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Radiation Laboratory

LIGHT ABSORPTION OF SOLUTIONS OF THE
TRI-VALENT IONS OF THE LANTHANIDE AND ACTINIDE RARE EARTHS
I. The lighter Lanthanide Elements in Aqueous Perchloric Acid.

By

D. C. Stewart

Berkeley, California

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LIGHT ABSORPTION OF SOLUTIONS OF THE
TRI-VALENT IONS OF THE LANTHANIDE AND ACTINIDE, RARE EARTHS
I. The Lighter Lanthanide Elements in Aqueous Perchloric Acid.
D. C. Stewart

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ABSTRACT

The absorption spectra of the perchlorates of the lighter rare earth elements (lanthanum through terbium, with the exception of promethium) have been determined in aqueous solution over a wave length range of 220 to 1100 mμ, using a Beckman quartz prism DU spectrophotometer. The values obtained are compared with those available from the literature, and the data are presented graphically to show the change in the molar extinction coefficient of the solutions with change in wave length of the incident light.

This work was performed under the auspices of the Atomic Energy Commission.

September 22, 1948.

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LIGHT ABSORPTION OF SOLUTIONS OF THE
TRI-VALENT IONS OF THE LANTHANIDE AND ACTINIDE RARE EARTHS
I. The Lighter Lanthanide Elements in Aqueous

D. C. Stewart

Introduction

Data on the absorption spectra of the trivalent rare earth ions in aqueous solutions are scattered widely throughout the literature and were obtained by a number of different workers with widely varying instruments and materials. The most thorough investigation available, that of Prandtl and Scheiner⁽¹⁾, is an exception, but unfortunately their results were presented in a form which makes them of little use for analytical purposes, although their study was a remarkably thorough one with an instrument of very high sensitivity. The present investigation, while undertaken primarily to obtain curves for comparison with the trivalent actinides (Seaborg⁽²⁾), also sought to obtain data suitable for analytical use. This first report will consider the results largely from the latter point of view, and will consist chiefly of a presentation of the data found.

With the double purpose of actinide comparisons and of obtaining reference curves, an attempt was made to satisfy the following experimental conditions:

(1) Use of an instrument of the type used in determining the light absorption in aqueous solution of the trivalent ions of the actinide series and of a type widely used for analytical purposes.

(2) Determination of the spectra with the rare earth ions in media thought to be non-complex forming, and in solutions of approximately the same ionic strength for each separate element considered.

(3) Determination of the absorption over as wide a spectral range as possible.

(4) Maintenance of controlled temperature conditions.

These specifications were not completely met in all cases. In general, however, the absorption spectra were determined with the rare earth ions in perchloric acid solution at a 0.15 M R^{+++} concentration, and 0.1 M HClO_4 ($\mu \approx 1$). The same Beckman DU quartz prism spectrophotometer was used for the various determinations over a spectral range of 220 - 1100 millimicrons. For most of the runs, the temperature was controlled by means of a water jacket* to $25 \pm 0.2^\circ \text{C}$. Experimental difficulties necessitated occasional divergence from these conditions, and such variations are indicated in the following report or in the various included tables of data.

Literature

Such review as will be given of the literature in this field consists primarily of the tabulated comparisons given in Tables 3-10. A comprehensive discussion of the theoretical aspects of the subject has recently been given by Yost, Russell and Garner⁽³⁾. The origin of the sharp absorption lines found in the spectra of the rare earth ions in aqueous solution was a matter of dispute for some time, but now, as these authors point out, it is generally accepted that the sharp peaks occurring in the visible portion of the spectrum are due to forbidden transitions within the 4f electron shell itself, whereas the broader absorption peaks in the ultraviolet are

* Designed by L. B. Magnusson of this laboratory.

probably due to transitions between the 4f and outer electron shells.

The inter-4f shell transitions are thought to be changes between states having varying values of the L or S quantum numbers, which accounts for the lack of absorption in the visible region for Ce^{+++} and Yb^{+++} where only one L value is possible. These 4f shell transitions are forbidden, the high peaks on the curves being somewhat illusory with their apparent intensity being accounted for by the high rare earth ion concentration in solution as compared to their concentration in the case of gas phase spectra determinations. The diffuse quality of the absorption peaks in the ultraviolet is thought to be indicative of the perturbation effect of surrounding ions on electron changes occurring in the outer, less-shielded electron shells⁽⁴⁾.

No attempt will be made to review the older work on rare earth absorption spectra, the references to which can be found in the publications of Jones, Strong, and Anderson^(5,6,7) and of Yntema⁽⁸⁾. These investigators give quite complete surveys of the information to the time of their writings.

Some work has been done on the influence of the solvent on the absorption spectra of the rare earths. Of the earlier studies, those of the Jones group at Carnegie Institution (referred to above) deserve special mention for their extent and thoroughness. They worked primarily with praseodymium, neodymium and samarium salts. Besides trying a large number of pure solvents, they worked with various water-organic solvent mixtures and found that the rare earth spectra were comparatively unchanged in such cases until the proportion of H_2O fell below 15-20%. Beyond this point, the observed spectra were a composite of those of the salts in pure water and in

pure organic solvent.

They found that the spectra of the rare earths in solution as iodide, bromide and chloride were very similar and did not change markedly with concentration. The nitrates, however, did show different spectra, particularly in concentrated solutions. Adding large amounts of CaCl_2 or AlCl_3 to NdCl_3 solutions did not seem to affect the spectrum to any great extent.

Ozumasa and Okuno⁽⁹⁾, and Ozumasa⁽¹⁰⁾, working with neodymium and praseodymium, found that there was a redward shift of the spectrum which roughly followed the decrease in the dielectric constant of the solvent used. This shift was more marked for the nitrate salts than for the chlorides. A similar displacement was noticed with increasing concentration in aqueous solutions, again particularly for the nitrate. Adding 0.496 M $\text{Mg}(\text{NO}_3)_2$ to 0.012 M $\text{Nd}(\text{NO}_3)_3$ caused a marked red-ward displacement. Dolejsek and Zadkevic⁽¹¹⁾ also observed a displacement towards the red end of the spectrum with decreasing dipole moment of the solvent, but observed that it was a smaller effect than with other light absorbing substances.

Fialkovskaja and Katchenov⁽¹²⁾ have reported that the substitution of deuterium oxide for water as the solvent causes a slight blue-ward shift of the absorption spectrum of neodymium and praseodymium sulfates, accompanied by lessening in intensity and broadening of the bands.

Radoitchitch^(14,15), working with the acetyl acetonates of samarium and neodymium, studied the effects of a long list of solvents on their light absorption in solution. The spectra varied considerably with the solvent used, showing many displacements, changes

in intensity and loss or gain of certain lines. Comparing her samarium spectra to the 1086.9 Å line reported for samarium chloride in water,⁽¹⁶⁾ she seemed to get a uniform blue-wards displacement of the spectra when the acetyl-acetonates of these rare earths were dissolved in organic solvents.

Concentration changes can materially affect the spectrum found for the rare earth salts in solution. Prandtl and Scheiner⁽¹⁾ missed the very large absorption peak of praseodymium at 214 Å, probably owing to this fact. Larionov, Novikova-Minash and Seidel⁽¹⁷⁾ were able to find this peak only over a narrow concentration range (0.06-0.17% in 2 cm cells). Mukherji⁽¹⁸⁾ found a broad absorption band in praseodymium sulfate solutions (1/10 M), which could be broken into three components by diluting to 1/40 M. A similar situation occurred when he diluted a neodymium sulphate solution. Shishlovski⁽¹⁹⁾ reports the spectra of concentrated cerous solutions, or cerous solutions in borate or phosphate containing media to be very similar to those of the crystalline salts of trivalent cerium.

Berton and Berlinger - working with gadolinium crystals - have found the sulphate, citrate and oxalate to have the four narrow bands between 273 and 276 μ approximately in the same position, while they are displaced towards the longer wave lengths in the oxide, hydroxide, nitrate, orthophosphate and tartrate.⁽²⁰⁾

Freed and Weissman⁽²¹⁾ and Freed⁽²²⁾ have observed that $\text{Eu}(\text{NO}_3)_3$ shows a very different structure in solution from that of EuCl_3 . The spectrum of the latter was constant over a very wide range of concentrations. The nitrate spectrum showed a change below 0.01 M to become like the chloride. Freed suggests that there is a higher

symmetry of field around the nitrate ion than around the chloride in these solutions. Purvis⁽²³⁾ noted a very similar behavior pattern between solutions of the nitrates and chlorides of erbium and "didymium" as early as 1903.

Blank⁽²⁴⁾ dissolved Sm_2O_3 in a borax pearl, and by heating to 250°C , obtained a new absorption peak at 422 μ . The absorption of both Nd and Sm in borax solutions are much broadened in the 300-600 $^\circ\text{C}$ range, but do not show the usual sharpening in going from room temperature to liquid air temperature, although there is a slight increase in their intensities.

There have been some studies on the absorption spectra of the rare earths in the infrared, and the peaks found are listed in Tables 3-10, although most of the values are beyond the portion of the spectrum investigated in the present work.

Among these infrared studies are those of Freymann and Takvorian⁽¹⁶⁾ with concentrated aqueous rare earth solutions, those of Gobrecht⁽²⁵⁾ and Rosenthal⁽²⁶⁾ using rare earth salts dissolved in borax pearls, and the recent study by Stair and Faick, employing rare earth oxides dissolved in soda lime glass⁽²⁷⁾. Spedding⁽²⁸⁾ also obtained some infrared absorption in praseodymium solutions.

The research of Prandtl and Scheiner has already been mentioned. It has been of great value because of its scope, since it covers all of the rare earth series. These workers used "neutral chlorides", but give very little more detail on the composition of their solutions. Their chart (reproduced in Yost, Russell and Garner) indicates the rare earth concentration at which they were last able to observe absorption. They started with a 1 molar solution, then successively

diluted to $1/2$ M, $1/4$ M, etc. The number of levels at a given wave length indicates the concentration when the absorption was last observed. The chart is excellent for placing the absorption peaks, but cannot be used for quantitative comparisons. Contrasting this chart to Figures 1-8 of this report will illustrate the marked difference in the aspects of the curves obtained by the two different methods of presenting the data.

Rodden^(54,55) also made a systematic investigation of the nitrate solutions of the rare earths, using a double monochromator photoelectric Coleman spectrophotometer. He has adapted the resulting data for analytical use in some cases. The instrument used, however is not a very suitable one for the rare earths, since it gives a band of 5 mμ width, which introduces a considerable error, as will be discussed later, and does not permit the detection of any fine structure in the spectra.

Spedding and his associates^(52,53) at Iowa State College have determined the absorption spectra of some rare earth chlorides in solutions as an analytical tool in connection with rare earth purification by ion exchange techniques. These figures are of particular interest to the present investigation, since they are the only ones determined with the same type of instrument as that used in the work reported here.

Materials

The source and quality of the rare earth stocks used are summarized in Table I. The perchloric acid used was Baker and Adamson, reagent grade. A 2.93 M solution of this acid was prepared and its

strength determined by titration with a standardized sodium hydroxide solution. This was then used as a stock acid for preparing the rare earth solutions.

Equipment

A Beckman model DU photoelectric quartz prism spectrophotometer was used throughout this study, with a hydrogen discharge lamp as the light source in the spectral range below 3200 Å, and a tungsten lamp as the light source of wave lengths longer than 3200 Å. The instrument was calibrated against emission lines from a mercury vapor discharge lamp, the error of the calibration being of the order of about ± 2 Å at the 4046.6, 4358 and 5460.7 Å lines of the Hg emission spectrum. The phototubes used were those furnished with the instrument and each was used over the wave length range recommended by the makers. Silica cells of 1 cm. path length were used for most of the runs (occasionally of the 0.2-0.5 ml. capacity type*). In the case of the Tb^{+++} spectra, 5 centimeter micro-cells of the Kirk, Rosenfels, Hanahan⁽²⁹⁾ type were used in an effort to determine some of the smaller peaks. These longer cells would have been used more extensively save for the lack of a satisfactory method of reproducibly aligning the cells in the light beam. Quartz windows were used in these cells for the Tb^{+++} run.

The length of light path used in the calculations were those furnished by the maker of the cells. This dimension is given to 3 significant figures by the Beckman people, indicating an accuracy of $\pm 0.1\%$ for the 1 cm cells.

* Made by Pyrocell Manufacturing Company, New York City.

Water from a constant temperature bath was circulated through the Bakelite-copper constant temperature jacket for 30 minutes before each run. Rough checks indicated that the temperature within the cell compartment was held at $25 \pm 0.2^\circ \text{C}$.

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Procedure

In general, the sesquioxides of the various rare earths were available or could be easily made by ignition of the oxalate or bromate. These oxides were weighed on an Ainsworth Chainomatic analytical balance directly into micro volumetric flasks (0.5-5.0 ml). The calculated amount of 2.93 N HClO_4 was then added with a micro-pipette and the dissolved oxide solution diluted to the mark with distilled water. The comparison perchloric acid solutions were made in the same fashion from the 2.93 N HClO_4 stock, an attempt being made to keep the ClO_4^- concentration the same in the two solutions. The neodymium, samarium, and europium oxides dissolved quite readily. The oxides of lanthanum, gadolinium, praseodymium and terbium required either mild heating or standing overnight before dissolving to a clear solution.

Preparation of the $\text{Ce}(\text{ClO}_4)_3$ solution turned out to be a rather difficult process. If a hydroxide precipitate was thrown down from a cerous salt solution (to permit washing free of the anion), air oxidation to ceric hydroxide occurred at once. There also seemed to be a "polymer" of the type found with $\text{Pu}(\text{IV})$ ion⁽³⁰⁾, since the hydroxide precipitate could not be redissolved in the desired amount of perchloric acid, or even in much stronger acid concentrations. Several expedients were tried in order to avoid these difficulties.

The final preparation was made by dissolving a 10-12 mg piece of cerium metal in perchloric acid. $\text{Ce}(\text{ClO}_4)_3$ absorption is extremely high in the ultraviolet, so this cerous solution was further diluted by a factor of 10 for the determination in this range. Aliquots of this latter solution were ignited to CeO_2 and weighed on the micro-balance in order to fix the final Ce^{+++} concentration.

Table II summarizes the various solutions investigated and gives the temperature conditions for each run.

Praseodymium oxide from two different sources was checked in order to confirm the presence of the large absorption peak at 2140 Å. A second, more concentrated solution of $\text{Sm}(\text{ClO}_4)_3$ was also prepared in order to check some of the smaller peaks in its spectrum.

Europium salts of good purity were not available in any quantity so the europium used for this run was purified by the "Nalcite" ion exchange column technique described by Tompkins and his co-workers⁽³¹⁾. The starting material contained about 11% impurities (thorium, neodymium, cerium, lanthanum and samarium). The purified oxide showed no contaminating rare earths or thorium when examined spectrographically. The size of the spectrographic sample was such that 0.2% of any of these contaminants would have been observed.

The spectrophotometer was originally used with the sensitivity control half way to its counter clockwise limit. In later runs, this knob was turned to its full counter clockwise limit. Checks indicated that this did not introduce any error, and did give more stability to the galvanometer needle. In general, readings were made at 2 Å intervals in the range below 6000 Å, at 2.5 Å intervals from 6000 to 8000 Å, at 5 Å intervals in the 8000-10000 Å range and

at 10 Å intervals above 10000 Å. The absorption peaks were investigated as carefully as possible within the limitations of the instrument.

Results

The data obtained are presented graphically in Figures 1-8 and are compared to values reported in the literature in Tables 3 to 10. The peak heights are presented in terms of the molar extinction coefficient, ϵ . If Beers' and Lamberts' laws for the light absorption are combined, written in differential form and integrated, one obtains the expression:

$$\ln \frac{I}{I_0} = -kcl$$

In this expression, I_0 is the intensity of the light entering the absorbing medium, and I is its intensity at depth l . " c " represents the concentration of the absorbing substance, and k is a constant. If l is expressed in centimeters and c in moles per liter, k becomes α , the "molecular absorption coefficient" (32). The expression can also be written

$$\log \frac{I}{I_0} = - \frac{k}{2.303} cl = -\epsilon cl$$

where ϵ is then defined as the molar extinction coefficient.

It will be seen that $\frac{I}{I_0} \times 100$ is the percent of light transmitted.

If a new term, D , the optical density, is defined:

$$D = \log \frac{I_0}{I}$$

Then $\epsilon = \frac{D}{cl}$. Either the quantities D or % transmission may be read off of the Beckman instrument directly.

Lanthanum (Figure 1, Table 3). As would be expected from its lack of color, the lanthanum solution did not show any light absorption in the visible portion of the spectrum. Absorption was found, however, in the 2120-2140 Å range, and was still increasing in magnitude, at the lower limit of the instrument. The purity data available on the lanthanum used would not entirely rule out the possibility of this absorption being due to cerous ion contamination, but in this event, the very large cerous peaks at 238 mμ and 253 mμ should appear, which they do not. Freed⁽³³⁾ has reported that lanthanum ion in mixed lanthanum-cerium crystals of ethylsulfate or chloride shows no absorption in the 210-297 mμ range. Rodden⁽⁵⁴⁾ shows a small amount of light absorption at about 355 mμ in his curve for lanthanum nitrate solution.

Cerium (Figure 2, Table 4). Several interesting points may be observed from the data in Table 4. It cannot be said that the chloride ion and the perchlorate ion solutions show much difference in the position of the absorption peaks, but the sulfate solution⁽³⁴⁾ and concentrated hydrochloric acid solutions⁽³⁵⁾ both show marked red-ward shifts of the absorption peaks, a phenomena which has already been mentioned in connection with concentrated nitrate solutions. Presumably, this, in all cases, is due to a modification of the electrical field surrounding the ion by the formation of complex ions or, perhaps, by changes caused in its hydration shell. It is in the same direction as the effect of the decreasing dielectric constant of the solvent discussed under the literature survey.

The 210.5 mμ absorption peak reported by Bose and Datta⁽³⁶⁾

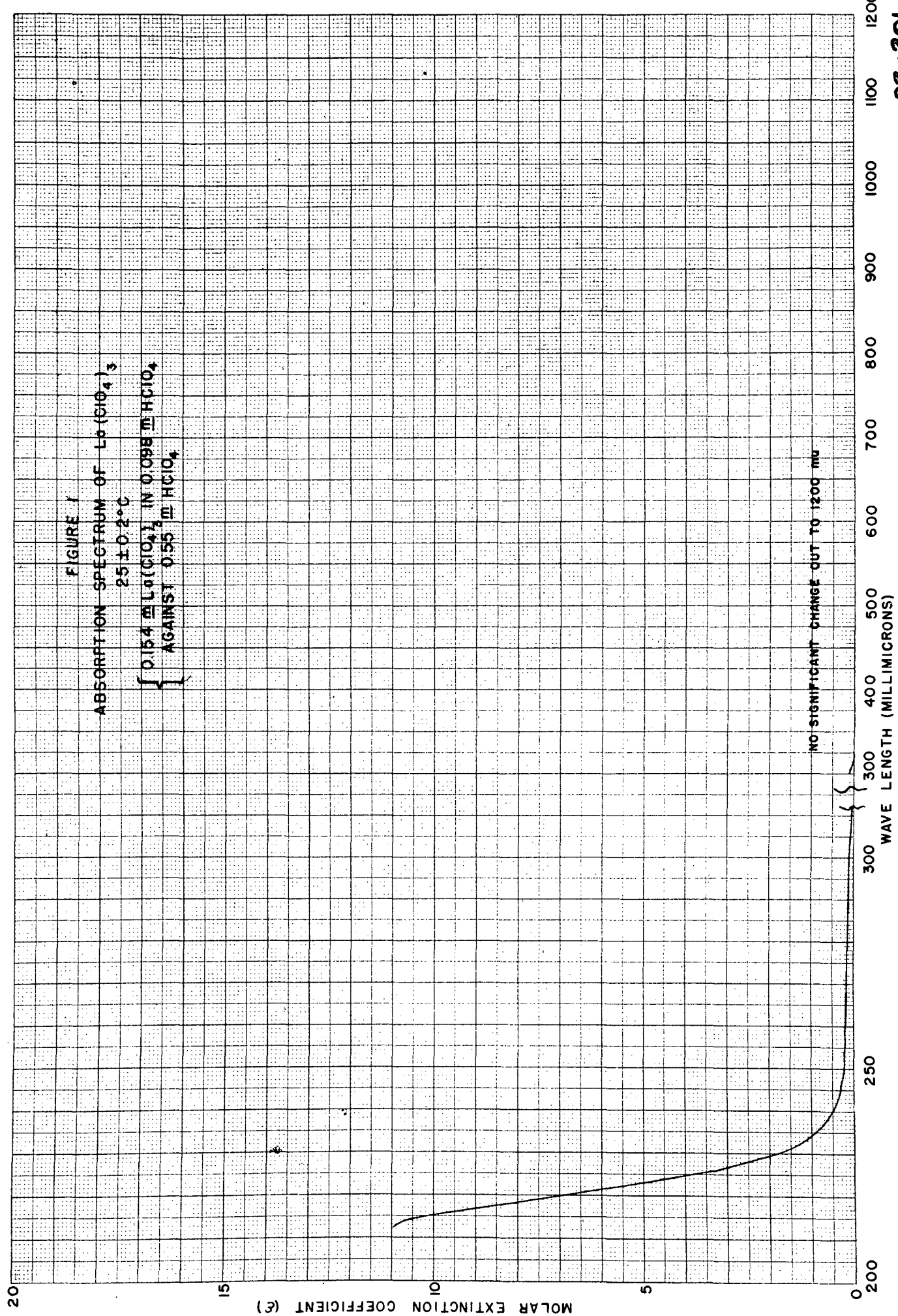
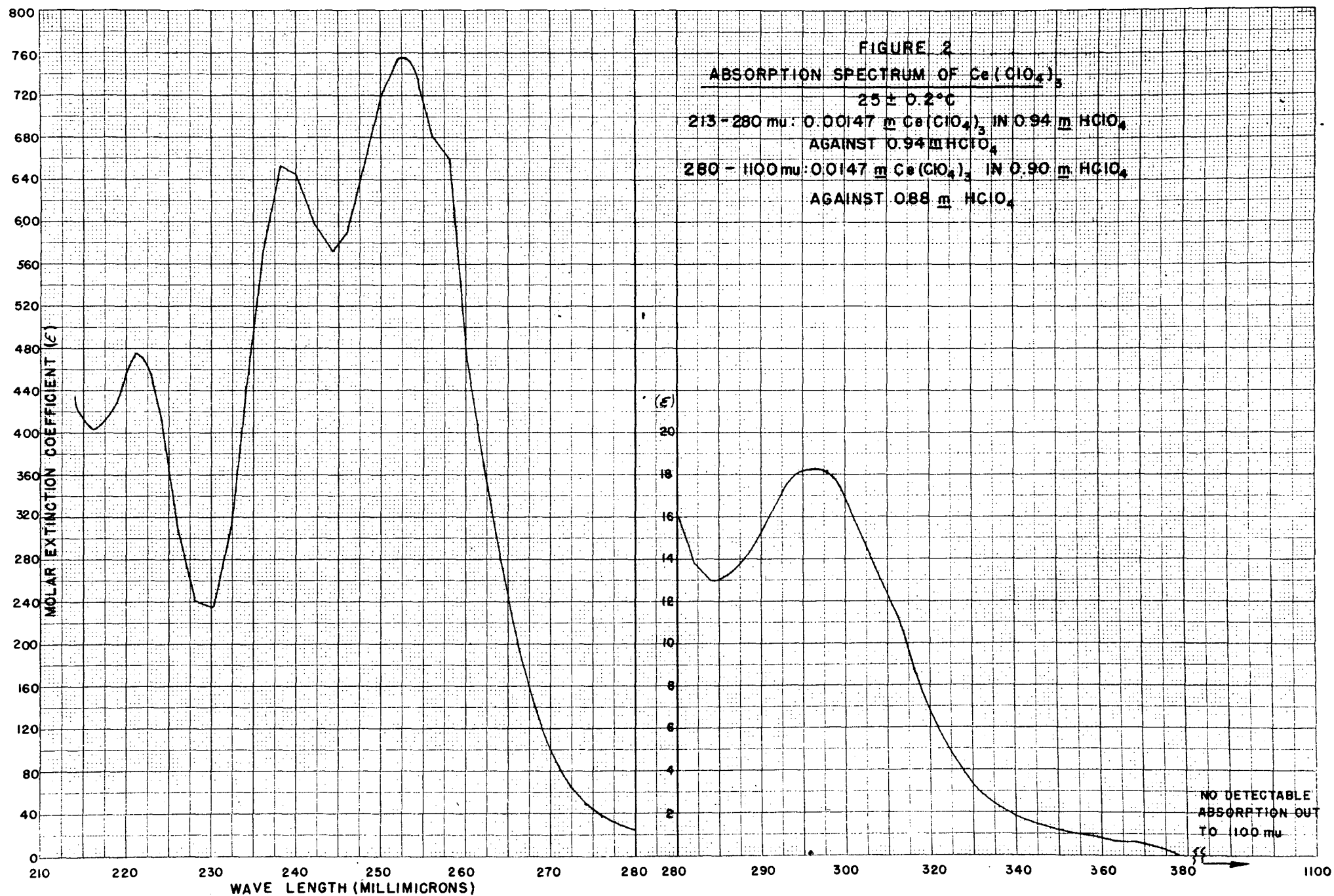


FIGURE 1
 ABSORPTION SPECTRUM OF $\text{La}(\text{ClO}_4)_3$
 $25 \pm 0.2^\circ\text{C}$
 { 0.154 M $\text{La}(\text{ClO}_4)_3$ IN 0.098 M HClO_4
 AGAINST 0.55 M HClO_4

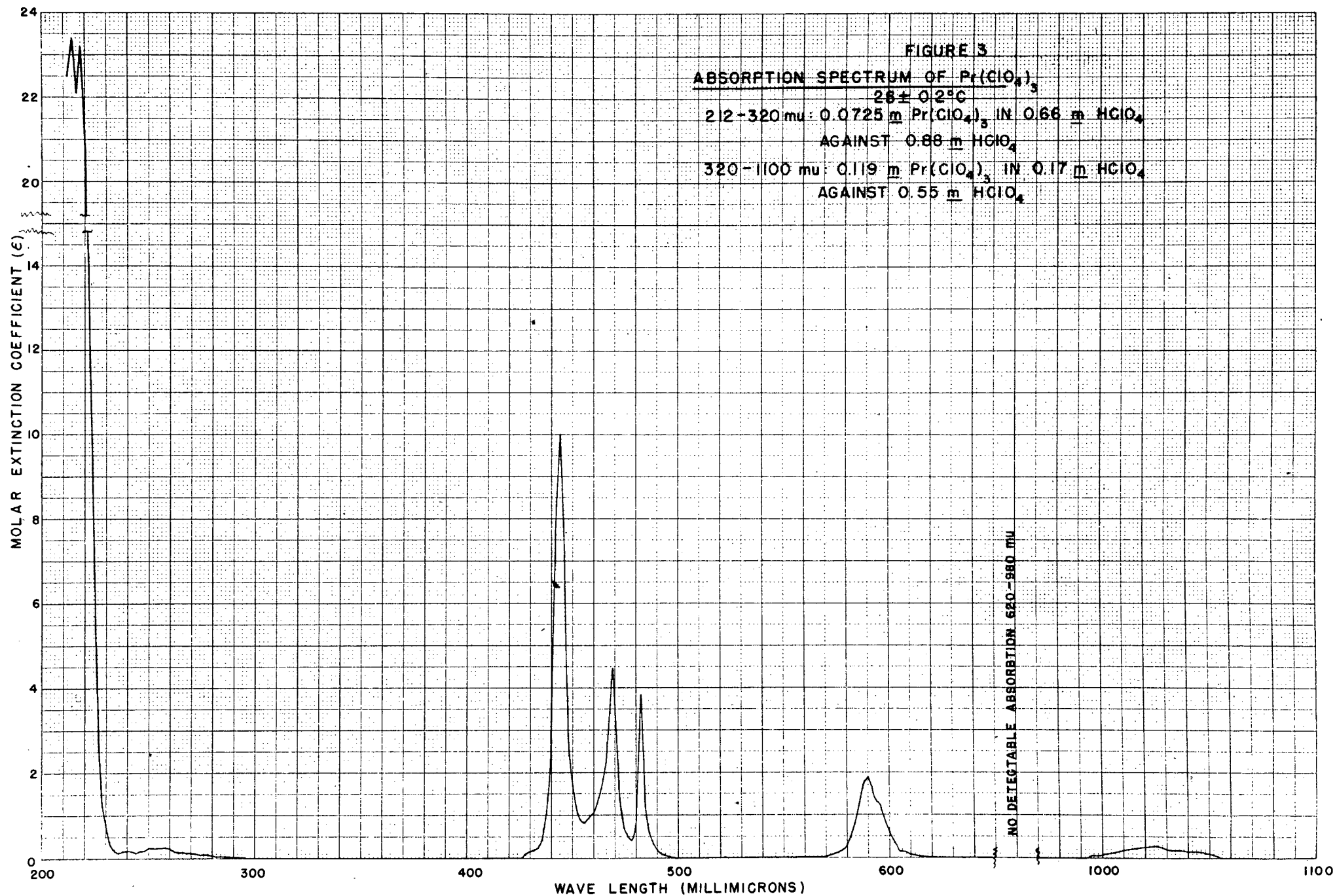


and by Wu and Kang⁽³⁷⁾ is perhaps partially confirmed in the present work, inasmuch as the extinction coefficient was still rising at the lowest limit of the Beckman instrument, but seemed to be leveling off to form a new peak.

The infrared absorption peak reported at 1650 μ by Rosenthal⁽²⁶⁾ is interesting inasmuch as it is the only absorption reported for cerium in solution by anyone in any but the ultraviolet portion of the spectrum. Rodden's⁽⁵⁴⁾ curve again shows a slight absorption at about the same point as for lanthanum ion (355 μ). This is at the lower end of the range and is probably an instrumental error.

The molar extinction coefficients given in Table 4 from the work of Roberts, Wallace and Pierce⁽³⁴⁾ were calculated from optical densities estimated from graphs published in their article, so some possibility of error is involved. Even so, the agreement between their data and the present study for the 238 and 253 μ peaks is rather good, although it is not very satisfactory for the smaller peak at 296 μ .

Praseodymium (Figure 3, Table 5). A very large amount of work has been done on praseodymium absorption, both in crystals and in solution. One of the most interesting points with respect to the present work is its confirmation of the ultraviolet absorption peak at 214 μ . As previously mentioned, this peak was missed by Prandtl and Scheiner, probably because it appears to come and go, depending on the solution concentration, as pointed out by Larionov, Movikova-Minash and Seidel⁽¹⁷⁾. This effect may account for the double peak observed in the present work. The peak is a very large one, and its presence was confirmed by the preparation of solutions using praseodymium from two different sources.



The present work missed the satellite peak at 597.7 mμ reported by Prandtl and Scheiner, and confirmed the one at 1000-1025 mμ reported by several other workers. It is interesting to note that Stair and Faick⁽²⁷⁾ found this peak in their praseodymium glass at approximately the same location as reported by various people working with aqueous solutions. No evidence was found in the present work for the 760 mμ peak reported by them.

In the case of references (40) and (41), k values (the molecular absorption coefficient), were estimated from their graphs, and converted into molar extinction coefficients by dividing by 2.303 before placing them in Table IV. In the case of reference (42), the percent absorption was presented graphically, and it was necessary to subtract this from 100% to get a "% transmission" to use in calculating the molar extinction coefficient by Beers' Law. The " ϵ " values given in Tables 5, 6 and 7 for the figures of Stair and Faick⁽²⁷⁾ on soda lime glasses were calculated by calling the difference between the transmission of the rare earth glass and the base glass the % absorption due to the rare earth ion. This was then subtracted from 100% to give a transmission figure for substitution into Beers' Law. A further assumption was made that the glass had a density of 3.5 so as to permit calculation of the rare earth concentration. The slight differences in thicknesses between the base glass studied and the various rare earth glasses were ignored on the assumption that they would be compensated for by the fewer number of base glass absorbing units per unit of length in the rare earth glass. It will thus be seen that the final " ϵ " values obtained are very approximate estimates, and are of value only as a

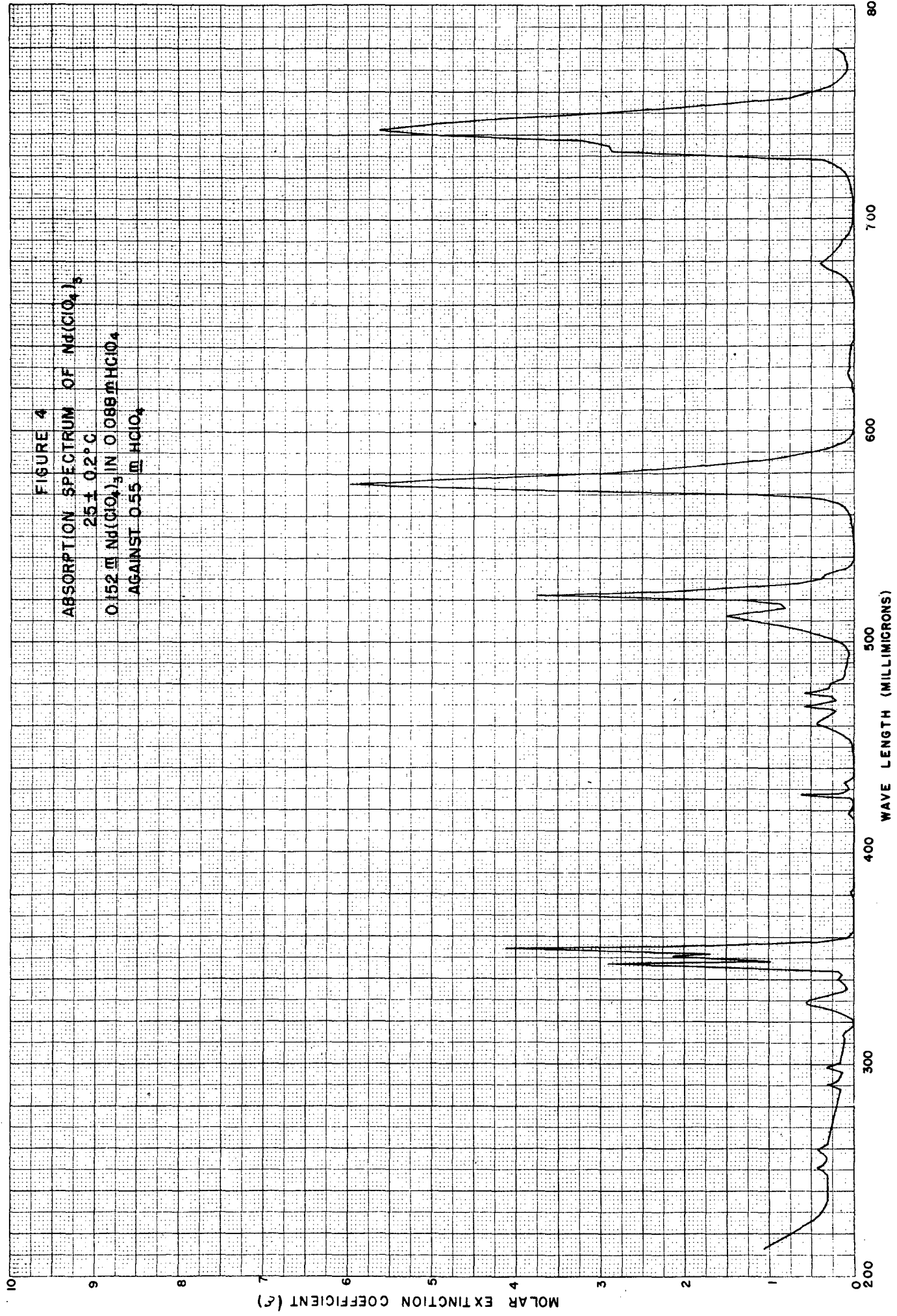
ready means of comparison between the peaks of the Stair and Faick study itself. It is interesting that the ϵ values thus calculated are roughly of the same order of magnitude (1/10) less than the present work in the case of both the praseodymium 1020 μ line and the samarium 1095 μ line.

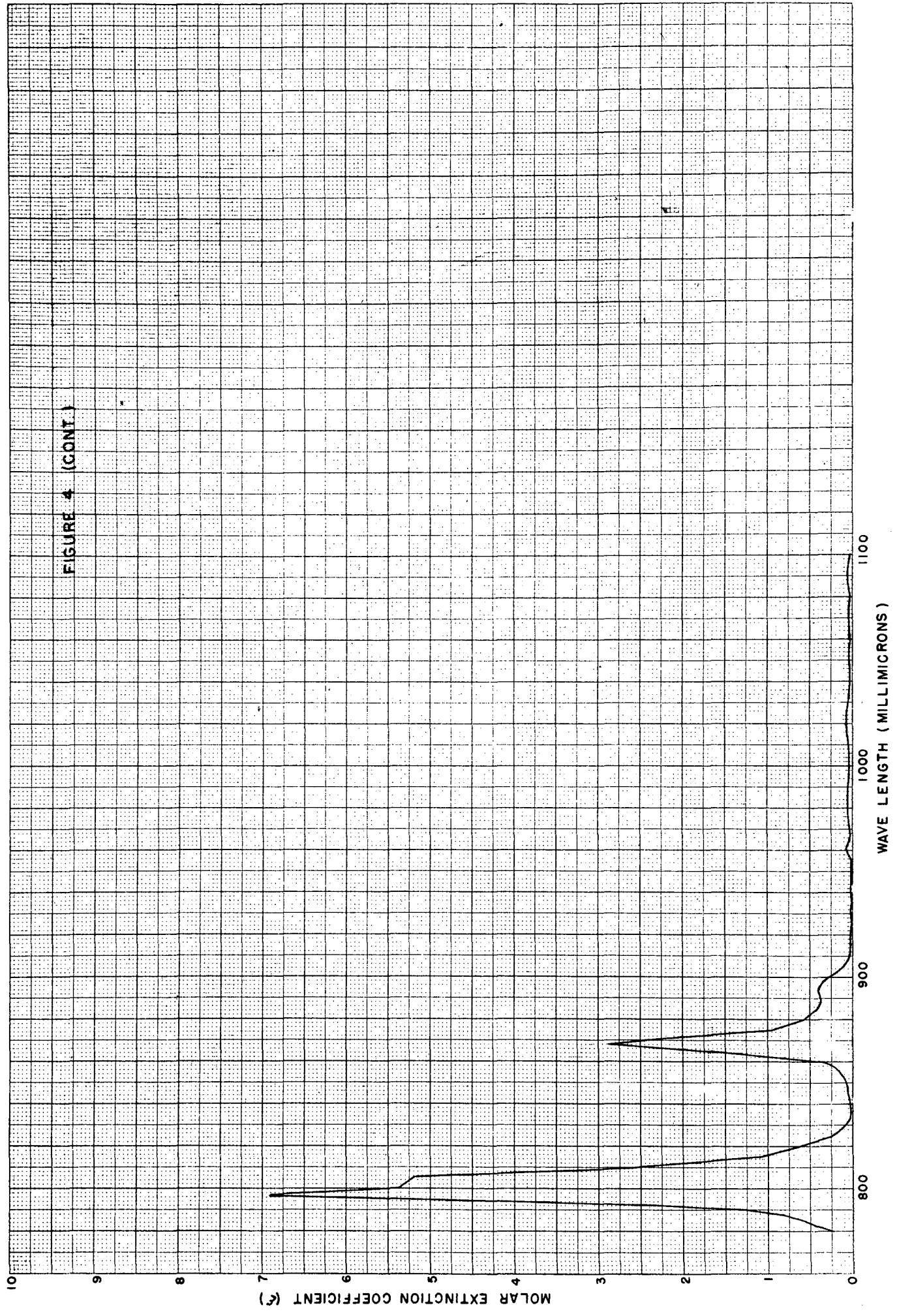
Consideration of Table IV shows that the infrared peaks at (approx.) 1020, 1440, 1540 and 1900 μ have all been reported by at least two workers. The peaks at 760 and 1650 μ have been reported only once in each case.

Neodymium (Figure 4, Table 6). More work has been done on the absorption spectrum of neodymium than on any of the other rare earths, save perhaps for praseodymium. It has a very complicated spectrum, particularly in the visible, which gives its solution a beautiful purple-violet color.

Again it was necessary to calculate ϵ values from the literature data for use in Table 6. In the case of references (45 and 46), the molecular absorption coefficient was presented graphically, and the values were converted to ϵ by dividing by 2.303. In reference (47), the % absorption was given, which necessitated conversion to % transmission by subtraction from 100%, and calculation of ϵ by Beers' Law. Again, the calculation of the value at 770 μ for the case where neodymium oxide was dissolved in soda lime glass (reference 27) was done by the rather dubious method described under the praseodymium discussion.

It will be seen that the ϵ values of the present work agree quite well with reference (46) in the 330-500 μ range, and with reference (45) between 500 and 600 μ . As would be expected, the





agreement at 740 and 795 μ with the data of Spedding, et al⁽⁵²⁾, is good, since the same type of instrument was used in both cases. The probable reason for the lack of agreement which is otherwise observed in the various data reported will be discussed below.

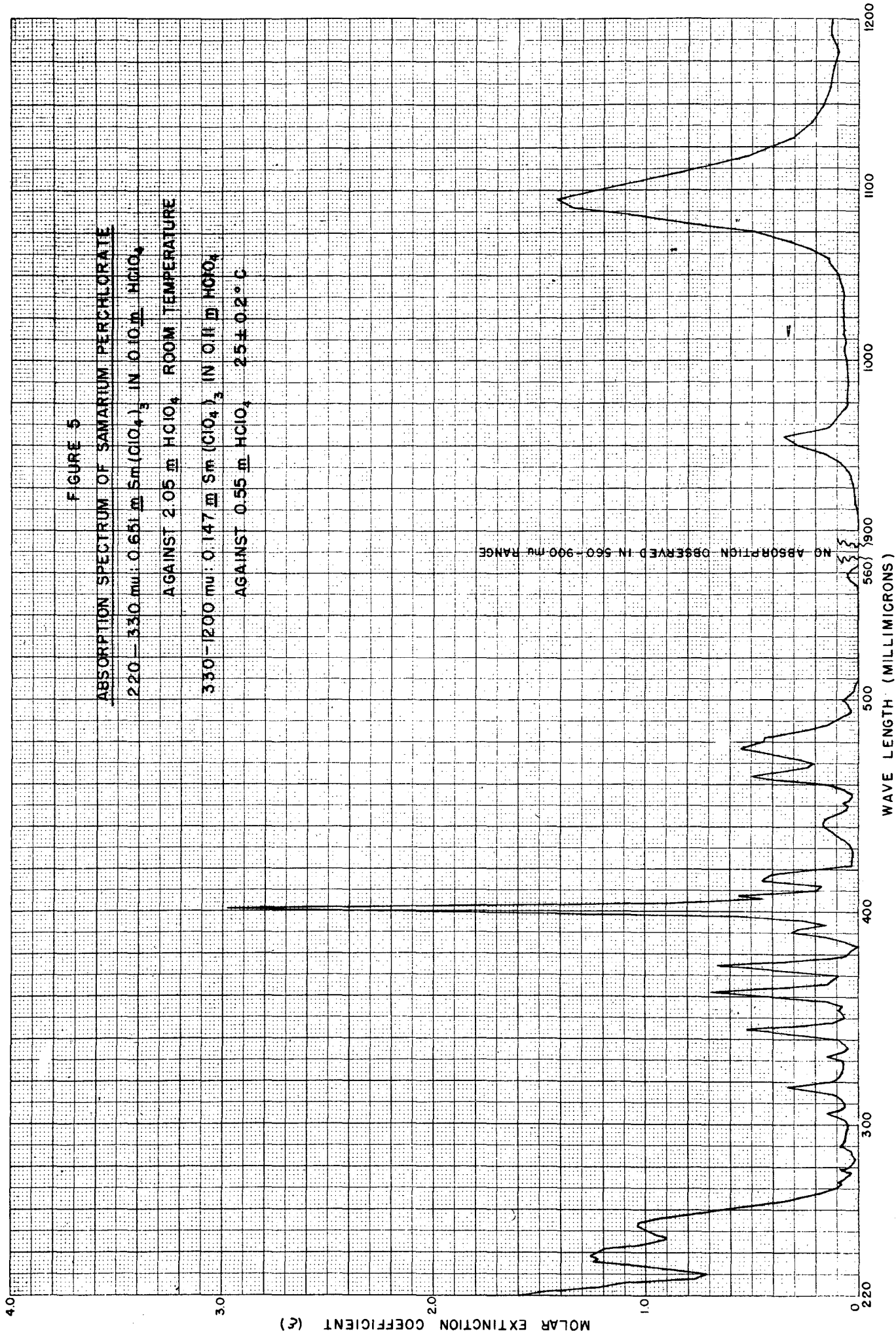
Some of the fine structure reported by Prandtl and Scheiner and by Yntema⁽⁸⁾ was missed in the present study, as was the 794 μ peak reported by Hoogschagen, Snook and Gorter⁽⁴⁵⁾. A very small, previously unreported peak was observed at 960 μ .

Samarium (Figure 5, Table 7). In general, all of the peaks reported by Prandtl and Scheiner for samarium were found in the present work, although several of them appeared only as shoulders on the sides of other peaks. In addition a new peak was found at 252 μ . The three new peaks at 523.5, 530 and 581 reported by Franzen, Woudenberg and Gorter⁽⁴⁹⁾, were not found. One of these had been previously reported by Yntema⁽⁸⁾ (530 μ).

The chief feature of the samarium spectrum is its relatively large number of infrared peaks. Only two of these could be observed with the Beckman instrument (955 and 1095 μ), but many more exist at longer wave lengths as is shown in Table 7.

In this case, the 940 and 1075 μ absorption peaks of samarium oxide dissolved in a borax pearl as reported by Rosenthal⁽²⁶⁾ would seem to be shifted towards the blue side when compared to results of other workers using aqueous solutions.

The Table 7 values for ϵ from references (41) and (49) were again calculated from k values estimated from their published curves, and the ϵ values of samarium oxide in soda lime glass were calculated by the method described under praseodymium results.

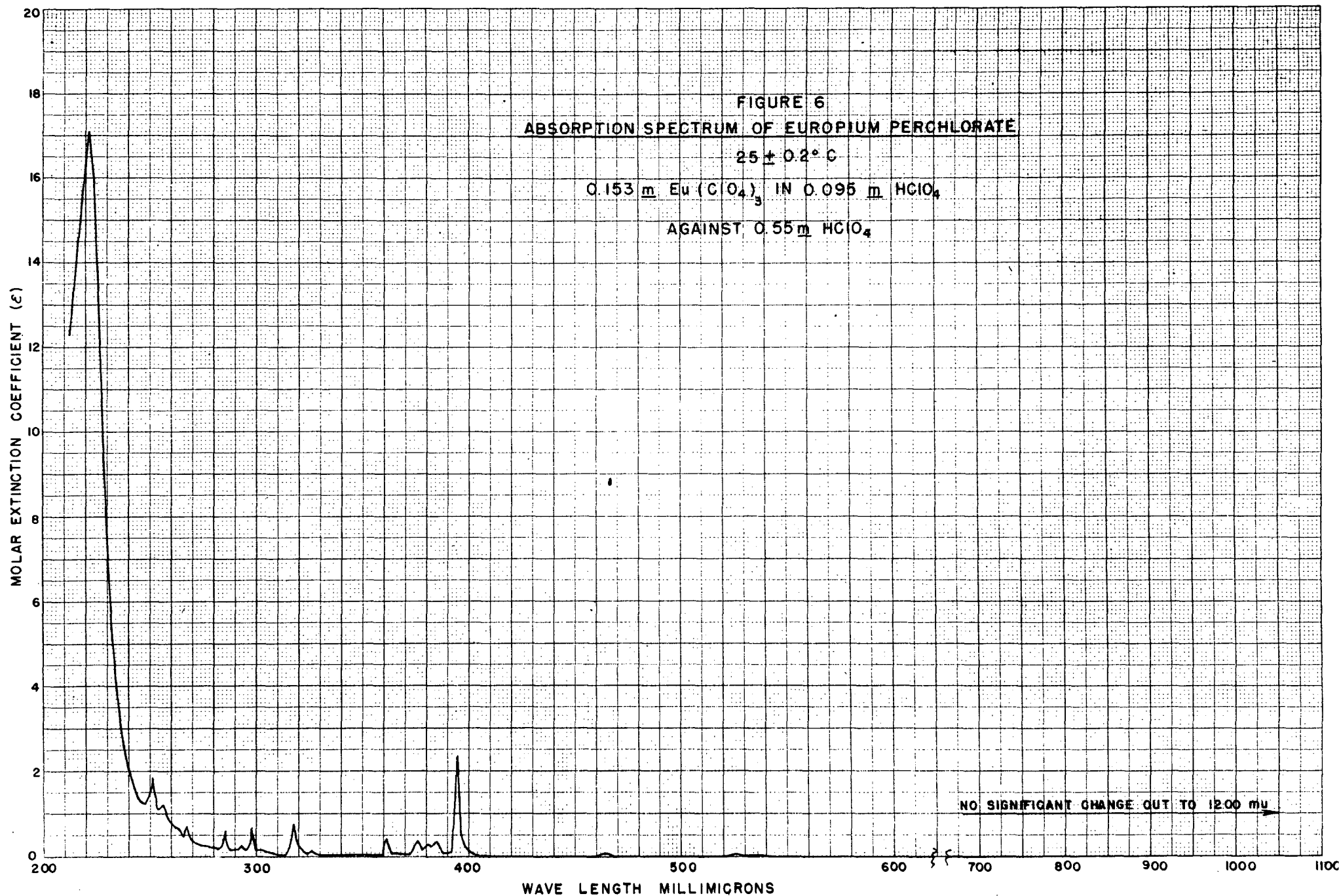


Promethium (Element 61). A supply of this element was not available for the present study. The only information available so far is that of Lantz and Parker⁽⁴⁸⁾. They determined the absorption spectrum of $\text{Pm}(\text{NO}_3)_3$ in 0.1 M HNO_3 , using a Beckman LD Spectrophotometer. The approximate values and peaks below are taken or calculated from their curves:

<u>Wave Length (mμ)</u>	<u>ε</u>
495	11.8
548	11.2
568	11.2
627	4.2(shoulder)
683	4.2
697	4.4
733	5.2
778	3.0
805	2.3

They believe that a large instrumental error was present below about 600 mμ. They ran a $\text{Nd}(\text{NO}_3)_3$ curve on the same instrument, and the results are listed in Table 6 for comparison with the present work. It will be seen that, in general, they are lower. It is probable that their instrument requires a broader effective band width than the DU model. The error which thus results will be discussed further on in this report. This would suggest that the ε values above may be too low, at least for the more reliable readings above 600 mμ.

Europium (Figure 6, Table 8). A new peak in the ultraviolet (at 222 mμ) was found in the present study, while several of the smaller peaks reported by Prandtl and Scheiner were missed. Their



peaks at 316.8 mμ and 374.9 mμ appeared only as shoulders on adjacent peaks in the present work.

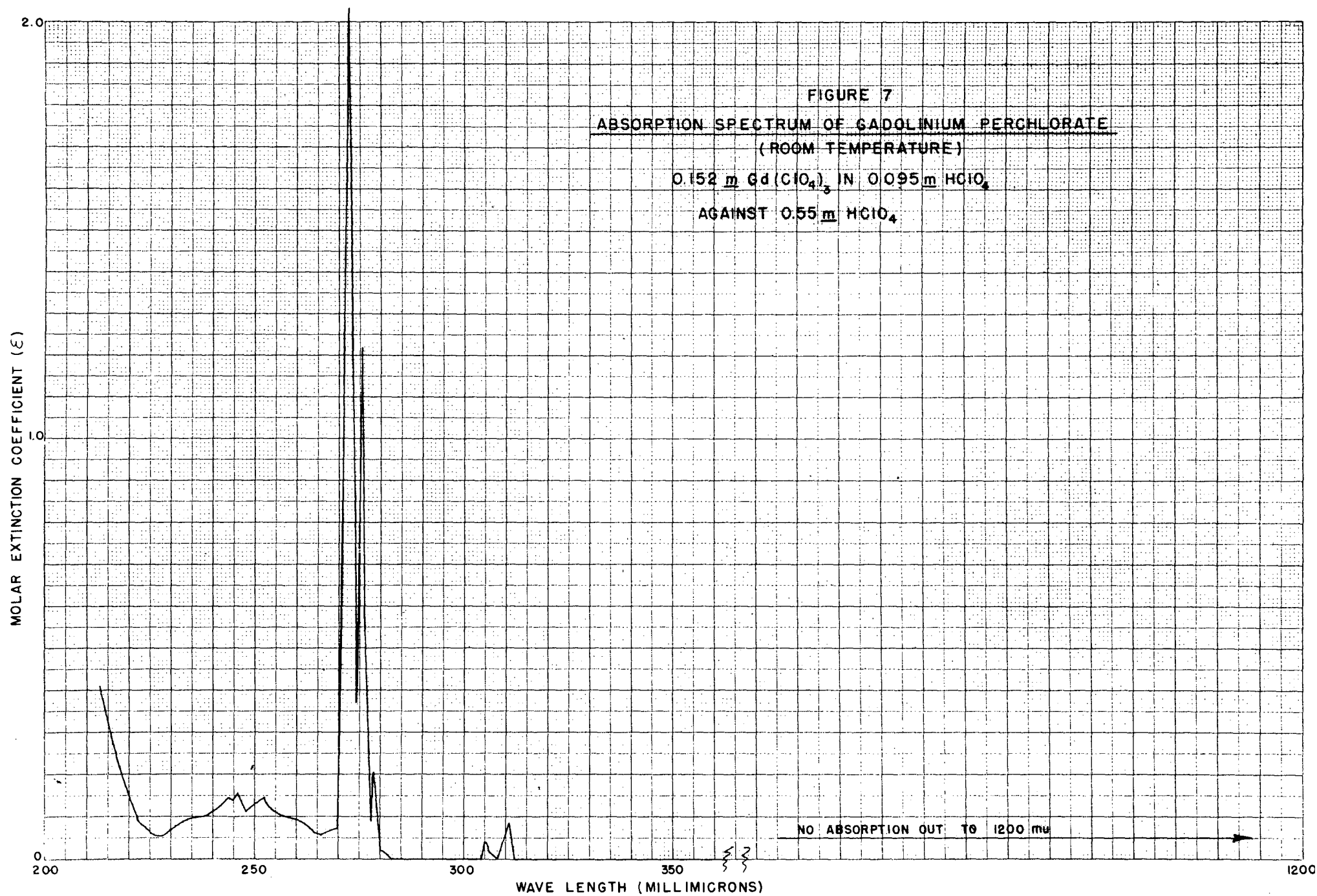
The redward shift produced by nitrate ion as compared to chloride ion is shown very well in the 464 mμ group studied by Freed and Weissman⁽²¹⁾.

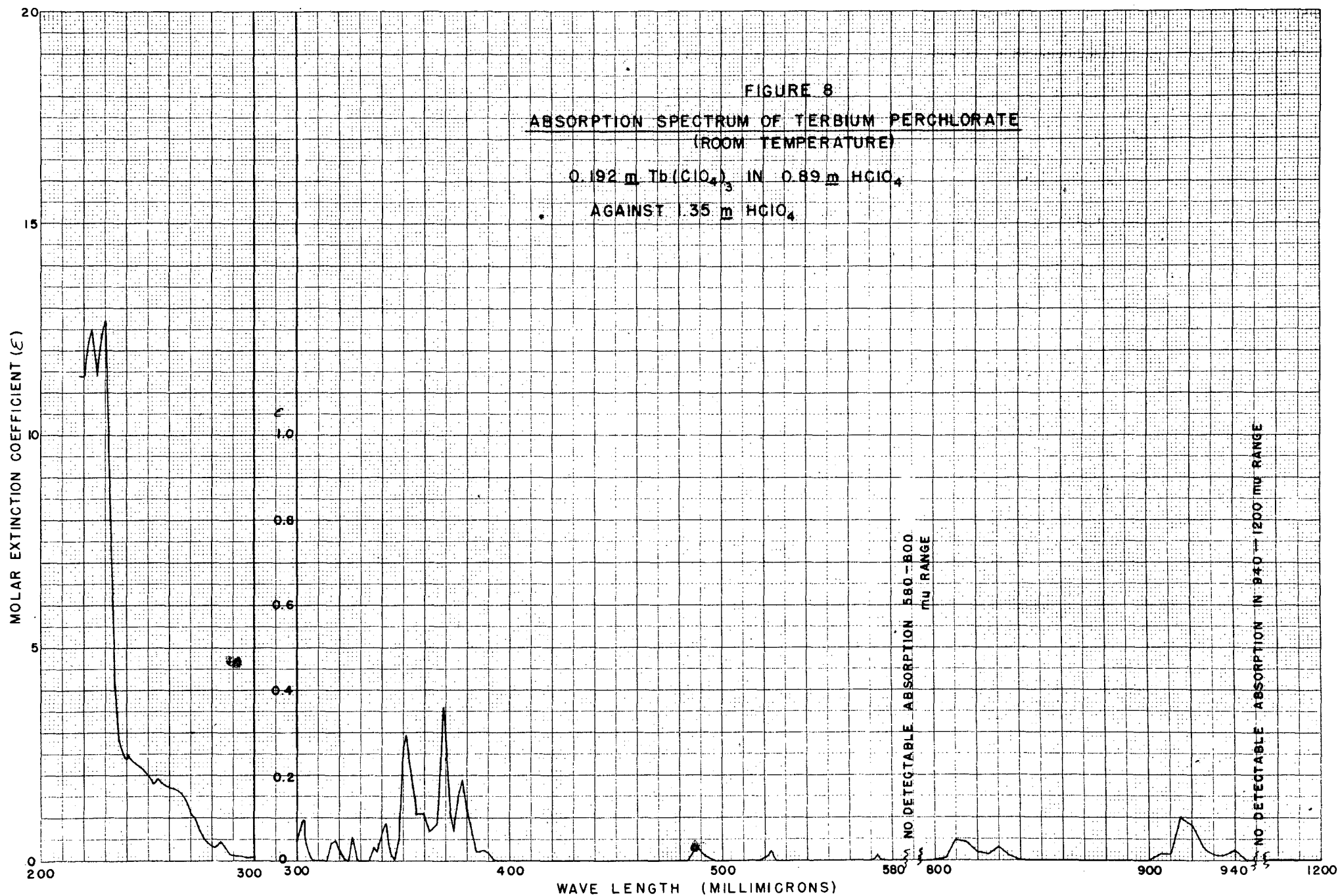
The only absorption reported for europium at wave lengths greater than 536 mμ is a peak found at 2133 by Rosenthal⁽²⁶⁾ using his borax pearl technique.

Gadolinium (Figure 7, Table 9). Very little data has been published on the absorption of gadolinium ion in solution. Such absorption as there is occurs in the ultraviolet - a fact which is presumably tied into the stable structure given to gadolinium by its half filled 4f shell.

The present work confirmed the peaks reported by Prandtl and Scheiner. The absorption peaks are very sharp and the 275.2 mμ peak could not be resolved from the 275.6 mμ absorption.

Terbium (Figure 8, Table 10). Several new peaks were observed for terbium absorption in the ultraviolet and in the near infrared, but some doubt is cast on their validity by the apparent dysprosium contamination present in the stock used. It is quite probable that the peaks seen in Figure 8 at 255, 325, 338, 351, and 388 mμ are from this source. The material used was reported as having less than 1% dysprosium present, but it seems quite likely that the level of contamination must have been somewhat higher. Because of this, it cannot be definitely said that the peaks at 224, 230, 815 and 915 mμ are due to terbium, rather than dysprosium absorption. Hoogschagen, Scholte and Kruyer⁽⁵⁰⁾ report sizeable dysprosium peaks at 805.5 and





at 909 mμ. No information is available on dysprosium absorption in the ultraviolet. The height of the 224 and 250 mμ absorption peaks shown in Figure 8 might be an argument for their being really due to terbium absorption rather than to the dysprosium contamination.

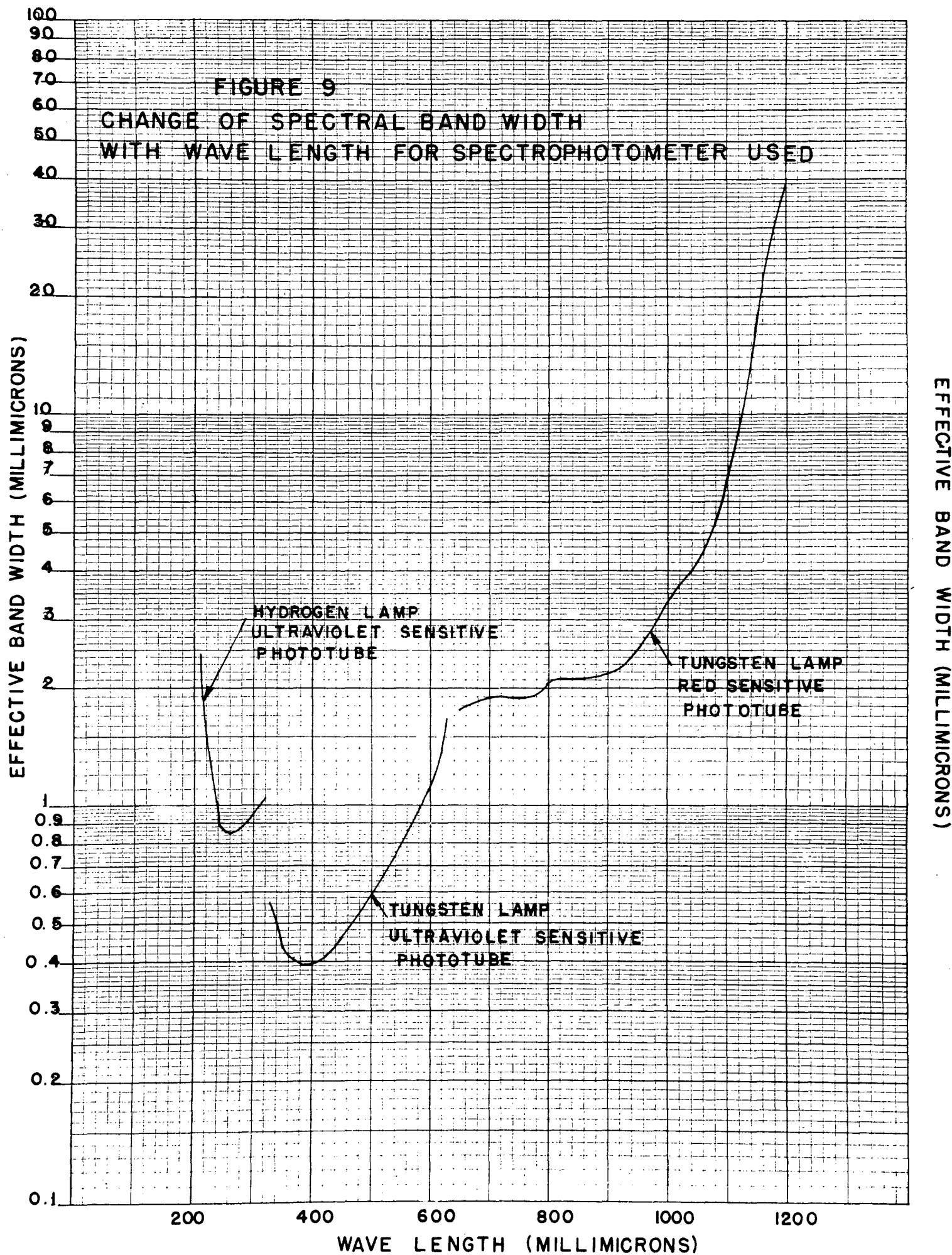
Discussion

The Dutch group, headed by Gorter^(40, 41, 43, 45, 46, 50), have been about the only other systematic investigators of the quantitative aspects of rare earth light absorption in solution. They have used their curves to graphically integrate an expression giving the electron transition probabilities represented by the various peaks. A similar calculation could be made on the basis of the data of the present work, although the results would probably have meaning only over a limited spectral range because of some of the errors discussed below.

The chief error in the present work arises from the limitations of the spectrophotometer in measuring absorption bands as narrow as those occurring in these rare earth solutions. Since many of the bands measured in the present study are of the order of a few angstroms in width, passage of wider light bands through the instrument results in a "light leak" around the peak, and a lower optical density reading is obtained as a result. The band width which can be obtained at any given wave length with the Beckman instrument is the resultant of two different effects, first, the intensity of the source for light of that wave length, and secondly the degree of dispersion of the light by the prism at that wave length. In the ultraviolet, the dispersion is excellent, but the benefit is largely

lost due to the lack of a high-intensity source of light of short wave lengths. The Beckman people furnish information⁽⁵¹⁾ which can be combined with the experimental slit openings found necessary at a given wave length to calculate the effective band width actually being used. Such calculations have been made for the present study and the results are presented graphically in Figure 9. It will be seen that the instrument gives quite satisfactory band widths in the 320-500 $m\mu$ range, but that considerable error is possible at either end of the spectrum when sharp absorption peaks are being measured. The widths in the 320-500 $m\mu$ range may be much better than shown in the graph, since the experimental slit widths are so small that the formula does not properly apply.

The effect of this can best be seen in Table 6 by comparing the data found with those of Hoogschagen, Snoek and Gorter^(45,46) on the absorption of neodymium solutions. These workers apparently did not get very narrow band widths in their first experiments over the 340-480 $m\mu$ range, and later repeated the work after redesigning their equipment. It will be seen that their second set of data agrees quite well with that of the present work in that range - both being much higher than their first figures. Above 500 $m\mu$, however, their figures start to show marked increases over those found in this study - the difference undoubtedly being due to the wider effective band widths being required at the longer wave lengths by the Beckman instrument. Presumably many of the other differences in the ϵ values reported in Tables 3 - 10 could be accounted for on the same basis. Most of the published work makes no mention as to the extent of this band width error in the figures given.



No studies have been made on the validity of Beers' Law (linear change in ϵ with concentration) in these rare earth solutions with the Beckman instrument as a part of the present work. On the basis of the discussion above, it would be expected that it would be followed fairly closely in the 320-500 m μ range, but that it would not be adhered to for peaks away from those limits. Fortunately, many of the rare earths studied have satisfactory peaks in this part of the spectrum, and these might be used for analytical purposes with the Beckman spectrophotometer.

The other errors involved in the present work are minor compared to this instrumental limitation. Weighing errors in preparing the solutions were of the order of $\pm 0.2\%$. Many of the solutions were made up in 2.0 ml volumetric tubes having straight sides. The error in reading the meniscus on such tubes is of the order of $\pm 0.5\%$.

No temperature control was used in the case of gadolinium or terbium, nor for some of the rechecks on the other rare earth solutions. The effect here is small, as is shown by the following data for gadolinium perchlorate absorption at the indicated wave lengths and temperatures:

<u>Wave length</u>	<u>Observed Optical Density</u>	
	<u>at 22° C</u>	<u>at 31° C</u>
272.8 m μ	0.308	0.311
275.5	0.184	0.182

The instrument will vary this much in reproducibility with these sharp peaks, and the indicated differences cannot be considered to be significant as far as small temperature changes are concerned.

Another possible source of error comes in the light absorption due to the perchlorate ion present. Before a measurement is made on the test cell with the Beckman instrument, the circuit is balanced at each new wave length against a cell which contains pure solvent. In this study, the perchlorate ion concentration in the solvent cell was adjusted as closely as possible to that of the test cell so as to eliminate any possible difference in perchlorate ion absorption. Table 2 indicates that the concentrations were not always exactly the same, so an error would come in if the perchlorate ion showed much absorption at that wave length. This is not of importance, save in the far ultraviolet, as is shown by Figure 10 which gives the light absorption of a solution of perchloric acid as compared to distilled water. There is substantially no light absorption by perchloric acid at wave lengths greater than 300 mμ.

Dr. B. B. Cunningham has pointed out that for some of the rare earths (praseodymium, gadolinium, neodymium), the observable ultraviolet absorption is not tremendously greater than the absorption due to the "forbidden" transitions in the visible range. This might be considered as evidence throwing some doubt on the current assumption that the ultraviolet absorption represents transitions differing markedly in probability from those of the visible.

Conclusion

A series of reference curves have been prepared showing the light absorption of the rare earth perchlorates from lanthanum through terbium, with the exception of promethium. The data for these curves have been compared with those found in the literature, and the sources of error in the present work have been discussed.

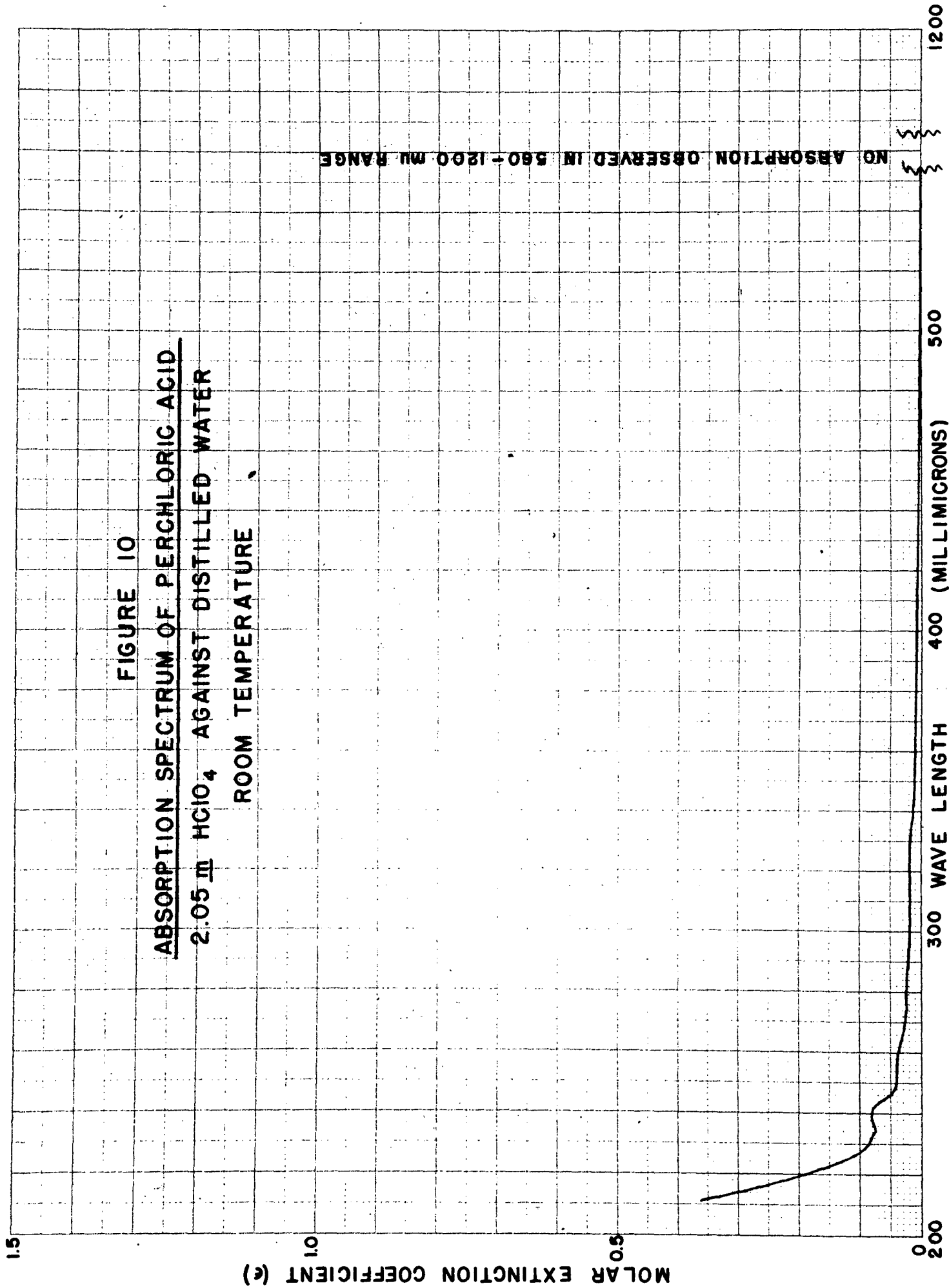


FIGURE 10
ABSORPTION SPECTRUM OF PERCHLORIC ACID
2.05 M HClO_4 AGAINST DISTILLED WATER
ROOM TEMPERATURE

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Table 1. Rare Earth Stocks Used in Preparing Solutions

Element	Compound	Source	Purity
Lanthanum	La_2O_3 Ignited from oxalate	Ames, Iowa Sample C-6-77A	No other rare earths detectable. Would not be able to determine up to 1% CeO_2 spectrographi- cally.
Cerium	Ce metal	Ames, Iowa Sample A-6-90	May be up to 1% La metal No other rare earths detectable.
Praseodymium	Pr_6O_{11}	E. R. Tompkins Clinton Labora- tories, Tenn.	No detectable impurities by radioactivity analysis after neutron pile irradiation
	Pr_6O_{11}	Adam Hilger Ltd Lab.No. 1533	No lines for rare earths, Co, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Si, Tl, V, Zn, Zr
Neodymium	Nd_2O_3	Hilger F546 Lab. No. 6783	Traces: Yb, Ca, Na, Fe No lines for: Ba, Er, Eu, Cd, La, Lu, Pr, Sr, Tb, Y
Samarium	Sm_2O_3	Research Chemicals Laboratory, Burbank, California.	Marked >99% pure
	Sm_2O_3	Hilger F548 Lab. No. 6784	Few Gd lines on spectrogram No lines for other rare earths.
Europium	Eu_2O_3	Purified this laboratory from "McCoy" $\text{Eu}_2(\text{C}_2\text{O}_4)_3$ 10 H ₂ O. Weighed as Eu_2O_3 .	Ce, Dy, Gd, Ho, Nd, Pr, Sm, Th and Y not detectable (Limit = 0.2%)
Gadolinium	Gd_2O_3	Hilger Lab. No. 1073	1 Yb line (barely visible) No lines for other R. E.
Terbium	Weighed as Tb_4O_7 after igniting $\text{Tb}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	National Bureau of Standards. "#50".	Dy - up to 1% Gd - up to 0.1% Y - Trace

Table 2. Rare Earth Solutions Used for Measuring Absorption Spectra

Element	Conc. R^{+++}	Final Solution Conc. excess $HClO_4$	Total Conc. ClO_4^-	μ	$HClO_4$ Conc. of Comparison Solution	Used for Spectral range: ($\text{\AA}$)	Temperature Control
Lanthanum	0.154 M	0.098 M	0.56 M	1.02	0.55 M	Complete	$25 \pm 0.2^\circ C$
Cerium	0.0147	0.91	0.95	1.0	0.94	280-1100 $\text{\AA}$	$25 \pm 0.2^\circ C$
	0.00147	0.94	0.94	0.95	0.88	214-280	$25 \pm 0.2^\circ C$
Praseodymium	0.0725*	0.665	0.88	1.1	0.88	212-320	$25 \pm 0.2^\circ C$
	0.119*	0.172	0.53	0.89	0.55	320-1000	$25 \pm 0.2^\circ C$
Neodymium	0.152	0.088	0.54	1.0	0.55	Complete	$25 \pm 0.2^\circ C$
Samarium	0.651	0.10	2.05	4.0	2.05	220-330	Room Temperature
	0.147**	0.11	0.55	0.94	0.55	330-1100	$25 \pm 0.2^\circ C$
Europium	0.153	0.095	0.55	1.02	0.55	Complete	$25 \pm 0.2^\circ C$
Gadolinium	0.152	0.095	0.55	1.01	0.55	Complete	Room Temperature
Terbium	0.192	0.89	1.46	2.03	1.35	Complete	Room Temperature

* From Clinton Laboratories (see Table 1)

** From Adam Hilger, Ltd. (see Table 1)

Table 3. Light Absorption by Solutions of Lanthanum Ion

Present Work		Ref. 16	54	
See Table 2		Chloride in H ₂ O 4M ²	Nitrate 25 g/l	
λ mu	ϵ	λ mu	λ	ϵ
212.3*	11.0	No absorption in 820-1160 range	355	0.06

* Not a peak. Absorption at lower limit of instrument.

Table 4. Light Absorption by Solution of Cerous Ion.

Present Work See Table 2		Ref. 34 38 Ce ₂ (SO ₄) ₃ in H ₂ O (0.0467-0.4863%)		35 Chloride? in H ₂ O (0.018-0.7%)			1 Chloride in weak acid	
				Chloride? in conc.HCl (0.007-0.35%)			Chloride? in EtOH (0.017-0.125%)	
λ m μ	ϵ	λ m μ	ϵ	λ m μ	λ m μ	λ m μ	λ m μ	λ m μ
213.8*	436							
221.0	476	223.0						
238.0	655	240.0	628	238.5	241.5	239.0	237.2	
					248.0			
253.0	755	254.0	738	252.5	258.5	252.0	253.0	
296.0-296.6	25	296.0	36	295.0	310.0	295.0	296.6	

* Not a peak. Absorption at lower limit of instrument

Table 4 (Cont'd)

36	39	16	26	37	54	
Chloride in H ₂ O M/1000- M/50	Chloride in H ₂ O 0.001M- 0.025M	Chloride in H ₂ O 8N	Oxide dissolved in borax pearl	Chloride or Sulfate	Nitrate 23.1 g/l	
λ	λ	λ	λ	λ	λ	ϵ
mp	mp	mp	mp	mp		
210.5 220-225 235-241				210.5		
250-255 297.0	255 296	No absorption in 820-1160 mu range				
			1650		354	0.17

Table 5. Light Absorption by Solutions of Praseodymium Ion

Present Work		Ref. 40 43*		42		41		52		53		26	
See Table 2		Chloride in (0.0594M- 0.1127M)		Chloride in H ₂ O "15%"**		Chloride in H ₂ O 0.169M Nitrate in H ₂ O 0.169M		Chloride		Chloride?		Oxide in Borax Pearl	
λ m μ	ϵ	λ m μ	ϵ	λ m μ	ϵ	λ m μ	ϵ	λ m μ	ϵ	λ m μ	ϵ	λ m μ	ϵ
214.0	23.4												
218.0	23.2												
444.0	9.8	444.0	9.1	443.6	0.87			444	6.2	444	7.3		
468.9	4.35	468.8	3.6	468.4	0.49								
482.5	3.85	481.9	3.6	483.2	0.34								
590.0	1.86	589.0	1.87	585.5	0.26								
		597.5		597.0	0.16								
1025	0.23					1020(Cl ⁻)	0.17						
						1020(NO ₃ ⁻)	0.16						
												1525	
												1650	

*Wave length assignments from Prandtl and Scheiner

Assumed to be 15% PrCl₃·7H₂O in calculating ϵ values*Glass density of 3.5 assumed in calculating ϵ values

Table 5 (Cont'd)

54	27**	1	17	8	44	28	18	16	25
Nitrate in H ₂ O 25 g/l	Oxide in soda lime glass (10% as oxide)	Chlorides in weak acid	Sulfate in H ₂ O (0.06-0.17%)	"Slightly Acid Chlor- ides"	Nitrates in H ₂ O	?	Sulfate in H ₂ O	Chloride in H ₂ O 4-8M	Borax beads (btw. 10- 50% Pr salt)
κ mu	κ mu	κ mu	κ mu	κ mu	κ mu	κ mu	κ mu	κ mu	κ mu
			215				256.0 260.5 273.0		
444	2.4	444.0		444.1					
470	1.7	468.8		469.0	468.4				
		481.9		481.9	482.0				
590	1.3	589.0		589.0	591.7				
		597.7		597.4	595.4				
1000	0.07	760 0.02 1000 0.03						1018.2	
		1450 0.5				1540			1440
		1900 0.6				1942			1920

Table 6. Light Absorption of Solutions of Neodymium Ions Part I

Present Work		Ref. 45		46		47		48		52	
See Table 2		Chloride in weak HCl 0.171M		Chloride in H ₂ O 0.061M 0.303M		Chloride in H ₂ O "2%"		In 0.1N HNO ₃		Chloride	
λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ
mu		mu		mu		mu		mu		mu	
250.4	0.41										
259.8	0.42										
290.5	0.28										
298.4	0.32	298.4	0.087								
313.8	0.13										
329.0	0.55			328.2	0.57						
340.0	0.20			340.0	0.26						
346.8	2.91	346.5	0.17	346.5	2.78						
350.7	2.13	350.4	0.32	350.4	2.08						
354.0	4.13	353.8	0.17	353.8	4.12						
380.8	0.026	380.6	0.06	380.6	0.04						
418.5	0.059	418.2	0.10								
427.2	0.60	427.2	0.28	427.2	0.76						
433.2	0.11	433.2	0.13	433.2	0.11						
461.0	0.42	461.2	0.52	461.2	0.50	441.5- 465.0	0.86				
469.4	0.57	469.1	0.48	469.1	0.59						
475.7	0.57	475.5	0.57	475.5	0.65	472.5- 480.0	0.51				
480.0	0.27	480.2	0.15	480.2	0.24						
509.0	0.9	509.0	1.69			503- 510	0.78				
512.3	1.50	512.9	1.70								
522.3	3.74	521.9	3.9			520.0	1.4	522	1.24		
532.0	0.35	532.0	0.43								
575.5	5.97	575.2	7.4			567.5- 577.0	1.6	575	1.73		
578	4.8	578.4	5.4								
623	0.059										
627.5	0.066	628.8	0.15								
636.5	0.053	636.9	0.13								

Table 6. Part II

53		54		27		1	8	44	18	16
Chloride?		Nitrate in H ₂ O 25 g/l		As oxide (10%) in soda lime glass		Chlorides in weak acid	"Slightly Acid Chlorides"	Nitrate in Water	Sulfate in Water?	Chloride in H ₂ O (N - 8N) (61)
Λ	ε	Λ	ε	Λ	ε	Λ	Λ	Λ	Λ	Λ
μy		μy		μy		μy	μy	μy	μy	μy
						250.4			250.5	
						258.9				
						259.8			260.0	
									273.0	
									277.5	
						289.9				
						291.7				
						298.4				
						299.7				
						313.8				
						328.2				
						340.0				
						346.5				
		350	1.7			350.4				
						353.8				
						355.7				
						380.6	380.3			
						418.2	418.5			
		430	0.06			427.2	427.3			
						429.6	429.3			
						433.2	433.1			
		465	0.33			461.2	461.2	460.5		
						469.1	469.1	469.2		
								473.5		
						475.5	475.5	475.2		
						480.2	480.3			
							486.9			
						509.0	509.1	508.8		
						512.9	512.3	511.2		
		520	1.6			520.7	520.5	520.6		
						521.9	522.2	522.4		
							525.3	524.5		
								528.5		
						532.0	531.9	532.4		
							572.6			
							573.1			
						575.2	574.8			
		578	3.5				578.2			
							581.6			
							582.3			
							588.8			
						622.8	622.8			
							625.1	625.3		
						628.8	628.6			
		635	0.11			636.9	637.4			

Table 6; Part II (Cont'd)

		685	0.39			678.6 687.7	672.0 678.6 687.7			
740	6.27	742	4.4							
795	7.78	800	5.1	770	0.35					
		865	1.3							866.0 875.5 889.1
				1630	0.038					
				2430	0.27					

Table 7. Light Absorption of Samarium Ions in Solution

Present Work		Ref. 49		41		54		52		53	
See Table 2.		Oxide dissolved in HNO_3 . 0.3-0.9M		Nitrate or chloride in weak acid. 0.283M		Nitrate in H_2O 25 g/l		Chloride		Chloride?	
λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ	λ	ϵ
$\mu\mu$		$\mu\mu$		$\mu\mu$		$\mu\mu$		$\mu\mu$		$\mu\mu$	
235.5	1.26										
238.5	1.26										
252.0	1.04										
273.0	0.095										
279.0	0.086										
289.7	0.083										
305.5	0.15										
317.5	0.34										
332.0	0.16										
344.5	0.52										
354.0	0.095										
362.0	0.69	362.0*	0.22			365	0.30				
374.6	0.66	374.6*	0.78								
390.5	0.31	390.5*	0.65								
401.6	2.98	401.6*	3.8			402	0.92	401	3.38	401	3.09
407.4	0.56	407.4*	0.59								
414.7	0.45										
416.0	0.43**	416.5*	0.54								
418.0	0.38**										
440-442	0.16	442.0*	0.15			440	0.11				
451.1	0.068	451.3*	0.05								
464.0	0.50	463.9*	0.56								
479.0	0.55	479.3*	0.56			480	0.44				
489.2	0.12**										
499.5	0.075	499.5*	0.07								
		523.5	0.008								
		530.0*	0.015								
558-559	0.054	559.3*	0.03								
		581.0	0.016								
955	0.35			949	0.39	950	0.30				
1095	1.42			1087	1.63						

*Wave length assignments from Prandtl and Scheiner.

**Appears as a shoulder on another peak.

Table 7 (Cont'd)

27		1	8	16	15	26	25
Oxide (10%) in soda lime glass		Chloride in weak acid	"Slightly acid Chloride"	Chloride in H ₂ O 8M	Ethyl Sulfate in H ₂ O	Oxide in Borax Pearl	Borax Bead Sm salt content 10-50%
μ	ε	μ	μ	μ	μ	μ	μ
		235.4					
		238.8					
		273.7					
		279.0					
		290.0					
		305.5					
		317.5					
		332.6					
		344.4					
		353.5					
		362.0					
		374.6	374.0				
		390.5	390.5				
		401.6	401.3				
		407.4	407.1				
		414.8	415.4				
		416.4	417.7				
		418					
		438.9-443	441.1				
		451.3					
		463.9	463.6				
		479.3	479.4				
		489.2	489.3				
		499.5	499.5				
			529.7				
		559.3	559.4				
1100	0.12		1100	950.8 1086.9	948.6 1087.9	940 1075 1217 1360 1465 1525 1595 1640	1250 1390
1470	0.38						1500 1560
1920	0.06					2033	
2620	0.12						
4100	0.3						

Table 8. Light Absorption of Europium Ions in Solution

Present Work		Ref. 1	21		26	16	8	53	56	54
See Table 2		Chloride in weak acid	Chloride in H ₂ O 0.01M-0.1M	Nitrate in H ₂ O 0.01M-0.1M	Oxide in borax pearl	Chloride in H ₂ O 3N	Slightly Acid Chloride	?	Chloride 0.268M	Nitrate 18.2g/l
λ	ϵ	λ	λ	λ	λ	λ	λ	λ	λ	λ
μ		μ	μ	μ	μ	μ	μ			
222.0	17.1									
251.3	1.84	251.3								
256.2	1.20	256.0								
267.4	0.686	267.6								
285.6	0.601	285.3								
		286.1								
293.5	0.268	293.0								
297.8	0.673	298.0								
316.8	0.490**	316.8								
317.7	0.739	317.9								
		320.4								
326.0	0.124	325.3-327.3								
361.7	0.418	361.7								
374.9	0.313**	374.9								
376.0	0.346	376.6							374.9	0.3
380.9	0.288	380.9							376.6	0.3
385.3	0.320	385.3							380.9	0.26
394.3	2.36	394.3							385.3	0.3
465.0	0.052	464.7	464.0	464.4				390	394.3	2.4
			464.5	464.8				2.65	399.0	0.13
			464.9	465.4					465.1	0.035
526.2	0.078	525.5					525.7		525.5	0.08
536.0	0.029	536.0					535.3			
					2133	No absorption in 820-1160 range				

** Appears as shoulder on another peak

Table 9. Light Absorption of Gadolinium Ion in Solution

Present Work		Ref. 1	16	27	53	54	
See Table 2		Chloride in in Weak Acid	Chloride in H ₂ O 5N	In Soda Lime Glass (10% as oxide)	?	Nitrate 25 g/l	
λ	ϵ	λ	λ	λ	λ	λ	ϵ
mu		mu	mu	mu	mu	mu	
243.6	0.145	243.6					
246.0	0.158	245.7					
252.2	0.147	252.1					
272.7	2.04	272.9			272.9	1.81	
275.6	1.22	275.6					
276.2	(0.572)**	276.2					
278.5	0.204	279.1					
305.0	0.042	305.1-305.5					
310.8	0.086	310.8					
			No absorption in 820-1160 range	No absorption in 500-2800 range		350	0.08

** Lost in the adjacent 275.6 mu peak.

Table 10. Light Absorption of Terbium Ions in Solution

Present Work		Ref. 1	16	26	54	56	
See Table 2		Chloride in weak acid	Chloride in H ₂ O 1N ²	Oxide in Borax Pearl	~0.16M Chloride	Chloride 0.412M	
λ	ϵ	λ	λ	λ	λ	λ	ϵ
mpu		mpu	mpu	mpu	mpu	mpu	
224.0	12.5						
230.0	12.7						
242.0	2.39	241.8					
(255)	(1.92)						
		305.2					
		311.1					
318.	0.047	316.0-319.6					
341.8	0.109	341.8					
(351.0)	(0.343)						
(358.0)	(0.140)						
369.0	0.294	369.4				369.4	0.26
378	0.183	375.2-379.7				377.3	0.13
487.5	0.031	487.0				487.5	
522.5	0.021	522.5					
573.0	0.016	572.8					
815-820	0.042						
915	0.099						
			No absorp- tion in 820- 1160 range	No absorp- tion in 500- 2500 range			

() Probably due to Dysprosium Contamination.

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