J. Inorg. Nucl. Chem., 1962, Vol. 24, pp. 393 to 398. Pergamon Press Ltd. Printed in England

HIGH PRESSURE FLUORINATION OF URANIUM OXIDES*

R. E. GREENE and G. S. PETIT
Technical Division, Oak Ridge Gaseous Diffusion Plant,
Union Carbide Nuclear Company, Oak Ridge, Tennessee

(*Received* 28 *November* 1960; *in revised form* 9 *October* 1961)

Abstract—A new method for the fluorination of uranium oxides to uranium hexafluoride has been developed. It uses gaseous fluorine at a pressure of about 1000 lbin^{-2}. The pressure is obtained by vapourization of liquid fluorine which has been condensed onto the oxide and an activator, potassium chloride, in a metal reactor at liquid nitrogen temperature. When the closed reactor warms within a safety shield, the fluorine vaporizes and a fluorination takes place very rapidly, usually before the reactor reaches room temperature. The reactor is again cooled and oxygen and unconsumed fluorine are separated from the condensed uranium hexafluoride by pumping. Based upon uranium, a 95 per cent yield of uranium hexafluoride, pure enough for isotopic analysis with the gas-type mass spectrometer, is obtained. The reactor also serves as the sample tube after the fluorination, which is completed in 15 min or less. Although the method is primarily used for the conversion of laboratory samples for uranium isotopic analysis, other applications may be feasible.

ONE of the oldest and most widely used methods for preparing uranium hexafluoride from uranium oxides uses colbaltic fluoride.(1)

$$U_3O_8+18CoF_3 \xrightarrow{375^\circ C} 3UF_6+18CoF_2+4O_2 \qquad (1)$$

Another uses gaseous fluorine at a pressure of one atmosphere or less.(2)

$$U_3O_8+9F_2 \xrightarrow{370^\circ C} 3UF_6+4O_2,\ \Delta H = -223\cdot 3 \text{ kcal/mole} \qquad (2)$$

These methods require about 3 hr for the preparation of 2 g of uranium hexafluoride with an expenditure of a minimum of one man hour per sample. A third method(3) uses liquid bromine trifluoride in a bomb reactor.

$$\tfrac{1}{3}\ U_3O_8+2BrF_3 \longrightarrow UF_6+Br_2+\tfrac{4}{3}O_2,\ \Delta H = -73\cdot 3 \text{ kcal/mole} \qquad (3)$$

It has been used routinely to fluorinate a sample in 30 min, but a larger amount of oxide is required, since some uranium hexafluoride is lost with the bromine in the purification step. A transfer of the uranium hexafluoride to a mass spectrometer sample tube is also necessary to separate the uranium hexafluoride from halogen compounds which interfere with the isotopic analysis.

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* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

(1) A. E. CAMERON, "Determination of the Isotopic Composition of Uranium", TID-5213, Chapter 2, Office of Technical Services, Department of Commerce, Washington D.C. (1950).

(2) J. J. KATZ and E. RABINOWITCH, *Chemistry of Uranium*, NNES, Div. VIII, Vol. 5, p. 399. McGraw-Hill, New York (1951).

(3) R. E. GREENE and G. S. PETIT, *Fluorination of Uranium Oxides With Bromine Trifluoride for Mass Spectrometer Assaying*, Carbide and Carbon Chemicals Company, K-25 Plant, August 25, 1954 (K-1137).

Although the chemistry and heat of reaction of the new method are essentially the same as that of equation (2), the reaction rate is much greater because of the high fluorine pressure; therefore, much higher temperatures are developed at the site of the reaction.

The new method has a number of advantages over the older ones. It eliminates tedious glass blowing, furnace heating, and lengthy distillation techniques. It produces a very pure product in high yield and eliminates transfer of the sample, since the reactor also serves as the spectrometer sample tube. With it, a fluorination can be completed in less than 15 min. A large heavy wall nickel reactor has been used to fluorinate as much as 10 g of oxide in one batch and temperatures as high as 550°C have been observed.

EXPERIMENTAL

Apparatus

The reactor is made from a packless diaphragm Monel angle valve. A connector seat is silver soldered to the diaphragm side of the valve and a standard $\frac{3}{8}$ or $\frac{1}{2}$ in. copper male flare fitting to the other. A section of copper tubing, 0·049 in. wall thickness and 4 in. long is pinched closed, Heliarc welded or silver soldered pressure tight, and fastened to the valve with a flare nut (Fig. 1).

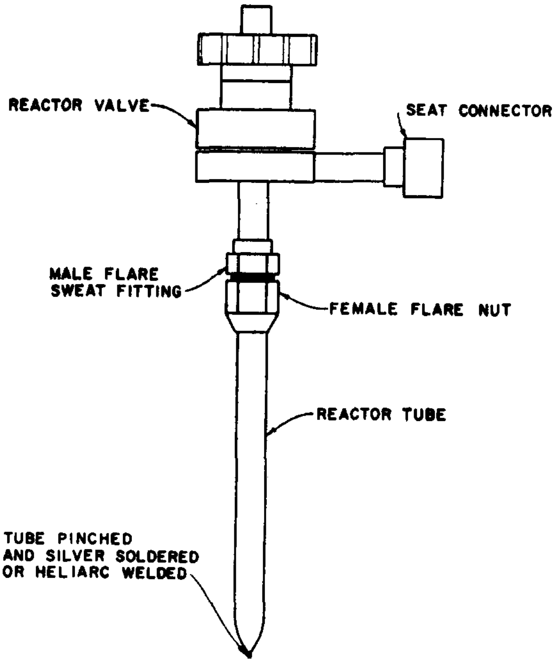

FIG. 1.—REACTOR.

The vacuum manifold (Fig. 2) and the fluorination manifold (Fig. 3) are constructed primarily of nickel and Monel. The fluorination system, except the fluorine tank, is installed in a fume hood.

A thermocouple is clamped to the lower portion of the reactor tube and connected to a suitable pyrometer.

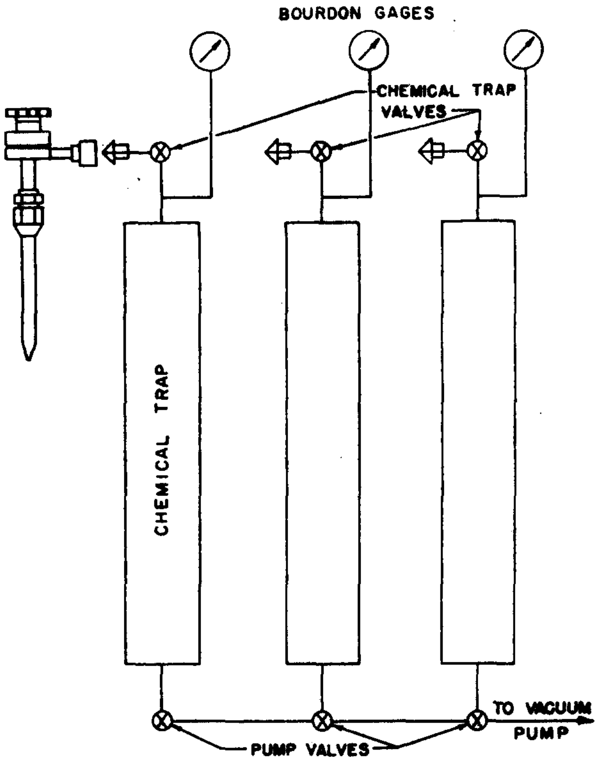

FIG. 2.—VACUUM MANIFOLD.

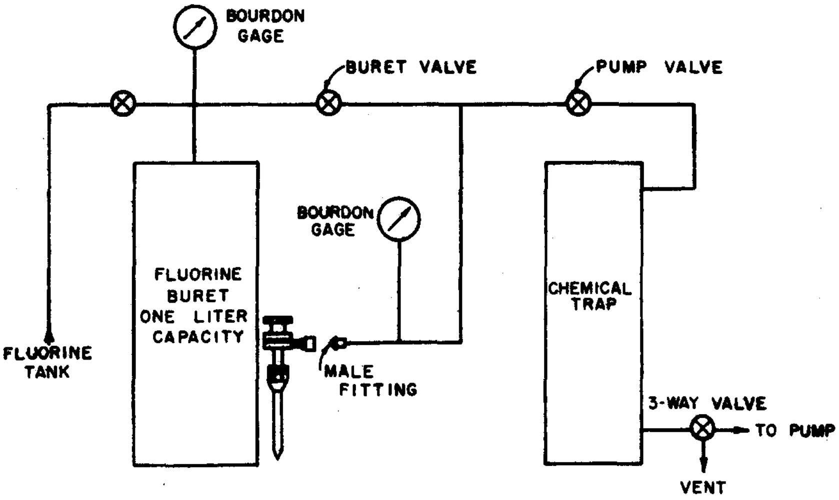

FIG. 3.—FLUORINE MANIFOLD.

An explosion shield encompasses the lower portion of the reactor during the reaction. It is made of 4 in. steel pipe so that a Dewar flask containing liquid nitrogen can be raised and lowered within it. The rear of the shield is perforated to relieve pressure in event of an explosion (Fig. 4).

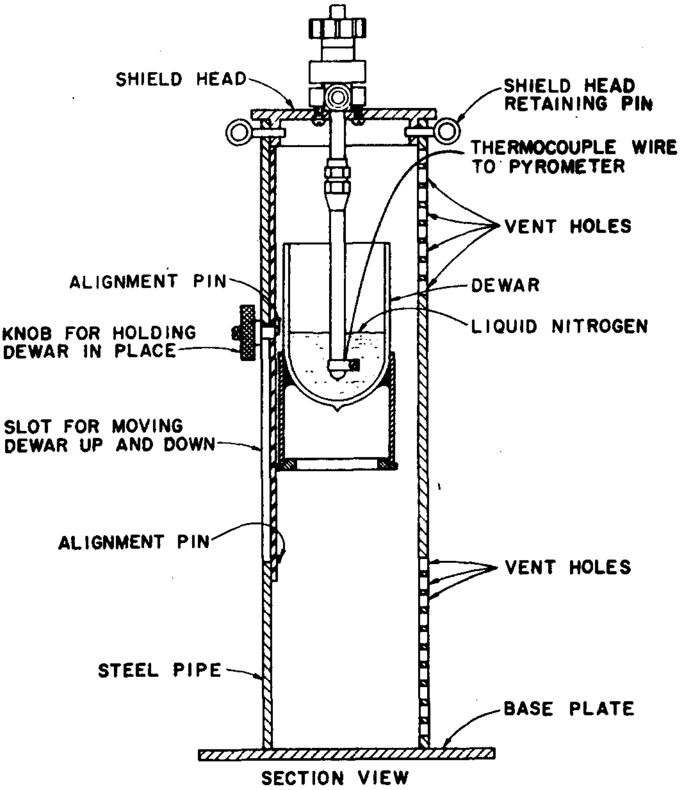

FIG. 4.—EXPLOSION SHIELD.

Procedure

A weighed quantity of uranium oxide, from 1 to 3 g, is mixed with about 1 mg of potassium chloride and transferred to the reactor (Fig. 1). The reactor is then assembled and evacuated without heating. The thermocouple is attached and the reactor placed in the safety shield. A quantity of fluorine which is at least three times the stoicheiometric amount required and sufficient to develop a fluorine pressure of at least 750 lbin^{-2} within the reactor, is measured into the burette. Some of this fluorine is admitted to the sample at room temperature to desensitize impurities that are highly reactive with fluorine. After 1 min, the Dewar within the shield is raised to immerse the lower portion of the reactor in liquid nitrogen, and the remainder of the fluorine is admitted. When the fluorine pressure drops to about 300 mm of mercury, the approximate vapour-pressure of fluorine at liquid nitrogen temperature, the valve of the reactor is closed. The line between the reactor and the burette is then evacuated, and the reactor is disconnected from the fluorine manifold. The Dewar containing the liquid nitrogen is lowered, permitting the liquid fluorine to boil and build up pressure. When the reaction takes place (usually before the reactor reaches room temperature), the reactor tube heats almost instantaneously to 200–400° C.

The reactor is cooled for about a minute in air, and then in liquid nitrogen to liquefy the fluorine and oxygen, which reduces the pressure. These gases are then removed using the vacuum manifold (Fig. 2). Reheating to about 100° C with the valve closed, followed by flash pumping at ice-brine temperature, purifies the uranium hexafluoride adequately for admission into gas-type mass spectrometers.

RESULTS

Several thousand oxide samples have been fluorinated by this method. The uranium hexafluoride is of high purity, and the yield is approximately 95 per cent.

Rush samples have been prepared for introduction into the mass spectrometer in less than 15 min. A 2 g sample of uranium oxide can be fluorinated with a total of 0·4 man hours of labour, including fabricating the reactor tube and cleaning the reactor valve.

DISCUSSION

Activators

The potassium chloride activator apparently serves only as an igniter or energy supplier rather than a catalyst since many materials initiate the reaction between uranium oxide and fluorine under high pressure. Iron oxides, potassium tartrate, and silicic acid in addition to the chlorides, bromides and iodides of potassium and sodium, have been observed to promote this reaction. Some impure samples of uranium oxides reacted with fluorine without the addition of an activator; however, purified oxide samples under the same conditions would not react with fluorine without the presence of some starter material.

All of the uranium oxides can be fluorinated using potassium chloride as the activator but potassium iodide is a much better activator for uranium tetrafluoride. With potassium iodide, yields of approximately 85 per cent have been achieved. With the proper activator the method may be useful for fluorinating a variety of other materials.

Fluorination of uranium metal

Fine turnings of metallic uranium react violently with fluorine under high pressure, usually bursting the reactor, whereas massive pieces do not fluorinate at room temperature with potassium chloride as an activator. Metal samples should be ignited to uranium oxide before fluorination.

Purity

Impurities in uranium hexafluoride prepared by the described method have been determined using recording gas-type mass spectrometers. Mass spectrum data show only trace amounts of chlorine, hydrofluoric acid, and chloryl fluoride (ClO_2F). The purity of the product is dependent upon that of the starting material, the fluorine, the amount and type of activator used, and the purification treatment after fluorination. The method has consistently produced samples that meet the stringent purity requirements for highly precise uranium isotopic measurements by mass spectrometry.

Explosions

Occasionally the reaction may burst the reactor tube. For this reason fluorinations are performed with the reactor tube in a shield of steel pipe. The cause of these infrequent explosions has not been determined, but they may result from an impurity that activates the entire charge of the reactor at once, producing a reaction more violent than the usual rapid burning. Some of the impurities that have been suspected are carbon, platinum, silver, chromium and boron. These impurities have been added in a concentration of approximately fifty parts per million to test samples of pure oxide, but these adulterated samples produced no explosions. Alteration of oxide surface area and slight traces of moisture appeared to make little difference in explosion susceptibility.

The tendency of impure oxides to cause explosions during fluorination can be reduced by treating them with hydrofluoric acid. This treatment consists of placing a few grammes of the oxide in a platinum dish, and covering with 48 per cent hydrofluoric acid, drying under an infra-red lamp, and igniting to the oxide in a steam atmosphere at 800°C. Uranium trioxide samples usually do not require the hydrofluoric acid treatment. The frequency of explosions has also been reduced by modifying the procedure in such a manner as to expose the sample first to gaseous fluorine at room temperature, which renders inactive those impurities which are highly reactive with fluorine.

Reactor tubes

Experience has shown that increasing the wall thickness of the copper reactor tubes from 0·032 to 0·049 in. reduced the frequency of tube ruptures to less than one in 500. The heavier walled tube withstands a pressure of nearly 9000 lbin^{-2} at room temperature, while the thinner ones rupture at approximately 5500 lbin^{-2}.

A new reactor tube is used for each sample, since a new tube costs no more than cleaning a used one.

Operating pressures

A special fluorination reactor was constructed with an attached pressure gauge for studying minimum initial reaction pressures with pure urano-uranic oxide. Reactions could not be produced below 750 lbin^{-2} of fluorine pressure at room temperature with potassium chloride as the activator: however, in routine operations where approximately 1000 lbin^{-2} fluorine pressure is used, the majority of the reactions start below room temperature. The reactions begin at a lower pressure with potassium iodide than with potassium chloride as the activator.

Prevention of isotopic and chemical contamination

In a laboratory where a range of isotopic concentrations of uranium is handled, care must be taken to prevent contamination of one sample by another. For this reason several vacuum systems are used to minimize accidental contamination. All reactor valves are coded and each valve is used for samples in a limited isotopic range. Each vacuum system is also restricted to a designated isotopic range.

The reactor, after being charged with fluorine and while still within the shield, is disconnected from the fluorine manifold before the reaction to avoid contamination of the manifold in event a leak of the reactor valve occurs. The use of a new reactor tube for each sample also greatly reduces the possibility of isotopic contamination.

Heat should not be used in the evacuation of the sample before fluorination. Heating the sample during evacuation causes a sudden rise in pressure, probably due to rapid vapourization of contained water, forcing some of the powdered sample into the evacuation lines and contaminating them. This phenomenon was observed with uranium trioxide in a glass system.

Contamination with organic materials must be prevented where fluorine is used. Organic solvents are never used in cleaning fluorination apparatus, as even small amounts of such material can cause serious explosions with fluorine.(4)

(4) R. H. LAFFERTY, J. C. BARTON and J. A. WESTBROOK, *Liquid Fluorine-CottonExplosion, Chemical and Engineering News*, Vol. 26, p. 3336. Amer. Chem. Soc. (1948).