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SEPARATION OF VARIOUS CATIONS BY REVERSED-PHASE PARTITION CHROMATOGRAPHY USING NEUTRAL ORGANOPHOSPHORUS COMPOUNDS

by

Jerome William O'Laughlin

A Dissertation Submitted to the
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DOCTOR OF PHILOSOPHY

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Approved:

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Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

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INTRODUCTION

The advent of the atomic energy and space age has caused a resurgence of interest in inorganic chemistry. Exceedingly pure substances are required in the construction of atomic reactors, in space technology and for many other new applications. Often trace impurities, in a few cases even in the parts per billion range, make these materials totally unsuitable for use or drastically alters their properties. This poses new and tremendously difficult problems for the analytical chemist whose job it is to come up with faster and more sensitive methods of analysis of these materials.

Exceedingly sensitive methods have been available to the analytical chemist for some time and more sensitive techniques are still being developed. The major problem, however, has usually been one of the specificity of a method rather than its sensitivity and it is very often the case that the more sensitive a method the less specific it is. A two-pronged attack on this problem has been the search for ever more sensitive and selective methods, and the search for faster and better methods of separation. This investigation will be concerned primarily with the latter.

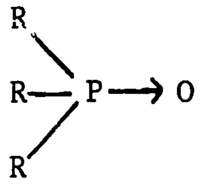
Classical separation techniques are often woefully inadequate for the separation of complex mixtures or of closely related substances. Fortunately several powerful new techniques have been developed. Two of the most powerful and versatile are the ion exchange and solvent extraction techniques.

Coupling chromatography and ion exchange, F. H. Spedding and others (68,69,70) achieved the separation of the lanthanides in a very pure form, a task practically impossible with classical techniques. The use of solvent extraction methods has increased in popularity enormously. Morrison and Freiser (45) list over six hundred references on the analytical applications of solvent extraction alone in a recent review article covering a two-year period.

The solvent extraction technique has some advantages over ion exchange for analytical separations. The extractant molecule itself is more amenable to change in its molecular structure designed to make it more specific than are ion exchange resins. It is also often more convenient to extract an aqueous phase, especially if a one-step extraction will suffice, than to set up an ion exchange column. On the other hand phase separation problems and the use of volatile and sometimes noxious solvents are certainly disadvantages.

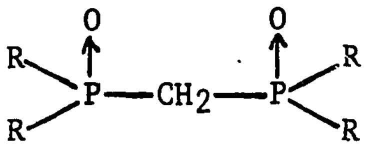
In recent years the use of long chain amines and various organophosphorus compounds as extractants has been studied extensively. The amines and organophosphorus acids function in a manner very similar to anion and cation ion exchange resins and indeed are often referred to as liquid ion exchangers.

Neutral organophosphorus compounds are also very effective solvent extractants and have received a great deal of attention. These compounds have the general formula



where the R may be an alkyl (or aryl) or an alkoxy group. When all three substituents are alkyl groups the compound is a phosphine oxide. The substitution of one, two, and three alkoxy groups for the alkyl groups gives phosphinates, phosphonates, and phosphates, respectively. These neutral molecules are believed to coordinate to a metal through the oxygen atom, possibly displacing a water molecule from the coordination sphere of the metal and forming a more hydrophobic species. In case the alkyl groups are sufficiently large the resulting complex is quite water insoluble and readily extracts into an organic phase.

The synthesis and solvent extraction properties of organophosphorus compounds having two functional groups have recently been studied by several members of the Ames Laboratory Staff (Ames, Iowa) including the author (46,60). The general formula for these compounds is

 .

The compound most extensively studied has been bis(di-n-hexylphosphinyl)methane, or HDPM. The behavior of HDPM as an extractant for uranium(VI) was compared with that of tri-n-octyl phosphine oxide, or TOPO (46). Numerous data have been obtained on the latter compound which is now widely used, especially by analytical chemists, and a compilation of these data has been recently published by White and Ross (74). HDPM appeared to be generally a more powerful extractant than TOPO (52) and in the case of the extraction of perchlorates the distribution coefficients were often very much greater for HDPM.

A paper by Weidman (73) on the separation of several of the transition metals by paper chromatography using tri-n-butyl phosphate, TBP, in methanol as the mobile phase suggested to the author that it would be of interest to study other separations using this technique. It seemed likely that the range of the method could be extended by the use of TOPO or HDPM in place of TBP. A systematic investigation was planned to study the movement of the various metal ions on paper using TBP, TOPO or HDPM in some suitable inert diluent as the mobile phase. It was planned to investigate the chloride, nitrate, and perchlorate systems. Besides the possibility of new separation processes, it was also thought that this would give a good comparison of TBP, TOPO and HDPM under a variety of conditions. It was anticipated that the R_f values obtained would be related to the partition coefficient and that a considerable amount of information could be rather quickly obtained.

Preliminary experimental work revealed, however, that the spots tended to tail (streak back toward the start line) rather badly. Although this problem could probably have been at least partially solved by careful attention to paper type, flow rate and other variables, another approach was taken. The paper was first impregnated with the organic extractant and then developed with water or an aqueous mineral acid solution. Initial experimental work using this technique was highly promising.

The latter technique which can be called reversed-phase partition chromatography has a number of advantages. Perhaps the most important is that it eliminates the need for a diluent (sometimes called the inert solvent). An increasing amount of evidence has pointed to the fact that the "inert" diluent often plays a significant role in solvent extraction work. The reversed-phase technique also has the advantage that prior equilibration of the mobile phase is not necessary and the problem of evaporation of some volatile diluent during the course of development is eliminated.

The objectives of the initially planned investigation were equally well served by using the reversed-phase technique with the added advantage of eliminating any specific effect due to the use of a diluent for the extractants. Therefore the planned systematic investigation was carried out using this technique. Some separations, particularly the separation of sodium, lithium and the alkaline earths, were investigated using column as well as paper chromatography.

A preliminary investigation of the infrared spectra of the adducts formed with HDPM by several metals and the mineral acids was carried out. It was also necessary to determine the solubility of HDPM in water and the various mineral acids used. No suitable method was available so a new spectrophotometric method for phosphine oxides was developed. The solubility study was then extended to TOPO and several related phosphine oxides.

The rather long names of the organophosphorus extractants make it advisable to refer to them in an abbreviated form. A list of the abbreviations used in this thesis and the compounds to which they refer appears in the Appendix.

REVIEW OF LITERATURE

A close relationship exists between partition data obtained by solvent extraction techniques and R_f data obtained by chromatographic techniques using the same extractants and a brief review of some of the more pertinent papers on the individual extractants is given.

Tri-n-butyl Phosphate, TBP

The first reported use of TBP as a solvent extractant was by Warf (72), who was looking for a solvent not attacked by cerium(IV) in nitric acid solutions. This report covered work done around 1945 and was first reported in the classified literature. The use of TBP as a solvent spread rapidly and a large number of papers appeared; however, many of the earlier papers were classified.

A number of conflicting reports appeared in regard to the distribution coefficients for metals into TBP. This was caused in part by the fact that the partial hydrolysis products, di- and mono-alkylphosphoric acids, were also powerful metal extractants with distribution coefficients three to four orders of magnitude higher than TBP (26). Furthermore these acid hydrolysis products, and in some cases the diluent, worked synergistically with TBP (1) to give extraction coefficients much greater than TBP alone. Kertes and Halpern (34,35) reported that hydrochloric (and perchloric) acid promoted the hydrolysis of TBP and the presence of acidic species facilitated the photo-reduction of uranium(VI) in the organic phase. This was reported to be much less important in the case of nitric acid which did not promote the hydrolysis of TBP. It is obvious that the possibility of hydrochloric and perchloric acid catalyzed hydrolysis of TBP should be considered in the interpretation of solvent extraction data on these systems, especially data obtained by radiochemical techniques.

The extraction of inorganic nitrates has been extensively studied; two papers of particular interest here are a paper on the separation of the lanthanides (22) and a paper by Oshima (54) covering the extraction of a number of metal nitrates and acids, and also giving infrared data on TBP-metal nitrate adducts. Nadig (47) has recently reviewed the literature on TBP-inorganic nitrate complexes and presented a large number of infrared spectra of these complexes. Siekierski (63) has discussed the influence of diluent on the distribution coefficient and Naito has discussed the mechanism of the extraction of acids (48).

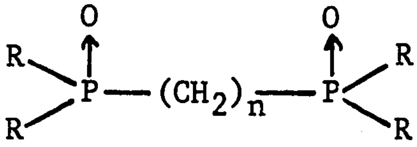
The extraction of most inorganic chlorides has been given by Ishimori and others (28) who compared their results with results obtained by Kraus and Nelson on the adsorption of metal chlorides on anion exchange resins. The extraction of metal perchlorates has received less attention. Kertes and Kertes (36) and Siekierski and Gwöźdź (64) have studied the extraction of perchloric acid by TBP. Hesford and McKay (23) and Naito and Suzuki (50) studied the extraction of uranyl perchlorate by TBP. Katzin (30) has reviewed the extraction of inorganic chlorides, nitrates and perchlorates into organic solvents, including TBP.

Tri-n-octyl Phosphine Oxide, TOPO

The synthesis, physical properties and use of TOPO as a solvent extractant were first reported by Blake and others (2). Recently White and Ross (74) reviewed the use of TOPO as a solvent extractant and gave a considerable amount of data on the nitrate, chloride, sulfate and phosphate systems. They claimed the perchlorate adducts were less soluble in cyclohexane, the diluent employed, and the perchloric acid system was, in their opinion, not attractive for analytical separations. Recently Ishimori and others (27) presented partition data for almost all the metal nitrates and chlorides in a convenient chart form as a function of acid concentration.

Bis(di-n-hexylphosphinyl)methane, HDPM

Blake and others (3) listed bifunctional compounds of the type

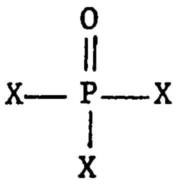


as potentially useful extractants for the uranyl ion in a classified report in 1952 (declassified in 1957) and proposed a reaction scheme for the preparation of the compound when n = 2. They postulated that this compound could form a seven-membered ring with the uranyl ion coordinating through the oxygens. They also postulated that the methylene compound (where n = 1), if it could be prepared, could form six-membered rings.

No further report on the actual synthesis of these compounds (where n = 1 or 2) appeared, however, until HDPM was synthesized in this Laboratory (52,60). The extraction of uranium(VI) with HDPM has recently been studied in some detail in this Laboratory and a report on this work has been accepted for publication (46). Additional data, not yet published, on the extraction of other metal perchlorates has been compiled and is given in Figure 3 of this thesis.

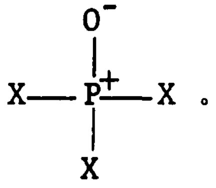
Nature of Metal Complex with TBP, TOPO, and HDPM

The nature of the phosphorus-oxygen bond in quadruply bonded phosphorus compounds such as the phosphine oxides has been reviewed by Larsson (39) who concluded the PO bond can best be described as a resonance hydrid with the limiting forms



$X-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle X}{|}}{P}}-X$

(I)



$X-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle X}{|}}{P^+}}-X$.

(II)

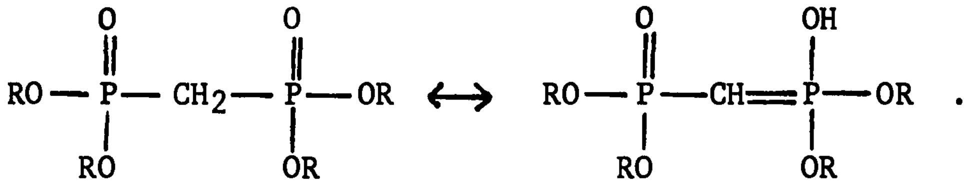
In compounds with strongly inductive substituents, as fluorine, structure I will predominate and with compounds of the tri-alkyl phosphine oxide type, structure II should be the chief contributor.

Cotton and others (10) state that in phosphine oxides coordination can take place only through the oxygen and discuss the shift in the PO stretching frequency on complex formation. Cotton reasons that the lowering of the PO stretching frequency on complex formation reflects primarily a decrease in the amount of $p\pi \rightarrow d\pi$ back-bonding from oxygen to phosphorus when the oxygen coordinates to a metal ion. Nadig (47) has recently correlated the PO shift on complex formation for TBP and TOPO with the ionic potential of the metal ion and reviewed the literature in this area.

The uranium nitrate complex with TBP has been shown to be a disolvate (44) and the general mechanism for the extraction of uranyl nitrate has recently been discussed by Naito and Suzuki (50). The uranyl perchlorate complex was reported to be a disolvate by Hesford and McKay (23) but Naito and Suzuki (50) claim, on the basis of infrared evidence, that, at least with TBP, the complex is a tetrasolvate.

It is assumed that the oxygen of the PO group enters the coordination sphere of the metal ion probably displacing water and that phosphates, phosphinates, phosphonates, and phosphine oxides all coordinate in the same manner. The PO stretch frequency shifts to lower frequencies in the order phosphates to phosphine oxides and seems to correlate with a rise in the distribution coefficients and with the basicity of the PO group (4,31).

It is believed (46,60) that the same type of coordination takes place with HDPM as with TBP and TOPO. The PO stretching frequencies in TBP, TOPO and HDPM are reported to be 1260 (54), 1150 (54), and 1164 (60) cm^{-1} respectively. The possibility of interaction between the PO groups in HDPM and how it affects the stretching frequency is not known. Addition of one, two or three additional carbon atoms in the chain between the PO groups giving HDPE, HDPP and HDPB, respectively, changes the frequency of the PO stretch to 1136, 1163 and 1155 cm^{-1} respectively[1]. No evidence for enolization for HDPM was found (46,60) similar to that postulated by Kosolapoff (37) of the type



$$RO-\overset{\overset{O}{\|}}{\underset{\underset{RO}{|}}{P}}-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{OR}{|}}{P}}-OR \longleftrightarrow RO-\overset{\overset{O}{\|}}{\underset{\underset{RO}{|}}{P}}-CH=\overset{\overset{OH}{|}}{\underset{\underset{OR}{|}}{P}}-OR \quad .$$

It was found, however, on the basis of partition data a 1:1 uranyl nitrate-HDPM complex formed in the presence of excess uranium as well as a 2:1 complex in the presence of excess HDPM (46).

Chromatography of Inorganic Substances

No sharp line separates reversed-phase partition chromatography from other types of chromatography. An ion exchange resin might be considered reversed-phase chromatography with the active functional group attached directly to the supporting phase. Kennedy and others (32) studied the adsorption of the alkali and alkaline earth elements on phosphorylated resins. Head and others (20), by impregnating cellulose with

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[1] John Mrochek, Ames Laboratory, Ames, Iowa. I.R. data on HDPE, HDPP and HDPB. Private communication. 1963.

urea and phosphoric acid and heating, obtained a cellulose phosphate which had interesting ion exchange properties. Reversed-phase partition chromatography differs from "direct" partition chromatography only through the convention of regarding the organic phase as the mobile phase. No attempt will be made to review the entire literature of inorganic chromatography, however, the recent review articles by Salmon (61) on ion-exchange chromatography and the text, Chromatographic Methods of Inorganic Analysis, (59) are very useful.

Reversed-Phase Partition Chromatography

Reversed-phase partition chromatography will be considered to be that technique where the hydrophobic phase is stationary and is supported by some inert material. This technique has had a limited use in organic chromatography (21) but at the time this investigation was started (1960) the only reference to reversed-phase partition chromatography of inorganic substances which the author had seen was a brief statement by Kertes and Beck (33). These authors were making a general study of the use of TBP in organic diluents in partition chromatography of metal nitrates and mentioned that a few experiments had been carried out on TBP impregnated papers. They reported that only a very slight migration of ions took place independent of acid concentration. Shortly later, however, Fidelis and Siekierski (12) reported the separation of the lighter rare earths on columns of kieselguhr impregnated with TBP. They published elution curves showing a sharp separation was possible for a number of the lighter rare earths when eluted from the column with nearly concentrated nitric acid (15.1 to 15.8M). The light rare earths were eluted first and rather good separation factors were obtained except for the europium-gadolinium pair. In a later paper (13) these authors extended this work to the heavier rare earths which are normally more difficult to separate. They obtained fair separations using 11.5M, 12.3M, 13.0M nitric and concentrated hydrochloric acid as elutrients. Gwóźdź and Siekierski (17) reported the separation of various oxidation states of plutonium using this technique and Siekierski and Sochaka (65) reported the separation of calcium and scandium on TBP columns using 6M hydrochloric acid as the elutrient. Mikulski and Stroński (42) gave a separation of zinc, manganese, and cobalt from iron on a TBP column and in another paper (43) describe the separation of tin(II) and tin(IV) and of tin, tellurium and antimony.

Small (66) incorporated TBP into a crosslinked copolymer of styrene and divinylbenzene to give a material having useful properties as a column packing. He called this technique "gel liquid extraction" or GLX. He presented elution curves showing the separation of uranium and thorium, yttrium and thorium, and iron and yttrium nitrates, and in a later paper (67) showed the elution curves for rare earth nitrate mixtures.

Pierce and Peck (57,58) investigated the separation of the rare earths on columns packed with a polyvinyl chloride-polyvinyl acetate copolymer impregnated with di(2-ethylhexyl) orthophosphoric acid (HDEHP) using gradient elution with perchloric acid. Cerrai and others (7,8,9) also studied the separation of the rare earths on cellulose columns and paper treated with HDEHP eluting with hydrochloric acid.

Testa (71) reported the separation of a number of cations on paper treated with tri-n-octylamine. He reported the separation of zirconium and hafnium among other interesting separations. Cerrai and Testa also reported a number of separations using cellulose (5) and Kel-F (6) impregnated with TOPO as the column packing. Several different authors (14,18,19) have recently reported the use of a Kel-F column impregnated with TBP for the separation of uranium from a variety of other elements.

Dietrich described the use of a column packed with glass beads coated with TOPO to remove uranium from urine (11). Winchester (75) used an alumina column impregnated with HDEHP to separate rare earth mixtures. Fritz and Hedrick (15) described the separation of iron(III) on columns packed with Haloport-F impregnated with 2-octanone.

APPARATUS AND REAGENTS

Spectral measurements in the visible region were made with a Beckman, Model DU, or a Cary, Model 14, spectrophotometer. Flame photometric determinations were made with a Beckman, Model B, spectrophotometer fitted with a Beckman flame attachment and infrared spectra were obtained with a Perkin Elmer, Model 21.[1] A Sargent-Malmstadt titrator and a Burrell shaker were used for the batch partition studies. A Beckman, Model 76, pH meter was used for pH measurements. A General Electric, 100 watt, BH-4 mercury arc lamp was used for fluorescence work. A "Chromatocab"[2] and several "Chromatoboxes" manufactured by Research Specialties Co., Richmond, Calif. were used. The latter two items are illustrated on pages 136 and 138 in <u>Chromatography</u> (21). Ordinary Petri dishes were used for radial chromatography.

Columns of various lengths and diameters were used; a schematic of a typical column is illustrated in Figure 1. Also illustrated is the conductivity cell used to monitor the effluent from the column. The electrodes in the con-

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[1] The use of the flame photometer and the Perkin Elmer 21 was through the courtesy of Dr. V. A. Fassel of the Ames Laboratory, Ames, Iowa.

[2] The use of the "Chromatocab" was through the courtesy of Dr. J. S. Fritz of the Ames Laboratory, Ames, Iowa.

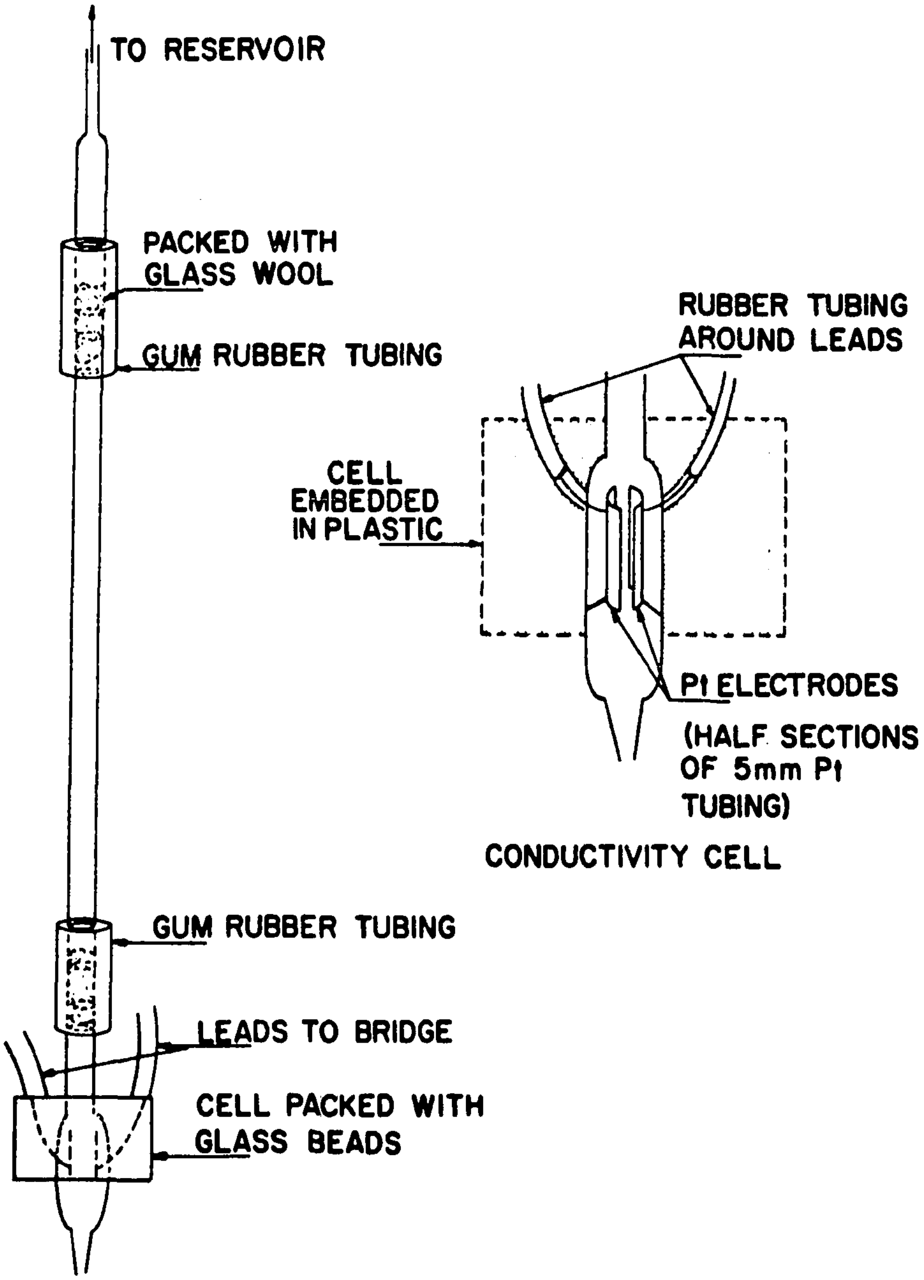

Figure 1. Schematic of column and conductivity cell

ductivity cell were prepared by splitting a short length of 5 mm. platinum tubing lengthwise. They were mounted in the cell with platinum leads as illustrated. The glass leads around the platinum wire leads from the cell were easily broken. For this reason the entire cell was embedded in plastic to make it less fragile. A constant temperature bath controlled by a Precision Scientific Company mercury relay was used.

A schematic diagram of the bridge used for conductivity measurements is shown in Figure 2. The components were mostly Leeds and Northrup equipment. The model numbers are indicated. The unbalance signal from the bridge was fed into a Mosely, Type A-1, AC-DC converter. The DC signal from the converter was fed into a Sargent, Model MR, recorder.

The lanthanide salts used were prepared from the oxides which were Ames Laboratory stock.[1] The zirconium and hafnium salts were also Ames Laboratory stock. The other chemicals used were reagent-grade materials except for the organophosphorus compounds.

The tri-n-butyl phosphate used was obtained from the

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[1] Obtained through the courtesy of Dr. F. H. Spedding and Dr. J. E. Powell of the Ames Laboratory, Ames, Iowa.

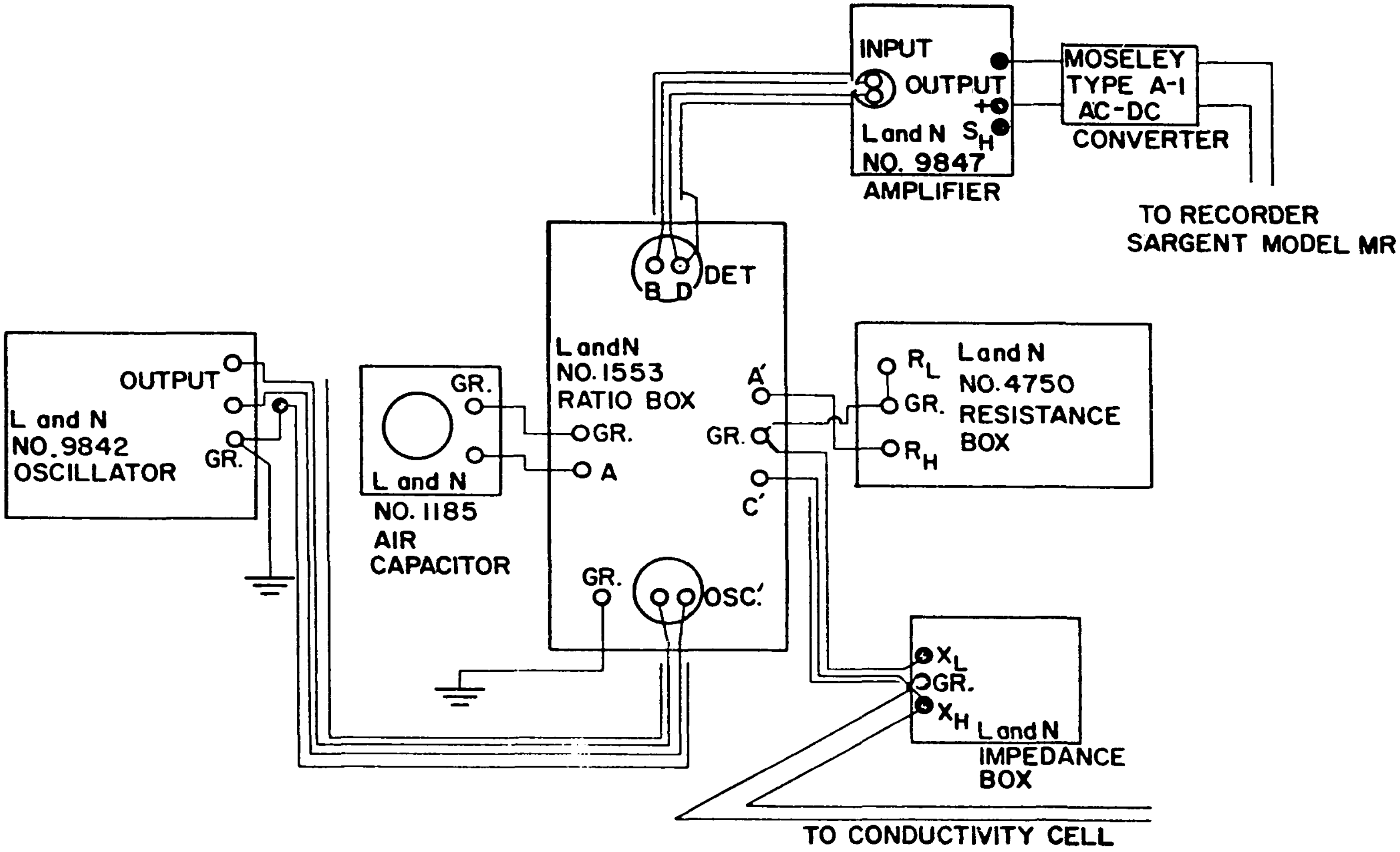

Figure 2. Schematic of bridge circuit

Fisher Scientific Company as a "purified" laboratory chemical. The tri-n-octyl phosphine oxide was an Eastman Organic Chemicals product. Both of the above compounds were used without further purification.

The bis(di-n-phosphinyl)methane was synthesized in this Laboratory by Mr. John J. Richard. The synthesis, purification and analysis are given in a recently published paper (60). The other organophosphorus compounds used containing two phosphorus atoms per molecule were also synthesized by Mr. Richard or Mr. John E. Mrochek, also on the Ames Laboratory Staff. The sources of other organophosphorus compounds used are given in Table 3.

The paper used for the paper chromatographic work was obtained from the Carl Schleicher and Schuell Co., Keene, New Hampshire except for the paper strips used in the spiral work which were Whatman No. 1 paper. The cellulose used in some of the column work was a product called "Solka-Floc" marketed by the Brown Company, Berlin, New Hampshire. The Kel-F, a fluorocarbon resin, was Minnesota Mining and Manufacturing Co. Molding Powder Grade 3010 or 300. Both numbers refer to the same product[1] which is a low density (133

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[1] Bringer, R. P. Chemical Division, 3M Co., St. Paul, Minn. Properties of Kel-F. Private communication 1962.

lbs./cu. ft.), highly absorbent, white powder. The resin was received as a sample from the 3M Company and was a mixture of various particle sizes from less than 10 to greater than 300 mesh. The 60-80 mesh fraction was used in this work. It might be noted this resin is no longer commercially available and has been replaced by the chemically identical product, Kel-F-6061.[1]

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[1] Bringer, R. P. Chemical Division, 3M Co., St. Paul, Minn. Properties of Kel-F. Private communication 1962.

EXPERIMENTAL

Paper Chromatography

The techniques of paper chromatography are adequately covered in the recently published text, Chromatography, by Eric Heftman (21). The reader is referred especially to Chapter 7 by Karel Macek. These techniques were followed in this investigation and any important modifications will be noted.

Preparation of solutions

Solutions of the chloride, nitrate, and perchlorate salts for most of the metallic elements were prepared to be 0.1M in the metal and, where necessary, enough mineral acid was added to prevent hydrolysis.

For the initial work on direct chromatography 0.05M and 0.025M solutions of TOPO and HDPM in 1,2-di-chlorobenzene were prepared. Portions of these solutions were equilibrated with an appropriate aqueous mineral acid phase before use.

The solutions used to prepare the papers for the general survey of stationary phases, the results of which are shown in Table 3, were prepared to be, very approximately, 2% by weight in the particular extractant used. Many of these extractants were research samples and undoubtedly impure. For this rather qualitative survey, however, no further purification was made.

The solutions used to impregnate the paper for most of the remaining work were carbon tetrachloride solutions 20% by volume, 0.2M, or 0.1M in TBP, TOPO, or HDPM, respectively, unless otherwise indicated.

Preliminary investigation

Initially it was thought that a rapid evaluation of HDPM and various other recently synthesized organophosphorus compounds (60) might be made by means of paper chromatography. The metals were spotted on chromatographic sheets (23 inches square) and the sheets were developed with the 0.05 or 0.025M 1,2-dichlorobenzene solutions of TOPO or HDPM. The sheets were developed in the "Chromatocab". The sheets were placed in the box after spotting and allowed to come into equilibrium with the atmosphere in the box before development was started. This was accomplished by placing open dishes of the developing reagent in the bottom of the box. The developing solution was then added through holes in the lid of the cabinet to prevent loss of vapor within the cabinet. The descending technique was employed and the chromatograms were allowed to develop to within about one inch of the bottom of the paper.

It was expected that the movement observed would be a function of the acid concentration in the developing solutions and these were equilibrated with an aqueous acid phase shortly before use.

The location of the metal salts after development was determined by the methods described in the following section. Despite all precautions severe tailing occurred in almost all cases except with the perchlorates and a more promising technique was sought. The possibility of impregnating the papers with the organophosphorus compound and using water or aqueous mineral acid solutions as developing agents was tried. Preliminary experiments on the movement of iron(III), uranium(VI), and aluminum perchlorates and chlorides on papers impregnated with TOPO and HDPM seemed quite promising and a systematic investigation of this technique was undertaken.

Reversed-phase chromatography

The movement of the chloride, nitrate and perchlorate salts of the metallic elements was studied on papers impregnated with various organic extractants. Chromatograms were obtained on sheets (23 inches square) and the individual metal salts were spotted about two centimeters apart along the start line. These sheets were developed in the "Chromatocab" using water or a mineral acid solution as the developing agent. It was found that the ascending method of development gave more sharply defined spots and this technique was employed for all the reversed-phase work unless otherwise noted. Chromatograms were also obtained on filter paper disks and strips. The circular discs were developed using Petri dishes, one inverted over the other, as development chambers. A spiral development technique was employed for the strips using the "Chromatoboxes" to which reference was made previously. The use of the plastic "Chromatoboxes" was especially convenient for a few cases in which hydrofluoric was added to the developing reagent.

Spotting of samples The metal salts were generally spotted on the papers by adding 1 λ of the appropriate solution using a 100 λ micro-syringe. After some use it was observed that the metal needle of the syringe was being attacked, especially by solutions containing hydrochloric acid. This introduced iron onto the paper and caused the reduction of some easily reducible species. Consequently these solutions were added using an all glass lamda pipet or just spotting with a glass rod or clean applicator stick. The amount added could be judged reasonably well by the size of the spot. For sheet and strip chromatograms the spots were centered two centimeters apart. For circular chromatograms the spot was centered at the base of the wick. It might be noted that the developing solution was always fed onto the disk chromatograms by means of a wick approximately 1 mm. in width cut out from the center of the disk. The bottom of the wick fell into the developing reagent which was taken up by capillary action.

Preparation of papers The sheets and strips were prepared by slowly drawing them through a solution of the stationary phase in some volatile solvent, usually carbon tetrachloride. They were then allowed to air dry or, occasionally, a hair drier was used to speed the process. The circular disks were prepared by actually soaking the disks in the solution containing the extractant and then hanging them to air dry. The amount of extractant on the paper was determined by weighing before and after treatment and by the spectrophotometric method described in a subsequent section.

Detection of spots The location of most metallic species was determined by spraying the paper with an alcoholic solution of 8-hydroxyquinoline and treating with ammonia. Most metals showed up as yellow spots or were detected under ultraviolet light as either a fluorescent spot or a dark spot on a faintly fluorescent background. Sodium and lithium were detected by their fluorescence after spraying with zinc uranyl acetate. A good summary of methods of detection of spots is given in a text by Pollard and McOmie (59). A 0.1% aqueous solution of "Arsenazo I", a chromogenic agent originally prepared by Kuznetsov (38), was used for the detection of the lanthanides, uranium, zirconium, hafnium, and thorium. These elements showed up as blue spots on a pink background when sprayed with "Arsenazo I". Excess acid on the paper was neutralized with ammonia. More sensitive reagents, "Arsenazo III" and "Chlorophosphonazo III", recently described by Savvin (62) and Nemodruk and others (51), respectively, were synthesized by Mr. John Richard and proved useful in some cases. The latter reagent gave green colored spots with all the heavy metals, the alkaline earths and even sodium and lithium. Sodium and lithium gave rather weak colors and could not always be located with this reagent after development of a chromatogram. The alkaline earths could be detected, however, and the reagent is particularly advantageous in this case. This is because magnesium, which falls between calcium and strontium, does not develop a green color immediately but first turns a rose-pink color. Calcium, strontium, and barium turn green immediately after spraying and treating with ammonia. The rose-pink color of the magnesium comes out strongly on treating with ammonia and then fades to a green color.

Survey of extractants   A relatively large number of potential extractants had been obtained from various sources as free samples. Also a number of potential extractants other than HDPM had been synthesized by Mr. John J. Richard of this Laboratory. A rough idea of the potential these materials might have as extractants or stationary phases in chromatographic work was desired. Consequently four salts, uranium(VI), cobalt(II), nickel(II), and calcium perchlorate were chromatographed using the sectional radial technique on paper disks impregnated with 2% solutions of these extractants using water as the developing agent. The paper was cut in four sections and one element was spotted in each section.

Systematic investigation   The movement of the chloride, nitrate, and perchlorate salts of the metallic elements on sheets impregnated with TBP, TOPO or HDPM was determined. The sheets were generally developed by the ascending technique using water or solutions of the mineral acids as developing agents. In all cases the TBP, TOPO, and HDPM sheets were spotted at the same time and developed with the same solution for the same length of time, usually overnight or for about 14 hours.

Radial chromatography This technique was used, especially for elements with very similar R_f values, because it gave sharper separations. It was also used for studying the movement of the metal perchlorates with more concentrated solutions of perchloric acid. The smaller papers were much more convenient in this case. It might be noted that immediately after development the excess acid was neutralized with ammonia and after detection of the spots the papers were washed free of perchlorates. Actually the organophosphorus compound seemed to prevent any dangerous reaction of the perchloric acid with the paper. The paper only charred on heating without exploding. Naturally, considerable precaution is advised with these papers which have been soaked with perchloric acid. Perchloric acid much more concentrated than 5M could not be used with the papers at all and some work was done using glass fiber paper impregnated with HDPM. The difficulty in locating the zones in the presence of excess perchloric acid on the papers restricted this work to the heavier elements.

Chromatography of mineral acids It was found that the mineral acid moved in a characteristic way on circular papers impregnated with HDPM. The acids were spotted like the cations and developed with water. The zones were located by spraying with a neutral or very slightly basic solution of methyl red. The movement of perchloric acid as a function of the absorptivity of the paper was studied. The amount of acid taken up by the paper was determined by titrating a fixed area of the paper behind the acid front on papers developed with 0.1M acid. A blank was run on papers not treated with HDPM.

Column Chromatography

The possibility that separations on a somewhat larger scale than was convenient with paper chromatography might be achieved on columns was investigated. Only HDPM was investigated extensively as a stationary phase. A few runs were made using TBP and TOPO.

Choice of supporting phase

Cellulose was first considered as a supporting phase for the extractant. This material had been previously used for this purpose but it proved rather troublesome to obtain uniformly packed columns which still had an appreciable flow rate. Glass beads (around 100 mesh in size) had too low a capacity and this supporting phase was unsatisfactory. Kel-F powder (see Apparatus and Reagents section) which was used by

Hamlin in similar work (18) proved quite satisfactory as a supporting phase and was used. The Kel-F powder was slurried with the extractant and carbon tetrachloride. The excess solvent was allowed to evaporate while stirring continuously. It was found that one part HDPM to two parts Kel-F gave a suitable product. Less HDPM could be used but resulted in a lower capacity. Larger amounts of HDPM gave a sticky product which would not pack well. The TBP-treated Kel-F was prepared by passing a 2:1 chloroform-TBP solution through a column packed with Kel-F and drying the column by passing air through it. The resulting material was about 25% TBP by weight. The TOPO-Kel-F packing was prepared in exactly the same way as the HDPM-Kel-F material.

Preparation of column

The columns were prepared by packing the treated Kel-F in glass or, in some cases plastic, tubes of various lengths. A U-shaped glass tube was used for most of the column work. This permitted a longer column to be used and it was still compact enough to be totally immersed in a constant temperature bath. Initially the column was packed rather tightly but a somewhat more loosely packed column was found to be almost equally as efficient and gave less tailing. The powder is best added in small portions and the column tapped repeatedly after each addition to insure uniform packing. The plastic columns were prepared by filling lengths of polyethylene tubing with the packing material. The columns were all wet before use by slowly back flushing with distilled water. They were never allowed to go dry.

Addition of sample

The sample solution was usually added with a microsyringe through a gum rubber section at the top of the column (See Figure 1) without interrupting the flow of the elutrient through the column. The elutrient was forced through the column by a positive head of air pressure over the elutrient in the reservoir. This pressure was maintained constant with a Johnson air regulator. The pressure was adjustable hence the flow rate could be controlled. The above was not neeessary, of course, when larger columns with gravity controlled flow were used.

Monitoring of effluent

When water was used as the elutrient the effluent was monitored with a flow-type conductivity cell illustrated in Figure 1. The cell was placed in the bridge circuit shown in Figure 2. Any unbalance signal from the bridge was amplified, converted to a DC signal and fed into a recorder. The chart speed of the recorder was ½ inch per minute and the time axis was syncronized with the addition of the sample. The flow rate was measured during each run by weighing the effluent from the column in a given time interval. The peak height was not linear with concentration but was approximately so for small unbalance signals. For the determination of the shape of the elution curves the non-linearity was ignored.

When perchloric acid or a salt solution was used as the elutrient it was not possible to use the conductivity method. In this case the elutrient was collected in fractions and each fraction analyzed by a flame photometric technique. The fractions were evaporated to dryness and taken up in a solution which was 80% in acetone, 19% in water and 1% in glacial acetic acid by volume. The samples were diluted to 10 ml. and read. The 422.7 mμ, 271 mμ, 461 mμ, and 515 mμ bands were used for calcium, magnesium, strontium, and barium, respectively. A calibration curve was prepared for each element at the same time the samples were read.

Batch equilibrium and loading capacity studies

Batch loading capacity and equilibrium studies were made. One- (or two-) gram portions of the treated Kel-F-HDPM packing was shaken with 10- (or 20-) ml. of water or

0.2M perchloric acid containing various amounts of calcium perchlorate. The equilibration was carried out by shaking in sealed glass ampules for 12 to 14 hours. The aqueous phase was then analyzed for calcium either by titrating with EDTA or spectrophotometrically using o-cresolphthalein (41). The titrations were carried out using the Sargent-Malmstadt titrator at a pH of 10 using Eriochrome Black T as the indicator.

The aliquots of the aqueous phase taken for analysis were filtered through a glass wool plug on the bottom of the pipet to remove any particles of solid material. The aliquots were then taken to dryness twice, adding a small amount of perchloric acid each time, to remove any organic matter which may have dissolved in the aqueous phase.

No difficulty was observed when larger amounts of calcium were present but some interference was observed for the spectrophotometric analysis of trace amounts of calcium. This was believed due to small amounts of phosphate from the destruction of traces of HDPM when fumed with perchloric acid. Efforts to remove this phosphate on anion exchange columns were not too successful at these very low calcium concentrations because of high blanks.

The amount of acid taken up by one- and two-gram samples of Kel-F-HDPM was determined by titrating with standard base before and after equilibration.

Spectrophotometric Determination of Organophosphorus Compounds

A spectrophotometric procedure proposed by Young and White (76) for the extraction and determination of titanium (IV) with TOPO was adapted for the determination of phosphine oxides. The titanium procedure involved the extraction of a titanium(IV) thiocyanate complex from an aqueous acid phase into an organic phase containing TOPO. A yellow-colored complex was extracted into the organic phase which was the basis of the spectrophotometric method.

It seemed likely that if an organic phase containing a variable amount of TOPO or some other phosphine oxide was equilibrated with an aqueous phase containing an excess of titanium(IV) and thiocyanate the extent of color formation would be a function of the concentration of the phosphine oxide. Preliminary experiments indicated this was true and the system was investigated.

Standard Procedure

Aliquots (2- to 15-ml.) of a 10^{-4}M solution of the organophosphorus compound were placed in a 60-ml. separatory funnel. Then 40 ml. of a 6M chloride solution (2M in HCl and 2M in $MgCl_2$), 0.5 gram of potassium titanyl oxalate and 2 grams of potassium thiocyanate were added. Sufficient chloroform was added to make the volume of the organic phase 10 ml. The funnel was shaken for three minutes and the chloroform phase transferred to a 25-ml. volumetric flask. The aqueous phase was extracted twice more with 3- to 5-ml. portions of chloroform and the chloroform phases added to the 25-ml. flask. The contents of the flask were diluted to volume with chloroform and the absorbance read at 390 mμ (in the case of TOPO at 425 mμ) against a reagent blank using a one-cm. cell path.

Effect of several variables

Solvent Cyclohexane, the solvent used by Young and White, was unsuitable for use with HDPM because a third phase formed and adhered to the funnel walls. This was also the case with carbon tetrachloride. Chloroform and 1,2-dichlorobenzene were both usable. The former was used because it gave slightly superior phase separations although the molar absorptivity of the complex was lower than it is in 1,2-dichlorobenzene.

Titanium concentration The absorbance only changed slightly as the amount of titanium added (as the oxalate) was varied from 0.2 to 2.0 grams. The 0.5-gram amount was chosen arbitrarily.

Thiocyanate concentration The amount of thiocyanate added was varied from 0.5 to 4.0 grams and the absorbance increased steadily from 0.415 to 0.650. The presence of a large absorption band in the ultraviolet region due to the thiocyanate itself made an increasing contribution to the absorbance at 390 mμ as the thiocyanate concentration was increased. Consequently the two-gram amount of thiocyanate was arbitrarily chosen.

Concentration of acid The amount of acid present between the limits of 2 to 5M did not change the absorbance of the complex so long as the total concentration of chloride remained at 6M. The absorption increased somewhat when the chloride concentration was increased.

Solubility of Organophosphorus Compounds

An excess of the organophosphorus compound was equilibrated with water or a mineral acid solution by stirring at least 15 hours. The container was immersed in a constant temperature bath the entire time. Aliquots of the aqueous phase were taken for analysis by the spectrophotometric procedure described above. Two separate 5-, 10- and 15-ml. aliquots were taken from each equilibrated solution. Equilibrations were carried out for TOPO, HDPM, HDPE, HDPP and HDPB at various temperatures from 62° to 20°C. Separate equilibrations were also carried out for these compounds at 0°C. by keeping the container in an ice bath. In this case the samples were only equilibrated for about four hours.

The fact that the solubility was inversely related to temperature made it necessary to cool the pipets used to aliquot the samples at 0° and 20°C. to prevent the compound from coming out of solution and sticking to the pipet walls.

Spectrophotometric analysis

The procedure described above was used with some slight modifications. A 10-ml. aliquot of the equilibrated sample was added to the volumetric flask and then 30 ml. of a solution 3M in hydrochloric acid and 3M in magnesium chloride. The rest of the procedure was the same as described above.

The possibility that different results might be obtained when the organophosphorus compound was initially in the aqueous phase rather than the organic phase was investigated. The aqueous phase was extracted with several portions of carbon tetrachloride. The carbon tetrachloride extract was evaporated down to a fairly small volume and then combined with chloroform to give a total volume of 10 ml. and the rest of the procedure carried out as above. The results were the same as in the above procedure but considerably more erratic as might be expected. Initially it was attempted to evaporate the aqueous aliquot to a smaller volume before analysis but the results were exceedingly erratic and low as might be expected from the inverse relationship between the water solubility and temperature of these compounds.

Chromatography of Organophosphorus Compounds

It was found that many of the organophosphorus compounds had R_r values between 0 and 1 when chromatographed on paper using alcohol-water mixtures. Mixtures 40 to 60% in ethanol were suitable for chromatographing many of these compounds. This was a useful technique in checking the purity of a particular compound.

Detection on paper

It was found that the zones containing the organophosphorus compound showed up a bright yellow color after spraying with a hydrochloric acid solution containing titanium(IV) and thiocyanate. The titanium and thiocyanate concentration were not critical. The reagent was prepared by adding 0.5 g.

of $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, 5.0 g. of KCNS and 5 ml. of concentrated hydrochloric acid to 100 ml. of water. This method of detection was also quite useful for the identification of treated papers.

Infrared Spectrophotometry

The infrared spectra of a number of metal and acid adducts with HDPM and related compounds were obtained. It was thought some information could be gained on the nature of the adsorbed species.

Preparation of samples

Solid uranyl nitrate, perchlorate, and acetate salts were mixed with HDPM with mole ratios of HDPM to metal varying from 2 to 0.5. The mixtures were heated at 60°C. for 63 hours in an effort to obtain homogeneous solutions. The resulting material was a viscous sticky substance but somewhat cloudy. The infrared spectra were obtained on the Perkin Elmer 21 using capillary cells (NaCl).

Solid uranyl nitrate and perchlorate salts were also weighed into small volumetric flasks and covered with 10 ml. of a 0.05M solution of HDPM in 1,2,2 trichloroethylene such that the mole ratios of HDPM to uranium were .46, .92, 1.3, 1.8, and 4.6. Analysis of the perchlorate and nitrate salts for uranium gave results of 39.70 and 51.45 % uranium, respectively. The samples were shaken overnight to effect dissolution of the uranium. The uranium salts dissolved completely but a viscous liquid second phase appeared in the perchlorate solutions. This phase disappeared on the dilution of the samples to 25 ml. with 1,2-dichloroethane and a homogeneous solution was obtained. These solutions were read on the Perkin Elmer 21 against a reference solution prepared in the same manner.

A series of solutions prepared exactly as above but with the HDPM in 1,2-dichloroethane were prepared. In this case homogeneous solutions were obtained with both the nitrate and perchlorate salts except in the case where the mole ratio was 0.46 where excess salt remained. These solutions were also read on the Perkin Elmer 21.

Both the above solutions contained some water (the salts were hydrated) and evidence of attack on the cell windows was observed. The latter set of solutions were dried with magnesium perchlorate and the infrared spectra again obtained. It might be noted that the uranyl salts are not soluble in these solvents in the absence of HDPM.

It had been observed in the solubility studies that a viscous material formed when HDPM, HDPE, HDPP, or HDPB was equilibrated with a mineral acid. The solid compounds completely disappeared and only a viscous acid adduct remained. The infrared spectra for the HDPM adducts with hydrochloric, nitric, perchloric and acetic acid were obtained. The spectra for the perchloric acid adducts of the other compounds were also obtained.

It was also found that when magnesium perchlorate was shaken with a 0.1M solution of HDPM in carbon tetrachloride a second clear, viscous phase formed. The infrared spectra of this material was also obtained. Uranyl chloride and anhydrous niobium pentachloride both dissolved in 0.1M HDPM in carbon tetrachloride to give yellow colored solutions. After some time a viscous yellow material appeared in the uranium solution but the niobium solution remained clear indefinitely. The infrared spectra of both solutions were obtained before any phase separation took place in the uranium solution.

RESULTS AND DISCUSSION

Paper Chromatography

Paper chromatography falls under the more general category of partition chromatography. The theoretical groundwork for the latter was laid by Martin and Synge (40). Recently a very lucid account of the theoretical basis of partition chromatography was given by J. Calvin Giddings and Roy A. Keller in Chapter 6 of Chromatography edited Eric Heftman (21). Some of the material particularily pertinent to this work is summarized here.

The movement of substances on paper chromatograms is usually described in terms of R_f values (or R_r values for radial chromatography). R_f is defined as the distance traveled by the zone to the distance traveled by the solvent front. The authors mentioned above prefer to discuss R_f in terms of a parameter R. This is considered a basic quantity equal to the fraction of solute molecules in the solvent (mobile phase) at any one time. It follows that R is related to the velocity of migration of the zone. The fraction of solute in the solvent moves with the velocity, v, of the solvent. The average velocity of the solute, u, is then equal to Rv. R is also related to the partition coefficient and it is readily shown that

$$R = \frac{A_m}{A_m + K_D\ A_s}$$

where A_m/A_s is the relative volume fraction of the mobile phase, as compared to the stationary phase, and K_D is the partition coefficient. It is stressed by these authors that R_f does not necessarily equal R. The reason for this is that the velocity of the solvent front, v_f, often exceeds the velocity, v, of the solvent at the point the zone is located. Also it is an error to assume A_m is constant for all zones regardless of R_f value. The amount of solvent associated with a unit area of paper varies from solvent source (greatest value) to the solvent front. These two factors work in opposite directions so often R_f values are closely related to R values. It should not be expected, however, that R_f values will be the same for ascending as for descending chromatography and no simple relationship exists between R_r values (the fraction of the radial distance to the zone to the radial distance to the solvent front) and the R_f values. It is not true that $R_f = R_r{}^2$.

The sample is usually applied in a small spot but it changes in shape and size on development due to diffusion and nonequilibrium conditions caused by the partition kinetics.

Consequently the spot usually acquires an elliptical shape since the slow kinetics affect only the longitudinal flow. There is also less eddy diffusion in the lateral directions and even under ideal conditions the spot will be an ellipse after development. Tailing (trailing to the rear) and bearding (streamers ahead of main body of spot) suggest non-linear isotherms or slow kinetic steps or both. Multiple spots from a single substance indicate a slow rate of formation or decomposition of some species of that substance.

Preliminary results

The R_f values for a number of metal chlorides spotted on Orange Ribbon paper and developed with 0.1M or 0.2M solutions of HDPM or TOPO in 1,2-dichlorobenzene, respectively, as a function of the acid concentration of the aqueous acid phase used to equilibrate the mobile phase are given in Table 1. The R_f values of zero signify a rather low partition coefficient into the TOPO or HDPM phase. The larger values suggest the partition coefficient is high. It is to be noted that the elements known to form strong chloride complexes have higher R_f values. It would also appear HDPM is a more powerful extractant for the lanthanides than TOPO from 6M hydrochloric acid. The spots tended to tail rather badly, however, and the data are only presented for later comparison with reversed-phase results.

Table 1. R_f values of metal chlorides as function of acid concentration

Element	TOPO			HDPM		
	3M	6M	12M	3M	6M	12M
Li	0	0	---	---	0	---
Be	---	0	---	---	0	---
Mg	0	0	---	---	0	---
Ca	0	0	---	---	0	---
Sr	0	0	---	---	0	---
Zn	.98	1	.86	.86	1	1
Cd	---	.80	.85	---	.88	?
Hg$^{(II)}$	---	0		---	0	---
Al	0	0	?	---	0	.32
Ga	---	1	.87	---	1	1
In	---	1	.82	---	1	1
Ti	---	0	1	---	0	.75
Zr	0	0	.8	---	0	.5
Hf	---	0	---	---	0	---
Sn$^{(II)}$	---	1	1	---	1	1
Cr$^{(III)}$	---	0	---	---	0	---
Mn$^{(II)}$	---	0	.3	---	0	.6
Fe$^{(III)}$	.02	1	1	.33	-	1
Co	.04	1	1	0	1	1
Ni	0	0	?	0	.15	?
Cu	.07	---	---	.04	0	---
Sc	.88	.95	1	.84	---	1
Y	?	.9	?	.94	1	1
La	.04	.6	0	.93	1	1
Ce	?	?	?	---	1	1
Pr	---	.9	0	---	1	1
Nd	---	.77	0	---	1	1
Sm	---	.76	0	---	1	1
Eu	---	.70	0	---	1	1
Gd	---	.78	.01	---	1	1

Table 1. (Continued)

Element	TOPO			HDPM		
	3M	6M	12M	3M	6M	12M
Tb	---	.81	.03	---	1	1
Dy	---	.84	.07	---	1	1
Ho	---	?	.07	---	1	1
Er	---	1	.08	---	1	1
Tm	---	1	.11	---	1	1
Yb	---	1	.14	---	1	1
Lu	?	.97	.19	.91	1	1
U	.97	---	---	.89	---	---
Th	.79	---	---	.60	---	---
Pt	---	---	.9	---	---	.1

When nitric acid was used to equilibrate the TOPO and HDPM the spots tailed so badly it was almost impossible to obtain any R_f values. Qualitatively, it was observed that scandium, uranium and thorium had large R_f values. Zinc also seemed to have a high R_f value and the lanthanides had R_f values around 0.5.

When perchloric acid was used to equilibrate the TOPO and HDPM solutions the appearance of the chromatograms changed remarkedly. Relatively little tailing was observed and the spots were well defined. The results obtained are summarized in Table 2. The lanthanides all moved practically with the solvent front with HDPM but not at all with TOPO. The alkaline earths were also observed to move with HDPM but not with

TOPO while the heavier metals moved with both TOPO and HDPM. A question mark in Tables 1 or 2 signifies an element that tailed so badly that it is not possible to give an R_f value.

Table 2. R_f values for metal perchlorates as a function of acid concentration

	1M $HClO_4$		3M $HClO_4$		6M $HClO_4$	
Element	HDPM	TOPO	HDPM	TOPO	HDPM	TOPO
Mg	.86	0	.94	0	.95	0
Ca	.94	0	.94	0	.94	0
Zn	.97	0	.96	0	.93	0
Al	.69	0	.83	0	?	0
Zr	.56	.96	.72	0	?	0
Fe	.94	0	.93	0	.92	0
Co	.89	0	.96	0	.95	0
Ni	.88	0	.88	0	.90	0
Cu	.79	0	.93	0	.93	0
Ag	0	0	0	0	0	0
U	.94	.99	.96	.99	.93	.98
Th	.91	.97	.95	.98	.92	.89
In	.93	0	.98	0	.92	0
Sc	.89	.95	.83	.93	.82	.96
Lanthanides	.95	0	.94	0	.95	0

Reversed-Phase Paper Chromatography

It was observed that reproducible results could be obtained much more easily by impregnating the paper with the organic extractant and then developing the paper with water or an aqueous solution of one of the mineral acids than could be obtained by direct paper chromatography. The results expected, in terms of R_f values, would be just the opposite of those obtained using the organic extractant in some "inert" solvent as the mobile phase. Species which had relatively high distribution coefficients would be expected to remain at the start line ($R_f = 0$) and those with very low distribution coefficients to travel near the solvent front ($R_f = 1$). The reversed-phase technique has the further advantage of eliminating the "inert" solvent which is usually required for the more powerful new extractants which are often solids.

Survey of Extractants

The results obtained on the use of various compounds as stationary phases for four different metals are given in Table 3. Sectional radial chromatography was used and the papers developed with water. The R_f values observed for the extractants themselves when developed on Blue Ribbon paper discs with 40 per cent ethanol are also given. The color of the various compounds when spotted on paper and sprayed with the titanium(IV) thiocyanate reagent used to detect the zones are given as well.

The purity of many of the compounds, which were obtained as research samples, is unknown. The names given in Table 3

Table 3. R_r values for U(VI), Co, Ni, and Ca with various extractants, their source and R_f values in 40% ethanol

Compound	Source	R_f	Ti(IV)-CNS	R_r			
			Color[a]	U	Co	Ni	Ca
Mono lauryl acid orthophosphate	2	--	PY	.53	.93	.93	.80
Phenylethylene thiophosphate	3	--	none	.98	1.0	.94	1.0
Mono-di-2-ethylhexyl acid orthophosphate	2	--	--	.16	.73	.74	.41
Iso-Amyl 2-ethylhexyl acid orthophosphate	2	--	none	.25	.38	.55	.25
Tri-iso-butyl phosphite	1	.80	PY	.76	.95	.89	.92
Triphenyl phosphite	1	.08	PO-Y	.23	1.0	1.0	.86
Triethylene diphosphite	1	--	none	--	--	--	--
Diphenyl phosphite	1	.91	O-Y	.48	.88	.88	.88
Tridecyl phosphite	1	.06	Y	.92	.96	1.0	1.0
2-(o,o-Dibutyldithiophosphate)ethylphenylphosphite	1	.08	PY	.25	.94	.94	.66
Tributylphosphite	1	.88	PO-Y	.83	1.0	1.0	1.0
Dimethylbenzene phosphonic acid	8	.90	O-Y	.90	1.0	.87	1.0
2-Chloroethylphenyl phenylmethane phosphonate	1	.85	O-Y	.45	1.0	.95	.98
Bis-(2-ethylhexyl)2-ethylhexanephosphonate	3	.06	O-Y	.30	.88	.93	.98

[a] Color Key = Y-yellow, O-orange, P-pale, V-very, D-deep.

Table 3. (Continued)

Compound	Source	R_f	Ti(IV)-CNS	R_r			
			Color[a]	U	Co	Ni	Ca
Bis-(2-Bromethylphenylphosphonato)ethane	3	1.0	PY	.76	.97	1.0	.95
Dibutyl butylphosphonate	7	.88	O-Y	.78	1.0	1.0	.90
Diamyl amylphosphonate	3	.53	O-Y	.57	1.0	.86	.86
Didecyl decanephosphonate	3	.05	O-Y	.98	.98	.92	.92
Dihexyl hexanephosphonate	3	.05	O-Y	.58	1.0	.98	.80
Phenylallyl allylphosphonate	1	.98	PY	.83	1.0	1.0	1.0
Dimethylallyl methylallylphosphonate	1	.99	DY	.82	1.0	1.0	--
Diallyl propene-2-phosphonate	1	.95	DY	.60	.71	.81	1.0
Di(2-ethylhexyl)ethylhexylphosphonate	7	.05	O-Y	.98	.98	.98	.98
Bis,beta chloroethyl vinylphosphonate	7	.98	VPY	.68	1.0	1.0	1.0
Dibutyl chloromethyl phosphonate	2	.93	PY	.80	.94	.89	.97
Di-2-ethylhexyl chloromethyl phosphonate	-	.07	VPY	.98	.94	1.0	.94
Di-propyl chloromethyl phosphonate	-	.95	VPY	.94	.94	.89	.89
Organic extractant #5	2	--	PO-Y	.42	.47	.47	.47
1-Heptyoctyl amine	6	.05	PO-Y	.40	.92	.92	.97
1-Undecyldodecyl amine	6	--	none	.96	.96	.96	.96
Tris [1-(2-methyl)aziridinyl] phosphine oxide	10	1.0	O-Y	.29	.57	.57	.86

Table 3. (Continued)

Compound	Source	R_f	Ti(IV)-CNS	R_r			
			Color[a]	U	Co	Ni	Ca
Tributyl phosphine oxide	4	1.0	Y	.15	1.0	.92	.92
Triphenyl phosphine oxide	5	.98	O-Y	.95	.92	.95	.95
Tri-n-octyl phosphine oxide (TOPO)	-	.13	O-Y	.50	.90	.95	.50
$(C_6H_{13})_2P(O)CH_2P(O)(C_6H_{13})_2$ (HDPM)	9	.08	O-Y	0	.24	.38	.10
$(C_4H_9O)_3PO$ (TBP)	-	.71	O	.98	1.0	1.0	.98
$(\phi)_2P(O)CH_2P(O)(\phi)_2$	9	.92	POY	.74	.73	.72	.83
$(\phi)_2P(O)CH_2C(O)($  $OCH_3)$	9	1.0	VVPY	.92	.84	.82	.95
$(\phi)_2P(O)CH_2C(OH)(\phi)_2$	9	1.0	Y	.94	.92	.97	.97
$(n\text{-}C_6H_{13})_2P(O)CH_2C(O)OCH_3$	9	.94	Y	.85	.98	.98	.75
$(\phi)_2P(O)CH_2C(OH)(\phi)H$	9	.83	PY	1.0	.97	.97	.97
$(C_6H_{13})_2P(O)CH_2C(OH)(C_2H_5)_2$	9	.87	DY	.24	.85	.68	.70
$(\phi)_2P(O)CH_2C(O)C_5H_{11}$	9	--	O-Y	.89	.95	.94	.97
$(C_6H_{13})_2P(O)C{=}CH(\phi)$	9	.63	Y	.92	.97	.92	.89
$(C_6H_{13})_2P(O)CH_2C(OH)(\phi)_2$	9	.21	PY	.92	1.0	1.0	.95
$(C_6H_{13})_2P(O)CH_2C(OH)(\phi)CH_3$	9	.78	Y	.90	.84	.92	.90
$(\phi)_2P(O)CH_2P(O)(C_8H_{17})_2$	9	.56	DY	.95	.90	.90	.90
$[2\text{-}(C_2H_5)C_4H_8]_2P(O)CH_2P(O)[2\text{-}(C_2H_5)C_4H_8]$	9	.95	Y	.34	.80	.80	.64
$(cyclo\text{-}C_6H_{11})_2P(O)CH_2P(O)(cyclo\text{-}C_6H_{11})_2$	9	.95	DO-Y	1.0	1.0	1.0	1.0
$(C_6H_{13})_2P(O)H$	9	--	Y	.92	.94	.94	.92

Table 3. (Continued)

1 Hooker Chemical Corp., Product Development, Niagara Falls, N.Y.

2 Victor Chemical Works, 155 N. Wacker Dr., Chicago G, Ill.

3 Shea Chemical Corporation, Adams, Mass.

4 Arapanoe Chemicals, Inc., 2800 Pearl St., Boulder, Colo.

5 Metal and Thermit Corp., Res. and Dev. Sect., Rahway, New Jersey.

6 Armour Research Division, Union Stockyards, Chicago 9, Ill.

7 Monsanto Chemical Co., St. Louis, Missouri.

8 Rodeny J. Davis, Ames Laboratory, Ames, Iowa.

9 John J. Richard, Ames Laboratory, Ames, Iowa

10 Interchemical, 67 West 44th St., N.Y. 36, N.Y.

for these compounds were taken directly from the bottle in which they were received.

The R_f values obtained are very approximate because considerably tailing occurred in many cases. The survey does indicate that the ability of HDPM to extract metal perchlorates is rather unique. Obviously many of these compounds might show considerably different behavior under other conditions. For example TBP is a very useful extractant although this is not evident from a survey such as this one.

The color, or lack of it given with the titanium(IV)-thiocyanate reagent was included because this indicates which compounds can be detected with this reagent. It does not necessarily follow, however, that the compounds giving a color can be determined by the spectrophotometric method for phosphine oxides described in another section. It is known that TBP, which gives an orange spot on paper, can not be determined with the procedure given.

Some variables which affect R_f values

Obviously the choice of the stationary and mobile phases are two very important variables. Only three different stationary phases - TBP, TOPO and HDPM - were considered in much detail in this investigation. The mobile phase was water or an aqueous mineral acid solution and the results of a systematic study of R_f values as a function of the acid concentration of the mobile phase is presented in a subsequent section.

Chromatographic techniques used It has already been pointed out that the R_f (or the R_r) values obtained might differ depending upon whether radial, spiral, descending or ascending chromatography is used. It was observed that bearding (streamers ahead of main body of spot) sometimes occurred when the descending method was used which made it difficult to calculate R_f values. This was likely due to non-equilibrium conditions between the mobile aqueous phase and the stationary organic phase caused by too rapid development. Radial results were dependent to some extent on the size of the wick used. If results on separate papers were to be compared it was necessary to cut the wicks on both papers the same size. This was conveniently done by using a razor blade to cut wicks on a small pile of papers at the same time.

Concentration of stationary phase As expected the amount of extractant per unit area of paper affected the observed R_f or R_r values and the capacity of the paper. Two papers soaked in 0.1M and 0.4M HDPM in carbon tetrachloride were found to have 1.07×10^{-6} and 3.84×10^{-6} moles of HDPM per square centimeter. These results were obtained by the weight differences of the papers before and after treatment. Very similar results were obtained by the spectrophotometric method described previously. These papers were spotted with 2 λ amounts of 0.1M calcium and magnesium perchlorate and developed with 0.1M perchloric acid. The results are shown in Table 4. It can be seen that the zones are smaller with paper 2 and the R_r values are smaller. The acid front refers to the distance from the start line to where perchloric acid no longer appears on the paper. Acid is taken up by the treated paper and when dilute acid is used to develop the paper an acid free zone appears immediately behind the solvent front.

Table 4. Effect of concentration of HDPM on R_r values[1]

	Paper 1 1.07×10^{-6} moles/cm^2	Paper 2 (3.84×10^{-6} moles/cm^2)
Acid front	.615	.462
Mg(leading edge)	.432	.277
Mg(trailing edge)	.273	.163
Ca(leading edge)	.228	.114
Ca(trailing edge)	.091	0

[1] Red Ribbon paper was used.

The capacity of the paper was determined by adding 10 λ and 20 λ of 0.1M magnesium perchlorate to paper having 1.2×10^{-6} moles/cm^2 of HDPM. The papers were developed with water and the magnesium zones cut out and weighed. The area was found from the known weight to area ratio. The results are given in Table 5. As the concentration of HDPM on the paper is increased the rate of development decreases and the amount of aqueous phase held per unit area of the paper probably decreases. Both these factors will also affect the R_r values. With larger amounts (<3.84 moles/cm^2) of HDPM on the paper the paper appeared slightly wet and sticky, and the rate of development was slower.

Table 5. Capacity of HDPM paper for $Mg(ClO_4)_2$[1]

$Mg(ClO_4)_2$ added (molesx10^6)	Area of zone (cm^2)	Moles HDPM in zone(x10^6)	Molar ratio HDPM/Mg
1	2.02	2.42	2.42
2	3.59	4.31	2.15

[1] Blue Ribbon paper was used.

Absorption characteristics of paper Paper discs of different absorptivities (correlated with the rise of distilled water on the paper in 30 minutes) were treated with HDPM (0.1M) and developed with 0.1M perchloric acid. The amount of acid held per unit area was determined by titrating the acid held by a disc of known size. Untreated paper was developed with perchloric acid at the same time and the amount of acid held per unit area determined. The results are summarized in Table 6. The R_r values are approximately the same but the amount of acid held is seen to be a function of the absorptivity of the paper.

Table 6. Movement of perchloric acid on HDPM-treated papers of different absorptivities

Paper type	Absorptivity[1]	R_r (acid front)	Acid held μ-eqs./cm^2)[2]	HDPM μ-moles/cm^2
Blue Ribbon	65-76	.67	.392	1.2
Red Ribbon	70-80	.61	.697	1.3
White Ribbon	95-100	.65	.703	1.3
Orange Ribbon	110-120	.70	.850	---
Black Ribbon	150-160	.70	.942	1.7

[1] Rise of distilled water in mm. per 30 min.

[2] Micro-equivalents of acid held per cm^2 by treated papers in excess of that held by untreated papers.

Movement of metal nitrates as function of acid concentration

The movement of various metal nitrates on papers impregnated with TBP, TOPO, and HDPM are shown in Tables 7, 8, and 9. Blue Ribbon paper sheets were used and treated with a 20% by volume, 0.2M, or 0.1M carbon tetrachloride solution of TBP, TOPO or HDPM, respectively. The papers were developed for 14

Table 7. R_f values for metal nitrates as function of nitric acid concentration on TBP treated papers

Element	Acid molarity .5M	3M	6M	9M	12M
Mg	1.0	1.0	1.0	--	--
Ca	1.0	1.0	1.0	--	--
Sr	1.0	1.0	1.0	--	--
Ba	1.0	1.0	1.0	--	--
Sc	1.0	.69	.59	.79	1.0
Y	1.0	.90	.76	1.0	1.0
La	1.0	1.0	.94	1.0	1.0
Eu	1.0	.92	.96	1.0	1.0
Gd	1.0	.92	.94	1.0	1.0
Tb	1.0	.89	.92	1.0	1.0
Lu	1.0	.84	.71	.91	1.0
Th	.54	.10	.06	.36	1.0[2]
UO_2	.32	.05	.07	.82	1.0
Zr	.92[1]	.19	.06	.07	.44[1]
Cr(III)	1.0	1.0	1.0	--	--
Mn(II)	1.0	1.0	1.0	--	--
Fe(III)	1.0	.95	.89	1.0	1.0
Co(II)	1.0	1.0	1.0	--	--
Ni(II)	1.0	1.0	1.0	--	--
Cu(II)	1.0	1.0	1.0	--	--
Ag	1.0	.11[1]	.08[1]	0	0
Zn	1.0	1.0	1.0	--	--
Cd	1.0	1.0	1.0	--	--
Hg(II)	1.0	.10	.10[1]	0?	1.0
Al	1.0	1.0	1.0	1.0	1.0
Pb(II)	1.0	1.0	1.0	--	--
Bi	.79	.95	1.0	1.0	1.0

[1] Tailed.

[2] Some Th at start line and some at solvent front.

Table 8. R_f values for metal nitrates as function of nitric acid concentration on TOPO treated papers

	Acid molarity				
Element	.5M	3M	6M	9M	12M
Mg	1.0	1.0	1.0	--	--
Ca	1.0	1.0	1.0	--	--
Sr	1.0	1.0	1.0	--	--
Ba	1.0	1.0	1.0	--	--
Sc	.01	.03	.07	.11	.44
Y	.11	.67	.92	1.0	1.0
La	.95	1.0	1.0	1.0	1.0
Eu	.11	.84	1.0	1.0	1.0
Gd	.11	.84	1.0	1.0	1.0
Tb	.08	.85	1.0	1.0	1.0
Lu	.07	.48	.87	1.0	1.0
Th	0	0	.02	0	.16
UO_2	0	0	.02	0	.10
Zr	0	0	.01	0	0
Cr(III)	1.0	1.0	1.0	--	--
Mn(II)	.98	1.0	1.0	--	--
Fe(III)	.89[1]	.64[1]	.54[1]	1.0	1.0
Co(II)	1.0	1.0	1.0	--	--
Ni(II)	1.0	1.0	1.0	--	--
Cu(II)	1.0	1.0	1.0	--	--
Ag	.17[1]	.15[1]	.07[1]	0	0
Zn	1.0	1.0	1.0	--	--
Cd	1.0	1.0	1.0	--	--
Hg(II)	1.0	.03	.14[1]	1.0	1.0
Al	1.0	1.0	1.0	1.0	1.0
Pb(II)	.96	.89	.97	--	--
Bi	.01	.60	.94	1.0	1.0

[1] Tailed.

Table 9. R_f values for metal nitrates as function of nitric acid concentration on HDPM treated papers

	Acid molarity				
Element	.5M	3M	6M	9M	12M
Mg	1.0	1.0	1.0	--	--
Ca	.95	1.0	1.0	--	--
Sr	1.0	1.0	1.0	--	--
Ba	1.0	1.0	1.0	--	--
Sc	.01	0	0	.05	.03
Y	.02	.09	.13	.43	.83
La	.02	.30	1.0	1.0	1.0
Eu	.02	.08	.27	.68	1.0
Gd	.02	.09	.29	.71	1.0
Tb	.02	.08	.22	.59	1.0
Lu	.03	.06	.06	.14	.38
Th	0	0	0	0	.05
UO_2	0	0	0	0	.03
Zr	0	0	0	0	.02
Cr(III)	1.0	1.0	1.0	--	--
Mn(II)	.56	1.0	1.0	--	--
Fe(III)	0	0	0	0	.05
Co(II)	1.0	1.0	1.0	--	--
Ni(II)	1.0	1.0	1.0	--	--
Cu(II)	1.0	1.0	1.0	--	--
Ag	.28[1]	.1[1]	.11[1]	0	0
Zn	1.0	1.0	1.0	--	--
Cd	.84[1]	1.0	.86	--	--
Hg(II)	.22	0	.2[1]	1.0	1.0
Al	?[2]	?[2]	?[2]	0[2]	.07[2]
Pb(II)	.94	1.0	1.0	--	--
Bi	0	.02	.60	1.0	1.0

[1] Tailed.

[2] Tailed badly, in case of Al with HDPM from start line to solvent front but with 12M HNO_3 most Al remained at start line.

hrs. using ascending chromatography.

The alkali and alkaline earth nitrates are not appreciably extracted from acidic solutions by TBP or TOPO (74) and the R_f values are all one except that calcium was retained slightly by HDPM. No appreciable retention of chromium(III), nickel, copper, zinc, cadmium or lead was noted in agreement with known partition data for TBP and TOPO. Although iron (III) is not reported to be extracted from nitric acid media by TOPO (74) it is significantly retained by TOPO, and somewhat by TBP, from 6M acid and is held at the start line on the HDPM paper up to 12M acid. Bismuth is retained somewhat by all three extractants and in agreement with partition data shows its lowest R_f (highest partition coefficient) with the most dilute acid. Aluminum was retained to some extent on the HDPM paper but tailed badly. This is presumably due to slow kinetics in the partition equilibria.

The lanthanides, scandium, yttrium, uranium(VI), zirconium and thorium show similar behavior. All are held progressively tighter by TBP, TOPO and HDPM in that order. All show a minimal R_f value on the TBP papers around 6M acid and show steadily increasing R_f values on the TOPO and HDPM papers. The minimum in a plot of R_f values or maximum in a plot of the partition coefficients as a function of acid concentration is expected on the basis of a competitive extraction of nitric acid and the metal nitrates (50,53). This was predicted for the extraction of uranium(VI) with TBP at 4M nitric acid. It should be noted, however, that Hesford and others (22) found the partition coefficients of the lanthanides into 100% TBP increased monotonically with nitric acid concentration. Furthermore, no minimum in the R_r values for the lanthanide nitrates was evident, Table 22, when radial chromatography was used. This is discussed in a subsequent section on the separation of the lanthanides. The lack of a minimum with TOPO and HDPM probably reflects the more basic character of the PO group in these extractants.

The separation of the alkaline earths from the lanthanides, yttrium, and scandium looks particularly promising with HDPM. Calcium and magnesium are used in the reduction process for the preparation of the lanthanide metals and yttrium and the determination of small amounts of calcium and magnesium in these metals is an important analysis. A separation is usually required and the possibility of using the reversed-phase chromatographic method is of considerable interest. A rigorous investigation of methods for the determination of small amounts of calcium and magnesium in yttrium metal is currently being made by Mr. D. L. Berner of this Laboratory.[1] Preliminary results on the separation of calcium and magnesium from yttrium using a column packed with Kel-F impregnated with HDPM and 3M nitric acid as the elutrient are quite promising.

Movement of metal chlorides as function of acid concentration

The movement of various metal chlorides on papers, impregnated and developed the same as described in the previous section, are shown in Tables 10, 11, and 12. Exceptions are the papers impregnated with TBP and used for the 6M and 12M runs where a 0.2M TBP solution in carbon tetrachloride was used to impregnate the paper.

Considerably better resolution of zones was often obtained on circular chromatograms and elements which did not show any separation on sheet chromatograms can often be separated. An example of this is the separation of zirconium and hafnium on TBP treated paper discs using 6M hydrochloric acid as the mobile phase. R_r values of 0.64 and 0.83 were obtained for zirconium and hafnium run separately. Two sharply separated zones were obtained for a mixture of these

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[1] Berner, D. L., Ames Laboratory, Ames, Iowa. Separation of calcium and magnesium from yttrium. Private communication. 1963.

Table 10. R_f values for metal chlorides on papers treated with TBP

	Acid concentration				
Element	0.5M	3M	6M	9M	12M
Be	.95	1.0	1.0	1.0	1.0
Mg	.95	1.0	1.0	1.0	.86
Ca	.95	1.0	1.0	1.0	.67
Sr	.95	1.0	--	1.0	--
Zn	.43	.39	.50	.77	.72
Cd	.52	.26	.37	.81	.75
Al	1.0	1.0	1.0	1.0	.82
Ga	.37	.03	0	0	0
In	.48	.08	.13	.20	.43
Sc	.95	.90	--	.28	.10
Y	.95	.90	.85	1.0	.82
Ti	.95	.94	.95	1.0	.47
Sn(II)	.1	.03	0	0	.19
Mo(VI)	.47	.02	0	0	.07
Nb(V)	.1	.04	0	0	0
Mn(II)	.95	.97	.91	1.0	1?
Fe(III)	.47	.02	0	0	0
Co	.95	.96	.89	1.0	.72
Ni	.95	.96	.89	1.0	.75
Cu	.94	.83	.83	1.0	.75
V(IV)	.95	.88	.92	1.0	.75
Cr(III)	1.0	.91	.91	1.0	1.0
Zr	.95	.87	.88	0	0
Hf	.95	.87	.89	.21	0
U(VI)	1.0	.12	--	0	--
Th	.95	.84	--	.54	--
Hg(II)	.13	.08	0	.64	0
Au	0	.02	0	0	0
Pt	0	.01	0	?	?

Table 11. R_f values for metal chlorides on papers treated with TOPO

Element	Acid concentration 0.5M	 3M	 6M	 9M	 12M
Be	.95	1.0	.89	1.0	1.0
Mg	.95	1.0	.86	1.0	1.0
Ca	.95	1.0	.80	1.0	1.0
Sr	.95	1.0	--	1.0	--
Zn	.05	.01	0	.09	.13
Cd	.05	0	0	.16	.18
Al	1.0	1.0	.86	1.0	1.0
Ga	.11	0	0	0	0
In	.05	.01	.02	.14	.14
Sc	.07	.02	--	.03	.04
Y	1.0	1.0	.97	1.0	1.0
Ti	.28	.10	.02	.03	0
Sn(II)	0	0	0	0	0
Mo(VI)	0	0	0	0	.05
Nb(V)	0	0	0	0	0
Mn(II)	.92	.75	.49	1.0	--
Fe(III)	.03	0	0	0	0
Co	.84	.20	.07	.28	.13
Ni	.98	.97	.84	1.0	.80
Cu	.78	.10	.05	.77	.43
V(IV)	.92	.88	.77	.87	.7
Cr(III)	1.0	.98	.77	1.0	.7
Zr	.02	0	0	0	0
Hf	.04	0	0	0	0
U(VI)	.04	0	--	0	--
Th	.08	.07	--	.04	--
Hg(II)	0	0	0	.06	.06
Au	0	0	0	0	0
Pt	0	0	0	.06	.05

Table 12. R_f values for metal chlorides on papers treated with HDPM

	Acid concentration				
Element	0.5M	3M	6M	9M	12M
Be	.99	.90	.79	1.0	.87
Mg	.99	.90	.83	1.0	.90
Ca	.99	.81	.79	.93	.90
Sr	.99	1.0		1.0	--
Zn	.02	.01	.01	.35	.27
Cd	.02	.01	.05	.21	.19
Al	1.0	.92	.87	?	.95[1]
Ga	.66	0	0	0	0
In	0	.02	.03	.67	.53
Sc	.05	0		.02	0
Y	.79	.80	.92	.65	.71
Ti	.11	.04	.02	0	0
Sn(II)	0	0	0	0	0
Mo(VI)	0	0	0	0	0
Nb(V)	0	0	0	0	0
Mn(II)	.90	.93	.78	1.0	.90
Fe(III)	.08	0	0	0	0
Co	.92	.89	.27	.64	.34
Ni	.96	.98	.86	1.0	.94
Cu	.76	.65	.44	.93	.70
V(IV)	.60	.39	.21	.43	.40[1]
Cr(III)	1.0	1.0	1.0	1.0	.97
Zr	.02	0	0	0	0
Hf	.04	0	0	0	0
U(VI)	0	0	0	0	0
Th	0	.01	0	0	0
Hg(II)	0	.02	.06	.11	.12
Au	0	0	0	0	0
Pt	.02	.02	.04	.12	.17

[1] Tailed.

two elements with R_r values of 0.63 and 0.82. Similar examples of this type will be given in subsequent sections on the separation of the alkali metal perchlorates and the lanthanide nitrates and perchlorates.

Recently Ishimori and others (27,28) have compiled the known data on the extraction of the metallic elements into TBP and TOPO solutions. They compared these data with data from Kraus on the adsorption of metal chlorides on anion exchange columns. The data in Tables 10 and 11 on the R_f values are almost the exact inverse of the data given by Ishimori as would be expected. The R_f values for the alkali metals were all one and are not given in the tables.

The close correspondence between the partition coefficient and the absorption behavior on anion exchange columns is of interest. It seems to suggest that the neutral extractant is acting as an anion exchanger. This may be the case if the PO group is protonated and the metallic species is extracted as an anionic chloride complex. This might be expected in the case of a strong acid with an anion capable of coordinating to a metal to give an anionic species.

It is of interest that in the case of scandium, yttrium, and lanthanum as well as with zirconium, hafnium and thorium the lighter member of each set has the lowest Rf value (highest partition coefficient) and the R_f value increases as atomic number increases. An increase in R_f (decrease in partition coefficient) is not apparent in the series zinc, cadmium, and mercury(II) nor is any decrease in the partition coefficients of the alkali and alkaline earths evident with increasing atomic number (27). Iron is also strongly retained at higher acid concentrations.

It is tempting to postulate the extraction of these latter metals as chloride complexes but White (74) claims this is not the case with the iron-TOPO system and that the evidence is not in favor of the adduct being $HFeCl_4 \cdot 2TOPO$. Katzin (30) reported that the species in the organic phase for the extraction of trivalent metal chlorides with many organic solvents was the neutral species $HMCl_4$. He also noted, however, that TBP seemed to coordinate differently than the normal organic solvents and, like the halide ions, was capable of calling forth lower coordination numbers of its partner cations than they might normally show. It would be expected that this would also be true for TOPO and HDPM.

The above suggests that with normal organic solvents the extraction of the chlorides may be thought of as involving the replacement of waters of hydration around the cations by halide ions. At high acid concentrations the activity of water is lowered and the formation of a neutral species, $HMCl_4$, with the metal showing a lower coordination number takes place. The organophosphorus extractants, however, seem capable of replacing waters of hydration even at low acidities (Note the low R_f values for Fe(III) with TOPO and HDPM in 0.5M acid). The species extracted by TOPO is reported to be $FeCl_3 \cdot 2(TOPO)$ (74).

The more highly charged cations are more extensively hydrated in aqueous solution and the waters of hydration should be even more difficult to replace. It is interesting that HDPM retains the rare earths, yttrium, scandium and the quadrivalent elements better than TOPO or TBP while TOPO seems slightly superior for zinc, cadmium and mercury as well as cobalt, copper, gallium, indium and possibly iron(III). It should be kept in mind of course that the TOPO concentration on the papers is twice as great as HDPM and HDPM might be equally as effective as TOPO even for the latter elements at the same concentration. The relative difference in the two groups of metals still exists, however.

Movement of metal perchlorates as a function of acid concentration

The movement of a number of metal perchlorates on TBP-, TOPO-, and HDPM-treated papers (Blue Ribbon) is shown in

Table 13. The R_f values show that almost all the metal perchlorates are retained better on the HDPM paper than on the TBP or TOPO papers. The most striking difference noted is the behavior of the lanthanides which all have R_f values of zero with HDPM, are slightly held by TBP and not at all by TOPO. Scandium is held better by TOPO than TBP at 0.5M and 3M acid but its R_f value decreases with acid concentration for TBP and increases slightly for TOPO. It is strongly held by HDPM.

Iron and aluminum tailed badly and R_f values for these elements are not too significant. The R_f value for nickel increases rapidly with acid concentration on the HDPM paper as do the R_f values of cadmium and manganese.

The lanthanides, scandium, yttrium, uranium and thorium were chromatographed on glass fiber paper impregnated with HDPM (0.1M HDPM in carbon tetrachloride) using 9M perchloric acid as the developing agent. It was not possible to use ordinary paper with perchloric acid this concentrated and the detection of the spots was difficult. The glass fiber paper was soaked in aqueous ammonia after development which neutralized the excess perchloric acid and precipitated the lanthanides on the paper. The paper was then sprayed with "Arsenazo" and all the zones except for lanthanum and cerium

Table 13. R_f values for metal perchlorates as function of perchloric acid concentrates on TBP-, TOPO-, and HDPM-treated papers

Element	0.5M $HClO_4$			3.0M $HClO_4$		
	TBP	TOPO	HDPM	TBP	TOPO	HDPM
Be	1.0	1.0	.32[1]	1.0	1.0	.34[1]
Zn	.78	1.0	.72	1.0	1.0	.92
Cd	.90	1.0	.06	1.0	.88	.86
Hg	.51	.70	.59	.64	.66	.69
Al	1.0	1.0	1.0 [1]	1.0	1.0	1.0 [1]
In	.89	.11	0	.88	.79	0
Tl(I)	0	0	0	0	0	0
Pb(II)	.64	.82	.14	.44	.44	.38
Mn	.94	1.0	.04	1.0	1.0	.84
Fe(III)	.93	0	0	.94	?	?
Co	.94	1.0	.92	1.0	1.0	.93
Ni	.94	1.0	1.0	1.0	1.0	1.0
Cu	.93	1.0	.87	1.0	1.0	.87
U	.71	0	0	.41	.06	0
Th	.95	.10	0	.83	.23	0
Y	.95	1.0	0	1.0	1.0	0
Sc	.77	0	0	.27	.04	0
Ce(III)	.92	1.0	0	1.0	1.0	0
La	.91	1.0	0	1.0	1.0	0
Tb	.90	1.0	0	1.0	1.0	0
Gd	.90	1.0	0	1.0	1.0	0
Tm	.89	1.0	0	1.0	1.0	0
Lu	.89	1.0	0	1.0	1.0	0
Acid front	.92	1.0	.97	1.0	1.0	

[1] Tailed, in case of Al from R_f = 0 to 1.

could be found. The results are shown in Table 14 and compared with R_f values for these elements with 9M nitric and hydrochloric acids.

Table 14. R_f values for the lanthanides, scandium, yttrium, uranium and thorium on HDPM-treated paper[1]

Element	9M HCl	9M HNO_3	9M $HClO_4$[1]
Sc	0	.05	.02
Y	.46	.08	.09
La	.46	.37	---
Ce	.47	.25	---
Pr	.47	.23	.13
Nd	.45	.23	.13
Sm	.36	.13	.13
Eu	.38	.14	.11
Gd	.43	.16	.11
Tb	.36	.09	.11
Dy	.36	.08	.08
Ho	.40	.07	.07
Er	.38	.06	.10
Tm	.37	.05	.08
Yb	.30	.04	.05
Lu	.28	.05	.04
U	0	0	0
Th	0	0	.02

[1] S & S glass fiber paper No. 26 used for 9M $HClO_4$.

The movement of the alkali, alkaline earth and several other metal perchlorates on HDPM-treated paper with water and rather dilute (.05M and .1M) perchloric acid was studied. The R_f values obtained are presented in Table 15.

Table 15. R_f values for metal perchlorates on HDPM-treated paper

Element	Descending		Ascending	
	H_2O	.05M $HClO_4$	H_2O	.1M $HClO_4$
Li	1	.67	.97	1
Na	1	.82	.92	1
Mg	.14	.10	.14	.24
Ca	.05	.01	.07	.04
Sr	.24	.37	.29	.85
Ba	.30	.37	.32	.85
Mn	.03	.01	.03	0
Co	.12	.05	.11	.11
Ni	.18	.19	.20	.54
Cu	---	---	.12	.14
Zn	---	---	.11	.07
Cd	.05	.02	---	---
Hg	.02	.01	.04	.01
Tl(I)	---	---	0	0
Pb	---	---	.05	0
Ce(III)	---	---	0	0
U	---	---	0	0
Acid front	---	.37	---	.85

As in the case of zirconium and hafnium chlorides, a number of separations of metal perchlorates were possible using radial chromatography which would not be evident from the sheet or strip results. It was found for example that sodium and lithium could be nicely separated on filter paper discs impregnated with HDPM. The alkaline earths could also be separated by this technique. The R_r values for sodium and lithium both when spotted separately and as a mixture are shown in Table 16.

Table 16. R_r values for sodium and lithium perchlorates on HDPM-treated papers on development with water (Blue Ribbon paper)

Run	R_r	
	Li	Na
1	.50	---
2	.63	---
3	---	.83
4	---	.75
5[1]	.63	.84

[1] In run No. 5 Be, Mg, Ca, Sr, Ba, and Al perchlorates were also present in the mixture. They all had smaller R_f values.

R_f and R_r values for the alkaline earth perchlorates on HDPM-treated paper are shown in Tables 17 and 18. The results in Table 17 are for spiral development in the "Chromotobox". Whatman No. 1 paper impregnated with 0.1M HDPM was used in the latter case. The results in Table 18 for the alkaline earths and aluminum were obtained on disc chromatograms using Red Ribbon paper impregnated with 0.1M HDPM in carbon tetrachloride. The zones were sharply separated but when barium was present the strontium and barium zones overlapped.

The displacement of strontium and barium by 0.1M perchloric acid permits an exceedingly sharp separation of these

Table 17. R_f values for alkaline earth metals and aluminum on paper treated with HDPM (Spiral development)

Element	R_f	
	H_2O	0.1M $HClO_4$
Be	.94	.11
Mg	.06	.26
Ca	.03	.11
Ba	.25	.64
Sr	.28	.64
Al	.04	.03
Acid front	---	.64

Table 18. R_r values for alkaline earth perchlorates spotted separately and in mixtures. Solvent - 0.1M $HClO_4$, Red Ribbon paper

Run	R_r values				
	Be	Mg	Ca	Sr	Acid front
1	---	---	---	---	.68
2	.31	---	---	---	.65
3	---	.46	---	---	.65
4	---	---	.39	---	.77
5	---	---	---	.65	.65
6	---	.52	.32	.78	.78
7	---	.53	.26	.72	.72

two elements from the remaining members of the group. All of the strontium and barium are displaced by 0.1M perchloric acid and the trailing edge is very sharp. Provided the capacity of the paper is not exceeded even trace amounts of barium and strontium can be separated from much larger amounts of the other members of the family.

The movement of a number of other perchlorates as a function of acid concentration is shown in Figure 3. The variation in distribution coefficient for the extraction of the metal perchlorates into HDPM in 1,2-dichlorobenzene is also shown.[1] It can be seen that the R_f values generally are what might be expected on the basis of the distribution data.

The partition coefficients are for the extraction of the metal perchlorates into a 0.1M solution of HDPM in 1,2-dichlorobenzene. In all cases 10 ml. of a 0.0334M metal solution was equilibrated with 10 ml. of the organic phase for ten minutes. The partition coefficients for the lanthanides all fell between one and ten so a different ordinate scale was used in Figure 3 for the lanthanides to better illustrate how the partition coefficient varied with acid concentration.

The length and position of the R_r scale on the right hand ordinate of each square were chosen so that the curves would roughly follow the log K_D plots. The R_f values read

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[1] The distribution data shown in Figure 3 are a compilation (mostly yet unpublished) of data obtained by a number of members of the Ames Laboratory Staff including K. E. Burke, J. W. Ferguson, J. E. Mrochek, and H. Sakurai, Ames, Iowa.

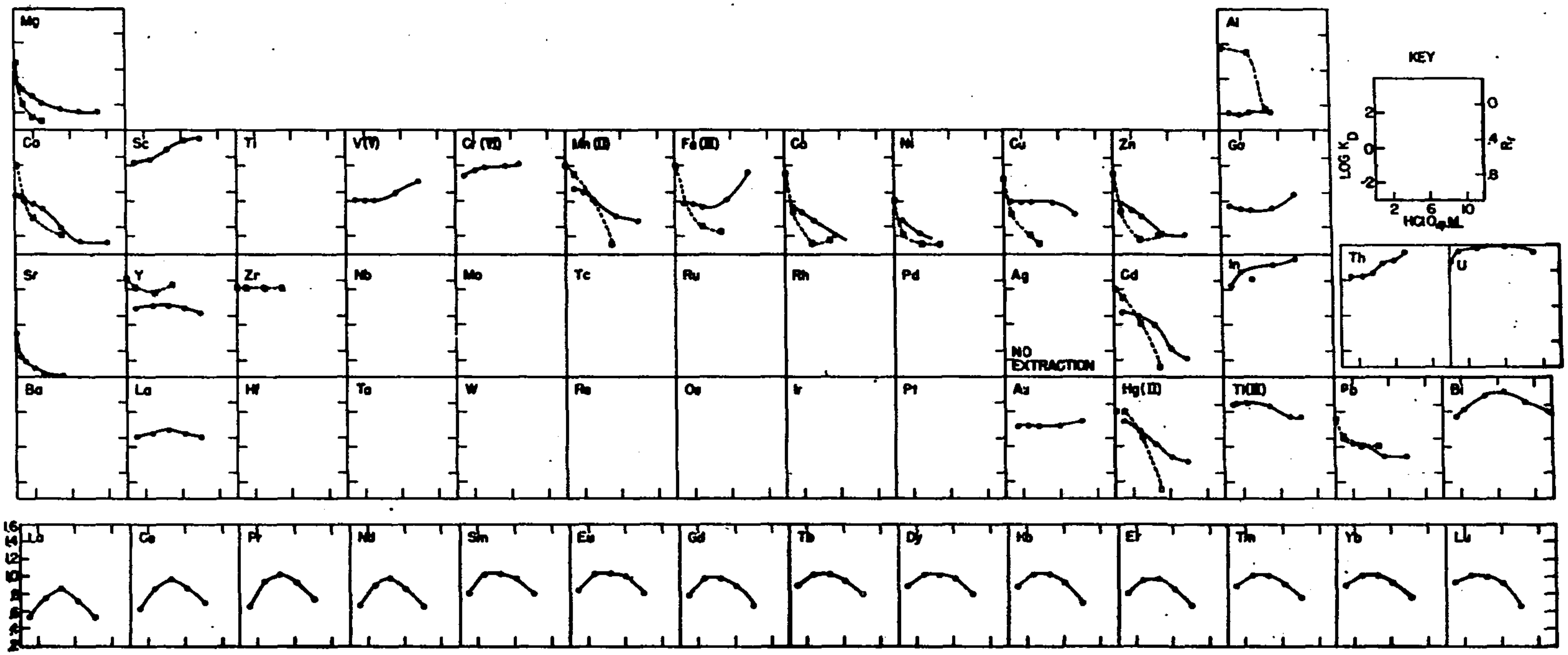

Figure 3. Partition coefficients and R_r values for metal perchlorates as a function of perchloric acid concentration

R_r data - □ and dotted lines
K_d data - ○ and solid lines

from 0 at the top to 1 at the bottom for the same reason. Blue Ribbon paper discs were used which were treated with 0.1M HDPM in carbon tetrachloride. Strontium and barium were displaced by the perchloric acid and showed R_r values of one. Aluminum tended to tail and the R_r values are questionable. The R_r values for yttrium were so low that the shape of the curve shown is not too significant. The R_r values for uranium, thorium, scandium, zirconium and hafnium were practically zero up to 5 M perchloric acid.

Like the sorption of the alkali and alkaline earth cations on a cation exchange resin, the alkaline earth metals are held more tightly on the HDPM-treated paper than the alkali metals. Within each group, however, the normal order is reversed. The order of adsorption on a cation resin like Dowex 50 is Ba > Sr > Ca > Mg > Na > Li. The order of decreasing R_f values on HDPM-treated paper (the order of increasing adsorption) is Na > Li and Ba > Sr > Mg > Ca. Kennedy and others (32) suggested such an inversion in the normal order took place on certain phosphorylated resins because the $-POO_2^{-2}$ group displaced water from the cations. This resulted in an adsorption sequence governed by the charge density of the unhydrated cation.

It seems likely that HDPM would be capable of displacing water from the hydrated cations and it is believed this is the explanation for the order observed. The stronger complex is formed by the smaller unhydrated cation within each group with the exception of magnesium. This is the order of increasing ionic potential again excepting magnesium. The R_f values for zinc, cadmium and mercury are also all lower than for calcium in agreement with their larger ionic potential as is approximately true for the other metals in Table 15 with the exception of nickel and thallium. Beryllium had an R_f value approximately the same as calcium in 0.1M perchloric and like aluminum probably hydrolyzed when water was used as the developing agent.

Miscellaneous chromatographic separations

Separation of mineral acids The mineral acids traveled in separate zones well behind the solvent front when chromatographed on circular discs treated with HDPM. No such separation was apparent by the ascending or descending method, however. The movement of the acids on Red and Orange Ribbon paper is shown in Table 19.

Separation of Zr, Nb, and Mo with hydrofluoric acid Zirconium, niobium(V), and molybdenum(VI) were spotted as the chlorides on Whatman No. I paper strips treated with 0.1M

HDPM and developed using the spiral method with 0.5M hydrofluoric acid. The R_f values observed were 0.43, 0.86, and .20 respectively.

Table 19. R_r values of mineral acids

Acid	R_r Red Ribbon	R_r Orange Ribbon
H_2SO_4	.18	.16
$HClO_4$	.16	.24
HCl	.38	.50
HNO_3	?	.92

R_r values for transition metals with DOPPO and HDPM

Di-n-octyl-2-pyridyl phosphine oxide, DOPPO, was obtained from Mr. John E. Mrochek (Ames Laboratory, Ames, Ia.) and used as the stationary phase for the radial chromatography of the alkaline earths and several transition metal perchlorates. It did not show any ability to hold the alkaline earths. The behavior of the transition metal perchlorates is shown in Table 20. A 0.1M DOPPO solution in carbon tetrachloride was used to impregnate the papers. It is seen that copper is held better by DOPPO than by HDPM.

HDPE, HDPP and HDPB as stationary phases The movement of the alkaline earth perchlorates on papers (Blue

Ribbon) impregnated with HDPE, HDPP and HDPB was compared with results obtained on HDPM-treated papers. The former three compounds were obtained from John E. Mrochek[1] and are exactly analogous to HDPM but with a two, three, and four carbon alkane bridge between the phosphorus atoms.

Table 20. R_r values for transition metal perchlorates of papers treated with DOPPO and HDPM

Element	R_r DOPPO	R_r HDPM
Ni	.35	.21
Co	.44	.12
Cu	.16	.17
Mn	.70	0

The HDPE was so water insoluble (See subsequent section on Solubility of Phosphine Oxides) that papers treated with it repelled water and it was impossible to obtain paper chromatograms. The R_r values obtained on papers treated with the 0.1M solutions of the remaining compounds are shown in Table 21. The R_r values were similar to those obtained with HDPM but they were slightly closer together and these compounds did not appear to have any advantage over HDPM when

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[1] Synthesis and properties of these three compounds will be given in a doctoral dissertation by John E. Mrochek, Ames Laboratory, Iowa State Univ., Ames, Iowa ca. 1963.

water was used to develop the papers.

Table 21. R_r values for alkaline earths perchlorates on HDPM-, HDPP-, and HDPB-treated papers developed with water

Compound	R_r		
	Mg	Ca	Sr
HDPM	.17	.24	.38
HDPP	.23	.26	.33
HDPB	.24	.33	.35

When 0.1M perchloric acid was used to develop the HDPP- and HDPB-treated papers, calcium and magnesium as well as strontium and barium were displaced by the perchloric acid and traveled with the acid front. Indium, scandium, thorium and uranium had R_r values of zero and the lanthanides had intermediate R_r values but all were held behind the acid front. These compounds would appear to be particularly useful for a group separation of the alkaline earth metals from heavier metals.

Separation of the lanthanides

The R_f values observed for the lanthanide nitrates and chlorides as a function of acid concentration of the developing agent are shown in Figures 4 and 5. These results were obtained on Orange Ribbon sheets treated with 0.1M HDPM

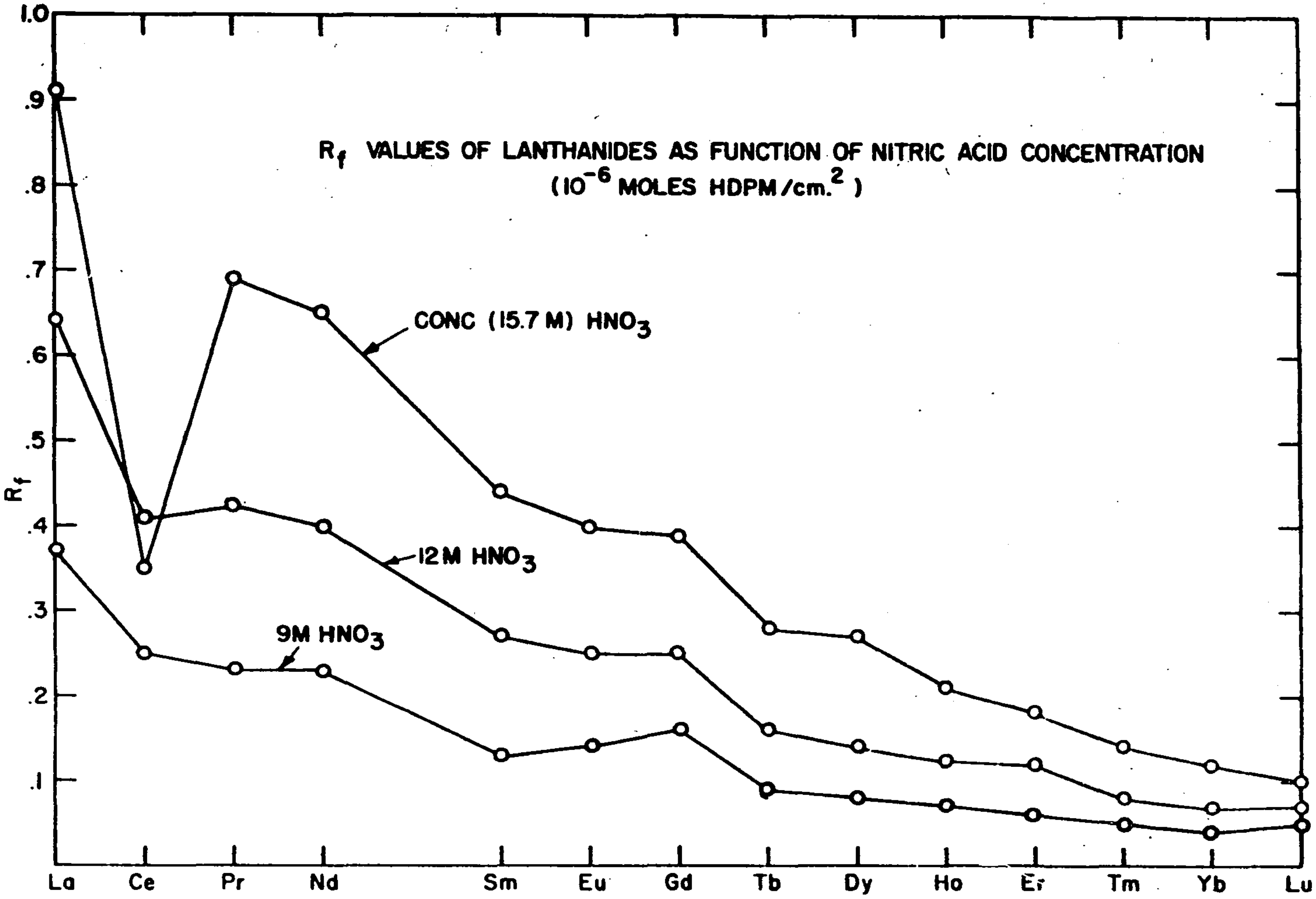


Figure 4. R_f values for lanthanide nitrates using ascending chromatography

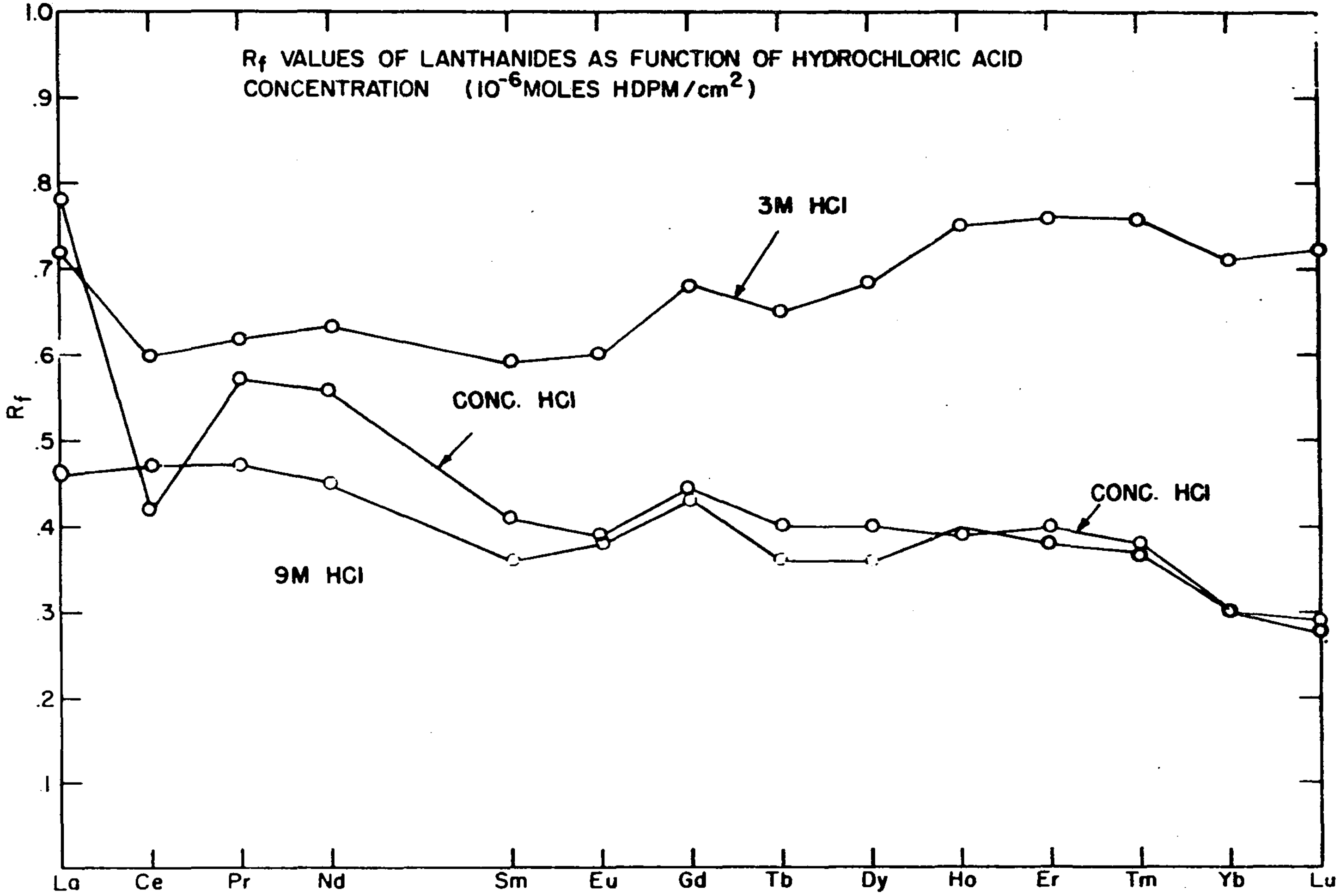


Figure 5. R_f values for lanthanide chlorides using ascending chromatography

using the ascending method of development. The R_f values for yttrium are not plotted but fell at the same point as dysprosium in 9M nitric and as erbium in 12M nitric. They fell at the same R_f as neodymium in 9M hydrochloric and slightly above erbium in 3M acid. The trends in R_r values for the nitric and hydrochloric acid systems observed for radial chromatography using Blue Ribbon paper treated with HDPM is shown in Figure 6 for three selected lanthanides.

The movement of lanthanum, terbium and lutetium nitrates on TBP-treated papers using radial chromatography as a function of acid concentration and the amount of TBP on the paper is presented in Table 22. Blue Ribbon paper disks were treated with carbon tetrachloride solutions 1 to 50% TBP by volume.

Table 22. R_r values for three lanthanide nitrates on TBP-treated papers

HNO_3,M	Element	%TBP				
		1%	5%	10%	20%	50%
15.7M	La	1.0	1.0	1.0	1.0	1.0
	Tb	.71	.67	.53	.52	.35
	Lu	.57	.33	.20	.28	.13
12M	La	1.0	1.0	1.0	1.0	1.0
	Tb	.93	.83	.75	.6	.6
	Lu	.83	.67	.5	.35	.25
9M	La	1.0	1.0	1.0	1.0	1.0
	Tb	1.0	.86	.90	.86	.75
	Lu	1.0	.72	.72	.66	.50

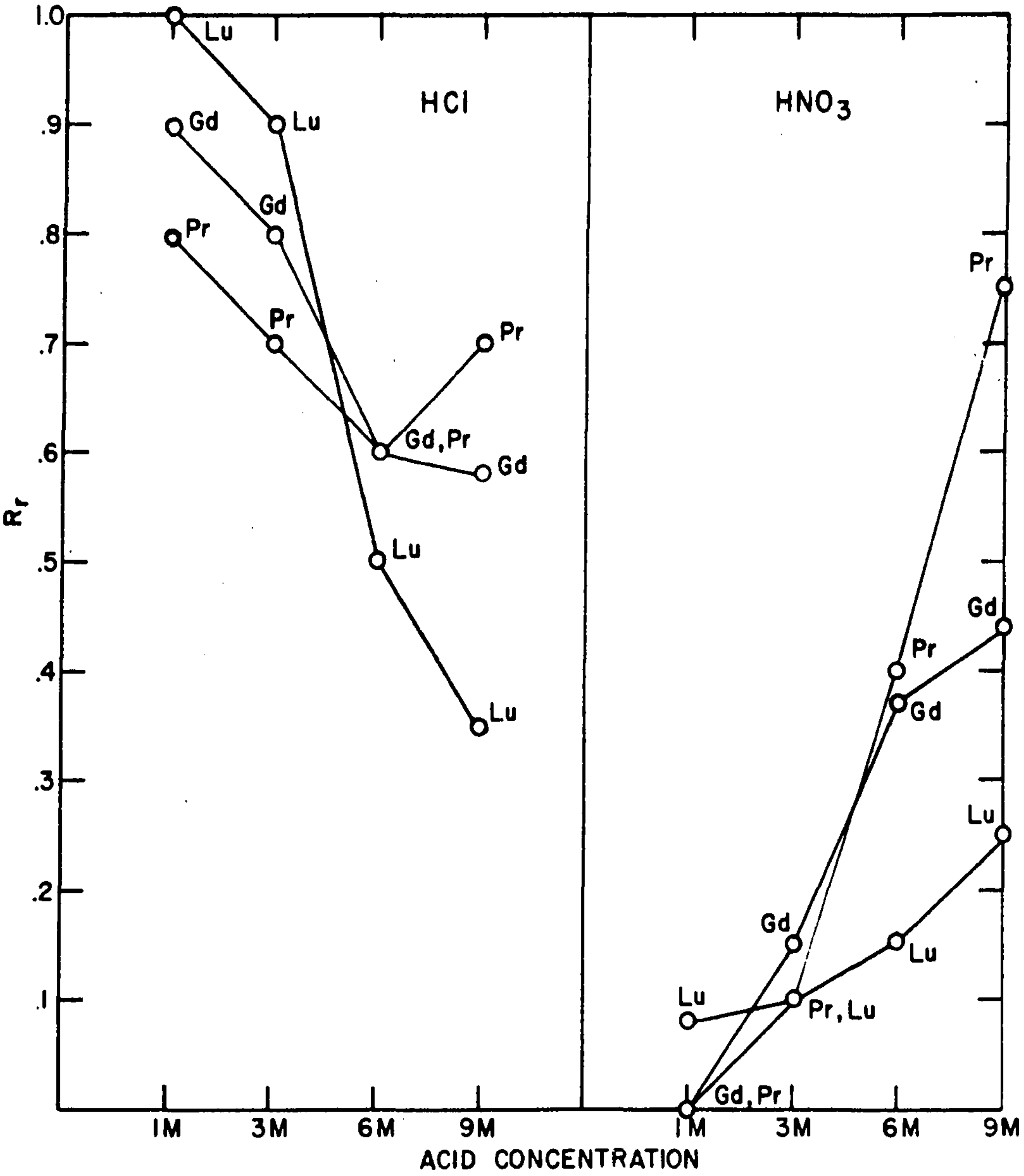


Figure 6. R_r values for several lanthanide chlorides and nitrates using radial chromatography

The R_f values for the lanthanide perchlorates on glass fiber paper impregnated with HDPM and developed with 9M perchloric acid are given in Table 14. The separation of terbium and lutetium, also on glass fiber paper impregnated with HDPM, using radial development gave R_r values of .22 and .36. The zones were sharply separated.

Hesford and others (22) noted that plots of the partition coefficient of the lanthanide nitrates into TBP were not a simple function of the atomic number as earlier postulated (56) nor did their results fit two straight line segments as suggested by Peppard and others (55) which meet at gadolinium. Their results did show a reversal at low acidities in a plot of partition coefficient against atomic number but not necessarily at gadolinium although there was a marked singularity there. Furthermore they observed an odd-even effect at lower acidities where the heavier, even-numbered lanthanides were somewhat better extracted than their odd-numbered neighbors. Gadolinium however, was extracted less than its odd-numbered neighbors. They also obtained a steeper slope for the increase in partition coefficient with atomic number for the lighter lanthanides with a break point at terbium for 15.6M nitric. Yttrium was found to show an effective atomic number near Z = 65 at low acidities and rising to Z = 71 in concentrated nitric acid. They observed that the partition coefficient for any given lanthanide increased monotonically with acid concentration and became quite large for the heavier lanthanides. The separation factor for lanthanide pairs also was largest at high acid concentrations.

Fidelis and Siekierski (12,13) reported the reversed-phase partition chromatography of the lanthanides using TBP supported on kieselguhr. They obtained good separations of the lanthanides and the order of elution was consistent with the above partition data.

White (74) reported that no extraction of the lanthanides occurred with 1M to 7M nitric, hydrochloric or perchloric acid with TOPO although some extraction had been observed from very dilute nitric acid, the maximum partition coefficient for europium occurring at 0.5M acid.

The R_f values for the movement of the lanthanide nitrates on HDPM-impregnated paper, Figures 4 and 6, indicate that, like TOPO, the partition coefficient is higher into HDPM at low acid concentrations. Above 1M nitric the R_f values are seen to increase (the partition coefficient to decrease) with acid concentration. Unlike TOPO the lanthanide nitrates are appreciably retained with HDPM and a plot of R_f values as a function of atomic number reveals a number of similarities to similar plots based on the partition of the lanthanides into TBP.

A distinct inversion in the order of R_f values as a function of acid concentration is seen in Figure 6 and the separation factor is seen to increase with acid concentration similar to what was observed with TBP. Because the R_f values are becoming larger with acid concentration no difficulty should be encountered in eluting the lanthanides from columns as Fidelis and Siekierski had with TBP (12,13) at high acid concentrations.

It should be noted, however, in Table 7 that the R_f values for the lanthanide nitrates by ascending chromatography showed a minimum at 6M nitric which was not observed when radial chromatography was used, Table 7. The R_r values in the latter case decreased with increasing amounts of TBP on the paper and increasing acid concentrations. The separation factor also increased in agreement with the partition data (22) and the column results obtained by Fidelis and Siekierski (12,13). No definite reason can be given for this difference in behavior of the lanthanide nitrates on TBP treated papers by the ascending and radial methods. The TBP on the papers greatly hindered the flow of solvent, however, and the solvent front only advanced a relatively short distance.

This made the determination of R_f values somewhat uncertain, especially when the ascending method was used since the spots became rather large. The fairly sharp zones obtained by radial development were more easily located with respect to the solvent front.

An odd-even effect might be imagined at least with 15.7M nitric in Figure 4 where the even-numbered lanthanides had somewhat higher R_f values but samarium and cerium are definite exceptions. Furthermore the even-numbered lanthanides would be expected by comparison with the TBP data to have lower R_f values. A definite singularity is seen at gadolinium, however, and the slightly higher R_f for this element is in agreement with the slightly lower than average partition coefficient into TBP. No singularity existed for cerium in the TBP extraction data and the unusually low R_f value obtained is believed to be due to oxidation to cerium(IV). The fact that cerium alone tailed badly and only in more concentrated acid supports this assumption. Cerium(IV) would be expected to have a very low R_f value.

The R_f values for the lanthanide chlorides, Figures 5 and 6 fall in a different pattern than for the nitrates. The R_f values, at least for the heavier lanthanides, decreased with increasing acid concentration which is just the opposite of the case with the nitrates. The R_f values initially decreased for the lighter lanthanides but reached a minimum around 6M acid and then increased. This resulted in behavior in concentrated acid very similar to what was observed with nitric acid. The largest separation factors were observed in concentrated acid where the R_f values decreased from lanthanum to lutetium. Again a singularity was observed with gadolinium and with cerium, the latter only with concentrated acid. Cerium tailed badly in the case of concentrated hydrochloric like in the case of nitric acid.

The lanthanide perchlorates were very strongly retained on the HDPM treated papers and had R_f values of zero unless the mobile phase was strongly acidic. Their movement on glass fiber paper treated with 0.1M HDPM and developed with 9M perchloric acid was previously given in Table 14. When the acid concentration of the mobile phase was greater than 9M perchloric it became increasingly difficult to detect the zones after development. The results in Table 14 indicate that the perchlorates behave somewhat like the nitrates except that no singularity was observed for gadolinium. The R_f values for erbium and thulium did break a regular monotonic decrease in R_f with atomic number.

Column Chromatography

HDPM-treated columns

Elution curves for the metal perchlorates of the alkali metals and barium on a HDPM column are shown in Figure 7. The curves were obtained using the apparatus shown in Figures 1 and 2. The column and conductivity cell were completely immersed in a constant temperature bath maintained at 25.0 ± .05°C. The order of elution is what would be predicted from the paper chromatographic results. The unsymmetrical shape of the curves suggest the partition coefficient might be load dependent. This was experimentally verified by obtaining elution curves for sodium perchlorate where the column load was varied from 0.1 to 10 micromoles, Figure 8. This increase in partition coefficient with concentration is not unexpected and represents a self salting-out effect.

Elution curves for sodium and lithium and the alkaline earth perchlorates on a longer HDPM column are shown in Figures 9 and 10 where water was used as the elutrient. Elution curves for barium, strontium, calcium and magnesium perchlorates were obtained using aqueous perchloric acid of various concentrations as the elutrient. The curves are shown in Figures 11, 12 and 13. It can be seen that, similar to the case on paper, barium and strontium are eluted almost

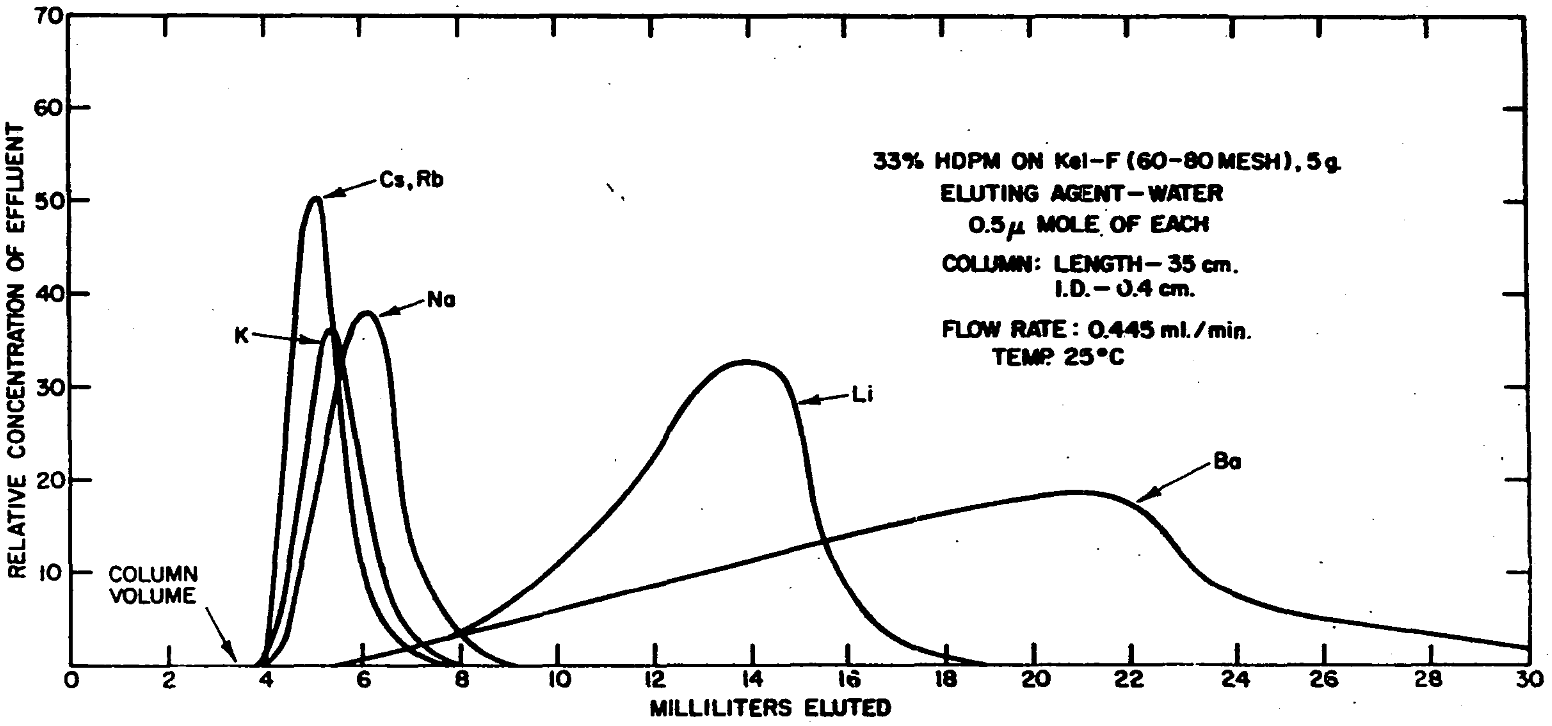


Figure 7. Elution curves for alkali metal perchlorates and barium perchlorate

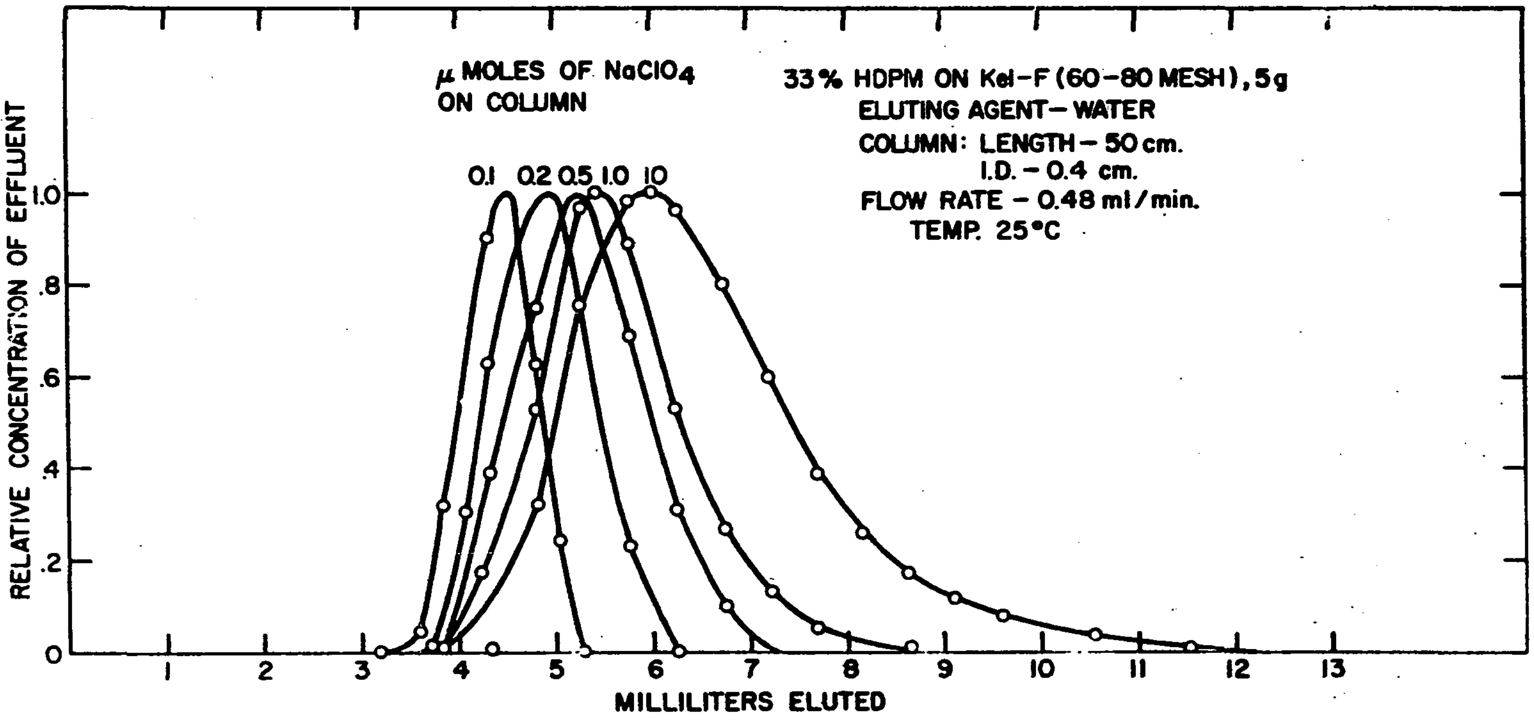


Figure 8. Elution curves of sodium perchlorate as a function of column load

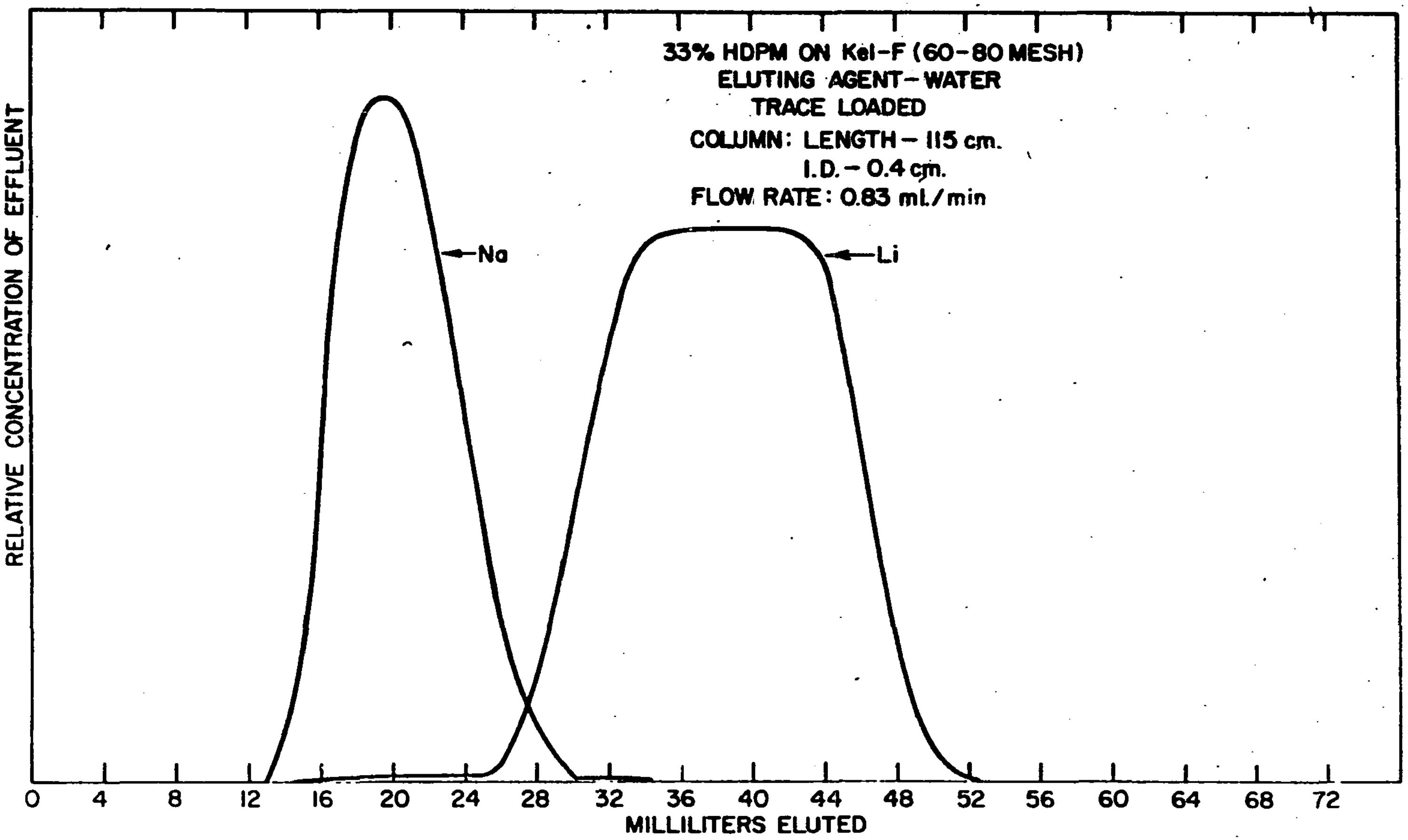


Figure 9. Separation of sodium and lithium on long columns

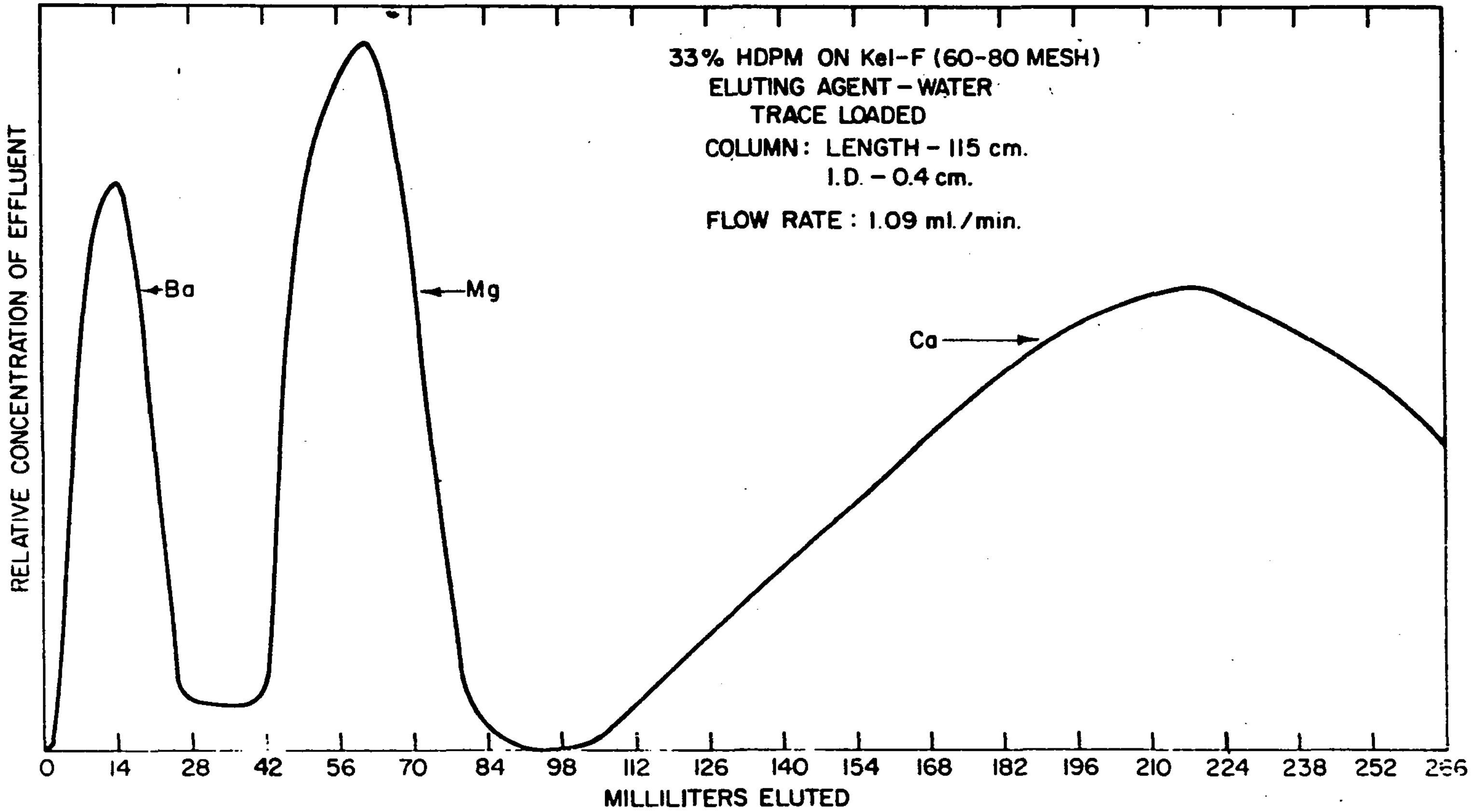


Figure 10. Separation of alkaline earth perchlorates on a long column

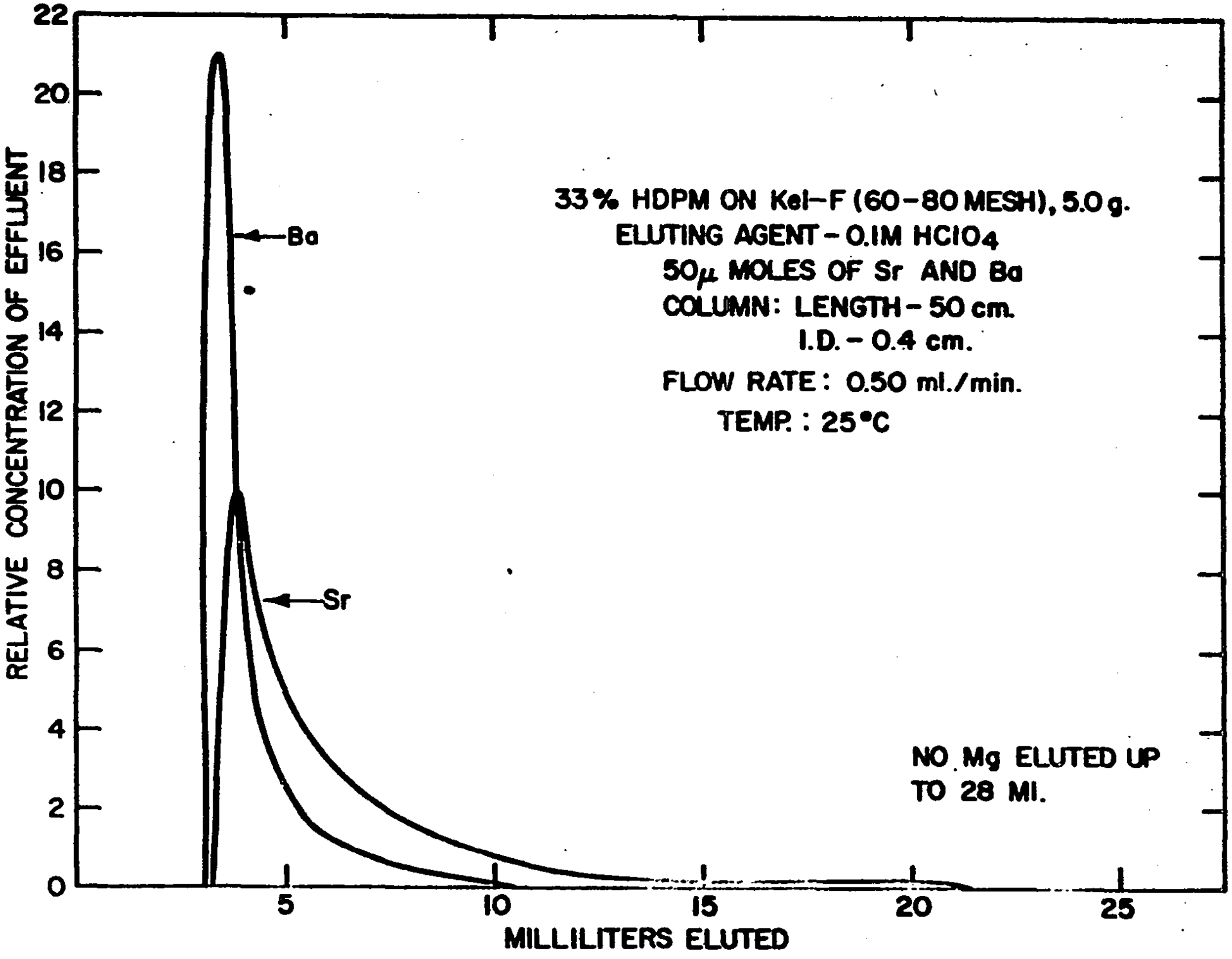


Figure 11. Elution curves for alkaline earths with 0.1M perchloric acid

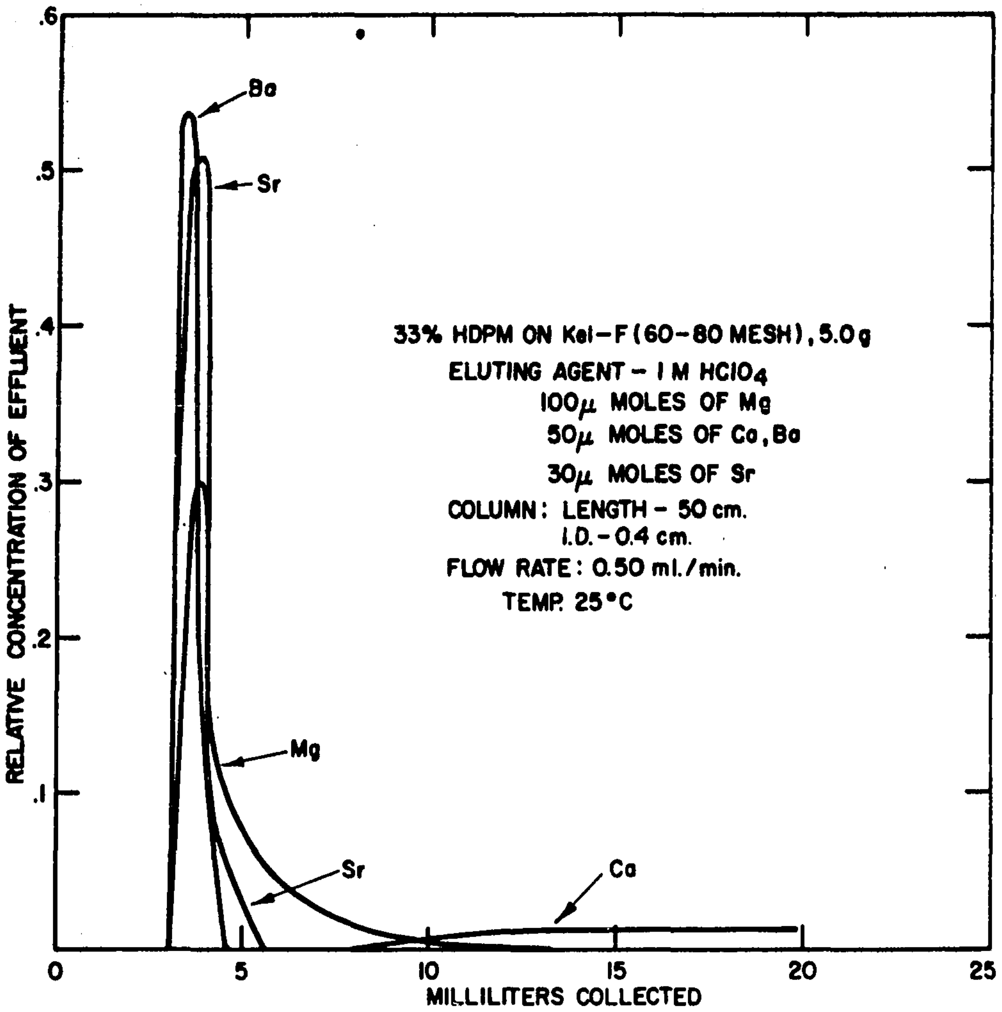


Figure 12. Elution curves for alkaline earths with 1M perchloric acid

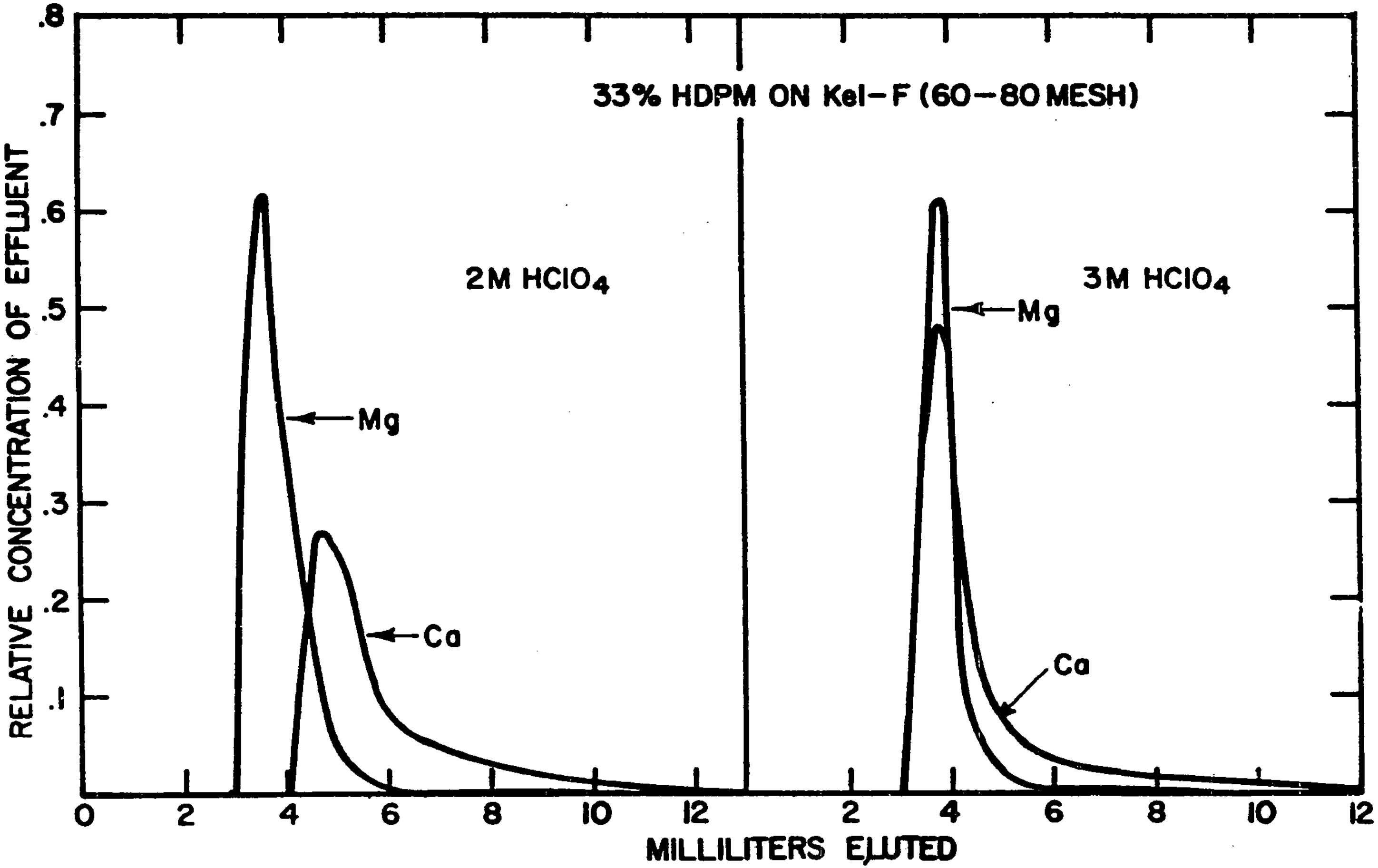


Figure 13. Elution curves for calcium and magnesium with 2M and 3M perchloric acid

immediately with 0.1M acid, Figure 11.

In the case where perchloric acid was used as the elutrient the conductivity method could not be used and the elution curves were obtained by collecting fractions of the elutrient and analyzing these fractions using the flame photometer. Attempts to evaporate off the acid and make conductivity measurements gave erratic results.

The elution order observed for the alkali and alkaline earth perchlorates, Ca < Mg < Sr < Ba < Li < Na < Rb < Cs, on the HDPM columns is the same as the order of increasing R_f values on HDPM-treated paper. The same explanation for this order applies. The possibility of separating the alkali metals both from each other and from heavier metals using only water as the elutrient is particularily attractive. It is not then necessary to introduce any other materials which might interfere with the subsequent determination of these metals. Furthermore the conductivity technique for detecting the alkali metals in water is exceedingly sensitive and parts per million amounts of the alkali metals in the effluent are readily detected. The possible application of this method to the determination of trace amounts of the alkali metals in the heavier metals is obvious. The major problem would be that traces of metal chlorides or nitrates are not appreciably retained on the column and would interfere unless first removed.

Naito (48) has shown that the partition of metals into an organic solvent like TBP (and it is assumed, HDPM) can be expressed by an overall mass action equation. This can be written for the particular case of a divalent metal perchlorate as

$$M^{+2} + 2ClO_4^- + x\ HDPM \rightleftharpoons M(ClO_4)_2 \cdot x\ HDPM.$$

This implies the addition of a salt containing the common ion, ClO_4^-, would increase the partition coefficient. This is observed in Figure 8.

Several factors complicate this simple relationship. The mean activity coefficient changes on the addition of another (or the same) salt and, if it decreases, tends to decrease the partition coefficient. Also in case a different cation (or the proton in case of an acid) is added it might compete with the first metal ion also decreasing the partition coefficient. The possibility that increasing the concentration of the common anion might complex the cation, possibly giving an anionic species, is a further complication not likely in the case of the perchlorate ion.

The presence of the perchlorate ion in the elutrient at a concentration large with respect to that of the metal salt on the column should result in a symmetrical elution curve. The bearding (trailing ahead of the main zone) observed with water as the elutrient due to a self salting-out effect would then be avoided. Unfortunately there is no soluble perchlorate salt with a lower partition coefficient into HDPM than the alkali metals and the retention volumes of the alkaline earth metals are already too large with water.

The use of perchloric acid as the elutrient for the alkaline earths has the advantage of providing a constant perchlorate concentration and the acid competes with the metal ion for the HDPM so that the retention volume is cut down. A gradient elution of the alkaline earths with increasing perchloric acid concentration should result (on the basis of Figures 11 to 13) in a good separation of these metals with the exception of barium and strontium.

TBP-and TOPO-treated columns

Elution curves for sodium, lithium and the alkaline earths on TBP and TOPO columns are shown in Figure 14. Water was used as the elutrient. The same elution order was observed as with the HDPM columns but the perchlorate salts studied were held much more tightly by the HDPM.

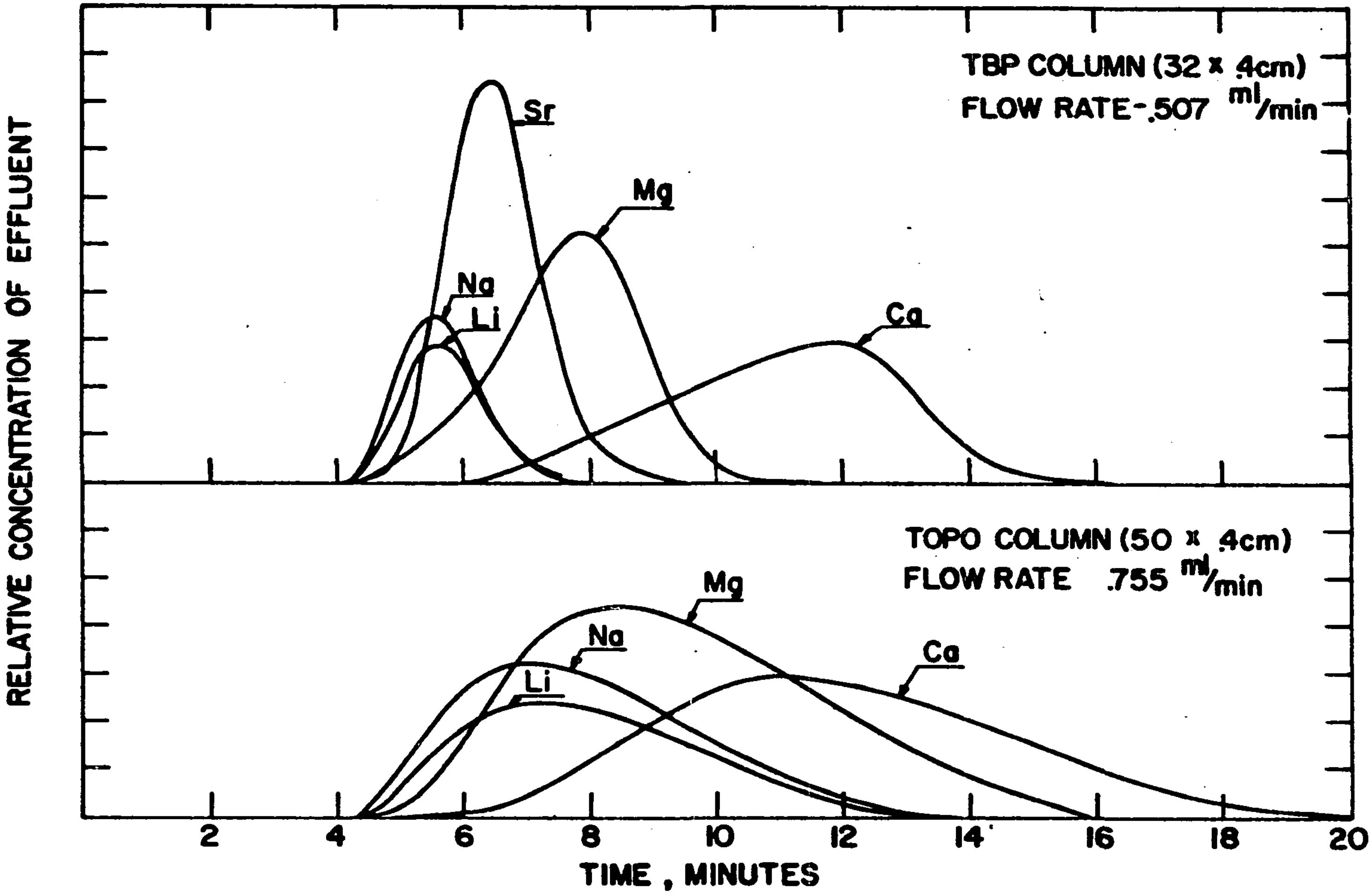


Figure 14. Elution curves for TBP and TOPO columns

Batch Partition Studies

The results of a series of batch partition studies between aqueous calcium perchlorate solutions and the Kel-F-HDPM mixture used in the above column work are presented in Table 23. The erratic and low values for log D for those cases in which the initial calcium concentration was less than 10^{-4} M are probably not too significant, although lower distribution values were expected (at least in those cases where the aqueous phase contained no perchloric acid) on the basis of the tear-shaped elution curves for calcium on columns of Kel-F-HDPM. When the initial calcium concentration was less than 10^{-4} M, the equilibrium concentration was in the 10^{-5} to 10^{-6} M range and the calcium determination was quite difficult. Normal calcium blanks for the water and possibly interference from the small amounts of phosphate from decomposition of the HDPM dissolved in the aqueous phase made calcium determinations at this level exceedingly difficult.

The molar ratio of HDPM to calcium perchlorate taken up by the HDPM-Kel-F phase as a function of calcium concentration is shown in Table 24. The ratio of millimoles of HDPM to millimoles of perchloric acid taken up by one gram of Kel-F-HDPM was found to be 2.48 for the samples in Table 23. The equilibrium concentration of perchloric acid for these

Table 23. Distribution of calcium perchlorate between solid HDPM on Kel-F and dilute aqueous perchloric acid or water

Initial conc.		Equilibrium conc.		Grams[1]	
$CaClO_4$, M	$HClO_4$, M	$CaClO_4$, M	$HClO_4$, M	HDPM-Kel-F	log D[2]
$9.67x10^{-5}$	0	$2.87x10^{-5}$	0	1	1.45
$9.67x10^{-4}$	0	$1.34x10^{-5}$	0	1	1.98
$9.67x10^{-3}$	0	$3.38x10^{-4}$	0	1	2.51
$4.83x10^{-5}$	0	$3.4x10^{-5}$	0	2	0.91
$4.83x10^{-5}$	.2	$8.5x10^{-6}$	.0680	1	1.62
$4.83x10^{-5}$	.2	$1.8x10^{-5}$	.0680	2	1.20
$4.83x10^{-4}$	.2	$1.45x10^{-5}$	.0680	1	2.45
$4.83x10^{-4}$	.2	$3.6x10^{-5}$	.0680	1	2.10
$4.83x10^{-3}$	.2	$8.0x10^{-5}$	.0680	1	2.78
$4.67x10^{-3}$	.2	$>5x10^{-5}$	.0680	1	2.95
$9.67x10^{-3}$	.2	$3.1x10^{-4}$	.0680	1	2.18
$9.67x10^{-3}$	.2	$3.1x10^{-4}$	.0680	1	2.18
$1.93x10^{-2}$	.2	$2.3x10^{-4}$	.0680	2	2.32
$1.93x10^{-2}$	.2	$3.6x10^{-4}$	.0680	2	2.13

[1] 0.77 millimoles HDPM per gram.

[2] $D = \frac{\text{grams of Ca per gram of HDPM-Kel-F (dry)}}{\text{grams of Ca per milliliter of aqueous phase}}$.

samples was 0.0680.

Table 24. Loading capacity studies for calcium perchlorate on Kel-F-HDPM

Initial conc., M	Millimoles in aqueous phase	Millimoles on 1 g. of Kel-F-HDPM	Ratio[1] $\frac{\text{moles HDPM}}{\text{moles Ca(ClO}_4\text{)}_2}$
0.05	0.50	0.237	3.25
0.25	2.5	0.247	3.10
0.50	5.00	0.281	2.74

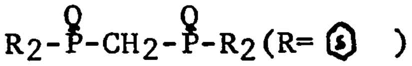
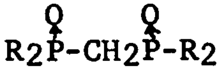
[1] 0.77 millimole of HDPM/gram of Kel-F-HDPM.

Chromatography of Organophosphorus Compounds

The R_r values observed for a number of organophosphorus compounds which were chromatographed on Blue Ribbon discs with 40 per cent (by volume) ethanol were shown in Table 3. The movement of several other compounds with various solvents is shown in Table 25. Both R_{front} (ratio of leading edge of zone to solvent front) and R_{back} (ratio of trailing edge to solvent front) values are given. It was observed that the leading edge was often diffuse and the R_{front} value uncertain. The trailing edge was usually sharp however.

By using an appropriate alcohol-water mixture, it appears likely that many of these compounds can be separated. The zones, especially the leading edge, were somewhat diffuse

Table 25. R values of organophosphorus compounds[1]

Compound	Solvent	Time of development	R_{front}	R_{back}
TOPO	50% EtOH	2 hrs.		.08
HDPM	50% EtOH	2 hrs.	1.0	.79
HDPE	40% EtOH	1.25 hrs.	.93	.36
R_2PHO (R=hexyl)	40% EtOH	1 hr.	1	1
 $R_2-\overset{O}{P}-CH_2-\overset{O}{P}-R_2$ (R=)	40% EtOH	1.5 hrs.	1	1
HDPM-TOPO	Dioxane-Water (50% H_2O)	1 hr.	1(.5)	.88(.23)
HDPM-TOPO	Pyridine-Water (60% H_2O)	1 hr.	1(.14)	.80(.22)
Impure  $R_2\overset{O}{P}-CH_2\overset{O}{P}-R_2$ (R=n-octyl)	40% EtOH	1.5 hrs.	1(.07)	.75(0)
(Same as above but Blue Ribbon paper)		4.5 hrs.	.83(.09)	.57(0)
(Same as above but Red Ribbon paper)		4.5 hrs.	.80(.03)	.53(0)

[1] Black Ribbon paper used unless the contrary indicated.

with Black Ribbon paper but considerably sharper with Red or Blue Ribbon. If two values for R_{front} and R_{back} are given, the second value is for a second (the slower moving) constituent. The impure sample of gem-bis(di-n-octylphosphinyl) methane was obtained from Mr. John J. Richard (Ames Laboratory, Ames, Ia.). It was thought that the sample contained a considerable amount of di-n-octylmethyl phosphine oxide and the appearance of two bands in the chromatogram substantiates this belief.

Spectrophotometric Determination of Phosphine Oxides

The absorption spectra for the complex formed with HDPM using the procedure given in the Experimental Section are given in Figure 15. The absorption maximum at 390 mμ was found to follow Beer's law within the range 5.4 to 27 μ-grams of HDPM per ml. The molar absorptivity based on the concentration of HDPM was 13,300 l./mole-cm. The same procedure was used for TOPO except cyclohexane or carbon tetrachloride were used in place of chloroform as the organic phase. The results with carbon tetrachloride showed less variation and this solvent was used. The molar absorptivity for the complex with either cyclohexane or carbon tetrachloride based on the concentration of TOPO was 14,200 l./mole-cm.

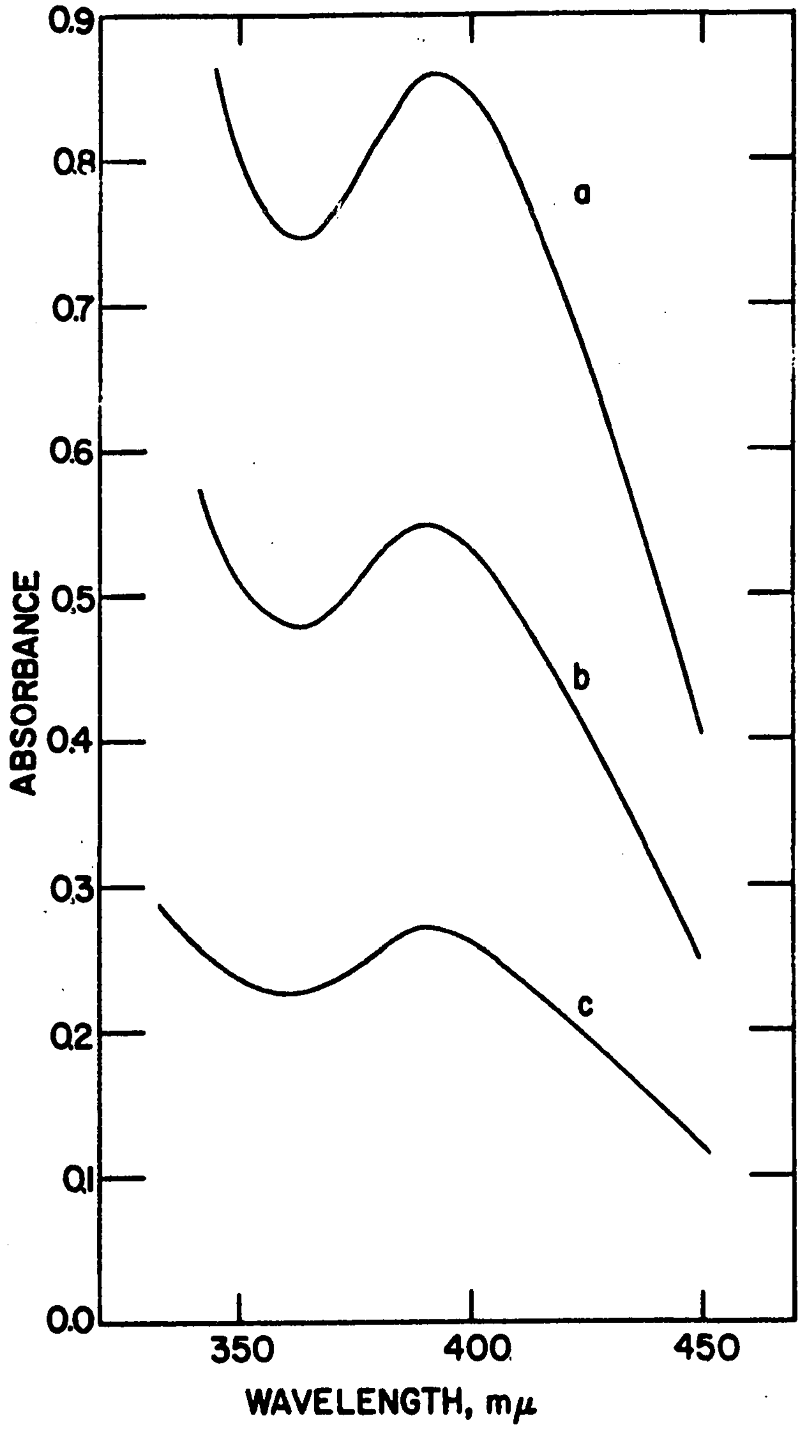


Figure 15. Absorption spectra for HDPM complex with titanium(IV) and thiocyanate
Standard procedure: curves a, b and c are for 15, 10 and 5 ml. aliquots of a 10^{-4} HDPM solution

Young and White (76) reported a molar absorptivity of 41,000 l./mole-cm. for this complex based on the titanium concentration. This suggests, as might be expected, that the combining ratio of TOPO or HDPM to titanium in the complex is greater than one. A combining ratio of TOPO to titanium of three would give a value of 42,000 l./mole-cm. for the molar absorptivity of the complex formed in the presence of excess titanium. This similarity to the value given by Young and White plus the fact that the spectrum of the complex formed using excess titanium is identical to that published by these authors suggest only one species with a combining ratio of three to one is formed. The molar absorptivity of the HDPM complex suggests a similar combining ratio but the change in solvent makes this less certain. The relative standard deviation for all the HDPM determinations was 4.7%.

Besides TOPO and HDPM the spectrophotometric method was used for the determination of HDPE, HDPP and HDPB. The absorption maxima for the latter compounds also occurred at 390 mμ and the molar absorptivities were about the same as for HDPM.

Solubility of Phosphine Oxides

The results obtained on the solubility of HDPM, HDPE, HDPP and HDPB in water as a function of temperature are presented in Figure 16. The inverse temperature-solubility relationship has also been reported for TBP (25) and tributyl phosphine oxide (24). The solubility of TOPO in water was also determined and found to be 1.5 mg. per l. at 25°C. and 2.8 mg. per l. at 0°C.

The solubility of HDPM in 1M hydrochloric acid at 25°C. was 26.5 mg. per l. and in 6M acid it was 64.1 mg. per l. In perchloric acid a viscous, sticky acid adduct formed with HDPM, HDPE, HDPP and HDPB which was highly insoluble in water-less than 1 mg. per l.

Infrared Spectral Data

Uranyl nitrate and perchlorate complexes with HDPM

The principal bands which appeared in the infrared spectra of the uranyl nitrate and perchlorate-HDPM systems other than those which appear in the spectra of HDPM (47,60) are tabulated in Table 26. The preparation of the solutions was described in the Experimental Section. The solutions with mole ratios of HDPM to uranium of 0.46, 0.92, 1.3, 1.8 and

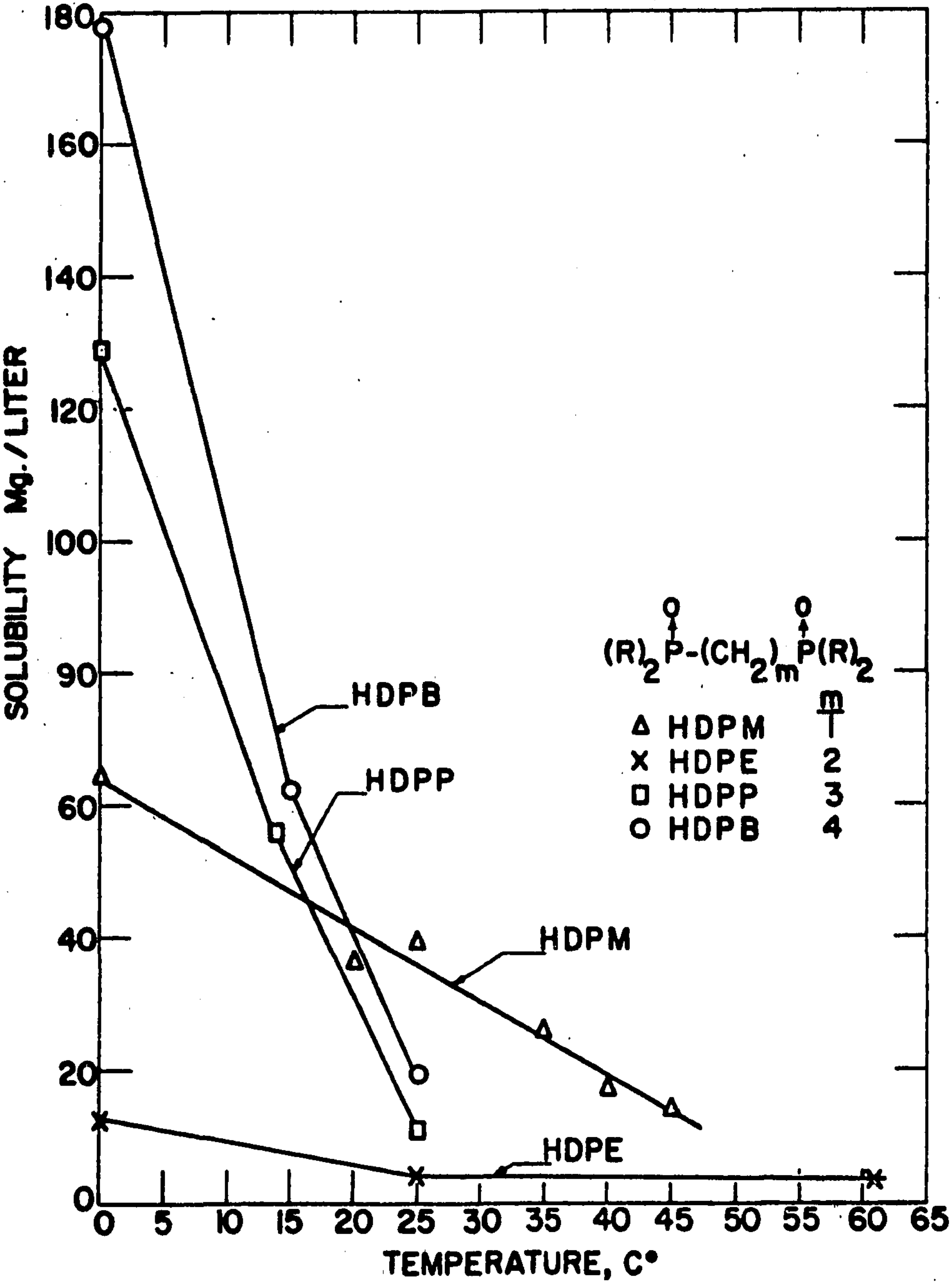


Figure 16. Solubility of HDPM, HDPE, HDPP and HDPB in water as a function of temperature

Table 26. Infrared bands for uranyl nitrate and perchlorate HDPM systems

Band assignment	Wave no. cm^{-1} (literature)	Mixed solvents		1,2-Dichloroethane	
		Nitrate	Perchlorate	Nitrate	Perchlorate
C_{2v} nitrate asym. str. ν_4	1531-1481 (16)	1530 W-S (5-1)	-----	1540 W-S (5-1)	-----
D_{3h} nitrate asym. str. ν_3	1390 (16)	1380 S (1-5)	1380 S (1-5)	-----	-----
C_{2v} nitrate sym. str. ν_1	1290-1253 (16)	-----	-----	1260 W-S (5-1)	-----
Unbonded P-O stretch	1164 (50,59)	1166 Sh-M (4-5)	1166 Sh (1-5)		
				1162-1150 W-M(1-5)	1166-1156 S(1-5)
Bonded P-O 1:1 complex	1130 (47)	1134 S(1)	-----	1130 M(5)	-----
Bonded P-O 2:1 complex	-----	1112 M(5)		1118 Sh(1)	1112 S-W (1-5)
Perchlorate organic	1090 (29)	[1090 Sh(4)]	Broad 1100 S(1-5)	1082-1070 S-W(1-4)	Broad 1080 S-M(1-5)
		1012 S-W (1-4)		1020 M-W (1-5)	1020 M-W (1-5)
N-O stretch	1034-970 (16)				
		1038 W(5)		1036 Sh-M (4-5)	1036 Sh-M (4-5)

4.6 are conveniently referred to as solutions 1, 2, 3, 4 and 5 in Table 26. A shorthand notation is used to indicate trends in the appearance or disappearance of a band with mole ratio and the type of band present. The symbols S, M, W, and Sh refer to strong, medium and weak bands or a shoulder on another band, respectively. The numbers in parenthesis refer to the solutions in which these bands appeared. For example the entry 1166 Sh-M(4-5) refers to the presence of a band at 1166 cm^{-1} as a shoulder in solution 4 and becoming a medium sized band in solution 5.

After complex formation the solutions in 1,2-dichloroethane were dried with magnesium perchlorate but the solutions in the mixed solvent were not dried. The spectral data for the solutions in 1,2-dichloroethane before drying were obtained but are not presented in Table 26. The main features in the undried case were the appearance of a band at 1390 cm^{-1} which disappeared after drying. The spectra were also less sharp and well defined before drying. It was observed that in the nitrate case for solution 5 (excess HDPM) well defined bands occurred at 1166 cm^{-1} and 1112 cm^{-1} before drying. On drying these bands appeared to move together and appeared at the wave numbers shown in Table 25. The brackets around the 1090 cm^{-1} shoulder for uranyl nitrate in the mixed solvents are to indicate that the band is not due to perchlorate (none present) although it occurs at this wave number. The 1380 cm^{-1} band which is shown as present in the case of the perchlorate salt is believed to be the ionic nitrate band. These bands are all false bands which occurred because of exchange with the cell windows (sodium chloride) in the slightly wet solutions. These bands occurred in the perchlorate solutions because the nitrates were run first and the nitrate which exchanged with the cell window was not washed off the windows with the solvent used. This nitrate exchange has been previously observed (53). No ionic nitrate bands were observed in the dried solutions.

It was also found that the band presumed to be due to unbonded P-O shifted to lower wavenumbers in the dried solutions. This band also shifted in the same direction as the mole ratio of HDPM to uranium increased.

The infrared spectrum of HDPM heated the same length of time, 63 hrs., as in the preparation of the solid complexes with uranyl nitrate, perchlorate, and acetate (Experimental Section) indicated some decomposition. Bands appeared at around 1670 cm^{-1} and 3480 cm^{-1} characteristic of acidic species. The solid complexes all had bands at 1166 cm^{-1} (unbonded P-O stretch) which were somewhat less intense in the cases of the 2:1 than the 4:1 ratios of HDPM to uranium. The nitrate also had a strong band centered at 1112 cm^{-1} which seemed slightly split. The acetate complex had a band at 1096 cm^{-1}. The perchlorate complex had a broad unresolved band covering the region 1112 cm^{-1} to 1070 cm^{-1} which was probably a combination of the bonded P-O stretch and the perchlorate band. No evidence of the ν_4 nitrate band was present in the case of the 4:1 complex but a small band at 1530 cm^{-1} was present in the case of the 2:1 complex. In both cases a band at 1380 cm^{-1} was present. A sharp band due to the U-O stretch in the uranyl group appeared at 920 cm^{-1}, 918 cm^{-1}, 922 cm^{-1} for the nitrate, perchlorate, and acetate complexes, respectively.

Magnesium perchlorate adduct

The spectra of the sticky adduct formed when magnesium perchlorate was equilibrated with a 0.1M HDPM solution in carbon tetrachloride was identical to the HDPM spectra except for the appearance of a broad band at 1080 to 1100 cm^{-1}. This is the region in which the perchlorate ion band appears (29).

Uranyl chloride and niobium pentachloride adducts

The spectra of the carbon tetrachloride solutions of the HDPM adducts with uranyl chloride and niobium pentachloride showed several bands not present in the case of pure HDPM. Neither niobium pentachloride nor uranyl chloride dissolved in carbon tetrachloride in the absence of HDPM. The new bands in the case of uranyl chloride occurred at 1122 cm^{-1} and 922 cm^{-1} and were assumed to be due to bonded P-O and to the U-O stretch in the uranyl ion. In the case of niobium pentachloride new bands occurred at 1134 cm^{-1}, 1053 cm^{-1} and 934 cm^{-1}, the first of which is probably the bonded P-O stretch.

Acid adducts of HDPM

The spectra were similar to that of HDPM except more poorly defined and the bands less sharp. The 1166 cm^{-1} band shifted to 1154 cm^{-1} for nitric and hydrochloric acids, to 1159 cm^{-1} for acetic acid, and to 1161 cm^{-1} for perchloric acid. In the latter case a strong band also appeared at about 1090 cm^{-1}. Bands at 3475 cm^{-1} and 1667 cm^{-1} were present in all the adducts.

Perchloric acid adducts of HDPM, HDPE, HDPP and HDPB

The principal features of the infrared spectra of these adducts are given in Table 27. Bands at 3475 cm^{-1} and 1667 cm^{-1} were observed in all the adducts. The wave numbers of the unbonded P-O stretch were approximately 1166 cm^{-1} when the spectra were obtained in solution in 1,2-dichloroethane for all the compounds in Table 26.[1] The wave numbers given previously for these compounds (Review of Literature section) were obtained on the solid compounds using the KBr pellet technique.

Table 27. Infrared bands of perchloric acid adducts

Compound	Observed bands cm^{-1}
HDPM	Strong band 1161, broad band 1090
HDPE	Slight shoulder 1118, broad band 1090
HDPP	Slight shoulder 1136, broad band 1090
HDPB	Very broad band 1080 to 1110

Discussion of infrared data

The ν_4 and ν_1 nitrate bands in the spectra of the uranyl nitrate-HDPM complexes in Table 26 strongly indicate the nitrate ion is covalently bonded to the uranium (16). Evidence from the partition of uranyl nitrate into HDPM (46) indicate two complexes, a 2:1 and a 1:1 HDPM to uranium species. The appearance of a band at 1112 cm^{-1} in the presence of excess HDPM in the case of uranyl nitrate where

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[1] Mrochek, John, Ames Laboratory, Ames, Ia. Spectral data on HDPE, HDPP and HDPB. Private communication. 1963.

the partition data indicate a 2:1 species exists suggest this band is the P-O stretch in the 2:1 species. This band is not seen in the presence of excess uranium but a band is present at 1134 cm^{-1}. This band also appears in the spectrum given by Nadig (47) of HDPM in carbon tetrachloride saturated with uranyl nitrate. It seems reasonable to conclude this is due to the P-O stretch in the 1:1 complex.

When the 1,2-dichloroethane solutions of the nitrate complex were dried with magnesium perchlorate the 1112 cm^{-1} band ascribed to the P-O stretch in the 2:1 complex disappeared and a new band appeared at 1130 cm^{-1}. Interestingly no band appeared at 1080 cm^{-1} (perchlorate band) in this solution even though there was excess HDPM but a band at 1080 cm^{-1} did appear in the solution containing excess uranium.

The spectra of the uranyl perchlorate-HDPM complexes were difficult to interpret because of the very strong perchlorate band at 1080 cm^{-1} which overlapped the general region in which the bonded P-O stretch is expected. The spectra in 1,2-dichloroethane dried with magnesium perchlorate all showed a definite band at 1112 cm^{-1}, the position of the bonded P-O stretch in the 2:1 complex. The band at 1020 cm^{-1} and 1036 cm^{-1} are apparently not N-O stretch bands because they also appear in the case of the perchlorate complex.

The spectra of the adducts formed with magnesium perchlorate and the mineral acids were all quite similar to HDPM alone except for the perchlorate band if the perchlorate ion was present and little information about the adduct can be obtained. It is of interest that the P-O stretch shifts very little if at all in the HDPM adduct but shifts under the perchlorate band with HDPE, HDPP and HDPB (Table 27).

A complete investigation of the infrared, the visible and the ultraviolet spectra of the complexes formed by various metal nitrates and perchlorates with HDPM would be a source of considerable information about the type of complex present. This was decided, however, to be outside the scope of this thesis. It should be noted that such an investigation is presently being made by Mr. John Mrochek of this Laboratory (Ames Laboratory, Ames, Ia.) for the complexes of uranium with HDPE, HDPP and HDPB as well as HDPM.

CONCLUSIONS

Reversed-Phase Partition Chromatography

Reversed-phase partition chromatography is a powerful and useful tool for the separation of the metallic elements. Closely related elements like zirconium and hafnium or mixtures of the lanthanides can be readily separated. The separation of various lanthanide mixtures can be accomplished on a filter paper disc impregnated with HDPM in about an hour. Sodium and lithium can be easily separated in the same manner.

This technique is very versatile. By proper choice of the stationary phase and the mobile phase a great variety of separations are possible. The three stationary phases investigated extensively in this thesis, TBP, TOPO and HDPM are generally more powerful extractants in the order given. Although the retention of most metals on paper or columns treated with the above three compounds can be varied widely by using different mobile phases, there are many other extractants suitable for use as stationary phases such as the phosphonic acids, long chain amines, and water-insoluble alcohols and ketones.

The technique is particularly suited to the separation of trace amounts of a strongly absorbed constituent from large amounts of less strongly absorbed elements or the concentration of some constituent from some very dilute solution. For example the separation of uranium from urine has been accomplished by this method (11). If necessary the substance absorbed on the column can readily be removed by stripping the extractant from the column with some organic solvent. Ashing procedures sometimes required with ion exchange resins and the possibility of introducing other metals is thus avoided.

The reversed-phase technique is also a simple technique which requires no elaborate equipment. Separations of trace amounts of many elements can be carried out on ordinary filter paper discs impregnated with the extractant using water or solutions of the mineral acids to develop the papers. The sharp separation of the zones obtained and their ready detection by suitable reagents makes the method a potentially powerful qualitative analysis scheme.

The method can be used on the tracer level using paper chromatography or easily scaled up for the separation of larger amounts of material on columns. Furthermore the behavior of elements on the column can usually be readily evaluated from their behavior on paper where their movement is much more easily followed.

The problem sometimes encountered in solvent extraction work of finding a suitable solvent for the adducts formed is avoided. For example many perchlorates give adducts with TOPO which are not soluble in the organic phase and for this reason White (74) states that the extraction of metals from perchloric acid media is not attractive. With the reversed-phase technique the strong retention of the metal perchlorates makes this media particularly advantageous for the separation of the alkali and alkaline earth metals.

TBP, TOPO and HDPM

Tri-n-butyl phosphate (TBP), tri-n-octyl phosphine oxide (TOPO) and bis(di-n-hexylphosphinyl)methane are all very useful compounds as stationary phases in reversed-phase partition chromatography. They all are very stable, even resisting attack by concentrated nitric acid, and they are all good extractants under the proper conditions. TBP can hydrolyze and its hydrolysis is promoted by hydrochloric and perchloric acids (34,35) and in this respect TOPO and HDPM are superior.

HDPM is particularly useful as a stationary phase on paper because it is such a powerful extractant. A very small amount on the paper, about 10^{-6} moles per cm^2 is usually sufficient to retain most cations under the proper conditions. Furthermore it is a very low melting compound which actually seems to soak into the paper fibers in the low concentrations used. The physical appearance of the paper and the flow of water over the paper are not noticeably altered by treatment with HDPM. Much larger amounts of TBP are required on the paper for suitable R_f values for most cations and TOPO is a solid which tends to crystalize on the paper. The larger amounts of TBP required on the paper alter the physical characteristics of the paper and this causes the aqueous mobile phase to move slowly and unevenly.

The mechanism of extraction of metals seems to be the same for all three, at least for metal chlorides and nitrates. All three apparently coordinate through the phosphoryl oxygen directly to the metal ion displacing water of hydration. TOPO and HDPM are capable of doing this even when the water activity is high and are more powerful extractants for the trivalent and quadrivalent metals than TBP, especially from weakly acidic solutions. They are also more basic than TBP and the mineral acids compete more successfully with the cations for TOPO and HDPM. Consequently plots of the partition coefficient (or R_f values) as a function of acid concentration show maxima (or minima).

The metal perchlorates show much lower R_f values (higher partition coefficients) with HDPM than with TOPO or TBP. Although the evidence is strongly against both phosphoryl groups in HDPM coordinating to the metal ion in the case of the nitrate or chloride complexes, it is possible that this does occur in the perchlorate complexes. This could be an explanation for the much larger partition coefficients of the metal perchlorates into HDPM. Attempts to determine whether both phosphoryl groups in each HDPM molecule were coordinated to uranium by a study of the decrease in the "unbonded" phosphoryl absorbance on the addition of uranyl perchlorate to a solution of HDPM in 1,2-dichloroethane gave inconclusive results. The results which were obtained, however, tended to show that only one phosphoryl group was involved.

Spectrophotometric Determination of Phosphine Oxides

The spectrophotometric method described for the determination of phosphine oxides based on the yellow adduct extracted into chloroform from an acidic solution of titanium(IV) and the thiocyanate ion is a sensitive and reasonably accurate procedure. It is somewhat empirical and requires close attention to experimental details but proved very useful for the determination of the solubility of TOPO, HDPM and related compounds in water. The same color reaction is involved in the detection of phosphine oxides on paper with the recommended titanium(IV)-thiocyanate reagent. The yellow to orange color given by many phosphates, phosphinates, phosphonates and phosphine oxides with this reagent on paper is extremely sensitive and is very useful for the detection of these compounds in paper chromatography.

BIBLIOGRAPHY

1. Blake, C. A., Baes, C. F., Brown, K. B., Coleman, C. F., and White, J. C. Proceedings of Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 28, 289 United Nations. 1959.

2. Blake, C. A., Brown, K. B. and Coleman, C. F. [Oak Ridge National Lab., Tenn.] *U. S. Atomic Energy Commission Report ORNL-1964*. 1955.

3. Blake, C. A., Moore, J. G., Whaley, W. M. [Oak Ridge National Lab., Tenn.] *U. S. Atomic Energy Commission Report ORNL-1480*. 1952.

4. Burger, L. L. [Hanford Atomic Products Operation, Richland, Wash.] *U. S. Atomic Energy Commission Report HW-44888*. 1947.

5. Cerrai, E. and Testa, C. *Energia Nucl*. (*Milan*) *8*, 510. 1961.

6. Cerrai, E. and Testa, C. *J. Chromatog*. *9*, 216. 1962.

7. Cerrai, E. and Testa, C. *J. Chromatog*. *8*, 232. 1962.

8. Cerrai, E., Testa, C. and Triulzi, C. *Energia Nucl*. (*Milan*) *9*, 193. 1962.

9. Cerrai, E., Testa, C. and Triulzi, C. *Energia Nucl*. (*Milan*) *9*, 377. 1962.

10. Cotton, F. A., Barnes, R. D. and Bannister, E. *J. Chem. Soc*. *1960*, 2199. 1960.

11. Dietrich, W. C., Caylor, J. D. and Johnson, E. E. [Union Carbide Nuclear Co., Y-12 Plant, Oak Ridge, Tenn.] *U. S. Atomic Energy Commission Report Y-1322*. 1960.

12. Fidelis, I. and Siekierski, S. *J. Chromatog*. *4*, 60. 1960.

13. Fidelis, I. and Siekierski, S. *J. Chromatog.* *5*, 161. 1961.

14. Fletcher, W., Franklin, R. and Goodall, G. C., [Technical Information Service Extension, AEC] *U. S. Atomic Energy Commission Report* TID-7629, 276. 1961.

15. Fritz, J. S. and Hedrick, C. E. *Anal. Chem.* *34*, 1411. 1962.

16. Gatehouse, B. M., Livingstone, S. E. and Nyholm, R. S. *J. Chem. Soc.* *1957*, 4222. 1957.

17. Gwóźdź, R. and Siekierski, S. *Nukleonika* *5*, 671. 1960.

18. Hamlin, A. G., Roberts, B. J., Loughlin, W. and Walker, S. G. *Anal. Chem.* *33*, 1547. 1961.

19. Hayes, T. J. and Hamlin, A. G. *Analyst* *87*, 770. 1962.

20. Head, A. J., Kember, N. F., Miller, R. P. and Wells, R. A. *J. Chem. Soc.* *1958*, 3418. 1958.

21. Heftman, Erich. Chromatography. New York, N. Y., Reinhold Publishing Corporation. c1961.

22. Hesford, E., Jackson, E. and McKay, H. A. C. *J. Inorg. Nucl. Chem.* *9*, 279. 1959.

23. Hesford, E. and McKay, H. A. C. *J. Inorg. Nucl. Chem.* *13*, 165. 1960.

24. Higgens, C. E. and Baldwin, W. H. *Anal. Chem.* *32*, 233. 1960.

25. Higgens, C. E., Baldwin, W. H. and Soldans, B. A. *J. Phys. Chem.* *63*, 113. 1959.

26. Irving, H. and Edgington, D. N. *J. Inorg. Nucl. Chem.* *15*, 158. 1960.

27. Ishimori, T., Kimora, K., Fujino, T. and Murakami, H. *J. At. Energy Soc. Japan* *4*, 117. 1962.

28. Ishimori, T., Watanabe, K. and Nakamura, E. Bull. Chem. Soc. Japan 33, 636. 1960.

29. Jones, R. N. and Sandorfy, C. Application of infrared and raman spectrometry to the elucidation of molecular structure. In Weissberger, A. ed. Techniques of organic chemistry. Vol. 9. pp 247-263. New York, N.Y. Interscience Publishers, Inc. c 1956.

30. Katzin, L. I. J. Inorg. Nucl. Chem. 4, 187. 1957.

31. Kennedy, J. and Deane, A. M. J. Inorg. Nucl. Chem. 19, 142. 1961.

32. Kennedy, J., Marriot, J. and Wheeler, V. J. J. Inorg. Nucl. Chem. 22, 269. 1961.

33. Kertes, A. S. and Beck, A. J. Chromatog. 3, 195. 1960.

34. Kertes, A. S. and Halpern, M. J. Inorg. Nucl. Chem. 20, 117. 1961.

35. Kertes, A. S. and Halpern, M. J. Inorg. Nucl. Chem. 19, 359. 1961.

36. Kertes, A. S. and Kertes, V. J. Appl. Chem. (London) 10, 287. 1960.

37. Kosolapoff, C. M. J. Am. Chem. Soc. 75, 1500. 1953.

38. Kuznetsov, V. I. Compt. Rend. Acad. Sci. U.R.S.S. 31, 898. 1941.

39. Larsson, L. Svensk Kem. Tidskr. 71, 336. 1959.

40. Martin, A. J. P. and Synge, R. L. M. Biochem. J. 35, 91. 1941.

41. Martin, J. V. Analyst 81, 348. 1956.

42. Mikulski, J. and Stroński, I. Nukleonika 6, 295. 1961.

43. Mikulski, J. and Stroński, I. Nukleonika 6, 775. 1961.

44. Moore, R. L. [Technical Information Service Extension, AEC] U. S. Atomic Energy Commission Report AECD-3196. 1951.

45. Morrison, G. H. and Freiser, H. Anal. Chem. 34, 64R. 1962.

46. Mrochek, J. E., O'Laughlin, J. W., Sakurai, H. and Banks, C. V. [gem-Bis(disubstituted phosphinyl)alkanes. II. Extraction of uranium(VI) with bis(di-n-hexylphosphinyl)methane.] [To be published in J. Inorg. Nucl. Chem. ca. 1963].

47. Nadig, E. W. Metal nitrate complexes with tributyl phosphate and with trioctyl phosphine oxide. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1963.

48. Naito, K. Bull. Chem. Soc. Japan 33, 363. 1960.

49. Naito, K. and Suzuki, T. J. Phys. Chem. 66, 983. 1962.

50. Naito, K. and Suzuki, T. J. Phys. Chem. 66, 989. 1962.

51. Nemodruk, A. A., Novikov, Yu. P., Lukin, A. M. and Kalinina, I. D. Zhur. Anal. Khim. 16, 180. 1961.

52. New organophosphorus reagents debut. Chemical Eng. News 38, No. 38, 57. 1960.

53. Oshima, K. J. At. Energy Soc. Japan 4, 8. 1962.

54. Oshima, K. J. At. Energy Soc. Japan 4, 166. 1962.

55. Peppard, D. F., Driscoll, W. J., Sironen, R. J. and McCarty, S. J. Inorg. Nucl. Chem. 4, 326. 1957.

56. Peppard, D. F., Faris, J. R., Gray, P. R. and Mason, G. W. J. Phys. Chem. 57, 294. 1953.

57. Pierce, T. B. and Peck, P. F. Nature 194, 84. 1962.

58. Pierce, T. B. and Peck, P. F. Nature 195, 597. 1962.

59. Pollard, F. H. and McOmie, J. F. W. Chromatographic methods of inorganic analysis. New York, N. Y., Academic Press, Inc., Publishers. 1953.

60. Richard, J. J., Burke, K. E., O'Laughlin, J. W. and Banks, C. V. J. Am. Chem. Soc. 83, 1722. 1961.

61. Salmon, J. E. Progress in nuclear energy, series IX, analytical chemistry. Vol. 2. Oxford, London, Pergamon Press. 1961.

62. Savvin, S. B. Talanta 8, 673. 1961.

63. Siekierski, S. J. Inorg. Nucl. Chem. 24, 205. 1962.

64. Siekierski, S. and Gwóźdź, R. Nukleonika 5, 205. 1960.

65. Siekierski, S. and Sochaka, R. J. Polish Academy of Sciences, Institute of Nuclear Research Report 262-V. 1961.

66. Small, H. J. Inorg. Nucl. Chem. 18, 232. 1961.

67. Small, H. J. Inorg. Nucl. Chem. 19, 160. 1961.

68. Spedding, F. H., Fulmer, E. I., Butler, T. A., Gladrow, E. M., Gobush, M., Porter, P. E., Powell, J. E. and Wright, J. M. J. Am. Chem. Soc. 69, 2786. 1947.

69. Spedding, F. H., Voigt, A. F., Gladrow, E. M. and Sleight, N. R. J. Am. Chem. Soc. 69, 2777. 1947.

70. Spedding, F. H., Voigt, A. F., Gladrow, E. M., Sleight, N. R., Powell, J. E., Wright, J. M., Butler, T. A. and Figard, P. J. Am. Chem. Soc. 69, 2786. 1947.

71. Testa, C. J. Chromatog. 5, 236. 1961.

72. Warf, J. C. J. Am. Chem. Soc. 71, 3257. 1949.

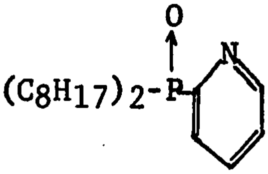
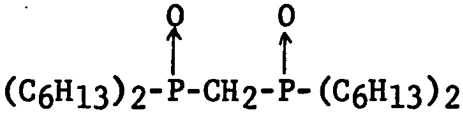
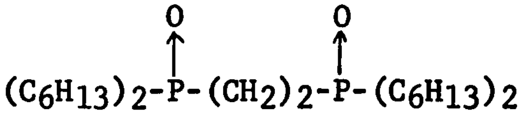
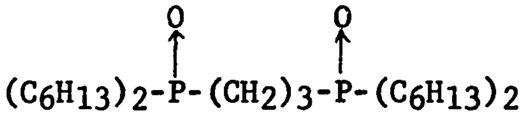
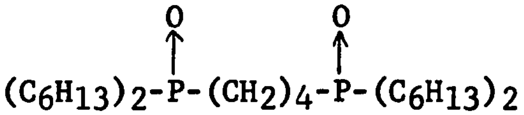
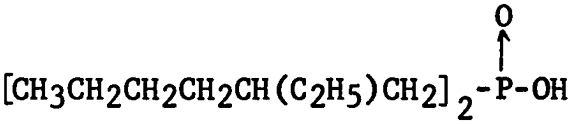
73. Weidman, G. Can. J. Chem. 38, 459. 1960.

74. White, J. C. and Ross, W. J. [National Academy of Sciences] U. S. Atomic Energy Commission Report NAS-NS-3102. 1961.

75. Winchester, J. W. [Oak Ridge National Lab., Tenn.] *U. S. Atomic Energy Commission Report CF-58-12-43*. 1958.

76. Young, J. P. and White, J. C. *Anal. Chem.* *31*, 393. 1959.

APPENDIX

Tri-n-butyl phosphate	TBP	$(C_4H_9O)_3\text{-P}\rightarrow O$
Tri-n-octyl phosphine oxide	TOPO	$(C_8H_{17})_3\text{-P}\rightarrow O$
Di-n-octyl-2-pyridyl phosphine oxide	DOPPO	
Bis(di-n-hexyl-phosphinyl)methane	HDPM	 $(C_6H_{13})_2\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-CH}_2\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}(C_6H_{13})_2$
Bis(di-n-hexyl-phosphinyl)ethane	HDPE	 $(C_6H_{13})_2\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}(CH_2)_2\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}(C_6H_{13})_2$
Bis(di-n-hexyl-phosphinyl)propane	HDPP	 $(C_6H_{13})_2\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}(CH_2)_3\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}(C_6H_{13})_2$
Bis(di-n-hexyl-phosphinyl)butane	HDPB	 $(C_6H_{13})_2\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-}(C_6H_{13})_2$
Di(2-ethylhexyl) phosphonic acid	HDEHP	 $[CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2]_2\text{-}\overset{O}{\overset{\uparrow}{P}}\text{-OH}$

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