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SPECTROPHOTOMETRIC DETERMINATION FOR THE FLUORIDE ION IN THE PRESENCE OF ALUMINUM AND PLUTONIUM

By

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SPECTROPHOTOMETRIC DETERMINATION FOR THE FLUORIDE ION IN THE PRESENCE OF ALUMINUM AND PLUTONIUM

INTRODUCTION

Analyses for the fluoride ion are reviewed in detail by Simons(2). Spectrophotometric methods based on reducing a colored thorium complex by precipitation of thorium fluoride are discussed, especially with respect to the many interfering metallic ions. Brownley and Howle(1) recommend removal of interfering cations by exchange on Dowex 50.

The proposed sample matrix was aluminum and plutonium nitrate. Since spectrophotometric methods generally offer accurate answers at a low time expenditure, the proposed investigation was to remove interfering metallics by ion exchange, then analyze for fluoride by bleaching a thorium-thoron complex.

SUMMARY

Fluoride, with no interfering cations, can readily be determined spectrophotometrically based on the reduction of the colored thoron-thorium complex. Aluminum nitrate and plutonium ions can be removed by extraction with 30 percent TBP from a sample six molar in nitric acid to a great enough degree that the same method can be used. The detection range is 0.003 M fluoride to 0.1 M fluoride. A recommended procedure is presented.

APPARATUS AND REAGENTS

Initial investigation was carried out with a Beckman Model DK-2 recording spectrophotometer. Routine calibrations were then made on a Bausch and Lomb "Spectronic 20" spectrophotometer.

A five-ml column, 1 cm in diameter, was used with the hydrogen form of Dowex 50 laboratory reagent grade cation exchange resin, 200-400 mesh.

Solutions consisted of 0.1 percent thoron (di-sodium salt of 0-[2 hydroxy-3,6-disulfo-1-napthylazo] benzene arsonic acid); 0.01 percent by weight of thorium ion in the form of thorium nitrate; 70 percent perchloric acid; 30 percent tri-butyl phosphate in Shell Spray Base; concentrated nitric acid; and standard fluoride solutions prepared volumetrically from crystalline, reagent grade, sodium fluoride. These reagents are individually stable, but the complex resulting from the mixing of thoron and thorium is unstable and must be prepared daily.

EXPERIMENTAL

Construction of the Standard Curve

The initial standard curve, with no aluminum present, was prepared by the following procedure:

1. Prepare Blank
    a. 6.200 ml H_2O
    b. 1.000 ml 0.1% thoron
    c. 10 drops 70% $HClO_4$

2. Prepare Reference
    a. 5.200 ml H_2O
    b. 1.000 ml 0.1% thoron
    c. 1.000 ml 0.01% thorium
    d. 10 drops 70% $HClO_4$
3. Prepare Samples
    a. 5.000 ml H_2O
    b. 1.000 ml 0.1% thoron
    c. 1.000 ml 0.01% thorium
    d. 10 drops 70% $HClO_4$
    e. 200 lambda fluoride standard

Several standard fluoride concentrations were used. The reference and each of the samples were run against the blank on the Beckman DK-2. The complex was found to absorb at 550 mu. A plot of log (reference absorbance peak height minus sample absorbance peak height) versus log (concentration) was prepared. This plot appears in Figure 1.

The second standard curve (4.3:1 aluminum to fluoride ratio) was prepared exactly like the initial curve, except for the sample size. In this case, a 500-lambda sample was used instead of 200 lambda. The resulting curve is shown in Figure 2.

Reducing Aluminum Interference

Removal of at least part of the aluminum would serve a two-fold purpose. Comparison of Figures 1 and 2 reveals the loss in sensitivity due to aluminum.

During initial investigations, it was noted that small variation in aluminum concentration at high (4:1) aluminum to fluoride ratios created a high (15-20 percent) analytical error. As the ratio dropped to 2:1, the effect was reduced markedly.

Aluminum was separated by the standard methods suggested by Scott(4); however, the fluoride carried on the aluminum each time. Ion exchange with Dowex 50 did not remove the aluminum complexed with fluoride. When plutonium was removed by extraction from a 6 M nitric acid solution into 30 percent TBP, the slope of the fluoride concentration curve was much greater than could be predicted on the basis of the aluminum concentration. In fact, the slope was quite analogous with Figure 1 (no aluminum). The implication was the aluminum was extracted by the solvent. Table 1 contains the results of a series of extractions to check this possibility.

TABLE 1: Successive extractions of 73.6 g/l $Al(NO_3)_3$ into 30% TBP* aqueous phase $Al(NO_3)_3$ concentration after extraction number.

N HNO_3	1	2	3
6	43.3 g/l	38.9 g/l	39.0 g/l
3	62.0 g/l	61.9 g/l	59.8 g/l
1	70.9 g/l	64.6 g/l	----

*30% TBP was pre-equilibrated with the appropriate nitric acid concentration.

From the data, it is apparent that the aluminum removal is a result of forcing the aluminum nitrate into the organic at a high acid concentration, but it is not an aluminum extraction. This corresponds to the documented extraction coefficient(3) for aluminum of 0.0003 for 4.7 M HNO_3 and 15% TBP.

This method of aluminum removal is adequate to permit determination of fluoride in the 0.003 M to 0.1 M fluoride range. Although this is not the full range experienced from an aluminum-free solution, it is sufficient for the analysis desired. A plot of percent transmission versus log concentration appears in Figure 3.

The samples in this case were read on the "Spectronic 20", and the percent transmission readings were obtained by setting the colorimeter to read 0% transmission with the reference and 100% transmission with the blank (see p.3). This allows a percent transmission reading for all samples, since they must fall between these two colors. It was found here that the useable range of percent transmission is 15% to 45%.

Reduction of the thoron-thorium complex was found to be time dependent. A curve showing percent transmission versus time appears in Table 4. For this determination a significant error would result unless a uniform time for color reduction were observed. For the purposes of this investigation, the time was set at five minutes after the sample was introduced.

DISCUSSION

The results obtained from this method are good to within ± 5%, if care is exercised. Although this seems rather large, the graph from which the concentration is read shows an error magnification of about seven times, so the analytical technique must be less than one percent to obtain an error less than seven percent. This magnification of error can be lessened either by increased sample size or weaker complex color, giving a steeper slope to the standard curve. Either conditions would result in a shorter curve range.

Recommended Procedure

1. Aluminum removal:
   - a. Pipet 500 lambda of sample into a 15 ml vial.
   - b. Pipet 1500 lambda water into vial.
   - c. Pipet 1 ml concentrated nitric acid into vial.
   - d. Pipet 3 ml 30% TBP in SSB into vial, and stir with a stainless steel stir bar for 15 minutes.

2. Label three 15 ml vials: 1, 2, and 3, respectively.

   Vial #1 (blank):

   6.500 ml water
   1.000 ml 0.1% thoron solution
   10 drops 70% $HClO_4$ (perchloric acid)

   Vial #2 (reference):

   5.500 ml water
   1.000 ml 0.1% thoron
   1.000 ml 0.01% thorium
   10 drops 70% $HClO_4$

   Vial #3 (sample):

   5.000 ml water
   1.000 ml 0.1% thoron
   1.000 ml 0.01% thorium
   10 drops 70% $HClO_4$

3. Zero the "Spectronic 20" colorimeter by setting the grating at 550 mu. Set to read zero percent transmission with reference (#2), and 100 percent transmission with blank (#1).

4. Add 500 lambda prepared sample, drawn from aqueous layer to Vial #3 and stir.

5. Read percent transmission of sample (#3) on the "Spectronic 20" at 550 mu. at exactly five (5) minutes after introduction of prepared sample into Vial #3.
6. Determine the fluoride concentration by referring to a calibration curve similar to Figure 3.

There is still a slight variance if the aluminum to fluoride ratio varies; however, little over-all effect is noticed due to the fact that $Al(NO_3)_3$ concentration can be determined by specific gravity checks.

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FIGURE 1: Complex Bleaching Vs. Log Conc. (No Aluminum Present)(Beckman DK-2).

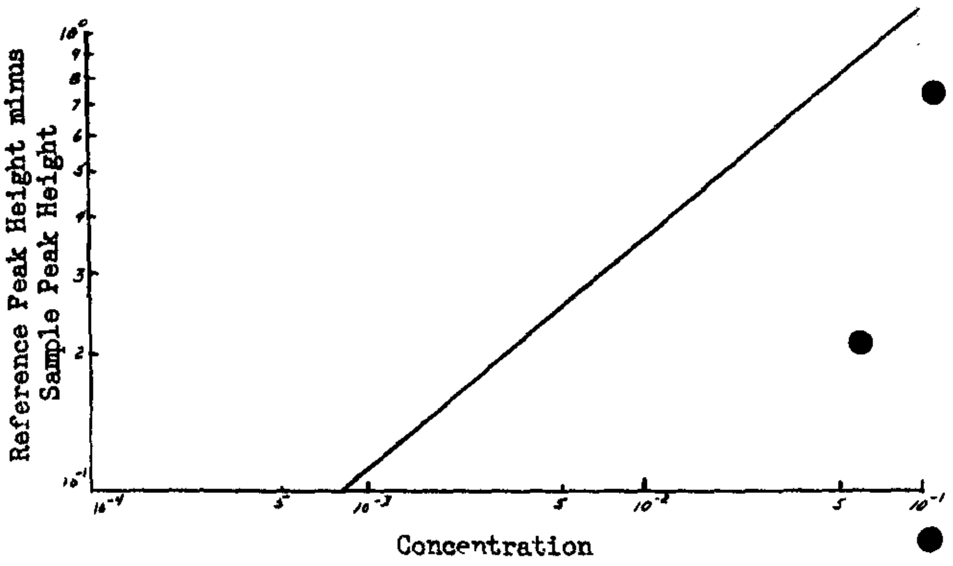


FIGURE 2: Complex Bleaching Vs. Log Conc. (4.3 to 1 Aluminum Ratio)(Bechman DK-2).

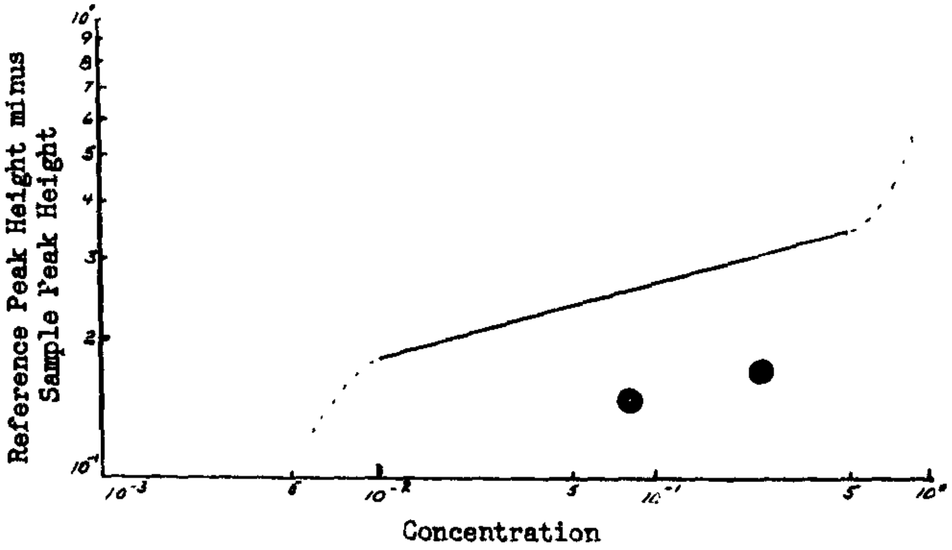


FIGURE 3: Complex Bleaching Vs. Log Conc. (Aluminum Extracted)(Spectronic 20).

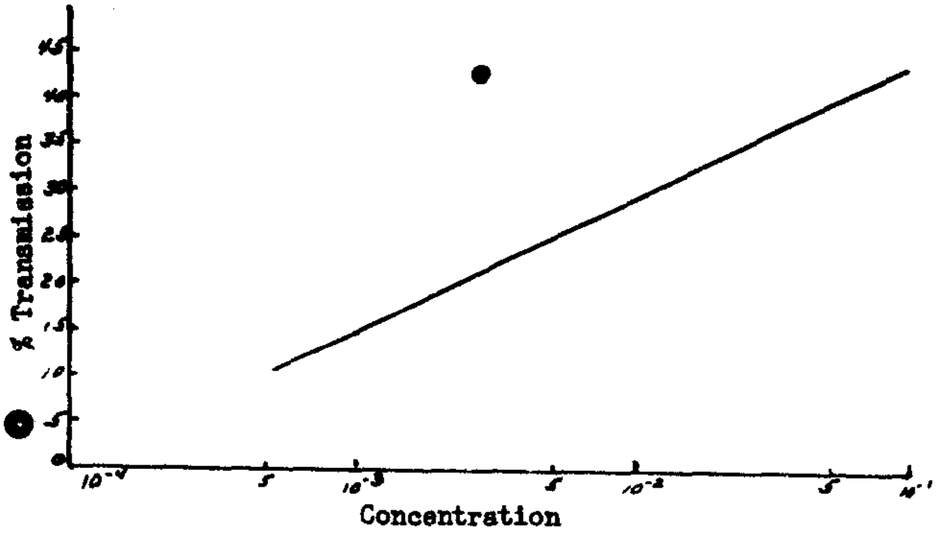
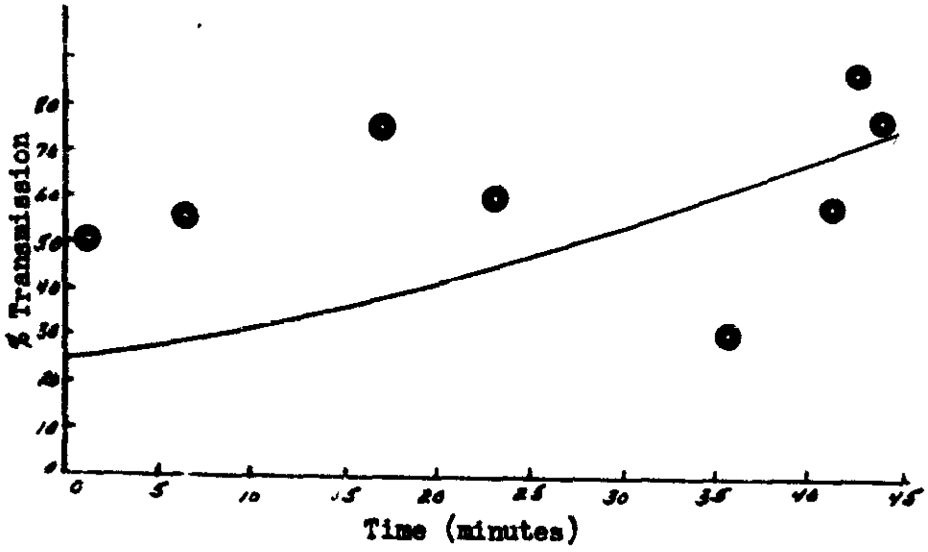


FIGURE 4: Time Dependence of Bleaching Process with Aluminum Present.



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