Handbook of the
Analytical Chemistry of

RARE ELEMENTS

A.I. BUSEV, V.G. TIPTSOVA, and V.M. IVANOV

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HANDBOOK OF THE ANALYTICAL CHEMISTRY OF RARE ELEMENTS

Foreword

This book is intended for use by laboratory workers, industrial chemists, and graduate students specializing in the chemistry of rare elements.

Knowledge of the theoretical principles of photometric, polarographic, potentiometric and other analytical techniques is a prerequisite for successful application of the material. A brief analytical description of the element precedes the description of laboratory methods.

The book describes the methods of determination of lithium, rubidium, cesium, beryllium, scandium, REE, yttrium, vanadium, niobium, tantalum, molybdenum, titanium, zirconium, hafnium, uranium, thorium, tungsten, rhenium, technetium, gallium, indium, thallium, germanium, bismuth, selenium and tellurium. It includes the most important organic reagents for these elements, masking compounds, and solubility products of certain sparingly soluble compounds. Methods for the isolation of rare elements by solvent extraction are also given.

Only the simplest, fastest, most selective and most reliable of the numerous analytical methods for determining rare elements have been included in this book. The methods do not require the use of unconventional reagents and can be applied in scientific research as well as in industrial laboratories.

The preparation of the analytical reagents is not described in detail, since in most cases it presents no difficulties.

Each chapter is provided with a list of references where additional information on the analytical procedures described can be found. Another source of useful information are the books on analytical chemistry listed on pages 16–21.

Platinum metals and inert gases, although formally regarded as "rare" elements, are not considered in this book. Determination of rare elements by spectroscopy, neutron activation methods and other techniques which have been excluded will be found in special textbooks. The spectroscopic methods for determining both rare and commonly occuring elements are, in principle, the same. Discussion of flame-photometric methods can also be found in special textbooks on spectroscopic analysis.

Numerous constants quoted in this book were taken from L. MEITES, ed., *Handbook of Analytical Chemistry*, McGraw-Hill Book Co., New York–Toronto–London, 1963.

The theoretical part of this book and the analytical treatment of rare elements were written by A.I. Busev. V.G. Tiptsova compiled the methods for the determination of vanadium, niobium, tantalum, tungsten, rhenium, gallium, indium, thallium, germanium, selenium and tellurium. The methods for the determination of lithium, rubidium, cesium, beryllium, scandium, lanthanum, cerium and the lanthanide elements, thorium, uranium, titanium, zirconium, molybdenum and bismuth were compiled by V.M. Ivanov. The entire book was edited by A.I. Busev.

We wish to acknowledge the help of Yu.A. Chernikhov, V.G. Goryushina and T.V. Cherkashina who reviewed the book and offered valuable advice, and the assistance of I.P. Alimarin and V.M. Peshkova in reading the manuscript. Special thanks are due also to M.A. Semenova and A.N. Buseva for their valuable help in preparing the manuscript for print. Any critical comments from readers will be most welcome.

EXPLANATORY LIST OF ABBREVIATIONS OF U.S.S.R. INSTITUTIONS AND JOURNALS APPEARING IN THIS TEXT

Abbreviation	*Full name (transliteration)*	*Translation*
GIREDMET	Gosudarstvennyi Naucho-Issledovatel'skii Institut Redkikh Metallov	State Rare Metals Scientific Research Institute
KhGU	Khar'kovskii Gosudarstvennyi Universitet	Kharkov State University
MGU	Moskovskii Gosudarstvennyi Universitet	Moscow State University
VKhO	Vsesoyuznoe Khimicheskoe Obshchestvo	All-Union Chemical Society
Zav. Lab.	Zavodskaya Laboratoriya	Industrial Laboratory
ZhAKh	Zhurnal Analiticheskoi Khimii	Journal of Analutical Chemistry
ZhNKh	Zhurnal Neorganicheskoi Khimii	Journal of Inorganic Chemistry
ZhAKh	Zhurnal Analiticheskoi Khimii	Journal of Analytical Chemistry
ZhFKh	Zhurnal Fizicheskoi Khimii	Journal of Physical Chemistry

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Rare Elements in Industry and in Geochemistry

About sixty elements in various groups of the Periodic Table are classified as rare elements. They include elements with a fairly high natural abundance as well as elements which are truly "rare". According to the accepted convention, a rare element is any element which has been produced on a commercial scale for a relatively short period of time, and whose practical uses are therefore of fairly recent origin.*

Thus the term *rare element* is to be interpreted as a *technologically new* or *relatively new element.*

The following elements are currently considered rare elements:

I. *Metals*:

1) Light elements: Li, Rb, Cs and Be;
2) rare-earth elements: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, Sc, and Y;
3) dispersed elements: Ga, In, Tl, Ge, Hf, and Re;
4) high-melting elements: Ti, Zr, Hf, V, Nb, Ta, Mo, W, and Re;
5) radioactive elements: Ra, Po, Ac, Th, Pa, U, Np, Pu, Am, Cm and other transuranium elements;
6) minor elements: Bi;
7) noble elements: Pt, Ru, Os, Rh, Ir, Pd, Au, and Ag.

* See SAZHIN, N. P. and G. A. MEERSON. Rare Elements in Modern Technology.—*Khimicheskaya Nauka i Promyshlennost'*, I, No. 5, 482. 1956.

II. *Non-metals*:

1) B, Se, Te;

2) inert gases: He, Ne, Ar, Kr, Xe.

Table 1 shows the abundance in the Earth's crust (lithosphere) of *technologically* rare elements and of common elements (for comparison). It will be seen from the table that some technologically rare elements occur in the Earth's crust in large

Table 1

AVERAGE CHEMICAL COMPOSITION OF THE LITHOSPHERE* (AFTER VINOGRADOV)

(Thickness 16 km, excluding oceans and atmosphere)

Element	Composition of lithosphere		Element	Composition of lithosphere	
	atomic %	wt. %		atomic %	wt. %
Oxygen	58.0	47.2	Cerium	$6 \cdot 10^{-4}$	$4.5 \cdot 10^{-3}$
Silicon	20.0	27.6	Gallium	$4 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$
Aluminum	6.6	8.80	Neodymium	$3.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$
Hydrogen	3.0	0.15	Scandium	$3 \cdot 10^{-4}$	$6 \cdot 10^{-4}$
Sodium	2.4	2.64	Lanthanum	$2.5 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$
Iron	2.0	5.10	Germanium	$2 \cdot 10^{-4}$	$7 \cdot 10^{-4}$
Calcium	2.0	3.6	Niobium	$2 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
Magnesium	2.0	2.10	Lead	$1.6 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$
Potassium	1.4	2.6	Arsenic	$1.5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
Titanium	$2.5 \cdot 10^{-1}$	$6 \cdot 10^{-1}$	Gadolinium	$1 \cdot 10^{-4}$	$1 \cdot 10^{-3}$
Carbon	$1.5 \cdot 10^{-1}$	$1 \cdot 10^{-1}$	Cesium	$9.5 \cdot 10^{-5}$	$7 \cdot 10^{-4}$
Barium	$5.7 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	Praseodymium	$9 \cdot 10^{-5}$	$7 \cdot 10^{-4}$
Phosphorus	$5 \cdot 10^{-2}$	$8 \cdot 10^{-2}$	Samarium	$9 \cdot 10^{-5}$	$7 \cdot 10^{-4}$
Manganese	$3.2 \cdot 10^{-2}$	$9 \cdot 10^{-2}$	Thorium	$7 \cdot 10^{-5}$	$8 \cdot 10^{-4}$
Sulfur	$3.0 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	Molybdenum	$6 \cdot 10^{-5}$	$3 \cdot 10^{-4}$
Fluorine	$2.8 \cdot 10^{-2}$	$2.7 \cdot 10^{-2}$	Dysprosium	$5 \cdot 10^{-5}$	$4.5 \cdot 10^{-4}$
Chlorine	$2.6 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$	Erbium	$5 \cdot 10^{-5}$	$4 \cdot 10^{-4}$
Nitrogen	$2.5 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	Hafnium	$5 \cdot 10^{-5}$	$3.2 \cdot 10^{-4}$
Lithium	$1.9 \cdot 10^{-2}$	$6.5 \cdot 10^{-3}$	Bromine	$4 \cdot 10^{-5}$	$1.6 \cdot 10^{-4}$
Strontium	$1 \cdot 10^{-2}$	$4 \cdot 10^{-2}$	Ytterbium	$3 \cdot 10^{-5}$	$3 \cdot 10^{-4}$
Chromium	$8 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	Thallium	$3 \cdot 10^{-5}$	$3 \cdot 10^{-4}$
Rubidium	$7 \cdot 10^{-3}$	$3.1 \cdot 10^{-2}$	Uranium	$2 \cdot 10^{-5}$	$3 \cdot 10^{-4}$
Vanadium	$6 \cdot 10^{-3}$	$1.5 \cdot 10^{-2}$	Tantalum	$1.8 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Zirconium	$4 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	Europium	$1.8 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$
Copper	$3.6 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	Selenium	$1.5 \cdot 10^{-5}$	$6 \cdot 10^{-5}$
Nickel	$3.2 \cdot 10^{-3}$	$8 \cdot 10^{-3}$	Holmium	$1.5 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$
Zinc	$1.5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	Tungsten	$1 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
Cobalt	$1.5 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	Lutetium	$1 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
Beryllium	$1.2 \cdot 10^{-3}$	$6 \cdot 10^{-4}$	Terbium	$1 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$
Tin	$7 \cdot 10^{-4}$	$4 \cdot 10^{-3}$	Thulium	$8 \cdot 10^{-6}$	$8 \cdot 10^{-5}$
Yttrium	$6 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$	Cadmium	$7.6 \cdot 10^{-6}$	$5 \cdot 10^{-5}$
Boron	$6 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	Antimony	$5 \cdot 10^{-6}$	$4 \cdot 10^{-5}$

Table 1 (continued)

Element	Composition of lithosphere atomic %	wt. %	Element	Composition of lithosphere atomic %	wt. %
Iodine	$4 \cdot 10^{-6}$	$3 \cdot 10^{-5}$	Gold	$5 \cdot 10^{-8}$	$5 \cdot 10^{-7}$
Bismuth	$1.7 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	Rhodium	$1.7 \cdot 10^{-8}$	$1 \cdot 10^{-7}$
Silver	$1.6 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	Iridium	$8.5 \cdot 10^{-9}$	$1 \cdot 10^{-7}$
Indium	$1.5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	Rhenium	$8.5 \cdot 10^{-9}$	$1 \cdot 10^{-7}$
Mercury	$7 \cdot 10^{-7}$	$7 \cdot 10^{-6}$	Radium	$9 \cdot 10^{-12}$	$1 \cdot 10^{-10}$
Osmium	$5 \cdot 10^{-7}$	$5 \cdot 10^{-6}$	Protactinium	$8 \cdot 10^{-12}$	$1 \cdot 10^{-10}$
Palladium	$1.6 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	Actinium	$5 \cdot 10^{-15}$	$6 \cdot 10^{-10}$
Tellurium	$1.3 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	Polonium	$2 \cdot 10^{-15}$	$2 \cdot 10^{-14}$
Ruthenium	$1 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	Plutonium	$7 \cdot 10^{-17}$	$1 \cdot 10^{-15}$
Platinum	$5 \cdot 10^{-8}$	$5 \cdot 10^{-7}$	Radon	$5 \cdot 10^{-17}$	$7 \cdot 10^{-16}$

* The quantitative determinations of helium, argon, neon, krypton and xenon are not reliable.

amounts. For example, titanium, which is usually regarded as a technologically rare element, is the tenth most abundant element in the Earth's crust, and lithium is the eighteenth most abundant element.†

Some very familiar elements, on the other hand, (mercury, antimony, cadmium, lead, tin), have a low abundance in the Earth's crust.

A distinction should be made between the concept of *technologically rare element* and *low-abundance element*. In geochemistry, various chemical elements are regarded as rare because of their low abundance in nature. The geochemically rare elements include a group of dispersed elements (rhenium, radium, polonium, etc.) which do not form independent minerals and are encountered as impurities in minerals and ores of other elements.

As a rule, the abundance of chemical elements in celestial bodies and on Earth depends on the stability of the atomic nuclei in stellar interiors. The stability of atomic nuclei steeply falls off as the atomic number increases to 28, and then it continues decreasing more slowly. The relatively low abundance of the light elements—lithium, beryllium, boron, and others—is due to the large cross-section of the reaction between these nuclei and protons, neutrons, and other particles. The low abundance of the heavy elements—thorium, uranium, and the transuranium elements—is due to α-decay and spontaneous fission.

The number of technologically rare elements is steadily decreasing owing to the increase in the production volume and improved production technology. According to some authorities, titanium no longer can be regarded as a rare metal, since its production is now quite considerable; moreover, it belongs to the most abundant

† Many of the so-called rare earths are in fact fairly abundant in nature.

elements in the Earth's crust. This example shows that the concept of *technologically rare element* will in future become obsolete.

In the last twenty years there was a considerable increase in the production of certain rare metals and their compounds (titanium, zirconium, niobium, germanium, indium, gallium, cerium, lithium, etc., and their hydrides, borides, iodides, carbides, and a wide range of alloys). Some rare metals and rare-metal compounds are now being produced in highest grades of purity for use in nuclear, semiconductor, and metallurgical industries (uranium, thorium, zirconium, etc.).

The most important uses of rare elements are the following:

1. *Nucleonics*:

Uranium, thorium (nuclear fuel), zirconium, beryllium (construction materials for nuclear reactors), bismuth.

2. *Electronics*:

a) germanium, as a semiconductor in solid-state rectifiers and amplifiers, radio instruments, radar equipment, remote-control systems, automatic control of machines, computers, etc.;

b) other elements (more than 15) and their salts, oxides, carbides, borides, etc.

3. *Electric and radio industry*:

a) tungsten, molybdenum, tantalum, and niobium, as filaments and electron-emitting components in lamps and radio tubes and in the manufacture of high-temperature electric furnaces and thermocouples;

b) zirconium, titanium, and tantalum, for the absorption of gases in vacuum instruments;

c) selenium, for the production of photoelectric devices;

d) other elements (more than 15) and their compounds.

4. *Chemical industry*:

a) vanadium and some rare earths, as catalysts;

b) selenium, tellurium, lithium, etc., in organic synthesis, and in the plastics and glass industries;

c) lithium, in the production of lubricants which are stable in a wide range of temperatures;

d) tantalum, for use in the construction of corrosion-resistant equipment.

5. *Production of special steels and alloys*:

a) tungsten, molybdenum, vanadium, niobium, titanium, zirconium, beryllium, indium, rare earths, cobalt, selenium, tellurium, etc. (some of them alloyed with iron), for alloying, deoxidation and modification of numerous ferrous and non-ferrous alloys;

b) titanium and its alloys, as construction materials;

c) molybdenum, niobium, titanium, zirconium and their carbides, borides, and silicides, in the production of heat-resistant alloys;

d) tungsten, titanium and tantalum carbides, in the production of hard alloys.

Many rare elements display valuable and virtually unique properties.

The Importance of the Analytical Chemistry of Rare Elements

Analytical chemistry is of major importance in the development of the modern rare-element industry.

The sources of rare elements (ores, minerals, alloys, etc.) are very numerous and of varied composition. Analytical methods are extensively employed in quality control of starting materials, industrial processes, and finished products, and also in prospecting for new sources of rare elements.

Analytical chemistry of rare elements also plays a very important part in geochemistry. Thus, determination of the relative content in rocks of rare elements which have similar properties, such as niobium–tantalum, zirconium–hafnium, tungsten–molybdenum, sulfur–selenium, rubidium–thallium, aluminum–gallium, nickel–cobalt, radium–cadmium, etc., leads to significant results.

Traces of some rare elements (Mo, V, etc.) are important in biochemical processes.

Chemical analysis using spectroscopic, photometric, polarographic and other rapid, accurate, and sensitive techniques is essential for the production of rare elements with minimum impurity contents for atomic, semiconductor, chemical and other modern industries.

Atomic, semiconductor, and metallurgical industries require nuclear fuel, and also construction and semiconductor materials of a very high purity. Thus, pure zirconium is one of the best construction materials for nuclear reactors, and even a trace of hafnium present as an impurity renders it unsuitable for the purpose. Semiconductor properties, especially those of germanium and silicon, are displayed only in impurity-free specimens. The impurity tolerance is not more than 1 impurity atom in 10^{10} atoms of germanium; it is even smaller in the case of silicon.