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IN MEMORY

OF

MY BELOVED MOTHER

LANTHANIDES	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	57	58	59	60	61	62	63	64	65	66	67	68	69	71	71
ACTINIDES	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103

"These elements perplex us in our rearches [sic], baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us - mocking, mystifying, and murmuring strange revelations and possibilities."

Sir William Crookes (February 16, 1887)

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
DCP	Directly Coupled Plasma
ICP	Inductively Coupled Plasma
LSC	Liquid Scintillation Counting
NAA	Neutron Activation Analysis
HEHØP	2-ethyl-hexyl hydrogen phenyl phosphonic acid
RPC	Reversed phase chromatography
ppm	parts per million
ng	nanogram
pg	pico-gram

ABSTRACT

This thesis describes contributions to the analytical chemistry of f-series elements. New procedures were developed for the isolation and determination of lanthanides and thorium in rock samples.

The thesis commences with an account of the history of f-series elements, their occurrences, applications and a review of the various analytical separation and instrumental methods. The limitations of these methods and the interferences are examined.

A new fluxing agent, potassium superoxide was introduced. Potassium superoxide mixed with potassium hydroxide is an effective flux for rock and ore samples. Potassium may be removed subsequently by precipitation with perchloric acid. Traces of cations with various charges i.e. Ca^{2+}, Eu^{3+} and Th^{4+} are not significantly carried down but silver (I) is partially lost to the precipitate.

The cation exchange behaviour of micro and trace quantities of thorium on Dowex 50-X8 in the presence of carbonate and phosphate has been studied. Carbonate causes loss of thorium to the column effluent at pH 10. In the presence of phosphate, thorium is incompletely sorbed in the pH range 2-4.5, the loss being maximum at pH 3.8. Outside this range, thorium is quantitatively sorbed and recovered. A method that does not employ ion exchange has been developed

for the microdetermination of thorium in phosphate solution. The phosphate is precipitated as bismuth phosphate and thorium is leached from the precipitate with ammonium carbonate solution and determined with Arsenazo-III. Uranium, molybdenum, and vanadium are removed with Alamine 336. The results obtained for a standard ore are in excellent agreement with the certified value.

The extraction chromatographic separation of lanthanides is studied. The 2-ethyl hexyl hydrogen phenylphosponic acid (HEHØP) is an effective extractant for lanthanides. The extractant is supported on Kel-F that had been modified by treating with phenylithium. Microgram quantities of various lanthanides were placed on the column, eluted with HCl and determined by DC plasma spectroscopy. The development of the chromatogram confirmed the "tetrad effect", in lanthanides. Quantitative recovery of lighter lanthanides are studied and the determinations carried out with DCP spectroscopy and by colorimetry with Arsenazo-III. The effect of SiO_2 matrix in the determination lanthanides with DCP are studied.

A separation scheme is developed for the determination of lanthanides in rock samples using the extraction chromatographic technique, followed by DC plasma emission spectroscopy. This separation scheme is also applicable in other instrumental techniques such as NAA and spectrophotometry.

CHAPTER I

GENERAL INTRODUCTION

The purpose of this chapter is largely to review the natural distribution, chemical behaviour and the applications of the f-series elements. These comprise the 4f and 5f series elements which are often referred to as lanthanides or rare earths and actinides respectively. The lanthanides and actinides are similar in their chemistry and as a group, these "inner transition series" elements are somewhat different from other elements. Another important factor is that these elements are usually associated with each other in nature. These parallels in fact made it easier to unravel the behaviour of the actinides in the early days of transuranium element production. In addition to being similar chemically, the two series also share the properties of magnetism, radiant energy absorption and emission characteristic of f-electron species. Important differences also exist, particularly in oxidation states, bonding and complex ion formation.

Thorium is frequently found to be the principal rarer element accompanying the lanthanides. Less frequent congeners include uranium, zirconium, hafnium, titanium, tantalum, niobium, beryllium and very rarely scandium. Therefore this thesis is directed towards the development of procedures for the separation and determination of rare earths and thorium in different environmental conditions at trace

levels.

Occurrence of the f-transition elements in nature

The 4f transition elements cerium to lutetium, atomic numbers 58 to 71, lanthanum and yttrium are so similar to one another in chemical properties, it is no surprise that they show strong geochemical coherence. This is because under most natural conditions all members share a common trivalent state but with anomalous behaviour occurring under some conditions for Ce^{4+} and Eu^{2+}. Although scandium and yttrium do not belong to the lanthanide series they exhibit pronounced lanthanide-like characteristics and are often regarded as belonging to the "rare earth" group. In the loose terminology of some authors, even thorium is discussed as though it were a member of the rare earth group. In spite of some likeness in properties, thorium is not as similar to the lanthanides as yttrium is and there are some significant differences.

The earliest known of the rare earths, yttrium, was discovered before the beginning of the nineteenth century (1794) in a rare Swedish ore gadolinite and it was separated in the form of an impure oxide. Since then, a total of 17 rare earths were isolated laboriously by relatively inefficient fractional precipitation methods.* The rare earths are not truly rare in nature. This is shown in Table 1 which

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* Promethium, a fission product does not exist in nature.

TABLE 1

Symbol	Abundance ppm	Symbol	Abundance ppm
La	18.3	N	46.3
Ce	46.1	Sn	40
Pr	5.53	Nb	24
Nd	23.9	Co	23
Pm	4.5×10^{-20}	Pb	16
Sm	6.47	Ga	15
Eu	1.06	Mo	2.5-15
Gd	6.36	Be	6
Tb	0.91	As	5
Dy	4.47	U	4
Ho	1.15	B	3
Er	2.47	Ta	2.1
Tm	0.20	Br	1.62
Yb	2.66	Sb	1.3
Lu	0.75	I	0.3
		Cd	0.15
Sc	5	Se	0.09
Y	28.1	Au	0.005

Comparison between the Crustal Abundances of the Lanthanide Elements (Source: T. Moeller. The Chemistry of the Lanthanides, Oxford: Pergamon Press, 1973, p. 46.)

compares the crustal abundance of the lanthanides, to that of some better known elements. The relative abundance of lanthanides is in remarkable agreement with the rule of D. Harkins (1):that elements of odd atomic number are always less abundant than those of even atomic number, which immediately precede or follow them.

The rare earths are highly dispersed in nature (2). They are lithophilic elements i.e. when allowed to distribute themselves among common silicate and sulphide phases, they overwhelmingly enter silicates. The rare earths occur in a variety of minerals chiefly in pegmatite dikes associated with igneous rocks and in deposits derived from the weathering of pegmatites. The rare earths are concentrated in the residual fluid that crystallizes as pegmatite by the process of fractional crystallization. Then rare earths are partially separated so that some minerals are richer in the lighter elements (the so-called cerium group) whereas others are richer in the heavier elements (the so-called yttrium group). The cerium group consists of La, Ce, Pr, Nd, Sm, Eu, and Gd; the yttrium group consists of Y, Tb, Dy, Ho , Er, Tm, Yb, and Lu (2).

Although a large number, about 160, mineral species (2a, 2b) are known to contain rare earths, only a few are rich enough to warrant their use as ores of commercial importance. They are bastnaesite, monazite and xenotime.

Bastnaesite: Bastnaesite, a fluorocarbonate, is the principal

source of rare earths today. The primary content of this mineral is light rare earths of 60-70%. About 55% of rare earths utilized today in the free world comes from the Molycorp's open pit mine at Mountain Pass, California. Other significant deposits are found in mainland China, Burundi, Sweden, and New Mexico, U.S.A.

Monazite: This is an orthophosphate of the cerium group with thorium silicate. Monazite constitutes the second most important ore source for the rare earths and accounts for about 40% of the free world production. The rare earths distribution varies in monazites found in different parts of the world. The monazite found in South Carolina, U.S.A. has a higher concentration of heavy lanthanides plus yttrium than does the Australian monazite, which is in turn richer in the heavier earths than the Indian monazite. The La and Ce content is higher in the latter two. The commercial monazite sources are alluvial and may be found in beach sand. The primary associated minerals are rutile, ilmenite, cassiterite and zircon. These sands were processed in the past for their Ti, Zr, and Sn content.

Xenotime: Xenotime is an yttrium orthophosphate and is the major source for the heavy lanthanides and yttrium. In xenotime, the light lanthanide concentration is smaller by a factor of ten, while the heavy lanthanide and yttrium concentrations are greater by a factor of ten to several hundred, compared to bastnaesites and monazites.

Other minerals which have been used as a source of rare earths are apatite [$Ca_5(PO_4)_3F$]; exenite [$Ln(Nb,Ta)TiO_6 \times H_2O$]; gadolinite [$Ln_2(Fe^{2+}, Be)_3Si_2O_{10}$]. Other future sources include allanite, fluorite, perovskite, sphene and zircon. In addition, uranium tailings have been used in the past as a source of heavy lanthanides and yttrium. In Canada, Elliot Lake ore contains 0.1% uranium and 0.05% rare earth oxides; other deposits are found in the Bancroft, Agnew Lake areas.

The 5f-transition elements, when they were discovered, resembled rare earths and were named rare earths belonging to the Second Series. However, shortly many scientists collectively referred to these elements as actinides which include actinium (Z = 89) through lawrencium (Z = 103). All these nuclei are unstable with respect to alpha emission. Of the actinide elements, thorium and uranium have rather long lives (1.39×10^{10} yr for $^{232}_{90}Th$ and 4.50×10^9 yr for $^{238}_{92}U$). Nuclei formed at the beginning of the earth's lifetime are still present in the lithosphere. Thorium is the most abundant element among actinides and has a radius quite similar to those of the lanthanides. It is therefore almost always associated with the lanthanides in nature. Also, there is considerable interest in thorium as this element is expected to be used as a nuclear fuel in the future. Therefore the review of the actinides will be limited to thorium in this thesis.

On the basis of physico-chemical data derived from experiments by Seaborg and other investigators, it is recognized that thorium is the first member of the 5f actinide series (3, 4, 5).

Occurrence of Thorium

Thorium was first discovered in 1828 by one of the nineteenth century's greatest chemists, Jons Jacob Berzelius (1779-1848) in the mineral thorite (6). According to Vinogradov (7) its average concentration in the earth's crust is 8×10^{-4} wt% about the same as for lead, but it is rarely encountered in a concentrate form. In alkaline rocks, the thorium concentration is much lower than in acid rocks (8). For example, its average content in granites is 1.2×10^{-3} wt% as compared with 5×10^{-4} wt% in dunites (5). In the hydrosphere, the thorium concentration fluctuates between 10^{-5} to 10^{-9} $g \cdot L^{-1}$ (9, 10). In iron meteorites, the average concentration of thorium varies between 0.9×10^{-6} and 4.3×10^{-6} wt%, while in stony meteorites it is 2.4×10^{-5} wt% (11).

Thorium minerals are usually found in igneous rocks, pegmatites, veins and placers. The most important commercial sources of thorium are the placer deposits. The chief minerals which contain thorium (11a) are monazite, thorogummite, huttonite, thorite and thorianite; the latter two minerals are rarely encountered and are of no practical value. Monazite contains 5 to 10% of ThO_2. Because thorium

is a fissionable material several countries, notably Brazil and India, remove and stockpile thorium as a strategic material and the Th-free monazite is exported. Commercial thorium deposits (15) also exist in Ceylon, Tasmania, Nigeria, the Scandinavian peninsula, Colorado, North Carolina, Idaho and other states in the U.S.A. Monazite containing about 7.5% thorium was found in concentrated form at several sites in the iron-bearing region of Marquette in Northern Michigan. In many parts of Canada (13, 14) the percent composition of ThO_2 is low. For example, Elliot Lake ores contain 0.028% ThO_2, Blind River and the Bancroft ores about 0.03 to 0.04%. Therefore thorium processing in Canada is limited. Although thorium is a fairly abundant element, only a few tonnes of thorium are extracted per year, mainly as a byproduct of rare earth extraction.

Electronic structure and physico-chemical properties of rare earths and thorium

Many chemists view rare earths as an unique class among the naturally occurring elements with similar chemical properties to one another and collectively they can be considered as one element. To a certain degree this is correct, but as one examines these elements more closely vast differences in their behaviour and properties become apparent. One of the obvious facts is the difference in the melting points of the lanthanide elements which vary by almost a factor of two across the series, La - 918°C and Lu - 1663°C

for example. The remaining trivalent lanthanide melting points lie between these two values. This difference is much larger than that found in many of the groups of the periodic table, e.g. the melting points of Cu, Ag, Au vary by about 100°C (1083, 961 and 1063°C) respectively.

In order to have a better understanding and appreciation of the anomalous chemical properties of the lanthanides, the more important properties will be discussed first. These include the electronic configurations and ionic radii.

Electronic Structure: The electronic configuration, known oxidation states and ionic radii of the rare earths are given in Table 2. They all form trivalent ions and in metals most of them have three electrons in their conduction bands. They all exist in dilute aqueous acid solutions as trivalent positive ions, except thorium which is tetravalent. While +3 is their characteristic oxidation state, under certain conditions Ce, Pr, and Tb exhibit a +4 oxidation state and Sm, Eu, Yb a +2 oxidation state. These exceptional oxidation states are striking examples of the rule, which states that empty, half filled and completely filled levels tend to be more stable states; Ce^{4+} and Tb^{4+} give up an electron to have an empty and half filled 4f level respectively; Eu^{2+} and Yb^{2+} gain an electron to have a half filled and completely filled 4f level respectively. The Ce^{4+}, Eu^{2+} and Yb^{2+} states are quite common and are utilized by industry to separate these three rare earths from the remaining rare earths

TABLE 2

Electronic Configuration, Known Oxidation State and Ionic Radii of REE and Thorium (ref. 16)

Element	Neutral atom electron configuration	Known oxidation state	Ionic radii, °A M^{2+}	M^{3+}	M^{4+}
Sc	$3d4s^2$	+3		0.745	
Y	$4d5s^2$	+3		0.900	
La	$5d6s^2$	+3		1.045	
Ce	$4f^1 5d6s^2$	+3, +4		1.01	0.80
Pr	$4f^3 6s^2$	+3, +4		0.997	0.78
Nd	$4f^4 6s^2$	+3		0.983	
Pm	$4f^5 6s^2$	+3		0.97	
Sm	$4f^6 6s^2$	+2, +3	1.19	0.958	
Eu	$4f^7 6s^2$	+2, +3	1.17	0.947	
Gd	$4f^7 5d6s^2$	+3		0.938	
Tb	$4f^9 6s^2$	+3, +4		0.923	
Dy	$4f^{10} 6s^2$	+3		0.912	
Ho	$4f^{11} 6s^2$	+3		0.901	
Er	$4f^{12} 6s^2$	+3		0.890	
Tm	$4f^{13} 6s^2$	+3		0.880	
Yb	$4f^{14} 6s^2$	+2, +3	1.00	0.868	
Lu	$4f^{14} 5d6s^2$	+3		0.861	
Th	$6d^2 7s^2$	+3, +4			0.99

elements by relatively cheap chemical methods. The other rare earths can be separated by making use of ion exchange or extraction chromatography. For most major uses it is not cost effective to separate the individual lanthanides, but it may be worthwhile to separate the lanthanides into groups of light, medium and heavy in order to optimize the chemical behaviour for some limited applications and in certain instrumental analytical determinations.

Ionic Radii: The ionic radii of the lanthanides and thorium are shown in Table 2. The ionic radii decreases smoothly and systematically from La to Lu, the total contraction being about 7.5%. This is due to the increase in the effective nuclear charge in passing from one lanthanide to the next. The lanthanide contraction also accounts for the decreased basicity on going from La to Lu and forms an important basis of various separation techniques. Also the contraction is significant in its effect on the properties of elements after the lanthanide sequence relative to those before lanthanum. For example, zirconium and hafnium have almost identical chemical properties because of the lanthanide contraction experienced by hafnium. The usual increase of radius down a group is fortuitously cancelled at hafnium and it is nearly identical in size to zirconium. Since the trivalent lanthanide ions are comparable in size with Na^{+} or Ca^{2+}, substitution for these ions is sometimes possible provided the electronic charge is compensated for by the addition or

removal of anion charge in some way.

Thorium: Thorium-232 is the first member of the naturally occurring radioactive disintegration series. Thorium has six naturally occurring isotopes. Thorium isotopes commonly found in nature are ^{232}Th and ^{230}Th. Thorium metal is highly electropositive and can be prepared by reduction of thorium oxide with calcium. Thorium metal has a high melting point (1750°C) and is highly reactive in the molten stage. The potential of the thorium-thorium(IV) couple has been estimated as +1.90 volts (17).

Thorium has generally been considered to be a lithophilic element of low geochemical mobility. Like U^{4+}, Th^{4+} is relatively immobile since it is adsorbed tenaciously on cation exchange resins and it is one of the last elements to be eluted when cation exchange columns are leached with acid (18). Thorium occurs in nature exclusively as the tetravalent ion (19). Reduction to Th(III) and Th(II) is much too difficult for it to occur in nature. Since thorium exists in solution as a comparatively small, highly charged cation, it undergoes extensive interaction with water and has a strong tendency to form complex ions with anions which may be present in solution.

Applications of Rare Earths and Thorium

The diverse uses of the rare earths fall into four categories. (a) Early uses depended primarily on the chemical similarity of the various lanthanides. (b) The second

major category depends upon the characteristics imparted by a given configuration in the 4f shell. (c) The third is based simply on the variable oxidation state of certain lanthanides. (d) The last is based upon nuclear properties.

(a) Applications based on similarity in chemical behavior:

Rare earths are often used as mixtures, thus the cost per unit weight is small which allows industry to employ the rare earths in a large number of applications. They find use as catalysts, primarily in zeolite molecular sieve catalysts for cracking petroleum. The exact catalytic role played by the rare earths is not known but the addition of 1 to 5% mixed rare earths to the $Na_2O \cdot Al_2O_3 \cdot nSiO_2 \cdot H_2O$ zeolite does increase the catalytic efficiency by a factor of three, permitting a significant reduction in capital investment. The addition of rare earths into steel controls the sulphur and thus improves workability and certain mechanical properties. The largest metallurgical application is the addition of rare earths to ductile iron to spheroidize the graphite. The use of mischmetal in lighter flints and artillery shell liners is based on the pyrophoric nature of the rare earths and cerium in particular (20). The mixed rare earth oxides are used in glass polishing. Another important application is the use of mixed rare earth fluoride in carbon arc cores.

(b) Applications based on the 4f electrons:

In this category individual rare earths of highest purity are employed. Isolation is achieved by ion exchange

or liquid-liquid extraction. Transitions between energy levels within the 4f shell leads to the utilization of lanthanides as activators in phosphors, lasers and carbon arcs. The largest use of the rare earths in the optical field is that of Eu^{3+} activators as the primary red colour in color television (21). Cerium, samarium and terbium are also important activators. Yttrium and lanthanum oxides are used as hot materials for the various rare earth phosphors. One of the newer applications is in medical x-ray intensifying screens (22). Yttrium and neodymium are used on one of the most important types of lasers.

The magnetic properties due to the 4f electrons and their interaction with the magnetic electrons of the first transition metal group elements in ferrites, garnets and the cobalt (iron-rich) intermetallic compounds accounts for the use of rare earths in microwave and bubble devices. The gadolinium/gallium garnet used as bubble devices for domain memory storage is a fairly recent industrial application (23). Another important application included in this group is the utilization of La, Ce and Y. Additions of about 0.1 to 0.2% to cobalt, nickel and chromium based superalloys improves their corrosion and oxidation resistance in various environments, including high temperature and salt water. A high strength magnetic alloy of Nd, Fe and B is being introduced into the automobile industry for starting motors. The newest growth market for Y_2O_3 involves the stabilization of the high

temperature cubic form of ZrO_2, so-called Y_2O_3 stabilized ZrO_2 (YSZ). YSZ has been used for many years as a ceramic material for thermal insulation (24). It has also been known for many years that because of the oxygen defects in this material the electrical resistivity varies linearly over several orders of oxygen pressure. It is planned to put this property to use in many applications. YSZ may be used to make ceramic auto engines and also to measure the oxygen partial pressure in automobile exhaust emissions.

(c) Applications based on unusual oxidation states:

The use of rare earths which exhibit variable oxidation states would be included in this category, i.e. Ce, Eu, Yb, and perhaps Pr, Sm and Tb. Cerium dioxide is used to decolourize flint glass in the manufacture of bottles and jars. This application is based on the oxidation-reduction reaction of Ce to keep the iron impurities in the Fe^{3+} State, since Fe^{2+} imparts a bluish colour to the glass. The addition of 1.5% cerium hydrate to glass produces the pink tint which is popular in today's fashion glasses. A Pr-Ce oxide combination is used in welders' goggles to filter out the blue, violet and ultraviolet radiation (26). Cerium can be used as an oxidizing agent in certain analytical titrimetric determinations.

(d) Appications based on nuclear properties: (27)

Several of the rare earths have high neutron capture cross sections and thus are used as control rod materials and

burnable poisons. The most likely candidates are Sm, Eu, Gd, Dy and Er. Gadolinium and samarium because of their large capture cross section are quite attractive in reactor shutdown and safety devices - other rare earths which have very low cross sections such as cerium and yttrium may be used as diluents in nuclear fuels (28).

Miscellaneous

There are many miscellaneous applications but only a few will be mentioned here. Cerium hydrate is added to silicone rubber gaskets which are used in aircraft windows and laboratory environmental chambers. The cerium improves the heat stability and helps maintain the colour and elastic properties of the silicone rubber under extreme temperature variations. Lanthanum chloride is used as an interference suppressor due to PO_4^{3-} (25) in the determination of Ca in the blood samples by atomic adsorption. The affinity of the lanthanides for phosphate is being investigated as a possible solution to fresh water lake eutrophication. A fairly recent application is the use of the intermetallic compound $LaNi_5$ as a hydrogen storage material. REE hydrides are also used as hydrogenation catalysts, for hydrogen purification, thermal compression, waste heat engines, heat pumps and refrigeration (29).

Applications of Thorium

The world consumption of thorium rose with the develop-

ment of the incandescent gas mantle by Auer Von Welsbach in 1885. The gas mantle was widely used and represented the largest single use of thorium. The consumption of thorium in 1970 was estimated to be about 270 tonnes. Of this 50% was still used for the preparation of gas mantles, 40% was used in metallurgical industry and the remaining 10% was used for refractories, catalysts and nuclear reactors. Earthly thorium stores more energy than all uranium, coal, oil, natural gas and other fuels combined which are non-renewable. In the future, the utilization of thorium in nuclear reactor systems could be very high. The potential for utilization of thorium in nuclear reactors depends on the fact that ^{232}Th, the major isotope found in nature, can absorb neutrons to produce fissile ^{233}U, allowing it to be used as a fertile material in a breedor reactor (30). Linus Pauling has stated that thorium will save the world from the energy crisis in the future (31).

The U.S. Bureau of Mines estimates that the demand for thorium in the year 2000 will be 50-620 tonnes for non nuclear uses and 700-6500 tonnes for nuclear energy purposes depending on the need for and the successful exploitation of thorium-burning systems. It is expected that even if the demand for thorium were to reach the higher values, no supply problems would be encountered for a considerable period of time, because thorium would be obtained as a byproduct of the rare earths and uranium processing industries.

CHAPTER II

REVIEW OF THE ANALYSIS OF ROCKS FOR REE AND THORIUM

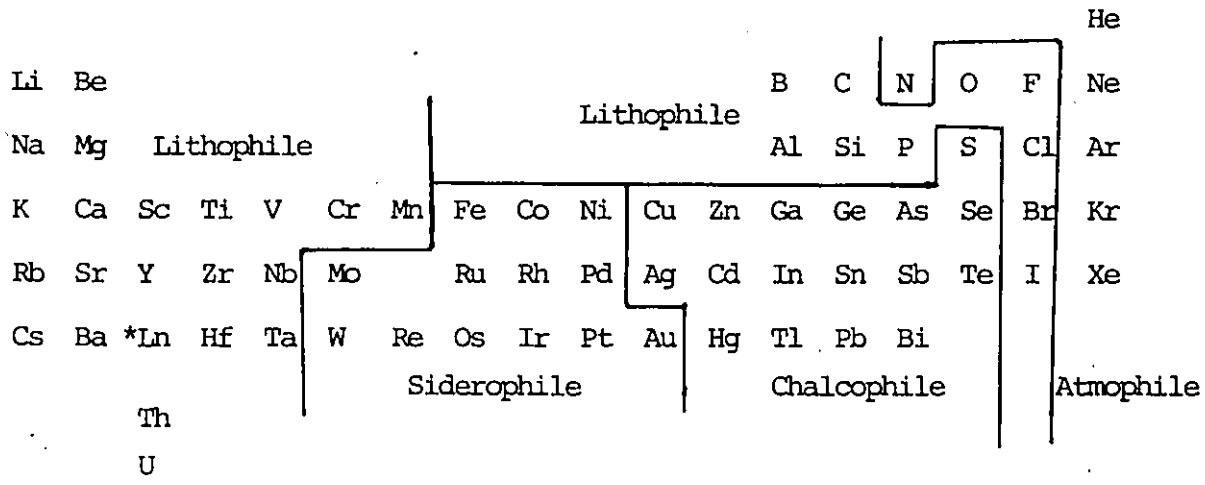
Analytical geochemists are engaged in elucidating processes governing the distribution of the chemical elements in various geochemical phases of the earth. One of the main purposes of analytical chemistry is to gain information about the composition of the great variety of rocks and minerals of which the earth is composed. For many of the eminent chemists of the eighteenth and nineteenth centuries uncharacterized minerals provided the challenge that led to the identification and subsequent isolation of the elements. In the nineteenth century, Berzelius, Fresenius, Lawrence Smith and others laid the foundations of the classical analytical scheme for the determination of all the major elements. Mineralogists and geologists have to be thankful for their painstaking care and accuracy.

By the year 1920 two notable text books had been published on rock analysis, "Manual of the chemical analysis of rocks" by Washington (33) and "The analysis of silicate and carbonate rocks" by Hillebrand (34). The methods described have been found to be too time consuming for today's requirements and from about 1950, various "rapid" analytical schemes began to be proposed as alternatives (35-40). Interest in the minor components of silicate rocks has continued almost uninterrupted to the present day, with current work emphasizing determination of elements at below parts per million (PPM) levels.

Rock analysis is one of the most difficult and complicated analytical tasks, especially at trace levels due to the fact that a rock might contain very many of the ninety naturally occurring chemical elements. The elements which are frequently encountered in rock analysis are shown in Figure 1. Geochemically, these elements can be differentiated on the basis of the reduction potential of the process $M^{n+} + ne \rightleftharpoons M$ relative to the half reaction $Fe^{2+} + 2e \rightleftharpoons Fe$. Elements whose reduction potentials are more positive than iron are called siderophiles. The majority of remaining elements whose reduction potentials are more negative than iron are classified according to their bonding potentials with oxygen and sulphur. Those which are associated in nature primarily with oxygen are lithophiles, while those associated with sulphur are chalcophiles. Lithophilic ions occur with rare gas structures and consequently are not readily polarized. Chalcophiles are more readily polarizable and therefore associate with the easily polarizable sulphide and arsenide ions. Secondary differentiation is influenced by the relative size of the cations, the bonding tendencies of the elements, fractional crystallization from the magma and densities of the compounds formed.

The analytical chemistry of the lithophilic f-series elements will be treated as a closely related group in this thesis. This has been deemed desirable in the context of the geochemical nature of association of the naturally occurring

Fig. 1. Geochemical Classification of the Elements[a] (32)



*Ln = Lanthanides

[a] Elements can display more than one type of behaviour

4f-series and of thorium, a representative of the 5f-series. The REE and thorium in most rock systems are present at the ppm or subppm levels and behave as trace elements, thus posing certain difficulties to the analyst in his determination. In this connection, trace elements are defined here as those elements whose presence in a rock does not significantly alter the stability fields of its major minerals. Analytical separation and determination of thorium will be dealt with in this thesis in view of the importance of thorium in industry and the environment.

Knowledge of the fundamental laws governing the distribution and the redistribution of elements, during metamorphic processes, etc., enables geochemists to predict the probability of the occurrence of economically interesting minerals in a particular geological environment. In the study of ore deposits, as well as in petrology, the distribution of trace elements casts light on the genesis of ore bodies. Knowledge of the genesis of mineral occurrences leads to a reliable forecast of the chemical and mineralogical composition as well as some structural aspects of potential deposits. The REE, because of their peculiar similarities, serve as a particularly suitable group of indicator elements. Also the presence of trace impurities of REE in materials such as high purity metals, semiconductors and glasses have an important influence on electrical, magnetic, mechanical, nuclear and optical properties. Quantitation of

REE in these materials helps to understand the above properties.

The geochemist is interested in the conditions that prevailed during formation of the constituent minerals. Particular interest attaches to the mineralization processes occurring during alteration of the rock by hydrothermal action. The mechanism of lanthanide leaching and migration is well established in the geochemical literature (41-45). Interpretation of the migratory processes is based primarily upon a recognition of the role of the lanthanide contraction. The early lanthanide ions are materially larger than those later in the series and the larger ions tend to be excluded from common rock forming minerals during the processes of crystallization; rather, they tend to remain in liquid solution in equilibrium with the crystals. It follows that the hydrothermal alteration of a rock may result in a change in the ratio of lighter to heavier lanthanides.

The equilibria between solid and fluid phases will be affected by the presence of complexing species such as Cl^-, F^-, and CO_3^{2-} ions, for example. The movement of the fluid phase within the geological structure will cause a displacement not only of the lanthanides but of all dissolved species, many of which may be metallic elements of commercial significance, e.g. Cu, Pb, Au, Mo, etc. The re-deposition of accessory minerals, can be expected to occur in proximity to depleted wall rock and therefore the geologist may infer the

presence of a pegmatite dike or other likely structure without the necessity of removing overburden at random. It is evident that rationalized strategies of prospecting for micas, molybdenite, zircon, niobium-tantalum and lithium minerals, beryl, spinels, to name but a few possibilities, may depend in future upon the technique of lanthanide analyses.

In order to find solutions to the general aspects discussed above, mainly trace element distribution, multi-element analytical tools are required. Thus, Goldschmidt introduced optical emission spectroscopy in the twenties and a decade later x-ray fluorescence spectroscopy was made available. In the nineteen-fifties, neutron activation analysis was introduced into geochemistry. The newest development is an induced or directly coupled plasma burner for the optical emission spectroscopy and mass spectrometry. In general, all these methods permit the detection of less than ppm levels with ever increasing reproducibility of results. Classical spectrophotometers and atomic absorption instruments have been much used for single element determinations. Unfortunately, all these instrumental methods suffer from more or less matrix or interelement interference effects, which restrict their applicability in some cases, thus calling for elegant separation techniques. The need and importance of separation techniques will be made evident in the next section where the matrix effects involved in neutron activation, emission spectroscopy and spectrophotometric methods will be discussed briefly.

Neutron Activation Analysis (NAA)

Neutron activation is one of the highly sensitive techniques for the quantitative determination of the rare earths. In this method, the sample is irradiated in a flux of thermal neutrons, generally in a nuclear reactor. The constituent elements absorb neutrons forming artificial radionuclides, the activity spectrum of which is measured and interpreted in terms of the amounts of the various elements present. An advantage of this nuclear technique is the fact that sensitivity limits can be fixed by the analyst via neutron flux and irradiation time. Furthermore, multielement determinations can be performed on a single aliquot of sample without chemical separations. This is termed non destructive instrumental neutron activation analysis. For multielement γ-ray measurements a high resolution detector of Ge(Li) type is used in connection with sophisticated multichannel analyzer.

Geochemists were involved in the development of NAA at an early period (46, 47) and they applied it to the rare earth determination (48, 49, 50). De Soete et al (51) have provided a detailed discussion of all aspects on neutron activation.

The multicomparator method is used for precise work. In this method, standards containing known amounts of the element of interest are irradiated with the samples and the induced activity is measured under the same conditions as the

samples. Errors arise in determination by neutron activation if the specific activity in the sample is not identical to that in the standard. There are certain interferences that yield activities, which are not strictly proportional to the amount of element present.

(a) If the matrix elements have high absorption cross sections, errors may arise due to shielding effects. This type of error can be avoided by irradiating a sufficiently dilute sample, or separating the elements having high absorption cross section prior to the irradiation. Gadolinium, for example, has the largest neutron absorption cross section (49,000 barns) thus causing the average neutron attenuation of 1% in a sphere of Gd_3O_3 which has 0.12μm radius and a mass of only 5×10^{-14}g. Massart and Hoste analyzed Lu in a 50 mg sample of gadolinite by dissolving the sample and irradiating an aliquot of a chemically separated rare earth solution (52). Turkstra and Van Droogenbroeck reduced the effect of self shielding in rare earth rich carbonatites by diluting the powdered sample with pure quartz (53).

(b) In certain cases the sample became highly radioactive upon irradiation. In such cases the post irradiation treatment has to be performed with great care behind proper shielding. For example, the γ-ray spectra of irradiated rock samples may be dominated at various times by the isotopes of Mn, Na, Sc, Fe, Co etc. from the matrix material, thus swamping the γ-ray spectra of lanthanides (54).

(c) The nuclide of interest may be formed by competing nuclear reactions such as (n, p); (n, α) and (n, f). The γ-ray spectrometer cannot, of course, distinguish between decaying nuclei from the intended parent and those from interfering elements.

Some of the important interferences in instrumental neutron activation (NAA) are given in Table 3. Boynton (57) and Bereznai discussed other types of interferences. Amongst the light rare earth group, the nuclides that are usable for neutron activation determination may also be formed as uranium fission products, even when La, Ce, Nd, Sm are totally absent in a given sample. The presence of uranium in a sample enhances the true values of La, Ce, Nd, Sm determined by INAA if appropriate corrections are not made for the interference. Recently Ila et al (59) reported that in a 5 hour irradiation, 1 mg of uranium is found to be equal to 0.28 mg of Ce and 0.23 mg of Nd. Therefore uranium must be separated while determining rare earths in uranium rich minerals or ores.

Another type of interfering nuclear reaction is the second order interference, for example of the type

$$^{a}X(n,\gamma)^{a+1}X \xrightarrow[\beta^-]{} {}^{a+1}Y(n,\gamma)^{a+2}Y$$

Interferences of this kind have been calculated by OpdeBeeck (60, 55). In cases where the nuclide ^{a}X has a large activation cross section, appreciable difficulties are encountered if trace amounts of the element Y are to be

TABLE 3 (ref. 56)

Parent isotope	Product isotope	Half life	Analytical γ-ray (Kev)	Interferences to be considered for various reasons (Kev)
^{45}Sc	^{46}Sc	83.8d	889.26	$^{160}Tb(879.4)$; $^{110m}Ag(884.7)$ $^{192}Ir(884.5)$; $^{46}Ti(n, p)^{46}Sc$
^{139}La	^{140}La	40.22h	328.8; 1596.4	$^{235}U(n,f)$; ^{24}Na; $^{239}(Np(334.3)$
^{140}Ce	^{141}Ce	32.45d	145.4	$^{235}U(n,f)$; $^{59}Fe(142.4)$; $^{175}Yb(144.86)$ $^{133}Pa(145.4)$; ^{182}Ta (152.4)
^{146}Nd	^{147}Nd	10.98d	91.03; 531.4	$^{235}U(n,f)$; $^{169}Yb(93.6)$; $^{140}Ba(537.2)$
^{152}Sm	^{153}Sm	46.44h	103.2	$^{235}U(n,f)$; $^{239}Np(99.6)(103.8)$ $^{153}Gd(103.2)$; $^{182}Ta(100.1)$
^{151}Eu	^{152}Eu	13.2y	121.78 1408.02	$^{169}Yb(118.2)$, (130.53); $^{133}Ba(123.7)$ $^{134}Cs(1400.4)$
^{174}Yb	^{175}Yb	101h	396.32	$^{233}Pa(398.5)$; $^{160}Tb(392.5)$; $^{131}Ba(404.3)$
^{176}Lu	^{177}Lu	6.71d	208.4	$^{239}Np(209.8)$; $^{131}Ba(216)$

determined via the radioisotope ^{a+2}Y in a sample of element X. If, for example, a dysprosium sample is irradiated for 22 h at a flux of 5×10^{12} $n \cdot Cm^{-2} \cdot S^{-1}$ for the determination of holmium, the ^{166}Ho activity produced by second order interference corresponds to 120 ppm Ho. Consequently this type of interference can be serious in cases where an element is to be determined in a matrix of an adjacent element.

The point which needs to be emphasized is that the purely instrumental neutron activation analysis is very much dependent on the composition of the sample and is useful in only a limited number of cases. Although improvements in γ-ray Ge(Li) detectors have considerably improved rare earth determinations, the nondestructive technique has lower sensitivities and greater chance of interferences. Therefore group separation whether based on classical or on modern methods is very desirable in order to improve the sensitivity, accuracy and confidence in the results. It may be desirable to analyze 5 to 10 g of sample. A chemical concentrating process would then be required.

Separation Methods

It is evident that economical and quantitative separation procedures are required. The procedures used for the separation of the REE as a group from the interfering elements have in most cases been based on classical hydroxide-fluoride or hydroxide-oxalate precipitation cycles using carriers. These procedures can be applied either before or after

irradiation of the sample. Several methods for the determination of the REE in silicate rocks based on radiochemical group separation and subsequent Ge(Li)γ-spectrometry have been published (61-65). By this means all fourteen elements can be determined with a precision and accuracy of $\pm$5% or better (62). A commonly used radiochemical separation procedure for the REE includes the following steps.

(i) Fusion of an irradiated sample in a Ni or Zr crucible with Na_2O_2 and NaOH in the presence of REE carriers.

(ii) Dissolution of the fusion cake with water or dilute acid.

(iii) Addition of NaOH or NH_4OH to precipitate REE hydroxides.

(iv) Separation of iron by extracting with isopropyl ether.

(v) Separation of Sc is an important part of the scheme, because Sc isotopes have strong γ-ray peaks in the spectra of rock samples and may interfere with REE peaks. Scandium can be removed either by diethyl ether extraction in the presence of ammonium thiocyanate or by precipitation of REE fluorides using NH_4HF_2 and HF. The precipitate of REE fluorides is separated by centrifugation, dissolved in a mixture of HBO_3-HNO_3 and the lanthanides reprecipitated as hydroxides with NH_4OH. This procedure may be repeated 2-3 times since about 50-80% of Sc is separated each time.

(vi) The final hydroxide precipitate is dissolved in

dilute hydrochloric acid and used for γ-ray measurement.

Yttrium is usually not determined along with the separated lanthanides, because it lacks suitable γ-rays. However, Steinnes (66) reported that Y may be determined by β-Counting of the isolated lanthanides plus yttrium fraction, but corrections for lanthanide interferences are required.

Before the advent of Ge(Li) detectors, methods based on group separation and subsequent chromatographic separations had to be used in order to obtain reliable data for many REE simultaneously. Separations based on elution from a cation exchange column with a suitable complexing agent have been most popular (67-68). Also, other types of separations such as anion exchange in presence of EDTA (70) and anion exchange in mixed solvents (71, 72) have been used.

There are separation steps described in the literature, which separate the REE from the matrix before irradiation, a technique which is not so common in activation analysis, but which is gaining popularity with the introduction of reversed phase chromatography in inorganic analysis. The advantages of preconcentration of the sample before irradiation will be described later in the discussion section in Chapter V.

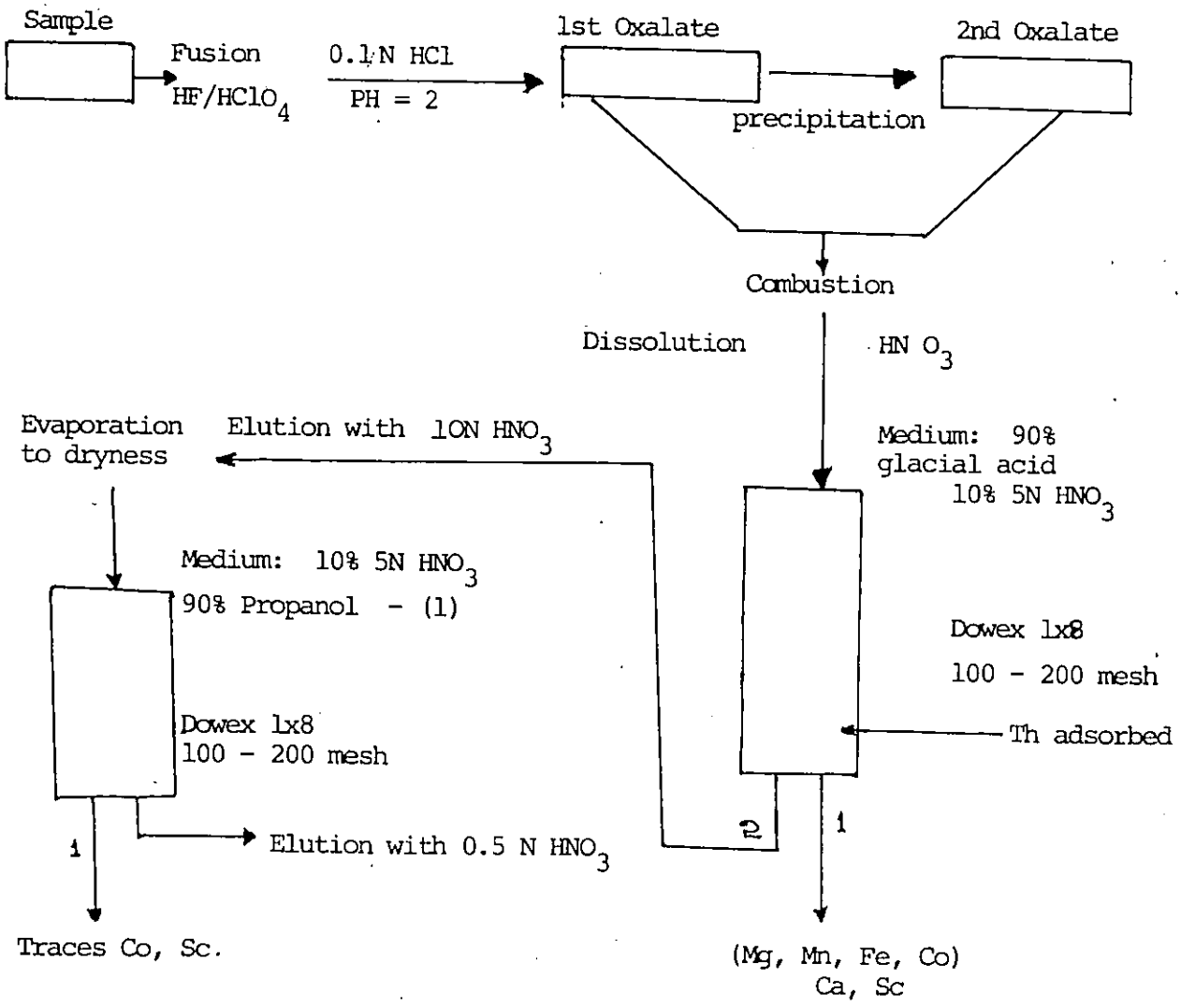
In a paper concerning the determination of rare earth impurities in metallic uranium, the interference due to bulk uranium was suppressed by passing the sample solution through a cation exchange column before irradiation (73).

The method developed by Klein (74) is based on

digestion of the sample by HF/ClO_4, double precipitation of the REE as oxalates with Ca as a carrier and decontamination of the combined oxalates from traces of Mg, Mn, Fe and Co as well as Sc and Th and the carrier by simple ion exchange operations. The scheme is shown in Fig. 2.

Fig. 2

Flow-sheet of the preirradiation separation of REE from silicate matrix by Klein (74)



In this type of chemical separation before activation, a blank should always be carried through the procedure. A blank problem does not exist with post irradiation procedure. Finally, it should be mentioned that the neutron activation technique is highly sensitive for the REE. It can be successfully employed for the determination of extremely low concentrations of REE in various natural samples, with a combination of chemical separations that increases the sensitivity and reduce interferences.

Spectrochemical Analysis

Optical emission spectroscopy is the oldest instrumental method known for analysis of terrestrial matter. In principle a minute quantity of sample is vaporized and excited to the point of light emission. The intensity of emitted radiation is measured and related to the elemental concentration. Excitation is achieved by means of DC or AC arc and spark discharges or flames (75, 76). This method is widely used in industrial laboratories but electrically generated plasmas for spectrochemical analysis are currently the subject of vigorous investigation and the plasma sources are being applied to the determination of geological materials at trace quantities. The following discussion will be limited to the plasma emission methods.

A plasma is any luminous volume of gaseous mixture in which a significant fraction of the atomic or molecular species are present as ions. There are three types of inert

gas electrical plasma sources now available, differing in the number of electrodes which are necessary to sustain the plasma.

1. DC Argon plasma jet (2 or 3 electrodes)(83)

2. microwave induced plasma (single electrode) (80, 81, 83) (not widely used).

3. Inductively coupled torches (electrodeless) (82-84)

These plasma spectroscopic methods provide several of the most useful and specific means for the determination of the rare earth elements at trace levels. Even though the chemical properties of the various lanthanides are very similar, the energy states of each atomic system are just as uniquely different for individual rare earth elements as they are for other elements. As a consequence, spectra produced by energy transitions between these states are also highly specific. Direct excitation of the sample with ICP or DCP provide sufficient detectability, precision and accuracy, if the sample is sufficiently pure. Because the physical properties of these plasmas offer excellent performance and operational advantages over arc and spark emission sources, most geochemical laboratories and many others appear to favour either ICP or DCP.

In general, environmental and geochemical samples provide diverse matrices that are exceptionally complex, both chemically and physically (85). The complexity of those samples raises the possibility that interelement effects of

various types or spectral interferences may introduce errors in the analytical determinations of rare earths. Some possible interferences are presented in Table 4 (102).

Types of interferences: High-temperature plasma is an efficient excitation source. As a consequence, all types of plasma atomic emission can be encumbered by many interference problems. The most significant of these are spectral interferences resulting from stray or scattered light, broadband continuum emission, broadened matrix element lines and direct spectral overlap. It is possible to eliminate or to minimize these interferences in several ways. One of these involves the use of a high dispersion, high resolution monochromator (86, 87). The echelle monochromator is particularly useful for this purpose. This monochromator has greater resolution than is necessary to provide reliable AES determinations when there are cases of suspected interference(86). The resolution and dispersion available allow a high degree of line-isolation and the effect of broadband background radiation is minimized. However, high resolution alone cannot alleviate every kind of spectral interference. Broadening of spectral lines in electrical plasmas can occur to such an extent that some close lines no longer are inherently resolvable. In some cases, alkali alkaline earth, Al, Ti, Si, W, Mn, Fe, and other matrix concentrations can be so high that they cause significant background signals and in some instances cause direct spectral overlap. In the case of

TABLE 4

Interference Data in DCP (ref. 102)

Element	Sensitive wave length nm	Matrix Elements, 100 mg.L^{-1}									
		*Al	Ca	Fe	Mg	Ti	W	Th	U	V	Nd	La
La	408.672	0.008	0.1	0.01	0.005	-	-	-	-	-	-	
Ce	418.660	0.06	0.3	0.1	-	-	0.3	-	2	-	-	
Pr	440.882	0.01	0.3	0.06	0.03			4		8	3	2
Nd	430.538	0.04	0.4	0.05	-	-	-	1	-	-	-	-
Sm	443.432	0.06	0.9	0.05	0.01	-	-	1	-	-	2	2
Eu	381.967	-	0.02	0.01	-	-	-	0.02	-	0.03	3	-
Gd	364.619	0.008	0.02	0.4	0.02	0.2	0.4	0.5	2	-	-	0.2
Tb	367.635	-	0.04	0.1	-	0.2	0.1	3	3	0.9	-	-
Dy	353.173	-	0.008	0.01	0.1	-	-	0.3	0.3	-	-	-
Ho	404.544	0.03	0.3	1	0.02	-	2	-	-	-	-	-
Er	369.265	0.02	0.03	0.06	0.01	-		0.4	0.7	0.1		
Tm	313.126	0.01	0.007	0.005	0.005	0.3	-	-	-	-	-	-
Yb	328.937	0.001	0.002	0.02	0.002	0.4	-	-	-	3	-	-
Lu	261.542	-	-	0.07	-	-	2	-	-	-	-	-

*Equivalent analyte concentration mg. L^{-1}

direct overlap, the operator must select a line different from the usual one for the element of interest.

Enhancement of spectral lines by matrix constituents has been reported to occur in DC plasma jets. This effect is most likely to occur in cases in which easily ionizable elements are present in large concentration. In such situations, it is advisable to use some form of matrix matching or matrix buffering - e.g. through addition of lithium to all solutions. The most satisfactory method is to isolate the analytes of interest from the matrix by employing some kind of effective separation technique. Recent extensive examinations of DCP jet enhancement interferences have not determined conclusively either the true nature of the interferences or the extent of the elements affected (88). A cursory examination of the literature shows that DC plasma jets have not been studied as thoroughly as other types of emission sources. Nevertheless, DC plasma jets are being used in many laboratories to provide reliable atomic emission analyses for a wide variety of constituent sample determinations.

Separation techniques: Since the REE are present in certain rock samples at PPM or sub PPM levels, separation of these elements as a group ordinarily should precede the analysis. This separation not only allows for preconcentration of the REE so that lower detection limits are possible, but also signifies the analytical problem of matrix effects, when geological samples of widely varying composition are encountered.

As described in the section on NAA, nearly every type of separation of the REE from a matrix can be found in the literature. In most cases ion exchange, extraction procedures and precipitation steps are suggested (91-94). One of the most interesting refinements is to concentrate the REE with the aid of a carrier. Yttrium has been used by Hettel and Fassel (89) as a carrier because its ionic radius is about the same as for Tb^{3+} and Dy^{3+}, so that in chemical properties yttrium is right in the middle of the rare earth series and closely resembles the whole group. Its emission spectrum is relatively simple, so that detection limits are not hampered by interfering matrix lines. Furthermore, any separation scheme devised can easily be monitored by a radioactive tracer, ^{90}Y, which is a β-emitter and easily obtained from ^{90}Sr. Non rare earths, such as Ca and Al (90) have also been used as carriers, particularly with precipitation separations.

ICP or DCP techniques together with creative sample preparations and elemental separations have lent themselves to a variety of geochemical applications, thus allowing for greater geochemical interpretation. An interesting separation and preconditioning scheme for the analysis of rare earth elements is described by Crock and Lichte (95). The method involves a low temperature multiacid digestion using hydrofluoric, nitric and perchloric acids. This is applicable when the REE are not present as resistant minerals (96). If

resistant minerals such as zircon are present a lithium metaborate fusion is used. After dissolution the sample is taken up in 50 ml of IN HNO_3. The solution is loaded on to a AG50W-X8 cation exchange resin that is pre equilibrated with IN nitric acid. The sample is then eluted with 130 ml of 2N nitric acid which is discarded. The REE content of the sample is eluted with 50 ml of 6N HNO_3 and 50 ml of 8N HNO_3 and the elutes are evaporated to dryness and the residue taken up in 10 ml of 8N HCl and loaded on to a pre-equilibrated AG1-X8 anion resin. The sample is eluted with 30 ml of 8N HCl, evaporated to dryness and taken up in 30% HCl for REE determination.

A gradient elution with nitric acid first removes most of the metal cations such as Al, Be, Ca, Mn, Th, Ti, U, V, and Zr from sample solutions. Iron is removed as a chloro-complex on an anion exchange column. The final solution contains predominantly REE and Y with minor amounts of other elements. One gram of sample can easily be taken up in 5 ml of 30% HCl. The authors claim that the procedure minimizes interelement corrections if it does not totally eliminate them. The authors have not mentioned scandium. separation from the lanthanides. They demonstrated the applicability of this procedure for trace analysis of certified standard geological samples for the lanthanides and yttrium. In the case of silicic samples one is in the favourable position of being able to evaporate silicon completely from the matrix; therefore some-

what larger sample amounts would lead to higher concentration of the traces under investigation.

The analysis of inorganic materials by the ICP technique exhibits a wide range of applications. A review of trace element determination in steels by Koch (97) discusses the use of ICP. The literature on emission techniques with respect to analysis of geological materials has been reviewed by Dinnin (98), Boyko et al (100) and Moore (101). Kiesl reviewed analysis of terrestrial and extraterrestrial materials dealing with the various steps of analytical chemistry required to reach satisfactory results, such as sampling, sample preparation, etc. (99). Emission spectroscopy is certainly one of the most useful analytical methods available for REE and will undoubtedly continue to be the method of choice.

Spectrophotometric Analysis

The absorption of radiation in the ultraviolet and visible range of the spectrum has been employed in analysis since the proposal of a general law for absorption of radiation by Beer in 1852. Beer's law (sometimes referred to as the Beer-Lambert or Borguer-Beer law) states that when a coherent monochromatic beam of light passes through a homogeneous absorbing medium, the radiant power will diminish in proportion to the number of absorbing molecules or ions in the light path. Mathematically this may be stated as

$$\log \frac{P_o}{P} = \log \frac{1}{T} = A = \epsilon bc$$

where

P_o = incident radiant power

P = transmitted radiant power

T = transmittance

A = absorbance

ϵ = molar absorptivity

c = concentration in moles per litre

b = thickness of cell in cm.

Adherence to Beer's law is one of the desiderata of a good analytical procedure.

Absorptiometric analyses in the visible and ultraviolet region can be carried out directly on the aquocomlexes of some of the lanthanides without the use of a secondary color forming agent. Although lanthanide absorption bands are sharp, their molar absorptivities are not as large as those of the colored complexes normally used in spectrophotometric analyses. Therefore, in the quantitative determination of the rare earths and thorium, the method normally involves the complexing of the analyte with an organic dye and the resulting change in the optical properties of the dye is measured. The colored solution differentially absorbs light of different wave lengths, the amount of metal-specific absorption being related to concentration of the analyte. Ease and simplicity are often compelling reasons for the selection of a spectrophotometric method of analysis of geological materials. In fact, color comparison can be applied

in the field without the aid of instruments (103). The continual increase in the number of applications has been documented in excellent review articles by Hargis and Howell (104). Comprehensive discussions of individual methods and experimental procedures for dealing with a variety of materials, including water, ores, rocks, and soils are given in standard texts such as those of Sandell (105) and Snell and Snell (106). The book by Jeffrey (40) is a valuable source of procedures dealing particularly with silicate rock analysis.

The molar absorption coefficients of most species used in trace analysis range from approximately 10^3 to 10^5 cm^{-1} mol^{-1} dm^3 at the wave length designated λmax, where ϵ has its greatest value. This enables many elements to be determined in geological materials at concentrations above about 0.1 $\mu g \cdot g^{-1}$, provided adequate separations can be achieved from the matrix.

Errors of photometric methods

As with other methods, spectrophotometric methods are subject to interferences. Apart from the obvious errors that arise from faulty procedure and from the instrument, serious interferences occur due to the presence of foreign substances. Very few color reactions are absolutely specific. Specificity and selectivity are relative terms, a matter of the degree of freedom from interference. Foreign substances may cause masking effects or render the desired color reaction unstable. The major constituent in which the trace impurities

are to be determined may be considered as a foreign substance which can cause errors simply because of its large quantity. More extensive discussion of absorptiometric errors can be found in the literature (107, 108) and in standard analytical texts.

Methods of determination of the rare earths and thorium with chromogenic reagents

Rare Earths:

The majority of methods for the determination of rare earths and thorium involve reaction with a chromogenic reagent to form a product with a high molar absorption coefficient. The choice of the reagent is governed by many factors such as simplicity and rapidity of the chemical procedure, chemical stability of the absorbing species, sensitivity and specificity. Because the reagents are seldom specific, chemical treatment is often essential, apart from the initial process of bringing the sample into solution. Several chromogenic reagents used for the determination of trivalent rare earths are shown below.

Element	Reagent	Reaction Conditions	Molar absorptivity ($Cm^{-1}mol^{-1}dm^3$)	Selectivity
Lanthanides	Arsenazo-III	pH 1-4	$5.5\text{-}6.5X10^4$	low
	Arsenazo-I	pH 1-4	$1X10^4$	low
	Antipyrine S	pH 2.5	$1X10^5$	low
	Alizarin red S		$1X10^4$	
	Carboxynitrozo (Ce)	pH 2-4	$1.6X10^5$	high
Thorium	Thoron (I)	pH0.7-1.2	$1.2X10^4$	high
	Arsenazo-III	pH 1-2	$1.2X10^5$	high

None of these reagents is specific for rare earths except Arsenazo-III which has been reported by Savvin (109) to be more selective. Cations which have radius of less than 0.7-0.8 °A show no color reactions with Arsenazo-III. These include elements commonly found in geological samples such as Al, Be, Ge, Ti, Sn etc. This reagent also forms complexes with a large number of other elements including thorium, uranium and zirconium at low pH and iron, yttrium, scandium and other elements at higher pH. Also interfering are oxyanions such as phosphate and sulfate which inhibit color formation.

Goryushina et al (110) developed a procedure to determine rare earth elements. To apply this photometric procedure it is necessary to separate the rare earth elements from all other elements that react with Arsenazo-III. This is accomplished by precipitation as hydroxides with ammonia, followed by precipitation as oxalates with calcium added as carriers.

Other methods used include precipitation with sodium hydroxide to remove aluminium and the alkaline earth elements, precipitation with hydrofluoric acid to remove iron, titanium, zirconium and other elements forming soluble fluorides, and chlorination to remove elements that form volatile chlorides including iron, titanium, aluminium and zirconium. A variety of procedures for determining total rare earths have been based upon combinations of these separation procedures. In most of these procedures there is a significant loss of rare earths amounting to 3-25%. Aladjem (111) has summarized much

of the information prior to 1966 on the spectrophotometric determination of the rare earths. Cerium is the only lanthanide that can be determined selectively in the presence of the other rare earths. This is possible by the oxidation of Ce (III) to Ce (IV). The latter quantitatively reacts with many colored reagents and organic dyes e.g. Tris-(1, 10 phenanthroline) iron (II), (Ferroin).

Thorium:

Among the reagents proposed for thorium, Arsenazo-III is appreciably more sensitive and in addition can be used in fairly strong acid solution (112, 113). This gives increased selectivity to thorium and only zirconium, hafnium and U (IV) interfere. Within limits zirconium and hafnium can be masked by oxalic acid, whilst uranium can be oxidized to U(VI).

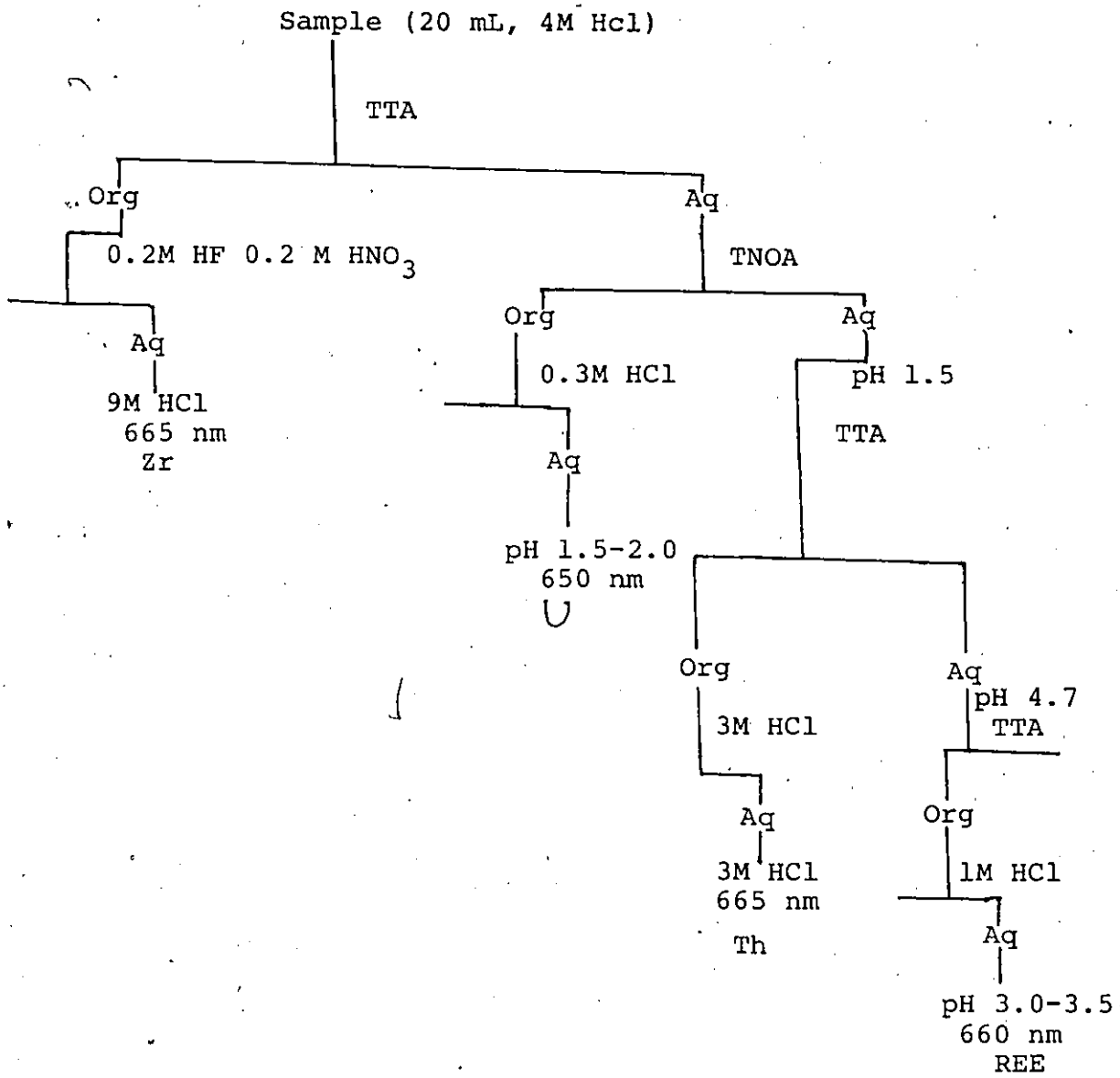
Ion exchange, column chromatography, solvent extraction and precipitation methods have all been advocated for the separation of thorium. None of these methods gives a complete separation in a single operation, and a number of authors have suggested combinations of two or more procedures. Anion exchange resins have been used to remove those elements that form anionic complexes in chloride solution from thorium and other elements that do not (114). Since rare earths interfere in the determination of thorium with Arsenazo-III, Korkisch and Dimitriadis (115) used an anion exchange resin in the nitrate form, eluting rare earths and other elements with nitric acid before recovery of thorium with 6M hydrochloric acid. A procedure for

determining zirconium, thorium and uranium in silicate rocks, all with Arsenazo-III following anion exchange chromatography in sulphate media has been described by Kiriyama and Kuroda (116). Culkin and Riley (117) used a solvent extraction procedure with tributyl phosphate to recover thorium, zirconium, hafnium and cerium from silicate rocks and to separate these elements on a column of cation exchange resin. Oxalic acid solutions were used to elute zirconium, hafnium and thorium and hydrochloric acid to elute cerium. The procedure developed by May and Jenkins (118) involves the decomposition of the sample by hydrochloric and nitric acids. Thorium and the rare earths are precipitated together as fluorides with calcium as carrier. Precipitation with potassium hydroxide and potassium iodate are used to complete the separation of thorium from other elements before photometric determination of thorium with Arsenazo-III.

A systematic separation of zirconium, uranium, thorium, and rare earths and subsequent photometric determination with Arsenazo-III was developed by Onishi and Sekine (150). Each metal is back extracted from the organic phase before determination. The outline of the procedure is shown in Figure 3.

Although some separations are inevitable in certain cases the need for separations can be avoided by the use of masking agents. The use of such agents in spectrophotometry and other analytical procedures has been well covered by the

Figure 3. Outline of Procedure: (ref. 150)



TTA - thenoyl trifluoroacetone

TNOA - tri-n-octylamine

Org - Organic phase

Aq - Aqueous phase

book by Perrin (119). For example, Savvin et al (109) described a spectrophotometric method for the determination of La, Ce, Pr and Nd in the presence of a 650 fold excess of Te(III) based on the color reaction of the rare earths with carboxynitrozo. Interference by Fe(III) and the heavy rare earths was suppressed by the addition of EDTA.

In conclusion photometric methods, especially for elements such as cerium and thorium, continue to be of interest, in spite of recent developments in the areas of AAS and ES, which make these methods superior for the determination of trace amounts of individual rare earths. New, more sensitive and selective reagents have been synthesized. In addition, techniques such as extraction photometric methods and the use of competing ligands to improve the selectivity of chemical methods continue to make spectrophotometric methods attractive. Moreover, although strong claims are made for the specificity of NAA and ICP spectroscopy, a certain amount of interelement interference still occurs (95).

OBJECTIVES OF THE INVESTIGATION

Investigations of certain problems in the chemical analysis of lanthanons and thorium at trace levels in rock samples forms the general subject of this thesis. The analyst in setting about the determination of the rare earths is presented with a difficult task, in view of the increasingly rigorous requirements of versatility, specificity, sensitivity and accuracy. At present, many trace elements can be determined at $ng \cdot g^{-1}$ and $pg \cdot g^{-1}$ levels with satisfactory accuracy and precision by using proper analytical techniques, that however involve a number of difficult problems. These difficulties mainly arise from low concentration of trace elements in various matrices. During the past two decades rapid development of electronic instrumentation has created powerful tools for trace element research. However, with geological, environmental, and biological samples, these tools can give erroneous results because of matrix effects when the limitations of the devices go unheeded.

This thesis is "sample-oriented"; that is, techniques for opening up, separations, and isolation of the analyte will occupy our attention ahead of the instrumentation used for the finish. We shall be at pains to emphasize the problems of handling real field samples. This has not been the case in some of the recently published work on the rare earths. Since one technique alone can seldom solve all the

problems presented in trace analysis of complex samples, an integrated approach was necessary. Multi-step procedures have been devised for thorium and lanthanides respectively. The reader is urged to believe that the costs in time of a multi-step procedure are amortized by the savings effected in avoiding errors.

In this thesis an attempt is made to answer the questions listed below.

(i) What are the special problems in trace analysis of f-series elements in rock samples?

(ii) Is there a powerful suitable flux, whose salt can easily be separated from the analyte species after fusion?

(iii) How does thorium behave in a strongly acidic cation exchange column in the presence of anions such as carbonate and phosphate?

(iv) How well can reversed phase partition chromatography be utilized in the separation of rare earths from rock samples?

(v) Is it possible to make separations of lanthanides into groups by employing the simple reversed phase chromatographic made at microgram levels?

CHAPTER III

POTASSIUM SUPEROXIDE AS A FLUX IN ORE AND ROCK ANALYSIS

The first step in a wet method of analysis is to put the sample into a suitable solution. An accurate analysis depends on the choice of reagents for decomposition, dissolution and subsequent separation of individual components of the sample. The development of such methods began with the alchemists. The earliest method utilized was thermal decomposition which served to liberate noble metals and mercury. The use of nitric and sulfuric acids was described in a 13th century Byzantine manuscript. Wet digestion with acids such as HNO_3, H_2SO_4, HF, HCl and $HClO_4$ are best suited for large sample throughputs and sample weights. Attention must be given to problems of contamination, losses of elements by volatilization and incomplete digestion of some refractory samples.

The conversion of rocks, minerals and ores to a soluble form often requires decomposition by fusion with a flux. M. H. Klaproth's (1743-1817) technique of fusing geological samples with potassium or sodium carbonate in a silver or platinum crucible greatly facilitated the analysis of minerals, especially silicates. Numerous other fluxes, acidic and basic, oxidizing and nonoxidizing, have been investigated since the time of Klaproth for use in decomposition of organic as well as inorganic materials (120, 121). Decomposition methods have to be reasonably rapid, should not

result in loss of analyte sought or contamination by interfering substances from vessels or added reagents. Fluxes should not introduce excessive amounts of salts and the flux salt must easily be removable from the analyte of interest. The chosen method must liberate or convert the analyte completely into a readily measurable form and ideally it should not require unusual or elaborate equipment. No universal decomposition method exists, so the analyst must often display patience and ingenuity in order to achieve the best compromise for each sample type met with.

In a program of rock analysis for earths at sub-p.p.m. levels, we have found it necessary to work with large samples and to effect a considerable reduction in the volume of sample solutions in order to achieve the desired concentrations of analyte. This presents no unusual problems when the rock is completely soluble in acids, but if it is necessary to resort to a fusion, the large quantity of added salt introduces the need for additional steps with their attendant uncertainties. If the analyte species are to be separated from the bulk of the salts, there is a problem of ensuring quantitative behaviour on the part of these species. This generally requires the addition of carriers which is effective when one employs neutron activation analysis followed by radiochemical separations. We have sought to avoid radiochemical techniques and have therefore chosen to remove the bulk of the sample salts that derive from the flux while

leaving the trace analytes in solution. While this is normally difficult, it is not impossible, in trace analysis.

It is in the nature of certain rare earth-containing rocks that a strongly alkaline and oxidizing fusion must be employed. Sodium peroxide is most commonly recommended as the flux. This substance is particularly effective for the decomposition of ferrosilicon, chromite, iron ores, platiniferous minerals, etc. Occasionally, procedures entailing the use of other peroxides, i.e. MgO_2 (123) and BaO_2 (124) have been recommended, but these peroxides do not long survive at elevated temperatures unless they are used in conjunction with alkali.

The separation of sodium salt is not straight-forward as it has been shown that in several suggested procedures selectivity was low and applicability was limited to a few particular cases (125, 126, 127). Girardi et al (128) have succeeded in selectively removing sodium by passing a strongly acidic sample solution through a column of hydrated antimony (V) oxide. However, the procedure is not promising for the separation of large quantities of sodium on a repetitive basis because the column cannot be regenerated.

In certain respects, the past can indeed reveal the future, at least with regard to further progress in sample treatment prior to analysis. In 1966, Suhr and Ingamells (129) suggested lithium metaborate ($LiBO_2$) as a fusion medium

for most siliceous rocks. This salt can be used to prepare samples for x-ray fluorescence. The authors also showed that the $LiBO_2$ melt can easily be converted to a stable acid solution by quenching and dissolving the melt in 3% HNO_3 (129). Silica does not precipitate. An excellent discussion of the use of lithium borate fusion in rock analysis is included in a review by Abbey, Aslin and Lachance (130).

Although this appears to be an attractive technique for the determination of lanthanides in rock samples, there are certain difficulties. Experiments performed on 200-500 mg samples of a variety of rocks and ores showed turbid solutions on quenching with 3% HNO_3 (131). In other cases, most of the quenched melt dissolved but a residue remained or a precipitate formed. These residues are usually small enough to be ignored if one is analyzing for major components. In trace determination of lanthanides, however, these residues or precipitates might well contain most or all of the trace lanthanides. Isolation and dissolution of such residues is difficult and the desired advantage of speed is sacrificed.

The residues might be produced in one or more of the following ways.

(i) Incomplete Attack: Trace elements often exist in rocks in the form of a few small discrete grains of a particular mineral. These grains might not be completely dissolved by the fusion procedure.

(ii) Conversion to Carbides: Several elements such

as Cr, Ti, W, Nb, Ta, Hf, Zr, Th, lanthanides may react with the walls of graphite crucible to form very stable carbides at high temperature. These carbides might not be dissolved by the acid solution used to dissolve the melt.

(iii) Hydrolysis: In the 3% HNO_3 solution suggested by Suhr and Ingamells for dissolving the melt, several elements (e.g. Sn, Ti, W, Nb, Ta) can produce insoluble hydrolysis products which in turn might adsorb the trace lanthanides.

(iv) Intercomponent Reactions: Phosphate and sulphate present in many rocks, can react with many of the above mentioned elements and others, to produce insoluble metal sulphates and phosphates in 3% HNO_3.

(v) Suspension of Graphite Particles: After dissolution of the melt, the solution sometimes contains graphite particles. However, it is never possible to be sure that all of the black particles seen in a particular solution are graphite.

Since quantities of lanthanides in natural rock samples are often in the order of micrograms, the types of behavior mentioned above would be difficult to identify experimentally, especially if the sample weight taken for analysis is small. We have therefore chosen rather to avoid the use of the above fluxes altogether and have employed potassium superoxide, KO_2, as a new strongly basic, oxidizing flux.

KO_2 is available commercially and it was found to be as effective as Na_2O_2 for decomposing various rock samples.

We normally use the potassium superoxide in admixture with KOH, the latter being added in order to reduce the cost of a sample analysis. We can now report a successful procedure.

Decomposition procedure: The powered rock ore is mixed with flux in the ratio of 1 part sample to 3 parts flux by weight. The flux is prepared by grinding a mixture of KO_2 (Alpha Ventron, Inc.) and KOH in a 1:3 ratio by weight. The sample-flux mixture is cooled and dissolved in dilute hydrochloric acid.

A nickel crucible suffered attack as expected but the zirconium crucible showed very little corrosion. Three standard reference materials* were tested and each one was fully decomposed. We were unable to judge whether KO_2-KOH differed from Na_2O_2 in ability to decompose silicate materials. The choice of the KO_2-KOH mixture would be governed by the need to remove the excess alkali salt from the sample solution. In some instances, one may wish to determine sodium and the KO_2-KOH flux, if sufficiently free of sodium, could be used to open up the sample.

Experiments were conducted to determine the efficiency of separation of the potassium from a selection of analytes at trace levels. We chose as analytes ions with charges from

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* The materials were the following: United States Geological Survey No. BCR-1, a basalt certified for rare earths; Energy Mines and Resources, Ottawa, Canadian Certified Reference Materials Project Nos. SY-2 and DL-1a. The former was a lanthanide-containing syenite and the latter was an arkose sandstone certified for uranium and thorium.

+1 to +4. These were namely Ag^{+}, Ca^{2+}, Eu^{3+}, and Th^{4+}.

Experimental

Materials: Carrier-free tracer quantities of ^{45}Ca and ^{152}Eu were supplied by Amersham Co., Arlington Heights, IL. ^{234}Th was isolated from uranyl nitrate by extraction with cupferron (132). Experiments with milligram quantities of the four analytes were carried out with aliquots of standard solutions of nitrate or perchlorate salts.

Determinations: A Beckman model 3133P scintillation counter was used for radio-chemical determination of ^{45}Ca and ^{234}Th. Aquasol-2 and Sentiverse were used as "cocktails" for ^{45}Ca and ^{234}Th, respectively. A gamma-ray spectrometer with a NaI(Tl) detector was used to count ^{152}Eu.

Thorium was also determined by a spectrophotometric procedure which made use of the complex with Arsenazo-III (133). The reagent was supplied by Aldrich Chemical Co. and was used as an aqueous solution with a concentration of 0.5 mg mL^{-1}.

Silver was determined turbidimetrically as AgCl (134).

Turbidimetry

Turbidimetry is an important analytical method which is based on the scattering of radiation by particulate matter (136). The suspension is placed in a spectrophotometer cuvette and the transmittance is measured with an ordinary spectrophotometer.

When light passes through a transparent medium in which solid particles are dispersed part of the radiation is scattered in all directions, giving a turbid appearance to the mixture. The diminution in power of a collimated beam as a result of scattering by particles is the basis of turbidimetric methods.

The attenuation of a parallel beam of radiation by scattering in a dilute suspension is given by the relationship

$$P = P_o e^{-\tau b}.$$

Where P_o and P are the power of the beam before and after passing through the length b of the turbid medium. The quantity τ is called the turbidity coefficient, or the turbidity; its value is often found to be linearly related to the concentration C of the scattering particles. As a consequence, a relationship analogous to Beer's law results; that is

$$\log_{10} \frac{P_o}{P} = KbC \qquad (1)$$

where $K = 2.5\,\tau/C$.

equation (1) is employed in turbidimetric analysis in exactly the same way as Beer's law is used in photometric analysis. The relationship between $\log_{10} \frac{P_o}{P}$ and C is established with standard samples, the solvent being used as a reference to determine P_o. The resulting calibration curve is then used to determine the concentration of samples.

Liquid Scintillation Counting as an Analytical Tool

Liquid Scintillation Counting (LSC) is the most sensi-

tive and versatile technique for the detection and measurement of radioactivity. The basic organic scintillator consists of a solution of one or more fluorescent aromatic solutes dissolved in an aromatic solvent (usually toluene or dioxan). The energy of the primary particle emitted by a radioactive sample is converted into light and a photomultiplier responds to this light energy by producing a charge pulse which can be amplified and counted by a scaling circuit. The technique is commonly used for counting a wide range of α and β emitting isotopes in many chemical forms.

In any method for radiation detection, the counting efficiency (the ratio of the observed counting rate to the rate of radioactive disintegrations in the sample) is greatest when the maximum number of emitted particles reaches the detector and interacts with it in the desired way. Losses in efficiency result when the particles escape in directions away from the detector or are stopped in it by some mechanism which does not result in a count. Beta rays lose their energy in passing through matter much more quickly than do x-rays or γ-rays of comparable energy, and thus have much shorter ranges. Absorption within the sample and between the sample and detector is most severe for low energy β-particles. In order to avoid such losses and to count with high efficiency, the distances to be travelled must be reduced as much as possible. This is the great advantage achieved in liquid scintillation counting.

In contrast to other nuclear detection methods such as Geiger-Muller or proportional counting or detection with NaI(Tl) crystals or semiconductor detectors, counting by LSC is unique in that the size and shape of the detector is flexible and usually is defined by the container. Most commercial counting systems consist of two phototubes and screw cap vial as in the arrangement in Figure 4. In general the radioactive substance is put into intimate contact with the scintillation solution by dissolving it, suspending it, or immersing it in the liquid solution of fluors. The whole "counting sample" then consists of the radioactive material, or solvent system, and scintillation solutes. Solvents are designated as primary or secondary according to their relative abundance and comprise the bulk of the counting sample. The scintillation solutes are designated as primary or secondary according to their function in the scintillation process, which may be outlined as follows (137). 1. The energy of the primary particle is transferred to the solvent. It may appear as energy of ionization, or excitation of the solvent molecule. It is the electronic excitation energy of the solvent which contributes most to the eventual formation of light quanta (138). Only about 5% of the total energy absorbed from a beta ray appears eventually as light. The remainder is degraded to quanta of lower energy (heat), or is consumed in chemical changes. 2. The excitation energy of the solvent is transferred to the molecules of the primary solute which is a fluor. This is

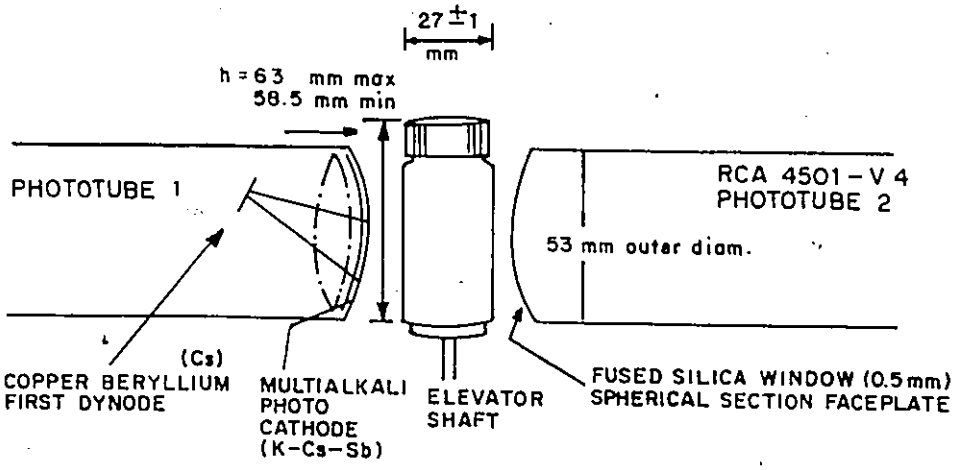


Figure 4 – Schematic diagram of standard counting vial and phototubes used for typical commercial LS counter (Packard TriCarb 3320).

believed to occur within approximately 10^{-9} seconds. 3. The excited molecules of the fluorescent solute return to the ground state by emitting quanta of light in the visible or near ultraviolet region. 4. If a secondary solute is present, it may absorb this light and re-emit it at a longer wave length. The purpose of introducing this solute is the achievement of a better match between the emission spectrum of the counting sample and the spectral response of the photocathode which detects the light.

The composition of individual scintillation systems varies and is designed for a particular use or type of sample. Commercial scintillation "cocktails" are available for sample preparation. A serious limitation of this technique is the variable efficiency caused by a reduction in the light quanta (quenching) due to the presence of certain chemical impurities or color formation. Therefore sample preparation for final detection is extremely important.

For many years workers have been incorporating inorganic isotopes into liquid scintillators (139). In a review on this subject Coursey and Moghissi (140) reported that 76 radionuclides of 57 different elements have been assayed using LSC techniques. McDowell et al used this technique for the determination of α-emitting actinides in phosphatic materials (141).

In our studies we have employed this technique for counting ^{234}Th and ^{45}Ca which possesses very favorable

characteristics, and decay through β-emission with half lives of 24.1 days and 164 days respectively. The E_{max} values for ^{234}Th and ^{45}Ca are favorable, being 0.263 and 0.254 MeV, respectively, and this provides good detection efficiency. There is a minimum of chemical preparation.

General procedure for potassium separation

An aliquot that contained between 1 and 10 mg of one of the selected analytes, Ag^{+}, Ca^{2+}, Eu^{3+}, or Th^{4+} was added to 50 mL of a solution that contained 225 mg of potassium as nitrate. The solution, contained in a 50 mL beaker, was cooled in ice and excess cold perchloric acid (20%) added. The precipitate was separated by filtration and washed with more of the acid.

^{152}Eu in $KClO_4$ precipitates was determined by counting the solid on a Metricel membrane filter disc. Counting was done at 0.24 Mev. In the case of the other ions, the precipitates were dissolved in hot water and the determinations carried out by one of the procedures specified earlier. Determinations were carried out similarly on the filtrates.

The results are shown in Table 5 . In the case of the radioactive ions, experiments similar to those described above were also carried out with carrier-free tracer quantities. The results of these separations were in general similar to those shown in the table except that the reproducibility was not as good.

TABLE 5

Percentage of Selected Cations Distributed Between $KClO_4$ Precipitate and Filtrate

Cation	No. of determinations	Percent found	
		precipitate	filtrate
Ag^{+}	4	10.9 ± 1.4	89.2 ± 1.4
$^{45}Ca^{2+}$,a,c	5	3.6 ± 0.4	96.5 ± 0.7
$^{45}Ca^{2+}$,b,c	3	0.8	
$^{152}Eu^{3+}$,c	5	0.3	
$^{234}Th^{4+}$,c	3	0.3	
Th^{4+},d	5		99.9 ± 0.4

a - Found in first precipitate and filtrate

b - Found after reprecipitation

c - Radiochemical determination. 2-10 mg of non-radioactive ion was present as well in each case

d - Determined spectrophotometrically with Arsenazo-III

DISCUSSION

With Eu and Th, the separations were efficient and quantitative after a single precipitation. Calcium required a reprecipitation of the $KClO_4$. Silver caused significant contamination of the precipitate. The behaviour of the four ions follows Goldschmidt's Rules which dictate that the contamination of a crystal should be minimal if the radius and/or charge of the foreign ion is dissimilar to that of the ions of the host substance. The crystals of $KClO_4$ are dense and very well formed and this leads us to feel that the behaviour of other ions also will be found to conform to Goldschmidt's rules. Of course it is important to add the perchloric acid to the sample rather than add the sample to the acid if co-precipitation of cations is to be minimized. Some divalent ions which have radii close to that of K^+ are Sr^{2+}, Ba^{2+}, Sn^{2+}, and Pb^{2+}. A decision as to whether or not these can be recovered quantitatively after a double precipitation must await further investigation.

The validity of our claim that KO_2-KOH is a useful flux has been tested by carrying out thorium determinations on the standard ore DL-1a (see footnote earlier). This work is reported elsewhere (133). In this connection we may point out that the small amount of unprecipitated potassium does not interfere with the determination of thorium with Arsenazo-III. This would not have been the case had Na_2O_2 been used as flux, for sodium interferes seriously with this reagent.

In our work, in which neutron activation follows the initial sample treatment, it is essential to achieve a quantitative retention of the trace analyte species with a minimum of interference from reagent material. Fortunately, the reagents that we use lead to acceptably small blank values. Potassium has a lower thermal neutron cross section than does sodium and the ^{42}K isotope produced upon irradiation has a shorter half life (12.4 h) than the sodium isotopes ^{24}Na(15.0 h) and ^{22}Na(2.60 y). Thus the interference by these latter two isotopes in γ-ray spectra may preclude the use of Na_2O_2 as a flux.

It is interesting to put KO_2 as flux into an historical context. Some excellent publications (120, 121, 122) deal with decomposition procedures and it appears from these that salts used for promoting fusion are limited to those that contain one of the following six anion types: CO_3^{2-}, $S_2O_7^{2-}$, O_2^{2-}, F^-, OH^-, BO_3^{3-} and polyborate. In addition, it was recognized in the time of Agricola, that fusion of certain oxides was facilitated by adding silica as well as alkali (135). This is a practice which seems to have fallen into disuse. Thus superoxide, after some centuries of analytical science, joins a very short list.

CHAPTER IV

PROCEDURES FOR ISOLATION AND DETERMINATION OF THORIUM

The generation of nuclear fission energy has led to the production of large quantities of actinides. The reprocessing, transport and storage of spent fuel and the permanent disposal of high level waste etc., carry a risk of accidental releases of actinides to the environment. Substantial amounts have already been spread as fallout from weapons testing and from processing facilities. The presence of actinides at significant concentrations in ecosystems would present a major health hazard. Therefore, it is of prime importance to characterize and model the chemical behaviour of the actinides in terrestrial and aquatic environments, particularly for the transuranic elements which do not normally exist in nature. The sources of these elements are both thorium and uranium which are relatively common elements in the earth's crust. Thus there is considerable interest in the behaviour of trace levels of the actinides in the environment, in particular of thorium and uranium. It is expected that thorium will be used as a nuclear fuel and this makes it important to determine it in the pregnant liquor and raffinate of uranium process streams if it is to be stockpiled now. Natural thorium is predominantly ^{232}Th which is an α-emitter of such low specific activity that the direct radiochemical determination of this element is not a sensitive method of analysis. Therefore a more sensitive chemical method of determination should be developed. Methods for thorium determination must incorporate a separation from the rare earths and other interfering elements such as U, V, Mo, Fe etc.

Separation of thorium from solutions that contain significant amounts of phosphate can be incomplete (142). Carbonate also complexes thorium strongly. As carbonate and phosphate are important constituents of ground water and other natural water systems, these two anions may play an important role in the complexation, adsorption, and other separations of thorium in natural samples. Phosphate is present in uranium process streams also.

Cation exchange is frequently used to isolate thorium from interfering elements, but published data do not lead to unambiguous predictions of the behaviour of thorium in the cation exchange process when carbonate and phosphate are present (143, 144). We have therefore investigated the absorption and recovery of thorium at microgram and tracer quantities as a function of pH. As the ion-exchange procedure is time-consuming owing to the necessity of evaporating a considerable volume of sulphuric acid (the eluate), an alternative method of separating phosphate was developed. This was incorporated into a complete method for thorium determination which was tested in the presence of uranium, molybdenum, and vanadium.

Preparations and General Experimental Procedures

Two methods, photometric determination with Arsenazo III and radiochemical counting, were used for determining thorium. Photometric readings were made with a Unicam Model

Sp 1800 spectrophotometer and ^{234}Th counting was done with a Beckman Model 3133P scintillation counter.

Standard thorium solution. $Th(NO_3)_4 \cdot 4H_2O$ (Baker, A.R.) was used as supplied. A stock solution containing 100 ppm Th was prepared by dissolving the salt in double distilled water and adding HNO_3 to give a final acid concentration of 1 M. The solution was standardized gravimetrically by evaporating aliquots to dryness in a crucible and igniting. Working solutions were prepared freshly by diluting the stock solution with 1 M HNO_3 to 5 ppm Th.

Arsenazo-III solution. A 50 mg quantity of the reagent was dissolved in 90 mL of water and the solution diluted to 100 mL.

Alamine 336 solution. 35 mL of this mixed tertiary amine, obtained from General Mills, Ltd., were diluted with petroleum ether and o-xylene (3:1 mixture, by volume) to 500 mL. Alamine 336 is described by its manufacturer as a water insoluble, symmetrical, straight chain, saturated amine. The alkyl groups are a C_8 - C_{10} mixture with C_8 carbon chains predominating. Its composition is reported as follows: tertiary amine content, 95%; secondary amine content, 1%; primary amine content, 0.2%; water 0.0% (145).

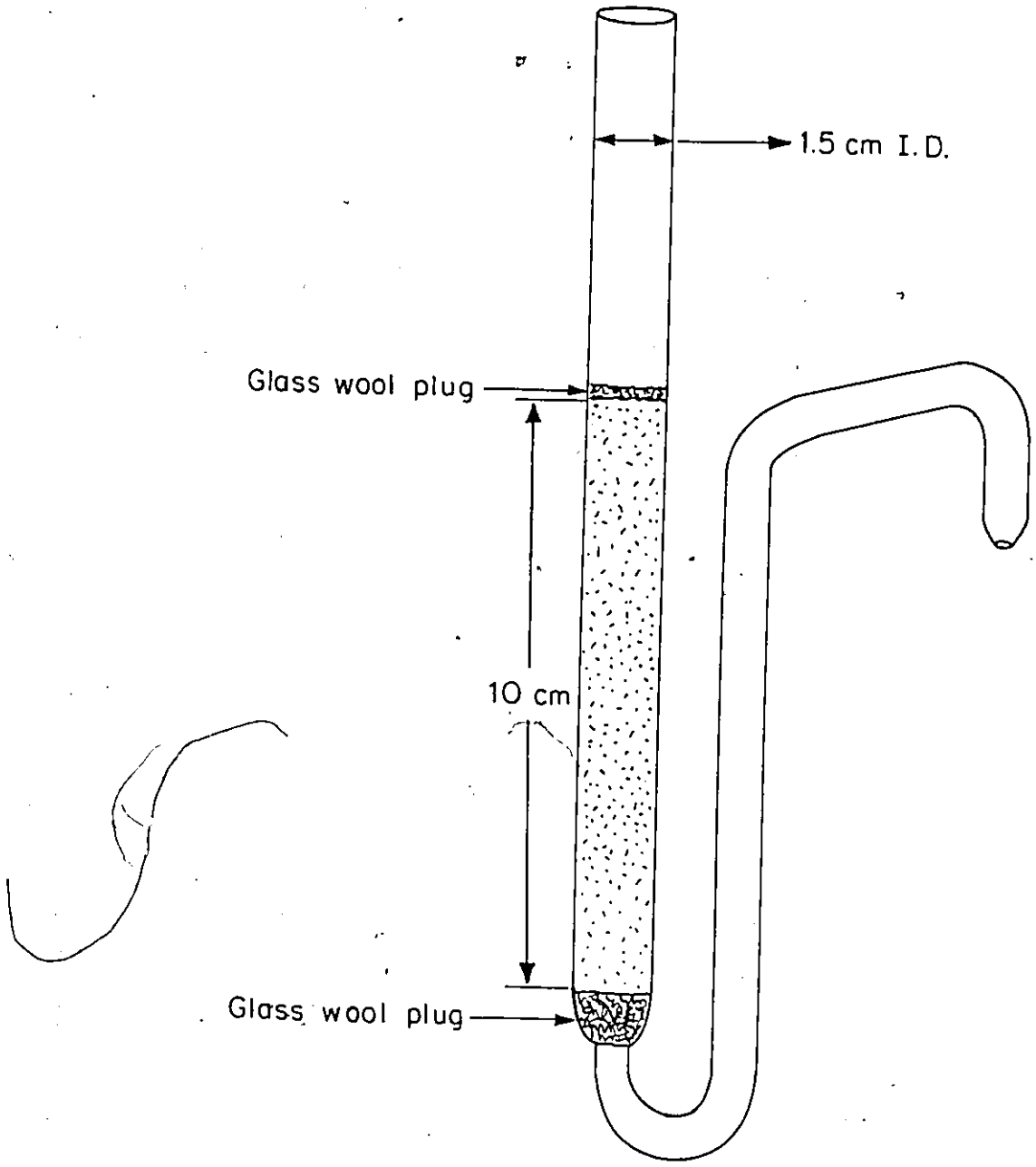
Carrier-free ^{234}Th tracer (132). A 2 g quantity of

$UO_2(NO_3)_2 \cdot 6H_2O$ (Baker, A.R.) in 10 mL water was converted to soluble carbonate complex by addition of saturated $(NH_4)_2CO_3$ solution until the initial precipitate of carbonate dissolved and 2 mL of 6% aqueous cupferron solution was added. ^{234}Th was extracted into 10 mL of chloroform at pH 8-8.5. The extraction was repeated once and the extracts were combined. The ^{234}Th was back-extracted with 10 mL of 3M HNO_3 containing 2-3 mL of saturated bromine water. The aqueous phase was washed twice with $CHCl_3$ and boiled for 2 min. to eliminate traces of $CHCl_3$. The volume was adjusted finally to 25 mL.

Preparation of cation exchange columns. Dowex 50-X8 (20-50 mesh, Baker) in the H^+-form was pre-washed with dilute H_2SO_4 followed by water. The height of the resin bed was 10 cm and the diameter was 1.5 cm. A similar column was converted to the NH_4^+ form by conditioning with 2 M NH_4Cl. See Figure 5.

Procedure 1 - Photometric determination. The sample solution was evaporated to dryness, 5 mL of 70% perchloric acid was added and the solution again taken to dryness after which 1 mL of conc. HCl was added and the solution again evaporated to dryness. One mL of conc. HCl and 5 mL of water were added and the solution was transferred to a 25 mL volumetric flask. A 5 mL portion of 8% W/W oxalic acid solution was added followed by 1 mL of Arsenazo-III solution. The solution was brought to volume with water. Absorbance was measured at 660 nm in a 1 cm cell. A calibration curve was prepared as

Fig.5. Cation Exchange Column.


1.5 cm I. D.
Glass wool plug
10 cm
Glass wool plug

described by Abbey (146) for the concentration range 0-1.2 g mL^{-1}. The standard curve passes through the origin and is valid up to 0.6 ppm. The slope of the curve was 0.58 absorcance units per ppm. Ammonium salts, when present, were destroyed with conc. HNO_3 and HCl (147).

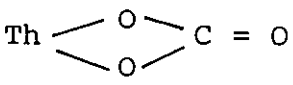
Procedure 2 - Scintillation counting. ^{234}Th was used as a carrier-free tracer. Sample solutions were evaporated to dryness, 1 mL of conc. HCl was added and the solution transferred with H_2O washings to a 20 mL scintillation vial (Fisher). The volume was 12 ± 1 mL at this point. A 3 mL portion of Sentiverse (Fisher) was added and the solution was mixed and counted in an open channel of the counter with the gain set at 280. The efficiency of the counter for ^{14}C (E_{max} = 0.156 Mev) was 95%. Since E_{max} for ^{234} Th is 0.263 Mev, we assume the efficiency for this isotope was in excess of 95%.

Cation Exchange Behaviour of Thorium

Microgram quantities and tracer levels of thorium in 1 M HNO_3 were absorbed by Dowex 50-X8 and recovered by eluting with 0.5 L of 1.8 M H_2SO_4. Procedures 1 and 2 were used in the determinations.

Effect of carbonate. - Solutions that contained 770 ppm of CO_3^{2-} caused cation exchange beds in the H^+ form to break up owing to CO_2 evolution. In the NH_4^+ form the cation exchanger behaved well.

The absorption of thorium from solutions of 1 ppm concentration was oompletely inhibited by the presence of CO_3^{2-} at a concentration of a mg mL^{-1} at pH 10. The relation between percent absorption and CO_3^{2-} concentration is shown in Figure 6 . This behaviour is similar to that of uranium and is attributed to the formation of anionic carbonato complex(es), e.g. $Th(CO_3)_5^{6-}$(143). At higher concentrations of CO_3^{2-} carbonato complexes of the type $Th(CO_3)_5^{6-}$ are formed. This anion is very stable in alkaline solutions and the structure is presumably as shown:

i.e. 

The thorium is larger in size than most transition metal ions and in fact it occupies about the same space as two smaller metal ions. The chelate may be regarded therefore as a psuedo five-membered ring and as such it is much more stable than most four-membered rings.

Effect of phosphate. - A study was made of the absorption of thorium on Dowex 50-X8 (H^+ form) as a function of pH and at a phosphate concentration of 520 ppm. Thorium was lost to the effluent in the pH range 2-4.5; the maximum loss (-30%) occurred at pH 3.8 as shows in Figure 7. Outside this pH range, thorium adsorption was quantitative and the element was quantitatively recovered by elution with 500 mL of 1.8 M H_2SO_4.

The work of Langmuir et al. leads us to suggest that

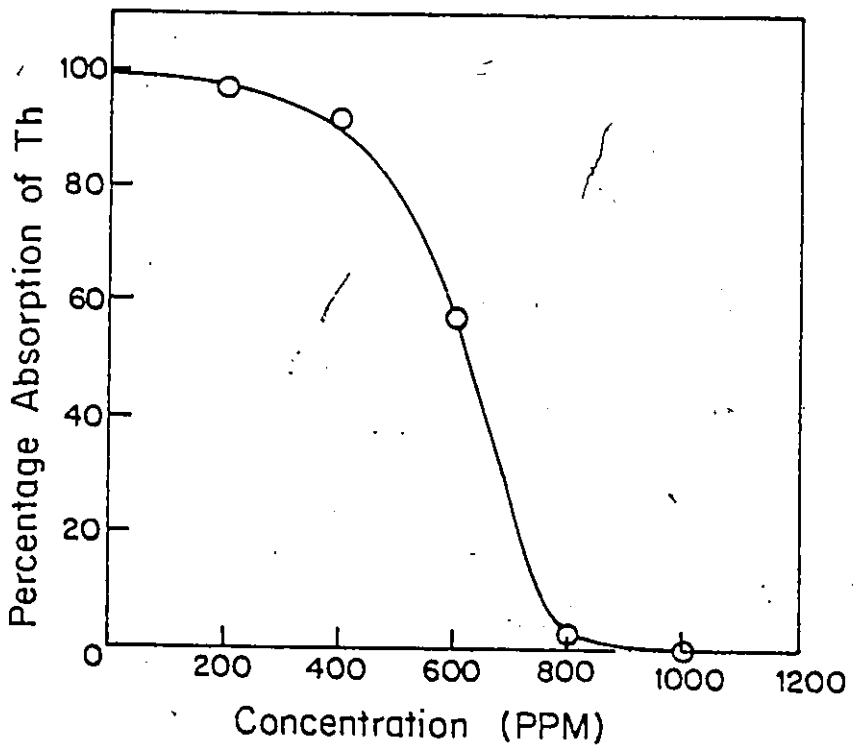


Fig.6. Relation between sorption of thorium on Dowex 50-X8 and carbonate concentration.

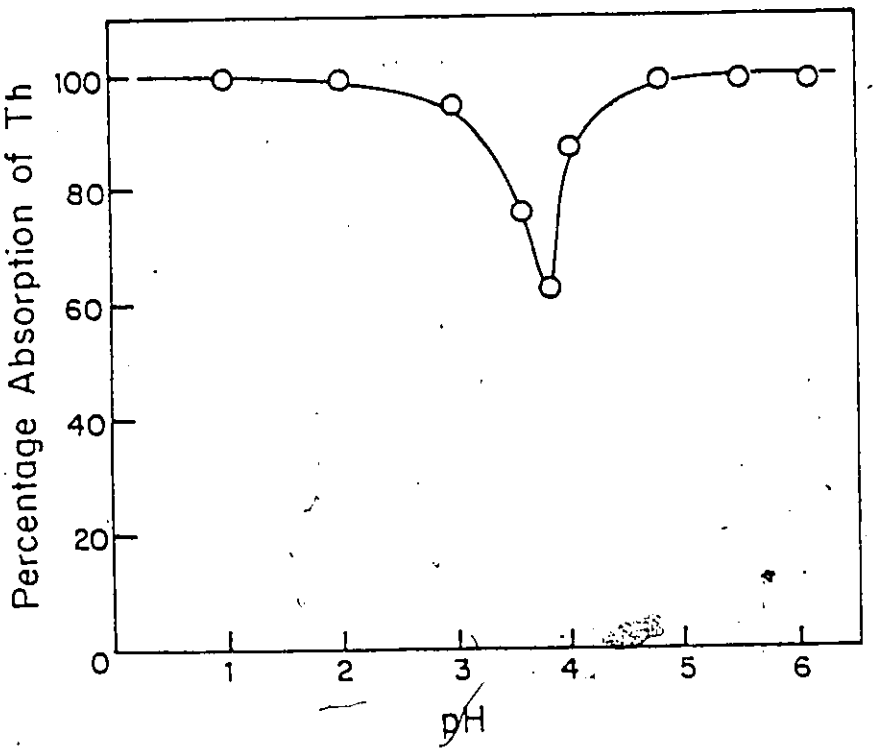


Fig.7. Relation between sorption of thorium on Dowex 50-X8 and pH, in the presence of phosphate (520 ppm PO_4^{3-}) (1.0ppm Th)

the following equilibria are responsible for the observed behaviour (148).

$$Th^{4+} + 2H_3PO_4 \rightleftharpoons Th(HPO_4)_2 + 4H^+$$

$$Th(HPO_4)_2 \xrightleftharpoons{OH^-} Th(Th(OH)_3)_m^{(4+m)+} + 2PO_4^{3-}$$

The species $Th(H_2PO_4)^{3+}$ and $Th(HPO_4)^{2+}$ are doubtless formed as well at pH values ≤ 2 and possibly higher.

At low pH values, cations are favored in the equilibria so that there is absorption by the resin. The neutral species $Th(HPO_4)_2$ is important at intermediate values of pH and this causes losses to occur. At higher pH values, hydroxo polycations form and these too are absorbed and tightly bound. The condensation polymerization is seen also with plutonium. Toth et al. report that polymerization occurs very rapidly with this element in aqueous HNO_3 (149).

Phosphate also interferes with the formation of the coloured Th-arsenazo III complex (150). We found that PO_4^{3-} at a concentration of 0.76 mg mL^{-1} prevented the appearance of the complex for a period of 7 h. After this, the absorbance increased to a maximum at about 30 h after which it decreased again. This is shown in Figure 8. The absorbance never reached the value that was observed when phosphate was absent. We are unable to account for the initial delay.

Separation of Phosphate

We have undertaken the development of an alternative

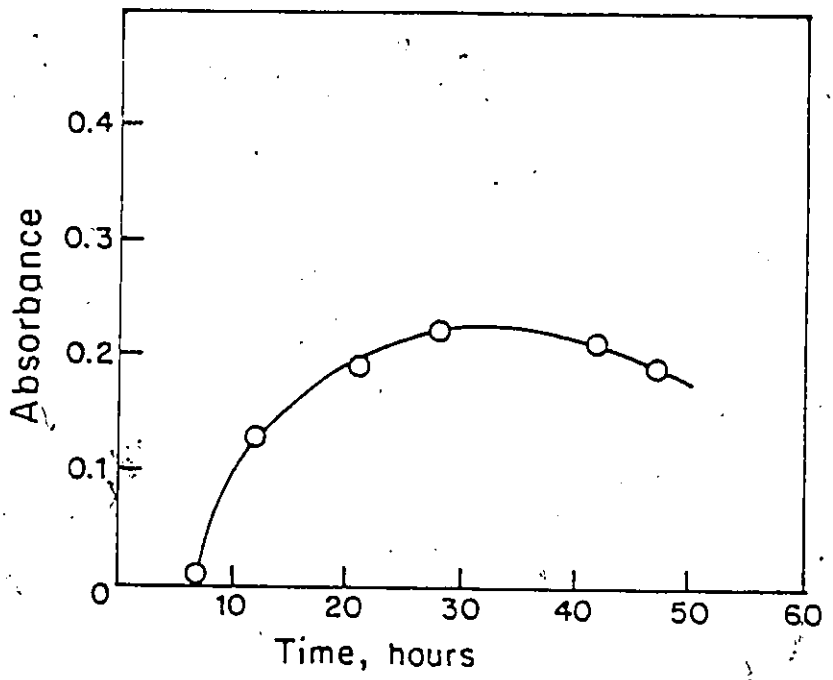


Fig.8. Effect of phosphate on the absorbance of thorium-Arsenazo-III.(1.0ppm Th)

method of ion exchange for the isolation of thorium from samples that contain phosphate, uranium, etc. In this approach, the lengthy evaporations of sulphuric acid solutions are avoided.

One step in the procedure that was developed consists of precipitation of phosphate by the addition of bismuth nitrate. The solubility product of $BiPO_4$ is reported to be 1.3×10^{-23} at 20°C (151). Not unexpectedly, the precipitate carries down much, if not all, of the thorium; however, we were able to leach the thorium from the precipitate with warm, saturated $(NH_4)_2CO_3$ solution. The added carbonate caused precipitation of the excess bismuth.

Procedure 3. A sample of thorium that contains phosphate is treated as follows. If the quantity of phosphate is insufficient to ensure good nucleation of $BiPO_4$, additional phosphate is added to bring its concentration to at least 0.5 mg mL^{-1}. A 0.1 M solution of $Bi(NO_3)_3$ is added slowly until the precipitation of $BiPO_4$ is complete. An equal volume of saturated $(NH_4)_2CO_3$ solution is added and the mixture kept on the steam bath for 40 min. The precipitates are removed on a medium frit filter and washed with saturated $(NH_4)_2CO_3$ solution. The $(NH_4)_2CO_3$ is eliminated by adding concentrated HCl and HNO_3 and boiling (147).

The efficiency of the separation was examined by treating solutions that contained 0.5 mg mL^{-1} of phosphate and 1.0 mg mL^{-1} of thorium. A trace of ^{234}Th was also

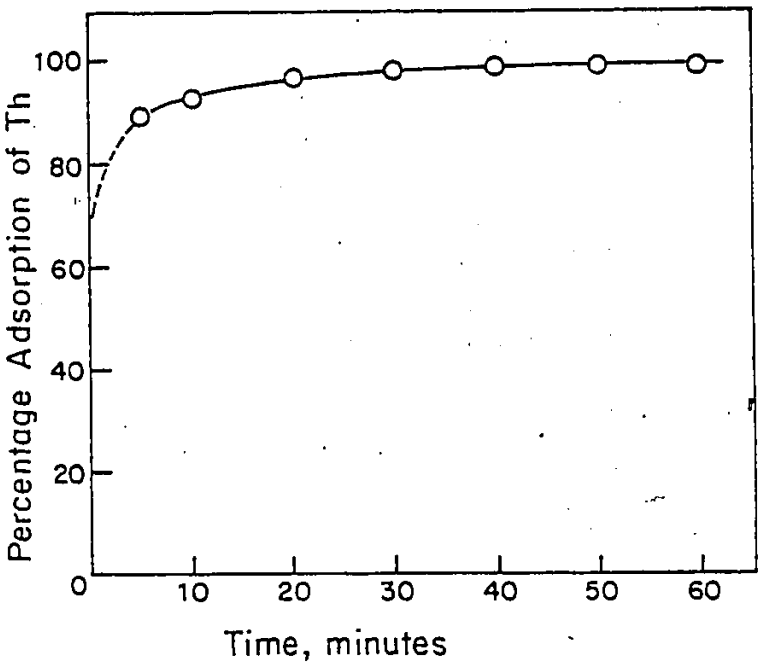


Fig.9. Incorporation of thorium into a precipitate Of Bismuth phosphate. (1.0ppm Th)

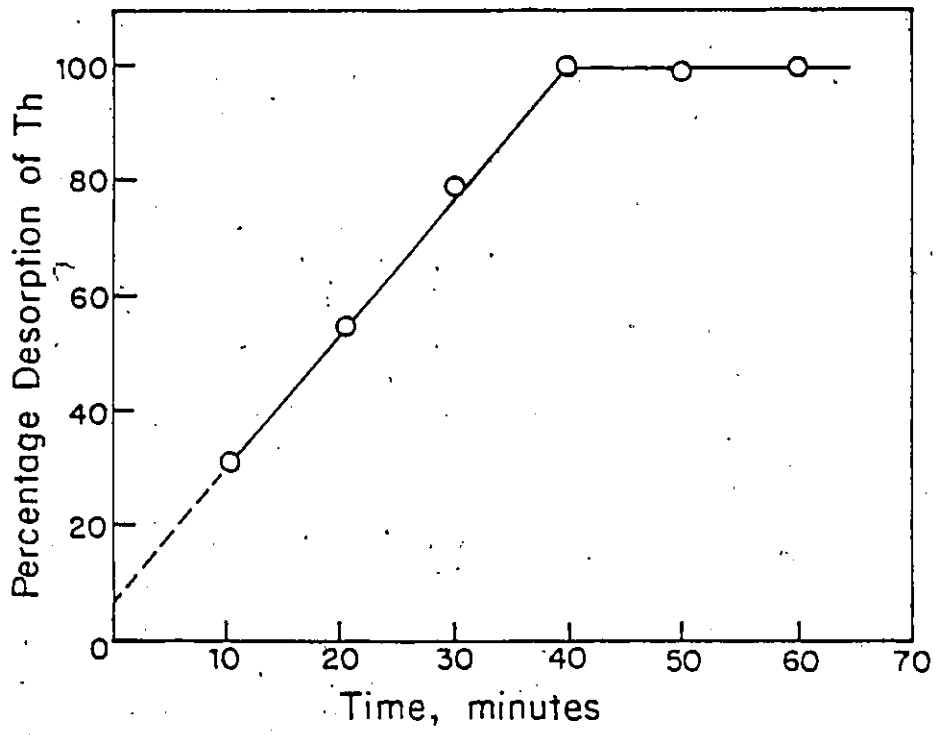


Fig.10. Leaching of thorium from a precipitate of $BiPO_4$ by heating with $(NH_4)_2CO_3$ solution.

present. The β activity of both precipitate and solution was determined. The results shown in Figure 9 show that the incorporation of thorium into the precipitate increased with time if the $BiPO_4$ precipitate was allowed to stand up to 60 min in contact with the mother liquor. The effect of leaching is shown in Figure 10. It is seen that 98 $\pm$ 2% of the thorium was recovered in the leachate in 40 min.

Another step was included in the procedure. This consists of a solvent extraction with tertiary amine, namely Alamine 336. This is necessary in the analysis of ores, concentrates and mill liquors. Uranium mill raffinate normally contains phosphate, molybdate, vanadate, and residual uranium. The following procedure is recommended :

Procedure 4. The sample solution should have a volume of ca. 25 mL. The pH of a sample solution is adjusted to 1.0 to 2.5 (no greater!) by adding dilute nitric acid. The sample is placed in a separatory funnel and shaken with an equal volume of Alamine 336 solution. The extraction is repeated once after readjusting the pH of the aqueous phase with the addition of a further 2 mL of 6.M nitric acid. The aqueous phase is subsequently boiled to expel traces of organic solvent. After cooling, Procedures 3 and 1 are applied.

Effect of UO_2^{2+}: In the absence of phosphate, neither U nor Th was extracted into a petroluem ether solution of Alamine 336. When various amounts of $UO_2(NO_3)_2$ and phosphate were

added to aliquots of standard thorium solution, uranium entered the organic phase. It is recommended that the concentration of uranium be no greater than 0.1 mg mL^{-1}.

The mechanism of extraction is discussed below. The ammonium salts of amines are formed upon protonation with strong aqueous acids:

$$(R_3N)_{org} + H^+ + X^- \rightleftharpoons (R_3NHX)_{org}.$$

The ammonium salts mainly exist as ion pairs i.e. $R_3NH^+....X^-$ where the radical R_3NH^+ can operate freely as an extractant for anionic metal complexes formed in the aqueous solution. The uranyl ion readily forms extractable anionic complexes in most aqueous acid systems (152, 153). Coleman and coworkers (153) found that the amine extractions of U(VI) from phosphate solution was qualitatively similar to the extraction from sulphate solution. A relatively low concentration of phosphate is sufficient to give an extractable uranyl complex at pH ~1 while thorium does not form an anionic complex under similar conditions.

Effect of molybdate. This element behaved in much the same manner as uranium. When both U and Mo were added to solutions containing Th as well as 3 mg of phosphate per mL at a pH of 1.0 - 2.5, both U and Mo were quantitatively removed by Procedure 4 and Th was quantitatively recovered in the aqueous phase (Procedures 3 and 1). It is well known that molybdate condenses with phosphate in acid medium and the heteropoly

species is extractable.

The molybdate ion tends to condense in acid medium (154, 155) according to reactions such as

$$7MoO_4^{-2} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6} + 4H_2O$$

condensation is favoured by certain foreign ions. The most efficient ion in this respect is phosphate. So this was added when extractions were carried out.

$$HPO_4^{2-} + 12\,MoO_4^{2} + 23H^+ \rightleftharpoons PMo_{12}O_{40}^{3-} + 12H_2O.$$

The resulting complex is called phospho-12-molybdate ion. In the extraction process, three molecules of amine are associated with one phospho-12-molybdate ion:

$$3R_3NH^+ + HPO_4^{2-} + 12MoO_4^{2-} \rightleftharpoons (R_3NH^+)(PMo_{12}O_{40}^{3-}) + 12H_2O$$

The ion quadruplet is soluble in the organic phase.

Effect of vanadate. Both U and Th were quantitatively extracted in the presence of vanadate at an initial pH $\lesssim$ 2. At pH $\gtrsim$ 2, only partial extraction of each element was observed. We believe that Th and U form extractable heteropoly species with vanadium at low pH. At pH 2-8, it has been reported (156) that the major species in vanadate solutions are $V_3O_9^{3-}$, $V_4O_{12}^{4-}$, $HV_6O_{17}^{3-}$, $HV_{10}O_{28}^{5-}$. and $H_2V_{10}O_{28}^{4-}$. Some of these anions might combine with Th^{4+} and UO_2^{2+} to form neutral heteropoly groups.

However, when phosphate was present also, V and U, but not Th, were extracted into the organic phase at pH 1-2.5. In this situation, uranium may form a complex similar to

phosphomolybdovanadate (151) which extracts in the protonated form. Thorium in the aqueous phase was isolated and determined by applying Procedures 3 and 1, respectively.

The results of the extraction experiments are shown in Table 6. The thorium recoveries were quantitative except when large quantities of interfering elements resulted in the formation of precipitates.

Analysis of a Certified Reference Material

The validity of the developed procedures was verified by analyzing a certified ore. The reference material chosen was an arkose sandstone supplied by the Department of Energy, Mines and Resources, Ottawa (CANMET) and bore the catalogue number DL-1a. The certified mean value for thorium in this material was 0.0076% and the 95% confidence limits were 0.0072-0.0079%. The material was reported to contain uraninite, brannerite and possibly monazite and uranothorite.

As sodium interferes in the determination of thorium with Arsenazo-III, we opened up the sample by fusion with a mixture of KO_2 and KOH.

Procedure 5. A 0.5 g portion of the finely powdered ore was mixed with 1 g of KO_2 (Alpha, Ventron) and 0.5 g of KOH in a zirconium crucible (158). The mixture was fused and heated to redness over an open flame for 3-5 min. The cooled crucible was placed in a 250 mL beaker and the melt dissolved with 50 mL of 2 M HNO_3. The solution was evaporated to

TABLE 6

Recovery of thorium in the presence of phosphate,* uranium molybdenum and vanadium

Th taken, μg	Other elements present, mg U	Mo	V	Th recovered μg
25.0(3)[b]	0.25	—	—	25.0±0.2
250.0(3)	2.5	—	—	248.9±0.7
25.0(3)	3.0	—	—	24.3±1.1
25.0(1)	—	—	—	X
600.0(1)	2.5	—	—	X
25.0(4)	0.25	37.0	—	24.8±0.4
250.0(3)	0.25	42.0	—	247.9±2.3
250.0(1)	0.25	76.0	—	X
25.0(3)	0.25	—	20.0	25.0±0.5
250.0(3)	0.25	—	30.0	249.1±1.6
250.0(1)	0.25	—	40.0	X

* In all cases $[PO_4^{3-}]$ = 3 mg/ml. Initial volume 25 ml.
b The number of replicate samples appears in brackets.
X Precipitation occurred; solvent extraction was not possible.

TABLE 7

Recovery of thorium in the precipitation of $KClO_4$

Quantity of K^+ precipitated (mg)	Thorium added (μg)	Thorium recovered (μg)
0	25.0	25.0
50.7	25.0	24.9
72.5	25.0	25.0
145.1	15.0	15.2
217.7	15.0	15.0
290.2	25.0	24.9

dryness on the steam bath. The residue was heated to dehydrate silicic acid and after adding 1 M HNO_3, the silica was separated on a Whatman No. 41 paper. The filtrate was again evaporated to dryness in order to render insoluble a further small amount of silicic acid. The residue was treated with acid as before and separated by filtration through a fresh filter. The two washed precipitates were combined and ignited at 700°C in a platinum dish. Silica was expelled with H_2SO_4-HF in the usual manner. The platinum dish was washed with 1 M HNO_3 and the washings added to the combined filtrates. The solution was made up to 100 mL volume and a 50 mL aliquot taken. This was evaporated to 30 mL volume and cooled in ice. Potassium was precipitated by adding cold 20% perchloric acid. The precipitate was separated on a medium frit filter and washed with more cold perchloric acid. The solution was evaporated to dryness and taken up in 30 mL of 1 M HNO_3. Procedures 4, 3, and 1 were then applied in that order.

The thorium values obtained with four samples of the ore were: 0.0074, 0.0072, 0.0075 and 0.0075%. The mean of these results is well within the 95% confidence limits provided for the ore. There were no rejected results.

The removal of potassium by precipitation as $KClO_4$ presented no difficulties. We tested the recovery of thorium for a range of potassium concentrations and found the thorium quantitatively in the filtrate in all cases. The results of these procedures are given in Table 7.

The procedure developed in the present work for solution samples is somewhat more rapid than that involving the ion-exchange procedure. The effects of possible dissolution of a small quantity of the ion exchanger are also avoided. The procedures are useful when a chemical method of determination is to be used. This applies also when it is necessary to obtain a chemical yield in a radiochemical assay.

CHAPTER V

MICRO SEPARATION AND DETERMINATION OF LANTHANIDES BY REVERSED PHASE CHROMATOGRAPHY FOLLOWED BY DCP EMISSION SPECTROSCOPY

Despite significant advances in instrumentation, it is evident from the review section that in a majority of cases, direct analysis methods do not enable one to determine all the lanthanides which may be present over a wide range of concentrations, without interference from matrix constituents. In many real sample analyses, preliminary separations and preconcentration of lanthanides are essential for eliminating interferences from minor or major matrix components. This results in greater sensitivity by lowering background effects. The closer that sample and reference materials are to being identical the more accurate is calibration. On the other hand, the advantage of an easier and seemingly more accurate calibration might be outweighed by the disadvantage of possible losses of trace lanthanides during the concentration procedure. Precipitation methods when applied to traces are inclined to lead to losses or, when carriers are used, there may be coprecipitation or occlusion. Moreover, precipitation methods lack selectivity. One rarely encounters selectivity equal to that of dipicrylamine toward potassium or dimethylglyoxine toward nickel. In general, oxalate shows modest group selectivity for lithophiles and dithiocarbomates show fairly good group

selectivity for chalcophiles.

Among the fast, effective separation and concentration methods, ion exchange and solvent extraction hold a very prominent place.

Ion exchange: In the ion exchange process a metal ion Ln^{3+} in solution exchanges with protons on a solid ion exchanger, a natural zeolite or a synthetic resin. The tenacity with which the cation is held by the resin depends largely upon the size of the ion and its charge. Selectivity of an ion exchanger towards elements as similar as lanthanides and actinides is not sufficient to ensure the desired separations. Various complex formation agents may be added to the aqueous phase to obtain larger differences in separation factors.

Solvent extraction: This technique is rapid, simple, and can sometimes be used to concentrate small amounts of substances. In a quantitative separation, it is an "all or nothing" situation. This means that one constituent is essentially all extracted from one phase, while the extraction of another constituent is practically nil. The main drawbacks of solvent extraction are troublesome emulsion formation, and the considerable manipulation that may be involved in making multiple extractions, each time carefully separating the layers, washing and finally back extracting. In these processes one is likely to lose sample.

Extraction Chromatography: This is a modification of the solvent extraction technique. A column is packed with a

solid support that holds stationary organic phase. In the sorption step an aqueous sample is added to the column and the various solutes are distributed between the organic and aqueous phases. The column is subsequently eluted with an aqueous solution whereupon the inorganic solutes move down the column at different rates and are thereby separated. Some authors term this technique "Reversed phase extraction Chromatography" (RPC). Extraction chromatography is actually a multistage separation process and it affords much more subtle separations than are possible with simple solvent extraction. Manipulation is minimal and the scope of possible separations is large.

The theoretical and technical aspects of extraction techniques including chromatography as applied to inorganic analysis have been treated in the monograph of Markl (159) and the monograph on "Extraction Chromatography" edited by Braun and Ghersini (160). In addition there are large numbers of comprehensive books on solvent extraction (161, 162, 163, 164, 165) and chromatography (166-170). It may suffice here to recall the following points.

(i) All chromatographic separations are based on the differential migration of solutes through a system of two phases, one of which is mobile.

(ii) The ability of any chromatographic system to perform separations depends upon both the selectivity and efficiency of the chromatographic system.

(iii) The selectivity is expressed in terms of the relative retention volume of the pair of components to be separated, while the efficiency is measured by the number of theoretical plates (or plate height) generated in the chromatographic column.

(iv) The plate height depends on operating conditions such as eluent flow rate, particle size and shape of the support material, stationary phase loading, temperature etc.

(v) The relative retention is a quasi-equilibrium property of a specific system that depends on the complexing ability of the extractant.

Extractants: The task of developing new extractants is usually directed at increasing selectivity. The principles of selectivity are still to be developed. In the chromatographic analysis, selection of the proper extractant is of paramount importance. The extractant should be such that the distribution coefficient of the analyte of interest differs from that of the unwanted matrix constituents by a factor of at least 10 to 100. The extraction system should conform to a number of other requirements also. The components to be separated should be readily extracted into the stationary phase. Both phases should be mutually saturated, so as not to change the composition or amount during the chromatographic process. There should be no interaction between the liquid phase and the support

material.

General principles for the selection of extractants are discussed by Zolotov and Petrukhin (171, 172). One of the principles is based on the concept of hard and soft bases and acids. According to this idea hard bases react preferably with hard acids and soft bases with soft acids. Extractants usually play the role of bases; oxygen-containing extractants being hard and sulfur-containing extractants being soft. Extractants with a basic nitrogen atom have an intermediate character. It is reasonable to use oxygen-containing extractants for hard cations which are usually lithophilic and sulfur-containing extractants for chalcophiles.

With the use of most selective extractants and simple new methods of multiple extraction, extraction chromatography has proved a viable alternative to ion exchange for the separation of adjacent lanthanides and actinides and also isolation of these elements as a group. The raising of this technique to a position competitive with ion exchange for such separations is mainly due to three important advances that began 25 years ago. These were (a) studies by Peppard (173) who developed acidic phosphorus-based extractants, (b) the development by Moore of long chain tertiary and quaternary amines as anion extractants (174), and (c) the development of new techniques of extraction chromatography, first successfully applied by Siekierski et al (175, 176, 177).

These developments constitute the foundation for the most effective separations of tripositive actinides and lanthanides. It is probably the main objective of this thesis to demonstrate the usefulness of extraction chromatography in rare earth analysis and to apply the findings to silicate rock analysis. The author has sought to maintain a simplicity in the operations of sample treatment. Industrial analysts have expressed some dissatisfaction toward high performance liquid chromatography instrumentation in the routine laboratory. The chromatography described herein consequently avoids instrumentation.

Table 8 lists some extractants that have been used, for inorganic ions. Several of those listed have only recently been investigated. Extraction chromatography was first applied to fractionate the lanthanides (178). From a selection of potential extractants, chromatographers early centered upon HDEHP as the extractant of choice and its use continues even though HEHØP is known to be more selective with a mean separation factor of 3.0 for lanthanides (176). In our studies we have selected HEHØP to evaluate the possibilities and limitations in fractionating lanthanides among themselves, and isolating them as a group from other matrix elements. HEHØP meets all the requirements for the chromatographic study of lanthanides. The synthesis of HEHØPis described in the experimental section.

Support material: Together with that of a suitable

TABLE 8

Extractants for Cations

Alkyl Sulphonic and Carboxylic Acids

HDEHP	bis(2-ethyl hexyl) phosphoric acid
HEHØP	2-ethyl hexyl hydrogen phenylphosphonic acid
OPPA	bis(2-ethyl hexyl) pyrophosphoric acid
HDOP	bis(n-octyl) phosphoric acid
DDCP	dibutyl-N, N-dietheyl carbamayl phosphonate

Extractants for Anions

$TLMANO_3$	tridodecyl methyl ammonium nitrate
Alamine 336	trioctyl and tridecylamines
Aliquot 336-S-X	trioctyl and tridecyl methyl ammonium salt.

extractant, the selection of the proper support material is very important in chromatographic analysis as it has the task to retain the extractant and maintain its stationary without adversely affecting the desired separation. An ideal support has to meet the following requirements.

1. To display good wettability by the stationary phase and to retain it in sufficient amounts. The fixed phase must not tear off the support with the flow of the mobile phase.
2. To be chemically inert, it must not dissolve or swell or react with stationary and mobile phases. It must not adsorb the components of the sample to be separated.
3. To consist of particles as identical as possible (spherical ones are the best), which allow the most uniform and reproducible column packing.
4. It should have a large enough surface to retain the stationary phase as a thin uniform film. Porous supports generally meet this requirement; but the pore distribution has to be within a narrow range of sizes, since the effect of different pore sizes is equivalent to that of different particle diameters. Pores must not be too narrow, as the equilibrium with the liquid retained in narrow and deep pores may be very slow leading to an additional broadening of the chromatographic peaks.
5. When applied for routine analyses or preparation purposes, it must be relatively cheap or permit regeneration.

There is no ideal support for reversed phase partition chromatography, so one must choose within a wide range of substances which partially meet the above-mentioned requirements. Silica particles or Kieselguhr are the support materials most often used in the reversed phase mode of high performance liquid chromatography (HPLC) (179, 180, 176). Kieselguhr is a diatomaceous earth consisting of about 90 wt % SiO_2, the rest is composed of Al, Fe, Na, Mg, Ca, Ti, traces of Cu and Mn. It is made organophilic by silanization. These materials have shown to be highly efficient and versatile for a large variety of separations. However, routine use of silica-based HPLC packings with either low or high pH mobile phases is difficult. At pH values less than 2, hydrolysis of siloxane bonds can occur, while above pH 7 dissolution of silica is possible (181). In particular these limitations imposed by the mobile phase restricts the utility of the silica-based packings. Also, the presence of unprotected oxygenated reactive sites such as hydroxyl groups diminish the nonpolar character of the support, thereby causing bleeding of the extractant. These sites may also adsorb various inorganic cations, and might lead to non reproducible chromatograms. In our spectrochemical determination of some lanthanides by DCP, the presence of a few ppm of silica caused erroneous results which are shown in Table 9 . The cause of the effect of silica on the determination of lanthanides is not apparent.

TABLE 9

Interference with SiO_2 Matrix

Element	λ, nm	Concentration ppm	Si added ppm	Percent Error
La	408.67	1.30	40	+22
			120	+22
			240	+22
		2.28	40	+23
			80	+19
Ce	418.66	0.56	83	+6
			166	+19
Dy	353.17	1.48	83	-47
			166	-32
Yb	328.94	0.96	83	+22
			166	+25

We have avoided the use of silica based material as inert support and have used phenylated Kel-F powder instead. The derivatization of Kel-F (Polychlorotrifluoroethylene) particles by organolithium reagents for use as HPLC packings was investigated recently by Siergeij and Donaldson (182, 183). They have applied this support for the separation of organic mixtures. We have chosen to use phenylated Kel-F powder as the support material as it meets almost all the requirements of a support material for reversed phase extraction chromatography. Preparation and characterization of phenylated Kel-F is described in the experimental section.

EXPERIMENTAL METHODS AND PREPARATIONS

Preparation of the lanthanide standard stock solutions

Accurately weighed quantities of rare earth oxides (specpure, 99.99% Johnson Mathey Chemicals Ltd.) were dissolved in 100 mL of 2% HNO_3 to give solutions with concentration of 1 $mg \cdot ml^{-1}$ of the element. Working standard solutions were prepared by diluting the stock solutions with doubly distilled water.

In the case of cerium, the stock solution was prepared as follows: A 0.3832 g. quantity of CeO_2 was digested with 15 mL of 70% perchloric acid, 10 mL of water and 2 mL of 30% hydrogen peroxide. The resulting solution was evaporated to dryness and 15 mL 1:1 sulphuric acid and 1 mL of hydrogen peroxide were added. The solution was evaporated to white fumes, cooled, and diluted to 100 mL with water in a volumetric flask.

Aluminum Standard Solution: An atomic absorption standard reference solution, containing 1000 ppm ± 1% Al, was obtained from Fisher Scientific Co.

Calcium: 0.675 g of $CaCO_3$ (Baker) was dissolved in a 500 mL volumetric flask. Sufficient hydrochloric acid was added to give 0.1 M acid concentration.

Scandium: An Atomic Absorption standard reference solution, containing 993 $\mu g\ ml^{-1}$, Sc in 2% HNO_3 was supplied by

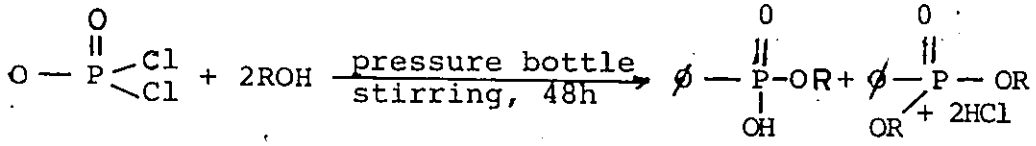
Aldrich Chemical Co.

Silicon: An Atomic Absorption standard reference solution containing 1000 μg ml^{-1}, Si in doubly distilled water supplied by Aldrich Chemical Co.

Alamine 336: A 25% V/V solution of alamine was prepared with a 1:1 mixture of petroleum ether (6·p40 - 50°C) and o-xylene.

Synthesis of Extractant

2-ethyl hexylhydrogenphenylphosphonic acid (HEHØP) was synthesized by alcoholysis of phenyl phosphonic dichloride (Aldrich) with 2-ethyl-1-hexanol (Aldrich).



The reactants were mixed in a 1:2 molar ratio in benzene and put into a pressure bottle. The reaction mixture was stirred for 48 h at room temperature. After completion of the reaction, the pressure was released carefully and the mixture was washed several times with water. The reaction mixture was taken up in ether and shaken with 15% NaOH in a separatory funnel. The aqueous solution was scrubbed with benzene to remove alcohol and unhydrolyzed diester and then acidified with concentrated hydrochloric acid to liberate HEHØP. This was taken up in anhydrous ether, dried with anhydrous magnesium sulfate and filtered. The solvent and other volatile materials were removed under reduced pressure. The structure and purity of the extractant was confirmed by proton and ^{13}C

NMR and mass spectrometry. The spectra are shown in Figs. 11, 12, 13, respectively.

The results of elemental analysis were C, 62.07%; H, 8.63%; calculated values for C, 62.21%; H, 8.57; O, 17.75%; P, 11.46%.

The 'H NMR spectrum was obtained for a solution in $CDCl_3$ with a varian EM 360 Spectrometer, operating at $60MH_Z$. Shifts are relative to TMS. Resonances appear at 7.2 - 8.0 ppm (multiplet aromatic H); 4.0 ppm (doublet of doublets $P-OCH_2$), and 0.3-2.0 (multiplet corresponding to fifteen aliphatic H atoms).

The ^{13}C NMR spectra was obtained in $CDCl_3$ with a varian FT80 instrument operating at 20.2 MH_Z. Shifts are in ppm and are relative to TMS peak and these are as follows: 132.0 (para CH, J_{c-p} = 2.2), 131.3 (meta CH, J_{c-p} = 9.8); 128.3 (ortho CH, J_{c-p} = 15.5); 124.2 (quaternary C); 67.8 (OCH_2, J_{c-p} = 6.2); 40.1 (CH, J_{c-p} = 7.2); 29.9 (CH_2); 28.8 (CH_2); 23.2 (CH_2); 23.0 (CH_2); 140 (CH_3); 10.4 (CH_3).

The mass spectrum was obatined with a VG 7070 E instrument. The electron energy was 70eV. The temperature of the ion source was approximately 200°C. Although a molecular ion peak is not seen, there are characteristic mass such as 77 for $C_6H_5^+$.

Phenylation of Kel-F powder

Kel-F 6061 (100% poly(chlorotrifluoroethylene) was

Fig.11. The ^1H NMR spectrum of HEHØP in $CDCl_3$.

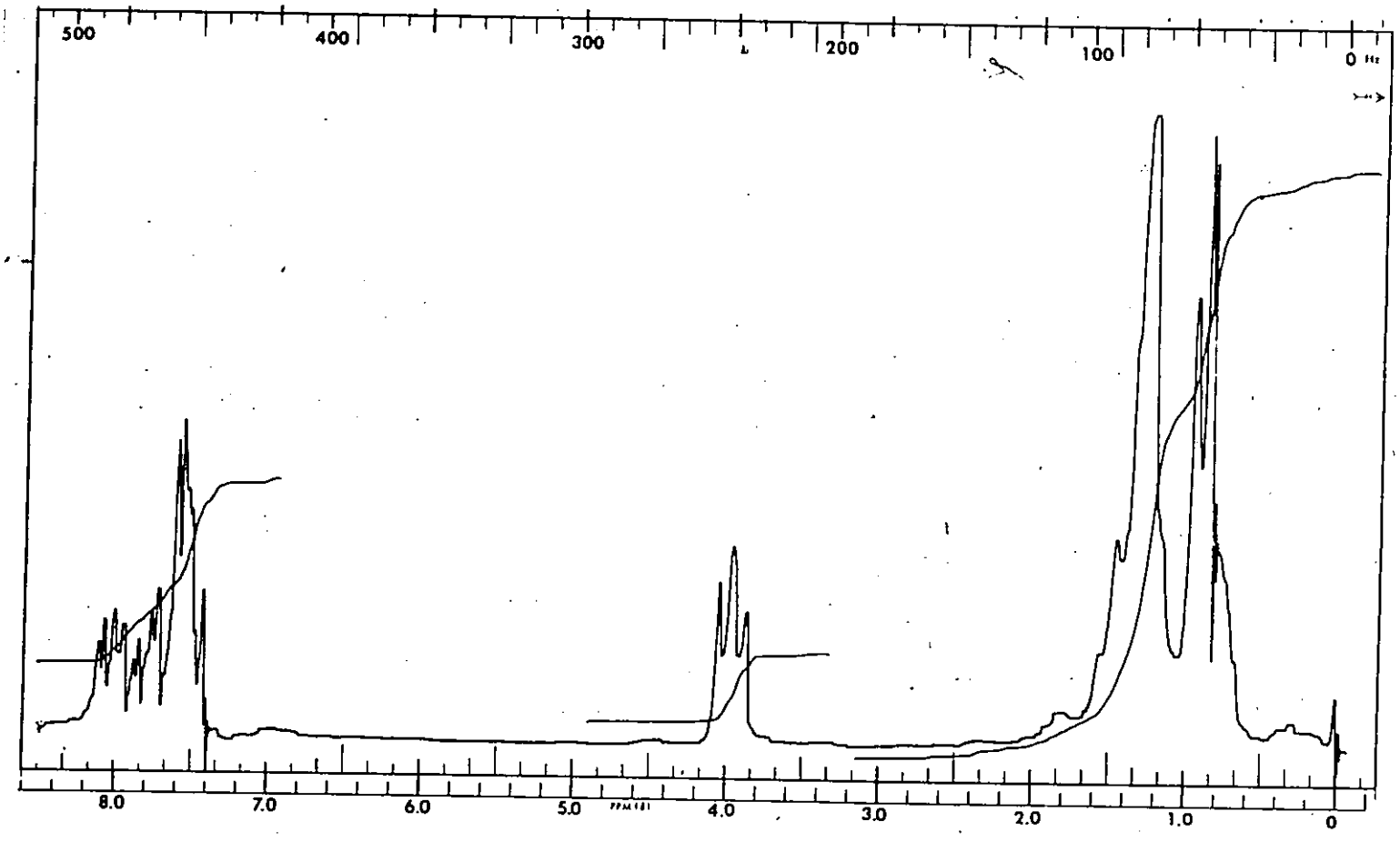
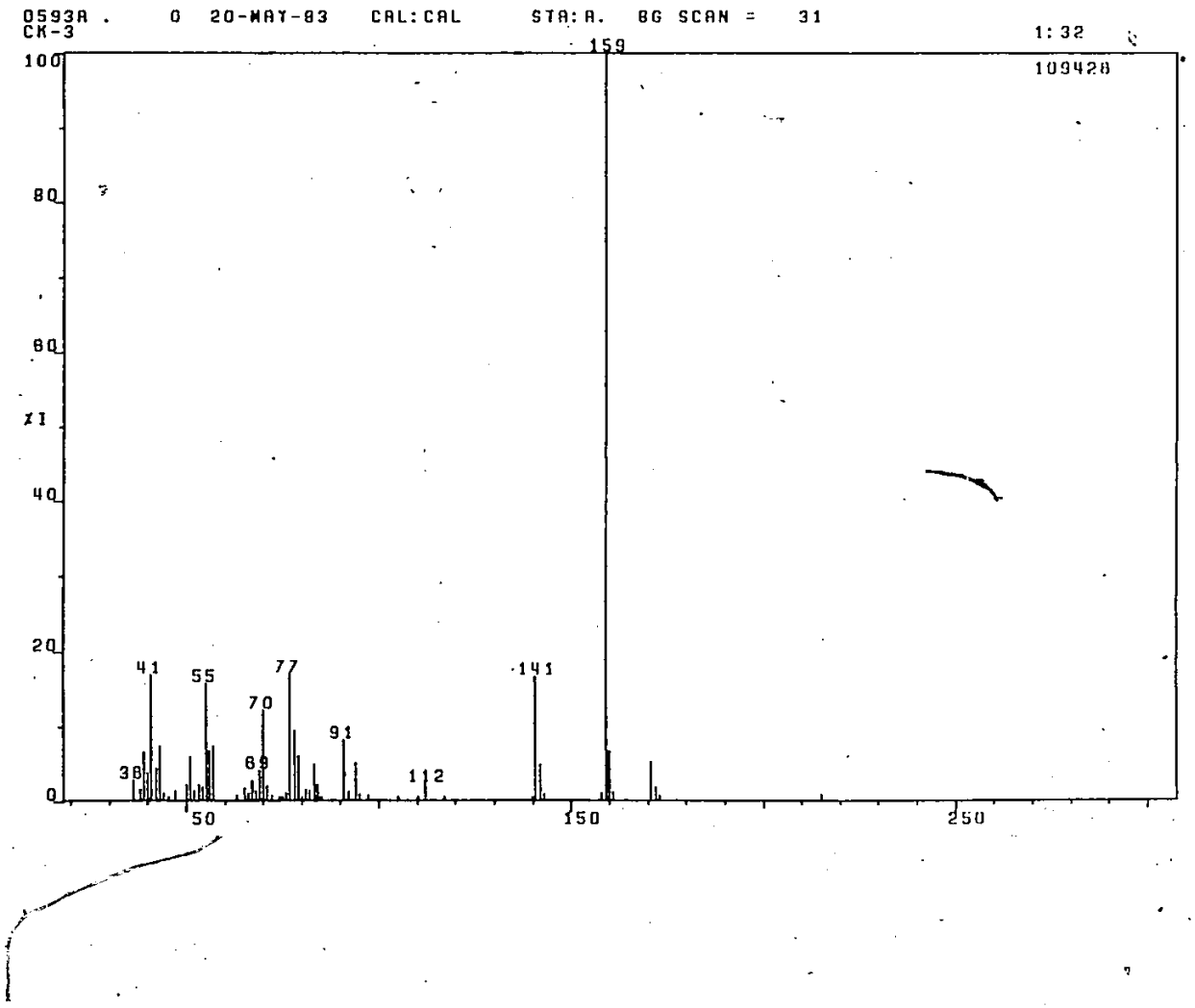

500
400
300
200
100
0 Hz
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

Fig.12. The ^{13}C NMR spectrum of HEHØP in $CDCl_3$.

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm(δ)

Fig.13. Mass spectrum of HEHØP .


0593A . 0 20-MAY-83 CAL:CAL STA:A. BG SCAN = 31
CK-3
1:32
109428
159
100
80
60
%I
40
20
0
41
55
77
70
91
69
38
112
141
50
150
250

obtained as a white 80 - 100 mesh powder from Afton plastics moulding company, Lakeland, Minnesota. It was reduced to 250 - 325 mesh in a shatter box that contained some dry ice. Sizing screens were used to select the desired fraction. The powder was further sized by stirring in a 15 cm high beaker filled with 2-propanol. The fraction which settled within 30 minutes was collected and sucked dry. Twenty-one grams of the dried Kel-F was mixed with 250 mL of dry THF (Aldrich Chemical Co.) and heated to 50°C. The mixture was purged with argon for 30 min. A ninety-five milliliter volume of 1.8 M phenyllithium was added dropwise and a green colour appeared in the reaction vessel. The mixture was heated under reflux for 3 h. Excess reagent was hydrolyzed by dropwise addition of 5 - 7 mL of distilled water. The product was separated by filtration and washed with hexane, acetone, 2 propanol, water and methanol. The dried product was brown.

Characterization of phenyl modified Kel-F

The phenyl modified Kel-F was identified as such by infrared spectrometry. Absorption bands at 3060 cm^{-1} and 3028 cm^{-1} and the overtones in the 2000-1660 cm^{-1} range clearly indicated the presence of substituted aromatic groups. Two characteristic bands at 758 cm^{-1} and 697 cm^{-1} confirmed the presence of monosubstituted benzene. The primary reaction occurring is the following:

Fig.14. Scanning electron micrograph of Kel-F 6061 .

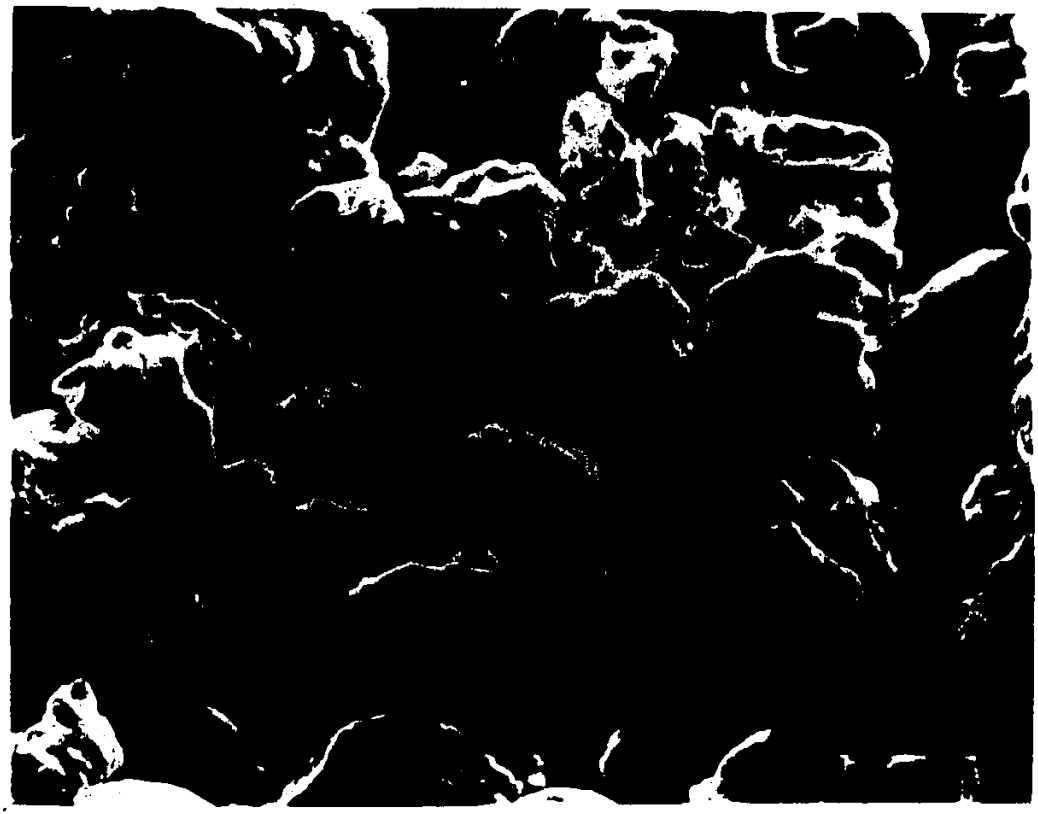
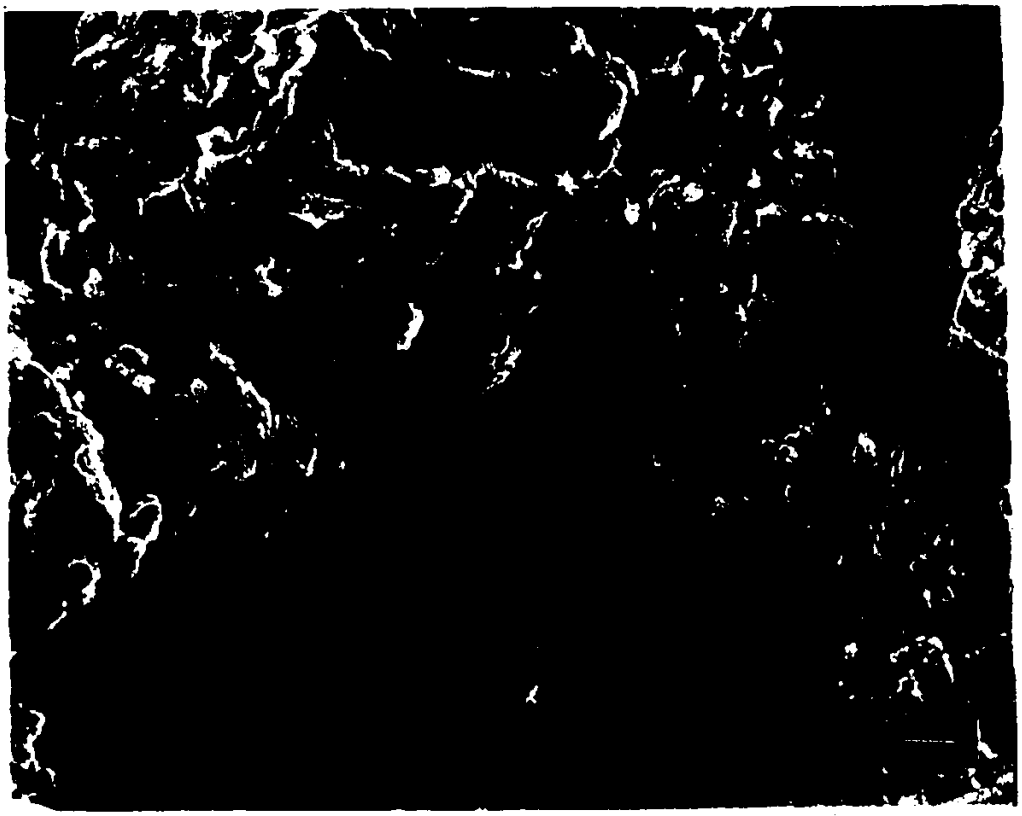


Fig.15. Scanning electron micrograph of phenyl Kel-F.

Fig.16. Scanning electron micrograph of phenyl Kel-F impregnated with extractant HEHØP .



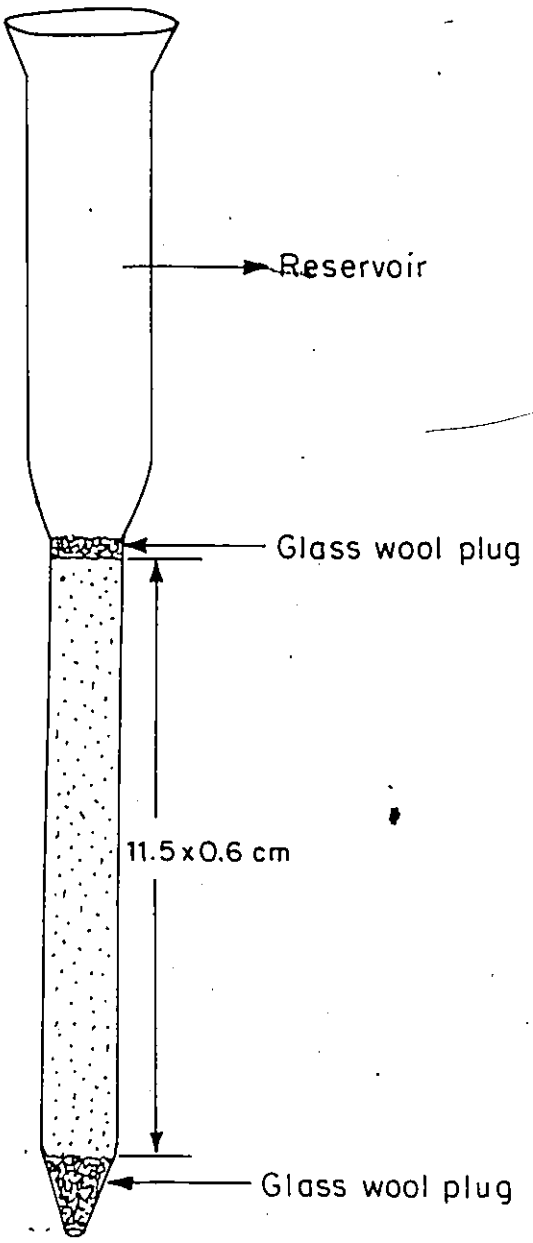
$$(CF_2\underset{Cl}{CF})_n + C_6H_5Li \longrightarrow -(CF_2\underset{C_6H_5}{CF})_n + LiCl.$$

An electron micrograph of underivatized, derivatized Kel-F, and impregnated with the extractant, HEHØP is shown in Figs. 14, 15, 16 respectively. It appears that the organolithium reaction increases the number of small particles which leads to a higher surface area.

Column Preparation

A weighed quantity of phenylated Kel-F powder was stirred with a known amount of complexing agent (HEHØP) dissolved in o-xylene. The solvent was evaporated under a heat lamp while stirring with a glass rod. The coated polymer was acidified and hydrated by stirring in 0.1 M $HClO_4$ or 0.1 M HCl for one hour. The wet material was transferred in small portions to a glass column and pressed gently into place with a flat ended stirring rod in order to remove voids. A plug of glass wool was placed at the bottom and on the top of the resin bed to prevent dislodging of the particles when solution was added. It also helped to prevent the top of resin bed from drying out if the liquid on top of the column was depleted. The column was washed with several column volumes of an aqueous solution of the same type as that to be used to transfer the sample. The aqueous solutions were equilibrated in all cases with HEHØP in order to prevent depletion of the extractant phase when

Fig.17. The schematic diagram of a chromatographic column.

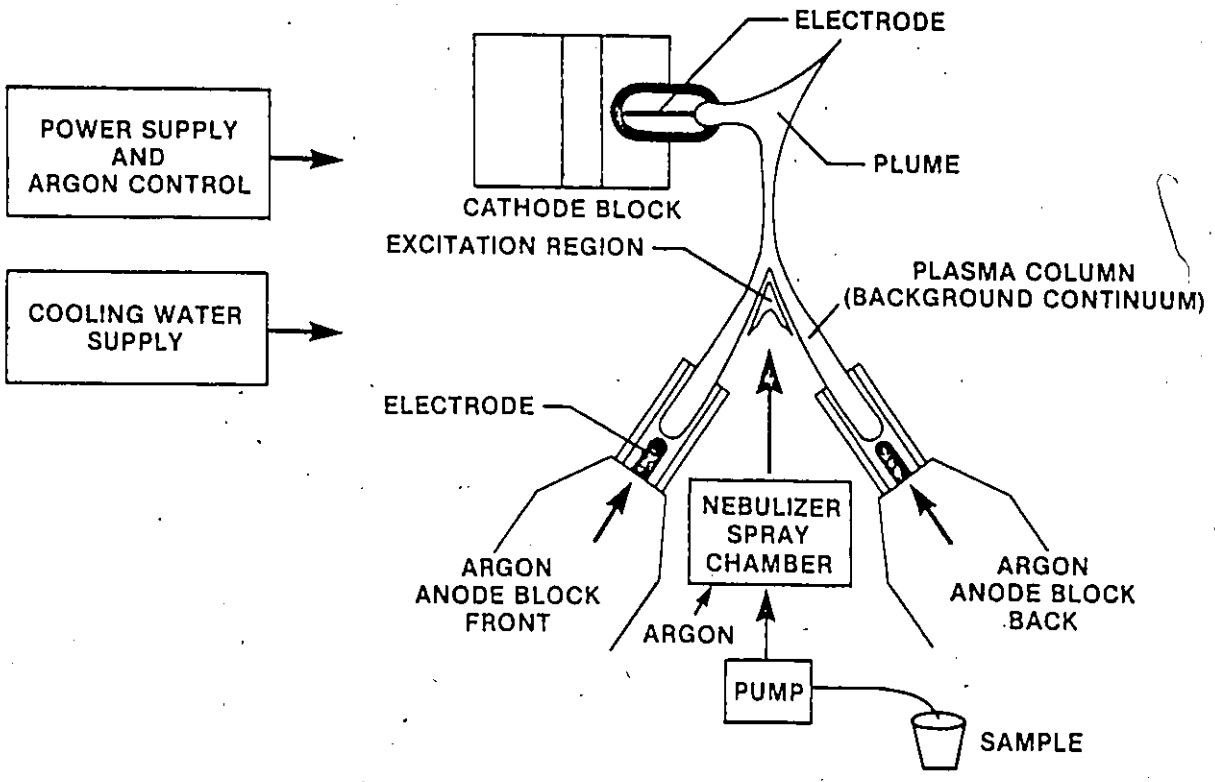

Reservoir
Glass wool plug
11.5 x 0.6 cm
Glass wool plug

the column was in use. All the acid molarities were determined by titration with standard base NaOH and phenopthalein as indicator. Empty glass columns were sometimes made hydrophobic by exposure to dimethyldichlorosilane vapour (in an oven). All columns were provided with a reservior for an eluent of an appropriate volume as shown in Fig. 17. The dead volume below the column bed was kept as low as possible. The reservoir was fitted on top with a ball joint to provide a means for the application of overpressure; if needed.

DCP Spectrometry

The atomic emission system utilized in this investigation was the Beckman-Spectrospan V combined with a high energy dc plasma excitation source with a high resolution Echelle grating. The instrument converts liquid samples into aerosol form and this is introduced into the excitation region. An Echelle grating and prism in the optics module separate the emitted light into its component wave lengths and creates a 2-dimensional spectral pattern 4" by 5" (10.2 X 12.7 cm) in area. This compact spectrum permits choice of wave lengths from 190 nm to 800 nm. The intensity of the emitted light at predetermined characteristic wave lengths is proportional to the concentration of the element. The signal was integrated for 5 seconds and the integration repeated twice under computer control.

Fig.18. The schematic diagram of the DC plasma jet.


POWER SUPPLY AND ARGON CONTROL
COOLING WATER SUPPLY
ELECTRODE
PLUME
CATHODE BLOCK
EXCITATION REGION
PLASMA COLUMN (BACKGROUND CONTINUUM)
ELECTRODE
NEBULIZER SPRAY CHAMBER
ARGON ANODE BLOCK FRONT
ARGON
ARGON ANODE BLOCK BACK
PUMP
SAMPLE

The computer uses a calibration to convert the measured voltage (for each channel) to a value representing the actual concentration of that element. The calibration was done by measuring two known concentrations of that element (a low and a high standard) prior to the test, and assuming a linear relationship between measured voltage and element concentration. Concentrations were provided as a printed output. The schematic diagram of the plasma jet is given in Fig. 18. This is a high energy dc argon plasma formed by a tungsten cathode and two carbon anodes in an inverted "Y" configuration.

The operating parameters were as follows; Argon (commercial grade 99.5%) was introduced at a flow rate of 7 litres min^{-1}. The sample uptake rate was approximately 2 $mL \cdot min^{-1}$. The temperature in the excitation region according to the manufacturer was 6000° - 7000° K.

Table 10 lists the analytical wave lengths used in this study. The wave length chosen were not necessarily the most sensitive, but they offer adequate sensitivity with minimal interferences.

TABLE 10

The Lanthanide Wave Lengths

Element	Wave length, nm
La	408.67
Ce	418.66
Pr	440.88
Nd	430.35
Sm	443.43
Eu	420.50
Gd	310.05
Tb	350.91
Dy	353.17
Ho	345.60
Er	369.26
Tm	313.12
Yb	328.94
Lu	261.542

RESULTS AND DISCUSSION

Extraction mechanism

The extraction of tripositive ions by mono-acidic derivates of phosphoric and phosphonic acids may be represented by the following equation (184)

$$M^{3+}aq + 3(HA_2)org \rightleftharpoons M(HA_2)_3org + 3H^+aq.$$

In this reaction, hydrogen ion is replaced in the weakly acidic extractant by a metal ion followed by solvation of the metal complex in the organic phase. It should be noted that HEHØP exists as a dimer in most diluents (185). The strength of the metal complex is dependent mainly on the size and charge of the metal ion. This of course, implies that in a regular series of elements such as the lanthanides and actinides, the order of extraction is dependent upon the contraction of the ionic radii with increasing atomic number. The smaller ion is bound tighter to the extractant, and is favourably distributed in the organic phase and is difficult to strip back with lower acid concentration.

Back extraction

We have prepared various synthetic samples consisting of lanthanides in 0.1 M $HClO_4$. An aliquot of 25 mL was taken in the separating funnel and an equal volume of 10% V/V

HEHØP was added and shaken for five minutes. After carefully separating the two phases, 7.5M HNO_3 was used to strip back all the lanthanides by shaking twice. The % of back extraction of some of the lanthanides is shown in Table 11. The aqueous phase was tested qualitatively with Arsenazo-III and by DCP emission spectroscopy which gave a blank colour and reading respectively. The results show that the back extraction is not more than 86% for lighter lanthanides and the percentage recovery gradually decreases with heavier ones. These results demonstrated the need for extraction chromatographic technique.

Chromatographic separation of lanthanides

Some preliminary experiments were carried out on the lanthanides, namely La, Pr, Nd, Sm and Eu. We adopted the following chromatographic procedure.

Chromatographic procedure

A few micrograms each of several lanthanide elements were mixed together in a 100 mL volumetric flask with 0.1 M HCl. The column length and internal diameter were 11.5 cm and 0.6 cm respectively. The percent extractant was 17.4 (W/W). By means of an Eppendorf pipette, a 0.05 mL sample was placed on the top of the column. Chromatographic development and elution of a first fraction was carried out with 0.7 M HCl equilibrated with HEHØP. The flow rate was

TABLE 11

Percent Recovery from HEHΦP by Double Back Extraction with 7.5 M HNO_3

Analyte	% Recovered
La	86
Ce	85
Pr	86
Sm	80
Eu	84
Gd	82
Dy	57
Yb	19

at 3 drops min^{-1} and was normally induced by gravity only. Forty drop portions of the eluate were collected in glass vials with the aid of a microfractionator. The samples were evaporated to dryness under a heat lamp and taken up in 5.0 mL of 0.1 M HNO_3. Each element was determined by DCP emission spectrometry. A blank was carried along with the samples. A second fraction was eluted with 1.2 M equilibrated HCl.

Quantitative recovery of lighter lanthanides

The glass columns used in this experiment were 0.6 cm I.D. X 11.5 cm long with a reservoir 2cm I.D. X 13 cm long at the top and a drip tip plugged with a glass wool at the bottom. The extractant percentage was 17.4 (W/W). Individual lanthanides were introduced on the column separately and they were eluted with specific volumes of acids of appropriate concentration and determined. Both spectrophotometric determination with Arsenazo-III and DCP spectroscopy were used for the determinations. In the DCP determinations the eluate was evaporated to dryness under a heat lamp and the residue was taken up in a specific volume of 0.1 M HNO_3. For colorimetry, the eluate was evaporated to dryness and the residue dissolved in 10 mL of 0.4 M HCl. The sample was quantitatively transferred to a 25 mL volumetric flask. One mL each of 50% ammonium acetate and of Arsenazo-III solution were added and the sample was diluted to volume with water.

Fig.19. Chromatographic separation of La, Pr, Nd from Eu .

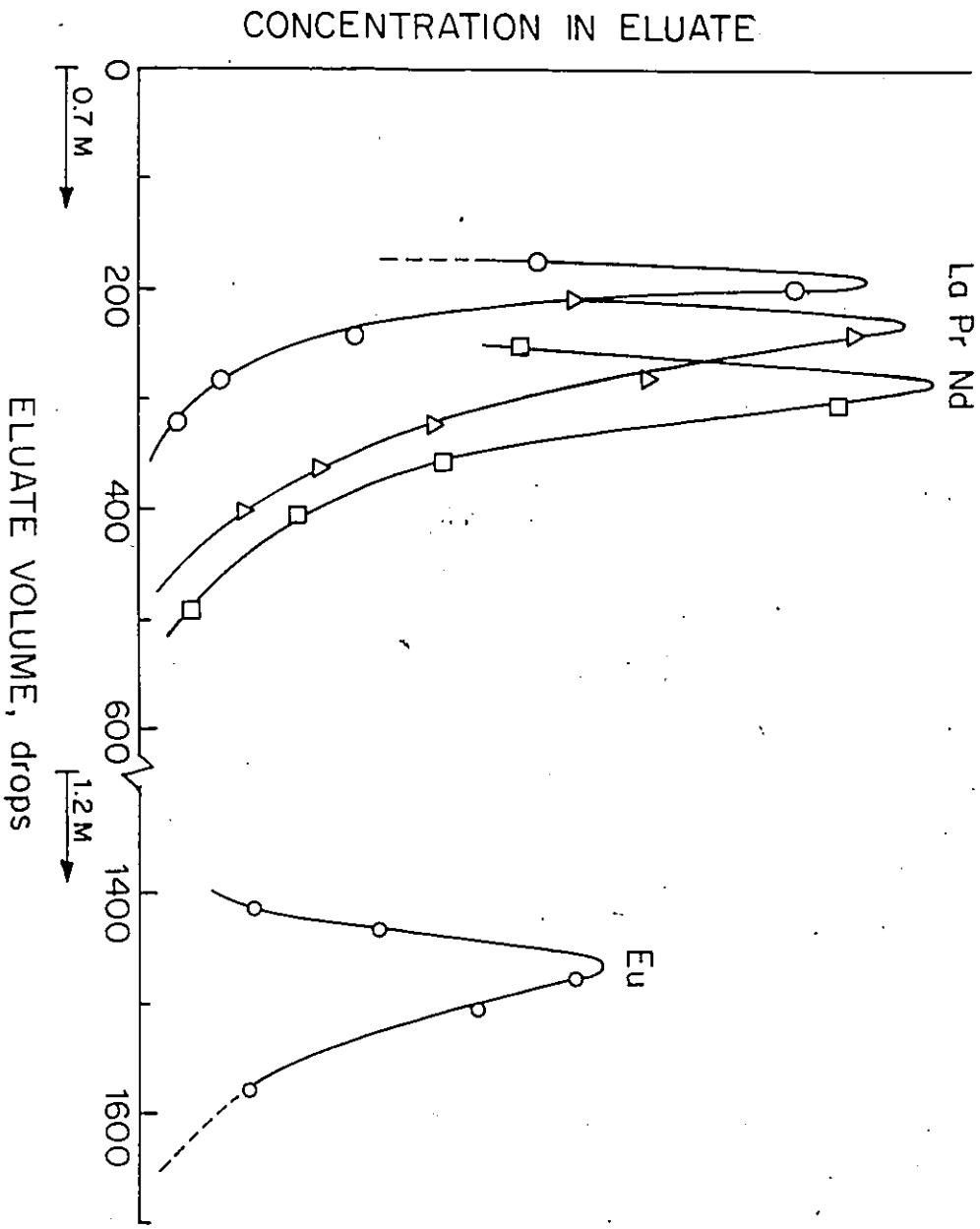
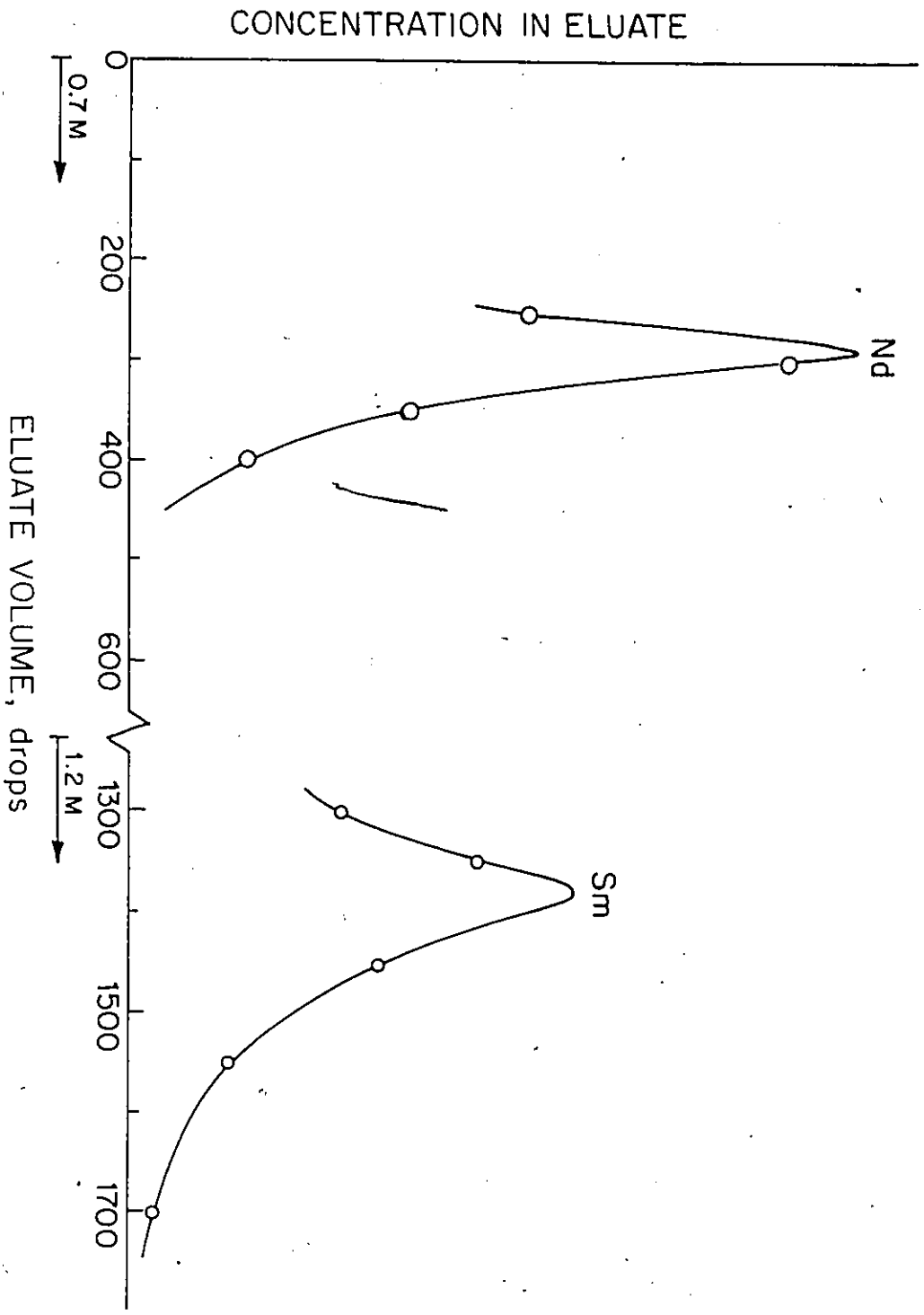

CONCENTRATION IN ELUATE
ELUATE VOLUME, drops
0
200
400
600
1400
1600
0.7 M
1.2 M
La Pr Nd
Eu

Fig.20. Chromatographic separation of Nd from Sm ..


CONCENTRATION IN ELUATE
0
0.7 M
200
400
600
1.2 M
1300
1500
1700
ELUATE VOLUME, drops
Nd
Sm

The absorbance was measured at 660 nm in a 1 cm cell with the reagent blank serving as the reference.

Conditions for the separation of lighter lanthanides into two groups were established. Figs. 19 and 20 show examples of such separations. Although separation between adjacent pairs is not quantitative, there is a remarkable gap between neodymium and samarium. Moreover, it was not possible to elute Sm and Eu with 0.7 M HCl. Therefore, we adopted a step-gradient elution technique. In the second step, we increased the acid concentration to 1.2 M.

The break in the elution curve between Nd and Sm is attributable to the "tetrad effect" described by Peppard et al (186, 187). Their plot of the logarithm of distribution coefficients or separation factors against atomic number displays a segmented curve with four sections. They tentatively generalized the "tetrad effect" hypothesis as follows:

> In systems involving all 15 lanthanides (III), the points on a plot of the logarithms of a suitable numerical measure of a given property of these elements VS Z may be grouped through the use of four smooth curves without inflections, into four tetrads with Gd being common to the second and third tetrads and the extending smooth curves intersecting additionally in the 60-61 and 67-68 Z regions. In a similar plot for actinides (III) an analogous tetrad effect is apparent with the curium point being common to the second and the third tetrads.

In their studies on the separation of the lanthanides by extraction chromatography with HEHØP, Fidelis and Siekierski (188) observed this effect and presented it as "Regularities in Stability Constants". The effect of

regularities consists in a definite sequence of four minima and four maxima in a separation factor along the series of lanthanides. The essence of the effect consists in some stabilization of the two pairs of electron configurations $f^3 - f^4$ and $f^{10} - f^{11}$, in addition to the stabilization of the f^0, f^7 and f^{14} configurations. These stabilizations result in the main division of the whole group of f-electron elements ($f^0 - f^{14}$) into two subgroups, $f^0 - f^7$ and $f^7 - f^{14}$, and in the further internal division of each of the two subgroups by the $f^3 - f^4$ and $f^{10} - f^{11}$ pair respectively. Therefore the name "double-double effect" was introduced (189). The stabilization of certain electron configurations has an influence on complex formation along the lanthanide series. We have noticed this stabilization between Nd and Sm. Samarium, being strongly complexed with HEHØP, needed a higher acid concentration for elution. Since the "tetrad effect" is well known in extraction chromatography, we have not proceeded further to confirm this effect in other subgroups in the in the series. We therefore studied the quantitative loading and recovery of individual lighter lanthanides and obtained excellent recoveries. The results are shown in Table 12.

The behaviour of the principal rock-forming elements was also studied. A 17.95 μg of aliquot of Al in 0.06 N HCl was loaded on to the column and the drops collected in 5 fractions. Aluminum was determined by Atomic Absorption Spectroscopy and the results are shown in Table 13. Similarly 27.0 μg of calcium was

TABLE 12

Quantitative Recovery of Lighter Lanthanides

Column length = 11.5 cm;
I.D. = 6 mm;
% extractant = 17.4 (W/W)

Analyte	μg, taken	μg, Recovered[a]	
La	20.2	20.2 ± 0.82	Eluted with
Pr	26.2	25.8 ± 0.77	0.7N HCl.
Sm	13.0	12.7 ± 0.51	Eluted with
Eu	11.0	10.9 ± 0.23	1.2N HCl.

(a) Triplicate samples, determined by both spectrophotometric method with Arsenazo-III and directly coupled plasma emission.

TABLE 13

Aluminum Recovery

Column length = 11.5 cm
I.D. = 6 mm
% extractant = 17.4 W/W
Eluent = 0.1 M HCl
Total Aluminum loaded on the column = 17.95 μg

Fraction Number	No. of drops	Al, found, μg
1	100	4.38
2	105	5.82
3	100	4.30
4	100	5.00
5	100	0.00
		Total 19.50

loaded on to the column, eluted with 0.1 M HCl, collecting the drops into several fractions. The fractions were analyzed qualitatively by flame emission spectroscopy. All the calcium was eluted out by about 200 drops. The extractant HEHØP has exceptionally strong extractive capacity for lanthanides, when the aqueous phase is acidic and it has high discrimination against extraction of the common elements particularly Ca, and Al.

In order to ensure against column saturation when working with higher concentrations of lanthanides and when doing rock analyses, larger columns than those described above were used.

Quantitative recovery of all the lanthanides

The length and the internal diameter of the column were 5 cm and 1 cm respectively in this experiment. The column material in this case was 35% (W/W) of HEHØP. Aliquots of all the lanthanides except promethium were mixed together in 0.1 M $HClO_4$. The volume of the sample introduced on the column was 25 mL. The column, charged with lanthanides, was initially washed with 50 mL 0.1 M $HClO_4$. Step-gradient elution with nitric acid was used, the final step being carried out with pre-equilibrated 7.5 M HNO_3.

The eluate was collected in two successive 100 mL fractions. These were individually evaporated to dryness and wet ashed with nitric and perchloric acids. The residue

was taken up in 0.1 M HNO_3 and determinations carried out by DCP emission spectroscopy.

We have also added to the synthetic sample, 200.0 μg, 541.0 μg and 7.9 μg of Al, Ca, and Sc, respectively. The sample was contained in 25 mL of 0.1 M $HClO_4$. It was loaded on to the column and eluted with 100 mL of 0.1 M $HClO_4$. The final elution was carried out with 7.5 M HNO_3. Calcium, was monitored in the effluent by flame emission spectroscopy. Scandium was tested for by Arsenazo-III. The sensitivity of the violet blue colour test was 0.2 ppm, Sc. The results are shown in Tables 14, 15 and 16.

Dissolution and separation procedure

After having established the conditions for quantitative recovery for all the lanthanides, we employed this method for the analysis of certified rock standard SY-2 1 g of powdered rock was weighed accurately into a Zr crucible and the dissolution of the sample was accomplished by fusion with KO_2 - KOH flux as described by Westland and Kantipuly (158). After fusion, the melt was dissolved in 50 mL of 5 M HCl. The solution was evaporated to dryness on a water bath to dehydrate silica. The precipitate was taken up in a small volume of 5 M HCl and filtered through Whatman paper. The filtrate was again evaporated to dryness in order to render insoluble a further small amount of silicic acid. The precipitate was treated with acid as before and silica

TABLE 14

Recovery of Lanthanides (5 - 40 μg samples)

Column: 5 X 1 cm
35% (W/W) extractant
Eluent: 7.5 M HNO_3

Element	Percent Recovered		
	Effluent	Eluate 7.5 M HNO_3	
		1st 100 mL	2nd 100 mL
La	0.0	100.6	0.0
Ce	0.0	101.2	0.0
Eu	0.0	97.5	0.0
Sm	0.0	95.0	0.0
Dy	0.0	100.4	0.0
Er	0.0	102.0	0.0
Tm	0.0	98.6	1.5
Yb	0.0	58.3	44.8
Lu	0.0	0.0	99.2

TABLE 15

Recovery of Lanthanides and Other Elements

Column: 5 X 1 cm
35% W/W extractant

Element	μg, taken	Percent Recovered				
		Effluent	Eluate 0.1 M HCl	Eluate 7.5 $MHNO_3$		
				1st 100 mL	2nd 100 mL	3rd 100 mL
La	50.0	0.0	0.0	99.6	0.0	0.0
Ce	30.0	0.0	0.0	102.0	0.0	0.0
Eu	20.3	0.0	0.0	103.0	0.0	0.0
Gd	27.1	0.0	0.0	100.0	0.0	0.0
Dy	22.3	0.0	0.0	100.5	0.0	0.0
Er	11.5	0.0	0.0	102.0	0.0	0.0
Tm	23.2	0.0	0.0	93.1	4.0	0.0
Yb	36.2	0.0	0.0	55.5	43.9	0.0
Lu	24.8	0.0	0.0	0.0	99.6	0.0
Al	200.0	94.1	7.7	—	—	—
Ca	540.6	93.1	11.0	—	—	—
Sc	7.9	39.2	60.5	—	—	—

TABLE 16

Recovery of Lanthanides and Other Elements

Column: 5 X 1 cm
35% W/W extractant

Element	µg, taken	Percent Recovered				
		Effluent	Eluate 0.1 M HCl	Eluate 7.5 M HNO_3		
				1st 100 mL	2nd 100 mL	3rd 100 mL
La	15.2	0.0	0.0	101.0	0.00	0.0
Ce	17.7	0.0	0.0	99.8	0.0	0.0
Eu	6.2	0.0	0.0	98.5	0.0	0.0
Gd	12.5	0.0	0.0	98.7	0.0	0.0
Dy	36.1	0.0	0.0	101.2	0.0	0.0
Er	10.0	0.0	0.0	105.0	0.0	0.0
Tm	49.7	0.0	0.0	98.1	1.7	0.0
Yb	10.7	0.0	0.0	60.5	41.2	0.0
Lu	15.5	0.0	0.0	0.0	99.7	0.0
Al	200.0	95.2	6.3	—	—	—
Ca	540.6	94.3	10.5	—	—	—
Sc	7.9	36.9	63.2	—	—	—

collected on a fresh filter. The two washed precipitates were combined and ignited at 850°C in a pt. crucible. The silica was volatalized by heating with a mixture of HF and $HClO_4$ in a platinum dish. We did not use HF - H_2SO_4 mixture for this purpose because it gives difficultly soluble anhydrous sulfates with a number of metals such as Ba, Ca, Pb which are present in rocks. The platinum dish was washed with 5 M HCl and the washings added to the combined filtrate. At this point the volume of the sample was ~ 100 mL.

Alamine extraction was carried out to remove the major elements which form anionic chlorocomplexes including iron and uranium. The aqueous phase which contains REE, Al, Sc, alkali and alkaline earths was evaporated down to about 50 mL, and potassium from the flux was removed by precipitating as $KClO_4$. Finally, the sample was taken up in 25 mL of 0.1 M $HClO_4$. This solution was loaded on to a 5 X 1 cm column consisting of phenylated Kel-F impregnated with HEHØP, extractant and conditioned with 0.1 M $HClO_4$. The sample was eluted with 100 mL of 0.1 M HCl. This eluate contained alkali, alkaline earth, Al, Sc etc., and was discarded. The lanthanides were held quantitatively on the resin and were eluted with 250 mL of 7.5 M HNO_3. This solution contains predominantly all the lanthanides and yttrium. The solution was evaporated to near dryness, wet ashed and taken up in 25 mL of 0.1N HNO_3 for DCP emission spectroscopic determination. The lanthanide values obtained by applying this

procedure on standard Canadian Sy-2 rock are shown in Table 17.

Qualitative tests for Ti^{4+} and Ce^{3+}

In the course of the separation procedure the following tests were applied while analyzing the Sy-2 rock sample to monitor the path of Ti^{4+} and Ce^{3+} at various steps.

In acid solution Ti^{4+} gives yellow colouration which can be attributed to HOO - $Ti(OH)_3$, peroxotitanic acid, whereas when Ce(III) is treated with NH_3 solution and excess H_2O_2, a yellowish brown colouration appears. Upon boiling the mixture, a yellow precipitation of $Ce(OH)_4$ separates.

General Discussion and Conclusions

New methods of determination of earths in geological materials have been described in the foregoing pages. The flowsheet for the separation of lanthanides is shown in Figure 21. It is designed to be applicable when either a spectrophotometric method or neutron activation analysis is to be employed at the finish. A potassium fluxing agent was developed for neutron activation work. The more conventional Na_2O_2 fusion could be substituted whenever atomic emission spectrometry is used or whenever it can be established that the separation of alkali in the chromatographic step is efficient enough for NAA to be used. It would probably be safe to use Na_2O_2, especially if cadmium or boron shielding

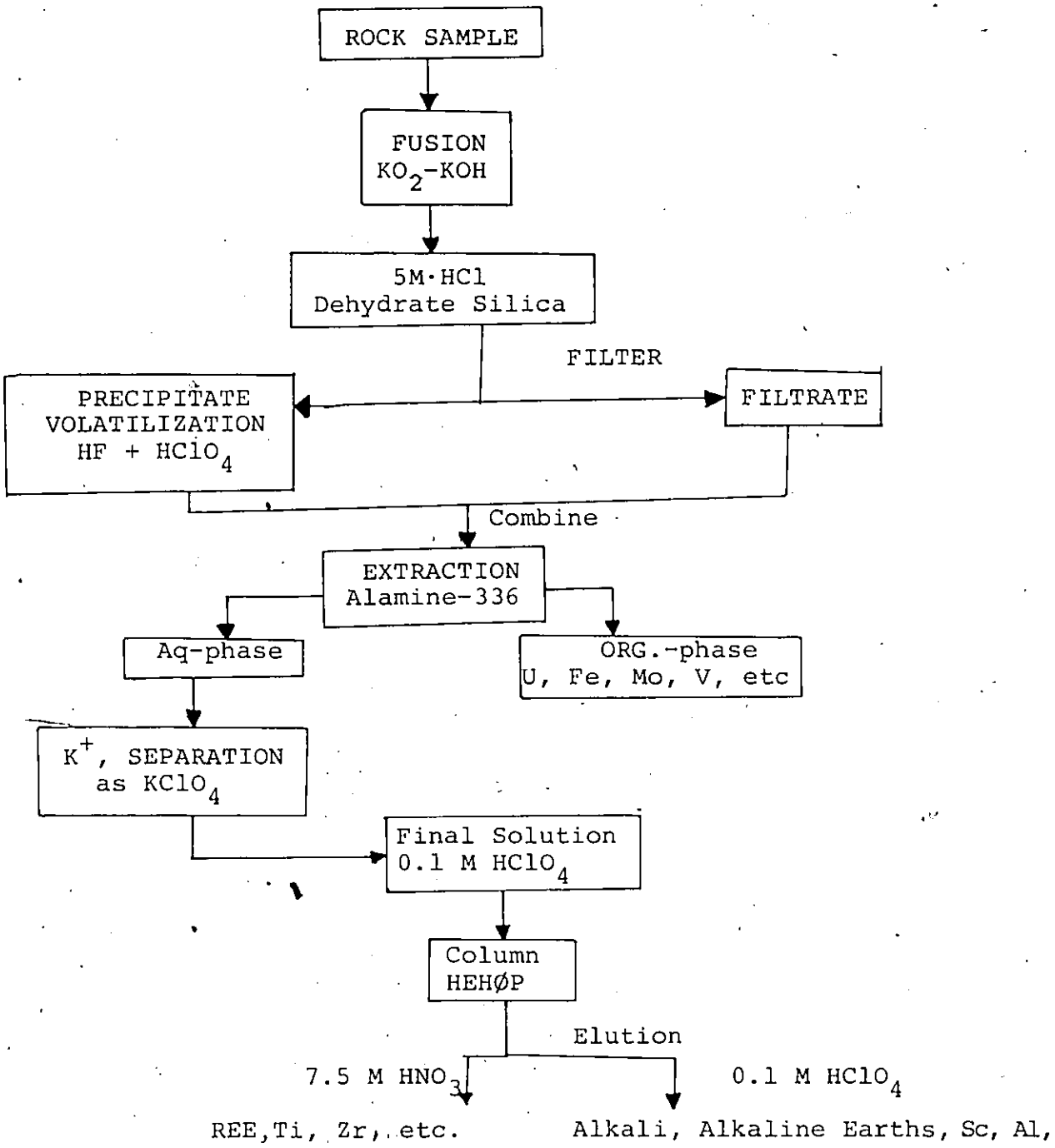
TABLE 17

Analytical Results of Canadian Sy-2 (Syenite)

Element	Literature ppm (190)	Found, ppm		
		Replicate 1	Replicate 2	Replicate 3
La	88	89.2	88.7	86.9
Ce	210?	205.2	203.1	206.2
Pr				
Nd	71?			
Sm	15?	13.3	14.7	13.9
Eu	2.4?	1.0	2.2	2.5
Gd				
Tb	2?			
Dy	20?	20.7	19.6	18.9
Ho				
Er	12?	10.2	11.1	10.5
Tm	2?	2.7	1.5	1.8
Yb	17	18.1	17.7	17.2
Lu	3?	2.6	2.2	2.7

Fig. 21

FLOWSHEET FOR DETERMINATION OF LANTHANIDES IN ROCK SAMPLES USING R P C FOLLOWED BY D C P (OR) N.A A



is used in the irradiation.

The separation of the lanthanide group into subgroups is a means of reducing inter-element interferences. Crock and Lichte (95) corrected for such interferences by a data processing procedure. Our analysis of the certified rock, employing fractionation of the lanthanides into sub-groups, gave very satisfactory agreement with the certified and literature values for that material. Analysts will therefore have an opportunity to choose between these alternative methods. We expect that our method of fractionation of the lanthanides will be found to be preferable when very low lanthanide values are encountered.

The separation scheme has been designed so that it can be used in NAA for the pre-irradiation separation of the lanthanides from a silicate matrix. This avoids the need for post-irradiation handling and this should make the procedure attractive to a wider number of geochemistry laboratories. The advantage of isotope dilution methods is lost and so it has been necessary to prove that each step in the procedure is quantitative. By largely avoiding precipitations, it has been possible to do this. Moreover, NAA blank analyses were carried out on most of the reagents involved and either nil or negligible blank values were encountered. The reagents, including the acids, solvents etc., were standard ACS laboratory grade only. There is therefore no extraordinary cost factor entailed in using the procedure.

The procedure described here is probably more rapid than post-irradiation separation schemes. This is for two reasons: (i) The extreme precautions of "hot" chemistry are avoided and (ii) there is no need to determine the so-called chemical yield, an added step.

It should be pointed out that there could be some further flexibility in decomposing the sample. For analyses at the sub-ppm level, it would be desirable, probably necessary, to work with samples weighing several grams. The author has in fact done this. The decomposition then consisted of treatment of the material with hydroflouric acid in a platinum dish. Silica was fumed off in the presence of perchloric acid in addition to the HF and the small residue was subjected to the fusion technique. The remaining matrix elements in 5 g samples did not cause any problems in the later extraction and chromatographic steps. Experiments to examine the application of the method to samples containing less than $1 \mu g \cdot g^{-1}$ have been begun. A neutron activation finish is to be used.

The author recognizes that further work is required. In particular, the method should be examined thoroughly at very low lanthanide levels and studies should be done comparing it with methods that do not fractionate the lanthanides. The author has not established the ultimate fate of thorium and zirconium in the procedure but it is believed that these elements remain permanently on the chromatographic column.

The fate of certain other elements, e.g. Nb, Ta, W, is not exactly known. Fortunately, these are rare in most cases and the specificity of modern instrumental methods of finish makes this question less important.

CLAIMS TO ORIGINAL RESEARCH

1. New procedures were developed to determine thorium at microgram levels. The procedure describes separations of thorium from phosphatic materials and other interfering elements such as uranium, molybdenum, vanadium, and iron, etc. The validity of the procedure was verified by application to a certified ore, an arkose sandstone.
2. The cation exchange behaviour of thorium at microgram quantities and trace levels was studied and the results interpreted.
3. A new flux KO_2 - KOH, was introduced into analytical science to fuse the rock samples. It was found that this flux has an added advantage over other fluxes, as potassium can easily be removed after fusion by precipitation as $KClO_4$. The co-precipitation of various cations such as Ag^{+}, Ca^{2+}, Eu^{3+} and Th^{4+} were studied while removing bulk potassium salt.
4. 2-ethyl-hexyl-hydrogen phenyl phosphonic acid (HEHØP) was found to be fairly selective for larger cations, such as lanthanides and actinides with high separation factors. It shows high discrimination against extraction of common elements like alkali, alkaline earths and aluminum, etc. Therefore the extractant was further studied to isolate and fractionate the lanthanides in rock analysis.

5. Extraction chromatography was used to study the separation of the lanthanide group into subgroups. The "tetrad effect" was exploited in order to achieve good separations.
6. Phenylated Kel-F was found to be an excellent support material with regard to its hydrophobic and hydrophilic characteristics and its ability to retain the extractant.
7. Separation scheme was developed to determine lanthanides in rocks, using a reversed phase extraction chromatographic technique, followed by DCP spectrometry. The procedure was verified by employing the separation scheme on a certified standard, Canadian syenite rock.

Some of the work described in the thesis has been published, and the remainder is in the process of publication.

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