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Studies of the Fractional Separation of the  
Rare Earth Elements

Reaction of the Anhydrous Chlorides with Ethyl Benzoate

by

Maryruth Claypool Jeffries

Submitted in Partial Fulfilment of the  
Requirements for the Degree of  
Bachelor of Science

from the  
Massachusetts Institute of Technology  
1945

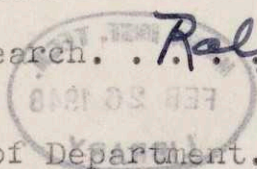
Signature of Author. . . *Maryruth C. Jeffries* . . . . .

Department of Chemistry, February 1945.

Signature of Professor

in charge of Research. . . *Ralph C. Young* . . . . .

Signature of Head of Department. . . . .



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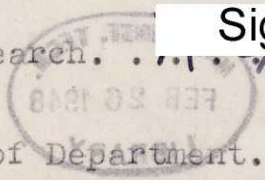
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The author wishes to express her appreciation to Professor R. C. Young, supervisor of this thesis, who was always ready with assistance and encouragement and whose constant efforts have made this study a most valuable and enjoyable experience.

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STUDIES OF THE FRACTIONAL SEPARATION OF THE RARE EARTH ELEMENTS  
REACTION OF THE ANHYDROUS CHLORIDES WITH ETHYL BENZOATE

I The Rare Earth Elements

Except for lanthanum, element number 57, there seemed to be no place in the periodic chart for a group of elements of atomic numbers 57 to 71 called the rare earths. When the structure of the atoms was determined it showed that all 15 members of this group should logically be placed in this one space. The outer orbits of all of the rare earths are identical, each member putting its additional electron in an inner shell. This accounts for the similarity of properties between the members of this group which is perhaps its most distinguishing feature. What differences there are vary gradually with the atomic numbers; the atomic weights rise from 139 to 175; the basicity decreases as the weight goes up. The colors of the ions fall into a definite pattern ranging from colorless thru green, red and yellow to colorless and back in the reverse order to colorless again.

In general, their properties fall halfway between those of aluminum and barium. They form insoluble hydroxides, carbonates, and oxalates. Their salts are hydrolyzed less than those of aluminum. The metals react vigorously with hydrogen and form hydrides, in this case resembling calcium and barium. All of the rare earths exhibit an oxidation number of three. However, cerium and praseodymium may also have a valence of four and samarium, europium and ytterbium a valence of two. Such exceptional com-



pounds are unstable and react with water except in the case of quadrivalent cerium. This property of change of valence is made use of to remove cerium and has been used to remove small amounts of samarium, europium and ytterbium.

It is not surprising that elements whose compounds are so similar are found together in nature. Three other elements, thorium, scandium and yttrium are found with the rare earths. Cerium makes up nearly one third of the deposits. The even atomic numbered elements are always more abundant than the neighboring odd numbered ones. The entire group forms about .001% of the earth's crust which is several times more abundant than tin, mercury, silver, cadmium, antimony, molybdenum, tungsten, bismuth, platinum, or gold. Deposits are found in many parts of the world, notably in Brazil and India where the heavy insoluble phosphates have been washed down toward the sea where they form huge beds. Cerium was used in gas mantles and is used on enamelware. An alloy of the rare earths and iron is used in gas lighters and the rare earth fluorides are used in searchlights. The oxides are useful as catalysts.



## II The Problem of Separation

The rare earth elements usually occur in deposits consisting of a large number or all of the group. Since their properties vary so slightly from one member to the next, no easy method of separation presents itself except for the cases previously mentioned. Any procedure used must be based upon the slight progressive differences between these elements and is necessarily some sort of fractionation process.

The difference in basicity which decreases with increase in atomic weight is the basis for several methods: fractional precipitation of the hydroxides by either organic or inorganic bases, fractional decomposition of the nitrates.

Variation in solubility makes possible fractional precipitations and crystallizations. Fractional crystallization is the present commercial method although the steps necessary are numerous if a pure product is desired; at present it is carried out only on a small scale.

There is, therefore, a need for a more efficient method involving fewer steps. Although many of the purposes for which the rare earths are used today require simply a mixture of these elements much more may be done with them when a cheap commercial supply of each member is obtainable in a fairly pure state.



### III The Method to be Used

A few years ago Young found that thorium bromide reacts with ethyl benzoate to form the benzoate and ethyl bromide. This suggested the possibility that the anhydrous rare earth halides might react similarly with organic esters and at differing rates, enabling a separation to be made because any unchanged chloride would be soluble in water, while the benzoate formed would be insoluble. The reaction rate was found to increase with increase in the atomic weight of the element.

In carrying out such a reaction it is necessary first to prepare the anhydrous chloride which is introduced into the reaction tube and covered with anhydrous ethyl benzoate. The mixture is heated over a bath boiling at the desired temperature. The ethyl chloride evolved is collected and measured as an indication of how far the reaction has proceeded. After about 30% of the chlorides have reacted the flask is cooled and the excess ethyl benzoate removed with petroleum ether. The residue is then extracted with water separating the insoluble rare earth benzoates of the portion which reacted from the soluble unchanged chlorides.

Fractionations of this type had already been made in this laboratory using mixtures consisting of known amounts of neodymium and lanthanum and of proseodymium and neodymium. However, the method had not yet been used on a natural mixture of the rare earths. Four samples of raw material were



available for this purpose: two rare earth oxide mixtures from the Maywood Chemical Co., some rare earth chloride crystals from Rohm and Haas Co. and an oxide mixture from the Lindsey Light and Chemical Co. All of these samples contained cerium which was to be removed before the fractionation was begun. It was decided to start on one of the oxide mixtures from the Maywood Co.

IV Methods of Control

If a separation method is to be studied there must be some way of determining the composition of the two fractions resulting from the partial reaction as well as an analysis of the original material. The lack of distinguishing properties between the members of the rare earth group makes analysis difficult in the same way as it does a separation; the elements cannot be determined one by one. One indirect method utilizes the fact that the magnetic susceptibilities vary progressively. By using a magnetic balance changes in composition may be observed. However, such a balance was not immediately available and other methods were used.

The average atomic weight may be calculated if the chloride in a weighed sample of the anhydrous chloride is known. This method was used; a few grams of the chloride were dehydrated by heating in HCl gas, weighed dissolved in H<sub>2</sub>O and the chloride precipitated with excess AgNO<sub>3</sub>. The AgCl was filtered and weighed.

Many of the rare earths have characteristic colors in ionized solution(Nd<sup>+++</sup>pink, Pr<sup>+++</sup>greenish yellow). The solutions studied were all pale pink indicating large amounts of neodymium present. The light absorption of the ions of these elements makes them adaptable to analysis by the spectrophotometer.

The calibration curves of percent transmission versus concentration of neodymium and praseodymium prepared by Vander



Weyden for the spectrophotometer and for the color analyser in the department of physics were available. Weighed amounts of the oxide to be determined were dissolved in HCl and diluted to a definite volume. Distilled water was used as a blank. From the percent transmission at a wave length of 443 millimicrons for praseodymium and 520 millimicrons for neodymium the molarity of these ions was found and the percent by weight in the oxide calculated. The results obtained on the spectrophotometer were most inconsistent and the curves made by the color analyzer were relied upon entirely.

## V Removal of Cerium

Cerium is the only one of the rare earths which can be easily separated by ordinary analytical methods. This is possible since cerium is the only one of the group whose valence four compounds are stable. All of the methods of separation tried were based upon the same principle: salts such as nitrates and bromates of quadrivalent cerium hydrolyze to form insoluble compounds while the other rare earths remain soluble in valence three.

The methods in the literature seem to be for the separation of pure cerium, not to obtain a cerium free rare earth mixture. A slight modification of the bromate method of Charles James was found to be very satisfactory.

200 grams of the mixed oxides were dissolved in 570 cc. of concentrated  $\text{HNO}_3$ . The  $\text{CeO}_2$  forms the complex  $\text{H}_2\text{Ce}(\text{NO}_3)_6$ . If any  $\text{Ce}_2\text{O}_3$  is present it dissolves in the nitrate as do the other rare earth elements present. The mixture was then evaporated on the hot plate until almost completely dry, driving off two molecules of  $\text{HNO}_3$  from the  $\text{H}_2\text{Ce}(\text{NO}_3)_6$  leaving  $\text{Ce}(\text{NO}_3)_4$  which then hydrolyzed to form the insoluble basic salt  $\text{OH-Ce}(\text{NO}_3)_3$ . Water was added and the precipitate filtered off. 40 grams of  $\text{KBrO}_3$  were added and the mixture was boiled. If any  $\text{OH-Ce}(\text{NO}_3)_3$  was still in solution it precipitated as the even more insoluble  $\text{OH-Ce}(\text{BrO}_3)_3$ . Any cerium present in valence three was oxidized up to valence four by the bromate ion forming  $\text{Ce}(\text{BrO}_3)_4$ . The solution was filtered



off and evaporated to complete dryness to drive off any  $\text{HNO}_3$  and prevent it from reacting with the marble later, introducing calcium into the solution. Water was then added to react with the  $\text{Ce}(\text{BrO}_3)_4$  to form insoluble  $\text{OH-Ce}(\text{BrO}_3)_3$  and  $\text{HBrO}_3$ . The precipitate was filtered off. To prevent the last reaction from reversing marble was added to remove the hydrogen ion. The mixture was boiled and filtered; the filtrate showed no cerium when tested with  $\text{NaAc}$  and  $\text{H}_2\text{O}_2$ .

$\text{NH}_4\text{OH}$  was added to a small portion of the solution and the hydroxides filtered off.  $\text{K}_2\text{C}_2\text{O}_4$  was added to the ammoniacal solution. Only a small amount of calcium was present.

Attempts to use chlorides in place of the nitrates,  $\text{CaCO}_3$  instead of marble or  $\text{KBr}$  in addition to  $\text{KBrO}_4$  were unsuccessful.

	$\text{CeO}_2$	$\text{Ce}_2\text{O}_3$
$\text{HNO}_3$	$\text{CeO}_2 + 6\text{HNO}_3 = \text{H}_2\text{Ce}(\text{NO}_3)_6 + 2\text{H}_2\text{O}$	$\text{Ce}_2\text{O}_3 + 6\text{HNO}_3 = 2\text{Ce}(\text{NO}_3)_3 + 3\text{H}_2\text{O}$
evap.	$\text{H}_2\text{Ce}(\text{NO}_3)_6 = \text{Ce}(\text{NO}_3)_4 + 2\text{HNO}_3 \uparrow$	
$\text{H}_2\text{O}$	$\text{Ce}(\text{NO}_3)_4 + \text{H}_2\text{O} = \underline{\text{Ce}(\text{NO}_3)_3^{\text{OH}}} + \text{HNO}_3$	
$\text{KBrO}_3$	$\text{Ce}(\text{NO}_3)_3^{\text{OH}} + 3\text{BrO}_3^- = \underline{\text{Ce}(\text{BrO}_3)_3^{\text{OH}}} + 3\text{NO}_3^-$	$6\text{H}^+ + 5\text{Ce}^{+++} + 21\text{BrO}_3^- \Rightarrow 5\text{Ce}(\text{BrO}_3)_4 + \frac{1}{2}\text{Br}_2 + 3\text{H}_2\text{O}$
evap.		
$\text{H}_2\text{O}$		$\text{Ce}(\text{BrO}_3)_4 + \text{H}_2\text{O} \rightleftharpoons \text{Ce}(\text{BrO}_3)_3^{\text{OH}} + \text{HBrO}_3$
marble		$2\text{HBrO}_3 + \text{CaCO}_3 = \text{Ca}(\text{BrO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$



## VI The Average Atomic Weight

Next the average atomic weight of the remaining rare earths was to be calculated by determining the amount of chloride in a weighed sample of anhydrous chlorides.

The filtrate from the cerium removal was heated to boiling and the rare earth oxalates precipitated by an excess of hot  $\text{H}_2\text{C}_2\text{O}_4$  solution. The oxalates were filtered by suction while hot and washed with hot dilute  $\text{H}_2\text{C}_2\text{O}_4$  and hot  $\text{H}_2\text{O}$ . The pink crystals were dried in air overnight. Three grams were ignited at  $600\text{-}750^\circ\text{C}$  for 2-3 hours. The oxide was dissolved in concentrated  $\text{HCl}$  and evaporated to dryness in the steam bath. It was then ground in an agate mortar and allowed to stand in a desiccator ( $\text{CaCl}_2$ ).

A Sweeney  $\text{HCl}$  generator was set up under the hood. It consisted of a small dropping funnel full of concentrated  $\text{HCl}$  which was slowly let into concentrated  $\text{H}_2\text{SO}_4$  thru a capillary tube. The  $\text{HCl}$  gas generated was led off thru the stopper of the large separatory funnel which contained the  $\text{H}_2\text{SO}_4$ . It was bubbled thru concentrated  $\text{H}_2\text{SO}_4$  to dry it and then passed into the reaction tube which was encased in a cylindrical furnace.

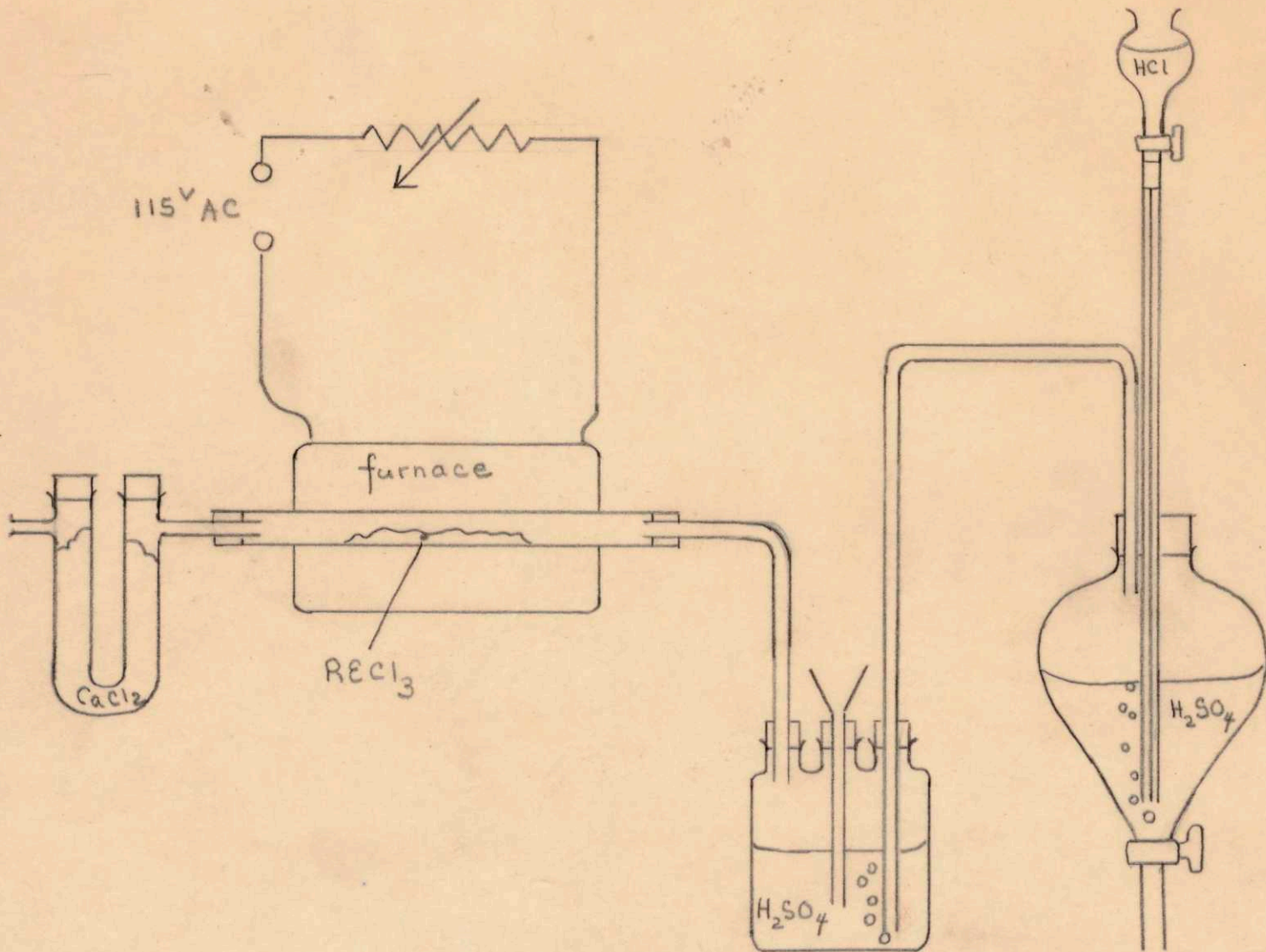
The chlorides were introduced into the center of the tube by placing them in a smaller glass tube and pushing them out in the proper spot by means of a solid glass rod which exactly fit inside the smaller tube. The apparatus was made as tight as possible. A straight tube led away



from the reaction tube. The generator was adjusted so that it bubbled steadily but slowly. The furnace was heated at  $100^{\circ}\text{C}$  for at least one hour then at  $200^{\circ}\text{C}$  and finally at  $300$  to  $330^{\circ}\text{C}$  for a final hour, during which a  $\text{CaCl}_2$  tube replaced the straight tube. The furnace was allowed to cool and then the  $\text{HCl}$  was replaced by dry  $\text{CO}_2$ . The chloride was removed quickly and weighed in a weighing bottle. The weighed chloride was dissolved in  $\text{H}_2\text{O}$ , acidified with  $\text{HNO}_3$  and excess  $\text{AgNO}_3$  added. The precipitate was filtered off into a weighed gouches, dried and weighed.

In some cases only 10/25 of the solution of the chlorides in  $\text{H}_2\text{O}$  was used. The remaining portion being precipitated as a check.





Apparatus for Preparation of the Anhydrous Chloride

Figure 1



## VII Preparation of the Anhydrous Chloride

A larger quantity of the anhydrous chloride was needed for the reaction with ethyl benzoate. The same HCl generator and furnace were used with a larger pyrex tube running thru the furnace. Attempts to use the hydrated chloride as before were unsuccessful with the larger sample; the surface was too small and water continued to condense at the ends of the tube for many hours.

About 15-20 grams of the hydrated chlorides were prepared as before and mixed with an equal weight of  $\text{NH}_4\text{Cl}$ . The mixture was heated in a crucible for three hours at  $200\text{-}220^\circ\text{C}$  to dry it completely. It was then introduced into the large tube and heated in a stream of anhydrous HCl at temperature slightly above  $400^\circ\text{C}$ . The  $\text{NH}_4\text{Cl}$  decomposes and condenses in the cooler ends of the tube but was pushed along by heating with a free flame. After no more  $\text{NH}_4\text{Cl}$  appeared to be coming off the furnace was cooled and finally the HCl turned off and dry  $\text{CO}_2$  run through. The chloride was then removed with as little  $\text{NH}_4\text{Cl}$  as possible and kept covered in a desiccator until used.



VIII Reaction with Ethyl Benzoate

If the anhydrous rare earth chlorides are heated with ethyl benzoate they will react forming insoluble rare earth benzoates and ethyl chloride gas. If the temperature is kept about 192°C some of the rare earth elements will react faster than others and the reaction will proceed at a rate such that a separation can be made between those which have reacted and those which have not.



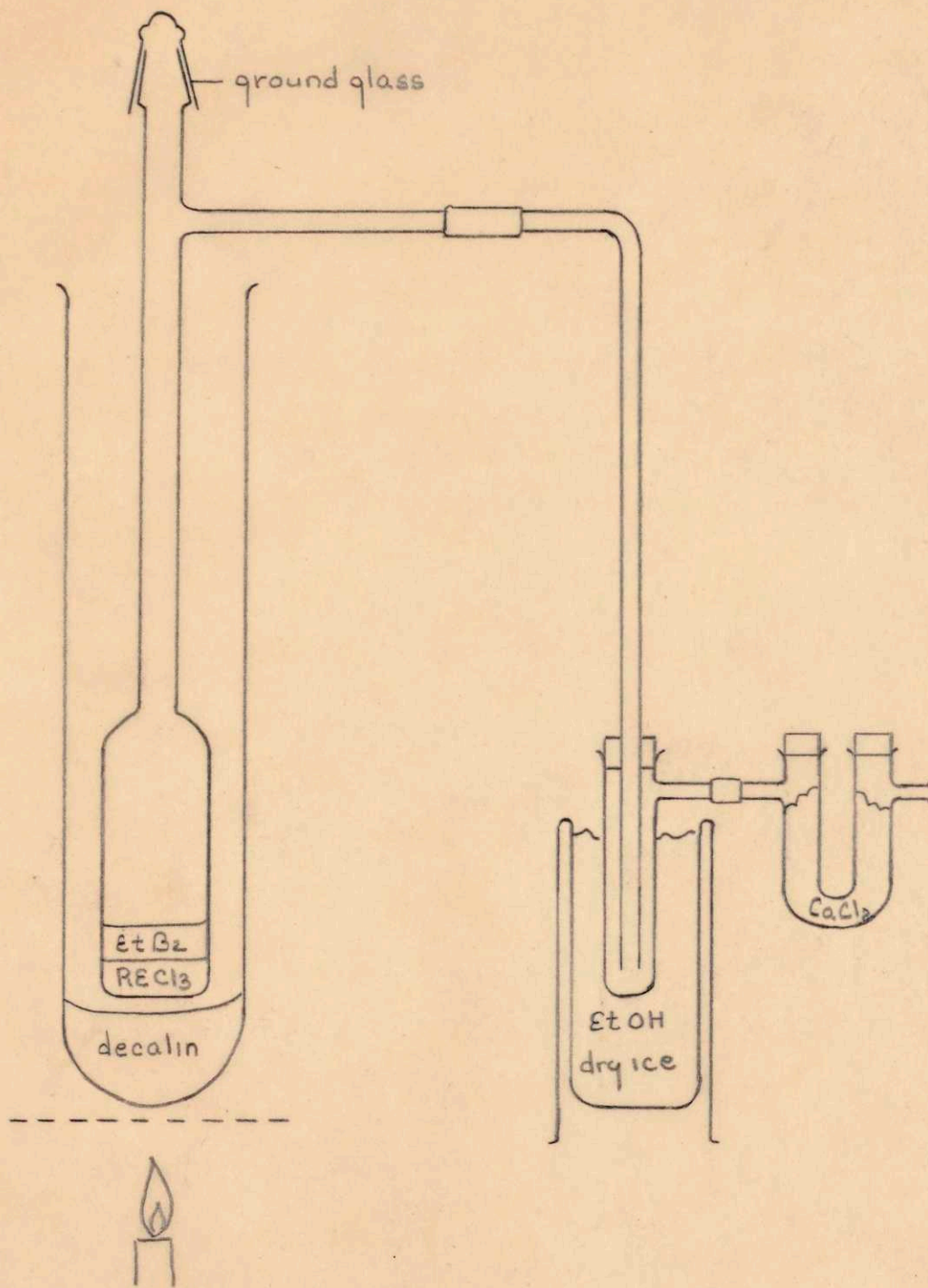
The apparatus consisted of a tube with a ground glass cap. A side arm led to a testtube which was placed in a mixture of dry ice and ethyl alcohol (-75°C) for condensing the ethyl chloride (B.P. 12.2°C); the testtube was open to the air through a CaCl<sub>2</sub> tube. Before the reagents were introduced the apparatus was filled with dry CO<sub>2</sub>. Ten grams of the anhydrous chlorides were placed in the bottom of the tube and covered with ethyl benzoate. A large testtube containing decahydro-naphthalene which boils at 195°C was placed around the inner tube and the bath kept refluxing gently for twelve hours. The volume of ethyl chloride which had condensed at the end of that time plus the estimated amount still in the reaction vessel<sup>1</sup> equalled about three cc. which indicated that about 35% of the chlorides had reacted. The apparatus was then cooled and the mixture extracted with petroleum ether to remove the excess ethyl benzoate. The residue was dried and then moistened with alcohol and extracted many times with small



amounts of cold water. The insoluble rare earth benzoates were thus separated from the soluble rare earth chlorides.

The filtrate containing the soluble fraction was heated and the oxalates precipitated with excess hot dilute  $\text{H}_2\text{C}_2\text{O}_4$ . The oxalates were filtered and ignited. 1.6830 gm. of the oxide were dissolved in  $\text{HCl}$  and diluted to 25 cc. for analysis with the color analyser.

The insoluble fraction was ignited, dissolved in  $\text{HCl}$ , filtered and the oxalate precipitated in hot solution, filtered off and ignited. 1.0916 gm. of the oxide were dissolved as above.



Apparatus for the Reaction with Ethyl Benzoate

Figure 2



## IX Summary of Results

It was not known to what extent the rare earth chlorides would be converted to the benzoates but it was hoped that those of lower atomic number from lanthanum to europium would be converted only to a slight extent so that the insoluble benzoates would consist mainly of the rarer elements of high atomic number. Changes in the composition of the fractions were followed by changes in the average atomic weight and by changes in the concentration of the two elements neodymium and praseodymium for which calibration curves had been previously obtained.\*

The change in average atomic weight was very small.

The values obtained were:\*\*

original material	141.1
insoluble fraction	141.0
soluble fraction	140.2

It is possible that the original sample contained yttrium and some scandium of atomic weights 89 and 45. These two elements are less basic than many of the rare earths and would have reacted quickly. The atomic weight of the insoluble portion would thus be lower than it would otherwise be and the average atomic weight of the soluble portion would be higher in comparison to the original material. However the difference does indicate some change in the expected direction.

\* Future work should include analysis by magnetic balance to determine the extent of reaction of one member of higher atomic number.

\*\* See table I for calculations.



The results obtained by the color analyzer\* were much more revealing. The changes in percent neodymium by weight in the oxide were:

original material	42.2%
insoluble fraction	52.0%
soluble fraction	39.7%

The differences were great enough to indicate a definite separation. This shows that lanthanum was changed very slightly, while the reaction was continued long enough for a large portion of the neodymium to react.

The changes in percent praseodymium are much smaller but still significant:

original material	18.1%
insoluble fraction	21.8%
soluble fraction	17.0%

The presence of neodymium lowers the apparent transmission for praseodymium but the correction factor is only 1/.996 and was therefore neglected.

These results of a fractionation of a natural rare earth mixture confirm the indications obtained in this laboratory by use of artificial rare earth mixtures that this new method holds out possibilities of fractionally separating the rare earths.

\*See table II for calculations.



TABLE I Average Atomic Weight Calculations

$$\text{equations: } \frac{3(35.5)}{\text{av. atomic wt.} + 3(35.5)} = \frac{\text{wt. of chloride in AgCl}}{\text{wt. of RECl}_3}$$

$$\frac{35.5}{107.9 + 35.5} = \frac{\text{wt. of chloride in AgCl}}{\text{wt. of AgCl}}$$

	RECl <sub>3</sub>	AgCl	chloride	av. atomic weight
original material	1.0816gm.	1.900gm.	.4695gm.	139.3
	1.0816	1.890	.4670	140.7
	1.0023	1.732	.4280	142.9
	1.0023	1.743	.4315	141.1
	1.0784	1.1213	.4630	141.4
		average	=	141.1
insoluble fraction	1.4068	2.4390	.6035	141.0
soluble fraction	1.8499	3.2248	.7990	140.2

Average atomic weight of original material = 141.1

Average atomic weight of insoluble fraction = 141.0

Average atomic weight of soluble fraction = 140.2



TABLE II. Color Analyser Calculations

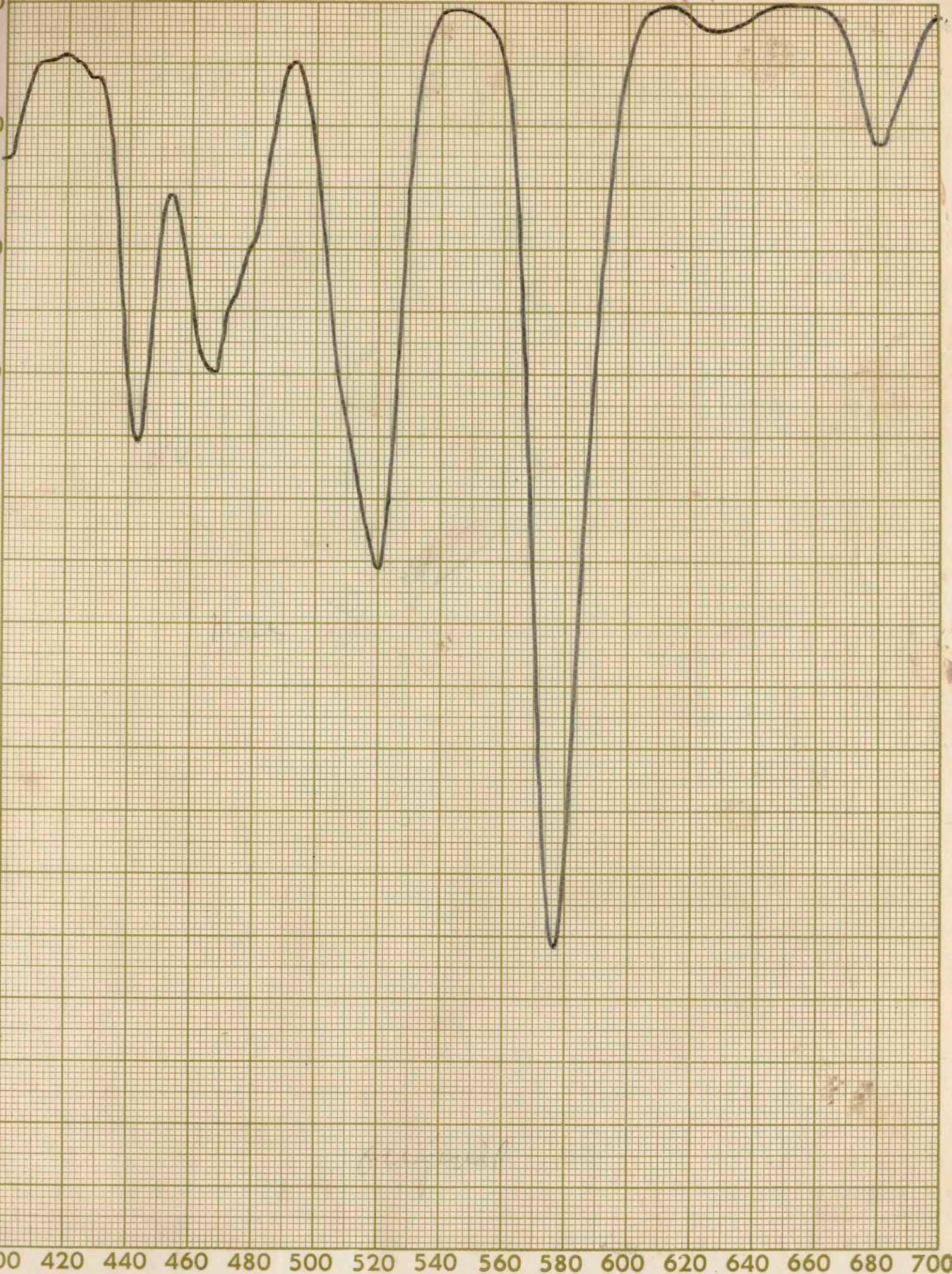
Neodymium	Absorption wavelength		Molecular weight			
	520 millimicrons		Nd <sub>2</sub> O <sub>3</sub> = 336.54			
	weight of oxide	volume	% trans- mission	molarity	% Nd	
original material	1.6830 gm.	62.5cc.	77%	.0675	42.2%	
insoluble fraction	1.0916	62.5	81	.0540	52.0	
soluble fraction	1.6830	62.5	78	.0635	39.7	

$$\frac{\text{molarity}}{2} \frac{336.54}{\text{wt. of oxide}} \frac{\text{volume}}{1000} = \% \text{ Nd}$$

Praseodymium	Absorption wavelength		Molecular weight			
	443 millimicrons		Pr <sub>6</sub> O <sub>11</sub> = 1021.52			
	weight of oxide	volume	% trans- mission	molarity	% Pr	
original material	1.6830 gm.	25 cc.	64.5%	.0715	18.1%	
insoluble fraction	1.0916	25	70.5	.0560	21.8	
soluble fraction	1.6830	25	66.5	.0670	17.0	

$$\frac{\text{molarity}}{6} \frac{1021.52}{\text{wt. of oxide}} \frac{\text{volume}}{1000} = \% \text{ Pr}$$



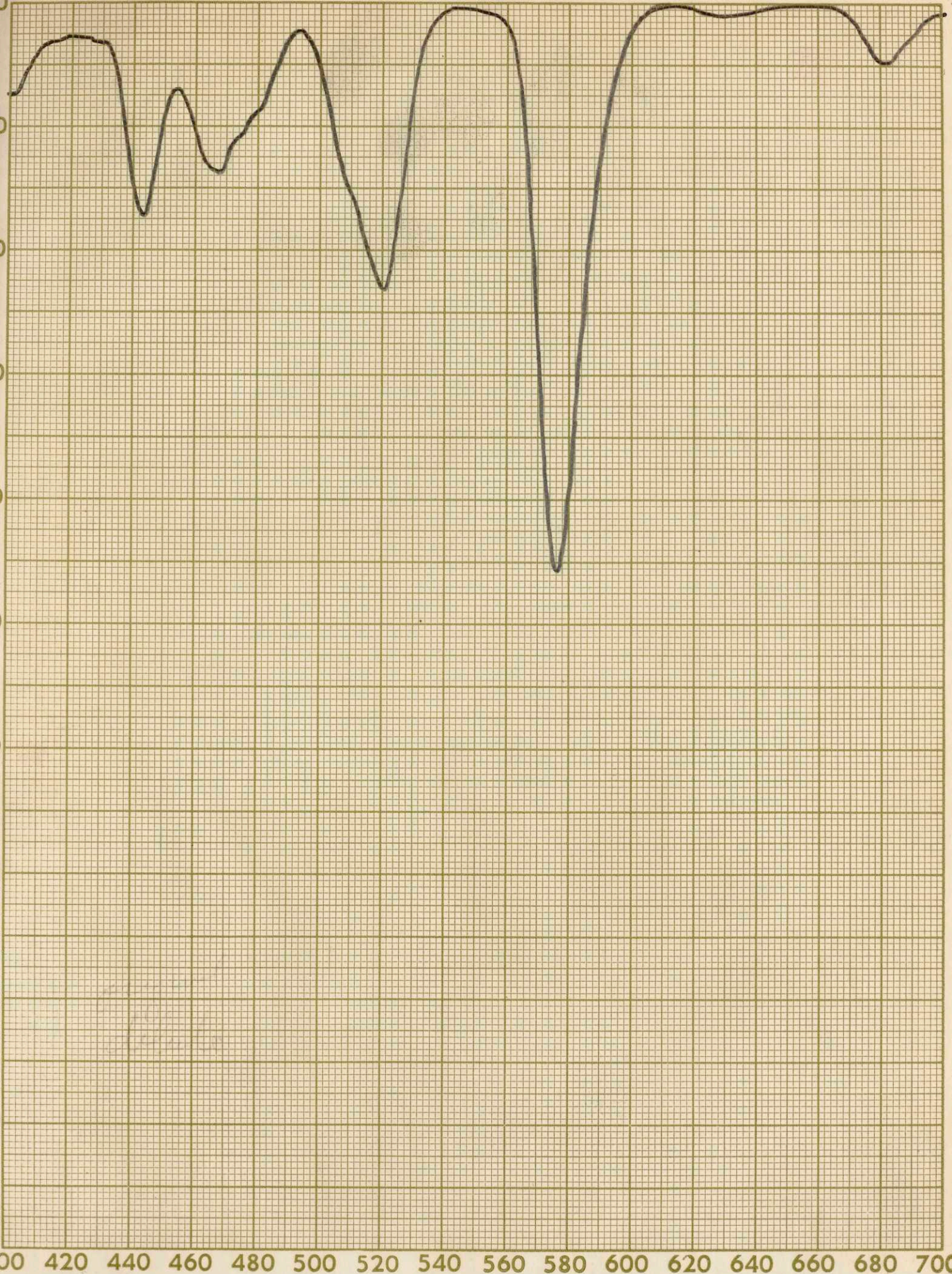


Date 1-19-45  
Test No. 30950

WAVELENGTH *Original*  
(millimicrons) *Concentrated*

Color Measurements Lab.  
Mass. Inst. of Tech. E



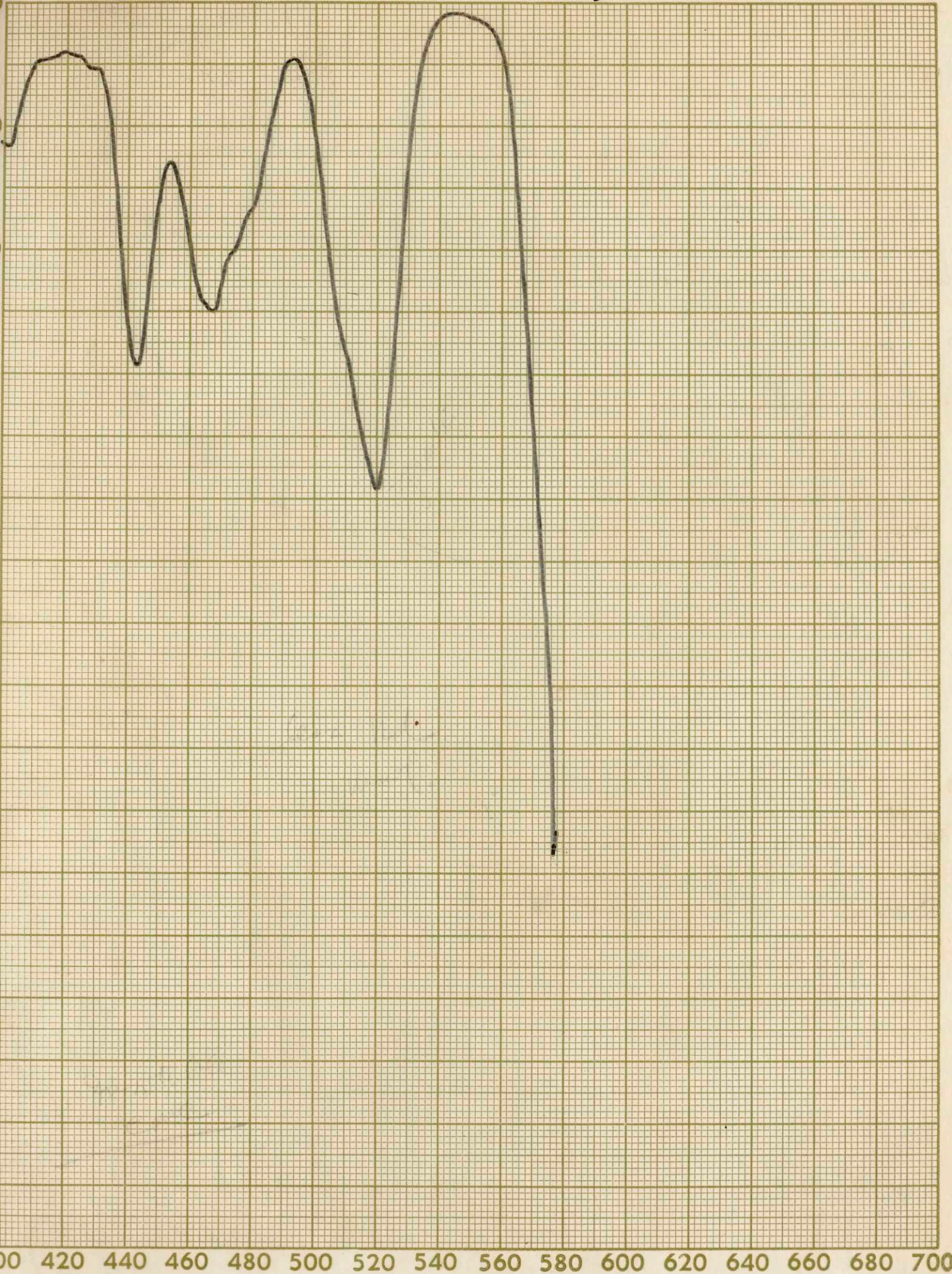


Date *1-19-45*  
Test No. *30951*

WAVELENGTH *Original*  
(millimicrons) *Date*

Color Measurements Lab.  
Mass. Inst. of Tech. *E*



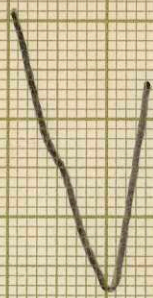


Date 1-19-45  
Test No. 30954

WAVELENGTH (millimicrons) *Insoluble Concentrated*

Color Measurements Lab.  
Mass. Inst. of Tech. *E*





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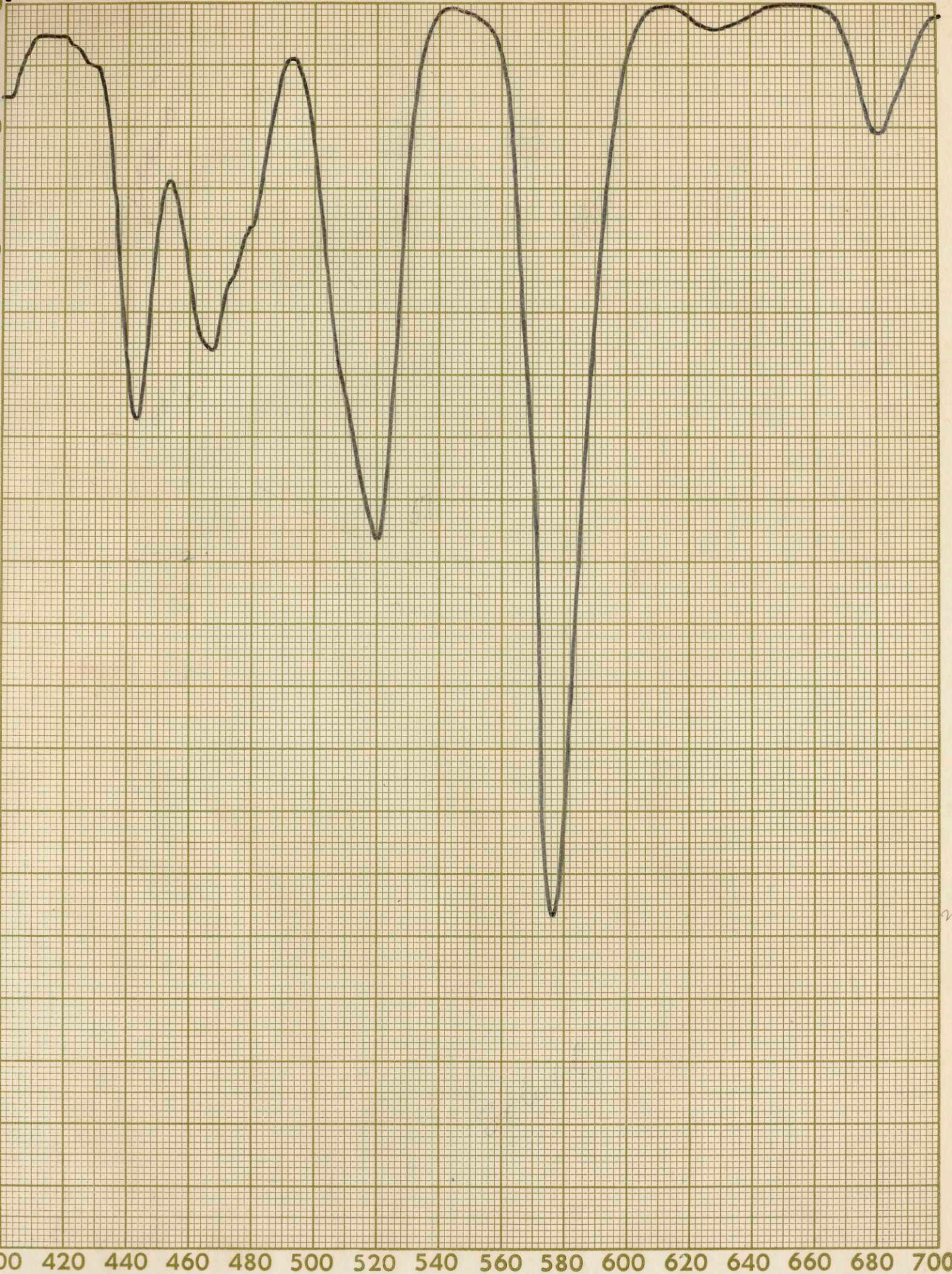
Date 1-19-45  
Test No. 30956

WAVELENGTH  
(millimicrons)

*Insoluble*  
*Dilute*

Color Measurements Lab.  
Mass. Inst. of Tech. E



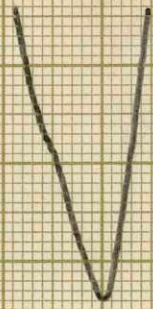


Date 1-19-45  
Test No. 30953

WAVELENGTH (millimicrons) Soluble Concentrated

Color Measurements Lab.  
Mass. Inst. of Tech. E





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Date 1-19-45  
Test No. 30955

WAVELENGTH  
(millimicrons)

Soluble  
Dilute

Color Measurements Lab.  
Mass. Inst. of Tech.

E



X Addendum

There was sufficient time for a few more experiments so a sample of rare earth chloride crystals from Rohm and Haas Co. was dehydrated and placed in the reaction tube with ethyl benzoate as before. Upon heating at 195°C a reaction started but soon stopped. Another portion of the same material prepared separately behaves similarly. The material was tested for cerium and a large quantity found present.

The ethyl benzoate was removed and ethyl oxalate added. At 154°C there was no reaction, at 177°C a slow reaction and at 195°C a very vigorous reaction. (The rare earth chlorides with cerium removed have been previously observed to react with ethyl oxalate at room temperature.) After extraction with water only a small quantity of an insoluble substance remained.

Cerium chloride does not react at 195°C to form ethyl chloride; a liquid was observed condensing just above the reaction tube.

These experiments seem to indicate that the cerium not only does not react as the other rare earths do but, if a large amount is present in a mixture, will prevent the other members from reacting.

The cerium was removed from a sample of the Rohm and Haas crystals. The anhydrous chloride was prepared and heated at 195°C with ethyl benzoate. The reaction was extremely slow.



It is possible that more cerium was left in this sample than was expected. Before any conclusions are drawn from these reactions the behavior of several more samples both with and without cerium must be observed. The liquid formed when one chloride is pure  $\text{CeCl}_3$  should be identified. If cerium prevents the rest of the group from reacting the amount necessary to have such an effect should be determined.



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