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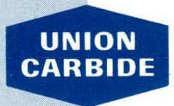
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DETERMINATION OF FLUORINE AND BORON IN
URANIUM-HYDROFLUOBORIC ACID SOLUTIONS

L. D. Keele

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT** **Contract W-7405 eng 26**



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ABSTRACT

A solution containing uranyl and fluoborate ions can be effectively analyzed for boron and fluorine after removing the uranium with a cation exchange column. The resultant effluent containing a mixture of acids (HF, H₃B₃O₃, and HBF₄) is reacted with a solution of calcium chloride, which precipitates the fluoride as the calcium salt (CaF₂). The resulting acid solution is analyzed by titrating to a methyl orange endpoint with a standard sodium hydroxide solution. Mannitol is added to the same solution, and the titration is continued to a phenolphthalein endpoint. The fluorine data yielded an absolute limit error of ± 0.48 percent (0.95) for a single determination; the boron data yielded an absolute limit error of ± 0.26 percent (0.95) for a single determination.

CONTENTS

SUMMARY	5
INTRODUCTION	6
METHOD FOR DETERMINING FLUORINE AND BORON	7
Analytical Procedure (General Description)	7
Reagents and Equipment	7
Reagents	7
Equipment	7
Analytical Procedure (Detailed Steps)	9
Calculations	10
Results	10
BIBLIOGRAPHY	11
ACKNOWLEDGEMENTS	12

SUMMARY

In the analysis of fluorine and boron in the same solution containing cations, anion exchange sorption is of special importance since this method can be applied to separate boron from numerous elements. In a solution containing the uranyl and fluoborate ions, the boron exists as an anion and can be separated from the uranium and other interfering elements by passing the solution through a Dowex 50 cation exchange column. The effluent from the column which contains three acids (H_3BO_3 , HF, and HBF_4) is reacted with calcium chloride. Calcium fluoride is precipitated, and equivalent quantities of hydrochloric and boric acids are released. The solution is boiled for one hour under reflux to complete the reaction. After cooling the sample, it is titrated to a methyl orange endpoint. Mannitol is added to the solution and the titration is continued to a phenolphthalein endpoint with a standard sodium hydroxide solution. In this type of analysis, the titration for fluorine does not interfere in the titration of boron in the same solution. This method was checked with synthetic solutions of uranyl fluoride plus boric acid.

INTRODUCTION

Determination of fluorine and boron in the same solution proved to be a difficult problem. These elements mutually interfere with each other since they form the fluoborate ion. In an effort to solve this problem, three methods were proposed: (1) the nitron procedure that is applicable to hydrofluoric acid solutions of uranium alloys (this procedure gave some promise but the time of analysis was too long); (2) the classical distillation of methyl borate in separation from other elements (this method is the most common, but is tedious, time consuming, and the blanks are erratic); (3) by passing the solution through a cation exchange column, precipitating the fluorine with calcium chloride, filtering the calcium fluoride from the solution, adding mannitol to the filtrate, and titrating with a standard sodium hydroxide solution to a phenolphthalein endpoint. The calcium fluoride was ignited and weighed for a gravimetric determination. This method was very much improved over the other two methods.

However, after searching for a better method, an adaptation of the method by Ryss and Polawoka for the analysis of gaseous boron trifluoride after it had been absorbed in water was considered. After removing the uranium by a cation exchange column, the precipitation of calcium fluoride with calcium chloride released equivalent amounts of hydrochloric and boric acids. The released amount of H^+ ion, equivalent to the F^- ion, was titrated with a sodium hydroxide solution to a methyl orange endpoint. After the addition of mannitol, the boric acid formed in the reaction was determined by continuing the titration with a sodium hydroxide solution to a phenolphthalein endpoint. This report describes the way the Plant Laboratory at the Oak Ridge Y-12 Plant^(a) has utilized this method for the determination of fluorine and boron in a uranium-hydrofluoboric acid solution.

(a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation's Nuclear Division.

METHOD FOR DETERMINING FLUORINE AND BORON

ANALYTICAL PROCEDURE (General Description)

A suitable sample of uranium-hydrofluoboric acid was pipetted into a beaker (pipette and beaker were of plastic) and diluted to 100 milliliters with demineralized water, then passed through a resin column (Dowex 50-8X 50-100 mesh). The resin was washed with 300 milliliters of demineralized water and the effluent caught in an 800-milliliter Teflon beaker. Fifty milliliters of two-molar calcium chloride were added to the effluent, then the solution was stirred with a Teflon-covered stirring magnet. Three or four drops of methyl orange indicator were added to the solution. The solution was titrated to an endpoint with standard (0.10 N) sodium hydroxide solution, then the solution was transferred to a round-bottom boiling flask and the flask connected to a water-cooled condenser. Using a heating mantle, the solution was boiled for one hour then cooled to room temperature by means of a water bath. Finally, the solution was transferred to the original beaker and titrated to a methyl orange endpoint for the second time with the standard sodium hydroxide solution. The total volume of sodium hydroxide was recorded. Mannitol (~ 40 gms) was added to this solution and the boric acid was determined by continuing the titration with the standard sodium hydroxide solution to a phenolphthalein endpoint.

REAGENTS AND EQUIPMENT

Reagents

Sodium Hydroxide - one-tenth normal

Hydrochloric Acid - six molar

Calcium Chloride - two molar

Methyl Orange - one-tenth percent

Phenolphthalein - one-tenth percent in ethanol

Resin - Dowex 50-8X (50 - 100 mesh)

Equipment

Beakers - Teflon - 800 mls

Column - polystyrene - one-inch ID, 16 inches long (Figure 1)

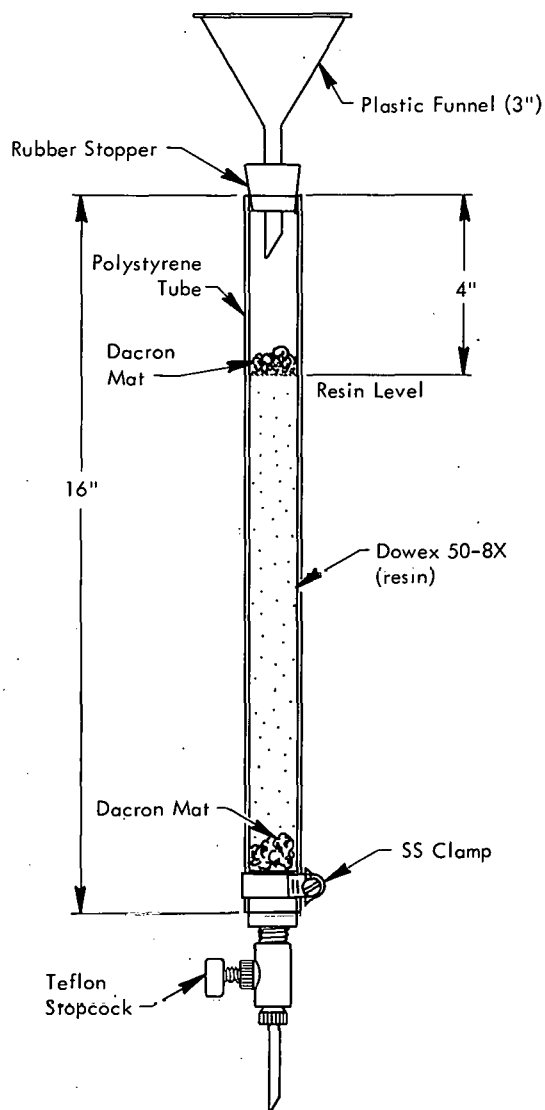


Figure 1. CATION EXCHANGE COLUMN.

Vials - plastic

Pipette - plastic - 5 mls

Boiling Flask - one liter with 24/40 female ground-glass fittings

Condensers - 24 inches long with 24/40 male ground-glass fittings

Heating Mantle - one liter size

Variac - control for heating mantle

Stirrer - magnetic

Stirring Bar - one inch long and Teflon covered

pH Meter - Beckman (pH 0 - 14)

ANALYTICAL PROCEDURE (Detailed Steps)

1. Prepare the Dowex 50-8X resin by washing it in a Teflon beaker with demineralized water and removing the fines at the same time.
2. Add 200 milliliters of six-molar hydrochloric acid and stir the mixture for two hours with a magnetic stirrer using a Teflon-covered stirring bar.
3. Make mats of Dacron thread and place them at the bottom and top of the column (Figure 1).
4. Fill the column within four inches of the top with hydrochloric acid-treated resin (Figure 1).
5. Wash the resin with demineralized water until the pH on the effluent water reaches 5.0 or higher.
6. Transfer the sample to the resin column with demineralized water.
7. Pass about 30 to 40 drops per minute of the sample through the column.
8. Wash the column with demineralized water until 400 milliliters of solution have transferred to a Teflon beaker.
9. After removing the Teflon beaker, use a small beaker and check the effluent with methyl orange until a straw-colored endpoint is reached.
10. Add this solution to the original beaker.
11. Add 50 milliliters of two-molar calcium chloride to the solution.
12. Titrate the solution to a methyl orange endpoint with 0.10 N sodium hydroxide solution. Record the number of milliliters as Volume 1 (V_1).
13. Transfer the solution to a one-liter, round-bottom boiling flask.
14. Connect the condenser to the flask.
15. Place the mantle on the flask.
16. Set the Variac on "60" for 20 to 25 minutes.
17. Boil the solution for one hour.

18. Remove the heating mantle.
19. Cool the solution to room temperature.
20. Titrate the solution to a second methyl orange endpoint with a 0.10 N sodium hydroxide solution. Record the volume as Volume 2 (V_2).
21. Add the titer (Volumes 1 and 2).
22. Add about 40 grams of mannitol to the solution.
23. Titrate the solution to a phenolphthalein endpoint with 0.10 N sodium hydroxide solution. Record as Volume 3 (V_3).

CALCULATIONS

$$\% F = (V_1 + V_2 - \text{blank}) \times \text{NaOH normality} \times \frac{\text{milliequivalent weight of fluorine}}{\text{weight of sample in grams}}$$

$$\% B = (V_3 - \text{blank}) \times \text{NaOH normality} \times \frac{\text{milliequivalent weight of boron}}{\text{weight of sample in grams}}$$

RESULTS

In ten determinations on a synthetic uranyl-fluoboric acid solution, the fluorine and boron contents were obtained as given in Table 1.

Table 1
DETERMINATION OF FLUORINE AND BORON CONTENTS

Sample Number	Fluorine (%)	Boron (%)	Sample Number	Fluorine (%)	Boron (%)
1	11.33	17.37	6	11.42	17.50
2	11.06	17.41	7	11.47	17.24
3	11.02	17.37	8	11.17	17.31
4	11.34	17.51	9	11.12	17.21
5	11.28	17.35	10	11.16	17.32

These accumulated data for the ten determinations were statistically evaluated. The fluorine data yielded an absolute limit error of ± 0.16 percent (0.95) for the mean and ± 0.48 percent (0.95) for a single determination; the boron data yielded an absolute limit error of ± 0.20 percent (0.95) for the mean and ± 0.26 percent (0.95) for a single determination.

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