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**DETERMINATION  
OF MICROGRAM QUANTITIES  
OF FLUORIDE IN METAL OXIDES**

C. E. PLUCINSKI

**MARCH, 1968**



**AEC RESEARCH &  
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OF FLUORIDE IN METAL OXIDES

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March 1968

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## DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE IN METAL OXIDES

### ABSTRACT

*A method for rapid and precise determination of fluoride in uranium and plutonium oxide was developed. The fluoride is separated from the oxide matrix by pyrohydrolysis and the amount measured with an electrode sensitive to fluoride ion activity. One to 100 ppm of fluoride can be determined in less than 15 min with a relative standard deviation of 3%.*

### INTRODUCTION

Corrosion of cladding resulting from the presence of small amounts of fluoride in reactor fuel elements may lead to their failure. The determination of the fluoride content of reactor fuel materials provides the essential quality control to minimize this possibility. The fluoride is most commonly determined colorimetrically after it is separated from the oxide matrix by pyrohydrolysis. Since the colorimetric method used in this laboratory has some disadvantages, an alternate method was sought. A study was undertaken to establish conditions under which the separated fluoride could be determined with a fluoride-sensitive electrode.

### SUMMARY AND CONCLUSIONS

A method for the precise and rapid determination of microgram quantities of fluoride in plutonium and uranium oxide was developed. The fluoride is separated by pyrohydrolysis, quantitatively collected in an acetate buffer

solution, and the amount measured with a fluoride-sensitive electrode. The use of 1- to 2-gram samples will permit the analysis of 1 to 100 ppm fluoride. From 2 to 100 micrograms of fluoride in  $U_3O_8$  have been determined with a relative standard deviation of 3% or less. A complete fluoride determination can be made in 15 min on samples containing less than 100 micrograms of fluoride.

Close control of pyrohydrolysis conditions is essential to assure quantitative fluoride recovery from the oxide matrix. With a reaction temperature of 850 °C and an air flow rate of 50 liters/hr or greater, up to 100 micrograms of fluoride can be quantitatively separated in 5 min.

Volatile products of the pyrohydrolysis reaction such as chloride, nitrate, and sulfate, if present in small amounts, do not adversely affect the fluoride electrode measurement. However, variations in both pH and ionic strength do affect the response of the fluoride-sensitive electrode to fluoride ion activity. These variations are minimized by making all

fluoride measurements in a buffer solution (0.001N in acetic acid and 0.001N in potassium acetate.) Accurate fluoride measurements can be made in less than 5 min using only 5 ml of solution.

## DISCUSSION

### LANTHANUM FLUORIDE MEMBRANE ELECTRODE

#### General Description

The lanthanum fluoride membrane electrode described by Frant and Ross<sup>(1)</sup> responds to fluoride ion activity in solution over more than 5 orders of magnitude. The electrode is similar in principle to that of a conventional glass electrode used for the determination of pH. Its response is Nernstian throughout its useful operating range (1M to  $10^{-6}$ M fluoride). Since the lanthanum fluoride crystal is permeable only to free fluoride ions in solution, the cell potential is given by  $E = \epsilon - RT/F \ln F^-$  activity, with  $\epsilon$  constant and independent of the composition of the sample. In practice, an empirical working curve is prepared by determining the potential across the fluoride-sensitive working electrode and a saturated calomel reference electrode immersed in solutions containing known amounts of fluoride added as the sodium salt. Any high impedance millivoltmeter can be used for this purpose.

The only significant interference with the fluoride determination is due to changes in pH. At high pH the fluoride electrode appears to respond to hydroxide ion as well as to fluoride ion. In solutions of low pH,

the electrode response is affected by an equilibrium shift of the reaction  $HF \rightleftharpoons H^+ + F^-$  which alters the amount of free fluoride ion in solution. Hence, at high pH, the apparent amount of fluoride ion in solution is increased producing a high electrode response while, at low pH, the amount of free fluoride ion in solution is decreased giving a low response. The presence of other cations which complex fluoride ion also gives low results since the fluoride-sensitive electrode responds only to free fluoride. This may or may not be an advantage depending upon whether total fluoride or free fluoride is desired.

Common anions such as  $NO_3^-$ ,  $SO_4^{2-}$ , and  $Cl^-$  which may interfere with the colorimetric determination of fluoride do not chemically affect the fluoride electrode measurement even when the ratio of foreign anion to fluoride ion exceeds 1000.<sup>(1)</sup> However, a change in ionic strength of solutions containing fluoride does affect the fluoride ion activity because of a change of the activity coefficient (see Figure 1). For most accurate measurement of fluoride ion activity, fluoride solutions must be maintained at constant ionic strength.

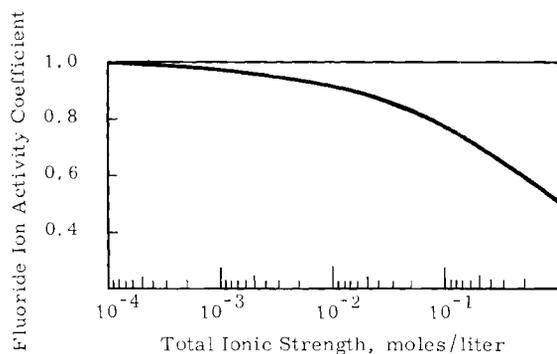


FIGURE 1. Effect of Total Ionic Strength on Fluoride Ion Activity Coefficient

### Development of a Solution for Absorption and Measurement

Both separation and measurement are essential steps for the determination of fluoride in uranium and plutonium oxide. The fluoride is separated by pyrohydrolysis and collected in an aqueous solution capable of effectively trapping the fluoride and also suitable as a medium for the fluoride measurement.

Historically, caustic has been used by others<sup>(3,4)</sup> to trap fluoride and other products separated by pyrohydrolysis. A solution 0.025N in sodium hydroxide was used as the pyrohydrolysis trap solution in this laboratory. But, because the high hydroxide ion concentration of this solution affects the fluoride measurement using a fluoride-sensitive electrode, an alternative trap solution was sought. Distilled water was effective in trapping the fluoride produced by pyrohydrolysis. However, the low ionic strength of very small amounts of fluoride in distilled water resulted in unstable solutions, and the fluoride results showed considerable variation (see Figure 2a). A buffer solution 0.001N in acetic acid and 0.001N in potassium acetate was used as a trap solution for up to 100 micrograms of fluoride and, like distilled water, was found to be effective in trapping fluoride (see Figure 2b). Obviously, the chemical trapping provided by a caustic solution is not needed. In addition to acting as an effective trap, the acetic acid-potassium acetate solution buffers both the pH and the ionic strength when only small

amounts of pyrohydrolysis products are present. Hence, the solution serves as an excellent medium for the measurement of fluoride with a fluoride-sensitive electrode.

### Calibration of the Electrode

The response of the fluoride-sensitive electrode was tested with standards containing  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$ M NaF in distilled water. A fluoride electrode and a saturated calomel reference electrode were immersed in each of the above solutions and the potentials measured. Three sets of such data were taken over a one-week period. Plotting of the logarithm of the fluoride concentration versus potential for each set of data resulted in a straight line as shown in Figure 3.

Because of fuel material specifications, only a narrow range of the fluoride response was utilized ( $5 \times 10^{-6}$ M to  $8 \times 10^{-5}$ M). For convenience, the units of fluoride measurement were converted from moles per liter to micrograms per 20 ml. Calibration curves were prepared by measuring the potentials of standard solutions containing 1.9, 3.8, 7.6, 11.4, 15.2, 22.8, and 30.4 micrograms of fluoride per 20 ml of water. Figure 2a is a graphic presentation of the data determined on 3 consecutive days. The considerable variation shown in these data thus prompted search for an alternate measurement medium.

Figure 2b presents the data for the same range of fluoride. These fluoride standards, however, were

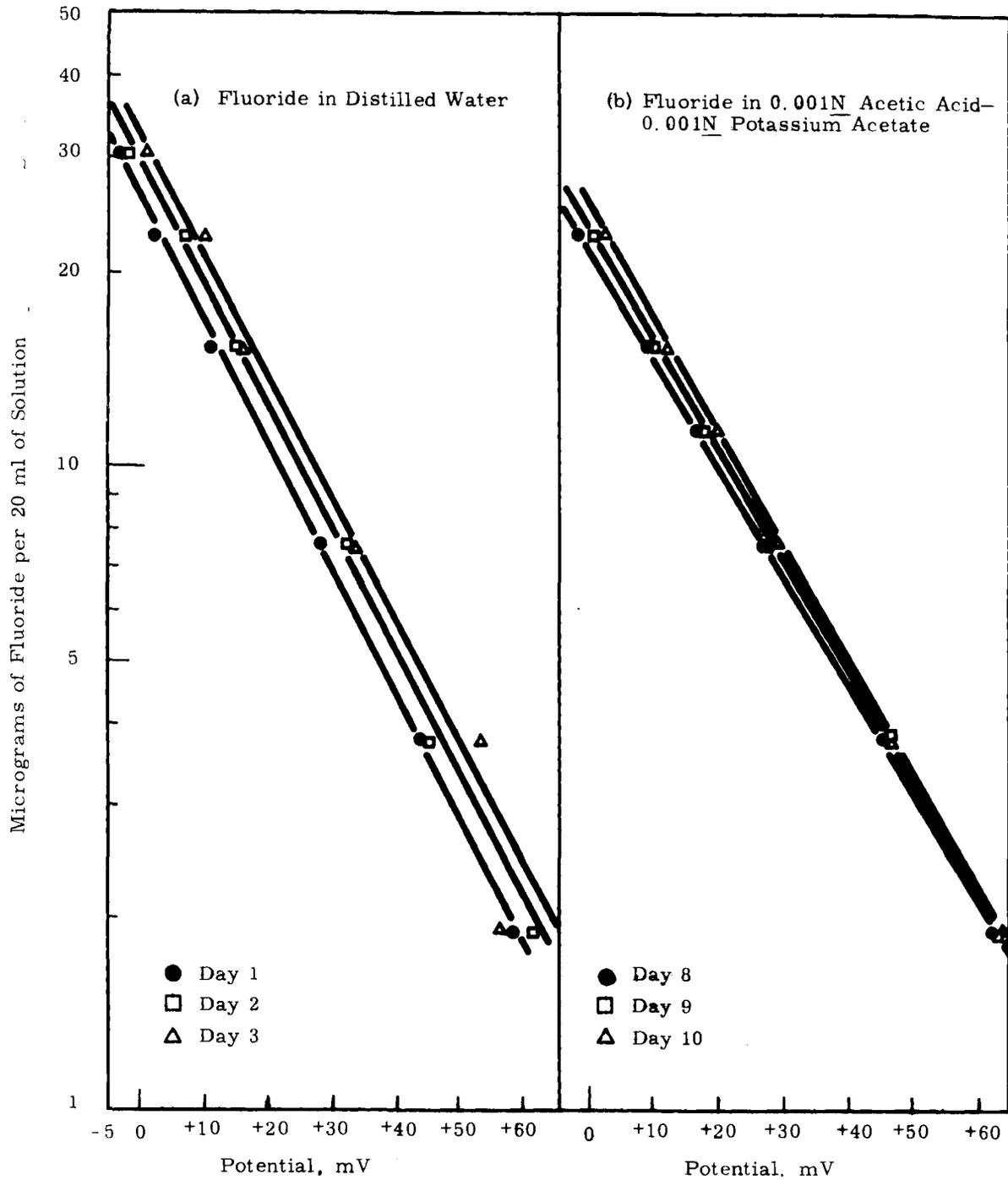


FIGURE 2. Calibration of the Fluoride Electrode

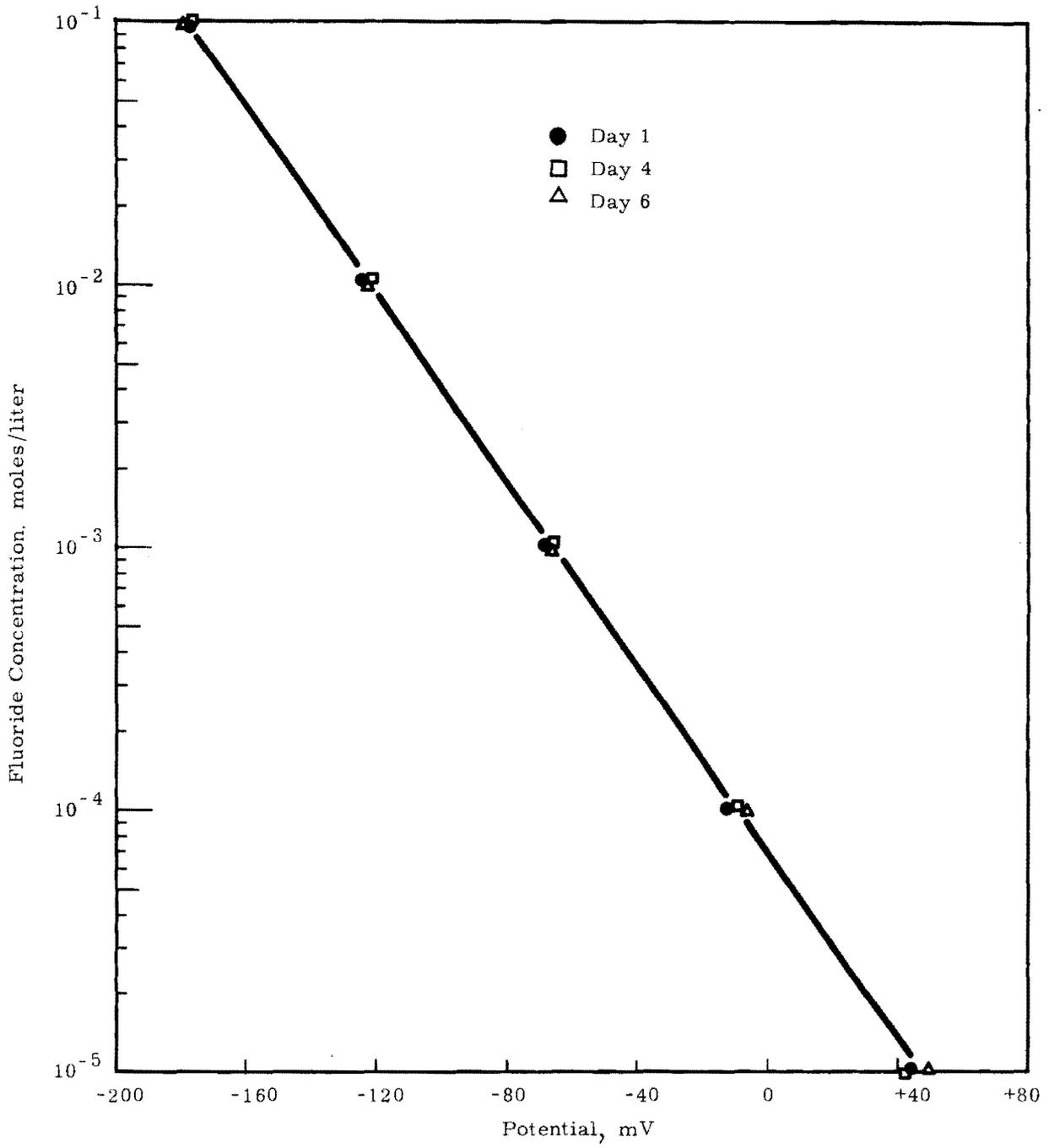


FIGURE 3. Response of the Fluoride Electrode

prepared in the buffer solution described earlier. While day-to-day variations are still apparent, data determined on the same day show considerably less variation than those shown in Figure 2a. The response of the fluoride electrode is more rapid in the buffer solution than in water alone, presumably because of the increased ionic strength.

#### DETERMINATION OF FLUORIDE IN $U_3O_8$

##### Standard Preparation

A standard containing a known amount of fluoride in  $U_3O_8$  was prepared to test the method. Some NaF, KCl, and  $U_3O_8$  were each passed through a 200 mesh screen to obtain particle size separation. Only that material passing through the screen was used to prepare the standard mixture. Exactly 12.5 mg of NaF and 10.8 mg of KCl were added to 56.54 g of  $U_3O_8$  which had been previously pyrohydrolyzed to remove traces of fluoride. The mixture was placed in a mixer mill shaker for about 3 hr to ensure homogeneity.

The mixture containing 100 micrograms of fluoride per gram and 75.7 micrograms of chloride per gram can be used as a standard for both fluoride and chloride. Only the fluoride was measured in this study and the presence of chloride did not affect the fluoride determination.

##### Pyrohydrolysis

The fluoride is separated by pyrohydrolysis<sup>(2,3,4)</sup> prior to its

measurement with a fluoride-sensitive electrode. The pyrohydrolysis apparatus used is a modification of that reported by Powell and Menis<sup>(3)</sup> and is described in the appendix. The reaction conditions were kept constant during all fluoride separations to ensure uniformity of operation. The reaction temperature was maintained at 850°C and an air flow rate of 50 liter per hr or greater was provided. A water temperature of 50°C provided sufficient water for the reaction of up to 100 micrograms of fluoride yet not enough to produce objectionably large amounts of condensate. Under these conditions, water collected in the trap solution amounted to only 1 to 2 ml. Quantitative fluoride recoveries easily resulted with the use of a 15-min reaction time. In fact, two samples were run for only 5 min under these conditions, yet excellent fluoride recovery resulted.

##### Fluoride Results

Varying amounts of the prepared standard containing from 1.7 to 102 micrograms of fluoride were weighed, mixed with 4.0 g of  $U_3O_8$  accelerator, and pyrohydrolyzed. The separated fluoride was collected in 20 ml of acetate buffer solution and the amount of fluoride was measured with the aforementioned fluoride-sensitive electrode. All results are presented in Table I.

The accurate measurement of both samples and blanks is necessary to determine accurately the fluoride content of samples. To determine

TABLE I. Determination of Fluoride in  $U_3O_8$ 

Sample Number	Reaction Time, min	Fluoride Blank Correction, $\mu\text{g}$	Fluoride Added, $\mu\text{g}$	Fluoride <sup>(a)</sup> Recovered, $\mu\text{g}$	Percent Recovery
1	15	2.9	6.4	6.4	100
2	15	2.9	15.4	15.0	97
3	15	2.9	8.4	8.1	96
4	15	2.9	1.7	1.7	100
5	15	2.9	10.1	9.9	98
6	15	2.7	9.8	10.0	102
7	15	2.7	5.6	5.6	100
8	15	2.7	7.6	7.8	103
9	15	2.7	17.5	17.1	98
10	15	2.8	11.7	11.5	98
11	15	2.8	5.0	4.7	94
12	15	2.8	18.4	18.2	99
13	15	2.8	51	49	96
14	15	2.8	49	47	96
15	5	2.8	47	46	98
16	5	2.8	102	100	98

(a) Corrected for blank.

the blank, 4.0 g of  $U_3O_8$  was pyrohydrolyzed under the same conditions established for sample mixtures. The amounts of fluoride in 4.0 g of  $U_3O_8$ , determined over a period of several days, are shown in Table II. The variation in blank is consistent with the sensitivity of the potential measurement,  $\pm 1$  mV. A potential difference of  $\pm 1$  mV is equal to  $\pm 0.1$  microgram of fluoride at the 3 microgram fluoride level (representative of the blank), to  $\pm 0.3$  micrograms of fluoride at the 10 microgram level, and to  $\pm 0.5$  micrograms of fluoride at the 20 microgram level (see Figure 2b).

TABLE II. Fluoride Blanks

Blank Runs	Fluoride, $\mu\text{g}$
Day 1	2.9
Day 1	3.0
Day 1	2.8
Day 2	2.6
Day 2	2.8
Day 4	2.8
Average	2.8
Standard Deviation	0.1

The calculated relative standard deviation of the 16 results presented in Table I is 3%. These data reflect not only the variation in the actual fluoride measurement but

also variations in weighing, standard preparation, electrode calibration, and pyrohydrolysis separation.

Although the results presented in this report were obtained from a  $U_3O_8$  matrix, the method is presently being applied with similar reliability to the determination of microgram quantities of fluoride in  $UO_2$ ,  $PuO_2$ , and  $PuO_2-UO_2$  mixtures. Since fluoride may also be separated from other oxides by pyrohydrolysis, and because the fluoride electrode measurement is not affected by the presence of small amounts of substances accompanying the fluoride during pyrohydrolysis, it should be possible to extend the method to the determination of fluoride in other materials.

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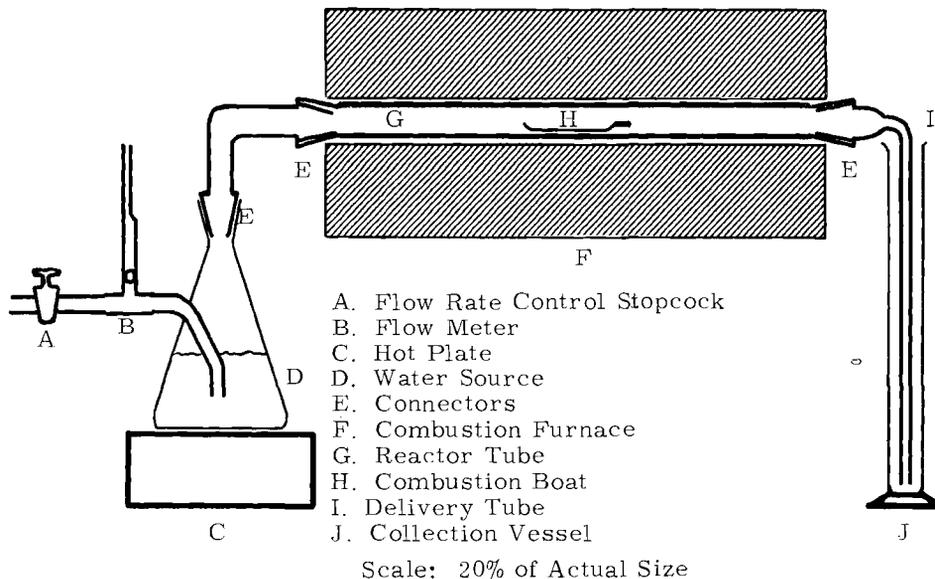
APPENDIX A  
DETAILS OF THE METHOD FOR THE DETERMINATION OF  
FLUORIDE IN METAL OXIDES

SEPARATION OF FLUORIDE BY  
PYROHYDROLYSIS

Apparatus

The apparatus consists of the components identified in Figure A-1. A compressed air tank (not shown) provides the system with forced air flow. The flow is regulated by a control stopcock, A, and measured with a calibrated flow meter, B. A 300 ml flask, D, contains the water needed for pyrohydrolysis reaction. A hot plate, C, provides control of the water temperature. Parts of the system are interconnected by 24/40 standard taper, ground glass joints, E, made of fused silica to

withstand the high temperatures near the furnace, F. The reactor tube, G, is made of fused silica. It is 13 1/2 in. long and has a 30 mm outer diameter with 24/40 outer joints at both ends. The heavy duty furnace, F, is 13 in. long with a 1 1/4 in. bore. The fused silica combustion boat, H, is 4 in. long and is made by cutting a 20 mm diameter silica tube lengthwise and flattening one of the ends to provide a handle. A delivery tube, I, and a graduated cylinder used as a collection vessel, J, complete the pyrohydrolysis apparatus. A pyrometer (not shown) is used to measure the furnace temperature when required. A variable transformer (not shown) is used to control



*FIGURE A-1. Pyrohydrolysis Apparatus*

the furnace power, thus providing the needed temperature control.

A reasonable assumption is that the efficiency of pyrohydrolysis reactions may depend upon both the conditions of the reaction and upon the physical structure of the apparatus. To ensure proper operation of the pyrohydrolysis apparatus under the established conditions, the aforementioned dimensions and the design shown in Figure A-1 must be closely adhered to.

#### Reagents

Powdered uranium oxide,  $U_3O_8$ , is used as an accelerator. The buffer solution is prepared by adding 50 microliters of glacial acetic acid ( $HC_2H_3O_2$ ) and 0.10 g of potassium acetate ( $KC_2H_3O_2$ ) to one liter of distilled water.

#### Procedure

1. Adjust the pyrohydrolysis apparatus to satisfy these conditions:
  - Furnace temperature -  
800 to 900°C
  - Air flow rate -  
50 to 60 liter/hr
  - Water temperature -  
40 to 50°C
2. Pour 12 to 15 ml of a previously prepared buffer solution (0.001N acetic acid and 0.001N potassium acetate) into a 50 ml graduated cylinder collection vessel, J, fitted with a delivery tube, I, which can be inserted at the end of reaction tube, G.
3. Weigh accurately 1 to 2 g of a powdered sample whose fluoride is to be determined and mix it with 4.0 g of powdered  $U_3O_8$  accelerator.
4. Pour the sample and accelerator mixture into combustion boat, H, and insert it in reaction tube, G, to begin reaction.
5. Immediately connect delivery tube, I, to the end of reaction tube, G, making sure that all ground glass connections are tight and that gas is bubbling through the solution.
6. Allow the reaction to proceed for 15 min. Five minutes may be sufficient, but should not be attempted without thorough experimental verification.
7. Remove delivery tube, I, from reaction tube, G. Wash down the walls of the delivery tube with buffer solution, and collect the wash solution in the graduated cylinder, J, containing the trapped fluoride. This removes traces of fluoride still remaining on the walls of the delivery tube.
8. Adjust the volume of the trap solution to  $20 \pm 0.2$  ml by adding more buffer solution.
9. Shake the solution in the graduated cylinder to ensure good mixing and pour it into a 22 ml sample vial for storage until the fluoride measurement can be made. Glass or polyethylene containers are equally suitable for this purpose.

10. Determine a blank by running 4.0 g of  $U_3O_8$  using the same procedure except that no sample is added.
11. The pyrohydrolysis apparatus and fluoride measurement should be checked for each series of determinations by running a standard sample containing a known amount of fluoride in accordance with instructions presented earlier in this report.

#### MEASUREMENT OF FLUORIDE WITH A FLUORIDE-SENSITIVE ELECTRODE

##### Apparatus

A fluoride electrode (Orion Model 94-09) and a saturated calomel reference electrode are mounted adjacent to the instrument which will be used to measure the potentials of the fluoride solutions. A Beckman Model 76 Expanded Scale pH Meter is satisfactory. Alternatively, a Model 401 Specific Ion Meter manufactured by Orion Research may be used for fluoride measurement. Its main advantage is a direct readout feature that makes the preparation of calibration curves unnecessary. This feature is especially useful when only one or two determinations are to be made.

The bottoms of one-ounce polyethylene bottles have been utilized as sample containers. They have been very satisfactory since they fit firmly around the two electrodes, requiring no additional physical support.

##### Reagents

Standards containing known amounts of fluoride in buffer solution.

##### Procedure

1. Allow the measuring device (pH meter or specific ion meter) to warm up before attempting any measurements. The following notes will apply to the Beckman Model 76 pH Meter.
2. Switch the meter to Standby position.
3. Pour 5 to 7 ml of sample solution obtained from pyrohydrolysis into a clean and dry polyethylene container and immerse the electrodes in the solution.
4. Rotate the container and contents for several seconds to mix the solution. This procedure ensures that the electrode tips are immersed in the solution and eliminates air bubbles which may have formed at the bottom of the fluoride electrode.
5. Switch the pH meter to read millivolts on the expanded scale.
6. Leave the solution in contact with the electrodes for 5 min, stir occasionally, and read the potential on the pH meter. Experiments have indicated some instability of the potential during the first 2 or 3 min. Therefore, for best results, a delay of 5 min is recommended before a final reading is made.
7. Record the potential, switch the pH meter to Standby, remove the

solution from the electrodes, rinse the electrodes with distilled water, and dry the electrodes.

8. Repeat Steps 3 to 7 for each determination of fluoride. Run samples, standards, and pyrohydrolysis blanks in exactly the same manner.
9. Solutions containing known amounts of fluoride in 0.001N acetate buffer are used to obtain calibration curves. It is not necessary to do a pyrohydrolysis separation to prepare calibration curves. Convenient units are micrograms of fluoride per 20 ml of solution plotted on the logarithmic scale

of semi-log paper versus the potential in millivolts on the linear scale (see Figure 2b in the text).

#### Calculations

1. Read the micrograms of fluoride of both samples and blanks from the prepared calibration curve.
2. Calculate the amount of fluoride in samples from the following equation:

$$\text{ppm fluoride} = \frac{\mu\text{g in sample} - \mu\text{g in blank}}{\text{sample wt in g}}$$

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