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A Reversed-Phase Thin Layer Chromatographic Separation Of The Light Rare-Earths With A Spectrophotometric Determination

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A REVERSED-PHASE THIN LAYER CHROMATOGRAPHIC

SEPARATION OF THE LIGHT RARE EARTHS WITH A

SPECTROPHOTOMETRIC DETERMINATION

A Dissertation

Presented to

the Faculty of the Graduate School

University of the Pacific

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

---

by

Leslie Arthur Whitaker

September 1967

This dissertation, written and submitted by

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is approved for recommendation to the

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Department Chairman or Dean:

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Dissertation Committee:

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Dated ___ September 6, 1967 _____

A REVERSED-PHASE THIN LAYER CHROMATOGRAPHIC SEPARATION OF

THE LIGHT RARE EARTHS WITH A SPECTROPHOTOMETRIC DETERMINATION

Abstract of Dissertation

In this study, two, three, four, five, and six rare earths were separated via reversed-phase thin layer chromatography. Selected sample spots were removed from the plate and determined by emission spectroscopy.

Di-(2-ethylhexyl)phosphoric acid was used as the stationary phase. This organic substituted inorganic acid is retained on the adsorbent through hydrogen bonding and is essentially hydrophobic, so that the aqueous mobile phase can pass over it without serious interaction between the two acids.

A small amount of hydrolytic decomposition of the HDEHP on the adsorbent occurs as the mobile phase moves up the plate. This formed what has been referred to as a double front. No ions including the impurities in the adsorbent were able to move beyond this double front boundary. This created distinct problems such as the obtaining of lower than expected R_f values for certain rare earths and the loss of ions with higher R_f values when they became involved with the double front.

Silica Gel HR, Silica Gel N, and MN-Cellulose 300 were selected and used as the adsorbents to retain the HDEHP for the separations. The most effective separations were found to take place on the cellulose.

There was little difference noted between aqueous HCl and HNO_3 as mobile phases. At times it appeared that better resolution of the Lanthanides was obtained with HNO_3, therefore, solutions of 0.5M to 0.75M HNO_3 equilibrated with HDEHP were employed for most of the separations.

The silica gels contain small quantities of iron and about eight other metallic impurities. When the mobile phase passed over the adsorbent, an interfering band of impurities was formed about 1.5 to 2 cm behind the solvent front. The purification of the silica gel partially solved this problem.

A solution of 8-hydroxyquinoline-kojic acid in 60% ethanol was used to locate the positions of the R.E.-HDEHP spots on the developed plate. With the exception of La, which fluoresces brightly under ultra-violet light, all of the lighter rare earths (Ce-Tb) have a deep blue coloration under the ultra-violet light following the spraying of the plate with the detection reagent and the exposure of the plate to an atmosphere of ammonia vapor.

A semi-quantitative analysis was obtained by the removal of selected spots from the thin layer plate and their subsequent analysis via emission spectroscopy. With the involvement of micro-quantities of the rare earths, a first-order emission spectrograph covering a wavelength range wherein the persistent lines of the rare earths will appear in their spectra is more desirable than a second-order instrument.

The stability of the R.E.-HDEHP coordination compounds increases with the decrease in the ionic radii of the rare earth cations; or stated in another way, their stability increases with increased atomic number, Z. Therefore, at any aqueous acid concentration, the R_f values increase with decreasing atomic number.

As the concentration of the stationary phase on the adsorbent is increased, the R_f values of the rare earths decrease.

ACKNOWLEDGEMENT

The University of the Pacific faculty is a pleasant and cooperative group with whom to pursue graduate studies and research in chemistry. I appreciate the time and effort extended in my behalf by the members of my dissertation committee.

Dr. Cobb's guidance and assistance through these years have been sincerely appreciated.

As most graduate students will attest, a man's research advisor with whom he works closely for a relatively long period of time is an important person in the total process. My association with Dr. Herschel G. Frye as a research advisor resulted in a period of continuous cooperation in all aspects pertaining to my research. The good will was always there. For all of this I am truly grateful.

To my fellow graduate students I extend my thanks for their encouragement, aid, and friendship.

And to a small group who have worked and waited patiently behind the scenes, I express great appreciation with the dedication of this dissertation to my wife, Joyce; my son, Craig; and daughters, Sally Ann and Lesliann.

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CHAPTER I

THE PROBLEM

An interest in the rare earth metals and the thin
layer chromatographic analytical method precipitated this
work towards a reversed-phase separation of seven of the
light rare earths with a spectrographic determination.

A literature search indicated a very ample amount
of research previously accomplished and currently taking
place in the continuous effort to effect a more complete
and expedient separation of these fourteen "peas-in-a-
pod" elements. The many trips to the library also re-
vealed new techniques and pathways which might be in-
vestigated and varied in this effort to separate and
identify some of these rare earths.

This work represents a micro-qualitative analysis
of the elements lanthanum (a sometime rare earth)
through gadolinium excluding the naturally occurring
radioactive promethium.

The separation and identification of these rare
earths, by virtue of the equipment and instrumentation
involved, was pursued with the intent that it might be
accomplished in any laboratory equipped with modern, but
perhaps not the most exotic instrumentation presently
available.

CHAPTER II

THEORY OF THIN LAYER CHROMATOGRAPHY

Thin layer chromatography as an analytical method is not new. More than thirty-five years ago Ismailov and Schraiber separated mixtures of organic compounds on layers of an adsorbent powder, and examined the rings formed under ultra-violet light (94). The chemist, however, was slow to recognize the potential of the method as evidenced by the fact that during 1958-59 only twenty TLC papers appeared in the chemical literature (88). In recent years the growth in interest and research in this method has been great.

Thin layer chromatography is an outgrowth of paper chromatography with distinct advantages over the latter. The preparation of plates is simple, small samples are a standard requirement, there is less tailing than in paper chromatography, and development time is shorter.

The chemical and physical processes involved in TLC are no different than those in paper or column chromatography. They include separations effected by adsorption, partitioning, and ion-exchange. Often, more than one of these processes is involved in the separation on the plate with one of the processes predominating.

Adsorption Chromatography.

Adsorption is defined as the adhesion of the molecules
of a gas, liquid, or dissolved substance to the surface (92).
The larger the interface, the greater the adsorption will be.
Consequently, the choice of adsorbent for a thin layer chromat-
ographic separation will be important for good resolution.
Adsorption from solutions is more complex in that both the
solute and the solvent compete for the adsorbent sites.

In adsorption chromatography, at constant temperature,
an adsorption equilibrium is established between the solute
on the adsorbent and the solute in the solvent. A constant
temperature plot of the concentration of the solute on the
adsorbent vs the concentration of the solute in the solvent
is referred to as an adsorption isotherm. Ideally, this ad-
sorption isotherm is a straight line. In practice, adsorption
equilibrium is not established immediately, consequently, the
adsorption isotherm is a curved line and the spots on the plate
are not elliptical as predicted, but are generally more spread
out either vertically or horizontally.

At constant temperature, the adsorption isotherm will
be nearer to the ordinate if the equilibrium favors solute on
the adsorbent. If the equilibrium favors solute in the solvent,
then the adsorption isotherm will be nearer the abscissa. These
conditions are shown in Figure 1 on page 4 (74). If the concen-
tration of the solute in the adsorbent increases rapidly as the
separation proceeds, the R_f value for that solute will be low;
whereas high concentration of solute in the solvent will

reflect a high R_f value. A solute not adsorbed will travel with the solvent and have an R_f value of 1.

CONCENTRATION
ON THE
ADSORBENT

A A′

B′
B

CONCENTRATION
IN THE
SOLVENT
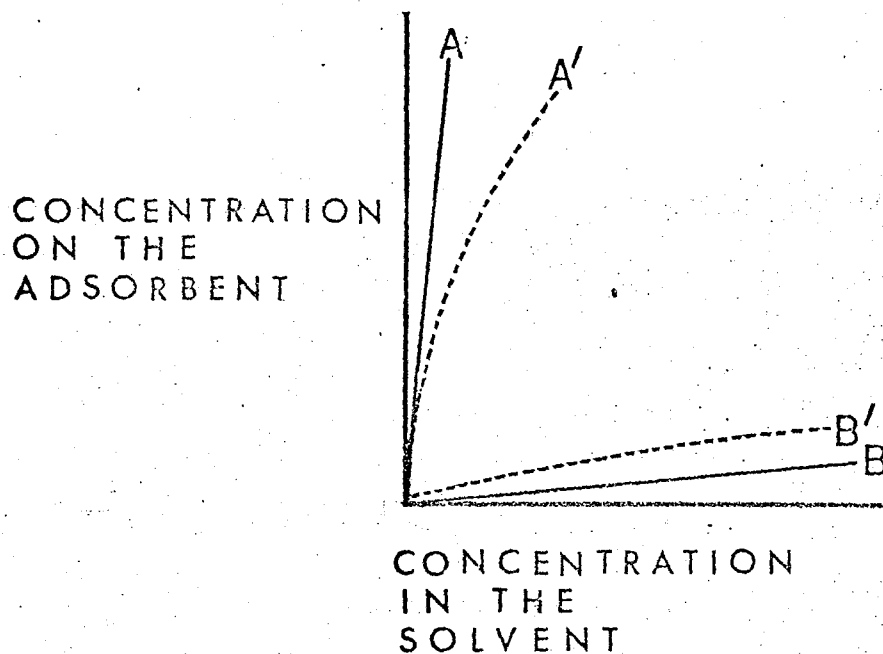
FIGURE 1

ADSORPTION ISOTHERMS

A and B Ideal Linear Isotherms
A′ and B′ Actual Non-linear
Adsorption Isotherms

Partition Chromatography.

Paper chromatography is the best example of this type of chromatography. The solute is partitioned between the liquid phases on a solid support.

In reversed-phase partition thin layer chromatography,

the adsorbent has a solvent adsorbed upon it. This solvent
is bound to the adsorbent, possibly through hydrogen bond-
ing as Bark, Duncan, and Graham (4) suggested for tributyl
phosphate-cellulose bonding. Also, the material on the
adsorbent must be hydrophobic in order that it will not move
along with the developing solvent. A material on the ad-
sorbent is referred to as the stationary phase in the
reversed-phase partitioning process. The solute placed on
the plate for separation is partitioned between the less
polar stationary phase and the more polar developer, or
mobile phase.

Partition chromatography has several advantages over
adsorption chromatography. Because the partition coeffic-
ient is independent of the concentration, the isotherms will
approach linearity (31). Another advantage is its suit-
ability for the separation of the more polar substances.
Hence, its frequent use in inorganic thin layer chromato-
graphy.

Ion-Exchange Chromatography.

Reversible heteropolar chemical bonds are formed be-
tween the moving compound and the adsorbent in ion-exchange
chromatography. A number of ion-exchange celluloses are pres-
ently available for TLC separations (25).

The R_f Value.

The R_f value is defined as the distance from the
position on the plate where the spots were originally placed
to their farthest point of migration divided by the distance

over which the solvent is adsorbed. The method used for
calculating this value is depicted in Figure 2 on page 7.

The R_f value is not considered to be as reproducible
in TLC as in paper chromatography (5). It is, however,
more reproducible in reversed-phase partition chromatography
than in adsorption chromatography. Standardization and care
in preparation of plates and subsequent procedures will en-
hance the reproducibility of R_f values. The principal
factors determining R_f values and the satisfactory repro-
duction of these values are listed in Table I on page 8 (6,
81, 2).

Holzapfel et al (37) determined that additional
thickness of the layer increases the R_f value slightly and
also the separation factors for the rare earths. In this
same research they found that increasing the load of the
stationary phase, di-(2-ethylhexyl) phosphoric acid, on the
adsorbent reduces the R_f values, but increases the separa-
tion factors of the Lanthanides.

The separation factor, β, can be calculated from
the R_M value, which in turn was calculated from the R_f
value.

$$R_M = \log_{10} \left[(1/R_f) - 1 \right]$$

and

$$\beta\,{}^{Z+1}_{Z} = 10^{R_M(Z + 1) - R_M(Z)}$$
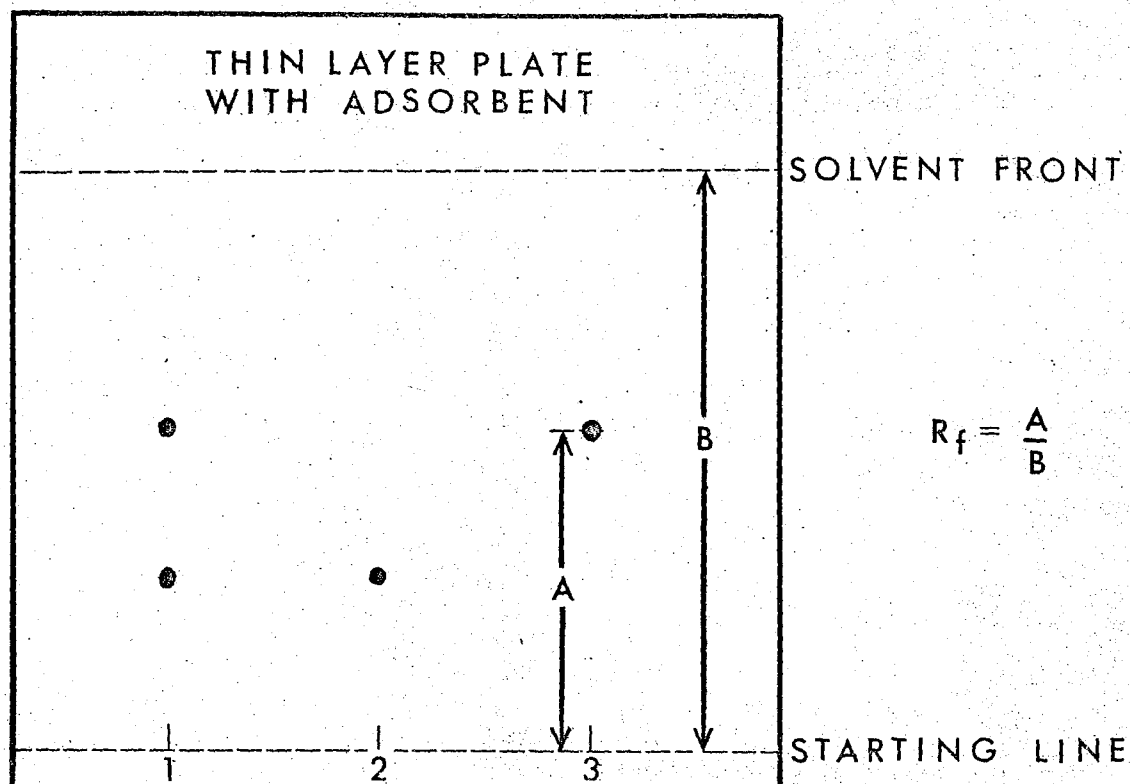
FIGURE 2

THE R_f VALUE IN
THIN LAYER CHROMATOGRAPHY

(1) MIXTURE OF TWO SUBSTANCES
(2) & (3) INDIVIDUAL SUBSTANCES

TABLE I

IMPORTANT FACTORS AFFECTING REPRODUCIBILITY OF R_f VALUES IN THIN LAYER CHROMATOGRAPHY

(1)   The activity of the layer

(2)   The degree of saturation
      within the chromatography
      tank

(3)   The quality and type of
      adsorbent

(4)   The quality of the developer

(5)   The distance from immersion
      line to spotted portion of
      the plate

(6)   The distance travelled by
      the solvent front

(7)   The thickness of the layer

(8)   The type of development;
      ie., ascending or descending

(9)   The size of the sample on
      the plate

(10) The temperature within the
      chromatography tank

Selecting a Solvent System.

The selection of a solvent system will not be discussed here in that it was not a factor in this research. However, excellent discussions of this phase of thin layer chromatography theory is available in texts by Bobbitt (5), Randerath (74), and one edited by Stahl (87).

The Selection of an Adsorbent.

The interdependence of the sample, adsorbent, and solvent makes their proper selection of importance if the separation is to be successful.

In selecting an adsorbent it is necessary to know the nature of the solubility of the sample, and whether it is acidic, basic, neutral, or amphoteric. Consideration must be given as to the possibility of a chemical reaction between the sample and the adsorbent; or a reaction between the sample and the binder in the adsorbent. Also, some adsorbents contain a fluorescent material for the detection of samples under ultraviolet light. With an aqueous solvent system this fluorescent material often causes a second front.

Brinkmann Instruments, Inc. has almost fifty different adsorbents available, so it is apparent that an adsorbent can be obtained for the separation of almost any type of material. Four of the most widely used adsorbents are listed in Table II on page 10.

Activities of adsorbents very greatly and since water is readily adsorbed and occupies active sites on the adsorbent,

TABLE II

ADSORBENTS USED IN TLC

SEPARATION	ADSORBENT	ACIDITY	ACTIVITY	TYPE OF CHROMA-TOGRAPHY	CARRYING CAPACITY
Nonpolar Acidic Nonpolar neutral	SILICA GEL	Acid	High	Adsorption or Partition	Highest
Nonpolar Basic Neutral	ALUMINA	Basic	High	Adsorption	Medium
Polar	KIESELGUHR	Neutral	Inactive	Partition	Low
Polar	CELLULOSE	Neutral	None	Partition (Ion-Exchange)	Low

the coated plates should be stored in a dessicator (23).

Sample Size in Thin Layer Chromatography.

The quantity of the substance to be separated which is placed on the plate is an important consideration because samples which are too large may exceed the capacity of the adsorbent material. The result will be tailing, a spreading of the spot on the plate vertically. This phenomenon makes a good separation unlikely. Generally, one must limit the quantity of the sample to two-digit microgram weights.

The volume of the sample solution spotted on the plate must also be considered. Too large a volume causes too much diffusion of the sample at the starting point, and a small concise spot at the end of the separation will not be a possibility. The diameter should not exceed one centimeter. A few microliters will limit the size of the spot to this dimension or smaller.

Methods of Development.

The moving of the solvent through the adsorbent with the resulting occurrence of the appropriate physical and chemical processes, resulting in the separation of the components originally mixed in the spot at the starting point is known as the development of the plate.

There are seven different methods available for the development of thin layer plates. All methods except for the radical method require that the plate be placed in a chromatography tank in a vertical position.

In the ascending method the solvent flow is from the lower portion of the plate upwards toward the top of the plate. In the descending method the solvent flow is reversed, and the solvent is fed to the upper portion of the plate via a filter paper tongue or strip. Horizontal development necessitates a feeding of the solvent from a supply of the liquid to the side of the plate using a filter paper strip.

Gradient elution necessitates the gradual change of the concentration of the developing solvent as the development proceeds.

The stepwise technique involves the placing of the plate in the developer in the tank in the vertical position. The plate is developed once, dried, and developed again in a more polar solvent than was used in the first elution. A double development is also a criterion of the two-dimensional development. The plate is developed once, dried, rotated ninety degrees from its first position and developed again. The separation may be enchanced even more if the concentration of the solvent is altered before the second development.

Finally, for a radial development, the plate may be in the tank vertically or in a special tank in a horizontal position. The spot is put on the adsorbent in the center of the plate and the solvent is fed to the spot via a filter paper wick, or for a plate in the horizontal position a special burette releasing very small droplets can be used.

As in the selection of an adsorbent, there would appear to be a method of development to fit the separation.

The Detection and Determination.

Occasionally the detection and determination in TLC will be the same. If, following a separation on the plate, certain spots have distinct colors, then little more is required at this point. However, many times, as is the case with the rare earths, the developed plate is the color of the adsorbent, white. When this situration exists an effort must be made to locate a reagent or reagents which will lend color to the spots, or which will result in their fluorescence under ultra-violet light. Often for similar substances being separated the color produced by a particular reagent will be the same for all spots. When this is the case, a determination of the chemical nature of each spot must be pursued.

If radioisotopes have been employed, a radiometric determination can be accomplished (13, 14, 15). Other satisfactory methods include atomic absorption spectroscopy, emission spectroscopy, and infra-red spectroscopy.

CHAPTER III

REVERSED-PHASE CHROMATOGRAPHIC SEPARATIONS

OF THE RARE EARTHS

In 1794, the discovery and isolation of yttria by the Finnish chemist Johan Gadolin, opened the door to an unending research problem; the separation and identification of the chemically very similar rare earth metals. In the years which followed until lutetium was positively identified independently by Urbain and von Welsbach in 1907 (91), nearly one hundred elements presumably having a place in the Periodic Table between lanthanum and hafnium were reported. The brilliant work of H. G. J. Moseley in 1913 conclusively narrowed the number of these metals with atomic numbers 58 through 71 to fourteen.

The methods utilized for the separation of the Lanthanides through the years provides more than enough material for a text unto itself. The discussion in this chapter deals primarily with a chromatographic technique incorporating two of the important methods developed earlier, ie., ion exchange and solvent extraction.

There is no mention in the literature of a purely reversed-phase chromatographic separation of rare earths prior to 1960. This date introduces a series of column separations extending to the present date.

A thin layer chromatographic separation of some of
the rare earths incorporating the reversed-phase technique
does not appear in the literature until 1964.

In the mid-fifties one of the pioneers in paper
chromatography, M. Lederer, was working toward paper chrom-
atographic separations of some non-adjacent rare earths and
also a small number of the lighter members of this series
of elements. In one of his papers (45) following a mention
of the remarkable ion-exchange preparative technique for
larger quantities of the rare earths as accomplished by
Tompkins (90), Spedding (86) and Boyd (39), Lederer stated
that he could easily envision other separation methods based
on complex formation. Among these possibilities be mentioned
inverse phase partition chromatography with complexed rare
earths. At this point his separations of non-adjacent rare
earths with ethanol-HCL solvent systems were successful but
not spectacular.

During 1956 a journal article appeared wherein Lederer
discussed the separation via paper chromatography of five
different rare earths (46). In this work he was approaching
the reversed-phase technique in that he had added an organic
solvent to his solvent system. Of the five organics which he
used, he concluded that only ammonium thiocyanate formed com-
pletely complexed ions with the higher rare earths. With no
criticism intended, it is interesting to note that Lederer
stated that along with the other three organics, tributyl
phosphate did not produce complexes with rare earths in dilute

hydrochloric acid. It is known that from acid solutions the rare earths enter the organic phase as compounds of the composition

$$M(NO_3)_3 \cdot 3(C_4H_9O)_3PO \quad (77),$$
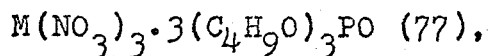
and the extraction of rare earth salts both in chloride and nitrate depends primarily upon the hydrogen ion concentration in the aqueous phase rather than on the type of acid (60). Perhaps only acid concentration separated success from failure with some of these organic compounds.

During this same period, Lederer also separated Y, Ce, and La on filter paper impregnated with Dowex-50 ion-exchange resin (47).

At this point the stage was set for the paper to be impregnated with the organic complexant wherein it becomes the stationary phase in the reversed-phase process. During 1962 Cerrai and Testa (12) did saturated filter paper with di-(2-ethylhexyl) phosphoric acid*, eluted with HCL and/or HNO$_3$, and reported many groups of two, three, and four rare earth separations.

Fortuitously, this period overlaps with the emergence of column and thin layer chromatography utilizing a long list of appropriate adsorbent materials.

Column Separations of the Rare Earths.

The reversed-phase chromatographic separation of the

*Di-(2-ethylhexyl) phosphoric acid is abbreviated HDEHP. The first H represents the ionizable hydrogen, and the DEHP is abbreviation for di-(2-ethylhexyl) phosphoric acid.

rare earths on a column is the predecessor of this type of separation via thin layer chromatography. There are certain advantages to the column separation. It is possible to place slightly larger quantities of the rare earths on the column which will ultimately make the determination of the individual earths less difficult. The technique of gradient elution may also be employed, and this gradual increase in the concentration of the mobile phase may enchance the separation. As an example, it is difficult to separate the adjacent rare earths, cerium, praseodymium and neodymium via reversed-phase TLC; however, this can be accomplished on the column through a gradual increase in the concentration of the mineral acid as the separation progresses. This is effective use of the gradient elution technique.

Also, the column prepared with the reversed-phase material on the adsorbent may be used more than once since the amount of residual rare earths following elution is minimal.

Thin layer chromatography is, of course, not without advantages as well. Perhaps the prime advantages of the TLC separation is the greater expediency in the initial preparations, shorter time required for a separation, and the simpler detection methods.

During 1962 Pierce and Peck (67, 68) reported column separations of the light and heavy rare earths, respectively, in separate journal publications. They reported the

separation of La - Gd inclusive using normal reversed-phase chromatographic techniques, and the separation of Tb - Lu inclusive using perchloric acid of gradually increasing concentration. In these and subsequent separations Pierce and Peck, and Hobbs (69, 70) used Corvic, a vinyl chloride-vinyl acetate copolymer, as an adsorbent; HDEHP as a stationary phase, and perchloric acid as a mobile phase.

Sochacka and Siekierski (84) achieved a clear separation of the adjacent rare earths, Ce-Pr-Nd, with HDEHP retained on kieselguhr. The kieselguhr had been previously treated with dichlorodimethylsilane. Winchester (93) also found siliconized kieselguhr to be an effective supporting material for column separations of the rare earths.

The Italians, Cerrai and Testa (13, 14, 15), using HDEHP on cellulose, achieved good separations of rare earth pairs such as La-Ce, Nd-Pm, Eu-Gd, and Gd-Tb. They also separated mixtures of rare earth, alkali, and alkaline earth metals. Gradient elution was necessary for the last separation.

Cerrai and Testa et al made their separations at temperatures ranging from 15 to 75 degrees centigrade and determined that a slight decrease in the separation factor at higher temperatures is offset by a higher column efficiency, and therefore a slightly sharper separation of adjacent pairs of rare earths.

At a later date, Cerrai et al (16, 17) accomplished a column separation and spectrographic determination of

trace amounts of rare earths in SAP material. [SAP is a product which results from the powder metallurgy of an aluminum powder containing alumina.] The importance of the separation lay in the fact that this SAP material was being considered as a possible structural material for thermal reactors, and the trace quantities of rare earths represented an unfortunate impurity because of their relatively high thermal neutron adsorption cross-sections.

The 3.4 meter Jarrell-Ash Ebert emission spectrograph was used for the determination. Cerrai et al devised a unique lower graphite electrode with a larger surface area than the normal electrode. This electrode could be loaded with five times the amount of sample that a regular electrode could handle. After arcing, this special electrode was rotated at a speed corresponding to a five second exposure for the surface equal to a single electrode surface (16, 17). Using the 3.4 meter spectrograph and this rotating graphite electrode yielded remarkable sensitivities of 0.120 ppm for Sm, 0.005 ppm for Eu, 0.017 ppm for Gd, 0.024 ppm for Dy and 0.06 ppm for Er. This was an impressive piece of research.

Other materials used as the stationary phase in column separations include di- and tributyl phosphate (44, 82, 28); 2-ethylhexylphenylphosphonic acid (29); methylenebis- [di(2-ethylhexyl)-phosphine oxide] (61); and thenoyltrifluoroacentone (55). Fidelis and Siekierski (29) have reported

that the 2-ethylhexylphenylphosphonic acid is a more selec-
tive extracting agent for the rare earths than is HDEHP.

In each of the column separations cited, the follow-
ing observation was made by those involved with the research:
For a given molarity of mobile phase acid, either HCl, HNO_3,
or $HClO_4$, the rare earths were eluted from the column in the
order of their increasing atomic numbers.

In each of the column separations using a reversed-
phase, radioisotopes of the rare earths were used in order
that the fractions removed from the lower portion of the
column could be analyzed via a measurement of their gamma
or beta radioactivity. This was the basis for a qualitative
and quantitative analysis of these cations. It is of inter-
est to note that only fifteen years earlier Yost had stated
in his text (95), "Radiochemical methods may prove useful
eventually when adequate trace radioisotopes are generally
available."

Thin Layer Chromatographic Separations.

Reversed-phase thin layer chromatographic separations
of the rare earths as reported in the literature are limited
to five or six in number.

Pierce and Flint (72) reported the separation of two
sets of three rare earths (La, Pr, Sm, and Tb, Gd, Eu) using
di-(2-ethylhexyl) phosphoric acid retained on Corvic. At
that time they found it necessary to purify the HDEHP accord-
ing to a procedure suggested by Stewart and Crandall (89).

Pierce et al were able to obtain good separations of La, Pr and Sm using a 0.25 $\underline{M}$ HCl solution as the mobile phase; and an equally satisfactory separation of Tb, Gd and Eu with 0.80 $\underline{M}$ HCl. They stated that the method of horizontal development yielded the most satisfactory results. The plates were sprayed with an 8-hydroxyquinoline solution (basic) for visualization as dark blue spots under ultraviolet light, and determined radiometrically.

Daneels, Massart and Hoste (24) approached the separation of pairs and one group of three Lanthanides on the plate in a different manner. They used HDEHP as the mobile phase rather than the stationary phase. This necessitated the developing of the plates with the acid, $HClO_4$, before the plate with the silica gel H was placed in the chromatography tank.

Since the heavier rare earths form more stable complexes with the di-(2-ethylhexyl) phosphoric acid, the use of organic acid as the mobile phase reverses the position on the plate of the separated elements. In a separation of Gd, Eu and Sm, the one with the largest Z, Gd, was carried the greatest distance along the adsorbent. Sm occupied the lowest position of the three on the plate.

No other publication describes the use of HDEHP as a mobile phase in a TLC separation.

The most complete investigation to date of a TLC separation of the rare earths has been accomplished by the

German chemists Holzapfel, Le Viet Lan and G. Werner (36, 37). Using HDEHP retained on silica gel D and a mobile phase of HNO_3 or HCl, they were able to separate all pairs of any of the adjacent rare earths except for Pr-Nd and Er-Y. Also they were able to separate five earths on a plate. They favored the HNO_3 as a mobile phase stating that it gave a better separation than HCl.

Using the method of two-dimensional elution, Holz-apfel and his coworkers were able to separate as many as nine Lanthanides on a single plate. The method and the elements separated are shown in Figure 3 on page 23. In the figure spots A and B are drawn to represent identical samples with seven micrograms of each of the nine rare earths to be separated. During the first elution the cerium earths are separated, but because of the low acid concentration the yttrium earths do not move. The plate was removed from the tank following the first development, dried, and rotated through ninety degrees before being placed in the tank again for a second development. Between developments the acid concentration in the tank had been increased to $4\underline{M}$. This time the mobile phase did not move across the cerium earths previously separated, but yielded a separation of the yttrium earths.

When HDEHP was used as the stationary phase in the separations discussed, the following observation could be made: The rare earth elements of high atomic numbers
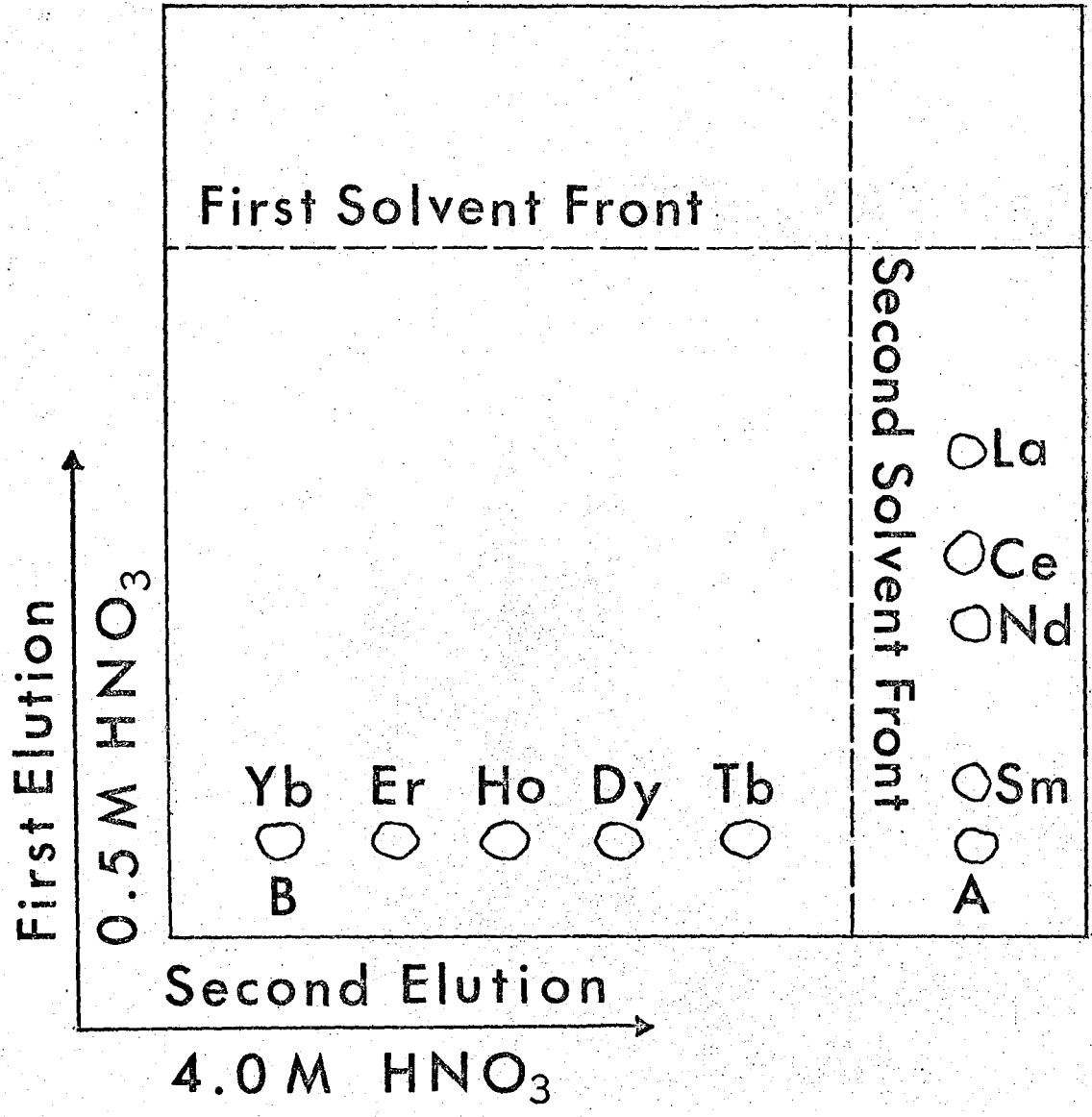
FIGURE 3

TWO—DIMENSIONAL
REVERSED — PHASE SEPARATION OF
CERIUM AND YTTRIUM RARE EARTHS

migrate on the plate at a slower rate than the elements of low atomic numbers at any concentration of acid used as the mobile phase.

CHAPTER IV

DI-(2-ETHYLHEXYL) PHOSPHORIC ACID

AS A STATIONARY PHASE

The analytical method of reversed-phase chromato-
graphy for the purpose of effecting separations of inorganic
ions, depends upon the partitioning of these ions between a
hydrophobic organic solvent extractant in the adsorbent and
a mineral acid. The organic liquids employed in this method
are a comparatively new class of substances which can be
considered to be cation exchangers which dissociate according
to the equation

$$H_aA = H^+ + AH^-_{a-1}$$
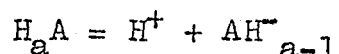
where AH^-_{a-1} is the anion of the inorganic acid which has
been esterified by organic chains.

Di-(2-ethylhexyl) phosphoric acid, commonly referred
to as HDEHP, is a diester of ortho phosphoric acid. This
acid when used as a reversed-phase material has great sel-
ectivity for the rare earth 3+ cations. The structural for-
mula for HDEHP is shown in Figure 4.

The importance of such a group of compounds as those
just described is aptly expressed by Cerrai (9).

All the advantages of selectivity and versatility
of liquid ion exchangers and in general of organic
extracting agents, can be transferred into the
field of chromatography.

A single extraction of a rare earth from the aqueous
phase into the organic phase does not yield a satisfactory

separation, but the placing of the solvent extracting material on an adsorbent as the stationary phase results in a multi-stage operation improving the separation appreciably.

$$CH_3(CH_2)_3 - \overset{\overset{\displaystyle C_2H_5}{|}}{CH} - CH_2 - O$$

$$O - \overset{\overset{\displaystyle }{}}{\underset{\underset{\displaystyle }{}}{P}} - OH$$

$$CH_3(CH_2)_3 - \underset{\underset{\displaystyle C_2H_5}{|}}{CH} - CH_2 - O$$
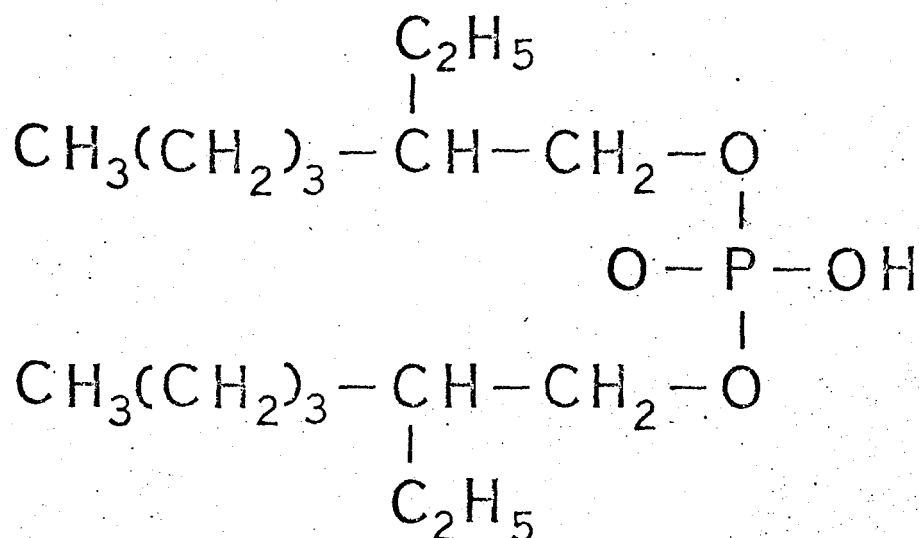
FIGURE 4

STRUCTURAL FORMULA
DI−(2−ETHYLHEXYL) PHOSPHORIC ACID

When the 3+ rare earth cations in aqueous solution as chlorides or nitrates are exchanged, the reaction occurs according to the equation:

$$RE^{3+} + 3(HDEHP)_3 = 3H^+ + RE\left[\overline{H(DEHP)_2}\right]_3 \quad (40).$$ The $H(DEHP)_2^-$ can be classified as an organic ligand, and the $RE\left[\overline{H(DEHP)_2}\right]_3$ as a coordination compound wherein the rare earth has a coordination number of six.

It is apparent that an effective reversed-phase chromatographic separation depends upon the hydrophobic character of both the reversed-phase material and the coordination compound formed as a result of the extraction.

Sheka et al (80) found that the solubility of the di-alkyl
phosphates in water at 25° C decreases with increase in the
length of the organic chain, and for HDEHP is in the order
of $10^{-4} - 10^{-5}$ moles per liter. The solubility of the
chelated rare earths varies slightly from the chelate of
the light rare earths to that of the heavier ones, being less
soluble in the heavier compounds.

The reaction representing the extraction and subsequent
formation of the chelate is a reversible one. If this were
not so, the separation on the plate would not be possible.
The chemical equilibrium is such that an increase in hydrogen
ion concentration will result in a decrease in the extraction
of rare earths by the organic acid. On this basis, the
aqueous mineral acid is a logical choice for a mobile phase
in the separation.

Hydrogen bonding in di-(2-ethylhexyl) phosphoric acid,
a monobasic di-ester, was investigated by Peppard et al (65).
Employing a standard sodium hydroxide titration of the acid,
they determined the equivalent weight of HDEHP to be 322, the
same as its monomeric molecular weight.

The molecular weight of the acid, determined via
freezing point depression in a standard Beckman type freez-
ing point apparatus, was 645, the dimeric molecular weight.
The HDEHP dimer is formed through intermolecular hydrogen
bonding between the -POOH, phosphoroxyl group, on each acid
molecule. Figure 5 on page 29 shows two structures for this
dimer.

Also of interest were the infra-red studies of HDEHP

(65). The regions of absorption for these derivatives of

phosphorus containing acids have been studied by Daasch and

Smith (22). The region of 2700-2500 cm^{-1} has been identified

as that of bonded OH, and in this region of the spectrum of

HDEHP a broad absorption band appears. There is no absorp-

tion peak at 3500 cm^{-1} which would evidence a free OH group.

The strong absorption at 1225 cm^{-1} is indicative of the

bonded P-O group in what is termed the phosphoryl region of

the IR spectrum. A P-O-C grouping wherein C represents an

aliphatic chain absorbs strongly at 1200-1350 cm^{-1}.

Peppard (65) found that the free OH group could not

be identified when HDEHP was placed in mineral oil and the

temperature raised to 135° C. This would indicate rather

strong hydrogen bonding in the HDEHP dimer (64). Actually,

this intermolecular hydrogen bonding in monophosphoric

acids is considered to be stronger than in the monocarboxylic

acids.

Figure 6 on page 30 is an infra-red spectrum of HDEHP.

The dimerization of the HDEHP does not alter the for-

mation of the R.E. coordination compound. One rare earth ion

complexes with three HDEHP dimers to yield a compound of the

type, M $\left[H(DEHP)_2 \right]_3$. A proposed structure for this coordina-

tion compound is shown in Figure 7.

Peppard et al (66) stated that HDEHP on a support with

mineral acid mobile phase offered considerable promise in the

(A) $R-O$ ... $O-H$---O ... $O-R^{29}$
     $\quad P \quad\quad\quad\quad P$
$R-O$ ... O---$H-O$ ... $O-R$

(B)

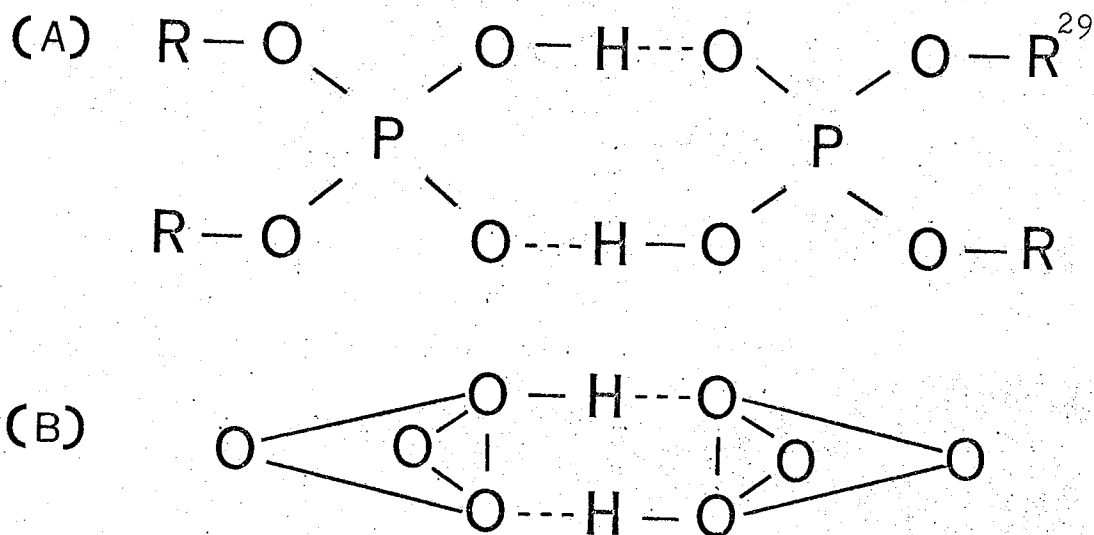# FIGURE 5

DI — (2-ETHYLHEXYL)
PHOSPHORIC ACID DIMER

(A) 8 MEMBERED RING
    FORMED AS RESULT
    OF HYDROGEN
    BONDING

(B) HDEHP STRUCTURE
    SHOWING THE
    PHOSPHOROXYL
    GROUP
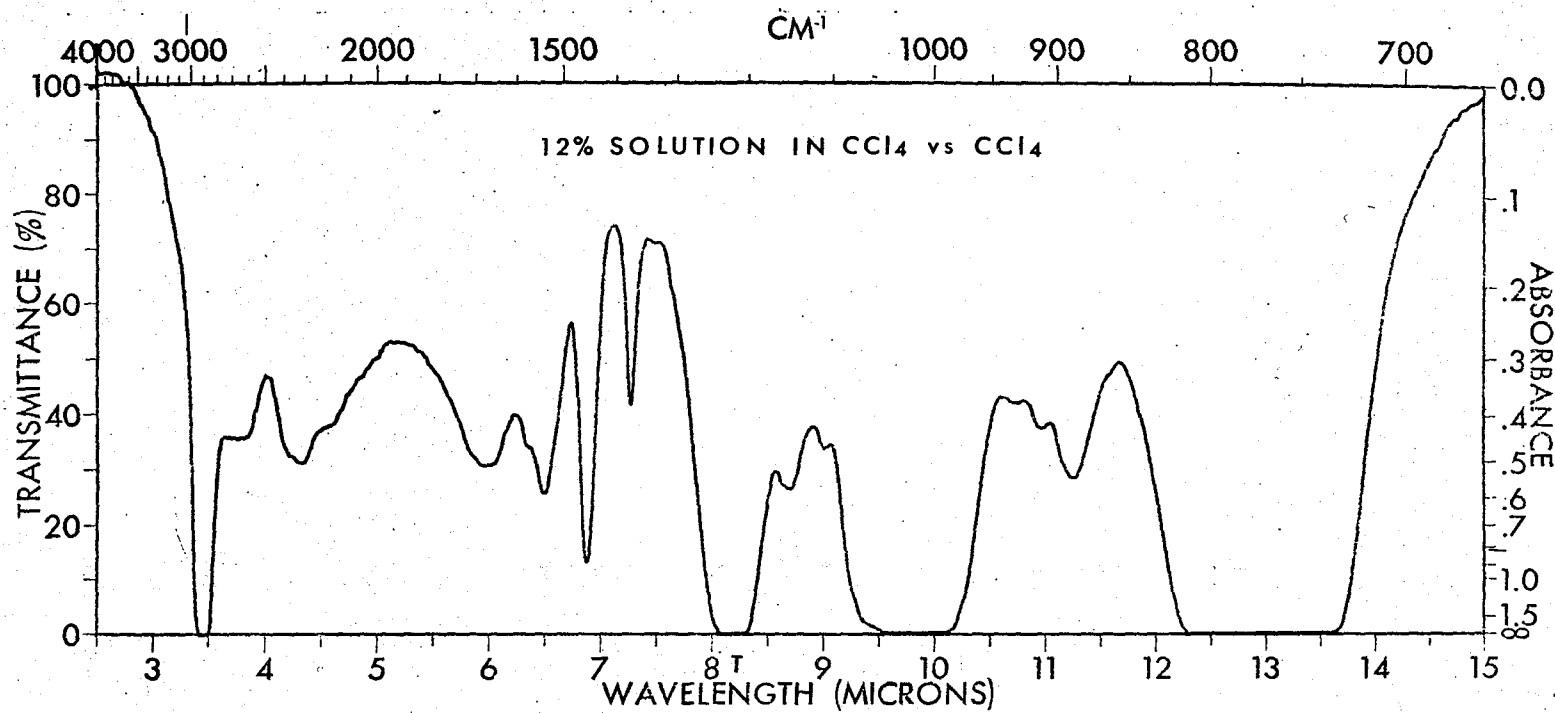
FIGURE 6

DI-(2-ETHYLHEXYL) PHOSPHORIC ACID
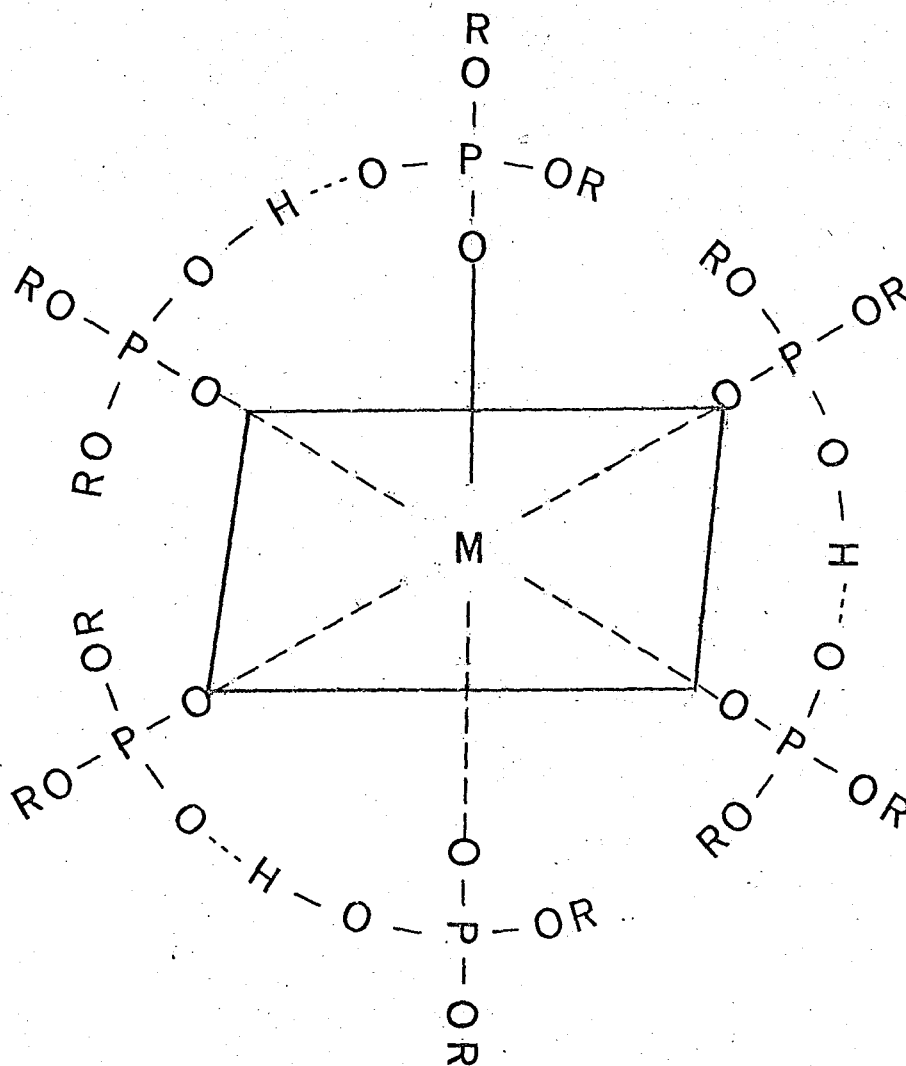
FIGURE 7

PROPOSED STRUCTURE
FOR CHELATE COMPOUND
OF R.E. AND HDEHP

R REPRESENTS
$$CH_3-CH_2-CH_2-CH_2-CH-CH_2-$$
$$\overset{|}{CH_2}$$
$$\overset{|}{CH_3}$$
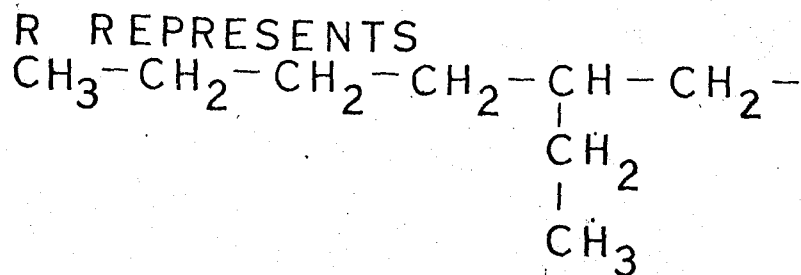
separation of lanthanides due to the steepness of the log
K versus Z curve (Z = atomic number). K is the symbol for
the distribution coefficient or extraction coefficient, and
may be defined

$$K = \frac{\text{Concentration of R.E. element in the organic phase}}{\text{Concentration of R.E. element in the inorganic aqueous phase}}$$

Peppard et al (66) determined K radiometrically.

A plot of log K versus Z yields a straight line.
When HDEHP is used in the separation of the rare earths,
the slope of the line is approximately 2.5.

The ratio of K_{Z+1} to K_Z results in a value known as
the separation factor, beta (β). For HDEHP as a reversed-
phase material in the separation of rare earths, Peppard
reported a mean separation factor between adjacent elements
of 2.5.

Separation factors for adjacent rare earths are
listed in Table III on page 33 (66, 69, 84).

When a plot is drawn for the individual earths of log
K versus log of the molarity of HDEHP in a diluent, lines
with a slope of +3 result. A similar plot drawn of log K
versus the log of the hydrogen ion concentration of the acid
mobile phase, the resulting lines have slopes of -3. This
would indicate that the value of the distribution constant,
K, has a direct third-power dependence upon the concentration
of HDEHP in the equilibrated organic phase and an inverse

TABLE III

SEPARATION FACTORS
FOR ADJACENT RARE EARTHS

La-Ce	Ce-Pr	Pr-Nd	Nd-Pm	Pm-Sm	Sm-Eu	Eu-Gd	Gd-Tb	Adjacent Rare Earths / Mobile Phase
2.8	1.5	1.3	2.7	3.2	2.2	1.5	5.0	HCL
2.7	Ce-Nd 1.55		2.1	2.7	2.1	1.7	5.5	HNO_3
2.98	2.05	1.38	2.16	3.05	1.9	1.4	4.9	$HClO_4$

third-power dependence upon the hydrogen ion concentration in the equilibrated aqueous phase.

Di-(2-ethylhexyl) phosphoric acid is an ideal reversed-phase material for separation of the Lanthanides for several reasons. The acid has a relatively large separation factor with the rare earths, the reaction rate with these metals is rapid, and it is quite hydrophobic. All of these are essential properties of the stationary phase for an effective separation on the thin layer plate.

A number of other organic compounds have been used as stationary phases in inorganic TLC separations with varying degrees of success. A great deal of research has been done with tributylphosphate (TBP) (28, 73, 82). This tri-ester of phosphoric acid has a separation factor of 1.6 with the rare earths. Fidelis and Siekierski (29) believe 2-ethylhexylphenyl to be superior to HDEHP as a stationary phase for the separation of the Lanthanides. Tri-isooctylamine (TIOA) (73), 2-ethylhexylphenyl phosphonic acid (HDEOP) (29), thenoyltrifluoroacetone (55), and di-isopentylmethyl phosphonate (54).

CHAPTER V

PROPERTIES OF THE LIGHT RARE EARTHS

RELATED TO THE SEPARATION

Particular properties of the rare earth elements are important in effecting a reversed-phase separation of the metal ions on a thin layer. These are the properties which will be discussed in this chapter.

The essential difference in the electronic configuration of the rare earths is in the number of electrons in the 4f orbitals. Table IV (56, 83) on page 36 describes the 4f, 5d and 6s electronic configurations and ionic radii of the light rare earths.

Because the 4f electrons are quite effectively shielded from interaction with ligand orbitals, complexation between rare earth cations and organic ligands does not involve the 4f electrons of the metals. Hybridization must occur through involvement of normally unoccupied higher energy orbitals in the rare earth ions such as the 5d, 6s, and 6p orbitals (60). Therefore, the complexes formed result from strong electrostatic attractions between the R.E. ion and the ligand. Consequently, R.E. complexes are more similar to the alkaline earth complexes than to the typical d-type transition metal complexes.

One piece of evidence to support the lack of involvement 4f electrons with ligand orbitals is the small effect

TABLE IV
LIGHT RARE EARTH PROPERTIES

Atomic Number (Z)	Element (Symbols)	Observed configuration			Ionic radii M^{3+} (Å)
		4f	5d	6s	
57	La	0	1	2	1.061
58	Ce	1	1	2	1.034
59	Pr	3	0	2	1.013
60	Nd	4	0	2	0.995
61	Pm	5	0	2	
62	Sm	6	0	2	0.964
63	Eu	7	0	2	0.950
64	Gd	7	1	2	0.938
65	Tb	9	0	2	0.923
		(or 8	1	2	

may increase following complexation, but peak shifts toward longer wavelengths are minimal. Any change which does occur in the spectra of the compounds from that of the 3+ ions is believed to occur due to interaction between the electric fields of the ligand molecule and the R.E. ion. This results in a partial breakdown of forbidden transitions in the 4f shell. (42)

Cations forming the most stable complexes are smaller than the rare earth metal cations, and the decrease in the radii of the rare earths as the atomic numbers increase* is not great enough to cause very large changes in the stability of rare earth complexes as the series progresses. However, this slight decrease in the size of the Lanthanide ions with increased Z is the key to the reversed-phase TLC separation with HDEHP in that the stability of the complexes formed with the ligand, increase with decreasing size of the cation (60).

Absorption Spectra of the Light Rare Earths.

With the exception of La^{3+}, all the light rare earths through Tb^{3+} absorb electromagnetic radiation somewhere in the wavelength range of 2,000 to 10,000 angstroms (56). This would indicate that their characteristic narrow spectra are fundamentally associated with the 4f electrons. La^{3+} does not have any 4f electrons. The remainder of those mentioned have at least one unpaired 4f electron.

*This decrease in radii is known as the Lanthanide contraction.

The colored tripositive ions, Pr, Nd, Sm and Eu, absorb radiation in the visible, and sometimes in the UV region. The colorless ions absorb in the UV or IR region. The very narrow absorption spectra are characteristic of the rare earths and the related actinide elements, but no others.

Emission Spectra of the Light Rare Earths.

Most of the rare earths were discovered with the aid of spectroscopy; and more specifically, emission spectroscopy.

The vaporization of a sample of ten to fifteen milligrams between graphite electrodes in an electric arc at five to eight thousand degrees centigrade, results in the moving of the element's electrons to higher energy levels. As these electrons fall back to lower energy levels, light of characteristic wavelengths for that element is emitted. In the emission spectrograph this light passes through a narrow 10-60 micron slit, a collimating lens, and then reaches the diffraction grating. The 1.5 meter Bausch and Lomb emission spectrograph has an Eagle-mounted grating. Generally, in an Eagle-mounted grating instrument a combination lens and dispersion piece is included (7). The grating is ruled upon the surface of a concave mirror. This gives a uniform reflection of light regardless of the wavelength. The diffracted light from the grating is either photographed on a thirty-five millimeter film strip, or recorded by means of photoelectric devices (20).

The developed film strip has dark lines at characteristic wavelengths where the diffracted light has exposed the film. For lighter elements, these spectra are generally less complicated with fewer lines. Rare earth spectra are quite complex; the fourteen elements yielding over 2,350 lines between 2,600 and 5,600 angstroms (7).

Inter-element interference makes analysis of the rare earth elements via spectroscopy one requiring much experience. In his text, Harvey states that the inexperienced spectroscopist should avoid the analysis of films containing rare earth spectra (32).

This means of detection of micro-quantities of the rare earth metals is still one of the most sensitive. Absolute spectrographic sensitivities for the light rare earths are given in Table V (20, 92).

TABLE V

DETECTION OF THE RARE EARTH METALS
ABSOLUTE SPECTROGRAPHIC SENSITIVITIES

RARE EARTH	LIMIT OF DETECTION IN MILLIMICROGRAMS IN TEN MILLIGRAM SAMPLE (D. C. ARC – GRAPHITE)	LIMIT OF DETECTION IN PARTS PER MILLION (D.C. ARC – GRAPHITE)
La	200	1–10
Ce	2000	100–1000
Pr	1000	1–10
Nd	1000	1–10
Sm	500	100–1000
Eu	200	1–10
Gd	500	100–1000
Tb	500	1–10

CHAPTER VI

EXPERIMENTAL DETAILS

The instruments, equipment and apparatus used and the necessary chemicals are listed in this chapter. A few items of the equipment designed primarily for use in thin layer chromatography are shown in Figures 8 and 9.

A discussion of the experimental procedures completes the chapter.

Instruments, Equipment, and Apparatus.

1. Stainless steel desiccating cabinet

2. Drying rack for glass plates

3. Long-short wave ultraviolet lamp

4. Aerosol reagent sprayer

5. Standard Mounting board

6. Desaga-Brinkmann 275 micron fixed thickness applicator

7. Ten microliter Hamilton syringe

8. Standard Desaga developing tanks with ground glass covers

9. Standard labeling template

10. Osterizer blender

11. Electrical air blast dryer

12. Sieve, 325 meshes to the inch

13. Glass plates
    20 x 20 centimeters
    10 x 20 centimeters

14. Bausch and Lomb 1.5 meter emission spectrograph

15. Graphite electrodes
    Electrode with cup L3900
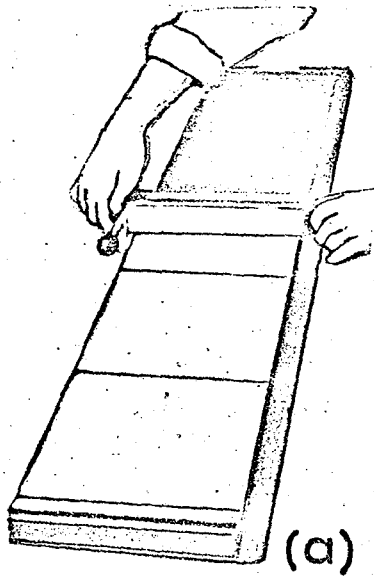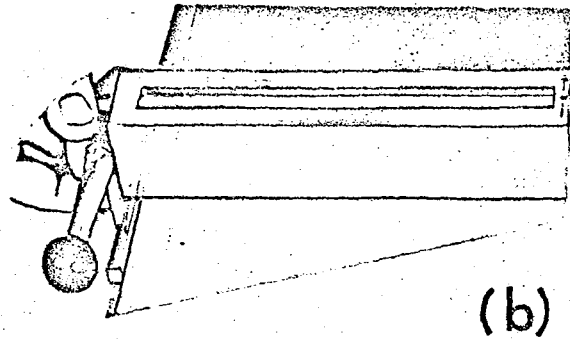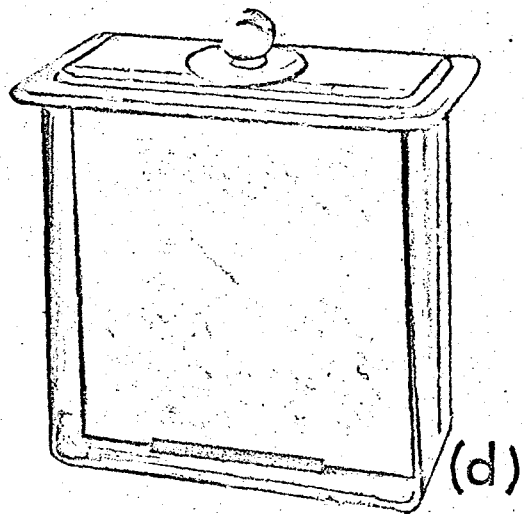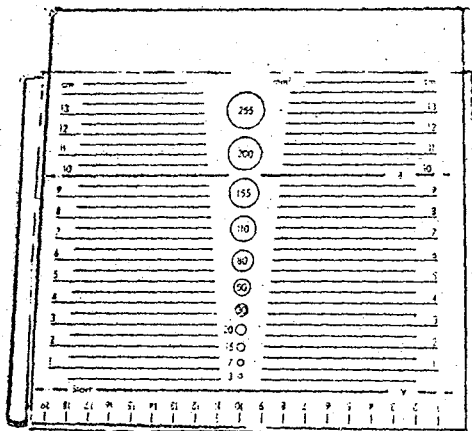
FIGURE 8

APPARATUS FOR THIN LAYER CHROMATOGRAPHY*

(a) Standard mounting board
(b) Desaga-Brinkmann 275 fixed thickness applicator
(c) 10 l syringe
(d) Standard Desaga developing tank
(e) Standard labeling template

*Permission Brinkmann Instruments, Inc. Westbury, New York
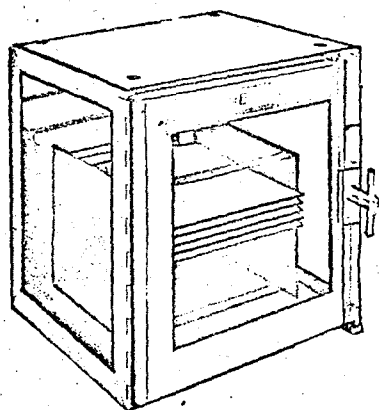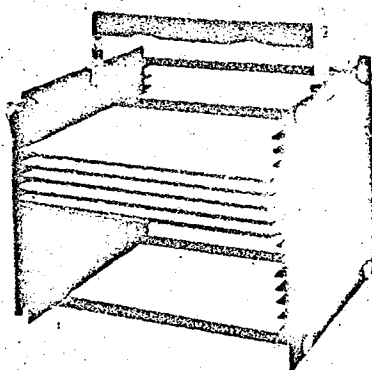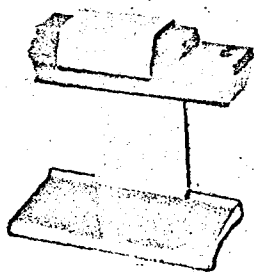
FIGURE 9

APPARATUS FOR
THIN LAYER CHROMATOGRAPHY[*]

(a) Stainless steel dessicating cabinet
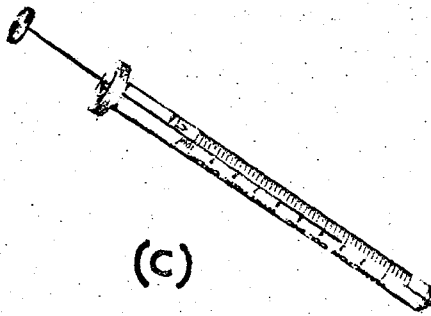(b) Drying rack for glass plates
(c) Long-short wave ultra-violet lamp
(d) Aerosol reagent sprayer

[*]Permission Brinkmann Instruments, Inc.
Westbury, New York

Upper electrode   Sp 2017
National Spectroscopic
A division of Union Carbide
Carbon Products Division
270 Park Avenue
New York, New York
10017

16.   35 mm film for the emission spectrograph
      Spectrum Analysis Number 1
      Eastman Kodak

      Chemicals.

1.   Rare Earth Chlorides
     American Potash and Chemical Corporation
     258 Ann Street
     West Chicago, Illinois
     60185

     Lanthanum   538ANH

     Cerium   237ANH

     Praseodymium   729.9

     Samarium   823

     Europium   1013

     Gadolinium   929.9

     Terbium   1805

     Purity of each rare earth chloride: 99.9%

2.   Adsorbents
     Brinkmann Instruments, Inc.
     Cantiague Road
     Westbury, New York
     11590

     Silica Gel HR

     Silica Gel N

     MN-Cellulose 300

     MN-Kieselguhr N

     Selectacel P

3. Di-(2-ethylhexyl) phosphoric acid
   K&K Laboratories
   6725 Sunset Boulevard
   Hollywood, California

4. 8-Hydroxyquinoline, Reagent
   K&K Laboratories

5. Kojic Acid, Reagent
   K&K Laboratories

6. 1-butanol, Reagent
   Wilshire Chemical Company, Inc.
   25324 South Broadway
   Gardena, California

7. Kodak Developer D-19

8. Kodak Indicator Stop Bath

9. Kodak Fixer

10. Kodak Hypo Clearing Agent

11. Kodak Photo-Flo 200

The remainder of the chemicals were obtained from the
department stockroom.

    Nitric Acid
    Hydrochloric Acid
    Sulfuric Acid
    Perchloric Acid
    Acetic Acid

    Ammonium Hydroxide

    Ethyl Alcohol
    Cyclohexane
    Acetone

    Aurintricarboxylic Acid Ammonium Salt

Experimental Procedures.

Successful separations via thin layer chromatography

are distinctly enhanced through concentrated effort on the

techniques involved in plate preparation, subsequent care

of the prepared plates, spotting of the plate with the sample

to be separated, and the means of detection of the spots on

the plate and the final determination.

When a glass plate was used for a separation, the

layer was readily removed with a single-edged razor blade.

The plate was then rinsed with warm water. A small amount

of cleansing powder was sprinkled on the plate, and it was

scrubbed with a sponge on both sides. The plate was rinsed

three more times; first with tap water, then a dilute sol-

ution of nitric acid, and finally with deionized water.

The plate could have been air dried, but drying with

a stream of warm air from a dryer lessened the chances of

streaking and water spotting.

At this point the clean plates were stored in a

closed cupboard so that the amount of dust settling on them

could be held to a minimum.

The standard mounting board was placed on a flat

surface and anchored on the end away from the spreader

starting point so that the board would not move when the

adsorbent was being spread on the plates. A thin stream

of water from a water bottle was sprayed along the length

of the board from one end to the other. This improved

adherence of the glass plate to the plastic board. The plates were then placed on the mounting board with a 5 X 20 centimeter plate on either end and five 20 X 20 centimeter plates between these. The small plate on either end permitted room for the DeSaga spreader to rest before the plates were spread and following the spreading of the plates with the adsorbent.

The adsorbent slurry was prepared in an Osterizer blender. Proportions of adsorbent and chemicals for the preparation of these different layers are given below.

1. 30 grams Silica Gel HR
   45 milliliters 1-butanol
   3 milliliters HDEHP

   Adsorbent supporting 0.1 ml HDEHP per gram

2. 30 grams Silica Gel N
   40 milliliter 1-butanol
   6 milliliters HDEHP

   Adsorbent supporting 0.2 ml HDEHP per gram

3. 20 grams MN-Cellulose 300
   90 milliliters 1-butanol
   4 milliliters HDEHP

   Adsorbent supporting 0.2 ml HDEHP per gram

The adsorbent and chemical were placed in the blender together and blended at high speed for two minutes, and at a low speed for thirty additional seconds. This produced a smooth slurry of the appropriate viscocity.

The slurry was poured into the DeSaga spreader as rapidly as possible and spread on the plates without delay to limit the amount of demixing which might have occurred.

The spreading of the adsorbent on the plate must be
accomplished slowly, deliberately, and with a minimum of
hesitancy along the way. Every hesitation yielded an ad-
sorbent ridge of greater thickness than the rest of the
plate.

The completed plates were air dried for five or
six hours and then placed in a desiccator cabinet over
anhydrous calcium chloride.

The spotting of the plates was the most painstaking
step of the total thin layer procedure. This was accom-
plished with a fifty microliter Hamilton syringe with
attached five centimeter needle. The volume of sample dis-
pensed was 0.5 to 1.5 microliter. The spot produced from
this volume of liquid had a diameter on the adsorbent of
from 0.5 to 0.75 centimeter. The two centimeter rule should
be adhered to here. The spots on the plate should be two
centimeters from the lower edge of the plate; two centimeters
apart and two centimeters from the edges of the plate.

After spotting, a few minutes was allowed for the
spots to dry completely. At this point they were visually
undetectable on the plate. The plate was ready to be placed
in the chromatography tank.

The tank was lined with three separate sized sheets
of Whatman No. 1 filter paper. One of these was cut to the
width of the tank and had a sufficient length to cover the
back, bottom, and one-half of the front of the tank. Another

piece was cut the width of the side of the tank and had a sufficient length to cover both sides as well as the bottom. Finally, a third piece was cut to fit the inside of the cover of the tank. These pieces of filter paper were appropriately placed in the tank after 250 milliliters of the solvent had been poured into the tank. A large plastic syringe was used to completely wet the filter paper with the developing solution.

Solvent saturation within the tank proved essential for a straight solvent front on the plate. The dampened filter paper lining most of the interior of the tank, plus the solvent itself, was at first expected to produce sufficient vapor pressure at room temperature. However, three small beakers of tank solvent with filter paper wicks running from one beaker to the next, placed in the front corners and front center of the tank proved essential to developing a straight solvent front. With this alteration the solvent front could almost be traced with a ruler's edge.

The plate was placed in the tank in as near to a vertical position as possible. Only a few millimeters of the adsorbent along the lower portion of the plate was immersed in the solvent. The spotted portion of the plate was not initially immersed in the solvent. The cover of the tank was replaced as quickly as possible to allow for rapid reestablishment of the vapor equilibrium within the tank.

Since the tank bottoms have a convex surface, a problem of leveling the plate occurred. Two plexiglas strips approximately 2 X 6 centimeters in length were laid on the bottom of the tank parallel to the ends of the tank. These made a level support for the plate.

The time required for the solvent to move ten centimeters up the plate beyond the position where the plate was spotted varied depending upon the concentration of the stationary phase, HDEHP, in the adsorbent, and also the type of adsorbent on the plate. Most plates required an average of sixty to ninety minutes for development.

When the ten centimeter line was marked on the plate with a stylus before immersion, the problem of determining when to remove the plate from the tank was simplified.

When the mobile phase had been adsorbed over the pre-determined distance, the plate was removed and placed vertically on a metal rack. The plate was partially dried by placing the adsorbent side of the plate away from an air blast dryer and allowing the warm air to move against the reverse side of the plate. Then the plate was air dried for another ten minutes.

After drying, the plates were sprayed with the 8-hydroxyquinoline - kojic acid reagent and immediately placed in an atmosphere of ammonia vapor for several minutes. When removed from the ammonia vapor tank and viewed under ultraviolet light, the individual rare earth spots

were a deep blue in color; Lanthanum fluoresced brightly.
While the plate was still under the ultraviolet light, the
spots on the plate were carefully outlined on the adsorbent
with a stylus.

The R_f values were calculated, recorded, and the
plate Xeroxed as suggested by Hilton and Hall (35).

The final step in the procedure was to scrape the
individual spots from the plate and place them in appropri-
ately labelled sample bottles, and an emission spectrum of
each sample was taken using the 1.5 meter Bausch and Lomb
emission spectrograph.

The film from the emission spectrograph was developed,
and each spectrum of the material from a spot on the plate
was then compared with standard spectrum film strips. This
was the final qualitative determination of the rare earth
separation on the plate.

CHAPTER VII

EXPERIMENTAL RESULTS

The Adsorbent.

Five different adsorbents were used in this separation with varying degrees of satisfaction.

(1) Selectacel P

This adsorbent is a product of Carl Schleicher & Schuell Company of Keene, New Hampshire. It is a cation exchanger prepared by the phosphoric acid esterification of cellulose. The adsorbent was selected for use in this separation of rare earth cations because of its high exchange capacity and capability of adsorption of cations from very acidic media.

Selectacel P was used only for a brief period of time because its adherence to the glass plate was not totally satisfactory, and the adsorbent was quickly washed off of the plate to the uppermost portion of its immersion in the acidic mobile phase. Of greater importance, little separation of the Lanthanides was effected on this adsorbent.

(2) Kieselguhr G

In an aqueous slurry Kieselguhr G is a neutral adsorbent containing a $CaSO_4$ binder. The use of this adsorbent was discontinued following the development of a few plates because of the possiblity of interference with the separatiom of the rare earths by the calcium ions of the binder in the adsorbent.

The carrying capacity of Kieselguhr is low which was
another factor in the decision not to continue its use as an
adsorbent in this separation.

(3) MN-Cellulose 300

This adsorbent without a binder is a product of
Macherey, Nagel & Company, a German firm. Like Kieselguhr,
cellulose is neutral in aqueous solution.

This was the first adsorbent upon which the HDEHP was
retained. The original method used for this procedure was
according to Cerrai & Testa (12,14). 16.12 g of HDEHP was
placed in 100 ml of cyclohexane (0.5$\underline{M}$ solution). This sol-
ution was mixed with 200 ml of 1$\underline{M}$ HCl wherein two phases
were formed. This mixture was shaken for several minutes,
and then set aside to await the formation of an organic and
an inorganic layer. Anhydrous Na_2SO_4 was added to the organic
layer following its separation from the inorganic layer in a
separatory funnel. After a few minutes the liquid was de-
canted from the solid Na_2SO_4 and 20 g of MN-Cellulose 300 was
added to the liquid. The cellulose in the HDEHP-cyclohexane
mixture was then stirred for 15 hours. At the appropriate
time the cyclohexane was filtered off, the cellulose dried be-
tween filter paper layers and then dried for 2 hours at 70° C.

For plate preparation this adsorbent is again slurried
with cyclohexane. The rapid evaporation of the cyclohexane
made it difficult to prepare a smooth layer, and adherence to
the plate following evaporation of the cyclohexane was poor.

The method ultimately used for the preparation of all
the plates subsequently developed in the research was due to
Holzapfel et al (36). The adsorbent was placed in an Oster-
izer blender with 1-butanol and the HDEHP and mixed at high
speed for two minutes, and then for one minute at low speed.
The 1-butanol evaporated more slowly than the cyclohexane,
and its greater viscosity seemed to aid in the spreading of
a smoother layer. This layer adhered well to the plate.

(4) Silica Gel N

This adsorbent is a Merck product and was selected
for this work because it contains no binder, no ultra-violet
indicator, and the iron content is only 0.01%. Even this
small quantity of iron present as an impurity proved to be
excessive. During the development with aqueous acid, the
iron and other impurities in the adsorbent were carried along
in an impurity front. When the dried plate was sprayed with
the detecting reagent, and placed in an ammonia atmosphere,
this front appeared as a yellow band approximately 1.5-2.0 cm
behind the solvent front. A drop of potassium thiocyanate on
the yellow band on the plate produced the typical red color-
ation of $Fe(SCN)_6^{---}$, hexanthiocyanatoferrate (III). This
resulted in the decision to purify the adsorbent according to
Seiler (79).

The purification of the silica gel was a time consuming
procedure. One hundred grams of the silica gel N was washed
with 100 ml of concentrated HCl plus 100 ml de-ionized water

and allowed to settle for 24 hours. After this length of
time the liquid was decanted from the solid and 200 ml of
de-ionized water was added, the mixture was stirred, and
then as much of the liquid as possible was removed by suc-
tion filtration. The washings with de-ionized water were re-
peated until the pH of the filtrate was 7. Each batch of 100 g
of silica gel N required no less than 25 washings to bring the
pH from 1 to 7.

When the adsorbent was once again neutral, each 100 g
was washed with 60 ml of absolute ethanol and 60 ml of benzene.
At this point the silica gel N was removed from the Buchner
funnel and oven dried for 24 hours at 120° C. Finally, the
dried silica gel was passed through a 325 meshes to the inch
screen sieve. The sieving of the adsorbent yielded particles
smaller than the original ones, and consequently a smooth layer
on the plate. However, in use the solvent was adsorbed much
less rapidly onto this purified product, and the development
time increased appreciably.

Perhaps it was the smaller particles of the silica gel
N following purification, but the adsorbent with HDEHP did
not adhere to the plate as well as it did prior to purification.
One gram of soluble starch was added per each 29 grams of silica
gel in an effort to solve the problem. This produced a more
brittle layer which had a distinct tendency to blister in the
atmosphere of the chromatography tank. The developed plate

could not be dried and sprayed with the detecting reagents without an appreciable loss of the layer.

The addition of starch was abandoned in favor of the addition of 1 g of sodium silicate per each 29 grams of the silica gel. This improved the adherence of the layer, but added another impurity to the adsorbent.

Following the purification, the line demarcating the impurity iron was reduced, but still visible.

An analysis of a sample removed from the impurity band of unpurified silica gel N by American Spectrographic Laboratories of San Francisco revealed the presence of the following impurities in the adsorbent:

ELEMENT	% IN 15 mg SAMPLE
Si	Principal Constituent
Mg	0.025%
Fe	0.010%
Pb	0.005%
Al	0.015%
Cu	0.080%
Ti	0.025%
Zr	0.001%
Ca	0.100%
Ba	0.001%

The impurity front shows clearly in Figure 10 on page 58. 0.5$\underline{M}$ HCl was used as the mobile phase in the developing of this unspotted plate. The adsorbent was unpurified Silica

Gel N with no reverse phase material. When the solvent front

had reached the line marked A, the plate was removed from the

chromatography tank, dried, and sprayed with the detection

reagent. In the dark under ultra-violet light, two distinct

bands were visible. Each of these bands was 2-3 mm wide. The

lower band was a deep brown color under UV whereas the upper

band was a light yellow in daylight and fluoresced brightly

under the UV light.

(5) Silica Gel HR

Merck produces Silica Gel HR with a binder of hydrated

silicon dioxide, no ultra-violet indicator, and a maximum of

0.001% iron. The fact that the silica gel N contains ten

times as much iron as the silica gel HR is significant. The

impurity band formed on silica gel HR as well as on the silica

gel N, but it was not as noticeable and less interfering to

the separation. Silica gel HR was not purified.

A troublesome phenomenon took place on both silica

gels and to a lesser extent on cellulose and kieselguhr dur-

ing development when these adsorbents were retaining HDEHP

as a stationary phase. A distinct second front was observed

during the development of the plate in the tank. This front

generally lagged 3-4 cm behind the solvent front and no rare

earth could migrate beyond it. In fact, it even held up the

impurity front. This reduced the R_f value of each rare earth

proportionately. G. Werner, an associate of Holzapfel, stated

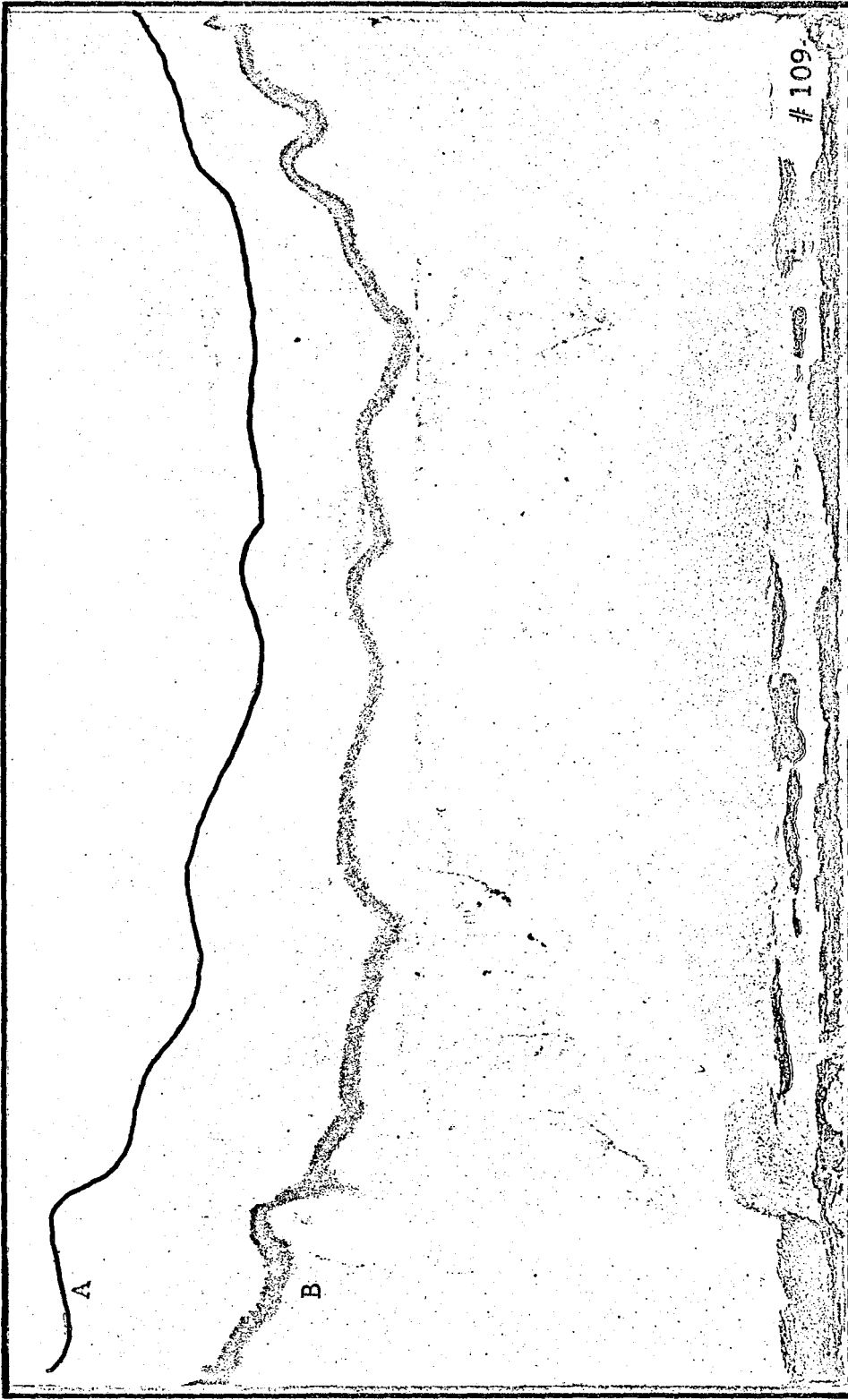in a personal communication that they had encountered this

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FIGURE 10

(A) SOLVENT FRONT (B) DOUBLE FRONT: HDEHP-ADSORBENT
HYDROGEN BONDS SEVERED BY AQUEOUS ACID MOBILE PHASE.

problem in their reversed-phase TLC work with the rare earths
(36, 37), and it was of a serious enough nature that they
could use only R_f values up to 0.8.

Double fronting, a nomenclature applied to this second
front in reversed-phase TLC, is believed to occur as the re-
sult of the cleavage of stationary phase-adsorbent hydrogen
bonds by the hydrogen ions in the mobile phase (4), and as a
result some of the stationary phase is moved along with the
acid, but cannot keep pace with it.

MN-Cellulose 300 resisted double fronting to a great
extent since the hydrogen bonds formed between the HDEHP and
the adsorbent are stronger than the silica gel-HDEHP hydrogen
bonds.

The Mobile Phase.

HNO_3, HCl, or $HClO_4$ have been employed most often as
the mobile phase in reversed-phase TLC separations of rare
earths. Holzapfel et al (36) and Winchester (93) made no
distinctions in the advantages of either HCl or HNO_3. HCl
was used in the work of Pierce and Flint (72), Cerrai et al
(13, 14, 15), Sochacka et al (84), and Peppard et al (66).
Daneels et al (24) stated that $HClO_4$ gave more reproducible
results in the separation of rare earths than did HCl.

Acetic acid was also tried as the mobile phase in
this work with no success. After the development, the drying
of the plate, and the spraying with the detection reagent,
no separation of the rare earths was apparent. The surface

of the plate had a smeared appearance as if the Lanthanides had been adsorbed in random directions. The failure was predictable by the organic nature of the mobile phase as well as the stationary phase. Peppard et al (65) has stated that in acetic acid both the monobasic and dibasic phosphoric acids are monomers due to solute-solvent interaction. Depolymerization of the organic derivatives of the phosphoric acid probably occurs due to the new hydrogen bonds formed between the acetic acid and the HDEHP.

In this work HNO_3 was favored as the mobile phase since this acid yielded slightly clearer separations than HCl, $HClO_4$, or H_2SO_4.

The Temperature.

Experimental evidence would indicate that temperatures higher than room temperature are beneficial to reversed-phase TLC separation of the rare earth metals.

Crouse and Horner (21) have stated that the extraction rate of the rare earths by the HDEHP increases with an increase in the temperature. A number of researchers with an interest in reversed-phase chromatographic rare earth separations, particularly those working with column chromatography, have maintained higher temperatures during the separations (13, 67, 68, 69, 80, 93).

Pierce and Flint (72) developed their thin layer plates at at temperatures ranging from 60-80°C, by placing their chromatography tanks in thermostatted air-baths. A ply-wood

cabinet with windows in the front for observation of the
plates in the tanks, an opening in the side of the box for
a forced-air dryer, and a thermometer through the top was
built for the work done in this research. This air-bath was
built to accommodate two chromatography tanks. Figure 11 on
page 62 is a drawing of this air-bath.

With this air-bath a number of plates were developed
at 45-55°C. At these slightly higher than room temperatures
the increase in vapor pressure within the tank was great
enough to cause the plates to sweat, and this did not improve
the progress of the separations. The lids of the tanks in
the air-bath were placed in such a manner as to leave a small
opening for escape of some of the vapor, but this upset the
vapor equilibrium in the tank and reduced the resolution of
the rare earths.

The results of separations at the higher temperatures
were not sufficiently improved over those at room temperature
to warrant the continued use of the air-bath.

Bobbitt (5) stated in his text on TLC that while the
importance of temperature variations cannot be overlooked in
paper chromatography, the effects of these variations in thin
layer chromatography has little effect.

The majority of the separations which were effected as
a part of this work were at temperatures between 25 and 30° C.
Generally, warm air from a forced-air dryer was circulated
about the back portion of the chromatography tank prior to the

placing of the plate in the tank for the purpose of establish-
ing vapor equilibrium. The temperature change due to this
procedure was minimal.

The Detection.

If the spots on the tin layer plate are not visible
following the development, a means of locating their position
on the plate must be implemented. This phase of the total TLC
procedure is often referred to as the detection (74) or the
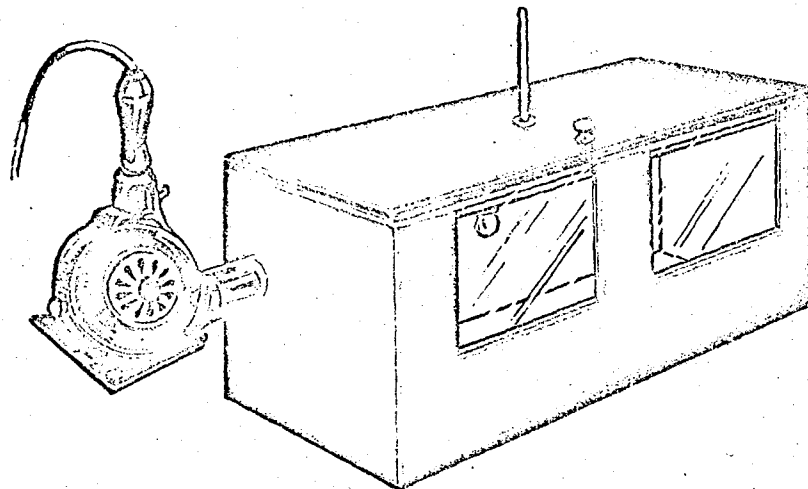visualization (5).

FIGURE 11

CIRCULATING AIR CHAMBER

The most frequent reference in the literature for the
detection of rare earths on the plate is to a 1% solution of
8-hydroxyquinoline in a 60% ethanol solution (12, 36, 37, 72,

73). The 8-hydroxyquinoline, also known as oxine, is an important organic precipitant. The precipitation is usually carried out in an ammoniacal medium. This reagent complexes with most of the transition metals plus the alkali and alkaline earth metals to form coordination compounds which in a large number of cases yield strikingly similar IR spectra (19). The rare earths form inner complexes with the oxine. For these metals there is some question as to the metal-ligand ratio in the complex formed (83). Charles et al (18) determined that the experimental molar ratios for the oxinate-metal are considerably below three. For example, the oxinate-R.E. ratio for La was determined to be 2.48. All others are also in a less than 3 to 1 ratio.

The dry adsorbent on the plate was sprayed with the 8-hydroxyquinoline and placed in an atmosphere of ammonia vapor. The ammonia vapor tank was prepared by pouring 750 ml of concentrated NH_4OH into a chromatographic tank. Four 25 ml beakers were also filled with the NH_4OH and placed in the corners of the tanks. A 10 X 20 cm glass plate was laid flat over the four beakers so that the thin layer plate would have a place to rest vertically in the tank without being immersed in the base. The plate was allowed to remain in the tank for two minutes, and when removed the spots on the plate had a faint yellow color.

The plate was viewed in the dark under ultra-violet light. With the exception of La which fluoresced a bright pale

blue, the other light rare earths appeared as deep blue spots. While still under the ultra-violet light, the spots on the plate were outlined with a stylus.

Another reagent suggested by Lederer (50) was prepared by mixing 5 g of 8-hydroxyquinoline plus 1 g of Kojic acid in a liter of 60% ethanol. This reagent was used for the detection of the Lanthanides on the majority of the plates since the addition of the Kojic acid to the oxine deepened the blue color under the UV light and enhanced the La fluorescence.

With the oxine-kojic acid reagent Eu fluoresced red-orange under the UV light after 48-72 hours. This was the only one of the rare earths used in this work (La-Tb) which developed a distinct color under the UV light after the plate was dried and stored.

All of the spots on a plate which had been sprayed with the oxine-kojic acid reagent began to darken after several hours in the laboratory atmosphere. Ce darkened the most. Its darkening almost to a black could perhaps be explained since the Ce(III) complex of oxine when exposed to the oxygen of the atmosphere is readily oxidized to Ce(IV) (60).

It was possible to view the plate again under the UV light several hours or several days later if the plate was sprayed again with the detecting reagent. This procedure could be repeated several times if necessary.

The Separation.

Plates with silica gel HR layers and spotted with the individual rare earths La - Gd were run at five different HNO_3 concentrations. During subsequent runs at each acid concentration, the quantity of HDEHP in the adsorbent was altered from 0.1 ml per gram of silica gel to a maximum of 0.3 ml per gram. It was determined that for a particular acid concentration the R_f values of the rare earths decreased with increasing atomic number. For the individual rare earth the R_f value increases with increasing acid concentration, and decreases with the increasing load of the stationary phase on the adsorbent. Table VI on pages 66 and 67 shows the trends in these variables. The R_M values listed in this table are from Stahl (87). The R_f values are average values derived from at least two and sometimes three plates run at each nitric acid concentration and HDEHP concentration.

Figure 12 on page 69 represents a plot of the R_M value[*] vs the log of the acidity of the mobile phase. This plot indicates the dependence of the zone-migration parameter, R_M, upon the acidity of the mobile phase. La, Ce, Pr, and Nd have slopes of approximately -2.6; Sm and Eu -3.4; and Gd has a slope of -5.5.

Figure 13 on page 70 shows the dependence of the zone-migration parameter on the concentration of the stationary phase retained on the adsorbent at varying acid concentrations. The plot is of R_M value vs HDEHP concentration in ml HDEHP per gram on silica gel.

[*] $R_M = \log \left[(1/R_f) - 1 \right]$

TABLE VI

RARE EARTH R_f VALUES
AT VARYING CONCENTRATIONS
OF HNO_3 AND HDEHP

| HNO_3 | R.E. | MILLILITERS HDEHP PER GRAM SILICA GEL HR | | | | | | | |
| | | 0.1 | | 0.15 | | 0.2 | | 0.3 | |
(M/1)		R_f	R_M	R_f	R_M	R_f	R_M	R_f	R_M
	La	.33	.308	.25	.477	.17	.689	.10	1.279
	Ce	.26	.454	.12	.865	.11	.908	.05	1.510
	Pr	.20	.602	.10	.954	.10	.954	.03	1.510
0.2	Nd	.21	.575	.07	1.12	.06	1.195	.03	∞
	Sm	0	∞	.02	1.69	0	∞	0	∞
	Eu	0	∞	.02	1.69	0	∞	0	∞
	Gd	0	∞	0	∞	0	∞	0	∞
	La	.69	-.347	.49	.017	.53	-.052	.21	.575
	Ce	.44	.105	.31	.347	.28	.410	.15	.753
	Pr	.39	.194	.27	.432	.24	.501	.12	.865
0.3	Nd	.36	.250	.23	.525	.19	.630	.12	.865
	Sm	.11	.908	.05	1.279	.03	1.51	0	∞
	Eu	.05	1.279	0	∞	0	∞	0	∞
	Gd	0	∞	0	∞	0	∞	0	∞

HNO$_3$ (M/1)	R.E.	MILLILITERS HDEHP PER GRAM SILICA GEL HR							
		0.1		0.15		0.2		0.3	
		R_f	R_M	R_f	R_M	R_f	R_M	R_f	R_M
0.5	La	.88	-.865	.78	-.550	.80	-.602	.59	-.158
	Ce	.83	-.689	.68	-.327	.65	-.269	.40	.176
	Pr	.78	-.550	.72	-.410	.61	-.194	.32	.327
	Nd	.78	-.550	.56	-.105	.40	000	.42	.140
	Sm	.30	.368	.28	.410	.12	.854	.06	1.195
	Eu	.20	.602	.12	.865	.05	1.279	.03	1.51
	Gd	.13	.826	.05	1.279	.01	1.996	00	∞
0.75	La	.92	-1.061	.84	-.720	.87	-.826	.75	-.477
	Ce	.91	-1.005	.72	-.410	.86	-.788	.65	-.269
	Pr	.90	-.954	.80	-.602	.76	-.501	.54	-.070
	Nd	.94	-1.195	.84	-.720	.76	-.501	.48	.035
	Sm	.76	-.501	.49	.015	.43	.122	.26	.454
	Eu	.52	-.035	.34	.288	.23	.525	.17	.689
	Gd	.39	.194	.26	.454	.13	.826	.05	1.279
1.0	La	.96	-1.38	.86	-.788	.95	-1.279	---	---
	Ce	.93	-1.061	.84	-.720	.88	-.865	---	---
	Pr	.92	-1.061	.80	-.602	.88	-.865	---	---
	Nd	.90	-.954	.84	-.720	.88	-.865	---	---
	Sm	.85	-.753	.71	-.389	.79	-.575	---	---
	Eu	.78	-.550	.54	-.070	.69	-.347	---	---
	Gd	.62	-.231	.34	.288	.37	.231	---	---

Each increase in the concentration of HDEHP on the adsorbent increased the time of plate development. A plate with 0.1 ml HDEHP per gram of silica gel with a 10 cm solvent run required 40-60 minutes for development. When the HDEHP concentration was double, the development time increased to 100-120 minutes, and approximately 150-160 minutes were required for a 10 cm development of a plate with 0.3 ml HDEHP per gram of silica gel.

HDEHP has a specific gravity slightly less than water (0.97), but it is more viscous. It is much like mineral oil in appearance. A load of 0.3 ml per gram of HDEHP on the adsorbent reduces the adherence of the layer to the plate. This layer flaked badly when dried and sprayed. The optimum concentration of the stationary phase on the adsorbent proved to be 0.2 ml per gram of adsorbent.

Figures 14 through 17 on pages 72-75 are Xeroxed TLC plates of the individual rare earths developed with varying mobile phase concentrations. Additional series such as this one were run with varying HDEHP concentrations. Two to three microliters with 5 micrograms per-microliter were spotted for each individual R.E. This was too heavy a load for a separation of the elements, but satisfactory for determination of individual R_f values.

The conclusion which was drawn from this phase of the work was that the most effective separation would probably
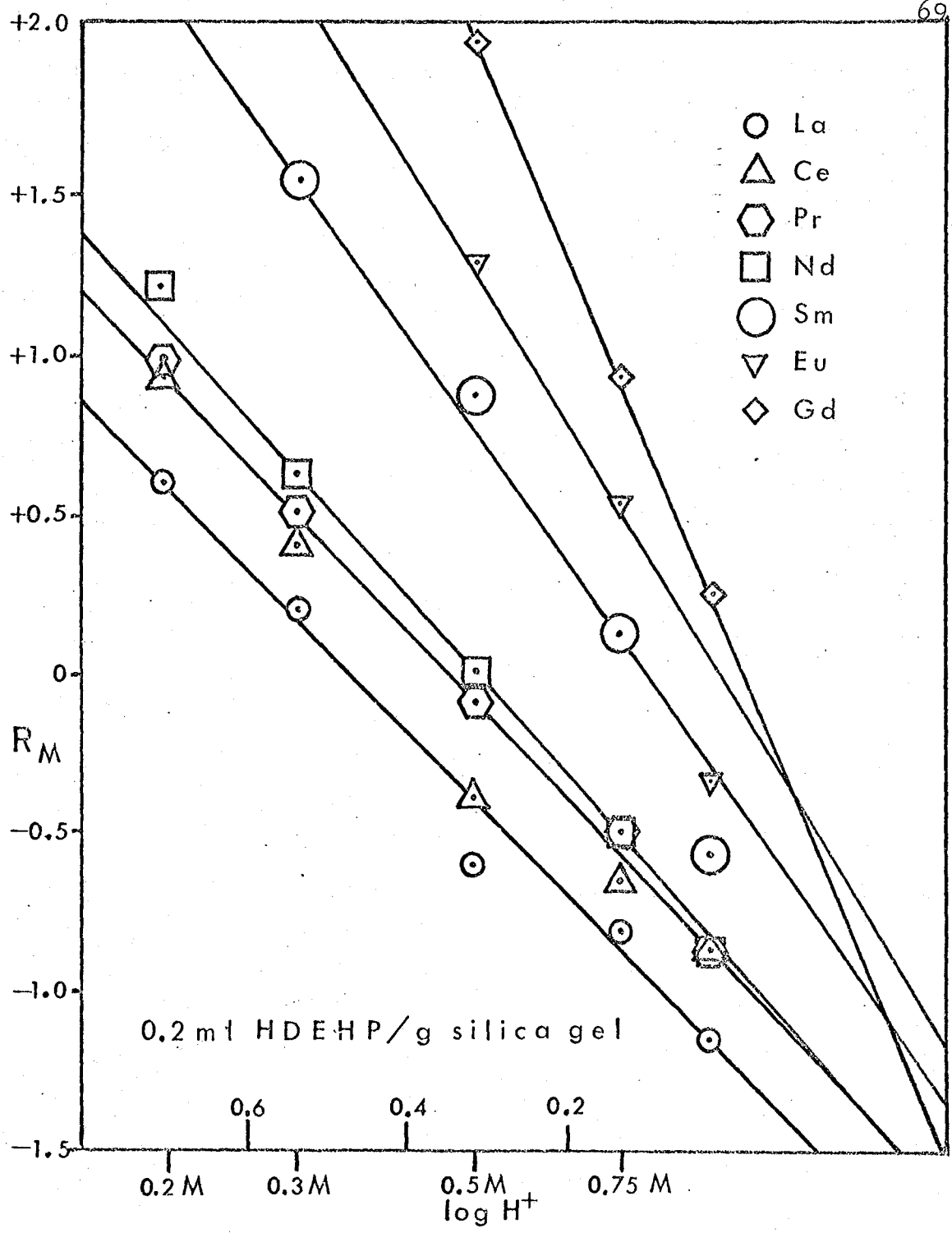
0.2 ml HDEHP/g silica gel

FIGURE 12

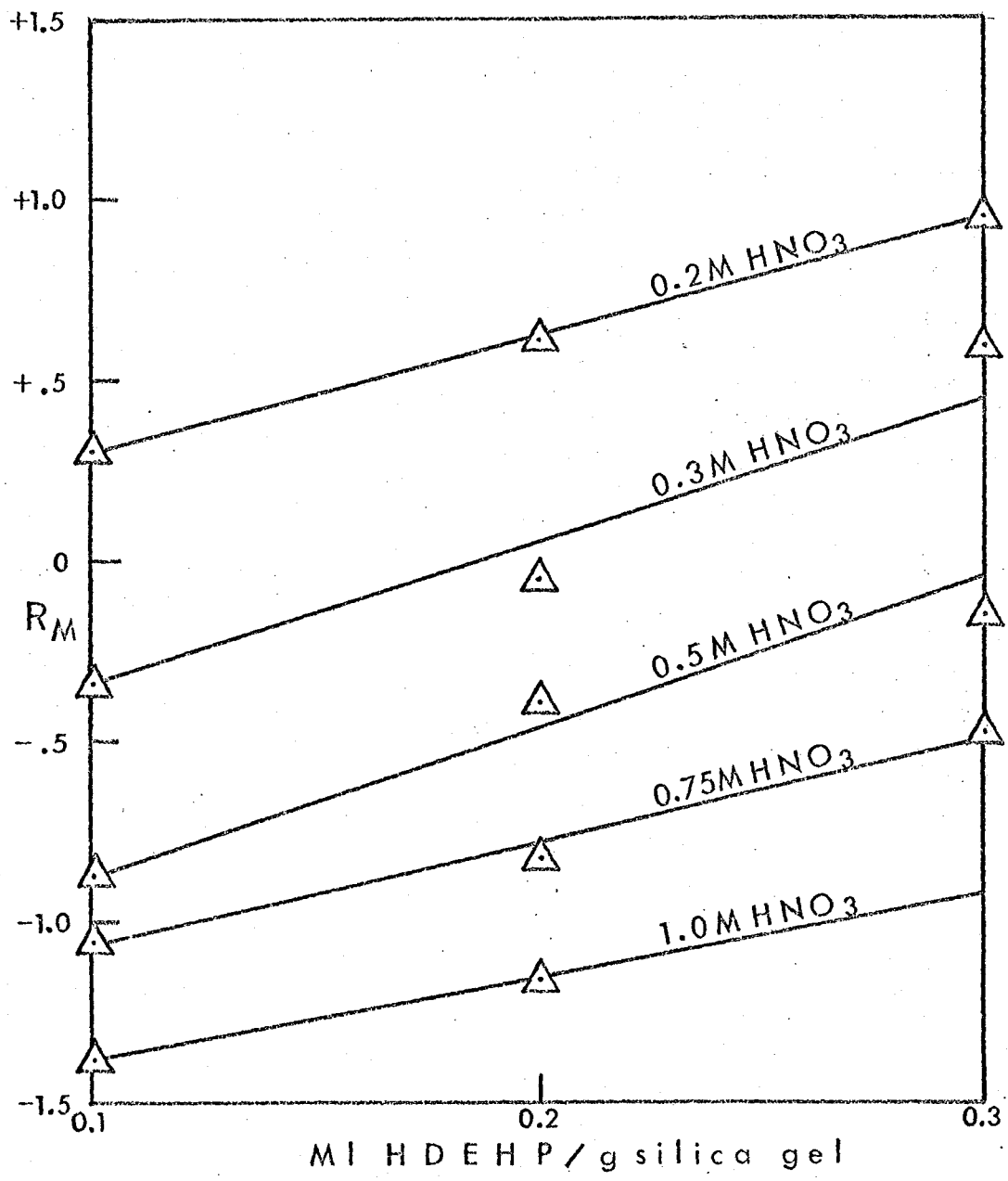R$_M$ vs H$^+$ ION CONCENTRATION

FIGURE 13

R$_M$ VS HDEHP CONCENTRATION

result from HNO$_3$ concentrations of 0.5 to 0.75 $\underline{M}$/l. It also appeared likely that a more efficient separation could be expected from a two-dimensional development as opposed to a one-dimensional development.

Reversed-phase two-dimensional TLC was attempted on a number of plates with individual and mixtures of the rare earths. The plate was developed in one direction, then removed from the tank and dried; the plate rotated 90° and developed in another tank containing an acid of higher concentration than that used in the first development.

The results of two-dimensional TLC were disappointing. After the plate was dried following the first development, the solvent front for the second development was always erratic. All of the two-dimensional determinations were run on either silica gel HR or silica gel N, and the silica gel was particularly susceptible to double fronting. Some of the HDEHP was moved along the adsorbent by nitric acid during the first development.. This destroyed the uniformity of the plate for the second development.

Figure 18 on page 77 is a copy of a plate developed two times in the same direction in an effort to a solution of the double-front problem. During the first development the nitric acid was allowed to pass over the full length of the adsorbent. When the plate was dried, the double front at A was clearly visible. Prior to the second development the adsorbent was spotted with the individual and mixtures of
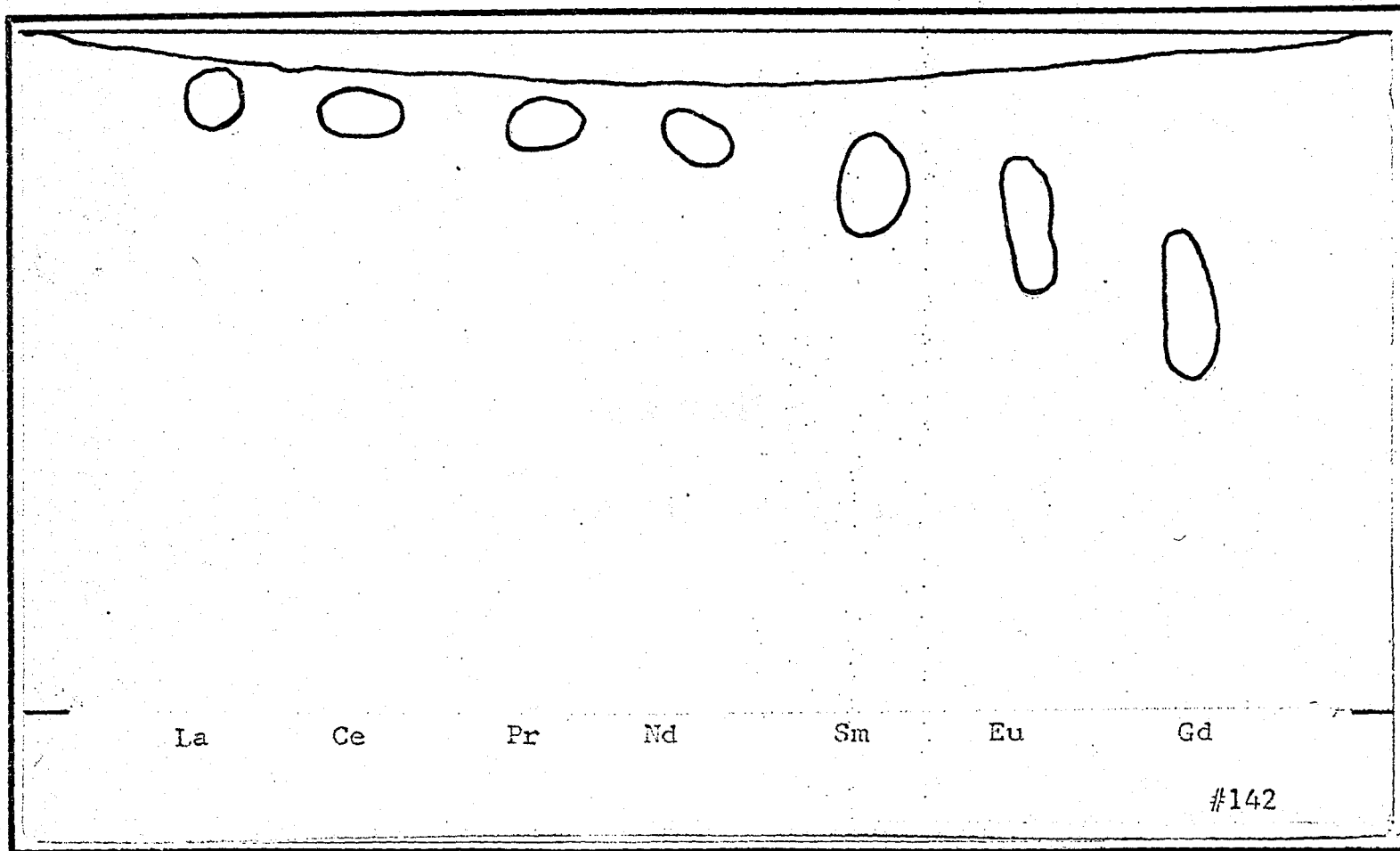
FIGURE 14

FIFTEEN μg EACH OF LIGHT RARE EARTHS ON HDEHP-
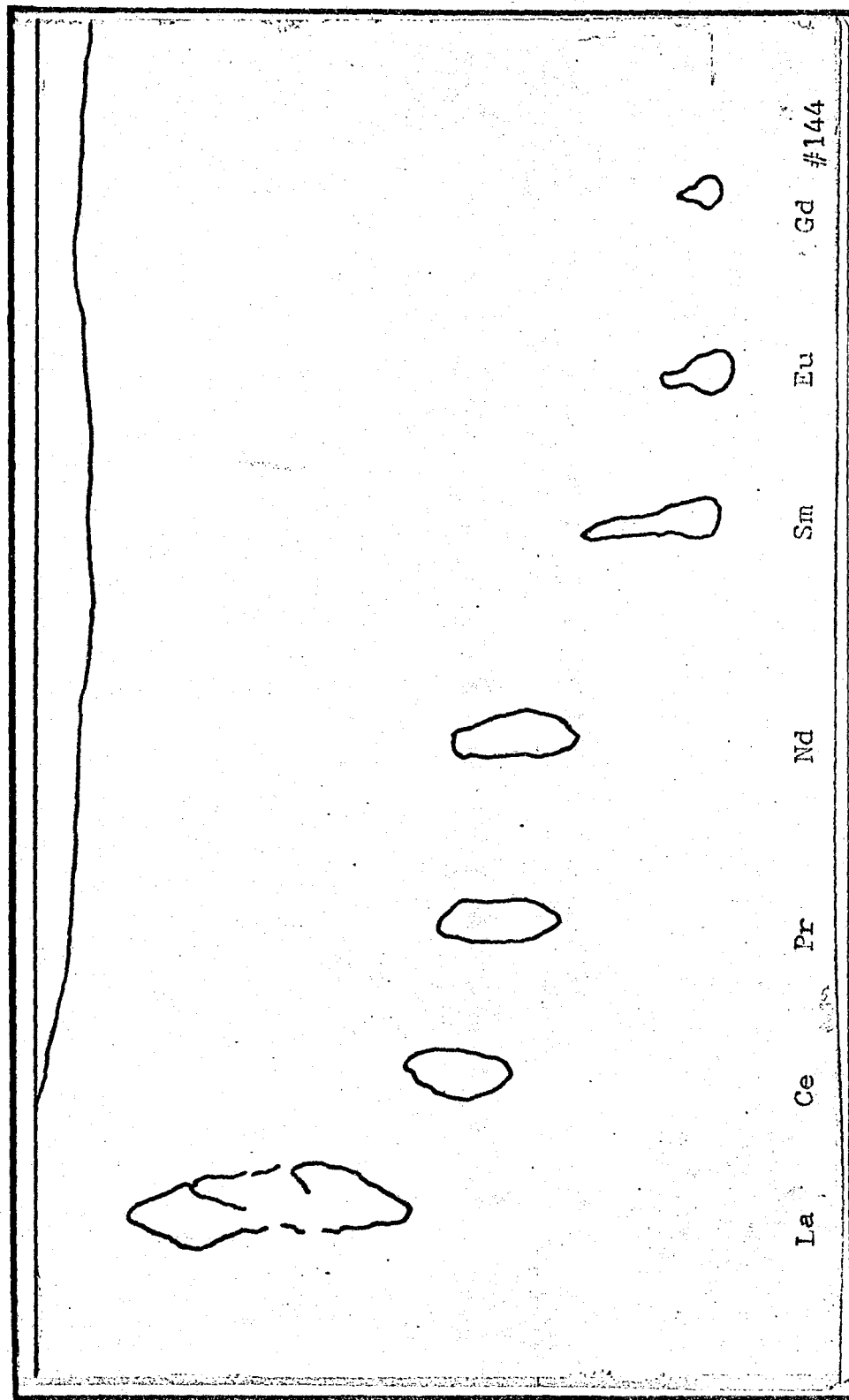SILICA GEL HR THIN LAYER. MOBILE PHASE 1.0M HNO_3.
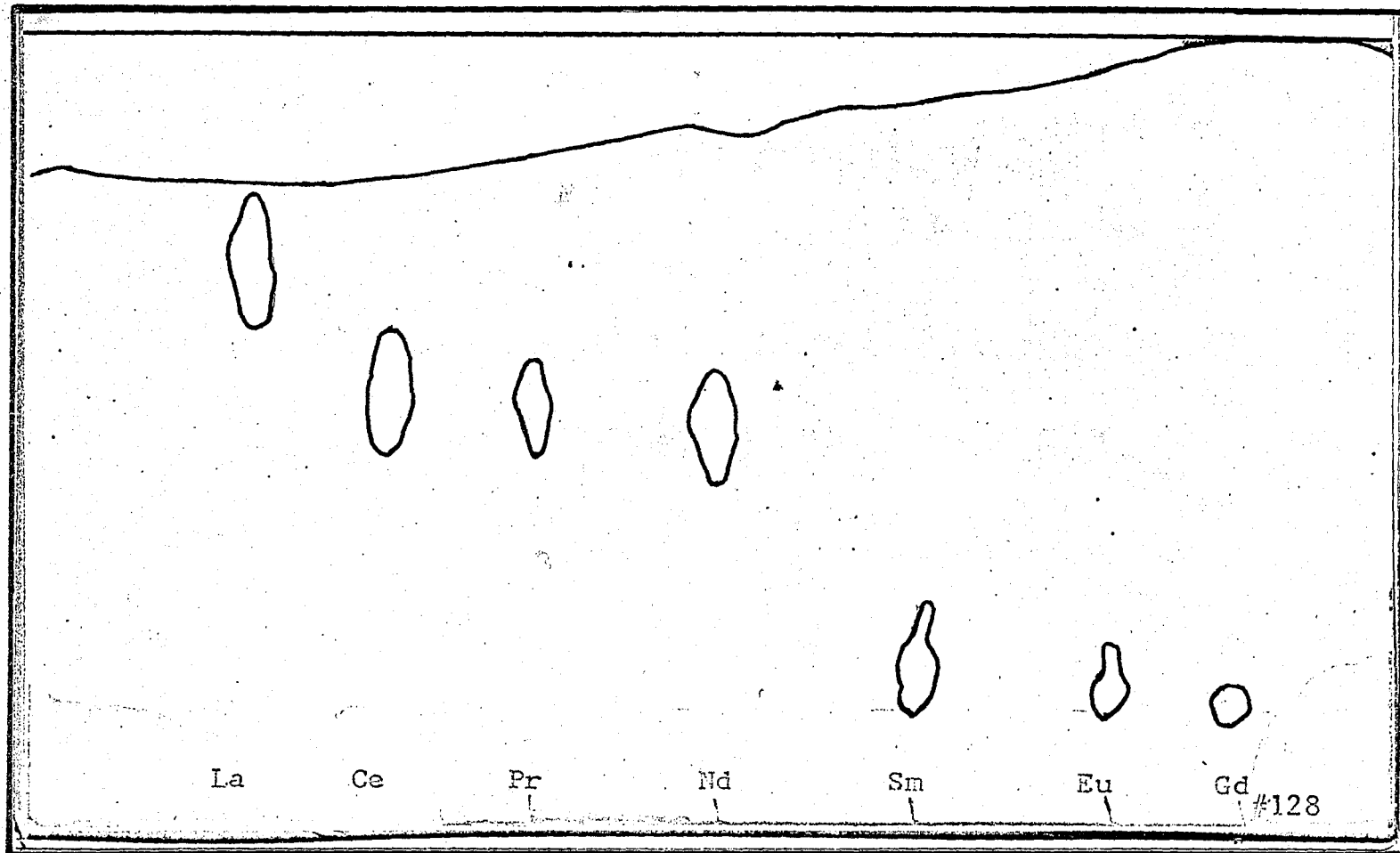
La   Ce   Pr   Nd   Sm   Eu   Gd   #144

FIGURE 15

TEN μg EACH OF LIGHT RARE EARTHS ON HDEHP-SILICA GEL
HR THIN LAYER. MOBILE PHASE 0.3M HNO_3.

FIGURE 16

FIFTEEN µg EACH OF LIGHT RARE EARTHS ON HDEHP-
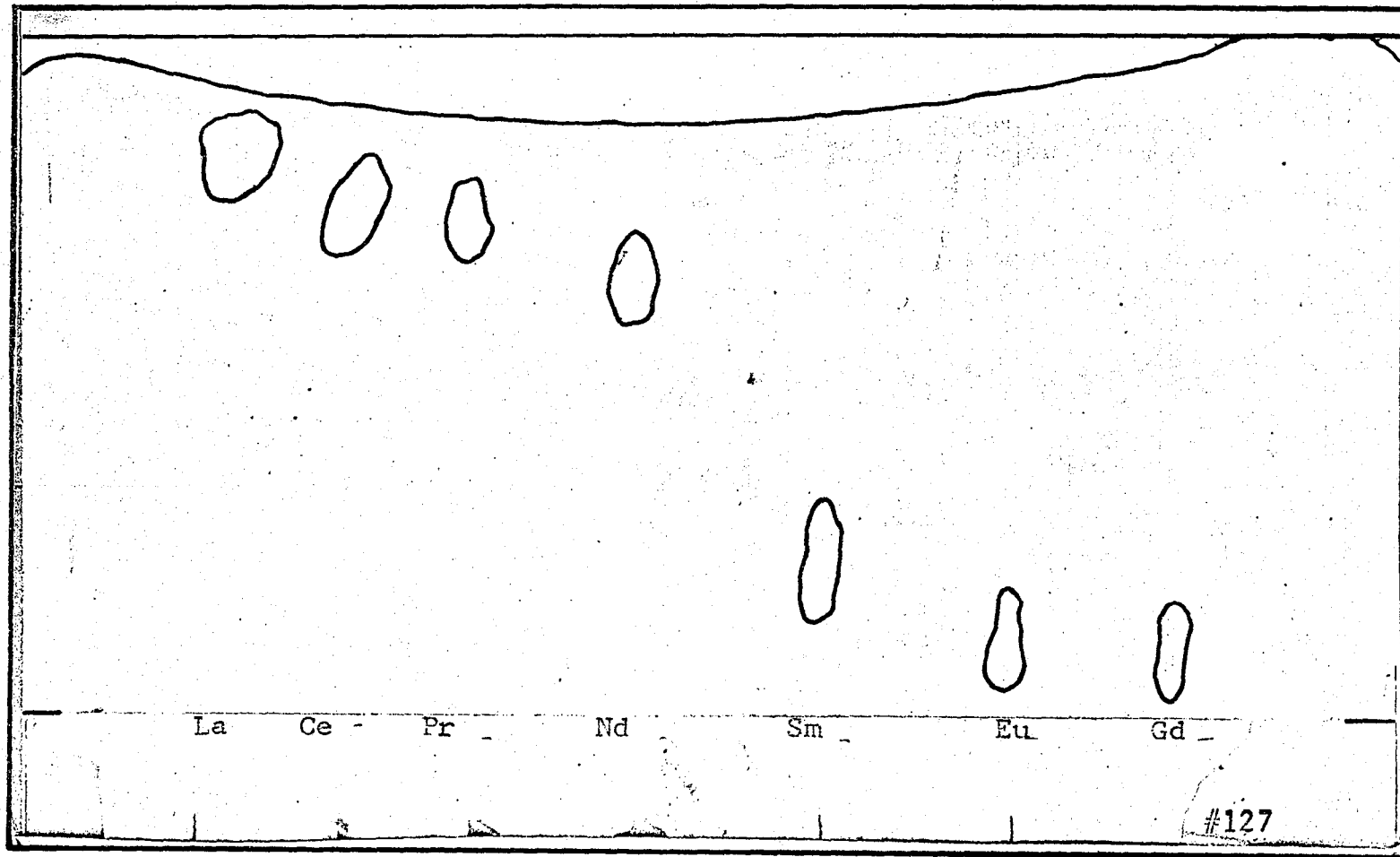SILICA GEL HR THIN LAYER. MOBILE PHASE 0.5M HNO$_3$.

74

La   Ce   Pr   Nd   Sm   Eu   Gd

#127

FIGURE 17

FIFTEEN µg EACH OF LIGHT RARE EARTHS ON HDEHP-
SILICA GEL HR THIN LAYER. MOBILE PHASE 0.75M HNO$_3$.

rare earths. To avoid an overlap of the double front, the
plate had to be removed from the tank after the acid had
moved only 7.6 cm during the second development.

The only practical solution to the double-fronting
proved ultimately to be a greater dependence upon cellulose
as an adsorbent for the separations.

A first glance at the individual R_f values at one acid
concentration was not encouraging when considering the pos-
sibility of a separation of a number of these cations. How-
ever, as was to be proven later, the R_f value of a rare earth
in a mixture may be slightly greater than the R_f of a pure
R.E. due to displacement analysis (81).

Figure 19 on page 79 shows an attempted separation of
Ce, Pr, and Nd. Table III on page 33 listed the separation
factors for adjacent rare earths. In this table it can be
noted that with HNO_3 as a mobile phase, no adjacent separation
factors are given for Ce-Pr or Pr-Nd, but only for Ce-Nd. The
separation factor of 1.55 for Ce-Nd is less than the average
separation factor for adjacent rare earths of 2.5. The low
value for the separation factor of Ce-Nd would indicate the
difficulty to be encountered in attempting to separate the
three rare earths in a single one-dimensional development.

The possibility that Ce(IV) might have a sufficiently
different R_f value from that of Ce(III) to warrant its use in
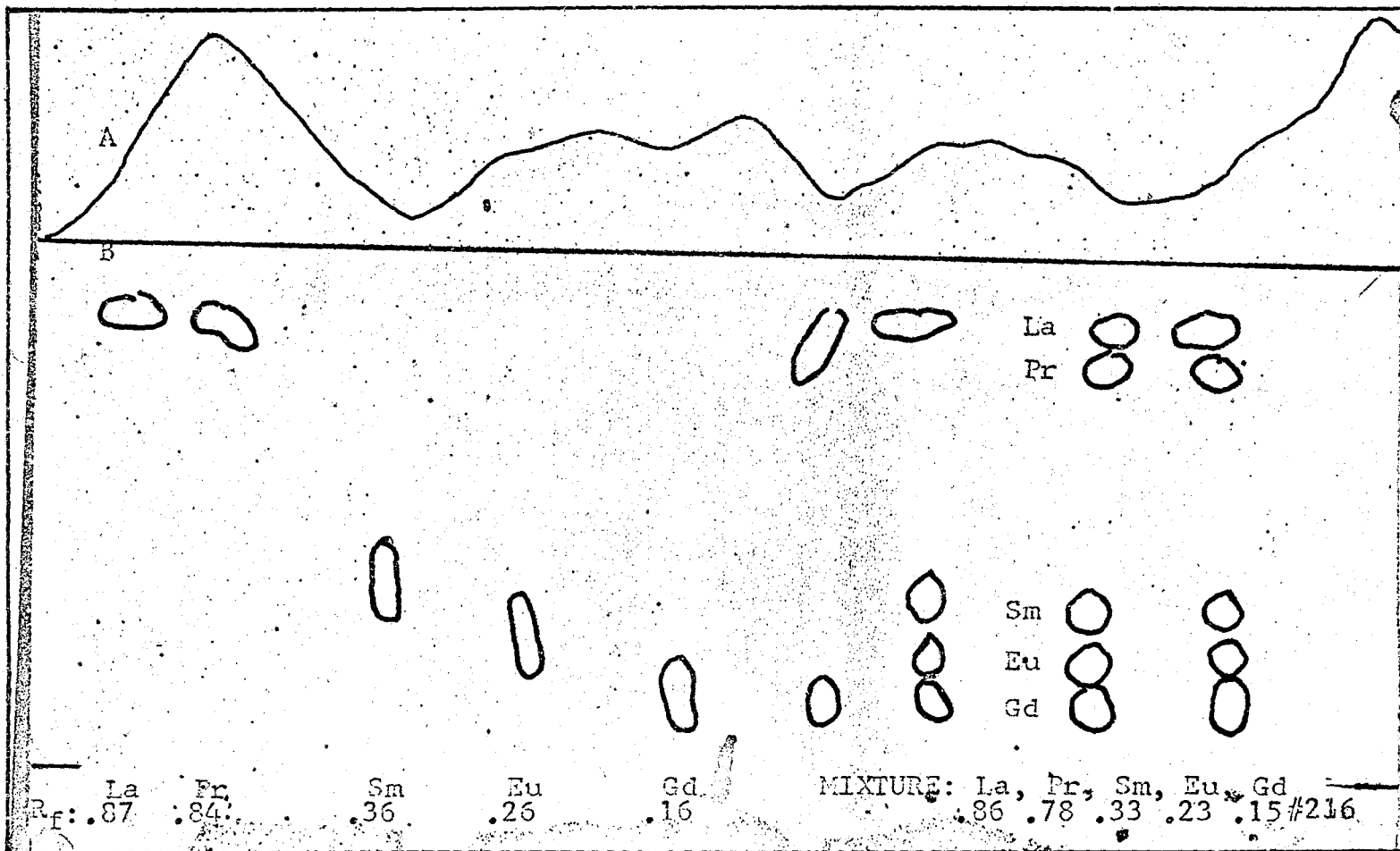the separation of Ce from Pr and Nd was suggested. The Ce(III),

FIGURE 18

(A) DOUBLE FRONT FROM FIRST DEVELOPMENT WITH NO SAMPLE. MOBILE PHASE 0.5M HNO_3.
(B) SOLVENT FRONT FOR SEPARATION OF 10 µg EACH OF FIVE LIGHT RARE EARTHS ON
HDEHP-SILICA GEL N THIN LAYER. MOBILE PHASE o.75M HNO_3.

Ce(IV), and a mixture of the two were run on cellulose with 0.5$\underline{M}$ HNO_3 as the mobile phase. Ce(III) had an average R_f value of .64 and C(IV) had an average R_f value of .61.

Figures 20, 21, and 22 on pages 81-83 are Xerox copies of two, three, and four element separations on silica gel HR.

Figure 23, on page 84, is a partial separation of the seven rare earths, La-Gd, on cellulose. As predicted previously, it was not possible to separate Ce, Pr, and Nd. They appear to gether with an average R_f value of .80.

A satisfactory separation of five of the light rare earths on MN-Cellulose 300 is shown in Figure 24 on page 85.

The maximum number of rare earths separated on a single plate in a one-dimensional development was six. The separation of La, Pr, Sm, Eu, Gd, and Tb on MN-Cellulose 300 with 0.75$\underline{M}$ HNO_3 is shown in Figure 25 on page 86.

One of the final separations is shown in Figure 26 on page 87. This was to be a separation of seven of the rare earth metals, however, a clear separation of the Pr-Nd pair was not possible.

The MN-Cellulose 300 retaining 0.2 ml HDEHP per gram of adsorbent proved to be the layer upon which the best resolution of the Lanthanides could be achieved.

The Determination.

The determination of the rare earths following the separation and detection was accomplished via emission spectrographic analysis.
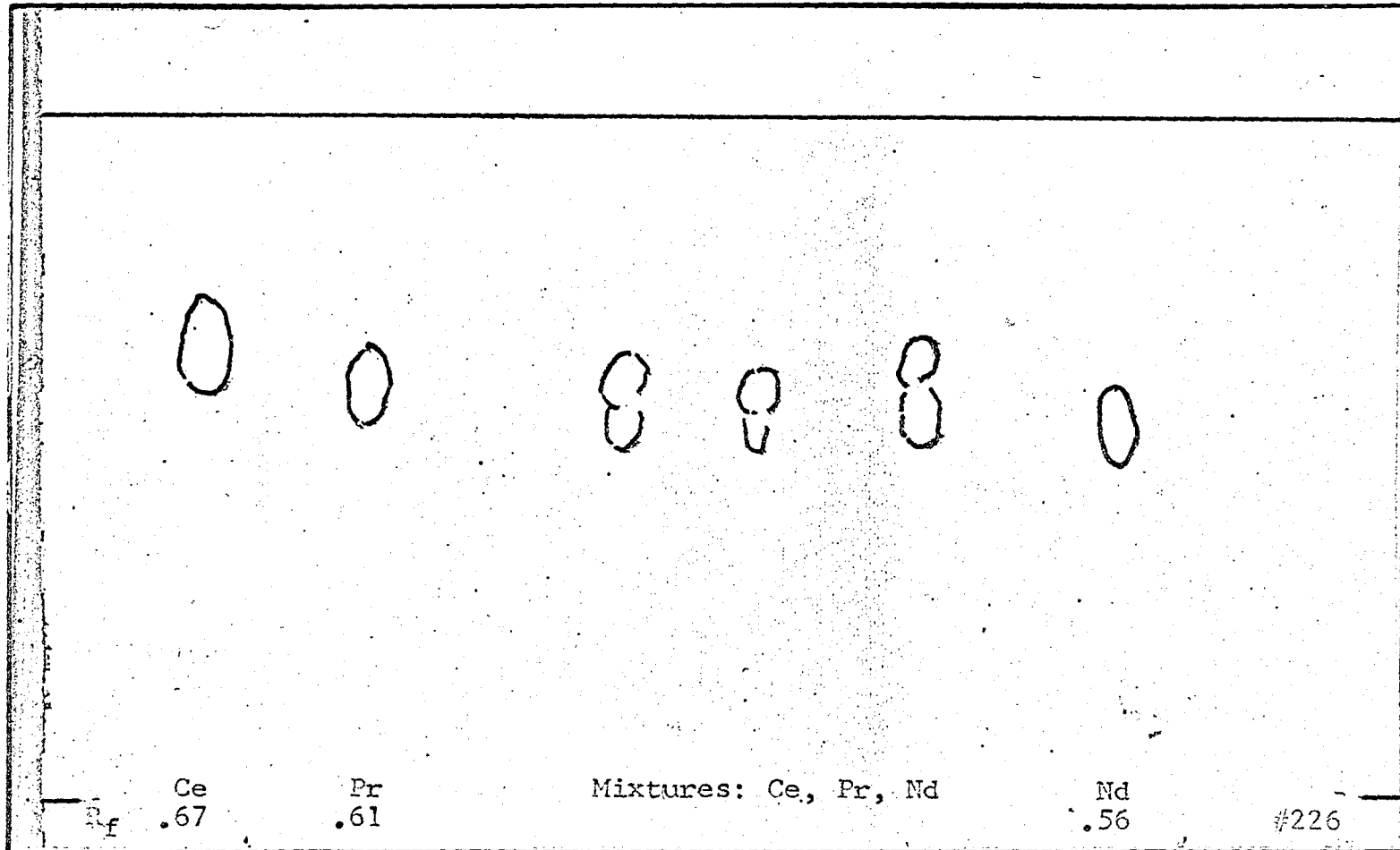
FIGURE 19

PARTIAL SEPARATION OF Ce, Pr, & Nd ON HDEHP-CELLULOSE THIN LAYER.
SAMPLE SIZE: 45 g EACH R.E. MOBILE PHASE 0.5M HNO_3.

The individual spots were carefully removed from the plate with a small blade. Figure 27 on page 89 is a copy of a plate after samples had been removed for spectrographic analysis. In a separation the quantity of each rare earth in a mixture rarely exceeds 5 micrograms. After a period of time it became apparent that in order to have a sufficient quantity of a rare earth for the determination that the separation must be accomplished several times on the same plate. This method would make it possible to have a quantity as large as 15-20 micrograms of a particular rare earth for the determination.

Each set of samples of the same rare earth from the plate was placed in the cup of the lower graphite electrode of the emission spectrograph, and emission spectra were obtained for these elements. Spectra of the pure rare earths were available for comparison and identification. In addition, the spectrum of the rare earth most likely to be identical to the one on the spot removed from the plate was included on the same film strip. In some instances a small amount of powdered graphite was mixed intimately with the plate sample to produce a steadier vaporization of the rare earth in the arc.

The 35 mm film strips exposed by the light diffracted from the instrument grating were developed according to the procedure suggested by Eastman Kodak in their Materials for Emission Spectrography (41).
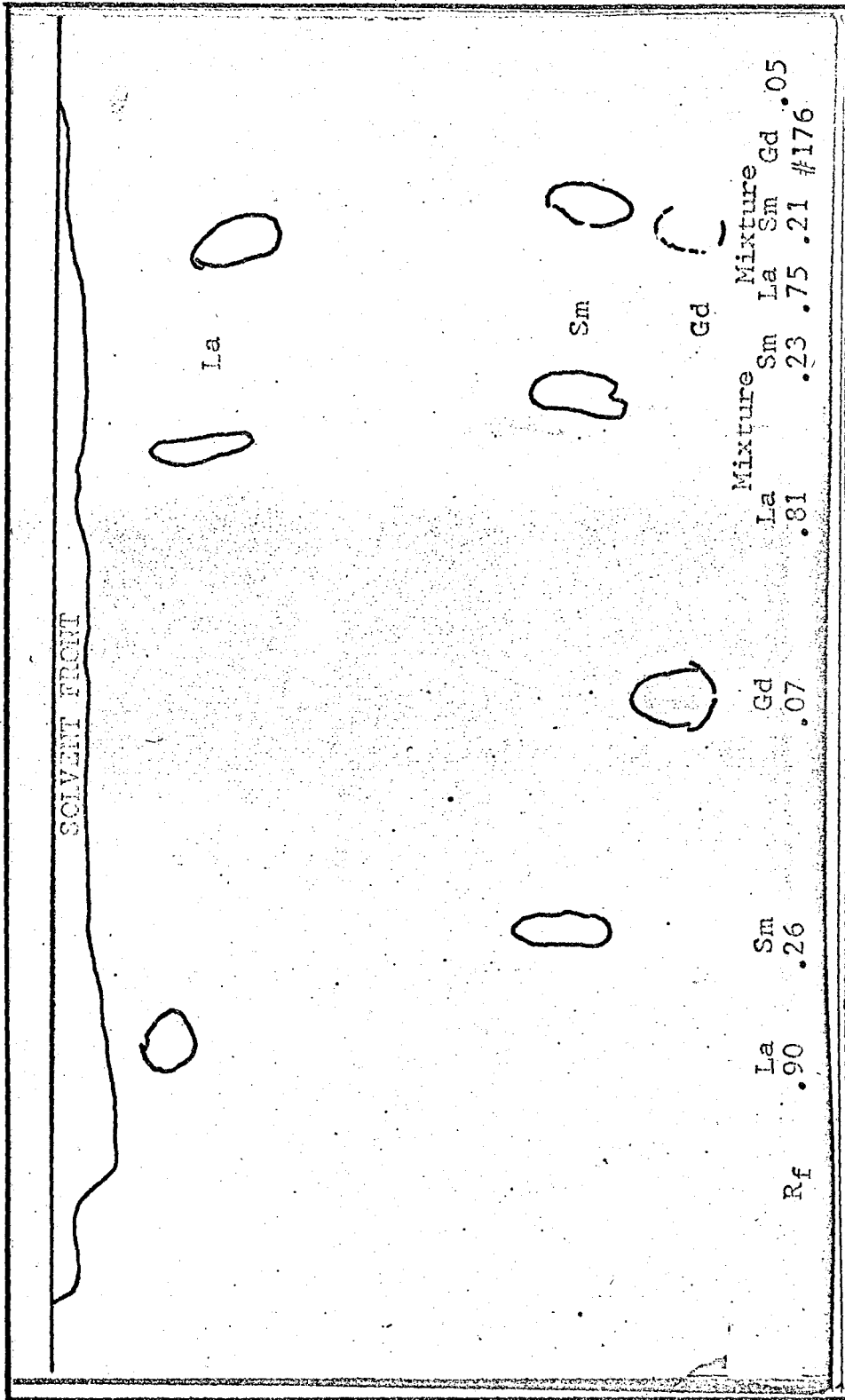
81

FIGURE 20

SEPARATION OF THREE RARE EARTHS ON HDEHP-SILICA GEL HR THIN LAYER.
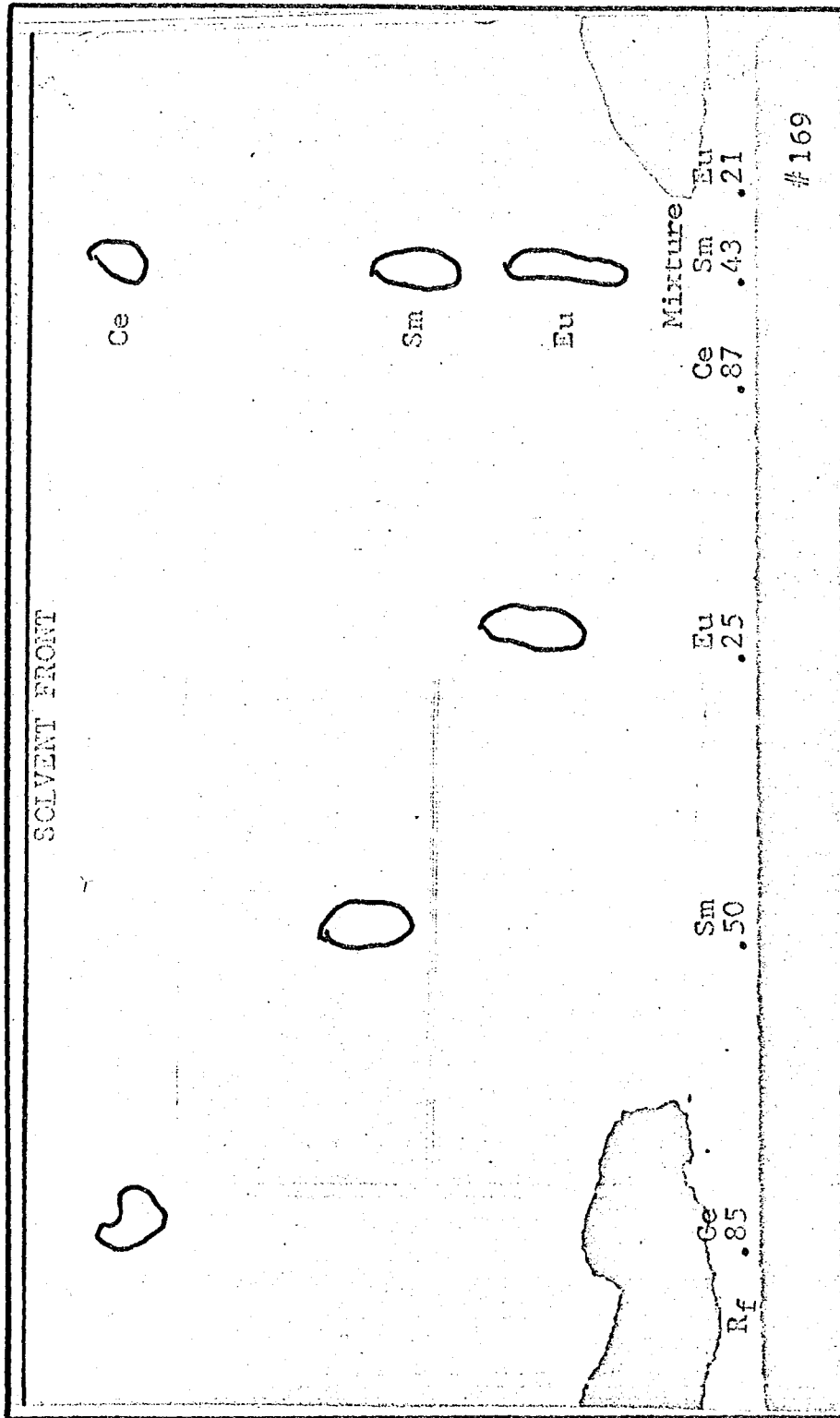SAMPLE SIZE: 6µg EACH R.E. MOBILE PHASE 0.5M HNO₃.

FIGURE 21

SEPARATION OF THREE RARE EARTHS ON HDEHP-SILICA GEL HR THIN LAYER.
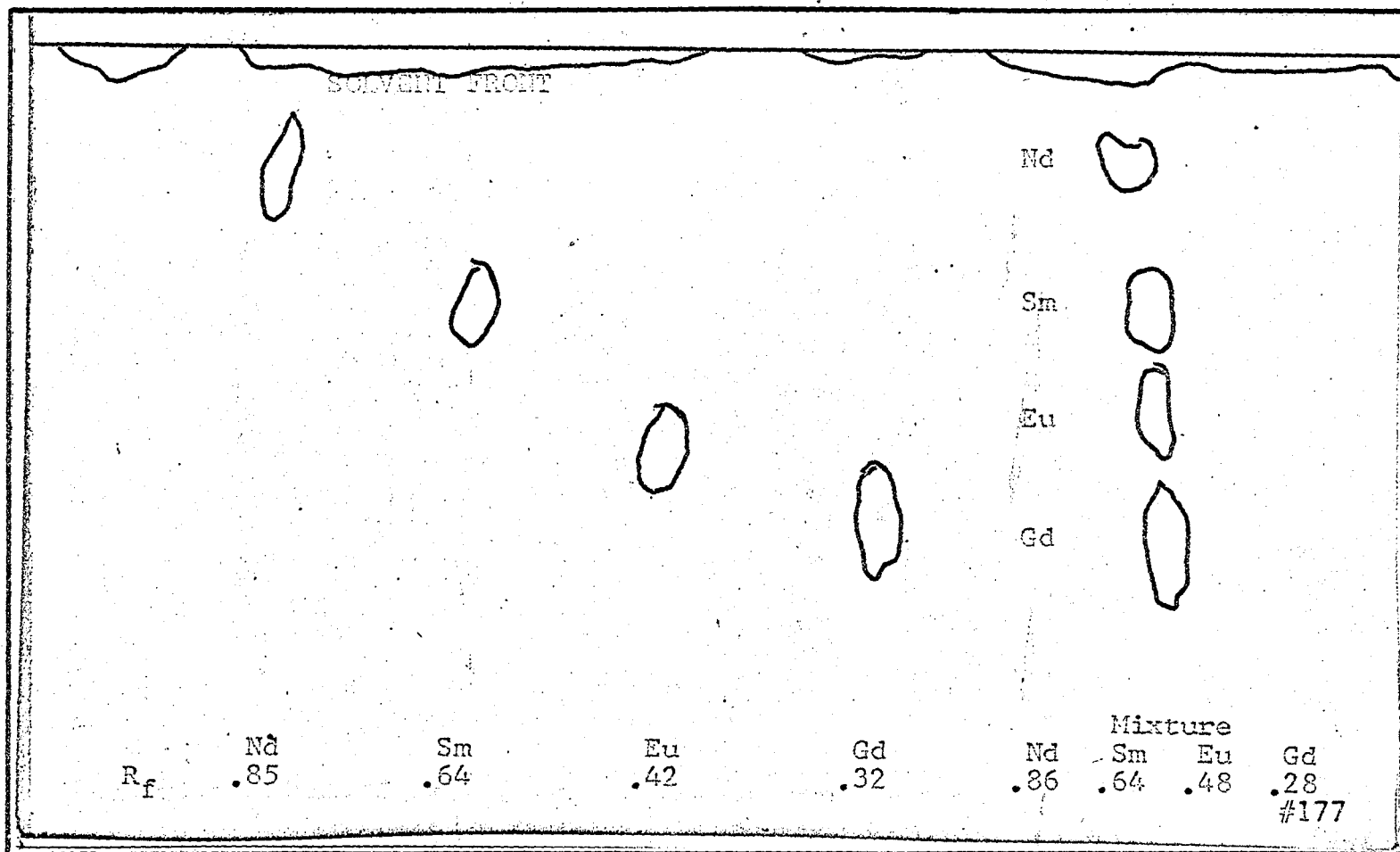SAMPLE SIZE: 6μg EACH R.E. MOBILE PHASE 0.75M HNO3.

FIGURE 22

SEPARATION OF FOUR RARE EARTHS ON HDEHP-SILICA GEL HR THIN LAYER.
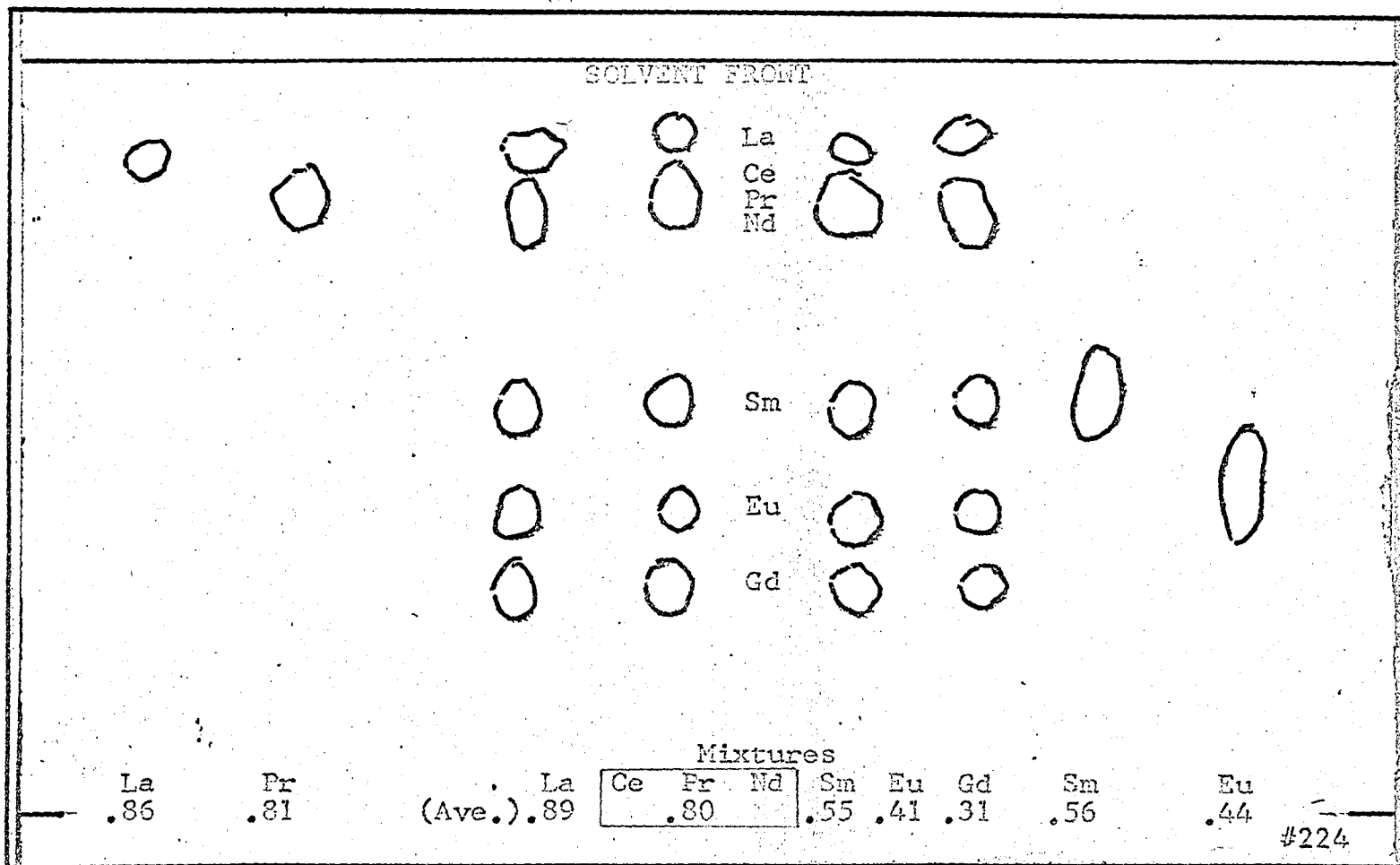SAMPLE SIZE: 6 µg EACH R.E. MOBILE PHASE 0.75M HNO₃.

FIGURE 23

SEPARATION OF SEVEN RARE EARTHS ON HDEHP-CELLULOSE THIN LAYER.
(POOR RESOLUTION Ce-Pr-Nd)
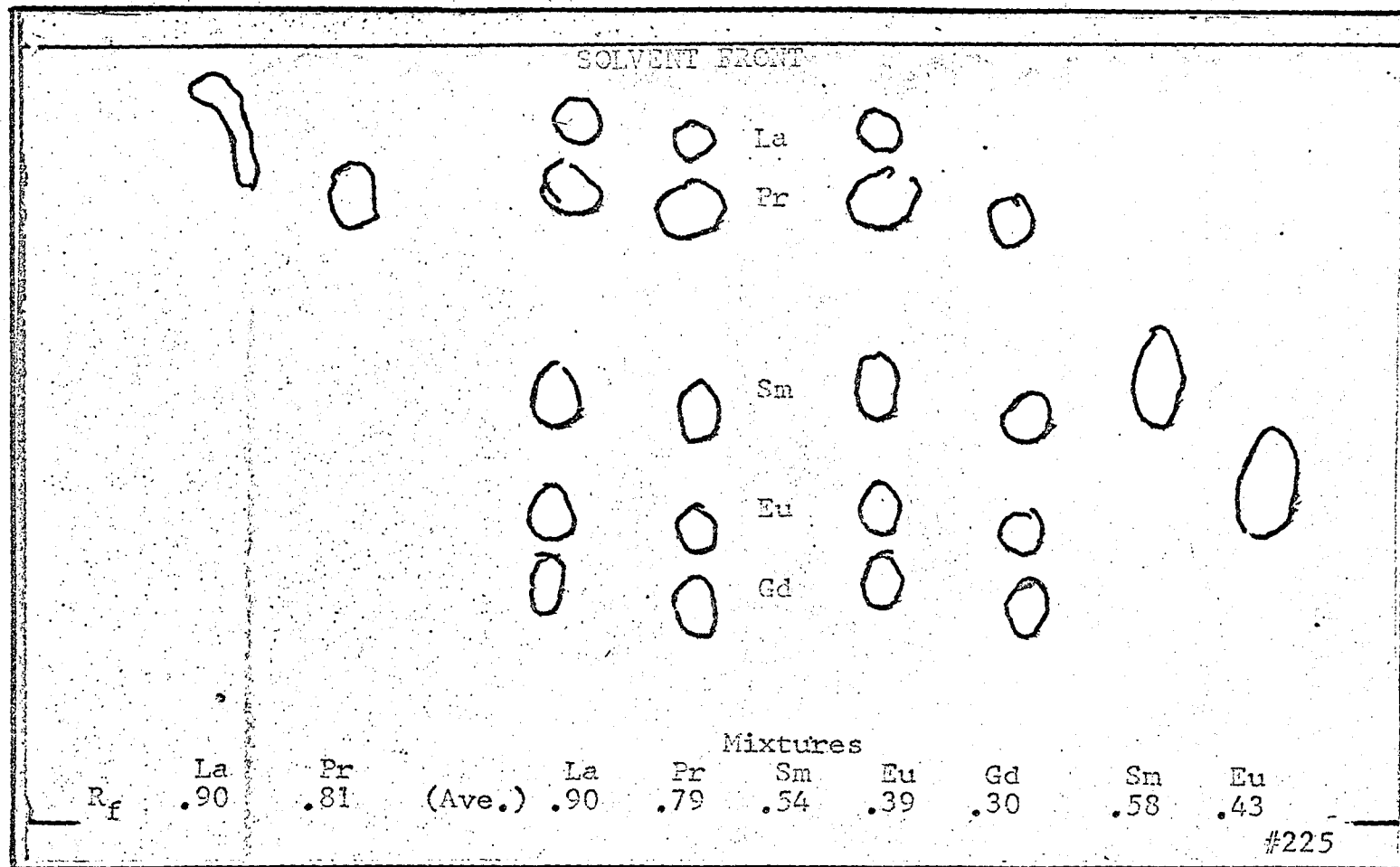SAMPLE SIZE: 5µg EACH R.E.   MOBILE PHASE 0.75M HNO_3.

FIGURE 24

SEPARATION OF FIVE RARE EARTHS ON HDEHP-CELLULOSE THIN LAYER.
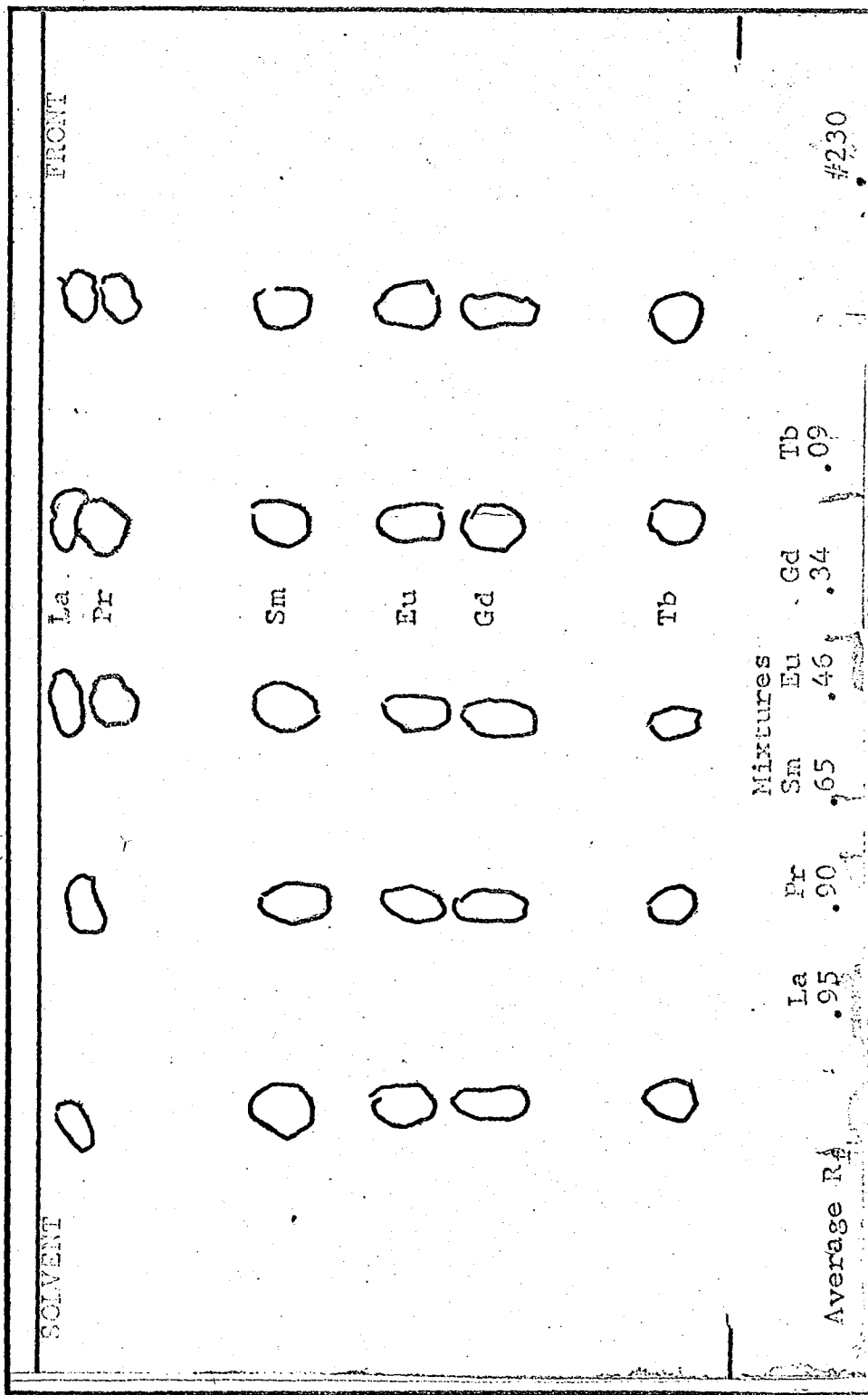SAMPLE SIZE: 5 μg EACH R.E.   MOBILE PHASE 0.75M HNO_3.

FIGURE 25

SEPARATION OF SIX RARE EARTHS ON HDEHP-CELLULOSE THIN LAYER.
SAMPLE SIZE: 5µg EACH R.E. MOBILE PHASE 0.75M HNO₃.

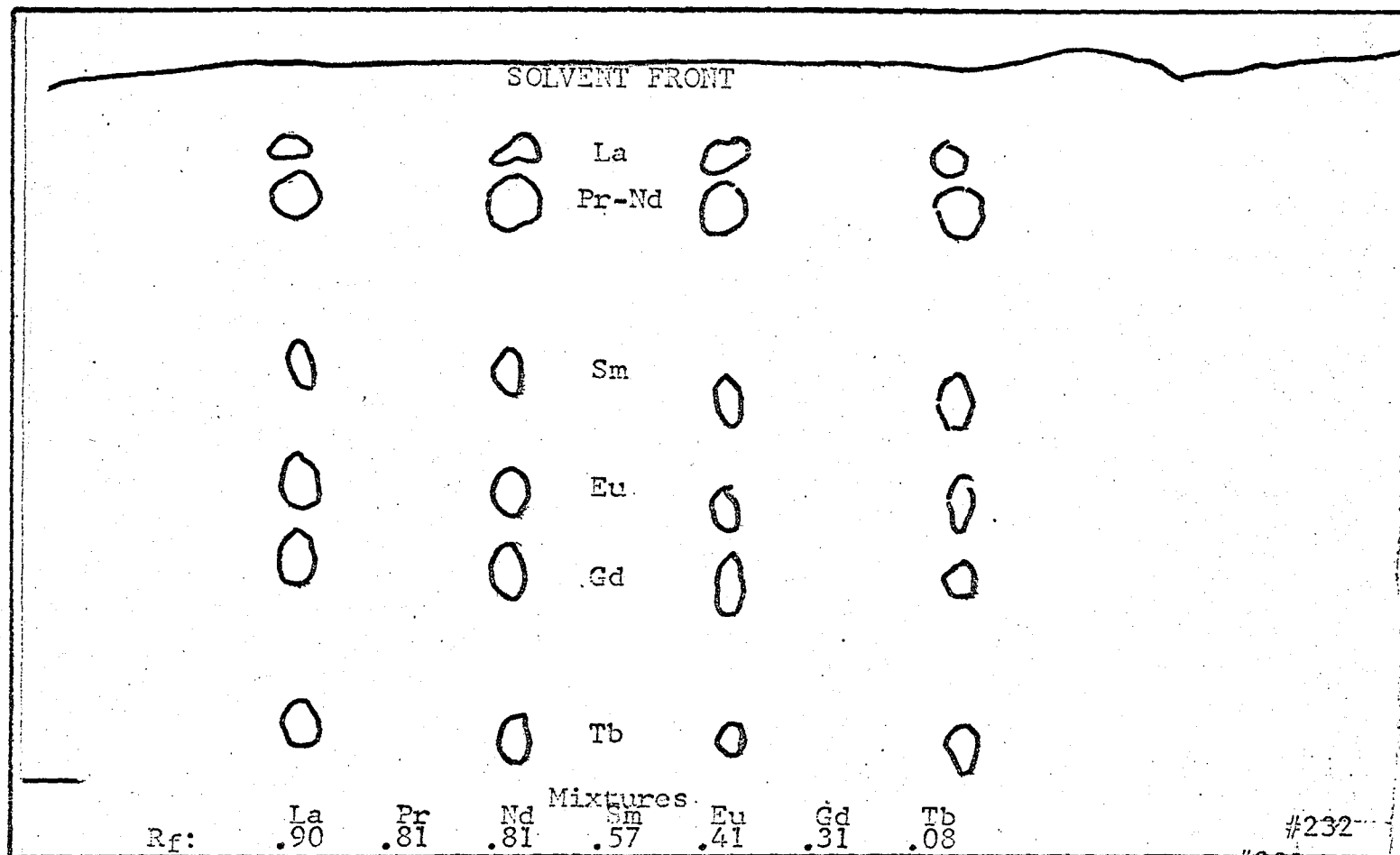|	La	Pr	Mixtures		Gd	Tb
			Sm	Eu		
Average R $_f$	.95	.90	.65	.46	.34	.09

#230

FIGURE 26

SEPARATION OF SEVEN RARE EARTHS ON HDEHP-CELLULOSE THIN LAYER.
(POOR RESOLUTION Pr-Nd PAIR)
SAMPLE SIZE: 5μg EACH R.E. MOBILE PHASE 0.75M HNO_3.

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Ahrens et al (1) discussed the linear relationship which exists between ionization potential of the element being analyzed and the arc temperature. The ionization potentials of the light rare earths range from 5.61 ev for La to 6.16 ev for Gd (83). The alkali metals can be vaporized in an arc temperature of 3800°K or slightly less. Due to their slightly higher ionization potentials, the rare earths must be vaporized at arc temperatures ranging from 4000 to 4500°K. Thirty volts across the terminals yields an arc temperature of 5000°K.

American Spectrographic Laboratories in San Francisco run rare earth samples at 13 amps which requires 70 volts across the terminals. According to Ahrens et al (1), 70 volts develops an arc temperature of 8000°K. Such high voltage did not produce favorable results with the instrument in this laboratory. An arc temperature of 7700°K will readily vaporize carbon with its ionization potential of 11.3 ev. When this high amperage and voltage were used with the 1.5 meter Bausch & Lomb emission spectrograph in this laboratory, the spectrum for carbon was excellent, but the rare earth spectra were disappointing.

The optimum conditions for emissions spectra of the light rare earths based on the preparation of standards were 40 volts and 7.5 amps.

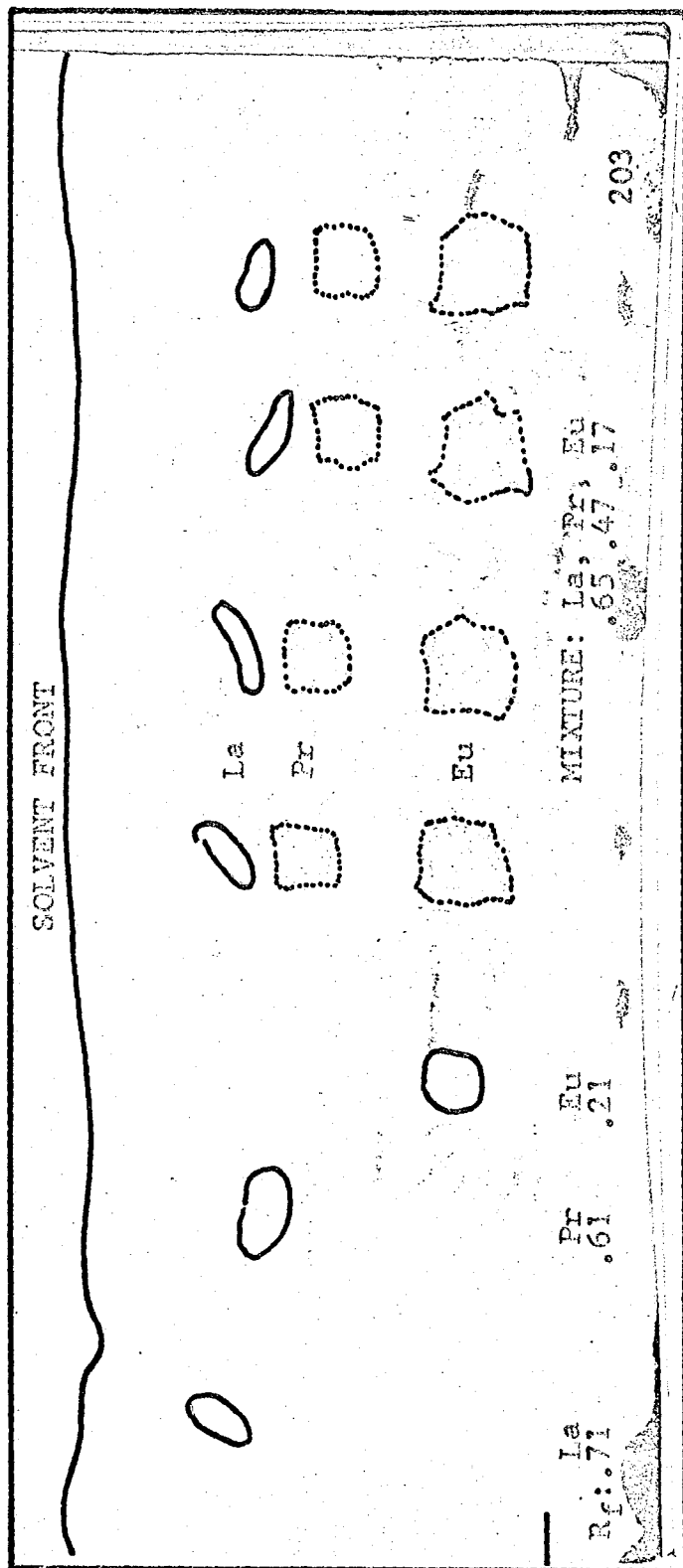The emission spectrograph in this laboratory is equipped with a Certified-Precision concave grating providing

FIGURE 27

HDEHP-SILICA GEL IR THIN LAYER WITH Pr AND Eu
SPOTS REMOVED FOR SPECTROGRAPHIC ANALYSIS.

dispersion of 5.2A/mm in the 2nd order; film coverage of 2250-3500A, and a resolving power of 80,000 in the 2nd order. Emission spectra of the seven light rare earths, La - Gd, taken with this instrument, appear in the appendix. The wavelengths which are identified were taken from Brode (7), Kerekes (38), and Meggers et al (53).

With a second order emission spectrograph, positive identification of the rare earths from the plate was difficult. There are a number of reasons why this was so.

In the arc spectrum for any element there are certain lines which persist in the spectrum to the lower limits of dilution of the element. These are known as the raies ultimes (7), and in a micro-sample of any element, one, two, or several of these lines may always be used to positively identify the element. None of these persistent lines for the rare earths appear in the second order spectra for these elements. The persistent lines are all derived from longer wavelengths of light than those appearing in the second order spectra. Brode (7) stated that the absence of persistent lines in the spectrum of an element should indicate that the element is not present in a sufficient concentration to be detected by the spectrographic method employed.

Because of the difficulty involved in making positive identifications of individual rare earths from the 35 mm film strips, selected samples from plates were sent to the American Spectrographic Laboratories in San Francisco. For the analyses

of these samples they used a 1.5 meter first order emission spectrograph. They have stated that they are able to detect a minimum of 5 micrograms of rare earth in a 15 milligram sample.

Semi-Quantitative Analyses

by American Spectrographic Laboratories

Plate #202

Sample: Sm

Sample Weight: 34 mg

ANALYSIS: (Sm)

A separation of Ce, Nd, Sm, Gd. 10 micrograms of each R.E. in mixture for spot on the plate. 4 Sm spots removed from plate for analysis.

Between 0.03 and 0.3% Sm Percentage represents 4.5 to 45 micrograms of R.E.

Plate #203

Sample: Eu

Sample Weight: 59.9 mg

Sample: Pr

Sample Weight: 27.0 mg

ANALYSIS: (Eu)

A separation of La, Pr, and Eu. 10 micrograms of each R.E. in mixture for spot on the plate. 4 Eu spots and 4 Pr spots removed from plate for analysis.

Between 0.1 and 1.0% Eu Percentage represents 15 to 150 micrograms of R.E. (Maximum Eu in sample: 40 micrograms.)

ANALYSIS: (Pr)

Between 0.03 and 0.3% Pr
Percentage represents 4.5 to
45 micrograms of R.E.

Also identified in
Pr sample.
(La)

Between 0.01 and 0.1% La
Percentage represents 1.5 to
15 micrograms of R.E.

La has the largest R_f value
of the rare earths included
in this separation. La pre-
cedes Pr on the plate.

Plate #207

Sample: Eu

Sample Weight: 19.0 mg

Sample: Sm

Sample Weight: 25.0 mg

Sample: Pr

Sample Weight: 18.7 mg

A separation of La, Pr, Sm,
Eu, and Gd.
10 micrograms of each R.E. in
mixture for spot on the plate.
4 Eu spots, 4 Sm spots, and 4
Pr spots removed from the plate
for analysis.

ANSLYSIS: (Eu)

Between 0.03 and 0.3% Eu
Percentage represents 4.5 to
45 micrograms of R.E.

Also identified in
Eu sample.
(Sm)

Between 0.003 and 0.03% Sm
Percentage represents 0.45 to
4.5 micrograms of R.E.

This impurity (Sm) has position
just above Eu on plate among sep-
arated R.E.

ANALYSIS: (Sm)

Between 0.003 and 0.03% Sm
Percentage represents 0.45 to
4.5 micrograms of R.E.

ANALYSIS: (Pr)

Between 0.01 and 0.1% Pr
Percentage represents 1.5 to
15 micrograms of R.E.

Plate #219

Sample: Should be
        primarily
        (Ce, Pr)

Sample Weight: 19.0 mg

ANALYSIS: (Ce, Pr)

A separation of Ce, Pr, and Nd.
5 micrograms of each R.E. in
mixture for spot on the plate.
Upper one-third of partially
separated rare earths spot re-
moved from plate for analysis.

Between 0.003 and 0.03% Pr.
Percentage represents 0.45 to
4.5 micrograms of R.E.

Neither Ce nor Nd identified
as impurities. This could
indicate that Ce had moved
beyond Pr on the plate, but
was not detected.

ANALYSIS: (Pr)

CHAPTER VIII

SUMMARY AND CONCLUSIONS

The spectrographic determination of rare earths separated by reversed-phase thin layer chromatography is a feasible method. It is practical in that the sample can be removed from the plate and a spectrum taken with no additional preparation of the sample. The prime requirements are a suitable first order emission spectrograph; good technique in the removal of samples from the plate, and the transfer of the samples to the graphite electrode. Of course, an understanding of the theory and techniques of thin layer chromatography and also of emission spectroscopy are essential.

At the present time in the United States, about 100 chemical researchers and graduate students are involved in studies of rare earth properties (97). Therald Moeller et al at the University of Illinois have been studying the structure and stability of rare earth coordination compounds. At probably the most important center for rare earth research, Iowa State University, Dr. Jack Powell, a pioneer in the study of these metals, is working on the stabilities of rare earth complexes. Also at ISU, Dr. Morton Smutz is working on the separation of rare earths by solvent extraction while V. A. Fassel continues his work directed primarily towards analytical methods involving emission spectroscopy. This concentrated effort on

rare earth research clearly indicates the importance that the scientific community places on the chemistry of these metals.

If the TLC separation of the rare earths is to be further improved as an analytical method, chemical research must also proceed in the direction of determining new organic solvents which will complex with the rare earths to form coordination compounds with an even greater separation factors than the average of 2.5 for the R.E.-HDEHP complexes.

In this study, the most effective resolution of the rare earths via thin layer chromatography resulted from HDEHP retained on MN-Cellulose 300 with nitric acid equilibrated with HDEHP as the mobile phase. The sample size spotted on the plate should be held to a minimum. One microliter containing 4-6 micrograms of each rare earth is a large enough sample. Good results can be obtained at room temperature. The plates do not need to be activated, but should be stored in a desiccator so that the water content of the adsorbent will be at a minimum.

The rare earths are detected the most readily with an oxine-kojic acid solution sprayed on the plate and exposed to ammonia vapor for the formation of the R.E.-oxinate precipitate. The plate is viewed in a dark room under ultra-violet light.

The separation of six rare earths via reversed-phase TLC would appear at this time to be nearly a maximum number in a single-dimensional development. Five of the Lanthanides

separated on one plate was the largest number encountered in the literature. However, the separation of seven or even eight could not be considered an impossibility.

The combining of one of the most sensitive analytical determinative methods, emission spectroscopy, with the expediency of the thin layer chromatographic separation for the purpose of analyzing samples composed primarily of light rare earths was conceived for this work when it was noted in the literature that the determinations were either a qualitative one based on the position of the R.E. spot on the plate; or a quantitative one based on radiological methods.

If the rare earths to be separated are not fission products, then the use of the radiological determination necessitates neutron bombardment of the rare earths to form the radioisotopes. A TLC--emission spectroscopic analysis eliminates the need for any special or unusual handling of the materials to be separated.

There are many laboratories with emission spectrographs, but which are not yet equipped with a radiological laboratory. This method of separation and determination can be used in this type of laboratory not just as a substitute, but as one which can be used with confidence because it is the combination of two sensitive and reliable analytical techniques.

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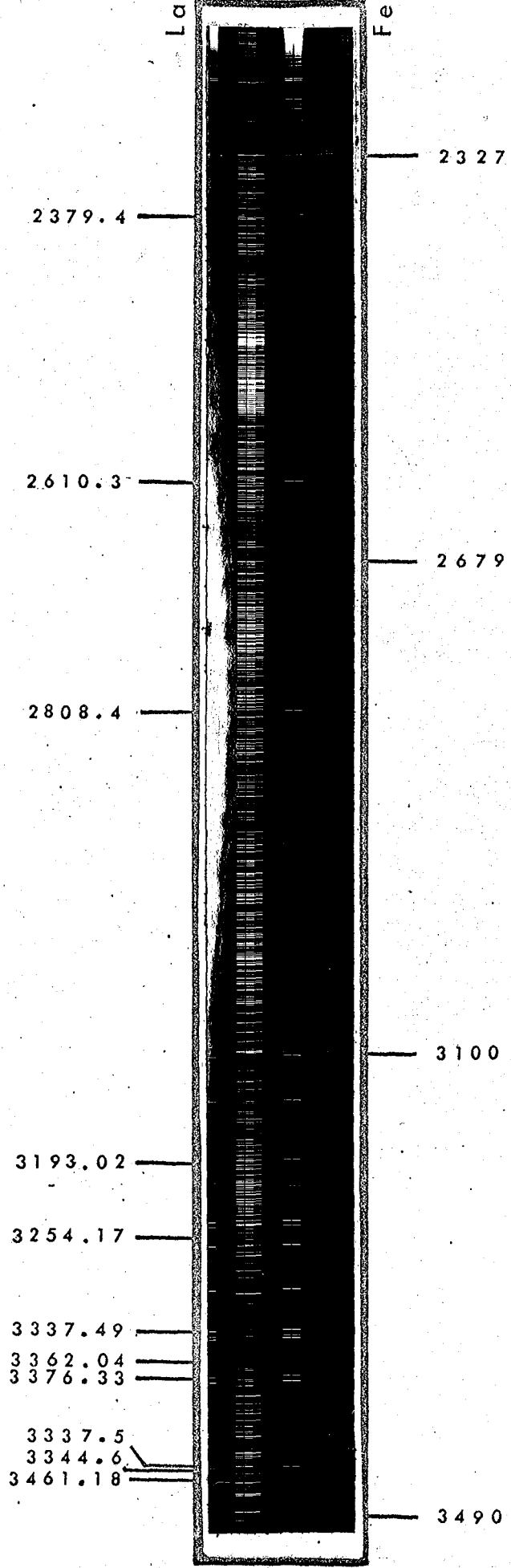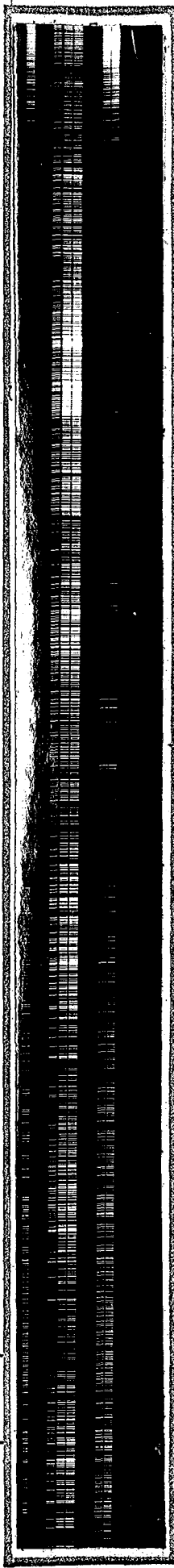
APPENDIX

FIGURE 28

EMISSION SPECTRUM OF LANTHANUM

	EXPOSURE TIME:	
	La	10 sec
	Fe	10 sec

SLIT WIDTH: 32μ
AMPERAGE: 7.5
VOLTAGE: 40

La / Fe

2327
2379.4
2610.3
2679
2808.4
3100
3193.02
3254.17
3337.49
3362.04
3376.33
3337.5
3344.6
3461.18
3490

104

FIGURE 29

EMISSION SPECTRUM OF CERIUM

EXPOSURE TIME:
Ce   15 sec
Fe   10 sec

SLIT WIDTH: 32μ
AMPERAGE: 7.5
VOLTAGE: 40

105
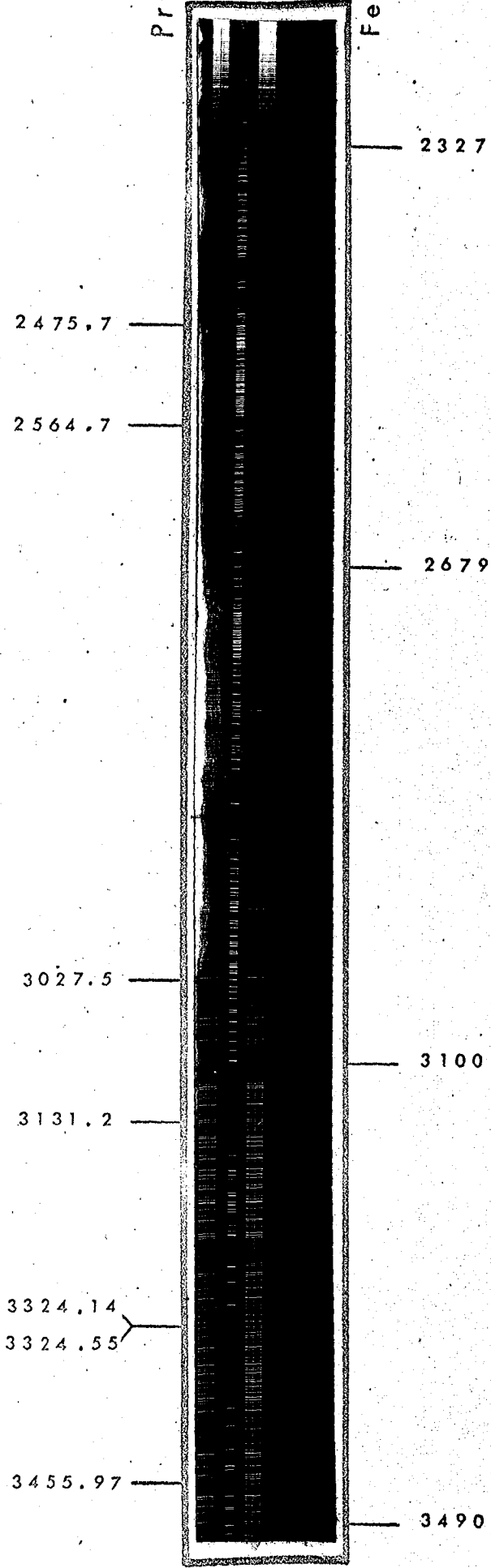
FIGURE 30

EMISSION SPECTRUM OF PRASEODYMIUM

EXPOSURE TIME:
Pr   20 sec
Fe   15 sec

SLIT WIDTH: 32 μ
AMPERAGE: 7.5
VOLTAGE: 40

106
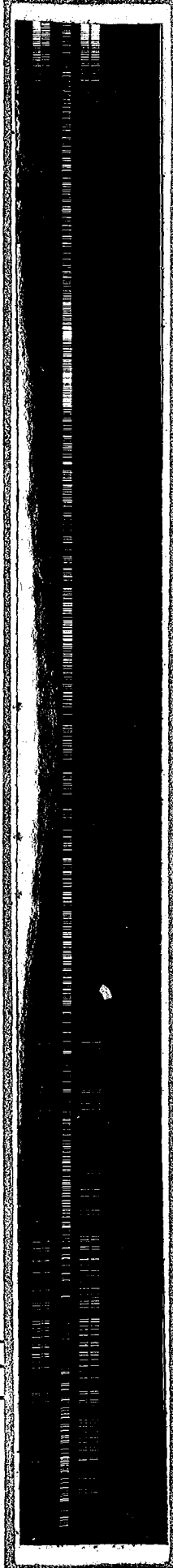
FIGURE 31

EMISSION·SPECTRUM OF NEODYMIUM·

	EXPOSURE TIME:
SLIT WIDTH: 32μ	Nd 10 sec
AMPERAGE 7.5	Fe 10 sec
VOLTAGE: 40	

107
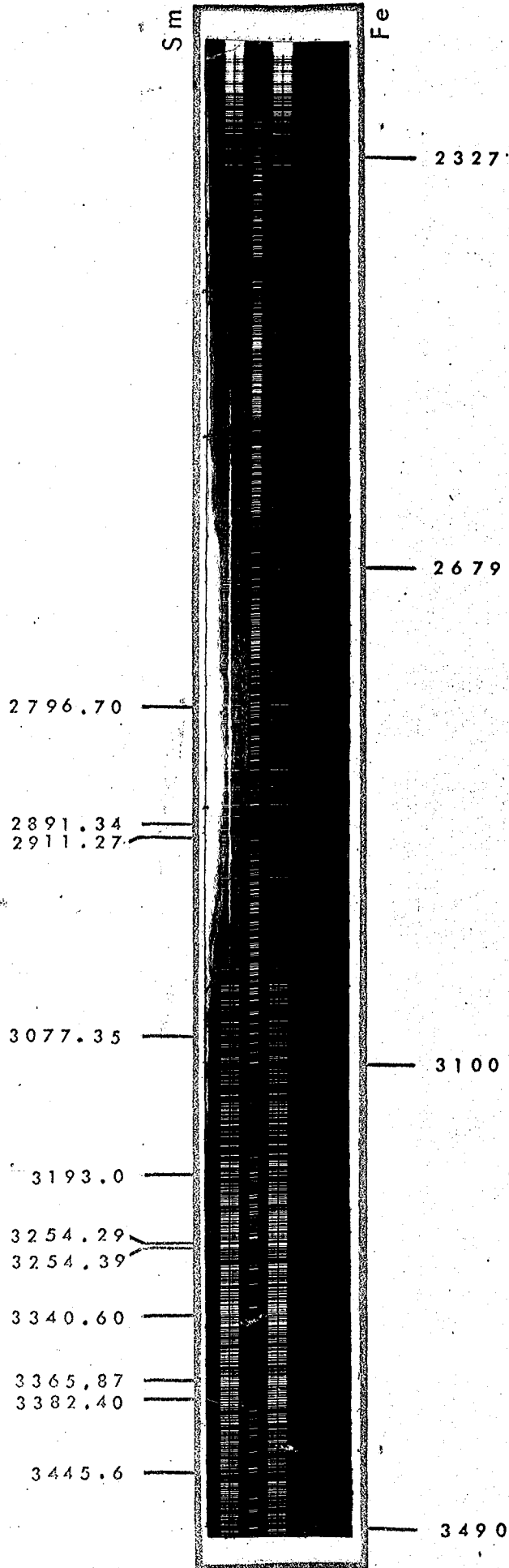
FIGURE 32

EMISSION SPECTRUM OF SAMARIUM

EXPOSURE TIME:
Sm   10 sec
Fe   10 sec

SLIT WIDTH: 32μ
AMPERAGE: 7.5
VOLTAGE: 40

108
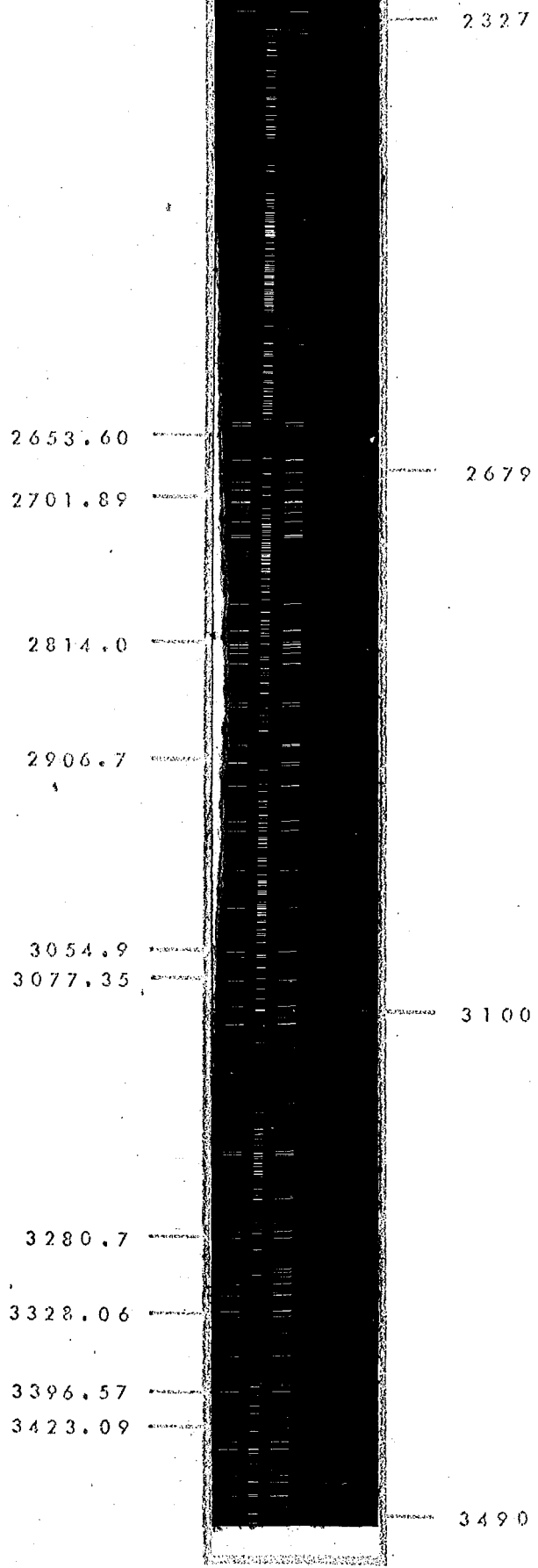
FIGURE 33

EMISSION SPECTRUM OF EUROPIUM

EXPOSURE TIME:
Eu   10 sec
Fe   10 sec

SLIT WIDTH: 32 μ
AMPERAGE: 7.5
VOLTAGE: 40

2327
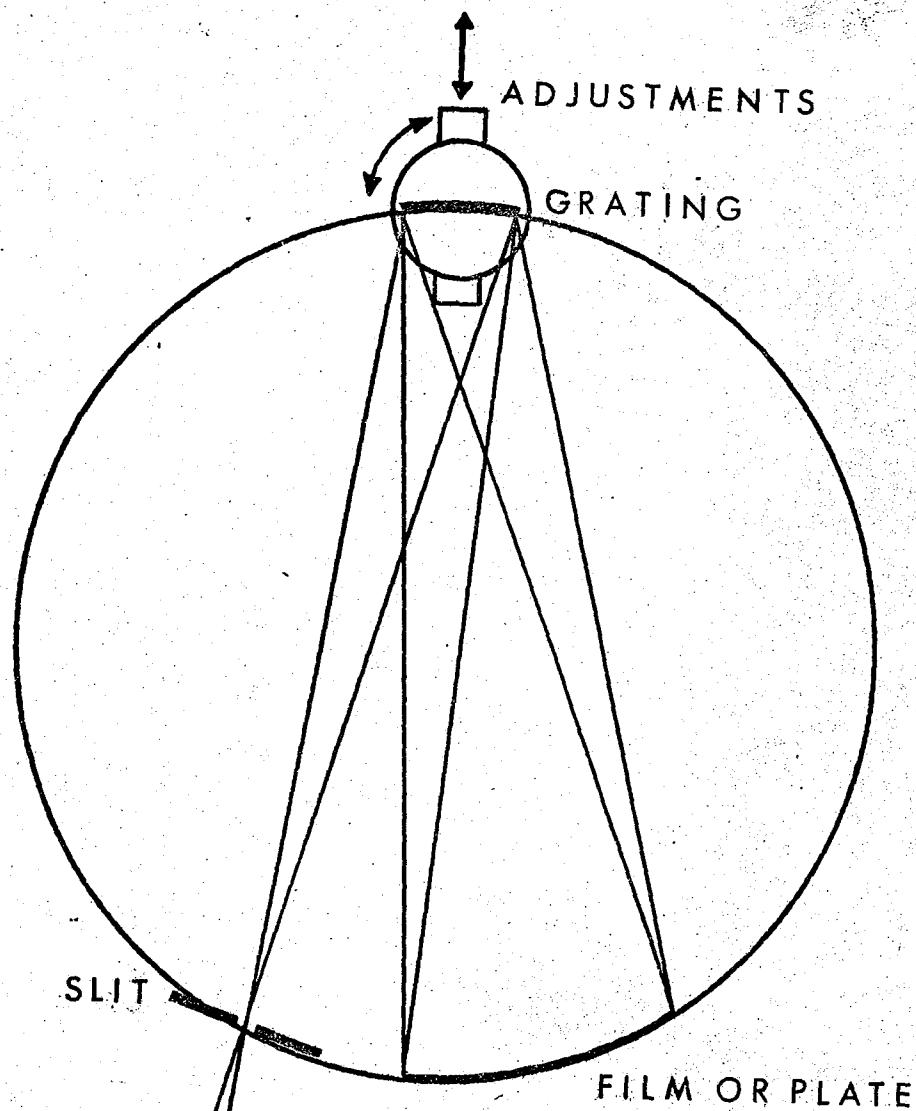2653.60
2679
2701.89
2814.0
2906.7
3054.9
3077.35
3100
3280.7
3328.06
3396.57
3423.09
3490

FIGURE 35

MODIFIED EAGLE MOUNTING