# SEPARATION AND PURIFICATION

3RD EDITION

PERRY AND WEISSBERGER
EDITORS

TECHNIQUES
OF CHEMISTRY
VOLUME XII

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# SEPARATION AND PURIFICATION

*Third Edition*

*Edited by*
EDMOND S. PERRY AND ARNOLD WEISSBERGER
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## TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

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VOLUME XII

# SEPARATION AND PURIFICATION

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# INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can be easily recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

It is my pleasure to acknowledge the collaboration of Dr. Edmond S. Perry in the editorial work on volumes of the preceding and the present series dealing with aspects of separation and purification:

Technique of Organic Chemistry, Vol. IV, *Distillation*, 2nd ed., Vol. XII, Kirchner, *Thin-Layer Chromatography*, Vol. XIII, Schupp, III, *Gas Chromatography*; Techniques of Chemistry, Vol. VII, Hwang and Kammermeyer, *Membranes in Separations*, Vol. XI, Scott, *Contemporary Liquid Chromatography*, and the present volume.

The authors and editors hope that readers will find the volumes useful and will communicate to them any criticisms and suggestions for improvements.

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# PREFACE

A collection of techniques useful for the isolation and purification of compounds appeared originally in 1950 as Volume III of the series Techniques of Organic Chemistry. In its second edition, published in 1956, the subjects of the first edition were divided into two treatises: *Separation and Purification*, Parts I and II; the latter bore the subtitle *Laboratory Engineering*. The second edition was also expanded to include a section on *diffusion methods*, comprising "Thermal Diffusion," "Barrier Separations," "Dialysis," "Electrodialysis," and "Zone Electrophoresis."

In the present edition, transferred to the more comprehensive series Techniques of Chemistry, the discussion of separation techniques and laboratory engineering is continued in two separate volumes: *Separation and Purification* and *Laboratory Engineering and Manipulations*.

For several reasons the diffusion methods have been deleted from the third edition. "Barrier Separations" has been expanded into Volume VII of the present series, *Membranes in Separations*, by Hwang and Kammermeyer. "Electrophoresis," likewise, will be treated in a separate volume, together with other electrokinetic methods. "Thermal Diffusion of Organic Liquids" was eliminated because little progress has been made in this technique since the previous edition.

We deeply regret the death of Lyman C. Craig. He had planned to write a fundamental and comprehensive treatise on countercurrent distribution and dialysis. The enlightenment that his unique mind and wisdom would have given is missed, as is his friendship. His renowned *Countercurrent Distribution* had a phenomenal effect on separation science. Although countercurrent distribution is now largely superseded by chromatography, the essentials of the method are retained and included in Chapter III, "Liquid-Liquid Extraction."

"Crystallization and Recrystallization" is to become part of a new volume. "Solvent Removal, Evaporation, and Drying" has been transferred to *Laboratory Engineering and Manipulations*.

To the remaining chapters of the second edition, which are all revised for the third edition, are added the following new chapters: "Purity," "Solvent Selection for Separation Processes," "Ion-Exchange Chromatography," and "Affinity Chromatography."

Other methods concerned with separation and purification are treated in separate volumes of the present or the parent series. They are in the series Techniques of Organic Chemistry, *Distillation* (Vol. IV), *Gas Chromatography* (Vol. V), and *Thin-Layer Chromatography* (Vol. XII); in the series Techniques of Inorganic Chemistry, the chapters "Gas Chromatography" (Vol. III) and "Ion-Exchange Techniques" (Vol. IV); and in the present series, "Liquid Chromatography" (Vol. XI).

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## TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

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VOLUME XII

# SEPARATION AND PURIFICATION

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# CONTENTS

Chapter I

# PURITY: CONCEPT AND REALITY

Morris Zief
A. J. Barnard, Jr.



## 1 THE EVOLUTION OF PURITY

For chemicals, the evolution of quality standards has proceeded from the rule of *caveat emptor* to specification "by sample or standard" to definition by physical and chemical measurements. This final stage became possible only with the development of measurement as a science and with an understanding of chemical combination; reliable results from routine chemical and physical analysis were also necessary.

Some early efforts to evaluate the quality of materials were associated with metals and alloys, particularly gold and silver. Possibly the earliest reference to a "purity" test appears in the Babylonian Tell "el" Amarna tablets of the fourteenth century BC. One tablet is a letter from the king of Babylon informing the king of Egypt that "of twenty *mines* of gold sent to him, only five came from the furnace as real gold." The analytical technique used was cupellation, in which base metals are oxidized and sink to the bottom of the

melt. It is intriguing that this early analytical report alludes to a fraud or at least a significant departure from expected purity.

The biblical reference to "trial by fire" is an allusion to a simple test for the purity of gold, namely, that only high-purity gold remains bright when fused in air. The technique for precious metals described in ancient literature as "degree of fineness" and in the Middle Ages as "touchstone" is based on examination of the color of the streak left when the sample is scratched with a rock (usually a dense flint). The simple touchstone method permits the detection of one part of either copper or silver in one thousand parts of gold.

No survey of the early period of purity can fail to mention the alchemist. In many ways the alchemist's quest for the *universal* substance parallels the modern chemist's demand for the *pure* substance. The recipes for the "philosopher's stone" contain directions for the purification of starting materials and ingredients. Failures in accomplishing the transmutation of base metals into precious metals were often ascribed to the presence of impurities, and their removal was attempted by repeated processing.

The historian F. J. Moore has observed that the alchemists should not be judged in twentieth century terms. They had no adequate theory on which to drape speculations. Assignment of meaning to chemical purity is difficult without some knowledge of the quantitative relations involved in chemical combination. Moore has stated that there was nothing in the knowledge of the alchemist's time from which one had the right to conclude that it was impossible to obtain gold from lead.

Science in many ways only refines old knowledge. The alchemical period contributed much of modern practical knowledge of equipment and elementary techniques for purification by precipitation, filtration, crystallization, distillation, and sublimation.

## 2 CONCEPTS OF PURITY

With the recognition that chemical compounds exist as molecules or ions of relatively invariant composition, chemical purity could be related to the degree of identity of such species. As Eyring [1] pointed out almost 30 years ago, a pure chemical compound is one in which a *single* molecular species is present. In equivalent terms, a chemical compound is pure if all molecules present are identical. The expression "singular molecular species," or its equivalent "identical molecules," is the operative expression, and the implications can be appreciated by simple examples.

Are various polymeric or associated forms of a molecule to be treated as "identical"? If not, "pure" water is a rarity. Do isotopic differences rule out molecular identity? If so, neither "high-purity" water nor standard reference

material hydrocarbons are especially pure because one in about 5000 hydrogen atoms is twice as heavy as the others. A final example to be credited to Eyring [1] is illuminating: in the most microscopic definition of purity, it would be maintained that two molecules having different energies are not identical. The third law of thermodynamics holds that all molecules of a (crystalline) substance are identical in energy only at absolute zero. Consequently, a pure compound exists only at absolute zero!

The more microscopic the viewpoint in defining a single molecular species, the more difficult it is to realize or to approach the pure chemical compound. In some ways, purity is therefore a relative property of a sample or simply a way of viewing or idealizing a sample.

A further complication appears if the concept of purity is considered from an operational viewpoint. With molecules, only a limited number of those present in the sample can be examined for "identity" or "nonidentity." The certainty with which the purity can be established is consequently limited by the uncertainties involved in this "examination" and the random errors associated with that process.

In practical considerations (see below), purity is often defined in terms of the percentage of the major constituent, often called an assay value. Here the "pure" system is implicit in the assumption of a reference standard, in the application of the laws of constant and combining proportions and in the use of atomic weights.

Another approach to defining purity is to record some property of the major constituent that is influenced by the presence of impurities. The mere recording of the boiling point or the melting point value or range is a simple example. The measurement of more than one property is especially helpful in the preparation of a highly pure material through repeated fractionation. A pure compound is considered to be attained when further fractionation fails to produce fractions with different properties.

Helium presents a fascinating case of fractionation [2]. Below 2.186°K, liquid helium passes to a "superfluid" form that has no viscosity and possesses the ability to penetrate minute openings. By use of these properties for the actual fractionation and for the analytical deductions, helium has been prepared with only one mole of impurity in $1 \times 10^{10}$ moles of the sample. This value corresponds to a purity expressed in mole percent of 99.99999999! Perhaps this is a unique and possibly limiting case.

Purity and impurity are two sides of the same coin. For real materials, the question is often not "how pure?" but "how impure?" Specific impurities are determined and usually expressed in terms of percentage or some other fractional part of the total sample. Even with a relatively pure material, there may be less concern about the exact expression of its purity than with the nature and content of impurities present. For example, a high iron content

in a glass fiber wave guide was initially believed to increase the attenuation of light passed; now it is known that only the iron(II) content is critical [3].

Ambrose [4] of the British Standards Institution has presented another interesting example. The lower pyridine bases, including the three isomeric picolines, have a refractive index in the range 1.50 to 1.51. Consequently, in refractometric measurements of one of the picolines, the presence of another as a minor impurity will have a negligible effect on the value obtained. However pyridine bases readily absorb water, which has a much lower refractive index of 1.33. A small content of water, therefore, would introduce a serious error. In contrast, if a picoline is to be used as a standard in infrared spectrophotometry, the presence of an isomeric picoline introduces serious error, but the presence of water can be easily tolerated.

Unlike the proverbial case of blind men examining an elephant, information must be pooled from numerous directions to provide a broad-based assessment of the quality, purity, and usefulness of chemicals.

## 3 NUMERICAL EXPRESSIONS OF PURITY

The content of a chemical species in a material can be expressed in various ways, depending on the data available and the intended purpose.

For a major or minor component, content is usually expressed in percent weight by weight (or weight by volume for solutions). For trace components ($10^{-2}$ to $10^{-4}$ %) or ultratrace components ($<10^{-4}$ %), other fractional parts are often preferable, notably parts per million (μg/g), parts per billion, and so on. Unfortunately, the European concept of a billion differs from that in the United States ($10^{12}$ vs. $10^{9}$). To avoid this difficulty, IUPAC commissions have proposed the use of parts per milliard (abbreviated ppM) to designate $10^{9}$. It is good practice in articles and monographs to define usages early in the text and also in tables, by such expressions as "... parts per billion (i.e., ng/g)."

Korenman [5] has urged that the Sorensen operator be used to record and report p% values (i.e., $-\log$%) for contents. The approach warrants more attention than it has received, and it is attractive, since for trace and ultratrace components, "order of magnitude" thinking is often appropriate. Some of these various modes of expression of content are highlighted in Table 1.1.

For metals, Melchior [6] has introduced the parameter "degree of purity" (i.e., Reinheitgrad), $R$, defined by the relation $R = -\log(100 - w)$, where $w$ is the weight percent of the major element. For $w$ values of 99.0, 99.5, 99.90, 99.95, ..., %, the $R$ values would be 0.0, 0.3, 1.0, 1.3, ...

The concept of "purity by difference" finds use as a simple index to purity. The percentages established for particular impurities are added and the sum is subtracted from exactly 100 to give a purity percentage. A chemical with

***Table 1.1*** Expressions of Content (w/w) [5]

| *Constituent* | *Percentage* | ppm (μg/g) | ppb (ng/g) | p% (= $-\log$ %) |
|---|---|---|---|---|
| Macro | | | | |
| Major | 1–100 | — | — | 0 to −2 |
| Minor | 0.01–1 | 100–1000 | — | 2–0 |
| Micro | | | | |
| Trace | ≤0.01 | ≤100 | — | ≥2 |
| Ultratrace | ≤0.0001 | ≤1 | ≤1000 | ≥4 |
| | 0.0000001 | 0.001 | 1 | 7 |

a single impurity at a content of 100 ppm (i.e., 0.01 %) would be described as 99.99 % pure. This index has greater validity for high-purity metals and nonmetals because the impurities are probably present in their elemental state. In the case of compounds, the exact nature of the impurities is not always determined. For example, all trace sulfur species may be codetermined and expressed as sulfate. Often for elements and simple inorganic compounds, the values for spectrographically detected impurities are added and the sum subtracted from 100 to give the "spectrographic purity." The value is not intended to imply that impurities not detectable by spectrography are absent. Purchasers of "spectrographic grade" materials sometimes have overlooked this point and have been surprised to find significant contents for nonmetals and their oxygenated species [7].

In the use of the purity-by-difference concept, significant figures have sometimes carelessly been ignored. For example, the sum of 0.001 % and 0.0002 %, each value expressed to the number of significant figures allowed by the precision of the measurements, is 0.001 %, not 0.0012 %!

An impurity content of 1 ppm (μg/g) corresponds to a purity by difference of 99.9999 %. For simplicity, this percentage can be read as "six nines" and the material is termed 6N [8]. Similarly, an impurity content of 0.5 ppm corresponds to 99.99995 % purity by difference and would be expressed as either 6N5 or 6N+. (It is interesting to contrast this approach with that using p%; the impurity content for the two examples reduces to 4.0 and 4.3 p%, respectively.)

For the description of high-purity forms of elements, the purity-by-difference concept has been refined by some workers with the listing of two values, one prefixed by "m" to designate reference to metallic impurities and the other by "t" to indicate that total impurities are considered, including

nonmetallic ones such as oxygen, carbon, and nitrogen [9]. In this system, for example, the expression m5N5 : t4N indicates the purity is 99.9995 % based on assessment of metallic impurities as 5 μg/g by spectrographic and spectrometric methods, but 99.99 % based on the assessment of both metallic impurities (5 μg/g) and nonmetallic ones (95 μg/g).

Purity values may also be reported in molar terms. Mole percentage values are often secured by methods of analysis based on colligative properties.

In materials science, notably semiconductor phenomena, the number of *atoms* of various impurities in a unit weight or volume may be of greater interest than the weight of the impurities. A convenient unit for this purpose is atoms per cubic centimeter.

## 4 WATER AND "POLYWATER"

Water has probably been subjected to more purification studies and by more techniques than any other substance. As noted in an earlier section, water can be considered "microscopically impure" even after extreme purification because a mixture of isotopes is present. The geonormal isotopic composition involves 99.98 and 0.02 atom percent for $^{1}H$ and $^{2}H$, respectively, and 99.76, 0.04, and 0.2 atom percent for $^{16}O$, $^{17}O$, and $^{18}O$, respectively. The isotopic composition of water from other planets may be different [10]. It is noteworthy that so-called heavy water, deuterium oxide, is now available even in drum quantities, with the price directly related to the atom percent of deuterium versus hydrogen present.

Purification of water by means of mixed-bed ion-exchange columns (strongly acidic cation exchangers containing sulfonic acid functionality plus strongly basic anion resins having pendant quaternary ammonium hydroxide groups) has largely supplanted distillation for the preparation of ion-free water. A single pass through the mixed bed yields water with a greater resistance than that obtained by three distillations in vitreous silica; 18 MΩ/cm at 25°C is routine in many laboratories (theoretical resistance at 25°C = 18.3 MΩ/cm). Membrane filters (0.22 μ) can now be supplemented with hollow fibers ($\sim$0.02 $\mu$) to separate additional quantities of particulate matter [11]. Granular carbon columns or distillation from permanganate can be adopted to remove organic material. The employment of ion-exchange resins, carbon, distillation, and membrane filtration in sequence represents the state-of-the-art approach for the elimination of inorganic, organic, and particulate materials.

The passage of water through an octadecylsilane-bonded reverse phase column removes organic impurities, which would interfere in gradient elution high-performance liquid chromatography [12].