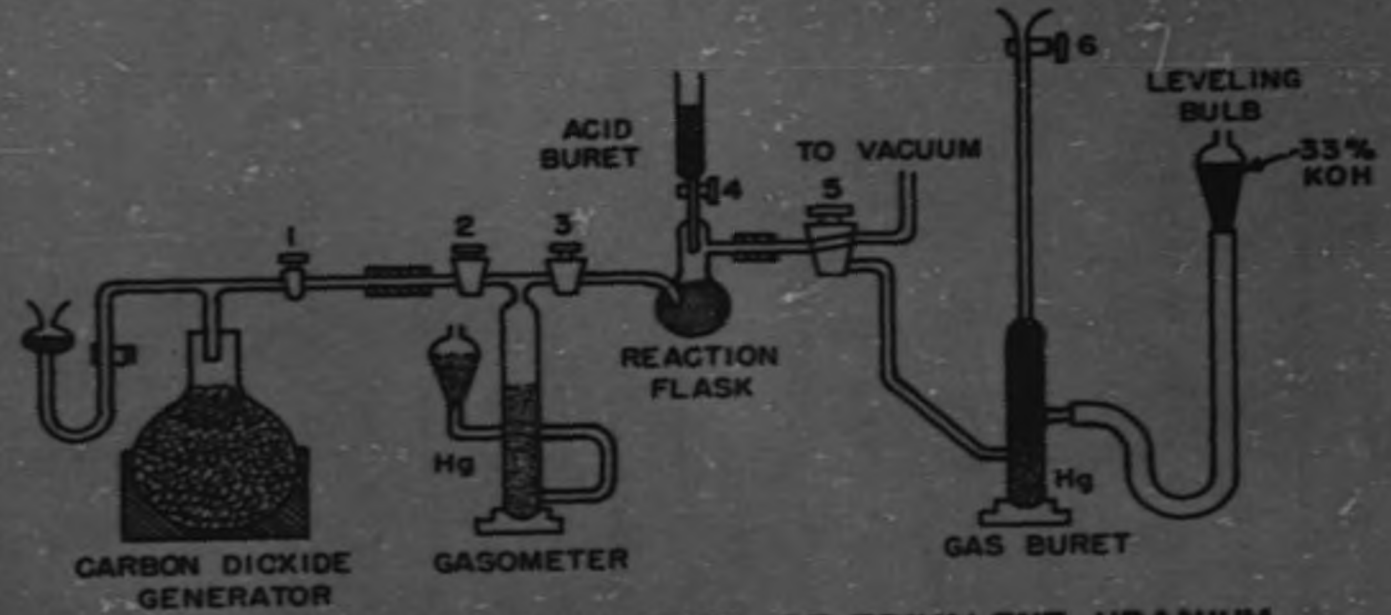
Calculation

$$\frac{(H_2, \text{ml} - \text{blank, ml}) \times 0.765 \times \text{observed barometric pressure in mm}}{\text{Temperature, }^\circ K \times \text{weight of sample, g}} = U^{+3}, \text{ per cent}$$
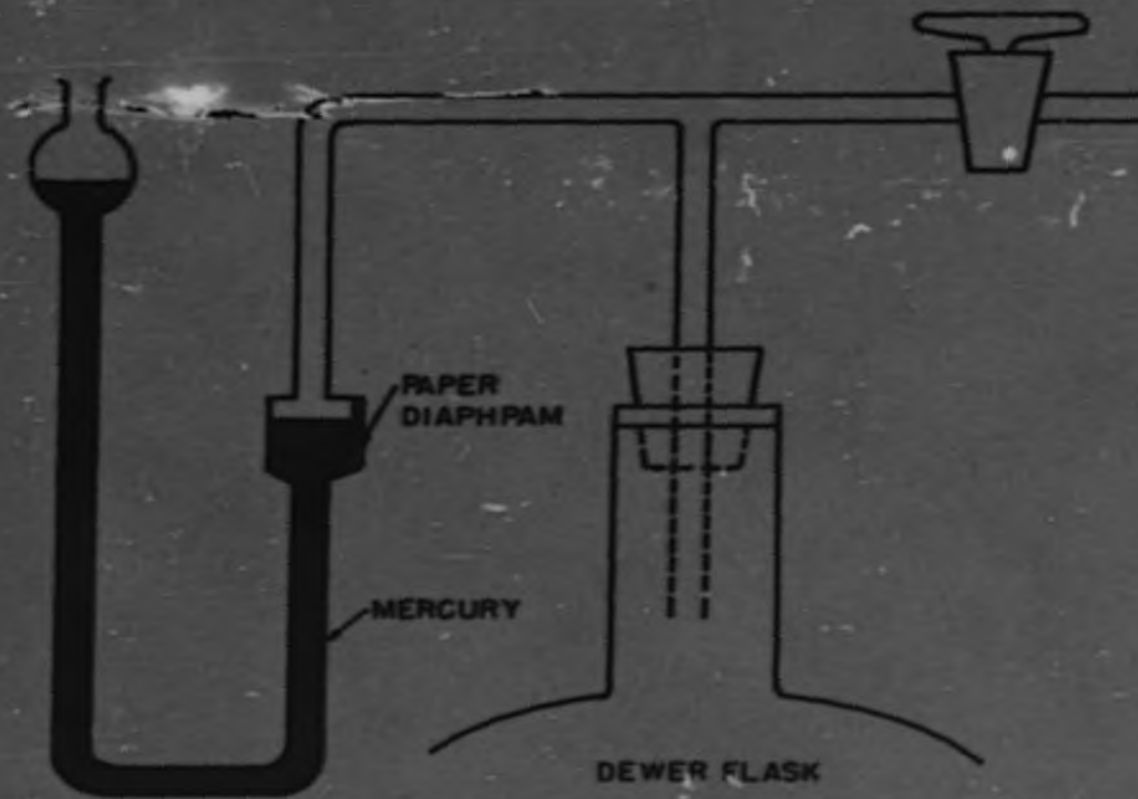
APPRATUS FOR THE DETERMINATION OF TRIVALENT URANIUM
BY THE HYDROGEN EVOLUTION METHOD
FIGURE 1.

PAPER
DIAPHPAM

MERCURY

DEWER FLASK

FIGURE 2 – SAFETY VALVE ARRANGEMENT FOR THE
CARBON DIOXIDE GENERATOR

END