

SHAHID BEHESHTY UNIVERSITY

MICRODETERMINATION OF RARE EARTH METALS (Ce, La, Eu)
BY COMPLEXOMETRY

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JUN

1993

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MICRODETERMINATION OF RARE EARTH METALS, La,Ce,AND Eu BY
COMPLEXOMETRY

A Thesis submitted By
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In part fullfillment of the conditions of admittance
to the Degree of

MASTER OF SCIENCE

of the Shahid Beheshty University

TEHRAN

JUN 1993

ACKNOWLEDGEMENTS

The research described in this thesis was carried out in the Fuel Department of the Atomic Energy Organization of Iran, and author thankful for this scientific cooperation.

The author wishes to thank professor Ali Masoumi and Dr.Hossein Ghafourian for the guidance and encouragement, for many helpful discussions and for their useful advice and suggestions during the course of this work.

She also wishes to thank MS Vahideh Mohadjeri for her assistance and cooperation during the course of this work.

To my dear

father and mother

whose sacrifice, kindness and enthusiasm

have always made

a friendly home atmosphere

for

pursuing my activities

57 58 59 60 61 62 63 64 65 66 67 68 69 70 71
La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

NOMENCLATURE (ACCORDING TO IUPAC RULES) :

Rare earth metals : Sc, Y and ⁵⁷La to ⁷¹Lu

Lanthanoids or Lanthanides = ⁵⁸Ce to ⁷¹Lu

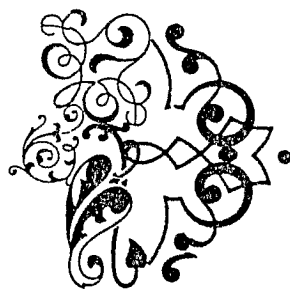
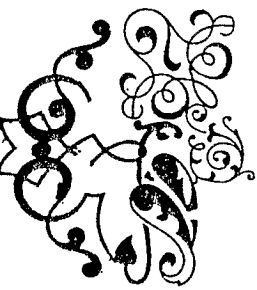
Lanthanons = LANTHANOIDES **OR** LANTHANIDES + La

NOMENCLATURE (ACCORDING TO PRACTICE) :

Lanthanides = ⁵⁷La to ⁷¹Lu

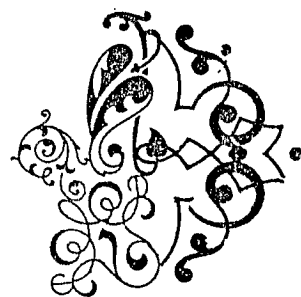
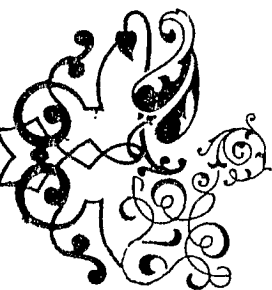
lights « CERICS » La, Ce, Pr, Nd, Pm, Sm, Eu, Gd

heavies « YTTRICS » Tb, Dy, Ho, Er, Tm, Yb, Lu



PART ONE

*Studying in
Lanthanides
Chemistry*



Abstract:

A simple, sensitive and selective method for solvent extraction and spectrophotometric determination of lanthanum (II) europium (III), and cerium(III) is described. The rare earth metals are extracted into chloroform solution of N-phenylbenzohydroxamic acid (PBHA) at pH 9-10 various parameters are studied to optimize the extraction conditions. The molar absorptivity is found to increase from 6×10^4 to $9.4 \times 10^4 \text{ l. mol}^{-1} \text{ cm}^{-1}$ with the increase in atomic number of the rare earths.

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INTRODUCTION

The lanthanides (Ce-Lu, atomic numbers 58-71) are unique among the elements, except for the closely similar actinides, in resembling each other so markedly both in elemental state and in compounds that changes in properties for a given oxidation state with increasing atomic number are largely changes in degree rather than in kind.

Typical examples are constancy of a particular thermodynamically stable oxidation state(+3) throughout the series, many instances of isomorphism when both oxidation state and anion are fixed, invariable co-occurrence in nature, the classically striking difficulty in separating one lanthanide from another, and small differences in the thermodynamic functions for particular reactions of lanthanide ions of a given charge type . Furthermore, both lanthanum (atomic number 57) and Yttrium (atomic number 39), elements treated here in as members of Group IIIA, are broadly indistinguishable from the lanthanides in so many respects that they are operationally classifiable with the latter. It is, of course, the problems of explanation associated with these situations that prompted early difficulties in the periodic classification of the lanthanides.

Discovery, History

The origin of lanthanide chemistry was the discovery by Swedish Army Lieutenant Carl Axel Arrhenius in 1787 of an unusual black mineral specimen near the Ytterby feldspar quarry not far from Stockholm.

In 1794 Johan Gadolin, a Finnish professor at the University of Åbo, separated from samples of this mineral about 38% of a new and previously uncharacterized "earth", or oxide in modern terminology. Although Arrhenius had termed the mineral Ytterite, Anders Gustaf Ekeberg in 1797 named it gadolinite and the earth Yttria. Shortly thereafter, in 1803, Martin Heinrich Klaproth, a German investigator, and, completely independently, Jöns Jacob Berzelius and Wilhelm Hisinger, in Sweden, isolated from another heavy mineral, originally found in 1751 by Axel Fredrik Cronstedt in a mine near Bastnas, Sweden, a similar but somewhat different "earth". This product was named ceria and the mineral from which it came cerite, both from the then recently discovered planetoid Ceres.

Although both yttria and ceria were believed to be simple compounds, differences in the properties of these substances as prepared by different investigators led ultimately to the belief that they were not.

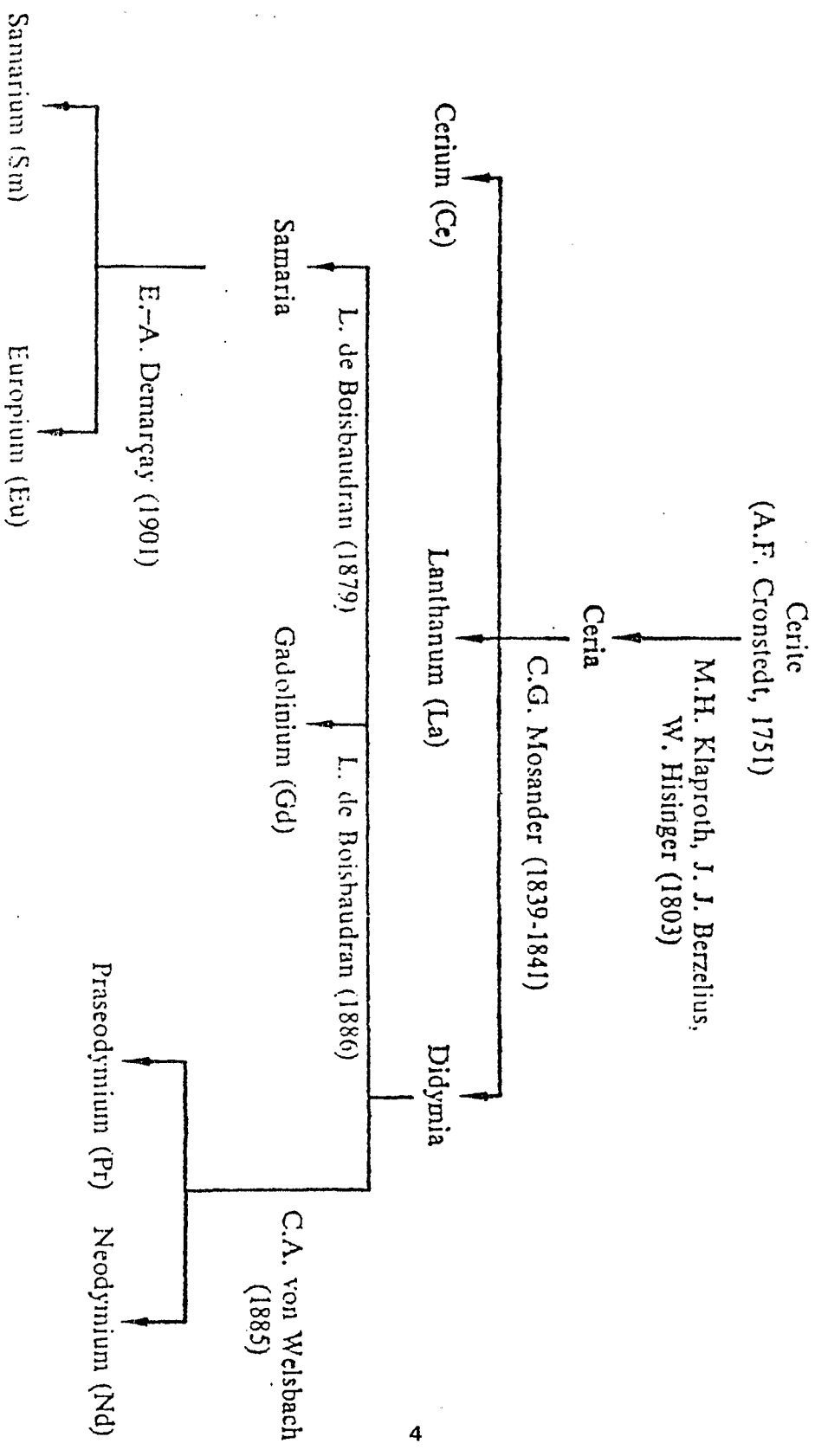
Absolute proof as to the complexity of each "earth" was obtained first by Carl Gustav Mosander, a Swedish surgeon, chemist and mineralogist.

During the period 1839-1841, Mosander Thermally decomposed a sample of nitrate obtained from Ceria, leached the product with dilute nitric acid, identified the insoluble product as Ceria, and ultimately recovered from the Solution two new "earths", lanthana (to be hidden) and didymia (twin brother of lanthana).

Similarly, in 1843, Mosander Separated from the original yttria three oxide fractions: a white fraction (yttria), a yellow one (old erbia), and a rose-colored one (old terbia).

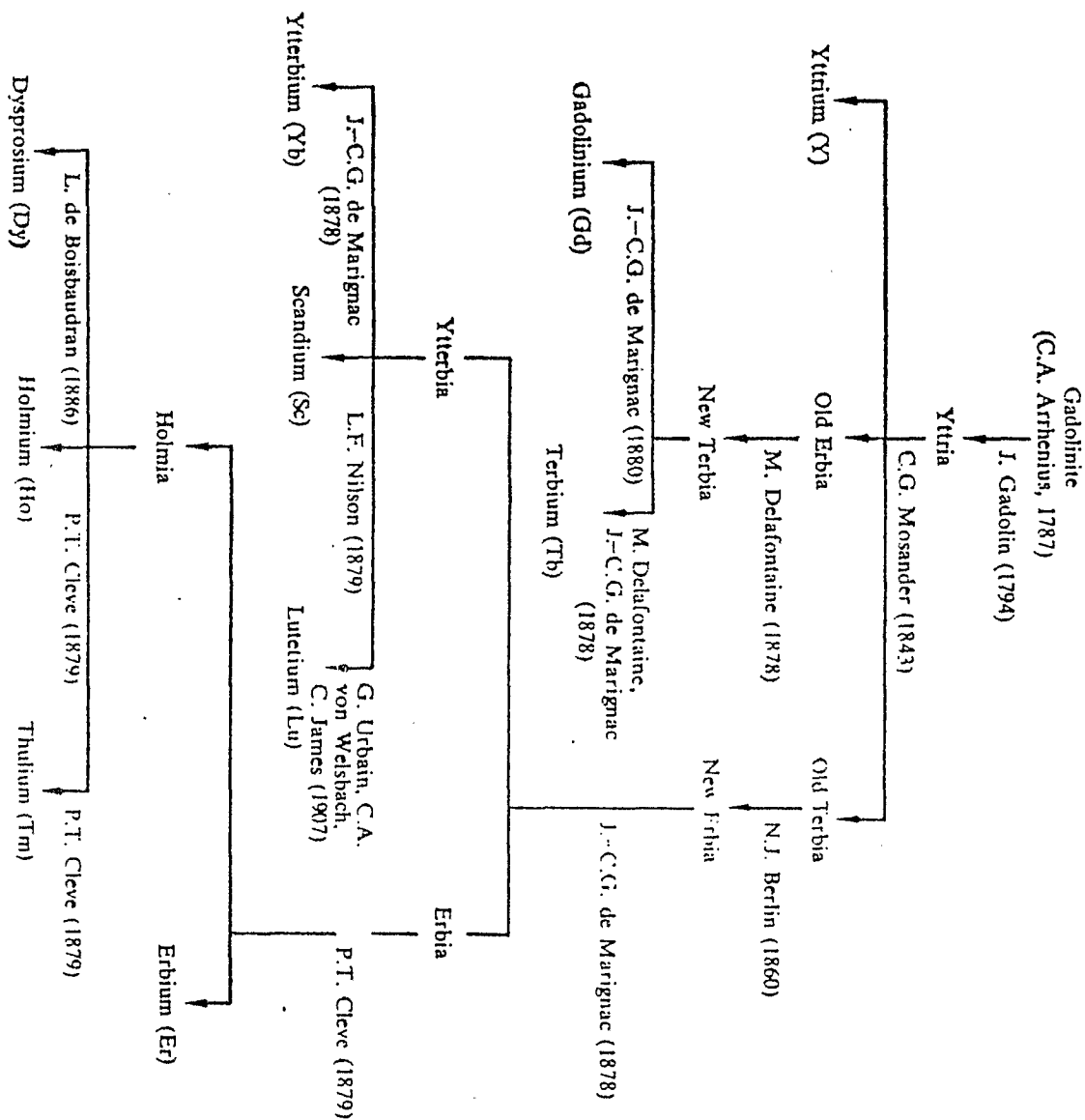
These observations were followed by an intense period of investigation of the complexities of both Ceria and yttria extending into the early 1900'S and involving many of the well-known investigators of those times. That there were duplications of effort, inaccurate reports, spurious claims as to discovery, and innumerable instances of confusion as a consequence of the limitations in communication, in definitive methods of characterization, and in clean-cut and rapid methods of separation is completely understandable. The summaries given in tables (1) and (2)

TABLE 1. HISTORICAL OUTLINE SHOWING THE ULTIMATE SIMPLIFICATION OF CERIA^a



^a Origins of names: Lanthanum—to lie hidden; cerium—Ceres; praseodymium—green twin; neodymium—new twin; samarium—the mineral samarskite; europium—Europe; gadolinium—Gadolin.

TABLE 2. HISTORICAL OUTLINE SHOWING THE ULTIMATE SIMPLIFICATION OF YTRIA*



* Origins of names: yttrium, ytterbium, erbium, terbium—Ytterby; gadolinium—Gadolin; dysprosium—difficult of access; holmium—Stockholm; thulium—Thule (ancient name of Scandinavia); lutetium—Lutetia (ancient name of Paris); scandium—Scandinavia.