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Chemistry

MASTER

DIRECT ESTIMATION OF FREE FLUORIDE ION
IN TWENTY PERCENT NITRIC ACID
ETCHING SOLUTIONS

W. C. Dietrich

INDEXED FOR SCIENCE ABSTRACTS

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
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ABSTRACT

Free fluoride ion was estimated directly in twenty percent nitric acid solutions containing fluoride, aluminum, beryllium, niobium, zirconium, and uranium ions by correlating the dissolution times of zirconium foils or siliceous films to reactive free fluoride ion.



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SUMMARY

Two methods have been developed for estimating free fluoride in twenty percent nitric acid solutions containing fluoride, fluoride-masking cations, and uranium(VI).

One estimation procedure correlates the dissolution time of a 0.28 cm^2 disc of zirconium foil when exposed to free fluoride ions. When uranium is present in large concentrations, a significant inhibitory effect on foil dissolution is observed. This uranium interference can be minimized by graphical compensation or by eliminating the uranium via a tri-*n*-octyl phosphine oxide extraction.

The second estimation procedure relates the dissolution time of a siliceous film to free fluoride. Film penetration was determined iodometrically by the reaction of oxidants in solution with the iodide-treated wooden substrate supporting the siliceous film. Uranium does not interfere in this procedure. This latter test, although far more qualitative, is suitable for field applications.



INTRODUCTION

Explosions have occurred during pickling, dissolution, or etching uranium-zirconium alloys by nitric acid.⁽¹⁾ This hazardous phenomenon was also believed possible with uranium-niobium alloys. Safe etching of these alloys may be possible by assuring the presence of uncombined fluoride ion. Therefore, a scheme of analysis was desired that was applicable to the rapid estimation of uncombined fluoride ion in the presence of uranium, zirconium, niobium, and twenty percent nitric acid.

A survey of the chemical reactions that are applicable to such an analysis disclosed that certain metals, such as aluminum, zirconium, and niobium which are very resistant to attack by nitric acid only, are readily attacked when hydrofluoric acid is added.⁽²⁾ The dissolution of these metals by hydrofluoric acid while in the presence of nitric acid offered a potential scheme of analysis.

An alternative analytical scheme would involve equating the dissolution time of siliceous films with free fluoride ion concentrations.



ANALYTICAL PROCEDURE

EQUIPMENT

Water Bath

A 12-inch Fisher tank and stand that was equipped with a stirring motor, a 500-watt immersion heater, and a Thermonic-Electronic temperature regulator set at 70° C was used as the water bath.

Reaction Cell

The reaction cell consisted of a 3/4-inch-diameter polystyrene cylinder, 2 1/2 inches long, that contained single-hole rubber stoppers.

Sample Loop

A thermostatted reaction cell and a 125-milliliter plastic sample bottle, series connected by plastic tubing to a sigmamotor pump (Figure 1), were the principal components of the sample loop.

Zirconium Foil

The foil was of one-mil uniform thickness, at least one inch wide.

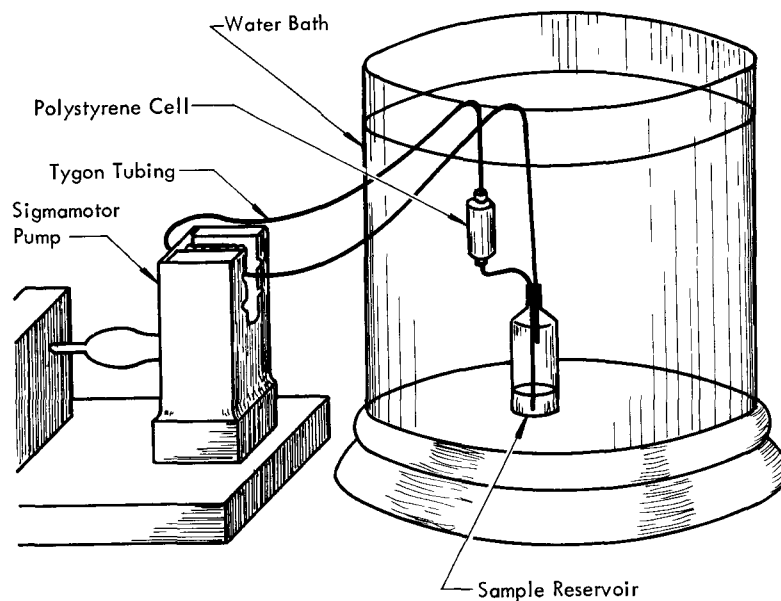


Figure 1. SAMPLE LOOP AND WATER BATH.

Wooden Sticks

Wood applicator sticks (6" x 1/2") were used that were made of smooth white birch.

Stirring Motor

Any unit that was geared down to about 100 rpm and equipped with a chuck capable of holding the wooden indicator sticks was suitable for the stirring operation.

REAGENTS

Sauereisen Solution

Sauereisen thinning liquid was diluted 1:3 with water.

Free Fluoride Indicators

Zirconium Foil - One-mil zirconium foil was sandwiched between layers of perforated plastic tape. For handling convenience, 12-inch lengths of one-inch plastic tape were stuck to a sheet of polyethylene and the excess sheet trimmed. Strips were folded in half along the major axis and six-millimeter holes punched one-half inch apart along the centerline of this folded strip. Next, the strip was unfolded to reveal the perforations with the centers parallel as well as normal to the major axis. The polyethylene film was peeled off and the perforated strip applied to the zirconium foil. The strip was turned over and another perforated plastic strip was applied to the remaining zirconium foil surface so that all perforations were aligned. Normal to the major axis but between adjacent holes, 1/2 by 1 inch rectangular specimens were cut, each containing duplicate reactive surfaces.

Wooden Sticks - A siliceous film covered the iodide-impregnated wooden substrate. Several wooden applicator sticks were soaked overnight in a saturated potassium iodide-methyl alcohol solution containing about one percent sodium thiosulfate. The impregnated sticks were protected from light to minimize oxidation of the iodide to free iodine. Next, the sticks were removed to permit them to air dry in the dark, then each stick was dipped into the siliceous Sauereisen solution, the excess liquid allowed to drain, and the coating air dried for about six hours. This process was repeated until six siliceous layers had been achieved. This coating process can be facilitated by using a 12 by 12-inch mounting jig drilled with many "snug-stick-fit" holes to dip, drain, and dry the sticks in a batchwise operation.

Other Chemicals

Potassium iodide, reagent grade; potassium bromate, reagent grade; and absolute methyl alcohol were also used in this work.

PROCEDURE

Free Fluoride Estimation by the Zirconium-Foil Indicator

Free fluoride can be estimated, using a zirconium-foil indicator, by observing the following steps:

1. Examine the sample history and estimate its uranium content. If it contains less than 30 milligrams of uranium per milliliter, proceed directly. If more, dilute the sample solution 1:1 with 20 percent nitric acid.
2. Insert a zirconium-indicator foil into the reaction cell and return cell to the bath.
3. Add about 100 milliliters of sample solution to the plastic sample bottle, transfer the bottle to the bath, and wait 40 minutes.
4. Turn on the pump (preset to 60 mls/min) then permit the sample solution to flow through the cell and past the zirconium foil surfaces.
5. Observe the time interval necessary for the flowing solution to perforate the zirconium discs. (A spotlight behind the indicator foil facilitates detection of the first breakthrough.)
6. Average the measured time interval to affect the perforation of the two discs and compare to a standard curve.

Free Fluoride Estimation by Indicator Sticks

Free fluoride can be estimated, using indicator sticks, by observing the following steps:

1. Insert a wooden stick into the chuck of the stirring motor.
2. Dip the free end of the stick into one inch of the sample solution containing five percent potassium bromate and immediately turn on the motor.
3. Record the time necessary to develop a dark discoloration on the stick.
4. Rinse the stick with distilled water and permit it to air dry for ten minutes.
5. Compare to known discoloration values.

EXPERIMENTAL INVESTIGATIONS AND RESULTS

In the following experimental investigations, all foil dissolutions were performed with metal specimens having an area of 0.28 cm^2 .

The time needed to dissolve the aluminum and zirconium-foil specimens by fluoride in 20 percent nitric acid solutions was estimated. Free fluoride in these solutions was varied by adding varying amounts of niobium, zirconium, aluminum, and beryllium ions to a 20 percent fluoride-20 percent nitric acid solution. Results from this study are graphically depicted in Figures 2 and 3.

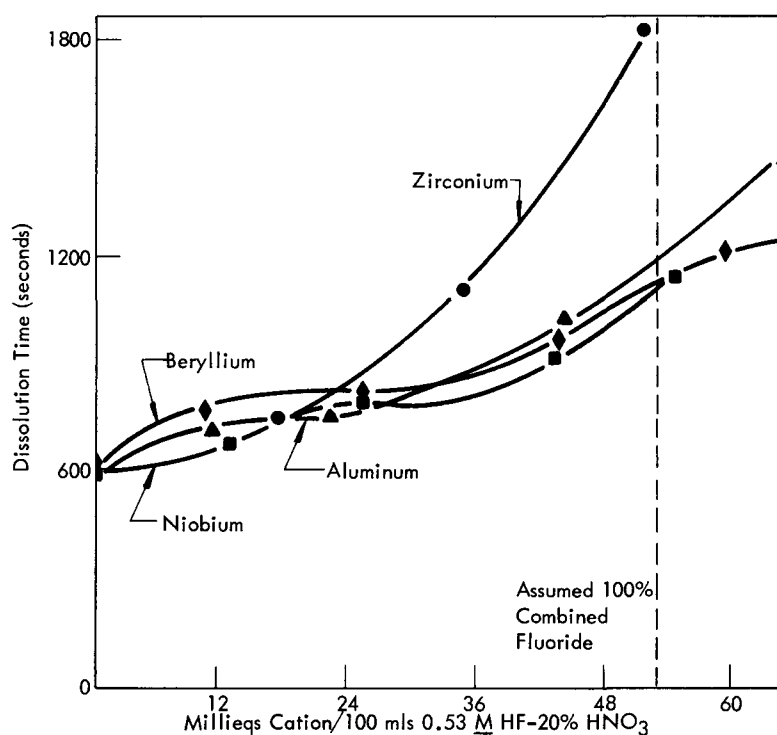


Figure 2. DISSOLUTION OF ONE-MIL ALUMINUM FOIL BY FLUORIDE ION IN HYDROFLUORIC ACID-NITRIC ACID SOLUTIONS SPIKED WITH CERTAIN CATIONS AT 25°C .

Dissolution times for zirconium foils were then determined. Estimated times for varying amounts of fluoride in 20 percent nitric acid solutions were found at 25°C and 90°C , and also at 70°C for solutions that were 0.2 M in uranium(VI). Data are graphically shown in Figures 3 and 4. The effect of uranium is clearly shown in Figure 5. Investigation of the 0.2 M uranium solutions was expanded to estimate the dissolution times at 70°C for solutions that were 0.2 M in uranium, 0.2 M in fluoride, 20 percent in nitric acid, and varying in amounts of niobium and zirconium ions. Figure 6 shows the results of the test.

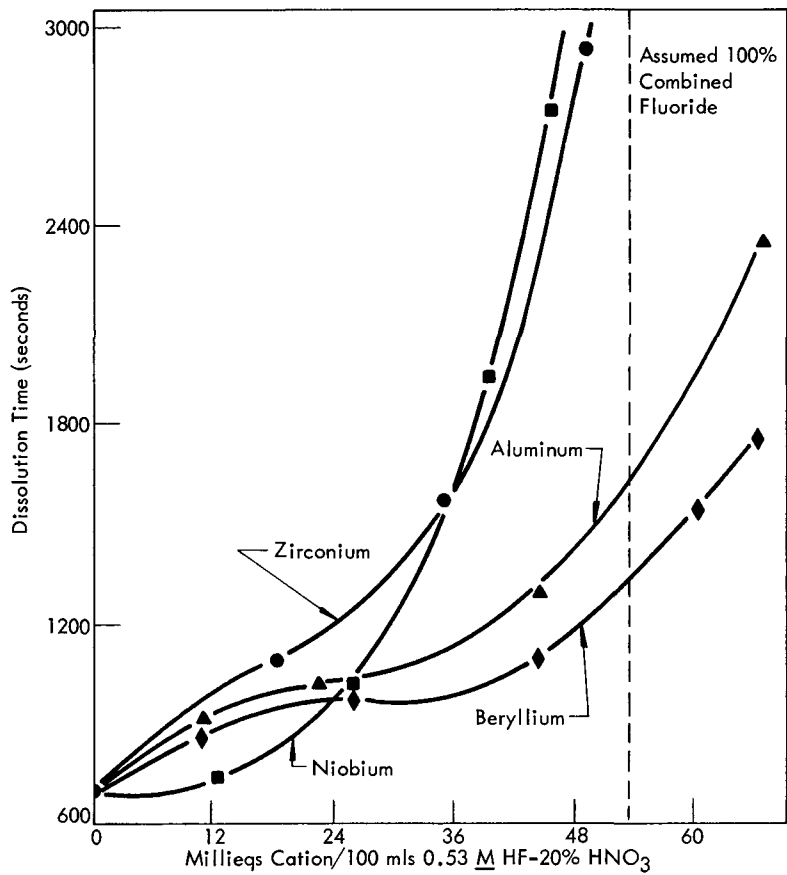


Figure 3. DISSOLUTION OF 4.5-MIL ZIRCONIUM FOIL BY FLUORIDE ION IN HYDROFLUORIC ACID-NITRIC ACID SOLUTIONS SPIKED WITH CERTAIN CATIONS AT 25°C.

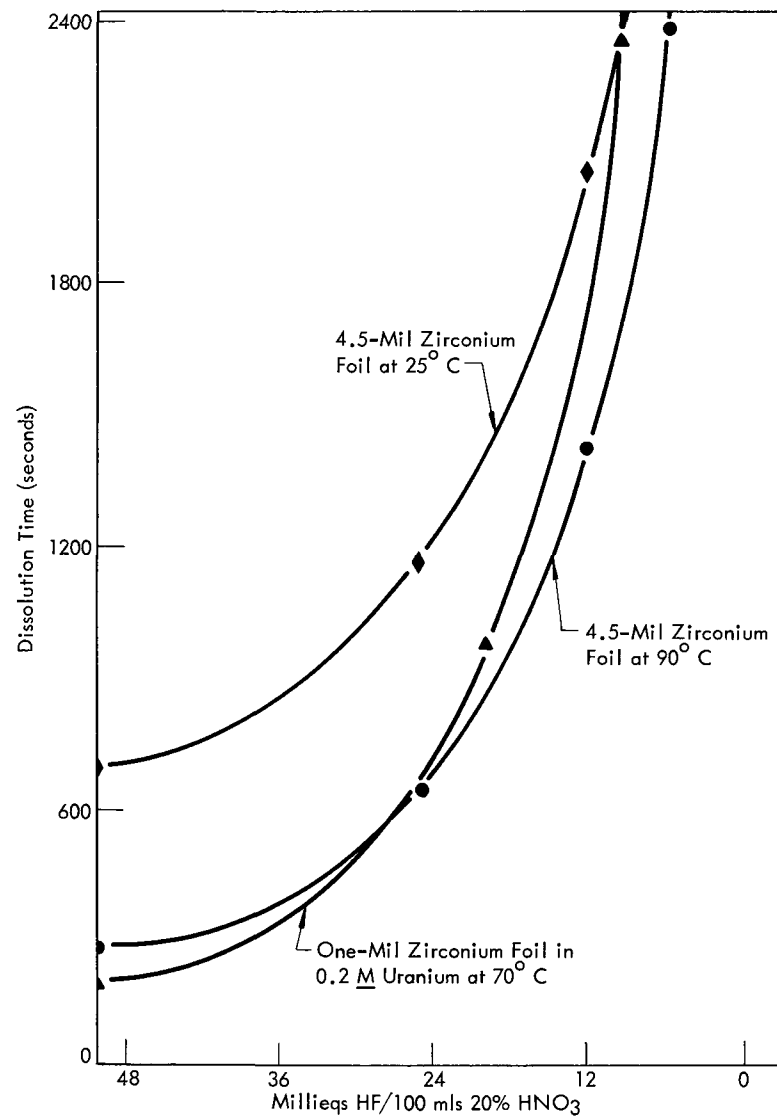


Figure 4. DISSOLUTION OF ZIRCONIUM FOIL BY FLUORIDE ION IN NITRIC ACID SOLUTIONS.

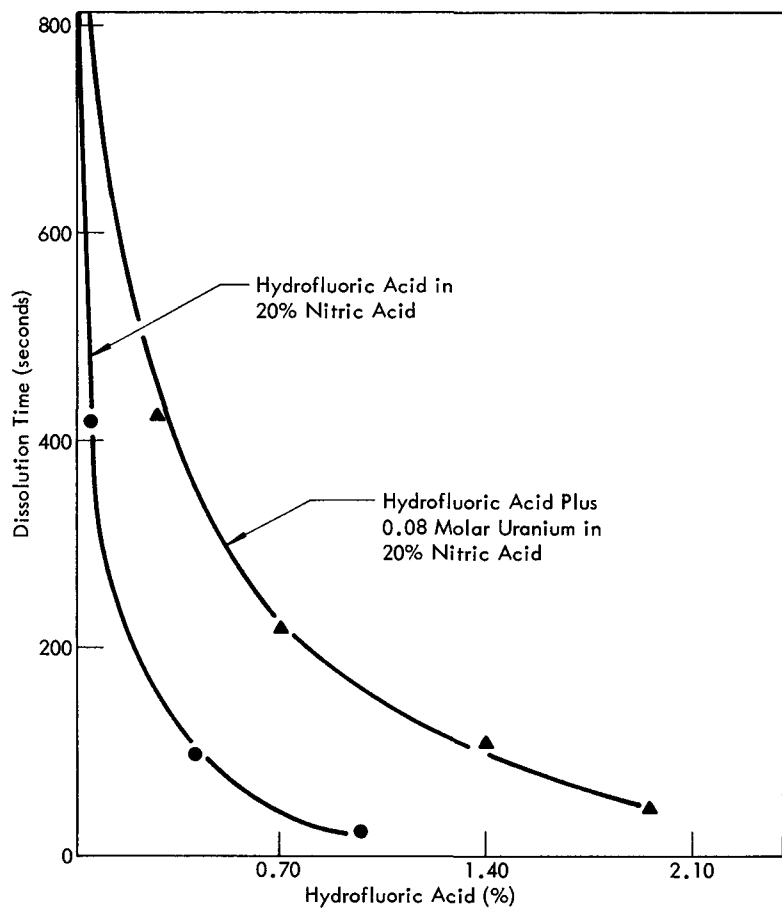


Figure 5. TIME REQUIRED TO DISSOLVE A ONE-MIL ZIRCONIUM FOIL BY FLUORIDE ION AT 70°C IN VARIOUS HYDROFLUORIC ACID SOLUTIONS.

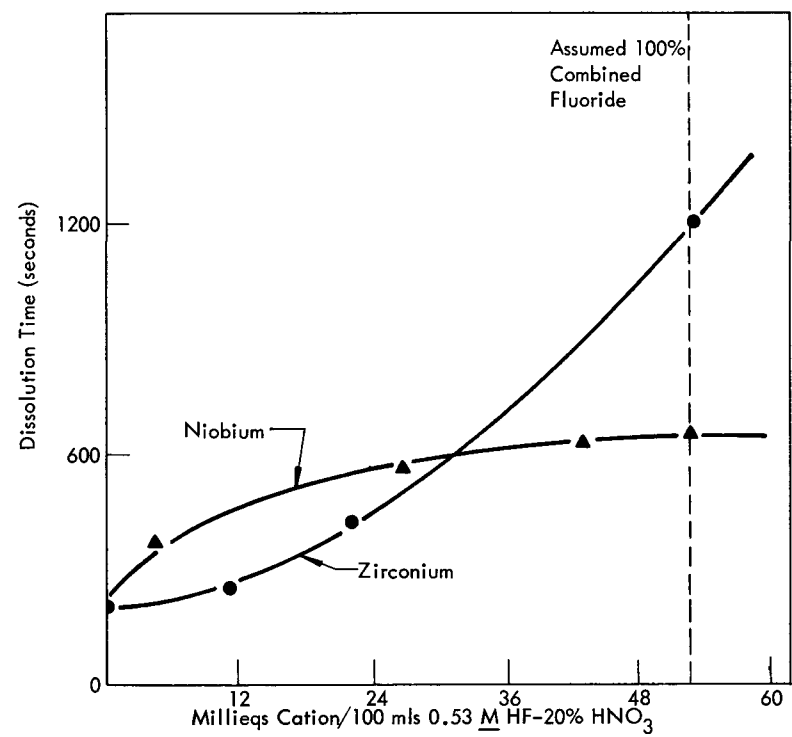


Figure 6. DISSOLUTION OF 1.3-MIL ZIRCONIUM FOIL BY FLUORIDE ION IN HYDROFLUORIC ACID-NITRIC ACID SOLUTIONS SPIKED WITH CERTAIN CATIONS IN 0.2 Molar URANIUM AT 70°C.

A history of a hypothetical etching bath was constructed by estimating the dissolution times in a 0.53 M fluoride-20 percent nitric acid solution containing increasing concentrations but fixed ratios of 1:9 and 1:12 niobium to uranium ions. Results are indicated in Figures 7 through 9. Free fluoride ion was also estimated in some of these solutions after removing uranium by a tri-n-octyl phosphine oxide extraction (Figure 10).

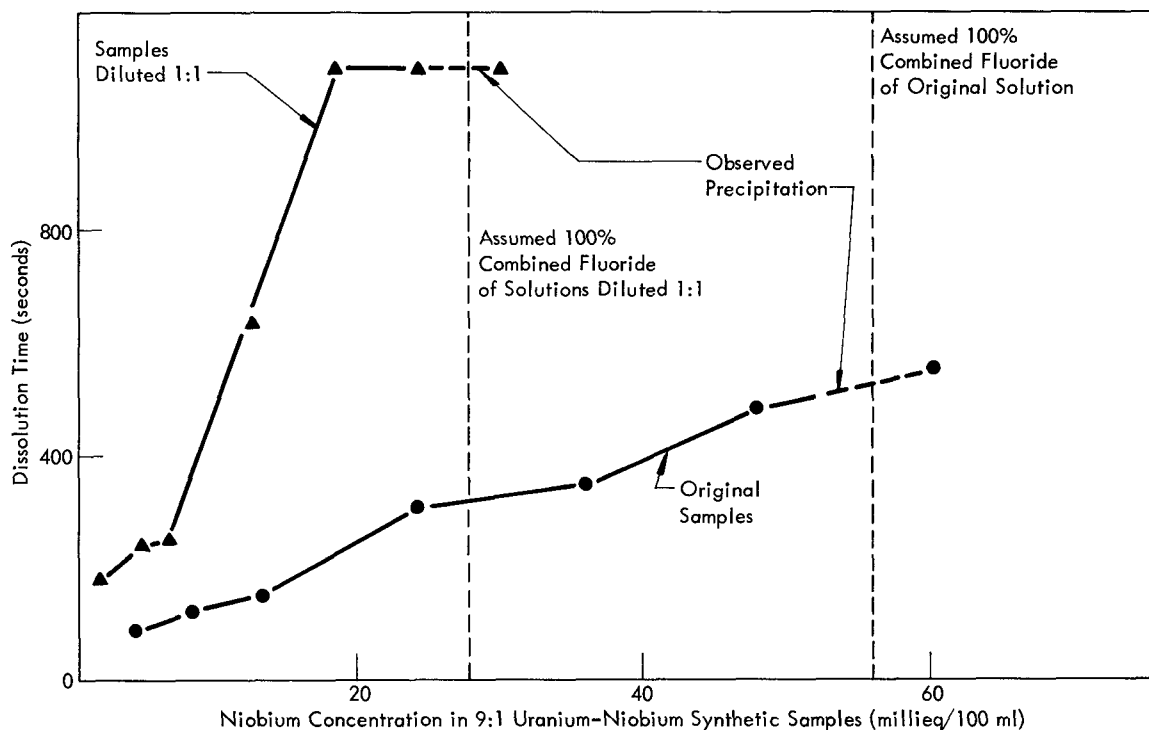


Figure 7. TIME REQUIRED TO DISSOLVE A ONE-MIL ZIRCONIUM FOIL BY FLUORIDE ION AT 70°C IN VARIOUS NIOBIUM SOLUTIONS.

Replenishing a given etching bath solution with free fluoride ion was investigated for various 9:1 and 12:1 uranium-to-niobium mixtures by adding sufficient hydrofluoric acid to attain two percent free fluoride (see Figures 11 and 12).

Free fluoride in synthetic etching-bath solutions was also determined by correlating the dissolution time of a fluoride-reactive siliceous film to the amount of free fluoride in solution. Detection of this film penetration was determined iodometrically by oxidizing an iodide-permeated wooden substrate with oxidants present in the sample. Starch and potassium bromate were added to the sample solution to assure marked color changes, Figure 13. These synthetic solutions contained various quantities of free fluoride and uranium in 20 percent nitric acid.

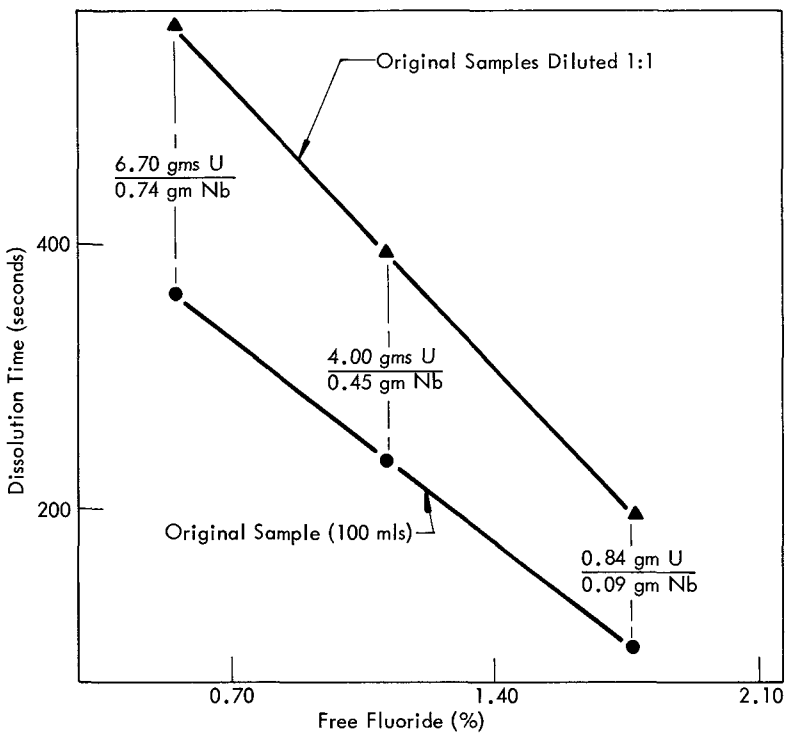


Figure 8. TIME REQUIRED TO DISSOLVE A ONE-MIL ZIRCONIUM FOIL BY FLUORIDE ION AT 70°C IN THREE URANIUM-NIOBIUM SOLUTIONS.

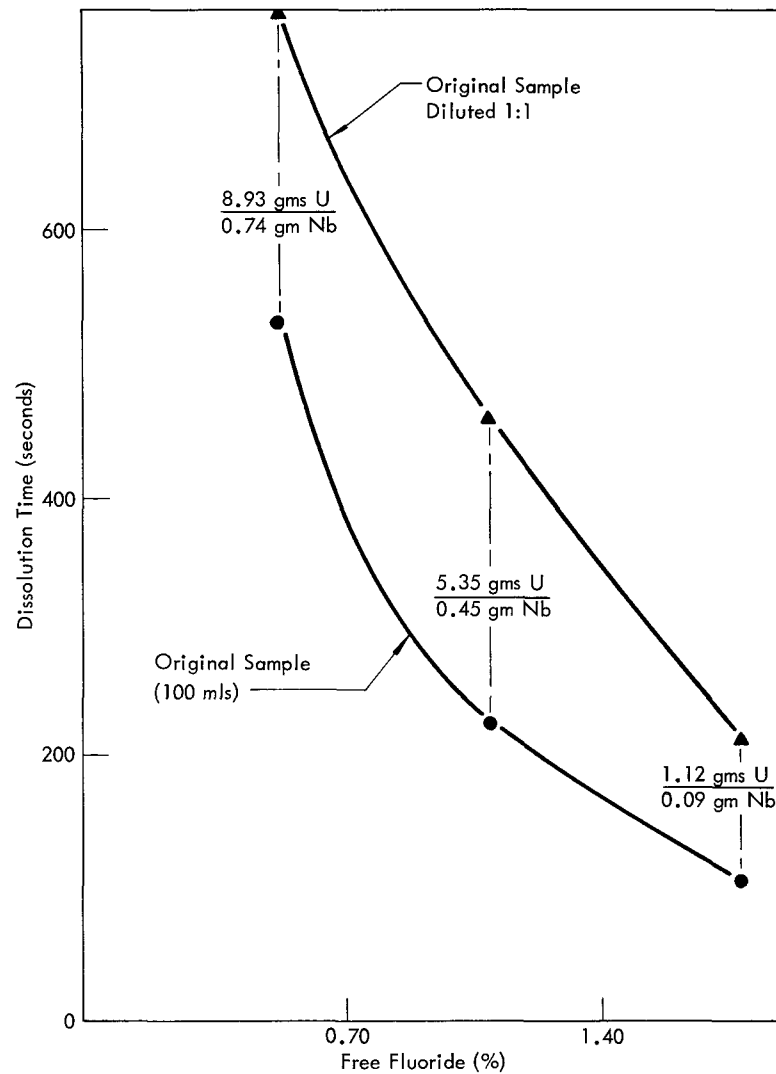


Figure 9. TIME REQUIRED TO DISSOLVE A ONE-MIL ZIRCONIUM FOIL BY FLUORIDE ION AT 70°C IN THREE OTHER URANIUM-NIOBIUM SOLUTIONS.

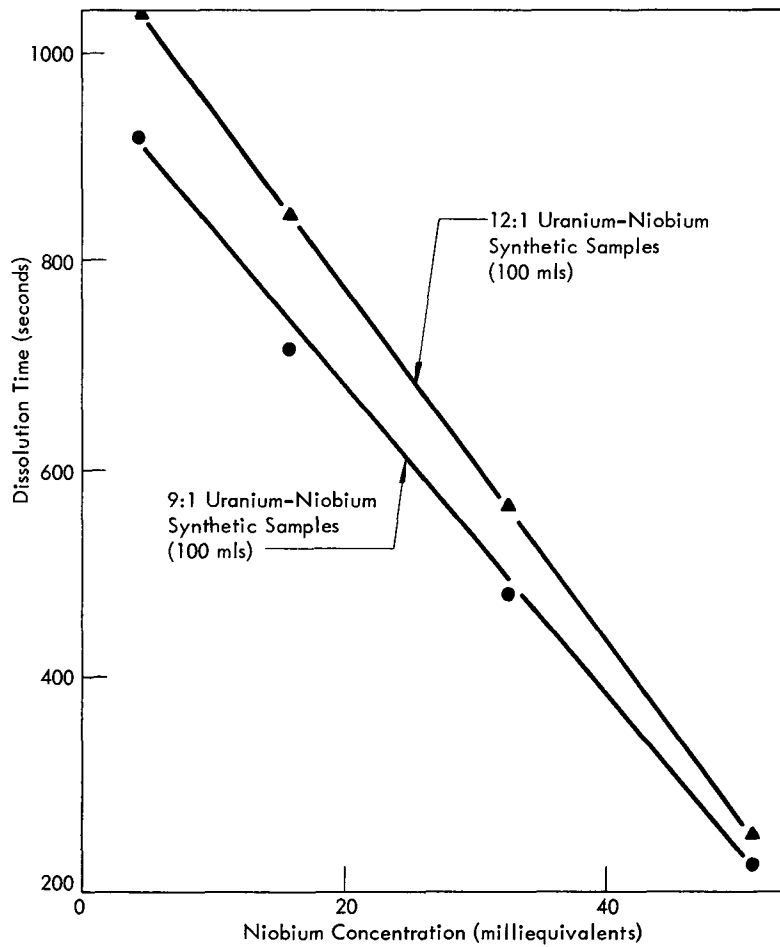


Figure 10. TIME REQUIRED TO DISSOLVE A ONE-MIL ZIRCONIUM FOIL BY FLUORIDE ION AT 24°C AFTER THE REMOVAL OF URANIUM BY EXTRACTIONS WITH TRI-N-OCTYL PHOSPHINE OXIDE-CHLOROFORM.

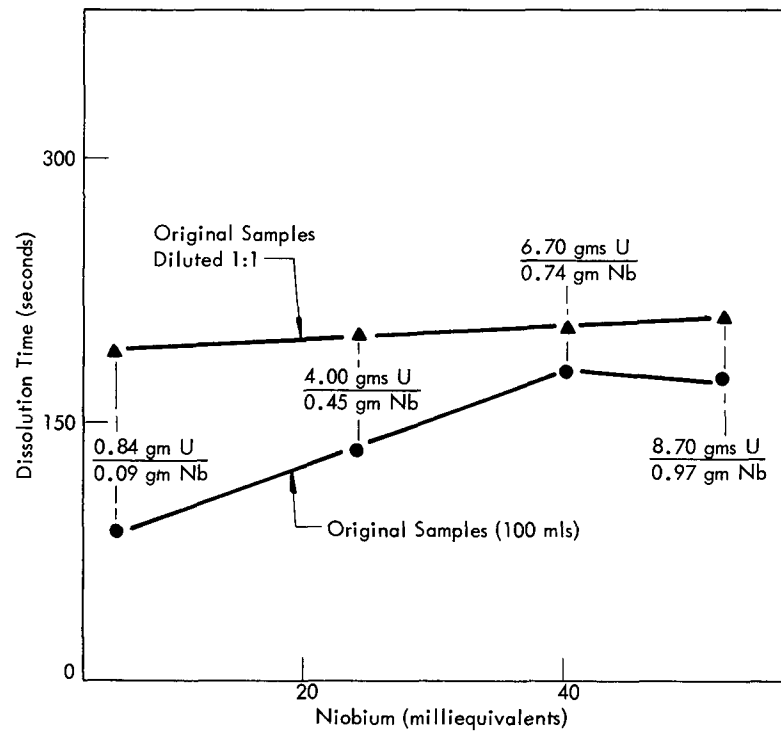


Figure 11. TIME REQUIRED TO DISSOLVE A ONE-MIL ZIRCONIUM FOIL BY FLUORIDE ION AT 70°C IN FOUR URANIUM-NIOBIUM SOLUTIONS AS A FUNCTION OF THE NIOBIUM CONCENTRATION.

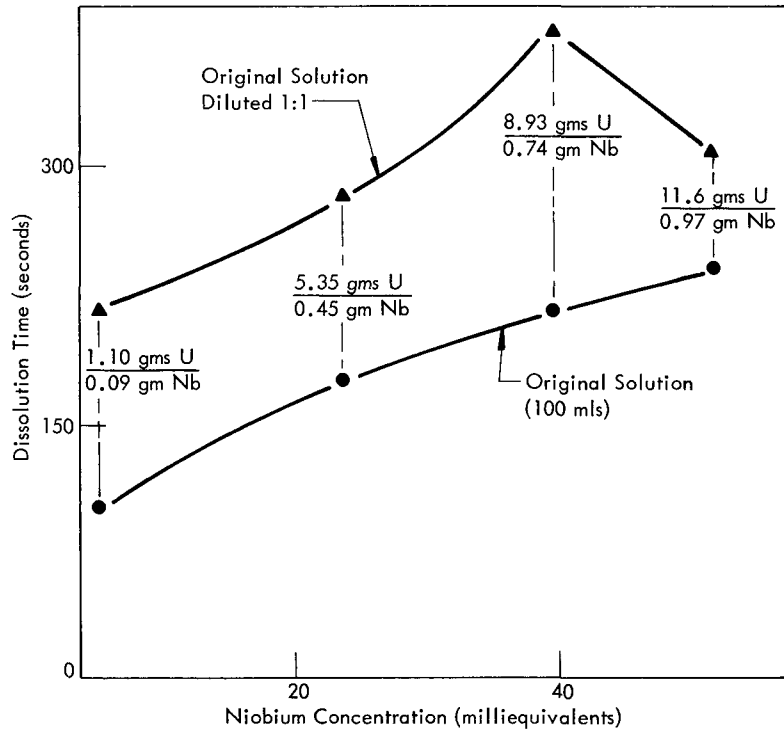


Figure 12. TIME REQUIRED TO DISSOLVE A ONE-MIL ZIRCONIUM FOIL BY FLUORIDE ION AT 70°C IN FOUR OTHER URANIUM-NIOBIUM SOLUTIONS AS A FUNCTION OF THE NIOBIUM CONCENTRATION.

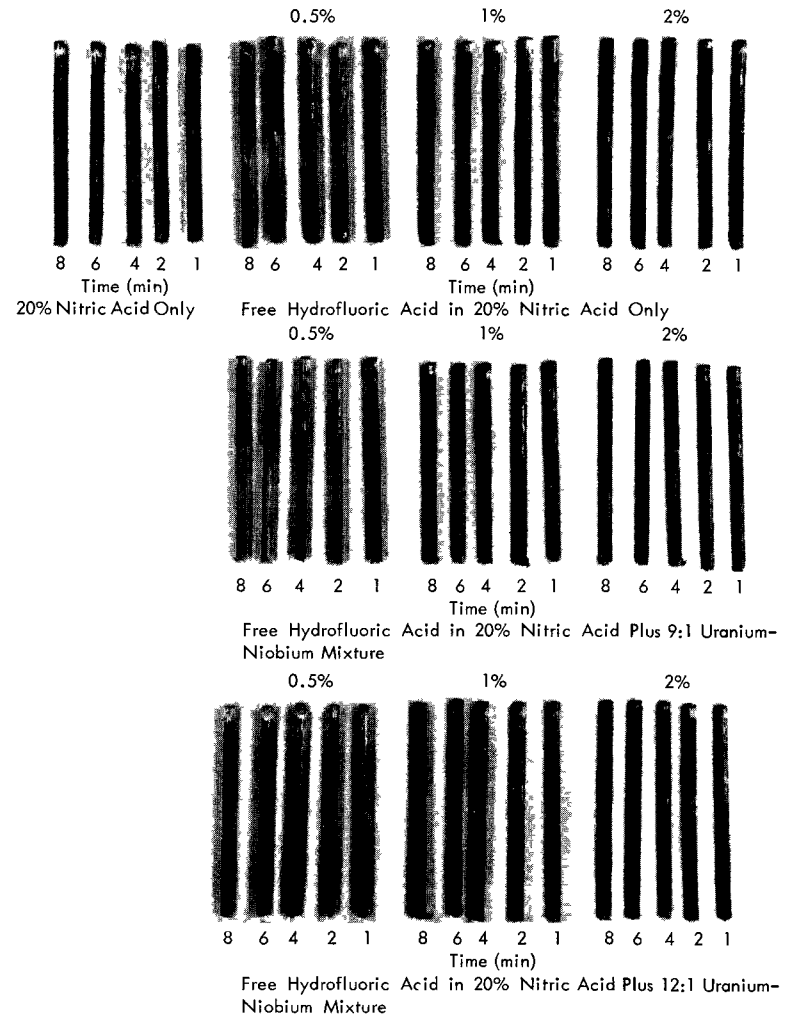


Figure 13. ESTIMATION OF FREE HYDROFLUORIC ACID BY COLORATION OF SAUERISEN-COATED POTASSIUM IODIDE-TREATED STICKS.

DISCUSSION

Reactions between uranium-zirconium and uranium-niobium alloys with nitric acid exposes an insoluble but highly reactive phase of the alloy which is explosive. Formation of this hazardous phase can be prevented by its ready dissolution in the presence of the free fluoride ion. Therefore, safe pickling, etching, or dissolving operations involving these alloys require assurance of the presence of free fluoride ion. It appears that a feasible analytical approach is to selectively dissolve aluminum, niobium, or zirconium metals by fluoride ions while in the presence of nitric acid.

A series of experiments was conducted to relate the time necessary to dissolve 0.28 cm² pieces of aluminum, niobium, or zirconium foils in varying concentrations of the free fluoride ion in 20 percent nitric acid solutions. It was found to be impractical to use a niobium foil indicator because of the excessively slow reaction rates encountered in initial experimentation. Aluminum and zirconium foils were then used in a comparative study where the fluoride ion concentration was fixed at 0.53 M in 20 percent nitric acid, then the "free" fluoride ion concentration was varied by adding different quantities of fluoride masking agents (such as the ions of aluminum, niobium, zirconium, and beryllium). Plots of the dissolution times for these foil specimens as a function of the concentration of the fluoride masking agents are presented in Figures 2 and 3 for solutions at 25° C. The abscissa units for the curves in these two figures are expressed as milliequivalents conveniently based on the assumed valences in the fluoride compounds of beryllium, aluminum, zirconium, and niobium. A study of the symmetry of the curves readily shows the superior performance of zirconium foil at low free fluoride ion concentrations. Special note should be given to the vertical dashed line at the 53-milliequivalent value (Figures 2 through 7). This line is a convenient reference that is presumptuously based on the "complete" conversion of the added free fluoride ion to combined fluoride.

An experiment was then conducted to relate the time necessary to dissolve 0.28 cm² pieces of zirconium foil in varying concentrations of the fluoride ion in 20 percent nitric acid solutions at 25 and 90° C. Some solutions were also spiked with uranium(VI) to give a uranyl ion concentration of 0.2 M. Results of this experiment are shown in Figure 4. The effect of uranium was clearly shown by another experiment, Figure 5. The curves in Figure 5 clearly show the inhibitory influence of uranium, principally caused by the formation of the very slightly soluble uranium tetrafluoride on the zirconium surface. Further study with uranium revealed excessive formation of this tetrafluoride at temperatures less than 60° C.

Estimation of free fluoride ions in etching-bath solutions was evaluated by preparing representative synthetic solutions. These solutions contained 0.53 M fluoride ions, varying quantities of zirconium or niobium ions, 0.2 M uranium(VI) ions, and 20 percent nitric acid. Any free fluoride was then estimated in these solutions by determining the time to dissolve the 0.28 cm² pieces of 1.3-mil zirconium foil. A

plot of these dissolution times as functions of the added masking agent is given in Figure 6. A study of the symmetry of these curves will reveal that 0.2 M uranium does not significantly alter the symmetry in the case of zirconium ions but seriously interacts with niobium ions. Also in the case of niobium, a copious white precipitate appeared in solutions with compositions near the vertical dashed line of Figure 6. This precipitate is believed to be $\text{UO}_2\text{NbOF}_5 \cdot (\text{H}_2\text{O})_x$ and dissolves upon the addition of excess hydrofluoric acid.

Evaluation of uranium effect upon the estimation of free fluoride in the presence of niobium was essential. A reasonable solution to the evaluation problem was to create a history of an etching-bath mixture from original makeup to depletion by the preparation and analysis of appropriate synthetic samples. The original mixture consisted of two milliliters of 48% hydrofluoric acid in 100 milliliters of 20 percent nitric acid. The synthetic samples were made to contain varying concentrations of uranium and niobium at a fixed ratio of nine parts uranium to one part niobium. Basis for this ratio was the simplifying assumption that the integrity of the uranium-to-niobium ratio in the metal alloy would not be violated in the solution during etching. The quantities of niobium were selected on the basis of the formation of $\text{H}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ ⁽³⁾ or one part niobium to mask five parts of fluoride. Successively increasing quantities of niobium were then added to the solution until complete masking of free fluoride was effected, as depicted by the dashed vertical line in Figure 7. Reference to this dotted region of the plot of dissolution time versus added niobium shows where $\text{UO}_2\text{NbOF}_5 \cdot (\text{H}_2\text{O})_x$ precipitated due to diminished free fluoride. The remainder of the curve shows a relatively shallow symmetry resulting in low sensitivity. Sensitivity was significantly improved by diluting the synthetic samples 1:1 with 20 percent nitric acid prior to foil dissolution (Figure 7). A plot of free-fluoride values at each corresponding niobium value results in the linear curve shown in Figure 8.

Evaluation of the uranium interference in free-fluoride estimation was extended by increasing the uranium-niobium ratio from 9:1 to 12:1. A plot of the free fluoride ion concentration versus the foil dissolution times for this increased uranium content is shown in Figures 9 and 10. Now, when these curves from the 9:1 and 12:1 systems are critically compared, the role of uranium can be seen to be inhibitory to foil dissolution by the formation of an insoluble uranium tetrafluoride film upon the zirconium foil surface. It should be noted that this interference incorporates a fail-safe feature in that extending dissolution times indicate depleted free fluoride content.

Depletion of free fluoride values beyond useful limits forced a decision to fortify the bath with additional hydrofluoric acid, or to discard the bath as useless for further etching. An experiment was designed to observe the behavior of a fortified solution. Several samples were prepared to contain two percent free fluoride ion that had varying amounts of uranium and niobium in ratios of 9:1 and 12:1 with 0.56 M free fluoride in 20 percent nitric acid. Plots of the data are presented in Figures 11 and 12. A study of the symmetry of these plots discloses progressive inhibition of foil dissolution by increasing uranium concentration in solutions with equal free fluoride

content. The anomalous change in the slope of the plot for the 1:1 dilution data, Figure 12, was surprising and not understood.

Reference to the curves in Figures 11 and 12 discloses that this inhibitory interference of uranium becomes serious beyond a concentration of 8 gms U/100 mls of solution when special compensation corrections would be required, such as comparing unknown solutions to known solutions with similar uranium concentrations.

This inhibitory role of uranium was eliminated by removing uranium from the samples with tri-*n*-octyl phosphine oxide—chloroform extractions. Free fluoride was then estimated in the purified aqueous phase at 24° C by measuring the dissolution time for a zirconium foil and comparing to a standard curve, see Figure 10. Longer dissolution times will be noted for the 12:1 uranium–niobium samples. The delay is a consequence of some hydrofluoric acid that transferred to the organic phase during the extraction. This loss could be minimized by diluting the samples 1:1 with 20 percent nitric acid prior to the extraction, then less uranium in the diluted aqueous would require fewer extractions. In either case, the prolonged dissolution times contribute to fail-safe features of the free fluoride ion. However, extraction is not necessary to the attainment of reliable results if the analyst will keep in mind the role excessive amounts of uranium will play in a given mixture. The analyst should also keep well in mind that foil-dissolution times are sensitive to the temperature of the sample solution as well as to the rate of flow.

An alternative but far more qualitative free-fluoride test was devised by using a fluoride-reactive but nonmetallic film incapable of reducing uranium(VI). Such a film was found by coating wooden sticks with several layers of sodium silicate. This siliceous film could then be dissolved by free fluoride during some measurable period of time. Detection of this film penetration was determined iodometrically by observing the oxidation of an iodide-permeated wooden substrate by oxidants present in the sample solution. Potassium bromate was added to the sample solution to assure a marked color change (Figure 13). A study of Figure 13 discloses progressive discoloration of the indicator sticks as a function of the free fluoride ion in solution. The top left group in Figure 13 was exposed to just 20 percent nitric acid solution with some bromate. Permeation of the sample solution resulted in some oxidation of iodide in the wooden substrate. Adjacent to the blanks are sticks exposed to 0.5 percent free fluoride in 20 percent nitric acid and some bromate. Comparison of these two groups readily discloses 0.5 percent free fluoride as the lower limit. Further comparison of remaining groups reveals reasonably good agreement within and between groups over the free fluoride and uranium concentrations studied. These iodide-pretreated, siliceous-coated wooden sticks permitted a simple approximation of free fluoride ion in the sample solutions tested. The presence of varying concentrations of uranium over the range studied did not interfere with the free fluoride ion approximation. A unique advantage of the stick test is its ready application to field-type processes.

The foil and stick tests used for estimating free fluoride in the etching-bath solutions should be well suited to many other fluoride-containing solutions since they permit a rapid and simple analysis of free fluoride in potentially complex mixtures.

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