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**REPORT**

No. 1722

LABORATORY METHOD NO. 9/13  
THE DETERMINATION OF SMALL AMOUNTS  
OF FLUORIDE IN URANIUM COMPOUNDS BY USE  
OF AN ION-SELECTIVE ELECTRODE

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2nd May, 1975



**NATIONAL INSTITUTE FOR METALLURGY**  
**NATIONALE INSTITUUT VIR METALLURGIE**

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### SYNOPSIS

A method is presented for the determination of fluoride in uranium metal and oxide at levels from 16 p.p.m. upwards. Uranium is separated from fluoride by extraction into a solution of di(2-ethylhexyl)-phosphoric acid (HDEHP) in carbon tetrachloride. The fluoride remaining in the aqueous phase is determined by potentiometric measurement with an ion-selective electrode. A correction is made for the fluoride lost during the dissolution or extraction step, or both, which is based on a determination of the apparent loss of fluoride on spiked samples that are taken through the whole procedure.

### SAMEVATTING

Daar word 'n metode voorgestel vir die bepaling van fluoried in uraanmetaal en oksied op peile van 16 d.p.m. en hoër. Uraan word van fluoried geskei deur ekstrahering in 'n oplossing van di(2-etieselheksiel)-fosforsuur (HDEHP) in koolstoftetrachloried in. Die fluoried wat in die waterige fase oorbly, word deur 'n potensiometriese meting met 'n ioonselektiewe elektrode bepaal. Daar word 'n korreksie vir die fluoried wat tydens die oplossing of ekstaheringstap, of albei, verlore gaan, aangebring wat gebaseer word op 'n bepaling van die skynbare verlies van fluoried met gesoute monsters wat dwarsdeur die hele proses geneem word.

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### 1. OUTLINE

The sample is dissolved in acid, and the uranium is separated from the fluoride by extraction into a solution of di(2-ethylhexyl)-phosphoric acid in carbon tetrachloride. The fluoride, after being buffered with a Total Ionic Strength Adjustment Buffer (TISAB)<sup>1</sup>, is determined potentiometrically by the method of standard additions with the fluoride-ion selective electrode.

### 2. APPLICATION OF THE METHOD

The ion-selective procedure outlined is essentially the procedure of Peters and Ladd<sup>1</sup>, but it incorporates certain modifications, which involve measurement by standard-addition potentiometry. As the procedure is not applicable in the presence of macroscopic amounts of uranium, this cation is separated by a liquid-liquid extraction step, which is based on published data<sup>2</sup> on the distribution of uranium between aqueous hydrochloric acid solutions and HDEHP in kerosene solutions. Carbon tetrachloride is used instead of kerosene because of its higher density and consequent convenience when it has to be discarded after successive extractions of uranium. The method is applicable to the determination of fluoride in uranium metal and oxide from 16 p.p.m. upwards. The recovery of fluoride is about 90 per cent, and it is necessary for a spiked sample to be taken through the entire procedure so that this loss can be corrected for.

### 3. APPARATUS

- (1) *Fluoride-ion electrode*  
Orion Research model 94-09A
- (2) *Calomel Reference Electrode*  
Ingold
- (3) *Electrolyte Bridge with Ceramic Plug*  
Ingold
- (4) *Digital Voltmeter*  
Solartron L. M. 1604 DC
- (5) *Compressed-air Stirrer*  
Quickfit catalogue number MU8/0.

### 4. REAGENTS

- (1) *Hydrochloric Acid*  
A.R. grade
- (2) *Nitric Acid*  
A.R. grade
- (3) *Hydrogen Peroxide*  
30 % solution A.R. grade
- (4) *Sodium Hydroxide, 2.5 M*  
Dissolve 100 g of sodium hydroxide (A.R. grade) in water and dilute to 1 litre.
- (5) *Sodium Hydroxide, 40 % (m/v)*  
Dissolve 40 g of sodium hydroxide in water. Cool, and make up to 100 ml with water.
- (6) *Phenolphthalein Indicator Solution, 1 % (m/v)*  
Dissolve 1 g of the reagent in ethanol, and dilute to 100 ml with ethanol.
- (7) *Di(2-Ethylhexyl)-Phosphoric Acid (HDEHP), 10 % (v/v)*  
Dilute 25 ml of the reagent to 250 ml with carbon tetrachloride (A.R. grade).
- (8) *Total Ionic Strength Adjustment Buffer (TISAB)*  
Add 17.65 g of diaminocyclohexanetetraacetic acid (CDTA) to approximately 500 ml of water. Add 40 % sodium hydroxide solution drop by drop until the salts dissolve. Then, add 300 g of sodium citrate dihydrate and 60 g of sodium chloride. Dilute to 1 litre, and adjust the pH value to 6 with hydrochloric acid.

## DETERMINATION OF FLUORIDE IN URANIUM

### (9) *Standard Sodium Fluoride Solution*

Dissolve 1,1050 g of the salt, dried at 150 °C, in 100 ml of water in a polythene beaker. Transfer the solution to a 1-litre volumetric flask, and dilute to volume with water. Store in a tightly stoppered polythene container.

1 ml  $\equiv$  0,5 mg of F.

### (10) *Diluted Standard Sodium Fluoride Solution*

Dilute 10 ml of the standard sodium fluoride solution (no. 9 above) to 1 litre with water.

1 ml  $\equiv$  5  $\mu$ g of F.

### (11) *Potassium Chloride Salt Bridge Solution, 5 % (m/v)*

Dissolve 12,5 g of potassium chloride in water, and dilute to 250 ml.

### (12) *Silicone Oil*

Orion number 94-00-03.

## 5 PROCEDURE

### 5.1. DISSOLUTION OF SAMPLES

#### 5.1.1. *Uranium Metal*

Transfer 1,0 g of the metal to a 250 ml beaker and add 25 ml of water. To another 250 ml beaker, add 10 ml of diluted standard sodium fluoride solution (1 ml  $\equiv$  5  $\mu$ g F), 15 ml of water, and 1,0 g of the metal. Add 2 ml of hydrochloric acid to each of the beakers, and, while the solution is reacting, make drop-by-drop additions of hydrogen peroxide. Warm the solution gradually to dissolve the yellow precipitate that forms. Add more hydrogen peroxide if there is any evidence of undecomposed sample, and boil gently until the solution has cleared. Transfer the solutions to 100 ml separating funnels and make up to 50 ml with water.

#### 5.1.2. *Uranium Oxide*

Transfer 1,0 g of the oxide to a 250 ml beaker, and add 25 ml of water. To another beaker, add 10 ml of the diluted standard sodium fluoride solution (1 ml  $\equiv$  5  $\mu$ g of F), 15 ml of water, and 1,0 g of the oxide. To each of the beakers, add 1 ml of nitric acid and dissolve the oxide by boiling gently. If a black residue is found, add 3 to 5 drops of hydrogen peroxide. The residue should dissolve when the solution is warmed, and a yellow precipitate should form. Dissolve this precipitate by adding 0,5 ml of hydrochloric acid and boiling gently until a clear solution is obtained. Transfer the solutions to 100 ml separating funnels, and dilute to 50 ml with water.

### 5.2. LIQUID-LIQUID EXTRACTION AND POTENTIOMETRIC DETERMINATION

- To each of the separating funnels, add 40 ml of HDEHP solution and shake for 1 minute. Allow the phases to separate, and discard the organic layers. Add a further 20 ml of HDEHP solution to each of the separating funnels, and again shake for 1 minute. Allow the phases to separate, and discard the organic layers.
- Add 10 ml of carbon tetrachloride to each of the separating funnels, and shake for 30 seconds to remove residual HDEHP. Allow the phases to separate, and again discard the organic layers. Repeat this extraction once more.
- Run the aqueous phases into the original beakers, add 2 drops of phenolphthalein and neutralize to the end point (pink) with 2,5 M sodium hydroxide solution from a graduated pipette. Note the amounts used.
- Evaporate the solutions to volumes of less than 25 ml – in this step residual  $\text{CCl}_4$  is removed – and transfer the solutions to 25 ml volumetric flasks, diluting to volume with water.
- Pipette 20 ml of each of these solutions into polythene beakers, and, using a pipette, add 20 ml of TISAB solution to each. Place the beakers in a tray of cold water, and allow them to stand for 20 minutes.
- In the following way, make a standard solution of approximately the same ionic strength as the samples. Pipette 1 ml of standard fluoride solution (1 ml  $\equiv$  0,5 mg of F) into a 50 ml volumetric flask, and add 2,5 M sodium hydroxide to within 0,1 ml of that present in the aliquot portion taken as described in paragraph 5e. Add 2 drops of phenolphthalein and hydrochloric acid until the pink colour is discharged. Now add sufficient sodium hydroxide to restore the pink colour. Add 25 ml of TISAB solution, and dilute to volume with water. In this solution, 1 ml should be equivalent to 10  $\mu$ g of F, and the ionic strength should be the same as that of the samples.

## DETERMINATION OF FLUORIDE IN URANIUM

- g. Measure the potential of the samples, using the fluoride-ion sensitive electrode (Note 1). In three 1 ml increments, add the standard solution (1 ml  $\equiv$  10  $\mu$ g of F solution - from step f), measuring the potentials after each addition (Note 2).
- h. Calculate the fluoride content of the samples.

### 6. CALCULATION OF FLUORIDE CONTENT

- Let  $X$  = F in unknown solution ( $\mu$ g)  
 $X_d$  = F added with standard addition ( $\mu$ g)  
 $V$  = volume of unknown solution (ml)  
 $V_d$  = volume of standard addition (ml)  
 $E_x$  = potential of unknown solution (mV)  
 $E_d$  = potential of unknown solution after standard addition (mV)  
 $S$  = slope of graph (mV/decade)(Note 3).

Then,

$$X = \frac{X_d}{\left\{ \frac{V + V_d}{V} \text{antilog} \left( \frac{E_x - E_d}{S} \right) \right\} - 1}$$

Therefore, F in sample =  $\frac{X \times 25}{20 \times M} = A_1$  p.p.m.,

where  $M$  = mass of sample (g).

It is convenient to use an Olivetti computer for this calculation.

To the concentration of fluoride determined by the above equations, apply a correction for the small fraction of fluoride lost during the extraction procedure. This is done as follows:

- Let  $A_1$  = fluoride found by above equations (p.p.m.)  
 $S_1$  = fluoride added to sample (p.p.m.)  
 $S_2$  = fluoride found in spiked sample (p.p.m.)  
 $A_2$  = true fluoride content (p.p.m.).

Then

$$A_2 = \frac{S_1}{S_2 - A_1} \times A_1$$

### 7. NOTES

- (1) Prepare the ion-sensitive electrode as described in an earlier report<sup>3</sup>.
- (2) The millivolt readings are taken once the rate of change of the readings is less than 0.03 mV per 30 seconds.
- (3) The value of  $S$  (i.e.  $2.3 RT/F$ ) at different temperatures is available in instruction manuals<sup>4</sup>. Should the value of  $X$  as calculated from the equation given be below 80  $\mu$ g of fluoride, recalculate the value, using a revised slope derived from the following table for solutions measured at 20°C.

Value for $X$ derived from theoretical value for $S$ $\mu$ g of F	Actual value of $S$ to be applied in calculation mV/decade
12 to 13	+49
13 to 15	+50
15 to 18	+51
18 to 22	+52
22 to 26	+53
26 to 30	+54
30 to 38	+55
38 to 55	+56
55 to 80	+57

## DETERMINATION OF FLUORIDE IN URANIUM

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## DETERMINATION OF FLUORIDE IN URANIUM

### 8. REFERENCES

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