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SPECTROPHOTOMETRIC DETERMINATION OF URANIUM
 BY THIOCYANATE METHOD IN ACETONE MEDIUM

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A method which is relatively free from both anionic and cationic interferences has been developed for the determination of uranyl ion. About one hundredth of a milligram of uranium per milliliter will develop an absorbance of about 0.20 in one centimeter cells. The molar absorbance index is approximately 3850. Relatively large amounts of copper, zirconium, tin, mercury, manganese, sulfate, fluoride, acetate, chloride and nitrate do not interfere. More than unit molar ratios of foreign ion/uranyl ion may be present if the foreign ion is fluosilicate, phosphate, citrate, nickel, chromium and iron. Lead, cobalt, and molybdenum interfere at low concentrations.

The thiocyanate method as developed by J. E. Currah and F. E. Beamish⁽¹⁾ and others^(2,3) has relatively high sensitivity and freedom from cation interferences. However, anion interferences have severely limited the applications of this method. Other spectrophotometric methods for uranium^(4,5,6) have been examined in this laboratory and found to require excellent separations of iron, copper, zirconium, and many other interfering cations. A thorough investigation of the thiocyanate method

2-197-1
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indicated that very good results (10.5 per cent) could be obtained at 375 μ using fresh aqueous ammonium thiocyanate solutions and using several drops of 10 per cent sodium thiosulfate to reduce interfering traces of iron. Stannous chloride, in the presence of uranium and ammonium thiocyanate in aqueous solution, as used by Currah and Beamish, was found to generate an interference peak around 375 μ , which was not too serious when the ammonium thiocyanate was fresh, but became large as the ammonium thiocyanate solution aged. It was found that if sodium thiosulfate were used to reduce the iron interference the ammonium thiocyanate solutions could be used for a week as opposed to about a day when reduced with stannous chloride. The use of amber bottles did not decrease the aging effect of the ammonium thiocyanate.

Although very good results could be obtained under ordinary conditions, the above method failed in extreme cases where large amounts of fluoride and fluosilicate were present with uranium. The conventional ether extraction of the uranium from an aluminum nitrate salted solution failed to give systems free from fluosilicate. This substance caused low results when present at a concentration of about 10^{-4} molar range in the final solution (see Figure 5).

Thus, for the purpose of obtaining a medium which would eliminate the anion interferences and yet retain the original sensitivity and freedom from cation interference, the authors turned to a system of lower dielectric constant in which the anions would be in a non-ionic form. In such a system only the stronger acids would remain fully ionised, thus minimizing anion interferences. Thiocyanic acid falls into the class of

very strong acids^(7,8) and the concentration of the thiocyanate ion would not be expected to decrease appreciably. Also, the use of a partially non-aqueous media might be expected to increase the stability of the uranyl-thiocyanate complexes. The former effect would effectively remove from solution many negative ions which compete for the coordination positions around the uranyl ion, but the latter might be expected to increase other cationic interferences.

The use of an acetone water media did, in fact, lead to a marked decrease in anion interferences and an increased absorbance index at lower thiocyanate concentrations. The use of acetone in a somewhat similar manner has been reported for cobalt^(9,10) and iron⁽¹¹⁾ thiocyanate.

Reagents

Ammonium thiocyanate, reagent grade, Baker and Adamson.

Acetone, reagent grade, Baker and Adamson. Saturated with ammonium thiocyanate at room temperature (3.25 - 3.50 M).

Stannous chloride, reagent grade, Baker and Adamson. Ten grams dissolved in ten milliliters concentrated hydrochloric acid, diluted to one-hundred milliliters and filtered through Whatman 42 paper.

Standard solutions were prepared from U. S. Bureau of Standards U_3O_8 , MS-ST.

Concentrated sulfuric acid, reagent grade, Baker and Adamson.

V-197-3

Apparatus

The Beckman Model DU Spectrophotometer was used for the uranyl ion analysis. Absorption spectra were obtained with the Cary recording spectrophotometer, Model 12, with the tungsten light source. The observed deviations of the absorbancy on the two instruments using identical solutions was ± 0.002 . Quartz cells were used throughout this work.

Procedure

A convenient sample size was selected to give a final uranyl ion concentration of $1.5 \times 10^{-4} \text{ M}$ (0.9 milligrams U/25 milliliters). This concentration will give an absorbance of about 0.60 in one centimeter cells.

Samples were pipetted into a small flask and one milliliter concentrated hydrochloric acid and one-half milliliter of concentrated sulfuric acid added. The sample was heated on a sand bath to the appearance of dense white fumes of sulfur trioxide, cooled and diluted with a few milliliters of water and transferred to a twenty-five milliliter volumetric flask. No pH adjustment was necessary. Twenty drops (approximately 1.0 milliliters) of 10 per cent stannous chloride was added, followed by fifteen milliliters of acetone saturated with ammonium thiocyanate (3.25 - 3.50 M). The solutions were well mixed after each addition. The final solution was diluted to twenty-five milliliters with distilled water.

Precipitates tended to form on addition of the acetone, but in all cases they redissolved on addition of water with the development of the correct color. Precipitation, however, can be avoided by bringing the volume of aqueous solution close to 10 milliliters before the addition of the acetone solution.

Ether extractions were made on solutions containing high concentrations of interfering ions. The solution was adjusted to 1.8 M aluminum nitrate and 0.75 M nitric acid. Three extractions were made using 2/1 ether-aqueous volume ratios. In the solutions containing large amounts of fluoride (5-15 M) an additional amount of aluminum nitrate was added to complex the fluoride. Sulfate ion interfered with this extraction. The final ether solutions were collected and evaporated over water. Mixed hydrochloric-sulfuric acid was added and the nitric acid removed by fuming. The final sulfuric acid solution was then handled as directed above.

The absorbancy was read with a Beckman model DU at 375 mμ. A blank was prepared with 0.5 milliliter concentrated sulfuric acid, twenty drops 10 per cent stannous chloride, and fifteen milliliters acetone-thiocyanate solution diluted to twenty five milliliters.

Standard curves, absorbancy vs uranyl concentration, were plotted using uranyl standards prepared from the MS-ST gravimetric standard. Beer's Law was obeyed in all cases within the limit of error of observation (see Figure 1). Concentration of the thiocyanate solution by evaporation of acetone must be avoided and new thiocyanate solutions were restandardized.

V-197-5

Cationic Interferences

Table I summarizes the cationic interferences tested. The absorption data in the thiocyanate-acetone medium used in this work are not well known and, therefore, scans of other ions are shown in Figures 2 and 3. It is evident that in some cases greater freedom from interference may be obtained by shifting the wavelength used. Zirconium was the only element tested which caused large deviations from Beer's Law, the interference depending somewhat on the previous treatment of the added zirconium. Cationic interferences were tested using the standard procedure excluding ether extractions.

Many of the cation-thiocyanate complexes fluoresce when irradiated with light of wavelength 350 m μ or less, and can cause negative error if the lower wavelengths are used. Figure 4 shows this fluorescence with a pure uranyl ion solution. When the solution was closest to the phototube the maximum amount of fluorescent light was received, decreasing the absorbancy and giving the false peaks shown in Figure 4. Appreciable fluorescence of solutions has not been observed when working at wavelengths 350 m μ or greater. Aged thiocyanate solutions showed increased fluorescence.

Anionic Interferences

Table II summarizes the anionic interferences tested. These tests were made using the standard procedure, excluding ether extraction. The lack of appreciable anionic interference is the result of the media adopted, the acetone decreasing the strength of all the acids markedly. Also, the acetone media increases the stability constants of the uranyl-thiocyanate complexes.

7-197-6

Sulfuric acid was selected for use in the standard procedure since it affords a simple way to bring a wide variety of solutions to a reproducible state by fuming. However, if the sulfuric acid concentration exceeds 1.2 N in the final twenty-five milliliter volume, two phases will appear. The interference of the fluosilicate ion was the most difficult to prevent in an aqueous media since it combines the properties of a strong complexing agent for uranyl ion as well as a relatively strong acid. Also, no appreciable separation of fluosilicate and uranyl ion can be made by ether extraction. Figure 5 compares the interference of fluosilicate in the aqueous and acetone media.

Precision and Accuracy of Method

Over a hundred analyses for uranyl ion have been made in this laboratory on a wide variety of solutions ranging from 10^{-2} to 5×10^{-5} molar in uranium. In routine work with the Beckman model B instrument the standard deviation in precision was ± 0.75 per cent and deviations from calculated values based on the MS-ST standard indicated that the standard deviations in accuracy were the same magnitude. The Beckman model DU with more manipulative care than ordinarily employed in routine work gave standard deviations in precision and accuracy of ± 0.5 per cent. These data were obtained by three different operators on about twenty samples. These data are shown in Table III.

v-197-7

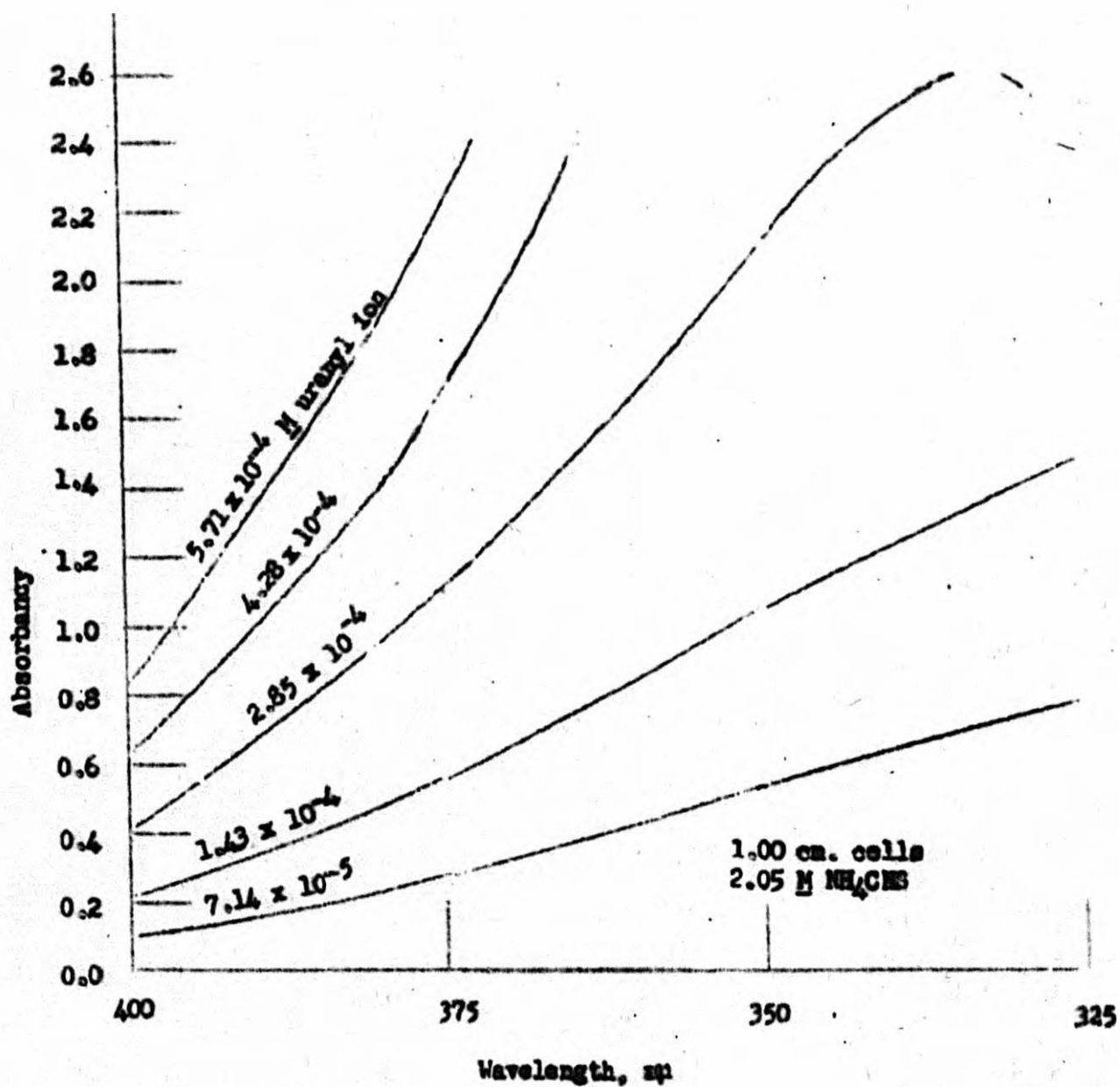


Figure 1

ABSORBANCY OF STANDARD URANYL ION SOLUTIONS DEVELOPED ACCORDING
TO THE STANDARD THIOCYANATE-ACETONE PROCEDURE

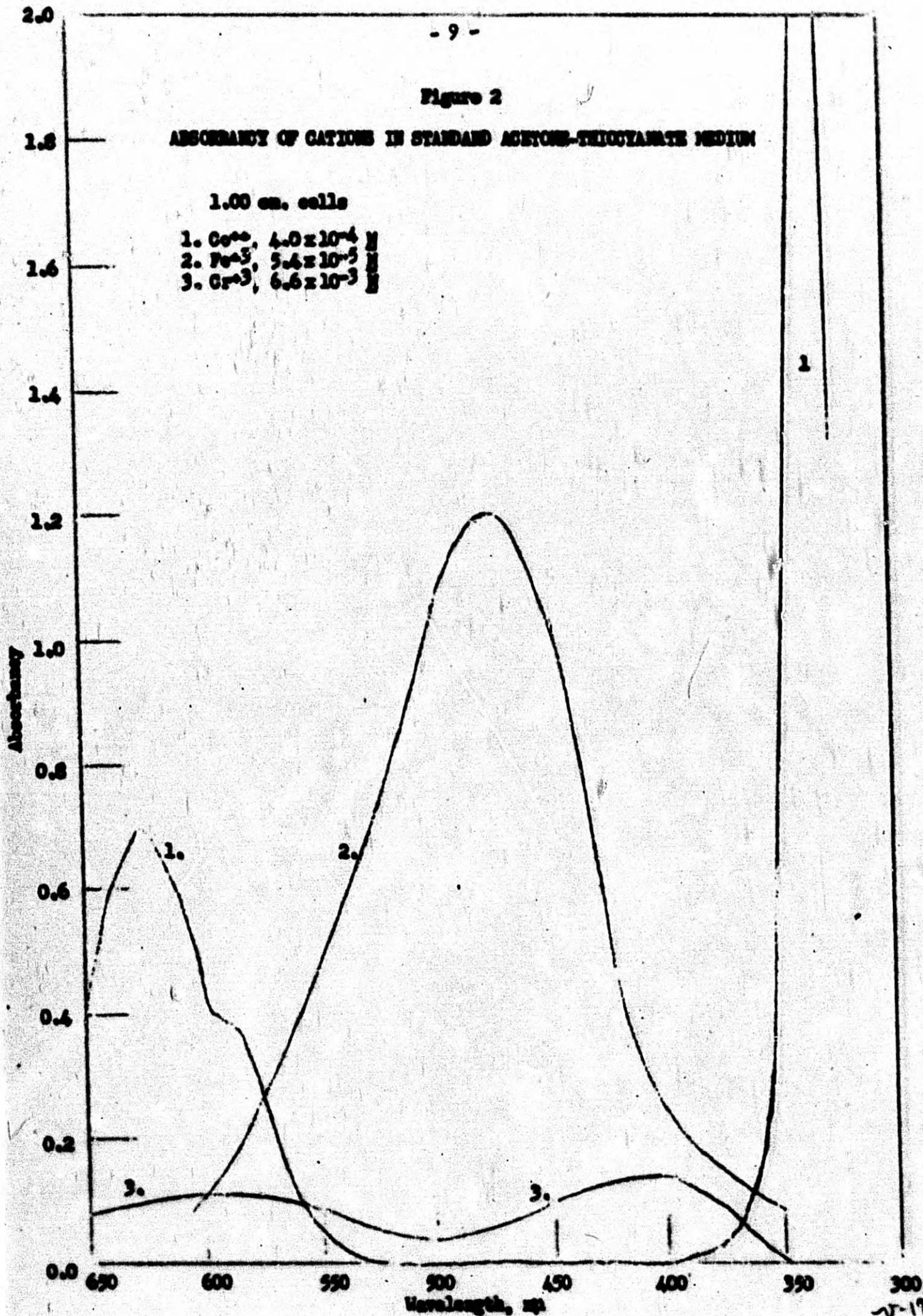
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Figure 2

ABSORBANCY OF CATIONS IN STANDARD ACETONE-THIOCYANATE MEDIUM

1.00 cm. cells

- 1. Co^{2+} , 4.0×10^{-4} M
- 2. Fe^{3+} , 5.4×10^{-5} M
- 3. Cr^{3+} , 6.6×10^{-3} M



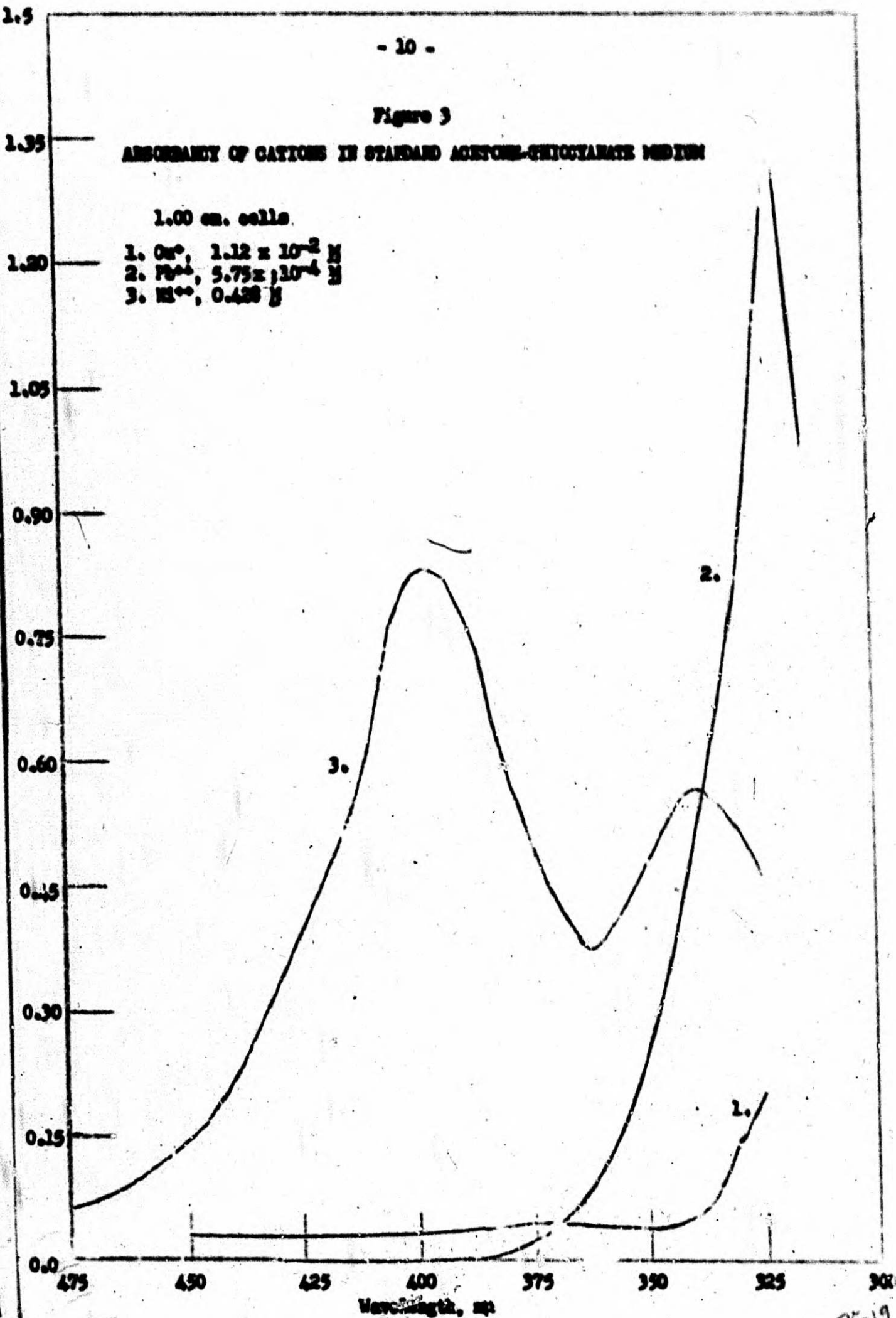
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Figure 3

ABSORBANCY OF CATIONS IN STANDARD ACETONE-THIOCYANATE MEDIUM

1.00 cm. cells

- 1. Cu^{2+} , $1.12 \times 10^{-2} \text{ M}$
- 2. Pb^{2+} , $5.75 \times 10^{-4} \text{ M}$
- 3. Ni^{2+} , 0.428 M



7-19

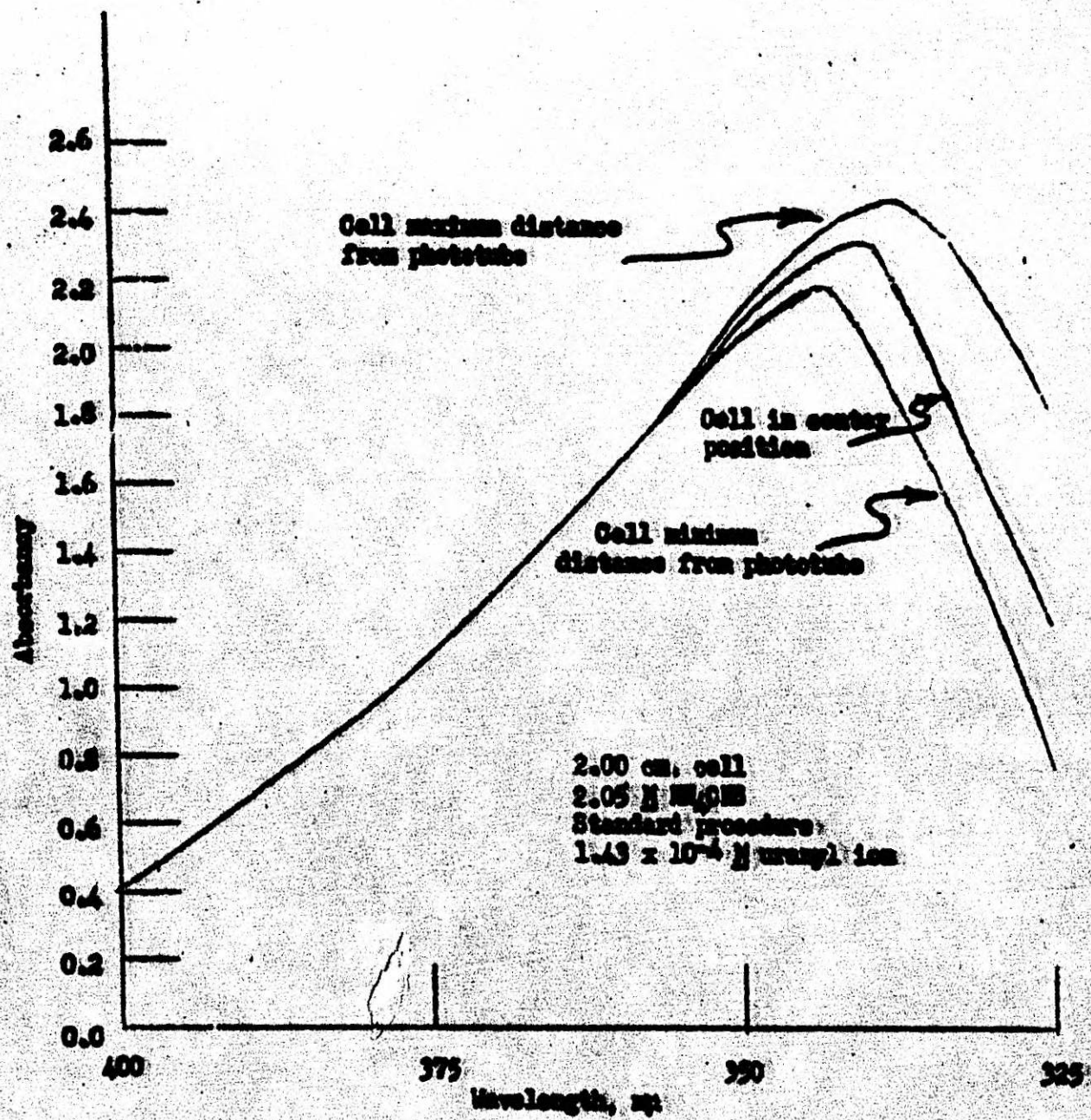


Figure 4

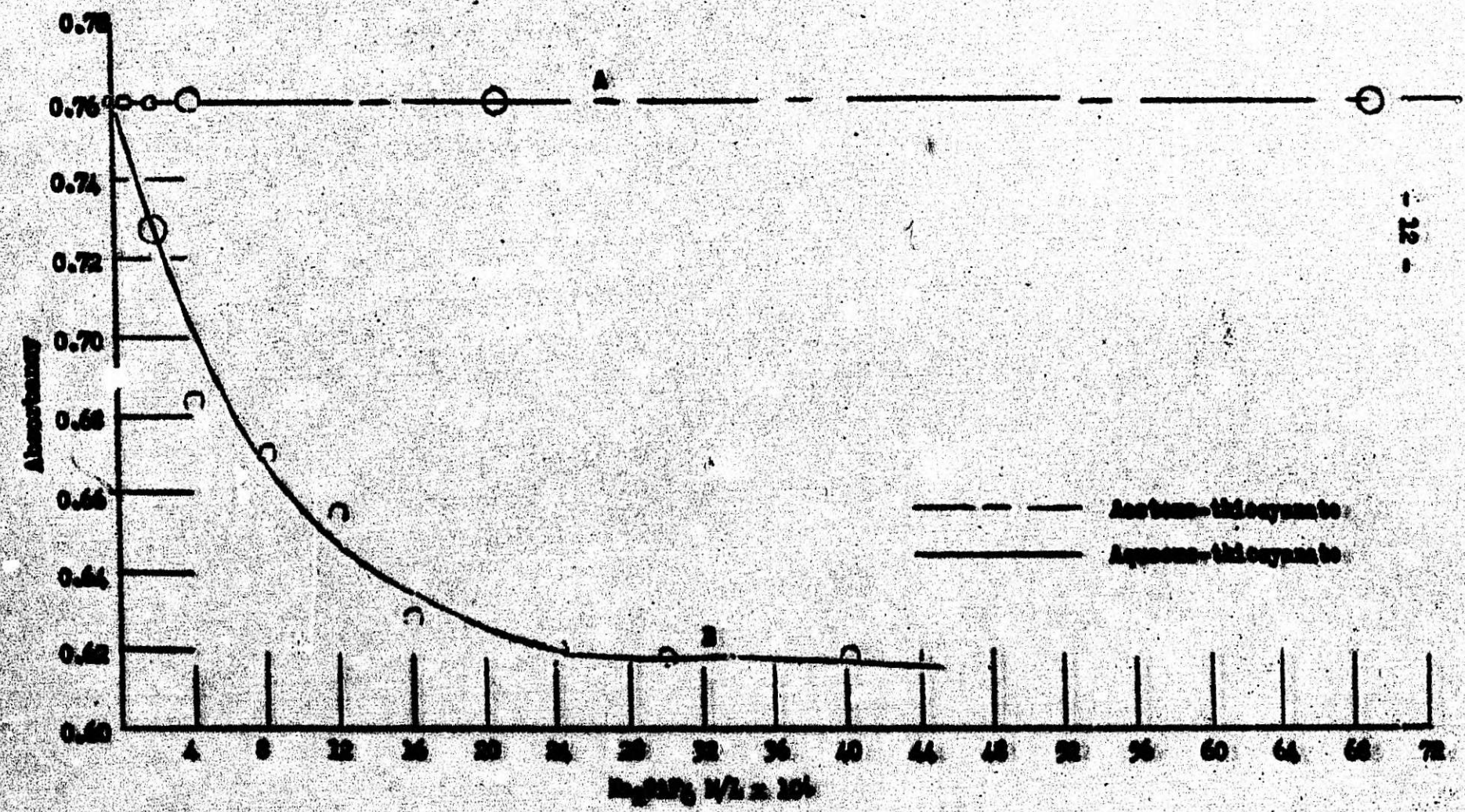
FLUORESCENCE OF URANIL THIOCYANATE COMPLEX

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Figure 5

INTERFERENCE OF FLUOSILICATE ON URANIL THIOCYANATE COLORIMETRIC PROCEDURES

A - 2.30 M H_2SiO_3
B - 3.30 M H_2SiO_3



5-197-12

Table I

CATIONIC INTERFERENCES AT 375 mμ, 1.00 cm. CELLS

Analytical procedure carried out as outlined in text.

Cation Added	Cation/uranyl ratio giving no error*	Cation/uranyl ratio giving ±1% error**	Remarks
Hg ⁺² ***	>10	-	Precipitates formed on addition of SnCl ₂ and redissolved on shaking or upon addition of thiocyanate solution.
Fe ⁺³ ***	0.5	2.0	More iron can be removed by using more than 1 ml. of 10% SnCl ₂ as called for in the standard procedure.
Ni ⁺²	2.0	10	
Cr ⁺³	2.0	8.0	
Mn ⁺	>10	-	
Cu ⁺² ***	5.0	20	
Zr	50	200	These errors apply to Zr sulfate complex. With Zr fluoride complex erratic results and somewhat more interference was obtained.
Al	250	1000	
Pb ⁺²	0.50	2.0	
Co ⁺²	0.50	2.0	
Sb ⁺⁴	>10	-	

* Limit of detection was 10.002 absorbancy unit.
 ** Determined at unit absorbance for uranyl ion ($\approx 2.5 \times 10^{-4}$ M).
 *** In following the standard procedure these ions are reduced by SnCl₂.

2-197-13

Table II
ANIONIC INTERFERENCES AT 375 mμ, 1.00 cm. CELLS

Anion added	Anion/uranyl ratio giving no error ^a	Anion/uranyl ratio giving 1% error	Remarks
NH_4NO_3	5000	-	The various oxides of nitrogen, N_2O_3 , NO_2 , N_2O_4 , etc., were not tested and will probably interfere.
H_2SO_4	5000	-	Large amounts of sulfuric acid, $>1.23 \text{ N}$, cause the acetone aqueous system to separate into two phases.
NaCl	1000	-	
K_2HPO_4	100	200	Precipitates formed on standing at higher concentrations. Negative error.
NaOAc	1500	-	Higher concentrations of NaOAc caused the formation of a white precipitate with SnCl_2 in the acetone medium.
Citric Acid	1000	2000	Positive error due to absorption of citric acid at 375 mμ.
NaF	25	-	Higher concentrations were not tested because of increased danger of etching of the cells.
NaI	1000	-	No mixed $\text{CNS} - \text{I}^-$ complexes were observed.
KMnO_4	10	-	Same as Mn^{++} (see Table I).
$\text{K}_2\text{Cr}_2\text{O}_7$	1.0	4.0	Same as Cr^{+++} (see Table I).
Na_2SiF_6	70	-	See Figure 5 for comparison of interference in aqueous solution.

^a Limit of detection was ± 0.002 absorbancy unit.

75-197-14

TABLE III

TESTS ON THE PRECISION AND ACCURACY OF THE METHOD
ON THE BECKMAN MODEL DU SPECTROPHOTOMETER

<u>SOLUTION NO.</u>	<u>OBSERVED MOLE/L URANIUM</u>	<u>CALCULATED MOLE/L URANIUM</u>	<u>STANDARD DEVIATION PER CENT</u>	<u>COMPOSITION OF SOLUTIONS</u>
1	7.47×10^{-3}	7.52×10^{-3}	-0.65	Solutions 1 - 5 contained uranium with chromium 10/1 and fluoride 1000/1. The solutions were extracted before analysis. Standard deviation = 0.40%.
2	7.52×10^{-3}	7.52×10^{-3}	+0.00	
3	7.49×10^{-3}	7.52×10^{-3}	-0.40	
4	7.48×10^{-3}	7.52×10^{-3}	-0.55	
5	7.54×10^{-3}	7.52×10^{-3}	+0.30	
6	1.423×10^{-4}	1.428×10^{-4}	-0.35	MS-ST Gravimetric standard pure uranyl perchlorate solutions analysed with no ether extraction. Standard deviation - 0.35%.
7	1.428×10^{-4}	1.428×10^{-4}	0.00	
8	1.432×10^{-4}	1.428×10^{-4}	+0.30	
9	1.421×10^{-4}	1.428×10^{-4}	-0.50	
10	1.430×10^{-4}	1.428×10^{-4}	+0.14	MS-ST Gravimetric standard solutions analysed with no ether separation. 1000/1 fluoride, 10/1 fluosilicate, 2/1 chromium, 2/1 copper. Standard deviation 0.35%.
11	1.435×10^{-4}	1.428×10^{-4}	+0.50	
12	1.425×10^{-4}	1.428×10^{-4}	-0.20	
13	1.422×10^{-4}	1.4×10^{-4}	-0.42	
14	1.433×10^{-4}	1.428×10^{-4}	+0.35	
15	1.436×10^{-4}	1.428×10^{-4}	+0.60	

V-197-15

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