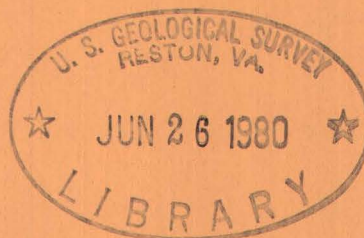


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# The absorption spectra of the complexes of uranium (VI) with some beta-diketones

By H. I. Feinstein



*Trace Elements Investigations Report 631*

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

Chemistry

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Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

THE ABSORPTION SPECTRA OF THE COMPLEXES OF URANIUM (VI)  
WITH SOME  $\beta$ -DIKETONES\*

By

H. I. Feinstein

October 1956

Trace Elements Investigations Report 631

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\*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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THE ABSORPTION SPECTRA OF THE COMPLEXES OF URANIUM (VI)  
WITH SOME  $\beta$ -DIKETONES

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ABSTRACT

The absorption spectra of the complexes of uranium (VI) with four  $\beta$ -diketones were determined under various conditions of pH, concentration of uranium, and alcohol concentration. Under optimum conditions, the maximum molar absorptivity (31,200) is obtained using 2-furoyltrifluoroacetone. This compares with about 4,000 and 19,000 for the thiocyanate and dibenzoylmethane complexes, respectively.

INTRODUCTION

There is a need for a sensitive colorimetric reagent for uranium. Reagents that have been proposed are listed by Ware (1945) and Rodden (1950). Among the types of reagents known to give colored products with uranium (VI) are the  $\beta$ -diketones (Sacconi and Giannoni, 1954) such as dibenzoylmethane (Yoe, Will, and Black, 1953). Although the structure of the complex produced is not definitely established, a coordination number of six and more has been suggested (Yoe, Will, and Black, 1953; Sacconi and Giannoni, 1954). Dibenzoylmethane is five or six times as sensitive as thiocyanate (Feinstein, 1955).

In the search for new reagents, four  $\beta$ -diketones were studied for sensitivity to uranium (VI). The molar absorptivity under optimum conditions varied from 20,600 for 2-thenoyltrifluoroacetone to 31,200 for 2-furoyltrifluoroacetone, whereas that for the uranium thiocyanate complex was 4,000.



This work is part of the program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

#### EXPERIMENTAL DATA

##### Apparatus

Quartz photoelectric spectrophotometer

1-cm corex cells

pH meter

##### Reagents and solutions

95 percent ethyl alcohol

(1+1)  $\text{NH}_4\text{OH}$ . Add one volume of concentrated  $\text{NH}_4\text{OH}$  to one volume of water.

(1+10)  $\text{NH}_4\text{OH}$ . Add one volume of concentrated  $\text{NH}_4\text{OH}$  to ten volumes of water.

7 percent nitric acid. Add 7 ml of concentrated nitric acid to 93 ml water and mix.

Standard uranium solutions were prepared by dissolving the required amount of 99.96 percent  $\text{U}_3\text{O}_8$  in enough (1+1) nitric acid to make a solution of the desired uranium concentration in 7 percent nitric acid.

2-thenoyltrifluoroacetone (TTA)

2-thenoylperfluorobutyrylmethane

2-furoyltrifluoroacetone

2-furoylperfluorobutyrylmethane

A 1 percent solution of TTA (equivalent to 0.045M) was prepared in 95 percent alcohol. The other diketones were 0.035, 0.049, and 0.033 molar, respectively, in 95 percent alcohol.

All the  $\beta$ -diketones were obtained from Graham, Crowley and Associates, Inc., Chicago, Illinois.

#### Procedure

Five milliliters of the standard uranium solution or of a blank of 7 percent nitric acid were placed in a 100-ml beaker; 25 ml of 95 percent alcohol, 15 ml of water, and 1 ml of reagent solution were added. The pH was adjusted using (1+1)  $\text{NH}_4\text{OH}$ , (1+10)  $\text{NH}_4\text{OH}$ , or 7 percent  $\text{HNO}_3$ , the solution transferred to a 50-ml volumetric flask, diluted to the mark with water and mixed. The pH after dilution is not more than 0.3 unit from the adjusted pH. Absorbance was measured immediately.

#### Concentration of reagents

The effect of reagent concentration upon the absorbance was studied for 2-thenoyltrifluoroacetone only. The results are given in table 1.

Table 1.--Absorbance as a function of 2-thenoyltrifluoroacetone concentration. Each solution contains 26 ml of 95 percent ethyl alcohol per 50 ml of solution, pH = 5.5,  $\lambda$  = 380 m $\mu$ .

1 percent TTA (ml)	Absorbance	
	Reagent blank vs. H <sub>2</sub> O	0.5 mg U vs. reagent blank
0.25	0.090	0.752
0.5	0.182	0.790
1.0	0.347	0.865
2.5	0.770	0.900
5.0	1.588	0.910

It will be noted that the net absorbance increases very gradually beyond a concentration of 1 ml of reagent solution per 50 ml of solution. Because of this and to keep the absorbance of the reagent blank down to a minimum, 1 ml of reagent solution was used in subsequent experiments.

#### Alcohol concentration

The effect of alcohol concentration, in the range tested, upon absorbance of uranium (VI)--2-thenoyltrifluoroacetone is nil (table 2). A concentration of 26 ml of 95 percent ethyl alcohol was used in subsequent experiments.



Table 2.--Absorbance as a function of alcohol concentration.  
 50 ml volume containing 0.5 mg uranium, 1 ml  
 1 percent TTA, pH = 5.5,  $\lambda$  = 380 m $\mu$ .

95 percent ethyl alcohol (ml)	Absorbance	
	Reagent blank vs. H <sub>2</sub> O	U vs. reagent blank
21	0.286	0.872
26	0.347	0.865
31	0.425	0.880

#### Absorption spectra

The absorption spectra of three  $\beta$ -diketones with uranium (VI) were determined at two levels of uranium (4 and 10 ppm), and of the 2-thenoyltrifluoroacetone--uranium complex at three levels (4, 10, and 20 ppm), and at various pH values. The absorption spectra of reagent blank vs. water and of complex vs. reagent blank at optimum pH are shown in figures 1, 2, 3, and 4. The effect of pH on absorbance is shown in figure 5, and tables 3, 4, and 5. All complexes obey Beer's law at optimum pH and wavelength. The results are summarized in table 6.

#### Interfering elements

A systematic study of the interferences was not made; however, it is known that many elements interfere with the dibenzoylmethane method (Yoe et al., 1953) and it would be necessary to effect a separation before these reactions may be applied to the determination of uranium.

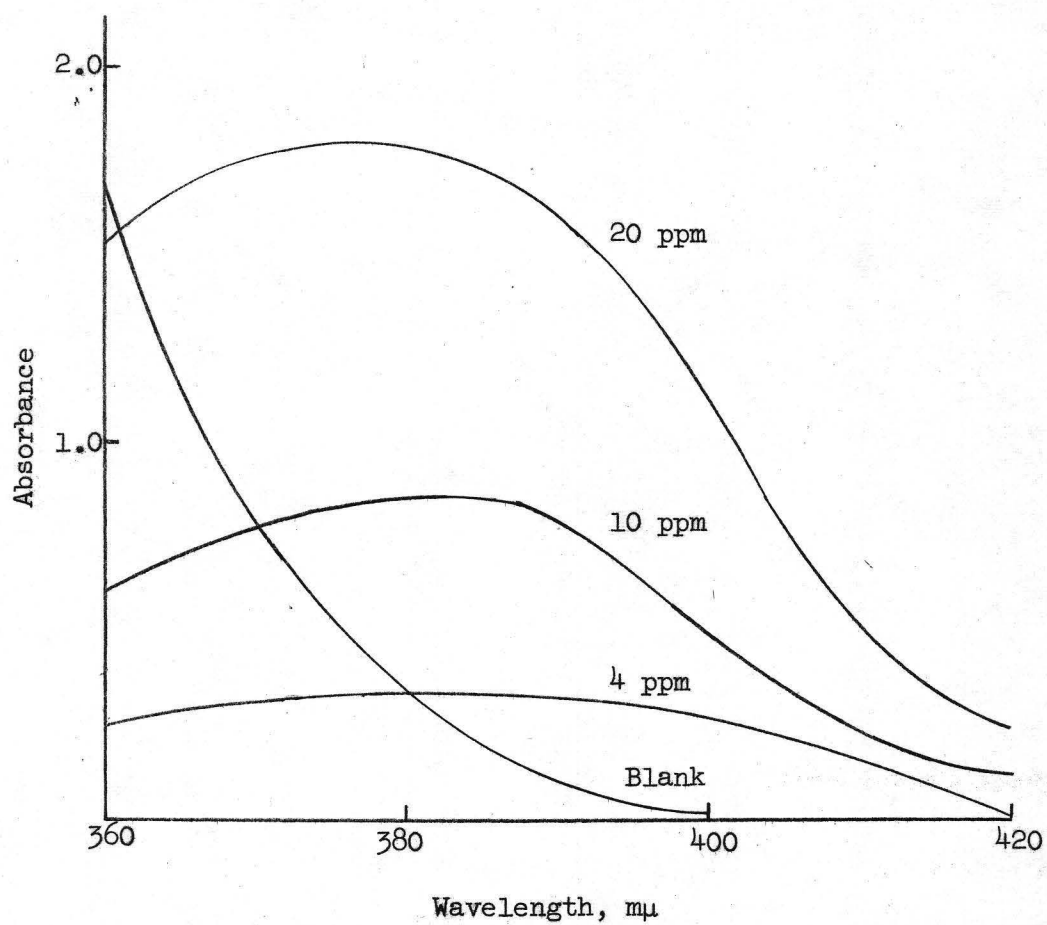


Figure 1.--Spectrum of U(VI)--2-thenoyltrifluoroacetone.

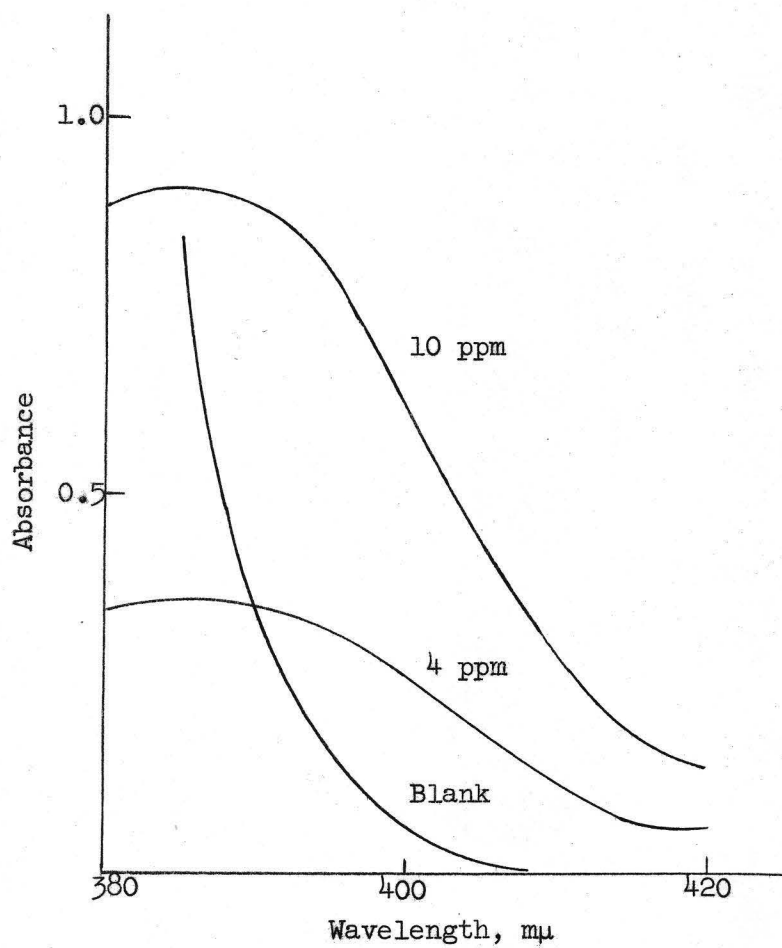


Figure 2.--Spectrum of U(VI)--2-thenoylperfluorobutyrylmethane.

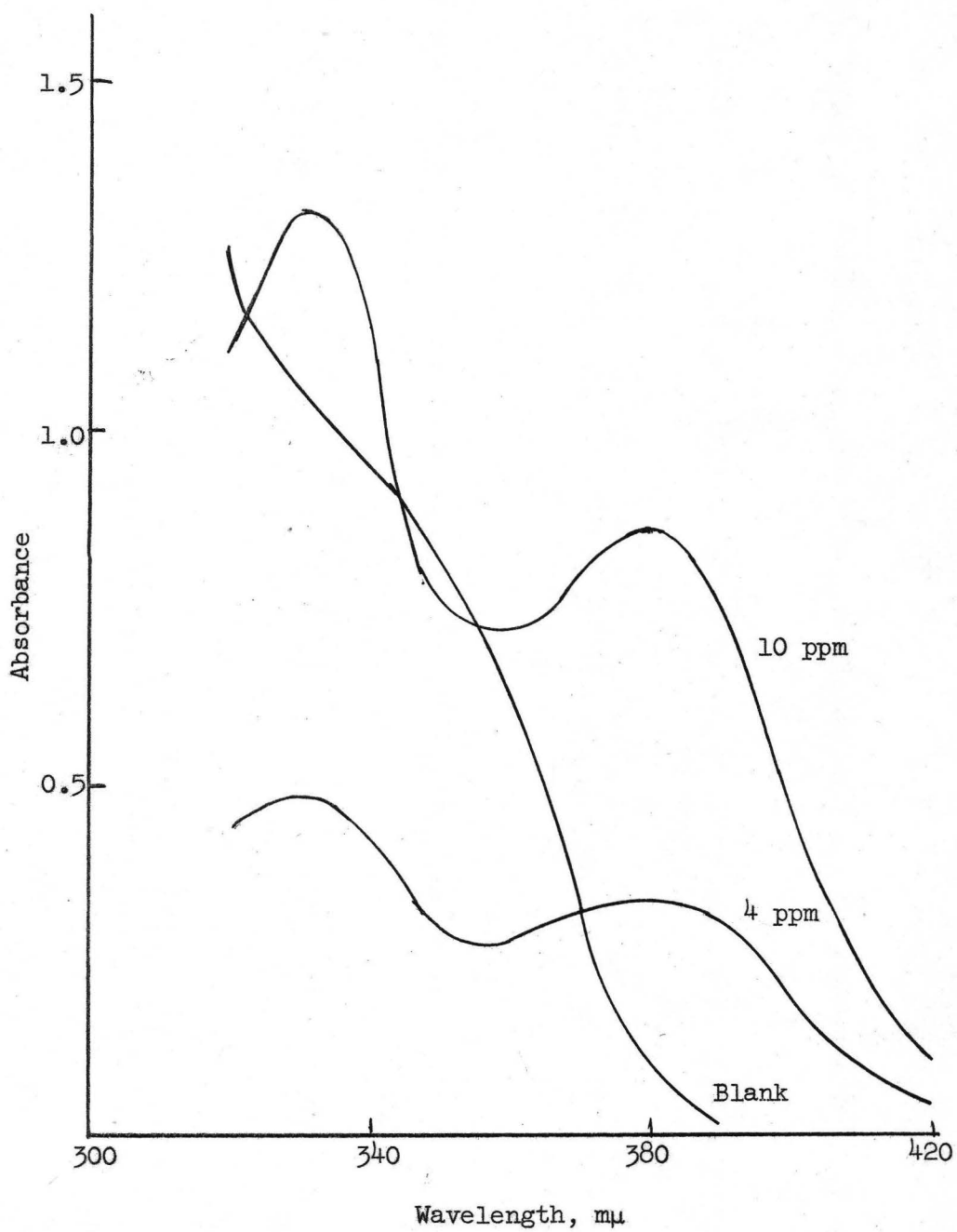


Figure 3.--Spectrum of U(VI)--2-furoyltrifluoroacetone.

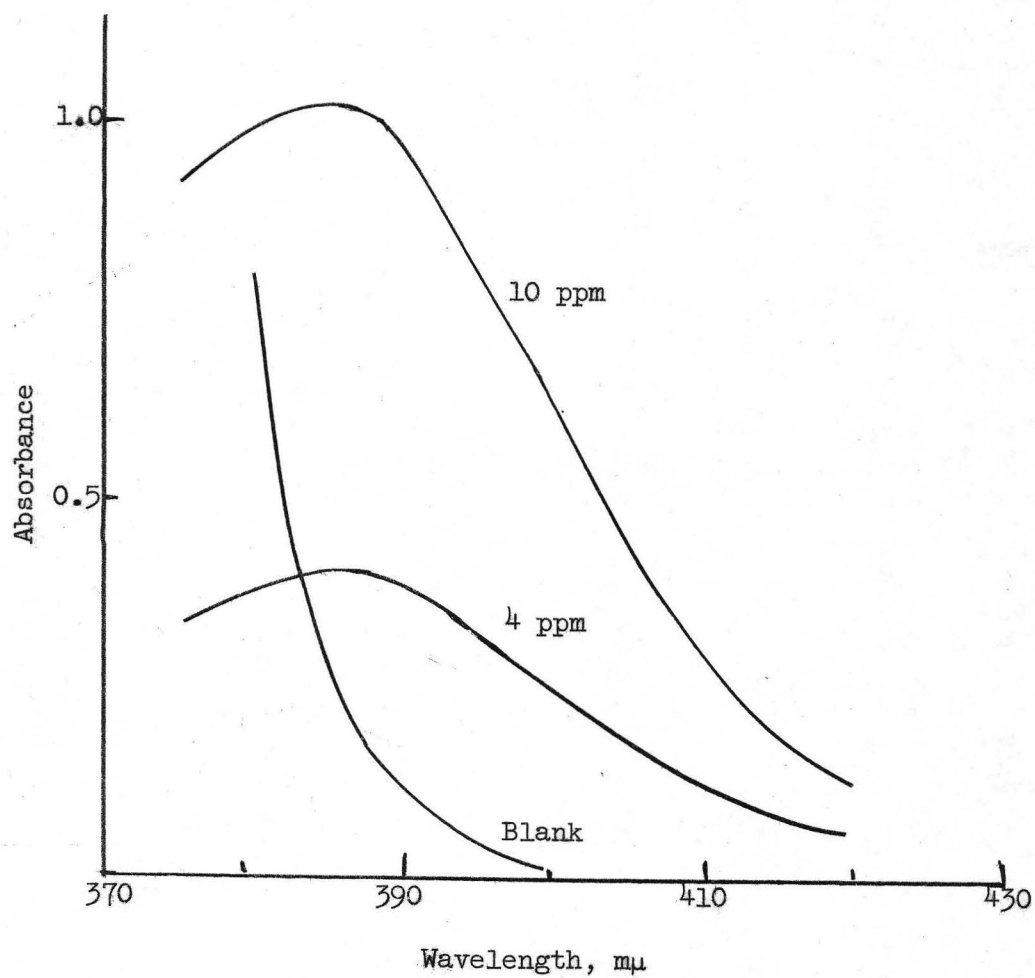


Figure 4.--Spectrum of U(VI)--2-furoylperfluorobutyrylmethane.

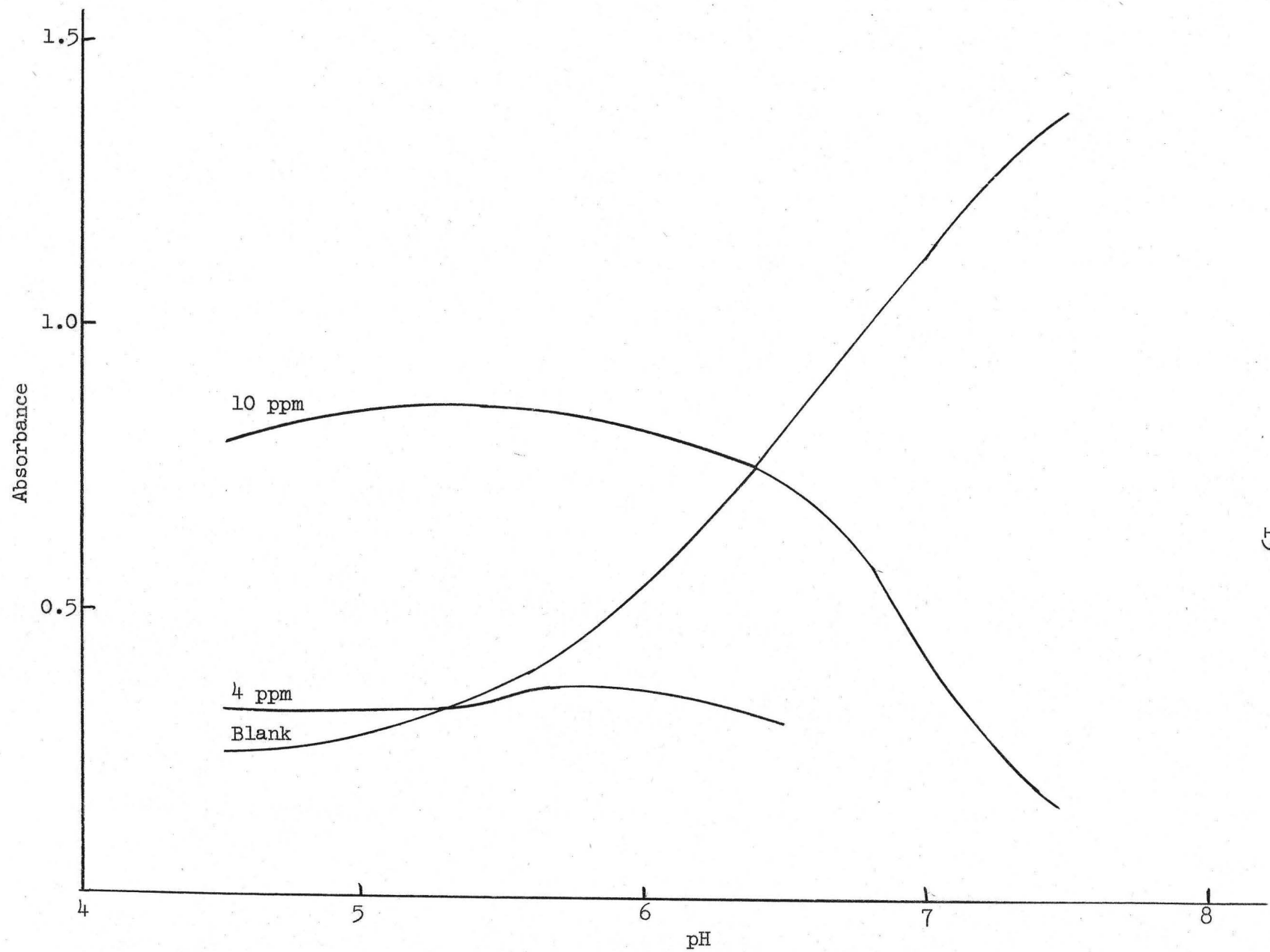


Figure 5.--pH and absorbance of U(VI)--2-thenoyltrifluoroacetone. Wavelength, 380 mμ



Table 3.--pH and absorbance of 2-thenoylperfluorobutyrylmethane.  
Wavelength 385 mμ.

pH	Absorbance		
	Reagent blank vs. H <sub>2</sub> O	U vs. reagent blank 4 ppm	10 ppm
4.0	2.93	0.286	0.760
4.5	2.45	0.297	0.778
5.0	2.04	0.297	0.792
5.5	1.168	0.341	0.800
6.0	0.955	0.382	0.892
6.5	0.850	0.353	0.900
7.0	0.796	0.364	0.895
7.5	0.791	0.335	0.805

Table 4.--pH and absorbance of 2-furoyltrifluoroacetone.  
Wavelength 330 mμ.

pH	Absorbance		
	Reagent blank vs. H <sub>2</sub> O	U vs. reagent blank 4 ppm	10 ppm
4.0	0.710	0.444	1.00
4.5	1.045	0.494	1.312

At higher pH values, a balance could not be obtained.

Table 5.--pH and absorbance of 2-furoylperfluorobutyrylmethane.  
Wavelength 385 mμ.

pH	Reagent blank vs. H <sub>2</sub> O	Absorbance	
		U vs. reagent blank 4 ppm	10 ppm
3.5	0.992	0.365	0.895
4.0	0.860	0.418	0.962
4.5	0.654	0.422	1.00
5.0	0.524	0.376	0.978
5.5	0.311	0.407	1.025
6.0	0.209	0.410	1.006
6.5	0.179	0.408	1.024
7.0	0.169	0.383	0.970
7.5	0.164	0.312	0.559

Table 6.--Summary of results.

Reagent	Optimum pH	Optimum wavelength mμ	Net absorbance		Molar ab- sorbptivity, ε 1/
			U vs. reagent blank 4 ppm	10 ppm	
2-thenoyltrifluoro- acetone	5.5	380	0.356	0.865	20,600
2-thenoylperfluoro- butyrylmethane	6.5	385	0.353	0.900	21,400
2-furoyltrifluoro- acetone	4.5	330	0.494	1.312	31,200
2-furoylperfluoro- butyrylmethane	6.0	385	0.410	1.006	24,000

$$\frac{1}{\text{Molar absorptivity, } \epsilon} = \frac{\text{absorbance}}{\text{molarity} \times \text{cell length in cm}}$$

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