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ABSORPTION SPECTRA IN FUSED SALTS

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ABSORPTION SPECTRA IN FUSED SALTS

BY

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B. S., University of Massachusetts, 1953

M. S., University of Massachusetts, 1955

A THESIS

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Graduate School

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This thesis has been examined and approved.

Alexander R. Cornell

Date

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This work was carried out in the laboratories of Charles James Hall under Dr. Helmut M. Haendler. I wish to acknowledge his help during this time. I also wish to acknowledge The Atomic Energy Commission which supported the entire investigation.

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INTRODUCTION

In the liquid metal fuel reactor the breeder blanket is a suspension of thorium bismuthide in bismuth. Breeding ratio can be a maximum only if neutron losses to the fission products are kept at a low level. It has been shown (1) that fission products may be extracted with a fused eutectic of magnesium chloride, sodium chloride and potassium chloride. The detection and assay of the fission products in the extract presents a problem. In attacking such problems, absorption spectroscopy is a well known and flexible tool. Ultraviolet and visible spectra are of great aid in obtaining such data. The literature on analytical applications of absorption spectroscopy in fused media is nil.

The spectral work for structural information in these media is more extensive. Quantitative spectra are reported for nickel(II)chloride in lithium chloride/potassium chloride mixtures (2); pure lithium chloride, pure cesium chloride, cesium tetrachlorozincate (II) and pyridinium hydrochloride (3); manganese (II) and manganese (VI) oxysalts in sodium hydroxide and potassium hydroxide melts (4); uranium (III) chloride, uranium (IV) chloride, dioxouranium (VI) chloride in a lithium chloride/potassium chloride eutectic (5); qualitative spectra have been investigated for a number of transition metal chlorides in a lithium nitrate/potassium nitrate eutectic (6); pure molten salts (7); and metal halides dissolved in a lithium chloride/potassium chloride mixture (8). The melts in which metal chlorides are dissolved are assumed to be composed of various metal complex ions. The pure salt spectra are interpreted in terms of charge-transfer spectra.

The work to be described herein is two-fold in purpose. The quantitative absorption spectra of eight anhydrous metal chlorides were observed in the ultra-violet and visible spectral region to obtain analytical as well as structural information. The structural study attempts to determine the species responsible for the spectral bands observed. The anhydrous metalchlorides observed in the fused magnesium chloride, potassium chloride, sodium chloride eutectic at 430°C are those of copper (II), cobalt (II), manganese (II), nickel(II), iron (III), uranium (III), uranium (IV) and dioxouranium (VI).

EXPERIMENTAL

Preparation of Chemicals. Copper (II) chloride dihydrate (reagent grade) cobalt (II) chloride hexahydrate, c.p., and nickel (II) chloride hexahydrate, c.p., were dehydrated at 185°C for twenty-four hours to prepare the corresponding anhydrous salts. These were stored in glass-stoppered bottles at 150°C in an oven. Anhydrous sublimed iron (III) chloride was of reagent grade. Manganese (II) chloride was prepared by the passage of dry hydrogen chloride gas over manganese (II) carbonate, reagent grade, at 300°C. Uranium (III), uranium (IV) and dioxouranium (VI) chlorides were prepared according to Inorganic Syntheses (8) as was chromium (III) chloride (9). Cesium tetrachlorocuprate (II) was prepared by allowing a solution of copper (II) chloride and cesium chloride in a 1:2 mole ratio respectively to evaporate to dryness (10). The manganese, chromium, uranium and complex copper salts were stored in waxed, screw-cap bottles in a desiccator. A sample of uranium (III) chloride was also supplied by Brookhaven National Laboratory. This was a product of The Rocky Mountain Chemical Co. The chlorides were analyzed for metal content only and found to be satisfactory. The analyses are shown in Table I.

TABLE I

ANALYSIS OF ANHYDROUS METAL CHLORIDES

Metal Chloride	Method	Results	
$CuCl_2$	Volumetric with Sodium thiosulfate(12)	calc found	47.26%Cu 47.57 47.59
$CoCl_2$	Gravimetric as pyrophosphate(13)	calc found	45.39%Co 45.52 45.31
$NiCl_2$	Gravimetric as dimethylgloximate(13)	calc found	45.28%Ni 44.96 45.06
$MnCl_2$	Gravimetric as pyrophosphate(13)	calc found	43.65%Mn 42.74 42.62
$FeCl_3$	Volumetric with potassium dichromate(13)	calc found	34.43%Fe 34.56 34.26
UCl_3	Volumetric with potassium dichromate(13)	calc found	69.08%U 67.75 69.50 68.80
UCl_4	Volumetric with potassium dichromate(13)	calc found	62.76%U 62.22 62.40 62.36
UO_2Cl_2	Volumetric with potassium dichromate(13)	calc found	67.79%U 67.14 66.87 67.36

The eutectic mixture was supplied by Brookhaven National Laboratory, Upton, Long Island, New York. The nominal composition of eutectic was 58% magnesium chloride, 24% sodium chloride and 18% potassium chloride by weight. This mixture melts at 398°C. The eutectic was received in lump form, broken into small portions, put in screwcap bottles and stored in a desiccator. It was always handled in a dry box.

When melted it was clear, remaining so as long as no hydrolysis occurred. In some fused samples there were small black particles which floated on the surface of the melt. They did not seem, however, to interfere with the spectrum. It was found advantageous to place the cell and melt briefly into the Meker burner flame before observing the spectrum as this resulted in a clear solution more quickly, and this solution did not seem to hydrolyze as readily.

Furnace. A copper rod was cut and reassembled to leave a hole to accept a 1 cm. path square cell (Fig 1). The block was 10 cm. high x 5 cm. in diameter and was nickel plated to retard oxidation. A ceramic tube was cut to fit around the block and wound with No. 18 Kanthal wire. It was insulated with No. 1500 Sauereisen cement, a vermiculite type. The furnace can operate to 730°C. In this work the temperature was held at 430 ± 3°C. A temperature fluctuation of this magnitude was found to have a negligible effect on absorbance measurements. Temperatures were controlled and recorded with a Leeds and Northrup Micromax Recorder using iron-constantan thermocouples. The furnace was mounted in a fixed position as close to the entrance slit as possible so as to admit the maximum amount of light. A metal clip held the cell in a fixed, reproducible position.

Spectrometer. A Perkin-Elmer Model 12-C Spectrometer was used for all absorbance measurements. The set-up used in the appropriate spectral region is shown in Table II.

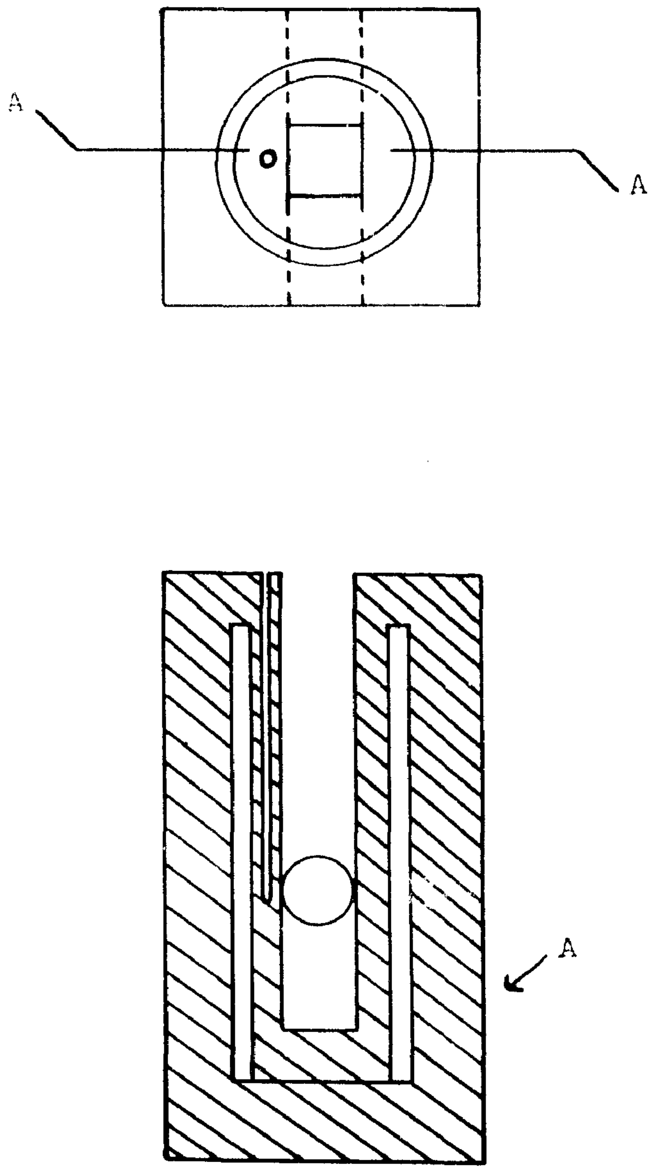


Figure I

Furnace

TABLE II

EXPERIMENTAL CONDITIONS FOR SPECTRAL REGIONS

	Ultra-violet	Visible
Range	230-400 m	400-650 m
Optics	quartz	glass
Cell	quartz	quartz
Detector	1P-28	1P-21
Source	H_2 lamp	Tungsten lamp
Source Operation	Beckman DU Power Supply	Variac
Calibration	H_2 lamp, Hg lamp, benzene vapor	Hg lamp, He lamp, H_2 lamp
Littrow Setting	Hg green 1142 drum	Hg green 495 drum

The chopped beam and tuned amplifier makes correction for the radiant energy of the furnace and sample possible. This is a single beam instrument necessitating the separate observance of solvent and solution spectra.

Density. Absorptivity values are given as 1./mole-cm. Therefore it is necessary to know the density of the eutectic. A standard Westphal balance was modified to permit direct determination of the density of molten eutectic or solutions. A nickel plummet was used as a bob. A set of copper wire weights was constructed to accompany the bob in order to make the balance direct reading.

The density of the eutectic was found to be 2.05g/cc. at 420°C. This is ten degrees below the temperature at which the spectra were observed. The data of Van Artsdalen (14) show that a 19°C change in temperature causes only a 0.010g/cc. change in density. The eutectic turns a violet color like that of pure nickel (II) chloride dissolved in the eutectic, due no doubt to attack on the bob by the eutectic. The resultant change of density of the eutectic is slight.

Optical Cells. These were supplied by the Pyrocell Mfg. Co., New York 28, New York (Fig. II). The cell is square with a 1 cm. path length and the optical section is 4 cm. high. A side arm is provided to allow passage of argon over the melt. The argon is passed over anhydrous magnesium perchlorate, Linde "Molecular Sieves", and phosphorous pentoxide in that order. The flow rate of argon is kept at about 80 cc./min. with a rotameter of 10-90cc./min. capacity as indicator. A cell cap reduces atmospheric contamination. This cap has an elongated neck through which a pyrex rod is placed and used as a stirrer. The transmittance of the cell increases from 60 to 80% in going from 230 to 280 mμ and remains at this level to 650 mμ (Fig. III). After the cells have been in use for some time etching appears at the gas-melt interface which reduces the transmittance, but very slight attack occurs at the optical surfaces. Care in transfer and high quality of solvent minimizes the attack. Immediate removal of the eutectic while molten after a run is imperative to prevent breakage of cells due to solidification of the solutions.

Procedure. Stoppered empty cells were weighed on an analytical balance, eutectic added in the dry box, and the restoppered cells weighed again. For the visible work a

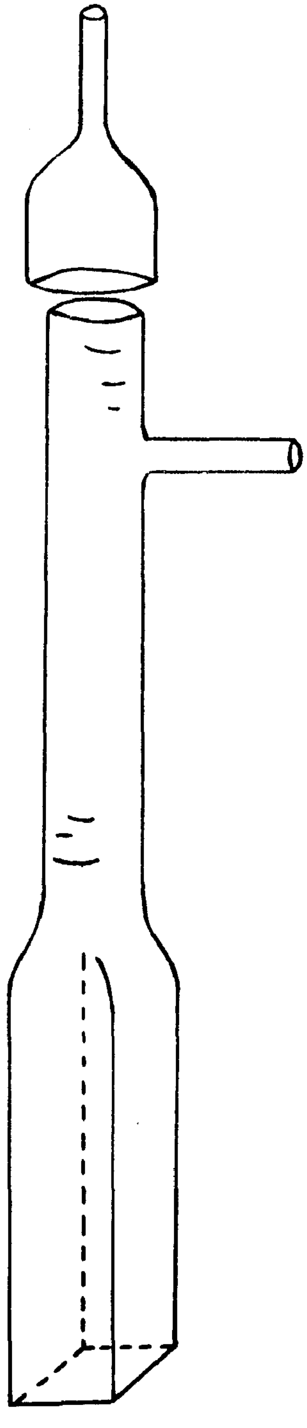
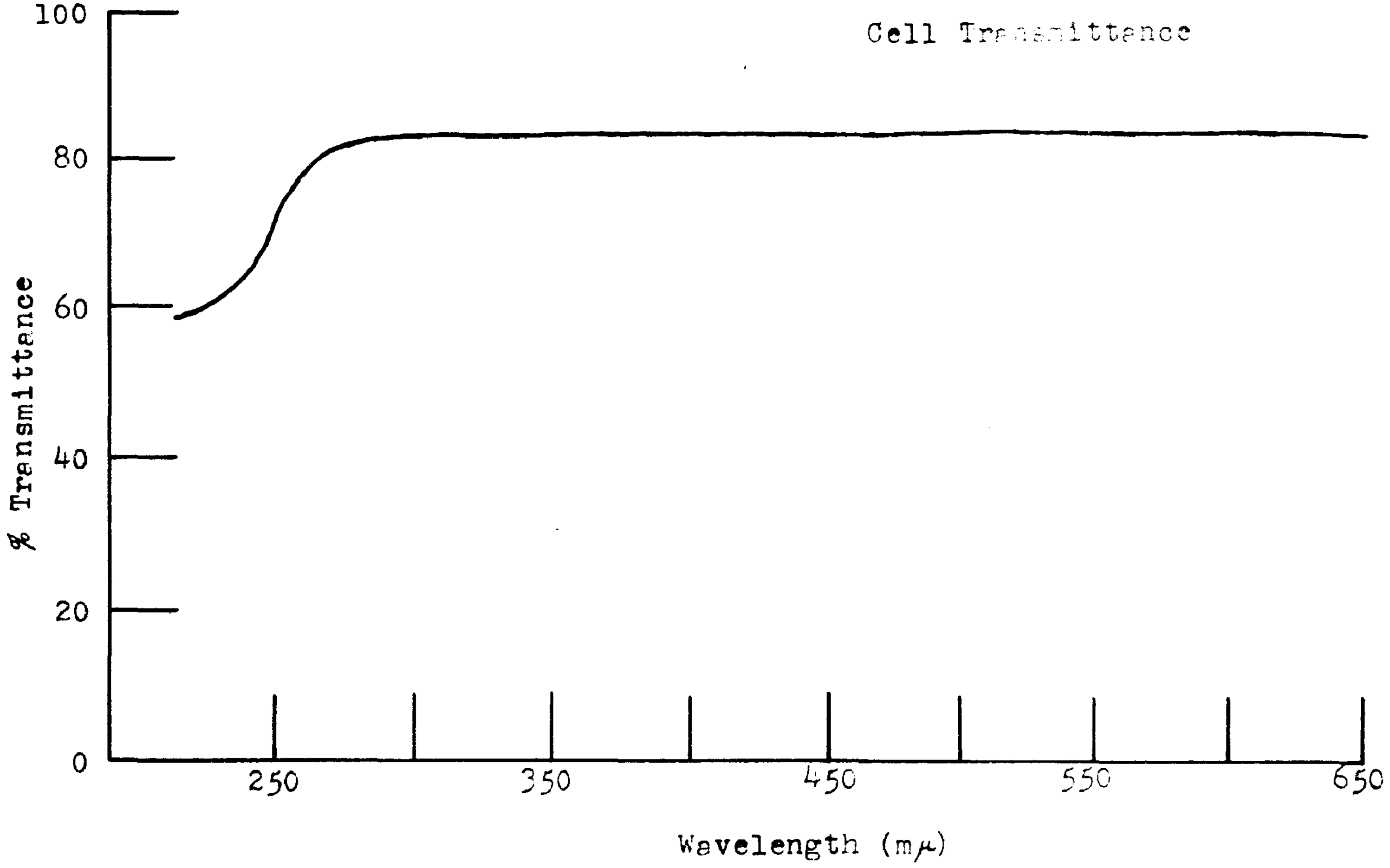


Figure II

Cell

Figure III

Cell Transmittance



Mettler Type H-5 balance was used. Samples of solute were weighed directly on a Berman torsion-type balance located in the dry box. A number of counter-weighted platinum weighing pans were constructed to permit weighing several solute samples at one time. The solute remained suspended in stoppered test tubes in a desiccator until needed for addition to the molten eutectic. The samples were added in air. Atmospheric contamination did not seem to have any effect, the transfer being rapid. All additions of solute were made in two successive increments, permitting consecutive measurements on solutions of different concentrations. Homogeneous solutions were obtained by stirring with a flamed pyrex rod. No vaporization of metal chloride was observed. In some cases a solution of low concentration (10^{-4} molar) of metal chloride was necessary because of the high absorptivity of the solute. These were called "master solutions". Such a solution was needed for copper(II) chloride. One was used for iron(III) chloride but in this case its use was to prevent hydrolysis of the metal salt. Copper(II) chloride solutions were made up by weight while the iron(III) chloride solutions were analyzed after make up. The analysis of these solutions are shown in Table III.

TABLE III

ANALYSIS OF MASTER SOLUTIONS

Metal Chloride	Method	Results
$FeCl_3$	Spectrophotometric as Thiocyanate(15)	found 0.4408g $FeCl_3$/grams-master solution 0.4223g $FeCl_3$/g master solution
$CuCl_2$	Weighing of $CuCl_2$ and Ternary Eutectic	6.35×10^{-3}g $CuCl_2$/g master solution

Determination of Spectra. The capped cell and eutectic are clipped in place and argon is passed through the side arm while the eutectic melts. The cell and melt are held in a Meker flame to insure a clear solvent. The spectrum of the solvent is taken, using narrow slit widths (0.06 - 1.0mm.), the practical lower limit being that obtainable with the maximum gain setting (16) at which concomitant noise could be tolerated. A sample of solute is added directly from a balance pan and the mixture is stirred until uniform. The spectrum is re-run with the same slit and gain conditions as used previously. The same procedure is followed for the second sample. Mixtures of uranium(III) and uranium (IV) chlorides as well as copper(II) and cobalt(II) chlorides were run in the same manner. The absorbances were then used to calculate the concentrations of metal chloride present. The absorbance range used for calculations was 0.1 to 1.0.

The absorption spectrum of the solute is then calculated on a point to point basis using the molten eutectic as a background for each solution. Some calculations on nickel

(II)chloride were made using the first solution as the background but poor agreement between runs was observed. The eutectic itself is highly absorbing (Fig. IV) at 225 mμ but the absorbance drops off quickly towards 300 mμ and remains small to 650 mμ. The concentrations of these solutions being low (10^{-2} - 10^{-3} molar), their density is taken as that of the pure solvent in computing molar absorptivities. When a "master solution" is used the amount of eutectic added in this manner must also be taken into account for most accurate results.

The Beer-Lambert equation was used to calculate absorptivities. It is given below and a sample calculation follows it.

$$\log I_0/I = \epsilon c l$$

where:

I_0 = incident beam

I = transmitted beam

ϵ = absorptivity (l./mole-cm.)

c = concentration (moles/liter)

l = cell path length (cm.)

Uranium(III)chloride at 450 mμ

$I_0/I = 0.275$

$c = 9.31 \times 10^{-4}$ moles/liter

$l = 1$ cm.

$$\frac{I_0/I}{(c)(l)} = 0.275/(9.31 \times 10^{-4})\ (1) = 295 \text{ l./mole-cm.}$$

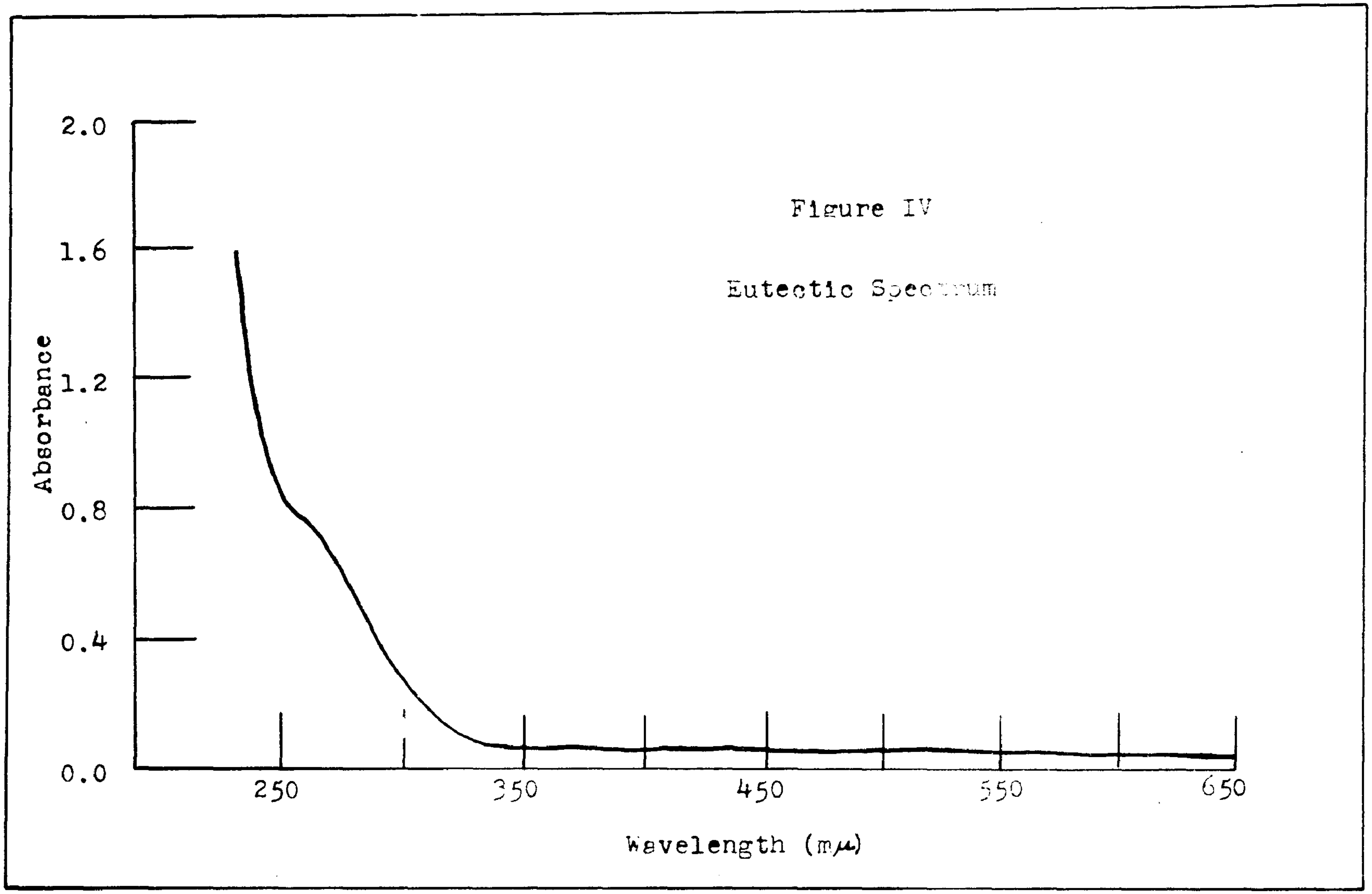


Figure IV

Eutectic Spectrum

RESULTS

The absorption maxima and corresponding absorptivities for the metal chlorides are listed in Table IV. The spectra are shown in Figures V - XII.

TABLE IV

ABSORPTION MAXIMA AND ABSORPTIVITY

Metal Chloride	Wavelength of Maxima, mμ	Molar Absorptivity l./mole-cm.
$CoCl_2$	262, 450, 610	198, 87, 149
$CuCl_2$	254	2770
$FeCl_3$	238, 282, 350	165, 118, 111
$MnCl_2$	233, 248, 272, 440, 480, 612	135, 102, 92, 42, 40, 32
$NiCl_2$	295, 470-490, 550, 610	398, 125, 96, 91
UCl_3	242, 330, 477	1656, 1219, 597
UCl_4	235, 405, 453, 613, 642	349, 166, 154, 112, 109
UO_2Cl_2	250, 450, 453	1804, 531, 550

The results presented are an average of several determinations. The absorptivities for each metal chloride are collected in the appendix.

The precision of absorptivity values vary with the magnitude of the latter as shown in Table V. The precision is computed from the final averaged values.

The colors of the solutions produced upon dissolving the metal chlorides in the molten eutectic are unique. The eutectic is colorless when molten. Some salts give a deeply colored solution in low concentrations while others must be relatively concentrated to produce any visible color.

TABLE V

REPRODUCIBILITY OF MOLAR ABSORPTIVITY

Absorptivity	Precision (Reproducibility)%
0 - 100	15%
100 - 1000	5%
1000 - 2000	3.7%
2000 - 3000	3.5%

TABLE VI

COLORS OF METAL CHLORIDE SOLUTIONS

Metal Chloride	Color	Concentration
$CoCl_2$	blue	(l)
$CuCl_2$	straw yellow	(l)
$FeCl_3$	yellow	(h)
$MnCl_2$	pink	(h)
$NiCl_2$	violet	(l)
UCl_3	red	(m)
UCl_4	green	(h)
UO_2Cl_2	yellow	(m)

The colors are listed in Table VI with low (l), medium (m), and high (h) designating the relative concentration needed for each color.

The sample of uranium(III)chloride supplied by Brookhaven National Laboratory was also run. Its spectrum was quite different from that of the material prepared above, Fig. X. The Brookhaven sample was a dull green color, while that prepared above was a dull violet to black as described in the literature (8). X-ray powder patterns were taken of each but neither gave a suitable result, apparently because of particle size.

Chromium(III)chloride is not as soluble in the eutectic as are the other salts. The insoluble portion floats on the surface of the molten eutectic and can be recovered after the melt has solidified. An approximation of concentration was made in this way. Its spectrum is shown in Fig. XIII; absorptivities are approximate.

The spectra of mixtures of uranium(III) and uranium (IV)chlorides were observed. The absorptivities of the single salts were used to calculate the concentrations of individual salts used. These were then compared with the known amounts. Both visible and ultra-violet were obtained for the uranium mixture while visible only was observed for copper(II) and cobalt(II) chlorides. Simultaneous equations using Beer's Law were set up for calculation purposes.

TABLE VII

MIXTURE CONCENTRATIONS FROM ABSORPTION SPECTRA

UCl_3 and UCl_4	240 mμ	330 mμ
UCl_3 present	4.8×10^{-4} m./l.	5.0×10^{-4} m./l.
found	1.3×10^{-4} m./l.	2.4×10^{-4} m./l.
UCl_4 present	6.8×10^{-4} m./l.	8.3×10^{-4} m./l.
found	1.7×10^{-4} m./l.	2.0×10^{-4} m./l.
	500 mμ	600 mμ
UCl_3 present	1.14×10^{-3} m./l.	1.14×10^{-3} m./l.
found	1.74×10^{-3} m./l.	1.35×10^{-3} m./l.

TABLE VII (Contd.)

	500 m μ	600 m μ
UCl_4 present	8.78×10^{-4} m./l.	8.78×10^{-4} m./l.
found	3.68×10^{-4} m./l.	7.43×10^{-4} m./l.
$CuCl_2$ and $CoCl_2$	650 m μ	630 m μ
$CuCl_2$ present	2.49×10^{-3} m./l.	2.49×10^{-3} m./l.
found	1.00×10^{-2} m./l.	2.55×10^{-3} m./l.
	500 m μ	600 m μ
$CuCl_2$ present	2.49×10^{-3} m./l.	2.49×10^{-3} m./l.
found	5.18×10^{-3} m./l.	5.29×10^{-3} m./l.
	600 m μ	620 m μ
$CoCl_2$ present	2.74×10^{-3} m./l.	2.74×10^{-3} m./l.
found	1.58×10^{-3} m./l.	2.79×10^{-3} m./l.
	600 m μ	470 m μ
$CoCl_2$ present	2.74×10^{-3} m./l.	2.74×10^{-3} m./l.
found	2.07×10^{-3} m./l.	7.7×10^{-4} m./l.

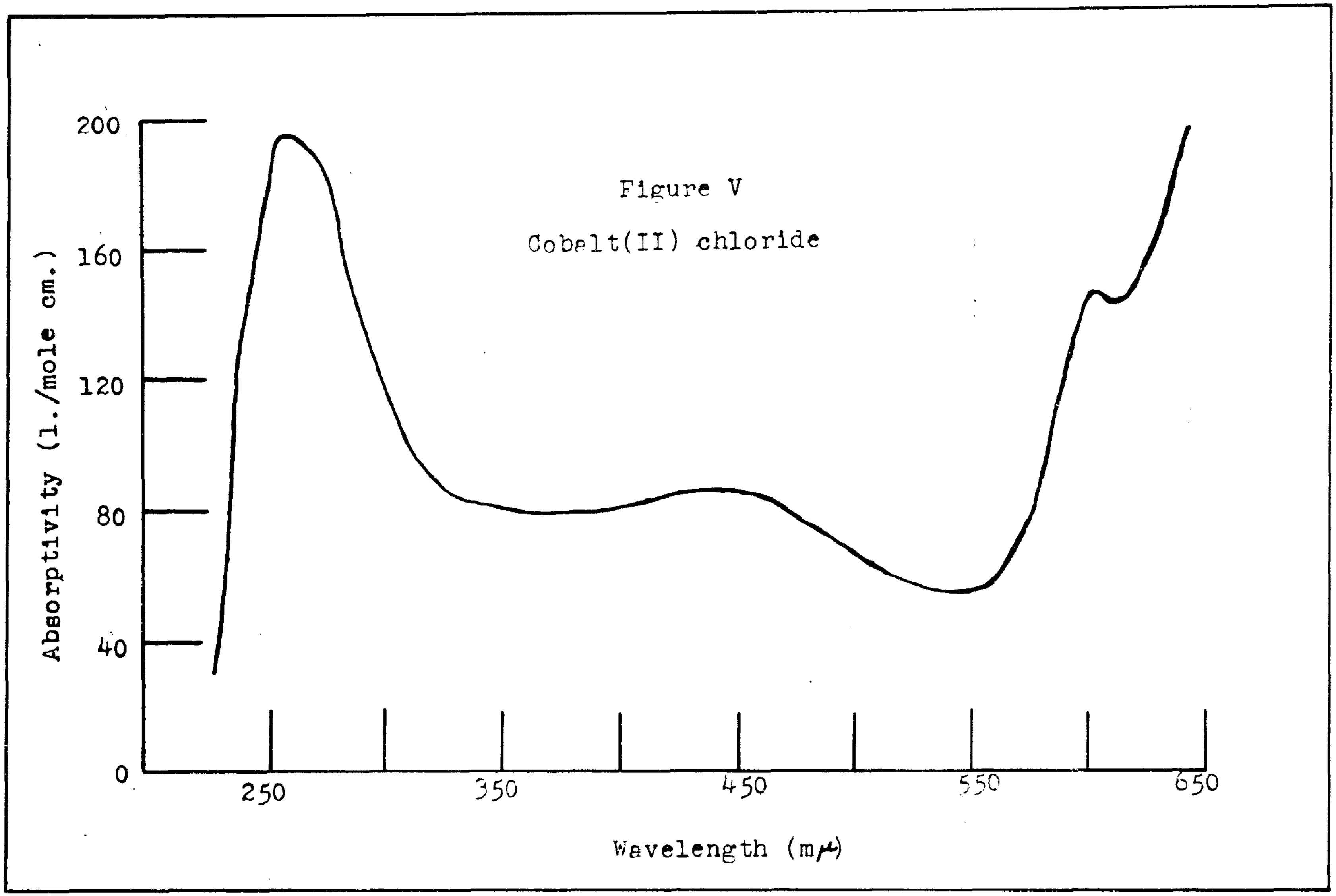


Figure V

Cobalt(II) chloride

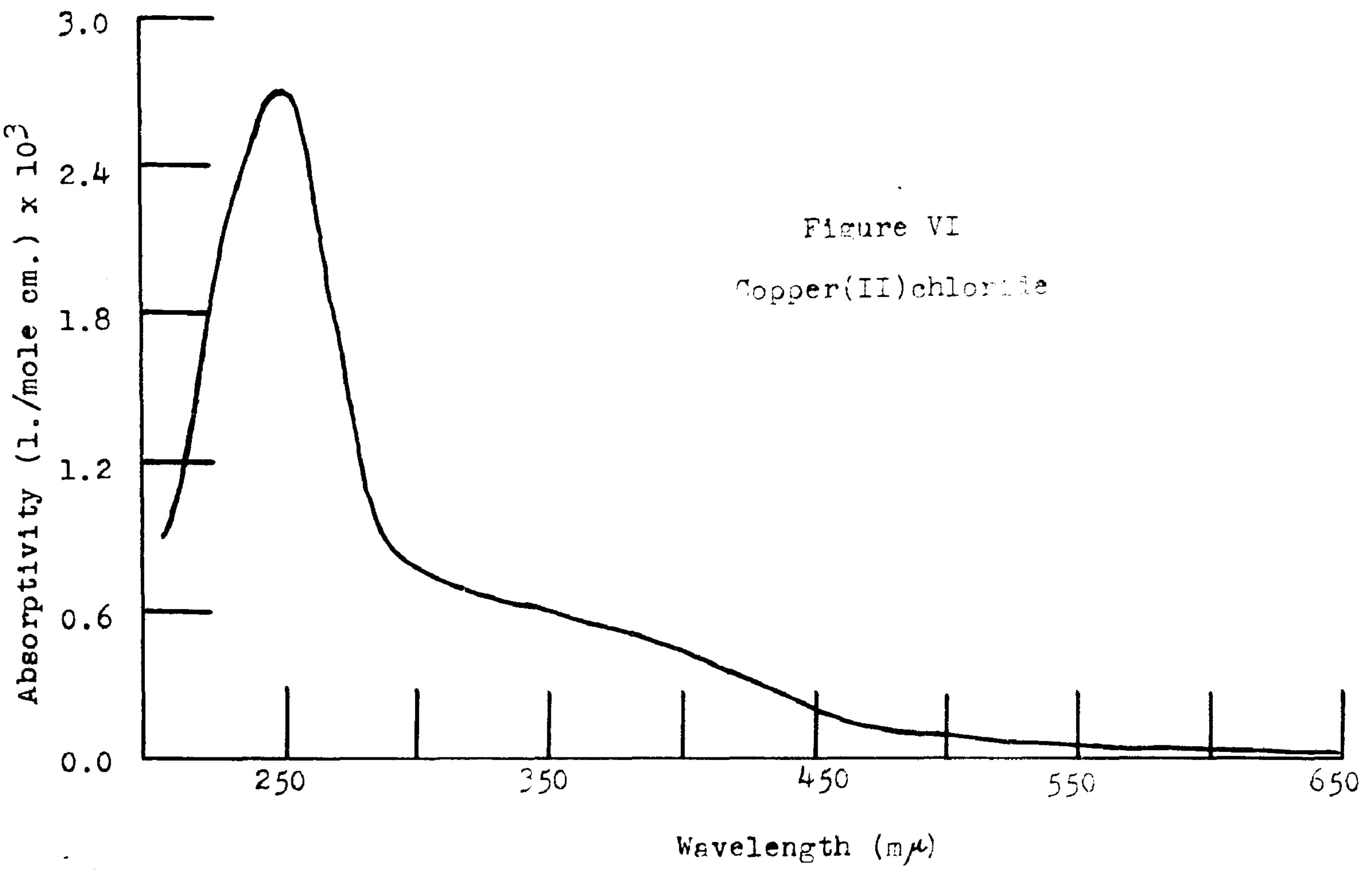


Figure VI

Copper(II)chloride

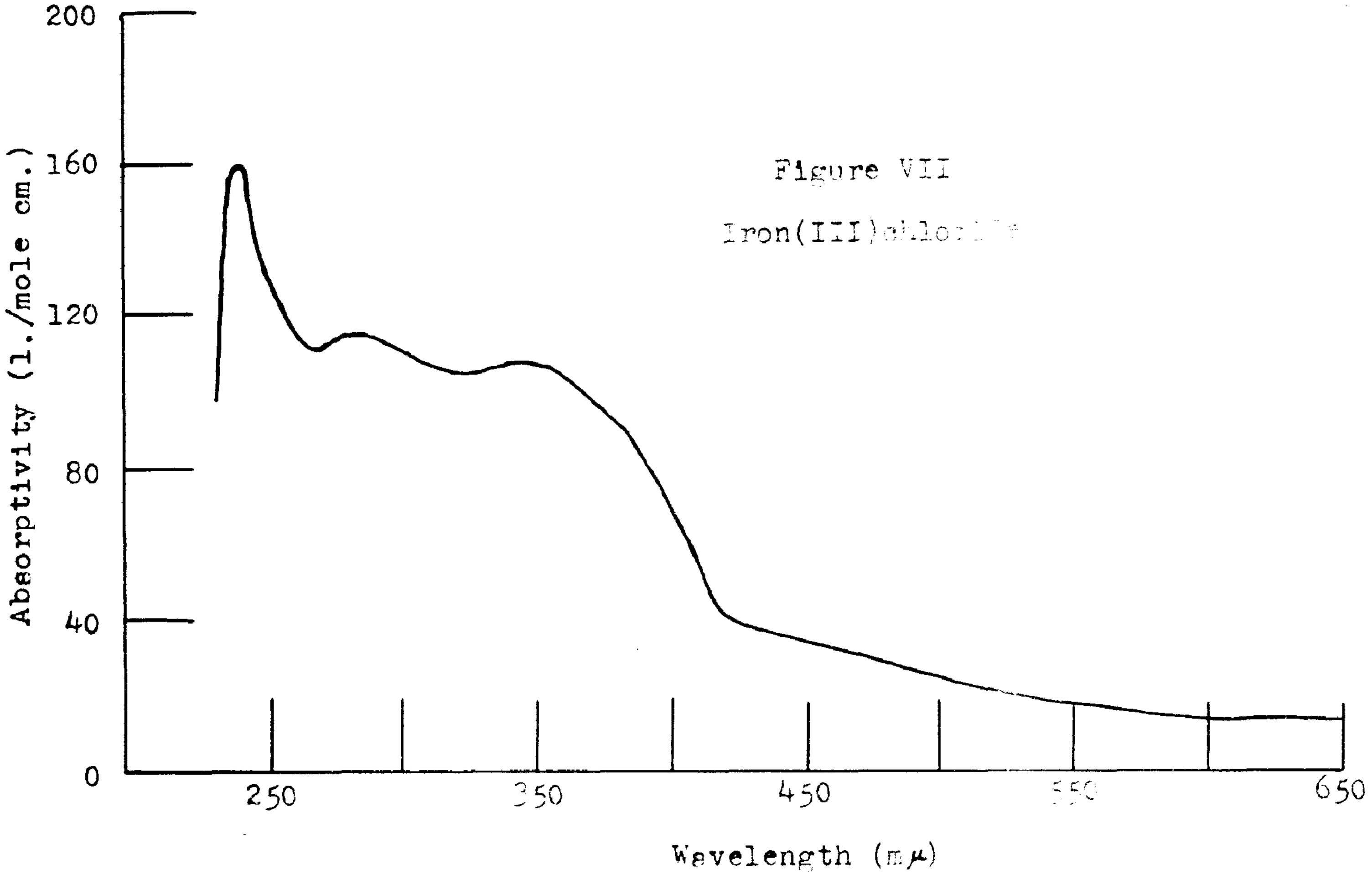


Figure VII

Iron(III)chloride

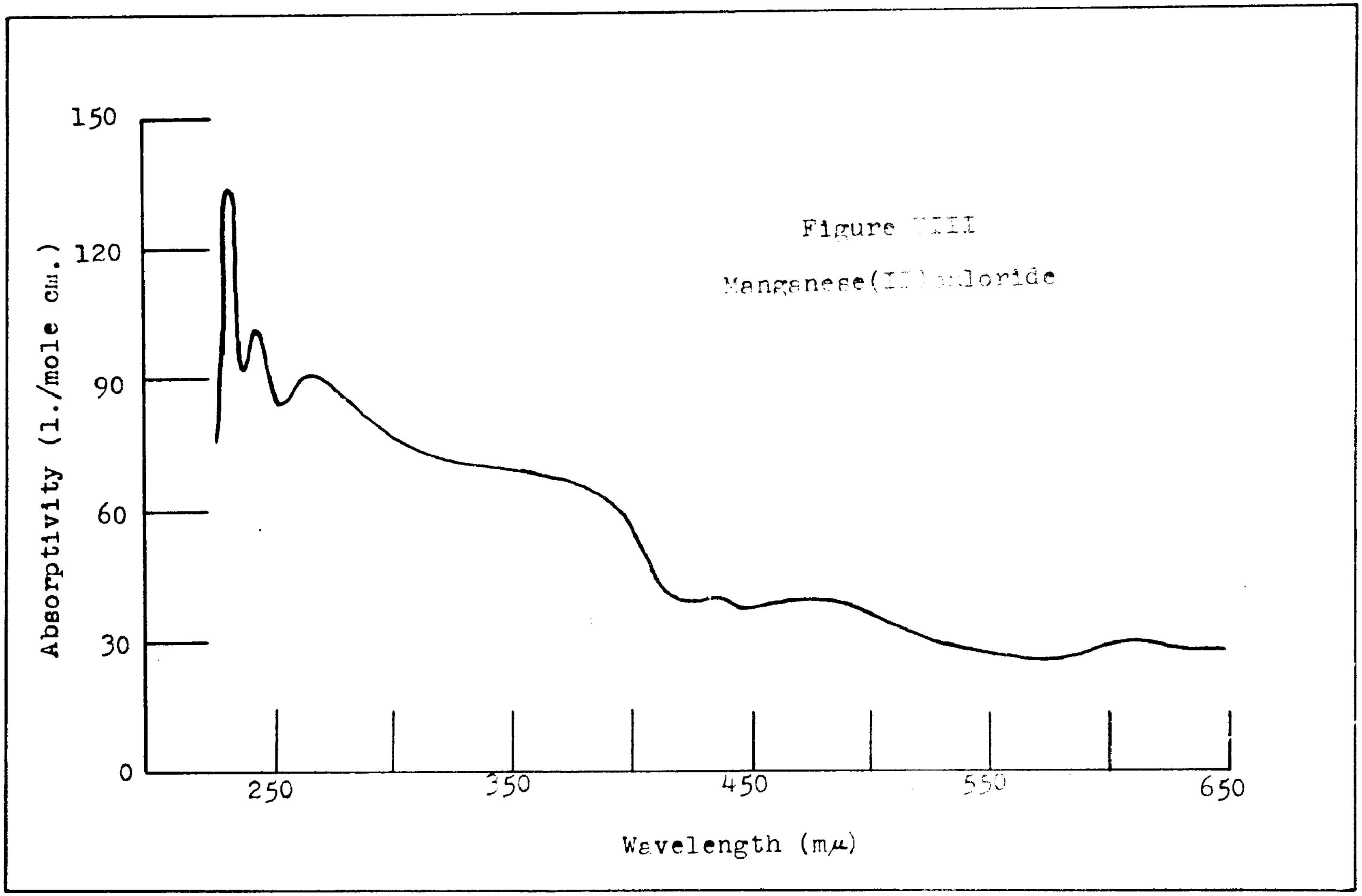


Figure VIII

Manganese(II)chloride

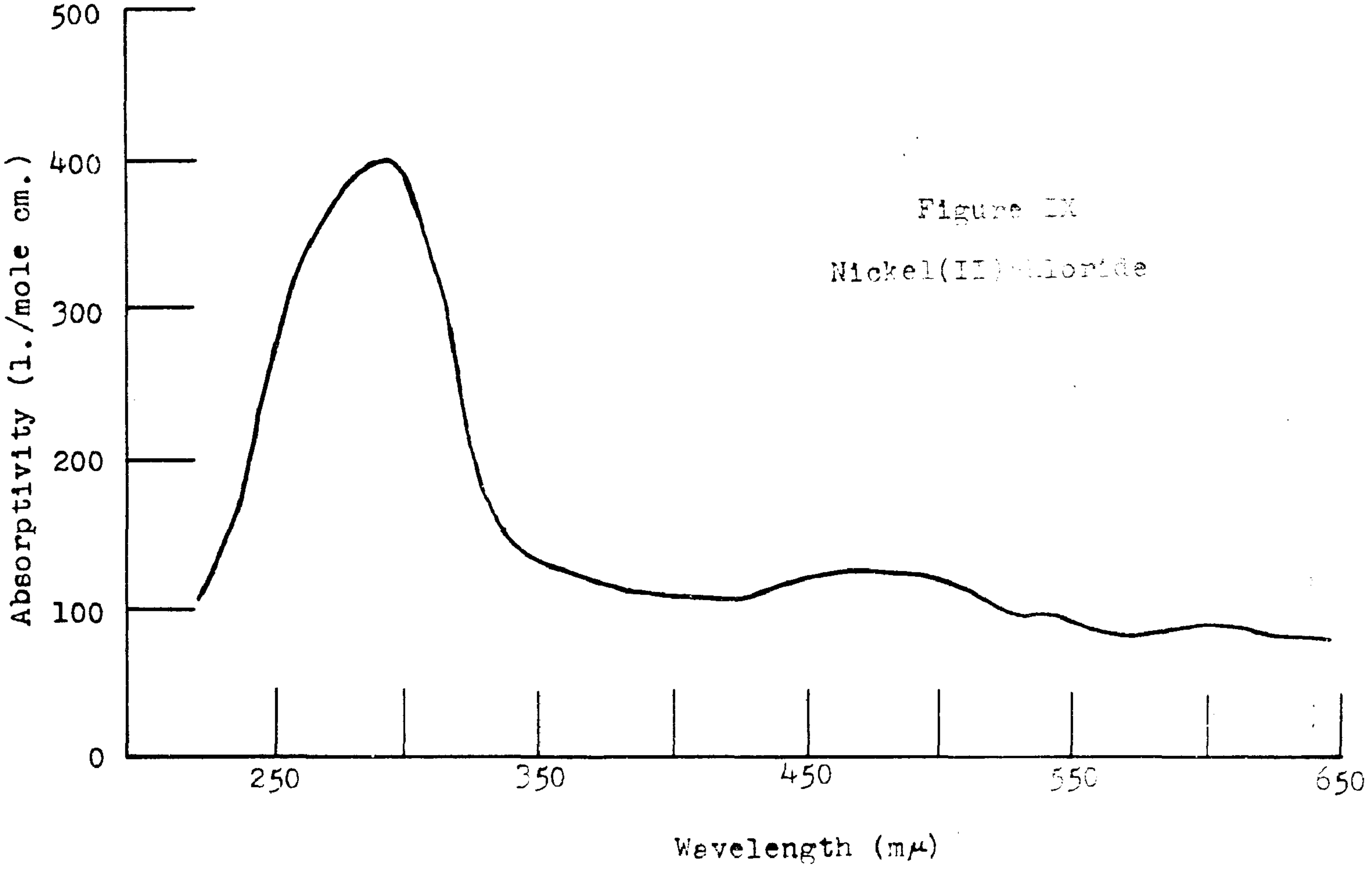


Figure IX

Nickel(II) Chloride

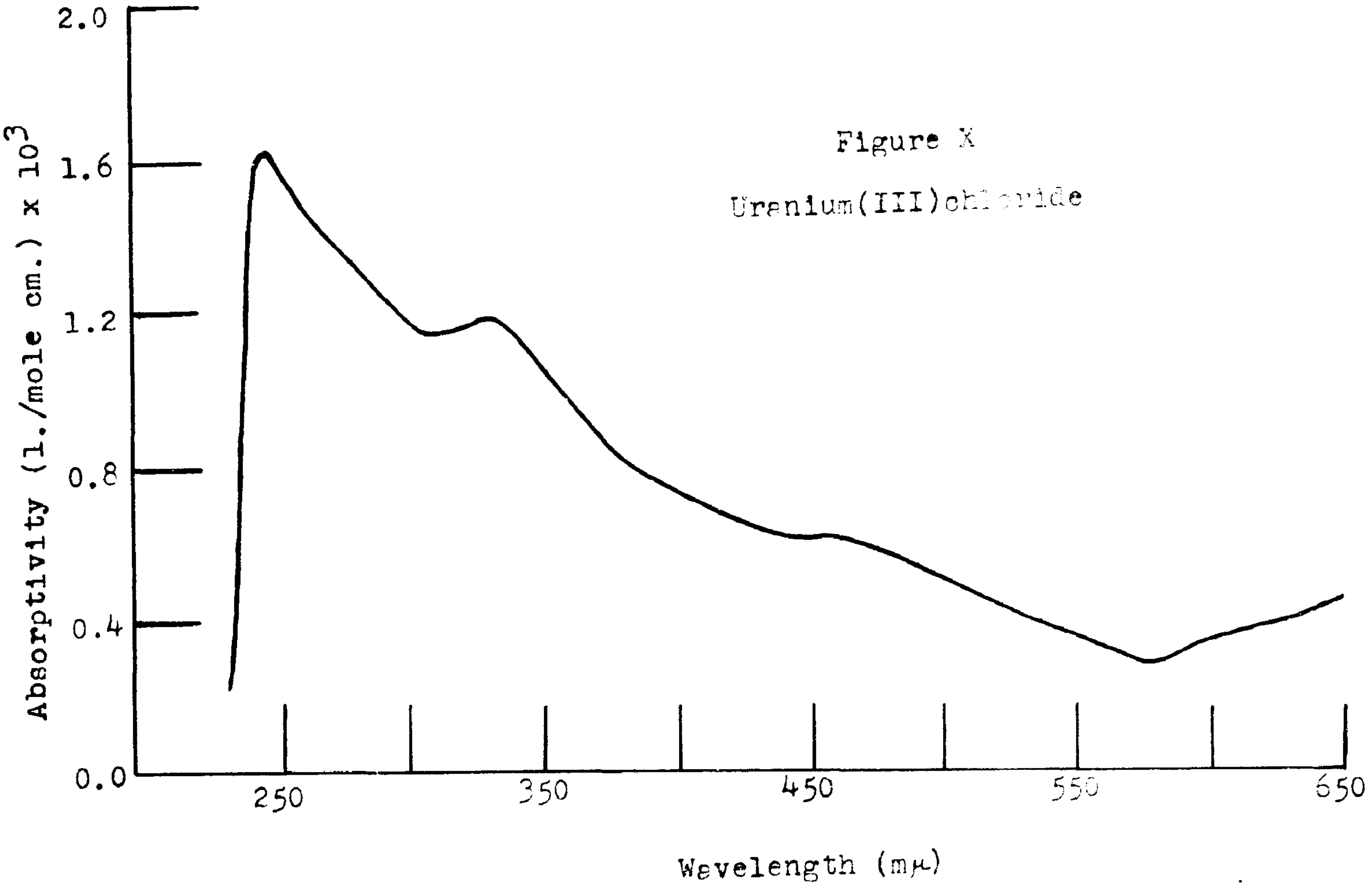


Figure X

Uranium(III)chloride

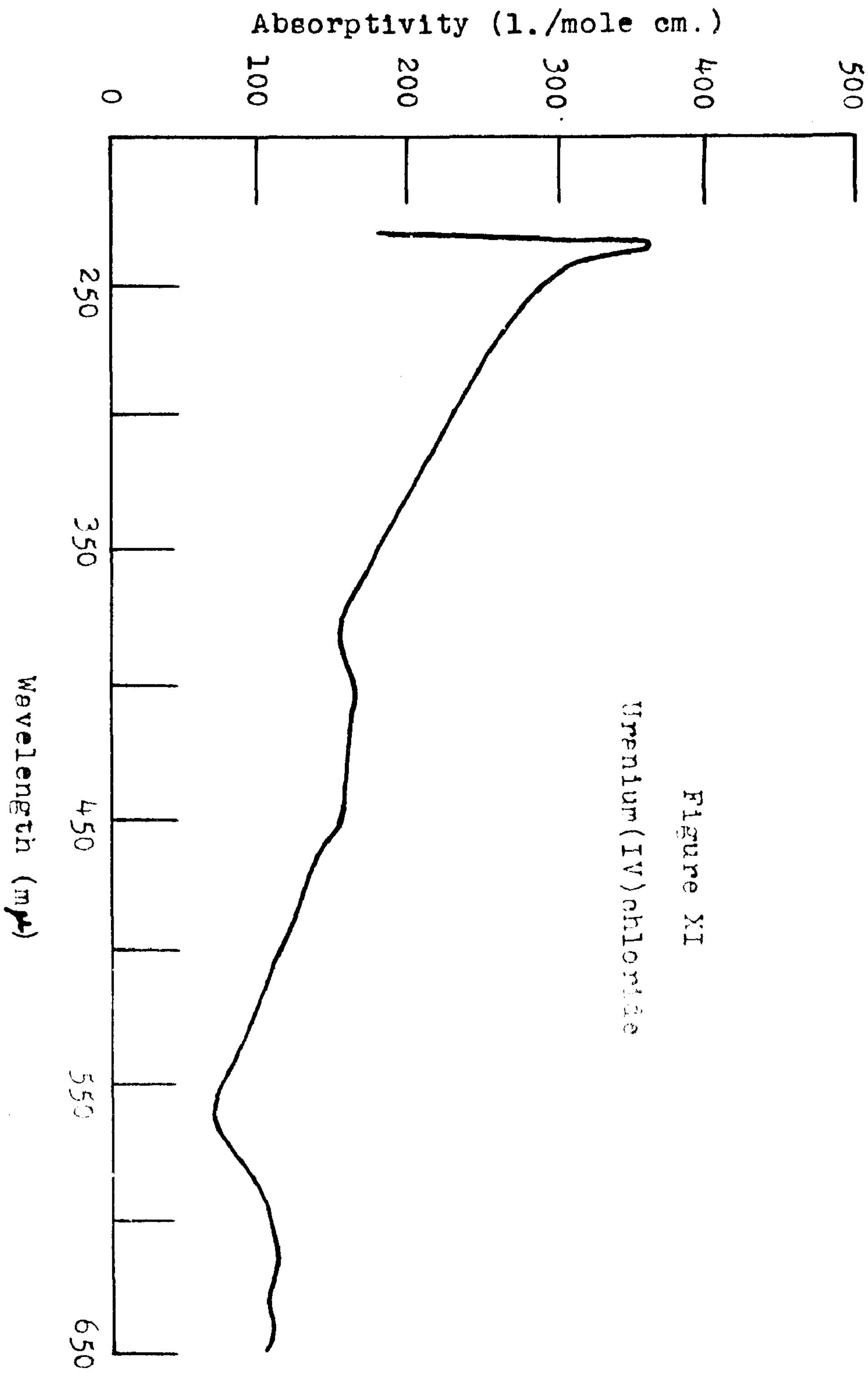


Figure XI
Uranium(IV)chloride

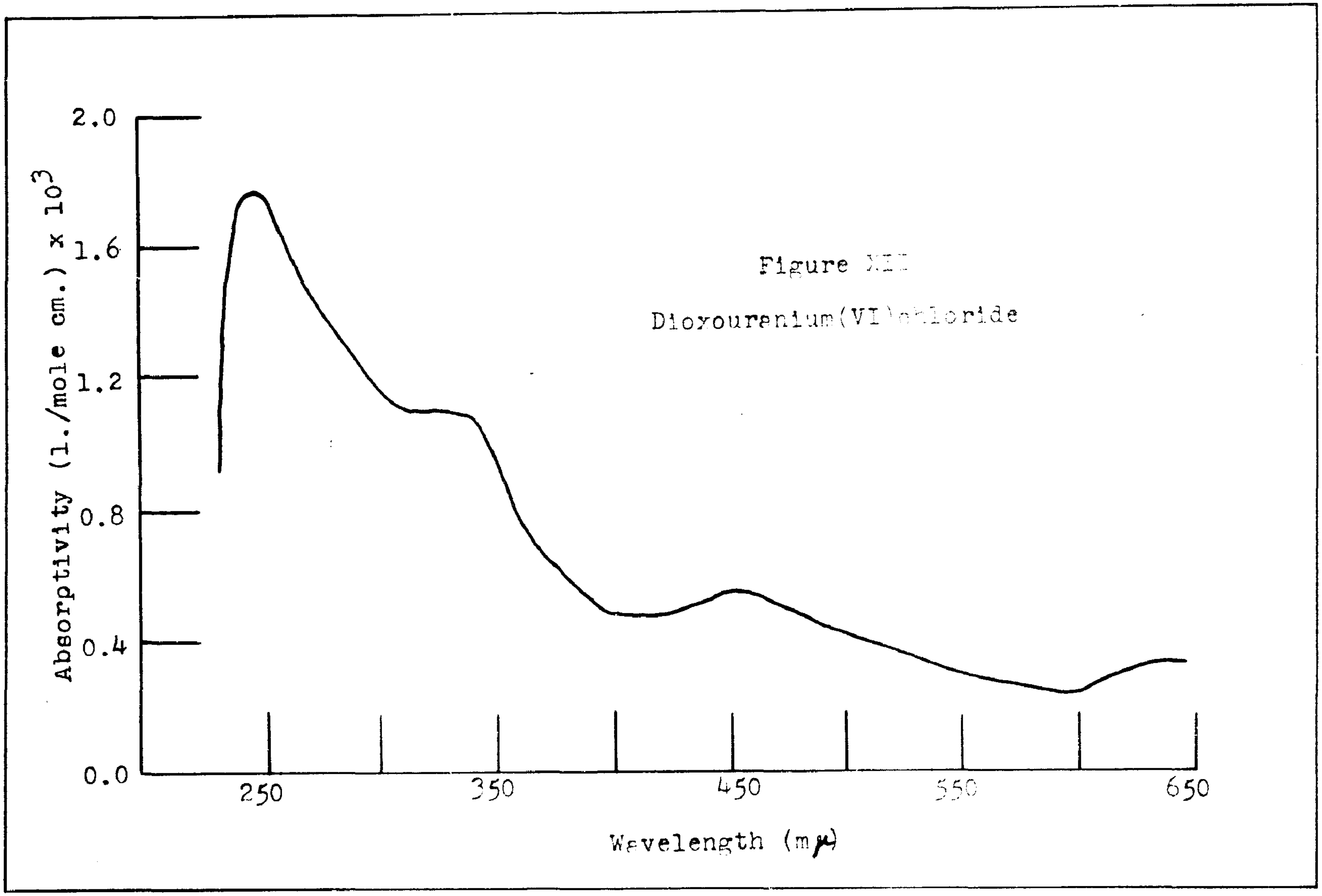


Figure XII

Dioxouranium(VI)chloride

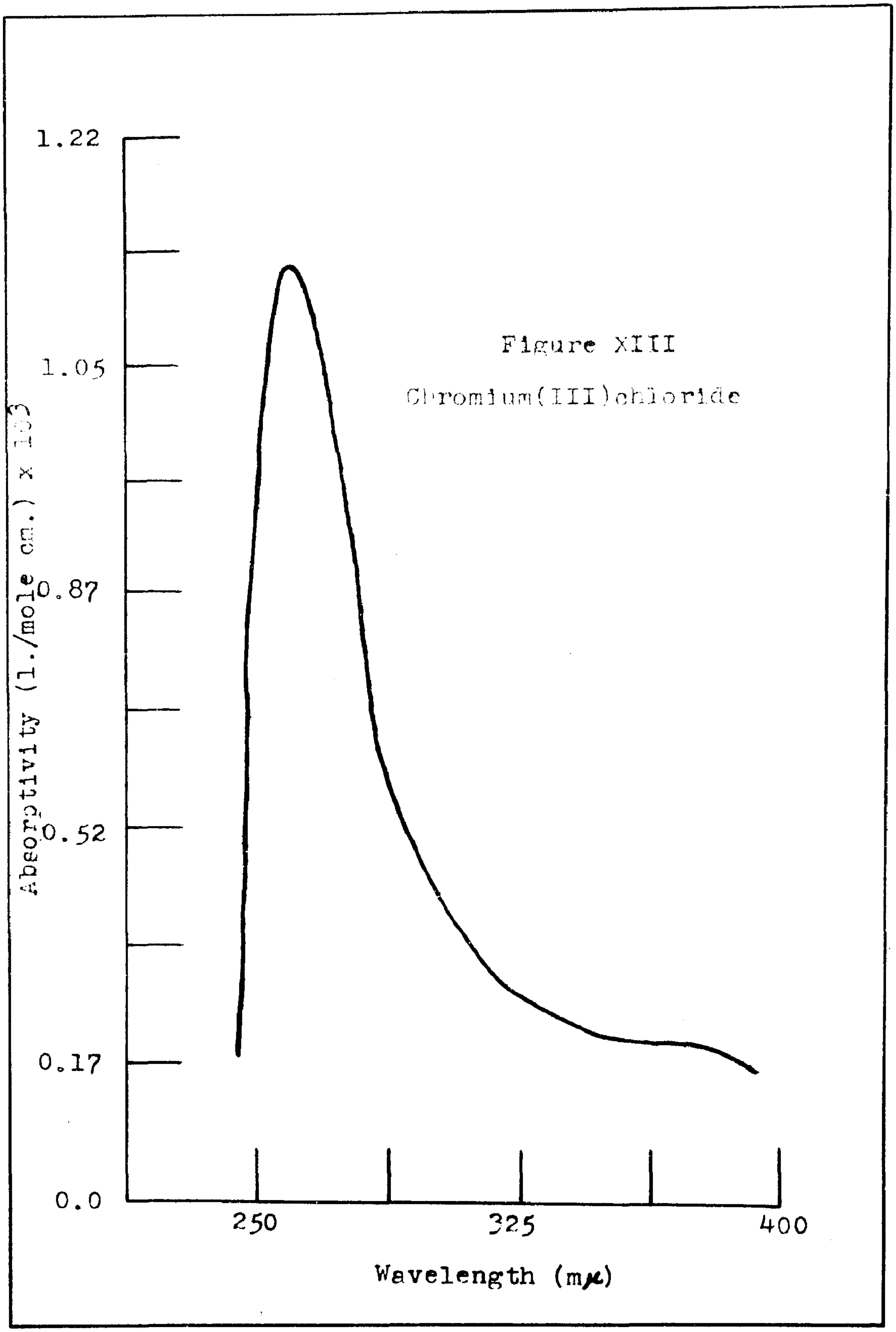


Figure XIII

Chromium(III)chloride

DISCUSSION

ANALYTICAL

For analytical applications the ultraviolet spectra show high sensitivity but low selectivity. The charge-transfer bands carry over a long way into the visible region. The bands are somewhat sharp, which gives a rapid change of absorption with change in wavelength, making accurate measurements difficult. In addition the charge-transfer band of the eutectic occurs in this region, adding to the difficulty of quantitative measurements. All salts studied have overlapping bands in the visible and ultra-violet and are close enough in intensity, in the visible especially, to make quantitative readings hard to obtain for mixtures of salts. This explains the results for the cobalt(II) - copper(II) where rapid changes in absorption with wavelength are observed. For the uranium(III) - uranium(IV) system the agreement is much better where the change is not as rapid.

Orgel(16) points out the fact that charge-transfer between elements in different oxidation states can occur. If this occurs in the uranium(III) - uranium(IV) system the use of individual absorptivities for calculations of concentration would not lead to good results. Smith(2) has shown that a change in solvent composition can also alter the observed spectrum. This occurs in both the uranium and cobalt-copper system where the molar absorptivities for the single salts were observed with different samples of ternary eutectic than when observed with the two component systems. If the eutectic composition were the same in each case, which is probably not so, then an error could be introduced here. The problem of hydrolysis is one which is always present in this work. It varies from run to run and could be a large factor in determining quantitative results.

ULTRA-VIOLET SPECTRAL REGION

All of the metal chloride solutions show absorption in the ultraviolet region, with considerable variation in the magnitude of the molar absorptivity. The absorption appears to be related to some common property of these systems rather than to some unique property of the individual metal ion or complex present. The most probable explanation seems to involve "charge transfer" spectra(16) the absorption being due to transfer of an electron from one of the ionic species in the solution to another.

The spectra of a large number of crystalline halides (17) have shown the spectra to consist of one or more maxima at wavelengths less than 250 mμ. Chlorides generally have a single maximum while bromides and iodides have a pair of maxima. For a given metal more energy is required to bring about the transfer of an electron from chloride than either bromide or iodide because of the decrease in electron affinity of these atoms. The same phenomena occurs for gaseous alkali halides in the region from 200 to 350 mμ(18) but the maxima are at greater wavelengths. Again the process is interpreted as a "charge-transfer" process. The process is shown in the following manner:

$$FeCl^{+2} \xrightarrow{h\nu} Fe^{+2} + Cl$$

Evans and Uri(19) have detected these chlorine free radicals. The radicals have been used to initiate a vinyl polymerization reaction.

The stable alkali and alkaline-earth ions do not show any charge-transfer in solution below approximately 200 mμ. Fig. IV shows the spectrum of the molten eutectic. This no doubt is the tail of the "charge transfer" band wherein an electron is transferred from a chloride ion to a neighboring alkali or alkaline earth ion.

In aqueous solutions anions have strong absorption bands(20) in the range 200-250 mμ with molar absorptivities commonly reaching 10,000 l./mole cm. with the lower limit being 1,000 l./mole cm. This in general agrees with the results reported here. It is known, however, that increased temperature tends to cause broadening and diminishing of absorption maxima.

Sundheim(7) has observed a region of transparency and a region of opaqueness for several molten salts. Solutions of silver(I)chloride show the same behavior in a lithium chloride-potassium chloride but his solutions were too concentrated to show any maxima. In a study of cadmium(II) bromide in a potassium bromide-lithium bromide eutectic Sundheim (8) identifies the spectra of these salts as being due to a "charge-transfer" process. Smith(2) identifies the first maximum of nickel(II)chloride in a lithium chloride-potassium chloride eutectic as being due to a charge transfer process. With this previous discussion it seems reasonable to conclude that a "charge-transfer" process is also taking place in the ternary eutectic of magnesium chloride-potassium chloride-sodium chloride.

In solutions which contain high concentrations of chloride ions it would be expected that complex ion formation would take place. Complex ions with one or more chloride ions may be present and no doubt the metal-anion ratios vary. Cesium tetrachlorocuprate(II) has a grouping of $CuCl_4^{=}$ as an anion(11). It would be expected that this ion would also be present in the ternary eutectic because of the high concentration of chloride ions and the law of mass action. The spectrum of Cs_2CuCl_4 shows a maximum at 250 mμ and an absorptivity of 3160 l./mole cm. as compared to a maximum of 2770 l./mole cm. at 254 mμ for copper(II)chloride in the ternary eutectic. Further work on complex salts has been reported by Thunberg(21).

VISIBLE SPECTRAL REGION

Cobalt(II)chloride. (Fig.V) The aqueous spectrum of cobalt(II)chloride in 12 M hydrochloric acid has been investigated by Jorgensen(22). He observes the same type of band as this work does at 610 mμ. This band is also intense for cobalt(II) systems of chlorides and bromides. Katzen(23) has investigated the spectrum of cesium tetrachlorocobaltate(II) at liquid nitrogen temperatures. At this temperature there are many more weak bands observed than in water at room temperature. However his profile spectra in the area from 600 to 635 mμ shows the same type peak as observed in the ternary eutectic. The crystal structure of cesium tetrachlorocobaltate(II) has been observed and shown to consist of the $CoCl_4^=$ anion. The similarity of our spectra with that of Katzen in the region of 610 mμ indicates that in the ternary eutectic the cobalt is present as the $CoCl_4^=$ anion. Gruen(6) has investigated $CoCl_2$ in a lithium nitrate-potassium nitrate eutectic and has shown that the same band appears upon addition of excess chloride.

Copper(II)chloride. (Fig.VI) Solutions of $CuCl_2$ in the ternary eutectic are a yellow-brown in color. When solutions of $CuCl_2$ in hydrochloric acid are evaporated or solutions of $CuCl_2$ in high hydrochloric acid concentration are prepared they are this same yellow-brown color. Moeller(24) has investigated the Cu-Cl system by the method of continuous variations and finds that as the Cu-Cl ratio approaches 1:10 the visible peak approaches 570 mμ. He is of the opinion that the predominant species in these solutions is the tetrachlorocuprate(II) anion. Helmholz and Kuhr(II) have shown that cesium tetrachlorocuprate(II) has the $CuCl_4^=$ anion as an entity. The ultraviolet spectrum of Cs_2CuCl_4 in the ternary eutectic shows a peak at 254 mμ with an absorptivity of 3160 l./mole cm. indicating along with the visible spectrum that the spe cies in solution is probably $CuCl_4^{=}$.

Iron(III)chloride. (Fig. VII) $FeCl_3$ is non-absorbing in the visible. This also has been found for $FeCl_3$ in lithium nitrate/potassium nitrate (6). Orgel's(25) work for a d^5 system shows that only weak bands should be found and the predicted tetrahedral bands for $FeCl_4^-$ are beyond 650 mμ. $FeCl_3$ in 12 M HCl as $FeCl_4^-$ has very low intensity bands at 619 mμ with a molar absorptivity of 0.49 l./mole cm.(26). $FeCl_3$ in 7.5 M HCl shows a low absorption band beyond 650 mμ. At high temperatures and because of the hydrolysis in these solutions these low intensity bands may not be observed.

A comparison of the spectrum of $FeCl_3$ in HCl and the $FeCl_3$ complex ($FeCl_4^-$) in isopropyl ether(27) show these maxima at 285, 320 and 365 mμ. The highest complex found in quantity is $FeCl_4^-$. The comparison of these wavelengths of maximum absorption with those of this work indicate that in the ternary eutectic the iron is present as $FeCl_4^-$. In compounds such as potassium tetrachloroferrate (III), $KFeCl_4$, cesium tetrachloroferrate(III), $CsFeCl_4$, and ammonium tetrachloroferrate(III), NH_4FeCl_4, the iron is four coordinate and the solids are yellow. The color of the solutions of $FeCl_3$ in the ternary eutectic is yellow.

Manganese(II)chloride. (Fig. VIII) Orgel(25) and Jorgensen(28) have predicted and the latter has found that manganese(II) should have absorption bands of low intensity based on calculations for manganese(II) in an octahedral field of six water molecules. There are six bands observed for manganese(II) which have absorptivities of the order 0.02 l./mole cm. These are low with respect to other absorptivities of transition metal ions. The absorptivities of manganese(II) in the ternary eutectic are lower relative to the other transition metals. The positions of the fused salt bands do not occur at the same places as for the aqueous solutions but two bands are observed in the fused eutectic. This would seem to indicate that manganese(II) in the ternary eutectic is also octahedrally surrounded by chloride ions.

Nickel(II)chloride. (Fig. IX) The spectra of this metal ion has been observed in the aqueous, solid and fused salt media. This work shows two absorption maxima at 470-490 mμ, 610 mμ and a shoulder at 550 mμ in the visible. The intensities in the ternary are greater than those of Smith(2) in a 59 mole percent lithium chloride/potassium chloride mixture. Low(29) shows the spectra of nickel(II) in a magnesium oxide matrix with the same "red-band" as Smith and this work. Holmes and McClure(30) in their examination of $NiSO_4 \cdot 7H_2O$, $NiSiF_6 \cdot 6H_2O$ and $K_2(Zn,Ni)\ SO_4 \cdot 6H_2O$ (1% Ni) found the same double peak in the red-band. Jorgensen(31) states that this band is due to a singlet state with some singlet-triplet mixing. Gruen(3) has substituted nickel(II) isomorphously for zinc(II) in Cs_2ZnCl_4 whose crystal structure shows zinc to exist tetrahedrally. This forces the tetrahedral configuration in nickel and this spectrum corresponds to that of nickel(II) in pyridinium hydrochloride. The spectra of nickel(II) chloride in lithium chloride is much different from the above and much more similar to that of the previously mentioned work. Gruen acknowledges the fact that the strong polarizing power of the lithium ion distorts the tetrahedral structure of the $NiCl_4^{=}$ ion. Sundheim(32) has investigated nickel(II)chloride in a lithium chloride/potassium chloride melt. He comes to the conclusion that the $NiCl_4^{=}$ is somewhat distorted from the tetrahedral configuration because of the lithium ions' ability to cluster about the complex ion. In the ternary eutectic the high percentage of Mg^{+2} could bring about the same circumstances and force a like distortion of the $NiCl_4^{=}$ ion.

Uranium(III)chloride. (Fig. X) Solutions of uranium (III)chloride in high hydrochloric acid concentration are red (33). The same color is observed for UCl_3 in the ternary eutectic.

Transference experiments with trivalent actinides in 1 M HCl show that the metal ion moves to the anode(34) and in 10 M HCl a much larger amount of the metal ion moves toward the anode. Diamond(35) et al are of the opinion that the only way to explain the change in elution of actinides on an ion-exchange column in 12.2M HCl is via chloro complexes. The reflection spectrum of UCl_3(36) shows a number of weak bands and one strong one at 634 mμ. The band in this work is at 640 mμ. The work of Jorgensen(33) shows a shift of the 521 mμ band to 540 mμ on increasing the HCl concentration from 0-6M to 12 M HCl which seems to indicate the presence of uranium(III) chloro complexes. The exact nature of these is not known.

Uranium(IV)chloride. (Fig. XI) UCl_4 is not a strong absorber in the visible when in aqueous solution. Jorgensen is of the opinion that in 12 M HCl uranium(IV) exists as the $UCl_6^{=}$ complex(33). The ion exchange behavior of uranium(IV) indicates that chloro complexes are formed(35). UCl_4 solid is eight coordinate(37) with four chlorides at a greater distance than the other four chlorides. In compounds such as Cs_2UCl_6 it is hexacoordinated. In solution hexacoordination is much more common then octacoordination. Gruen's(5) work seems to indicate in comparison with other spectra that uranium(IV) in solution is hexacoordinated. If this is so then uranium(IV) in high chloride concentration should exist as $UCl_6^{=}$. The profile spectrum of uranium(IV)chloride in the ternary eutectic compared with that of uranium(IV)chloride in a lithium chloride-potassium chloride eutectic is in good agreement(5).

Dioxouranium(VI)chloride. (Fig. XII) The crystal field has a small influence on the 5 f electrons of uranium(38) and since uranium(VI) has no 5 f electrons the effect should be negligible. The spectrum in water should be similiar to that in the ternary eutectic for the visible region. This is seen to be true from this work. Gruen(5) reports a band at 430 mμ. This seems to correspond to this work at 450 mμ. The charge-transfer band is wide and carries over into the visible for a good distance. The crystal field has a small effect on the electrons of the lanthanides and actinides and this is borne out somewhat with UO_2 where the absorption drops off with increasing wavelength(39).

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APPENDIX

TABULATION OF MOLAR ABSORPTIVITIES

Wavelength (mμ)	Molar Absorptivity (l./mole cm.)		
	$CoCl_2$	$CuCl_2$	$FeCl_3$
230	33	905	99
35	66	1376	153
36			151
38			174
40	112	1978	165
42			161
44			191
45	136	2377	145
250	168	2630	121
52		2694	
54		2770	
55	188		128
56		2743	
58		2670	
60	200	2620	118
65	199	2374	115
70	202	2096	116
75	198		117
80	189	1489	118
85			117
90	151	955	115
95			110
300	139	814	113
10	107	739	110
20	97	680	111
30	87	642	106
35			108
40	85	629	109
45			109
350	84	619	111
55			103
60	87		105
65			107
70	77	580	103
75			104
80	80		99
85			102
90	79		101
400	80	543	90
10	82	475	56
420	72	401	39

Wavelength (mμ)	Molar Absorptivity (l./mole cm.)		
	$CoCl_2$	$CuCl_2$	$FeCl_3$
430	88	356	38
40	89	275	38
450	86	236	41
60	88	196	43
70	85	160	45
80	79	125	40
90	74	93	31
500	68	88	25
10	66	83	20
20	64	81	18
30	61	79	17
40	57	56	16
550	55	42	17
60	57	35	13
70	62	29	12
80	74	18	12
90	101	18	11
600	130	13	10
10	149	11	10
20	145	10	10
30	144	9	9
40	174	8	9
650	209	8	9

Wavelength (mμ)	Molar Absorptivity (l./mole cm.)		
	$MnCl_2$	$NiCl_2$	UCl_3
230	76	116	214
33	135		
35	130	152	1016
38	96		
40	88	158	1577
42	95		1656
44			1635
45	102	184	1622
46			1632
48	102		1619
250	100	234	1620
55	93		1558
58	87		
60	86	313	1470
65	79	340	1451
70	92	353	1399
75	88	360	
80	88	373	1335
85		385	
90	84	395	1241
300	78	400	1192

Wavelength (mμ)	Molar Absorptivity (l./mole cm.)		
	$MnCl_2$	$NiCl_2$	UCl_3
305		389	
10	74	373	1170
15		351	1184
20	71	315	1199
30	72	270	1219
35			1137
40	71	185	1169
45			1198
350	69	150	1077
60	68	138	991
70	66	119	901
80	67	115	821
90	64	131	781
400	64	135	795
10	[illegible]	125	682
20	39	111	636
30	39	105	631
40	41	113	624
450	39	116	624
60	41	120	614
70	41	125	599
80	42	125	581
90	41	125	551
500	40	124	529
10	37	119	482
20	36	112	451
30	33	104	422
40	32	98	402
550	31	96	356
60	28	91	337
70	27	86	305
80	26	85	281
90	27	84	288
600	29	88	348
10	31	90	355
20	31	88	378
30	29	85	387
40	29	85	414
650	29	78	390

Wavelength (mμ)	Molar Absorptivity (l./mole cm.)	
	UCl_4	UO_2Cl_2
230	219	928
35	357	1559
40	365	1772
45	343	1735
46		1711
48		1780

Wavelength (mμ)	Molar Absorptivity (1./mole$^-$ cm.) UCl_4	 UO_2Cl_2
250	335	1804
55	331	1741
56		1737
60	312	1731
65	296	1661
70	275	1501
80	277	1430
90	260	1276
300	257	1195
10	240	1122
20	231	1124
30	219	1115
40	209	1043
350	198	942
60	178	784
70	161	677
80	161	595
90	156	505
400	165	489
10	168	494
20	161	479
30	159	481
40	157	497
45	157	
450	157	531
55	156	
60	146	501
70	137	498
80	132	481
90	125	460
500	118	429
10	110	383
20	103	379
30	95	331
40	88	338
550	76	312
60	70	297
70	79	284
80	91	266
90	103	260
600	108	270
10	112	290
20	112	313
30	107	337
35	110	
40	112	335
45	110	
650	107	335