

QUANTITATIVE CHEMICAL ANALYSIS

Third Edition

Daniel C. Harris

*Michelson Laboratory
China Lake, California*

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Cover Image: Permanent magnet levitates above superconducting disk of yttrium barium copper oxide in pool of liquid nitrogen. Box 16-1 describes the chemical analysis of the superconductor and Experiment 25-11 gives a procedure for the analysis. [Photo courtesy D. Cornelius, Michelson Laboratory, with materials from T. Vanderah.]

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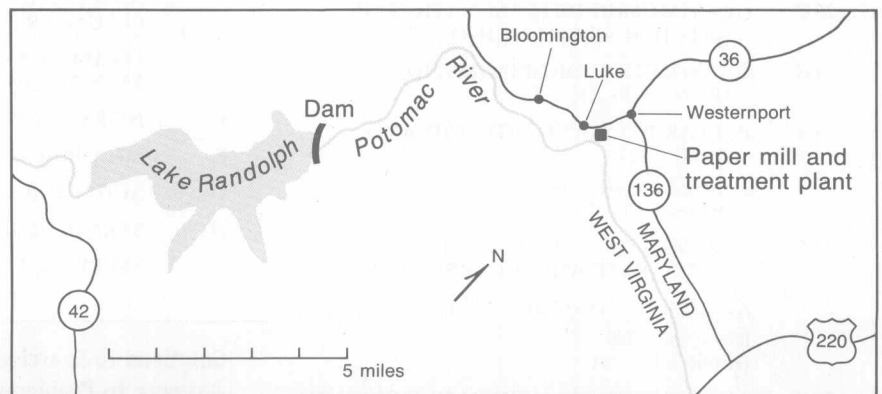
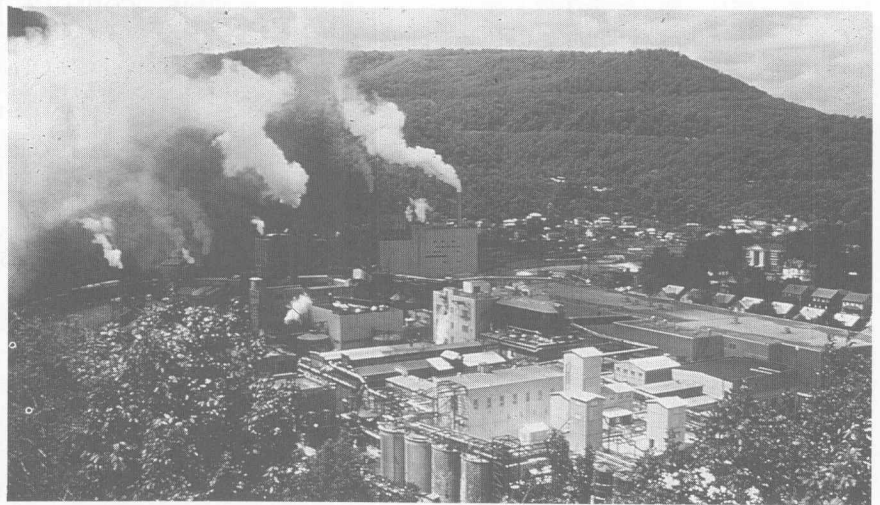
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Paper mill on the Potomac River near Westernport, Maryland. [Photo courtesy C. Dalpra, Potomac River Basin Commission.]

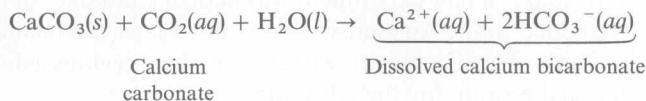


The Potomac River above the paper mill is acidic and lifeless. After passing the mill and water treatment plant, the neutralized river teems with life.

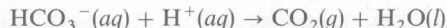
Preface

The North Branch of the Potomac River runs crystal clear through a beautiful section of the Appalachian Mountains. But for much of its length, the river is dead—a victim of acid drainage from abandoned coal mines. As the river flows past a paper mill and waste water treatment plant at Westernport, Maryland, the pH rises from a lifeless 4.5 to a fertile 7.2, in which fish and plants thrive. Something at Westernport is neutralizing the acid in the river. In the early 1980s a great dam was built at Bloomington, on the acidic part of the river, to serve as a reservoir and to provide flood control. The question arose of how to regulate the release water from the reservoir so as not to overcome the neutralization occurring at Westernport.

As in many environmental quality issues, analytical chemistry played a key role in solving this problem. Combining many of the techniques you will study in this book—including acid–base titrations, ion-exchange chromatography, atomic absorption spectroscopy, potentiometric titrations, and even gravimetric analysis—the chemistry at Westernport was unraveled and quantified.[†] The key source of neutralization is suspended solid calcium carbonate—from chemicals used to treat wood pulp—exiting the paper mill. Part of this solid is trapped at the treatment plant and does not enter the river. However, respiration of bacteria in the treatment plant produces a massive quantity of carbon dioxide that reacts with solid calcium carbonate to make soluble calcium bicarbonate:



The bicarbonate from the treatment plant neutralizes the acidic river, permitting life to thrive immediately downstream of the plant:



[†] D. P. Sheer and D. C. Harris, *J. Water Pollution Control Federation*, **54**, 1441 (1982).

By identifying and quantifying the chemistry at Westernport, operating rules for release of water from the reservoir at Bloomington were devised so that acidic water behind the dam would not overcome the neutralizing capacity of the paper mill.

In one way or another, almost every branch of science relies on analytical chemistry to answer the questions "What is it?" (qualitative analysis) and "How much is there?" (quantitative analysis). This text provides a foundation for understanding how the latter question is approached in the laboratory, although the two questions are usually intertwined.

In writing this text, my goals have been to provide a sound physical understanding of the principles of analytical chemistry and to show how these principles are applied in chemistry and related disciplines, especially the life sciences. I have attempted to present the subject matter of a traditional analytical chemistry course in a rigorous, readable, and interesting manner that will appeal to students whether or not their primary interest is chemistry. I intend the material presented here to be lucid enough for nonmajors, yet to contain the depth required by advanced undergraduates. My goals are reflected in the book's origins: it grew out of an introductory analytical chemistry course taught mainly for nonchemistry majors at the University of California, Davis, and out of a course taken by third-year chemistry majors at Franklin and Marshall College in Lancaster, Pennsylvania.

Although there is no way for one course to cover every topic in this book, the text is designed to satisfy the diverse needs of many analytical chemistry courses. Topics include statistics, chemical equilibrium, acid-base chemistry, electroanalytical methods, spectroscopic techniques, methods of separation, and laboratory procedures. Chapter 19 discusses spectrophotometric methods and can be easily covered out of its order in this book. Some problems in earlier chapters use spectrophotometry and refer the student to the beginning of Chapter 19.

Several major changes have occurred in this edition. The introduction to acids and bases has been moved forward to Chapter 5, to help pave the way for some acid-base chemistry used in Chapter 7. The introduction to electrochemistry in Chapter 14 was rewritten with the hope of reducing confusion about signs in the calculation of cell voltages. Instructors who have taught with the previous edition should pay particular attention to how signs are treated in this edition. Changes in the discussion of EDTA complex equilibrium are also intended to improve clarity. Chapters on chromatographic methods and spectrophotometric instrumentation were rewritten to incorporate a decade of advances. A new chapter on sample preparation appears at the end of the book. It collects aspects of sample preparation that were previously scattered through the book, and includes much material new to this edition. Numerous sections of the book were updated in small ways, new Boxes were added, a new experiment was added, and tables of formation constants were added to the Appendix. New Color Plates are included at the center of the book. The Computer Projects of the previous edition were deleted to help make room for the additions.

To help lighten the load of a very dense subject, the text is laced with interesting Boxes and Demonstrations and includes a color insert to illustrate the Demonstrations. There is an extensive Glossary at the back of the book. The collections of Exercises and Problems at the end of each chapter are vital, since only by attacking them can the student master this subject. The Exercises are the smallest set of problems; they cover all the most important,

sometimes complex, topics. Complete solutions to Exercises and short answers to Problems appear at the back of the book. Complete solutions to Problems appear in the *Solutions Manual to Accompany Quantitative Chemical Analysis*, available to instructors upon request. The manual may be made available to students through bookstores.

I am grateful to James P. Rybarczyk of Ball State University, Jerome W. O'Laughlin of the University of Missouri, and Timothy C. Donnelly of the University of California, Davis, who reviewed the Second Edition and then reviewed the entire manuscript for the Third Edition in excruciating detail. Detailed reviews of the previous edition used to plan this revision were also received from Joe P. Foley (Louisiana State University), Harry B. Mark (University of Cincinnati), Joseph Wang (New Mexico State University), John P. Walters (St. Olaf College), William E. Kurtin (Trinity University), Ned A. Daugherty (Colorado State University), Anna Brajter-Toth (University of Florida), and Dale Hawley (Kansas State University). A published review by Royce C. Engstrom (University of South Dakota) and a survey by David C. Lock (Queens College) and W. E. L. Grossman (Hunter College) were also helpful. Comments received from John G. Dorsey (University of Cincinnati), Lowell M. Schwartz (University of Massachusetts, Boston), Rollie J. Myers (University of California, Berkeley), George F. Atkinson (University of Waterloo), Robert de Levie (Georgetown University), Richard Ulsh (Elmira College), Gerald Seebach (Transylvania University), Jack Penciner (Tel Aviv University), Kenneth Sauer (University of California, Berkeley), Truman D. Turnquist (Mount Union College), and Donald C. Jackman (Pfeiffer College) were all appreciated. I especially savored letters from students.

At Michelson Laboratory I consulted a great deal with Eric Erickson, Mike Seltzer, Wayne Weimer, and Alice Harper, all of whom also helped check the solutions to problems for accuracy. The fine people at W. H. Freeman and Company, Gary Carlson, Stephen Wagley, Alice Fernandes-Brown, Julia De Rosa, and José Fonfrias, helped this edition to take form. New Color Plates were obtained with the help of Klaus Grohmann (Hunter College) and Ruth Anderson (Ohio State University) and were photographed by Ken Karp. No edition of this book would have gotten off the ground without the participation of my wife Sally, who typed the Solutions Manual, prepared the manuscript for production, compiled the index, proofread, and helped in numerous indescribable ways.

This book is dedicated to the students who use it, who occasionally smile when they read it, who gain new insight, and who feel satisfaction after struggling to solve a problem. I have been successful if this book helps you develop critical, independent reasoning that you can apply to new problems. I truly appreciate any comments, criticisms, suggestions and corrections from students and teachers. Please address correspondence to me at the Chemistry Division, Research Department, Michelson Laboratory, China Lake CA 93555.

Dan Harris
August 1990

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1 Units and Concentrations

The immediate goal of quantitative analysis is to answer the query “How much?” How much vanadium is contained in the ore? How much phosphate is bound to the enzyme? How much pesticide is contained in the groundwater? Some of the principles and methods that enable us to measure “how much” are the subject of this text. The ultimate goal of analytical chemistry is not just to measure “how much,” but to use that knowledge for some greater purpose. This could be a scientific investigation, a policy decision, a cost analysis, philosophical satisfaction, or myriad other reasons. We begin with a brief discussion of units of measurement.

1-1 SI UNITS

Scientists around the world use a uniform system of measurement known as the *Système International d'Unités*, whose units are called **SI units**. The fundamental units, from which all others are derived, are listed in Table 1-1. The standards of length, mass, and time are the familiar metric units of *meter* (m), *kilogram* (kg), and *second* (s). The other fundamental units of most concern to us measure electric current (*ampere*, A), temperature (*kelvin*, K), and amount of substance (*mole*, mol).

All the remaining physical quantities, such as energy, force, and charge, can be expressed in terms of the fundamental units. Some of these derived quantities are shown in Table 1-2, along with their names and symbols. Conversion factors relating some common non-SI units to SI units are listed in Table 1-3.

You can find the definitions of many terms used in this text in the Glossary at the back of the book.

Table 1-1
Fundamental SI units

Quantity	Unit	Symbol	Definition
Length	meter	m	The meter is the distance light travels in a vacuum during $\frac{1}{299\,792\,458}$ of a second. This definition fixes the speed of light at exactly 299 792 458 m/s.
Mass	kilogram	kg	One kilogram is the mass of the prototype kilogram kept at Sèvres, France. This is the only SI unit whose primary standard is not defined in terms of physical constants.
Time	second	s	The second is the duration of 9 192 631 770 periods of the radiation corresponding to the two hyperfine levels of the ground state of ^{133}Cs .
Electric current	ampere	A	One ampere is the amount of constant current that will produce a force of 2×10^{-7} N/m (newtons per meter of length) when maintained in two straight, parallel conductors of infinite length and negligible cross section, separated by one meter.
Temperature	kelvin	K	The thermodynamic temperature is defined such that the triple point of water (at which solid, liquid, and gaseous water are in equilibrium) is 273.16 K and the temperature of absolute zero is 0 K.
Luminous intensity	candela	cd	One candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540 THz and that has a radiant intensity of $\frac{1}{683}$ W/sr in that direction.
Amount of substance	mole	mol	One mole of substance contains as many molecules (or atoms, if the substance is a monatomic element) as there are atoms of carbon in exactly 0.012 kg of ^{12}C . The number of particles in a mole is approximately $6.022\,136\,7 \times 10^{23}$.
Plane angle	radian	rad	The radian is such that there are 2π radians in a complete circle.
Solid angle	steradian	sr	The steradian is defined such that there are 4π steradians in a complete sphere.

Table 1-2
Some SI-derived units with special names

Quantity	Units	Symbol	Expression in terms of other units	Expression in terms of SI base units
Frequency	hertz	Hz		1/s
Force	newton	N		$\text{m} \cdot \text{kg}/\text{s}^2$
Pressure	pascal	Pa	N/m^2	$\text{kg}/(\text{m} \cdot \text{s}^2)$
Energy, work, quantity of heat	joule	J	$\text{N} \cdot \text{m}$	$\text{m}^2 \cdot \text{kg}/\text{s}^2$
Power, radiant flux	watt	W	J/s	$\text{m}^2 \cdot \text{kg}/\text{s}^3$
Quantity of electricity, electric charge	coulomb	C		$\text{s} \cdot \text{A}$
Electric potential, potential difference, electromotive force	volt	V	W/A	$\text{m}^2 \cdot \text{kg}/(\text{s}^3 \cdot \text{A})$
Capacitance	farad	F	C/V	$\text{s}^4 \cdot \text{A}^2/(\text{m}^2 \cdot \text{kg})$
Electric resistance	ohm	Ω	V/A	$\text{m}^2 \cdot \text{kg}/(\text{s}^3 \cdot \text{A}^2)$
Conductance	siemens	S	A/V	$\text{s}^3 \cdot \text{A}^2/(\text{m}^2 \cdot \text{kg})$
Magnetic flux	weber	Wb	V·s	$\text{m}^2 \cdot \text{kg}/(\text{s}^2 \cdot \text{A})$
Magnetic flux density	tesla	T	Wb/ m^2	$\text{kg}/(\text{s}^2 \cdot \text{A})$
Inductance	henry	H	Wb/A	$\text{m}^2 \cdot \text{kg}/(\text{s}^2 \cdot \text{A}^2)$
Luminous flux	lumen	lm		$\text{cd} \cdot \text{sr}$
Illuminance	lux	lx		$\text{cd} \cdot \text{sr}/\text{m}^2$

Table 1-3
Some conversion factors

Quantity	Unit	Symbol	SI equivalent
Volume	liter	L	$*10^{-3} \text{ m}^3$
	milliliter	mL	$*10^{-6} \text{ m}^3$
Length	angstrom	\AA	$*10^{-10} \text{ m}$
	inch	in.	$*0.0254 \text{ m}$
Mass	pound	lb	$*0.45359237 \text{ kg}$
Force	dyne	dyn	$*10^{-5} \text{ N}$
Pressure	atmosphere	atm	$*101325 \text{ N}/\text{m}^2$
	torr	1 mm Hg	$133.322 \text{ N}/\text{m}^2$
	pound/in. ²	psi	$6894.76 \text{ N}/\text{m}^2$
Energy	erg	erg	$*10^{-7} \text{ J}$
	electron volt	eV	$1.60217733 \times 10^{-19} \text{ J}$
	calorie, thermochemical	cal	$*4.184 \text{ J}$
	British thermal unit	Btu	1055.06 J
Power	horsepower		745.700 W

Note: An asterisk (*) indicates that the conversion is exact (by definition).