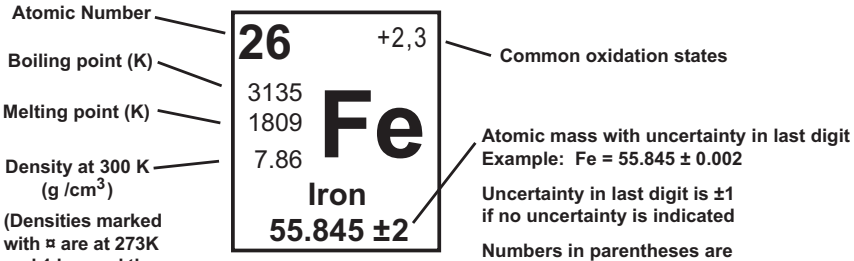
Quantitative Chemical Analysis

Ninth Edition

Daniel C. Harris

Periodic Table



Atomic masses from *Pure Appl. Chem.* **2011**, *83*, 359.
See Box 3-3 for explanation of atomic mass values used in this table

1	2	3	4	5	6	7	8	9
1 +1 20 14 0.0888¤ **H** Hydrogen 1.007 98 ±14								
3 +1 1615 454 0.53 **Li** Lithium 6.968 ±30	4 +2 2745 1560 1.85 **Be** Beryllium 9.012 182 ±3							
11 +1 1156 371 0.97 **Na** Sodium 22.989 769 28 ±2	12 +2 1363 922 1.74 **Mg** Magnesium 24.305 0 ±6							
19 +1 1032 336 0.86 **K** Potassium 39.098 3	20 +2 1757 1112 1.55 **Ca** Calcium 40.078 ±4	21 +3 3104 1812 3.0 **Sc** Scandium 44.955 912 ±6	22 +4,3 3562 1943 4.50 **Ti** Titanium 47.867	23 +5,4,3,2 3682 2175 5.8 **V** Vanadium 50.941 5	24 +6,3,2 2945 2130 7.19 **Cr** Chromium 51.996 1 ±6	25 +7,6,4,2,3 2335 1517 7.43 **Mn** Manganese 54.938 045 ±5	26 +2,3 3135 1809 7.86 **Fe** Iron 55.845 ±2	27 +2,3 3201 1768 8.90 **Co** Cobalt 58.933 195 ±5
37 +1 961 313 1.53 **Rb** Rubidium 85.467 8 ±3	38 +2 1650 1041 2.6 **Sr** Strontium 87.62	39 +3 3611 1799 4.5 **Y** Yttrium 88.905 85 ±2	40 +4 4682 2125 6.49 **Zr** Zirconium 91.224 ±2	41 +5,3 5017 2740 8.55 **Nb** Niobium 92.906 38 ±2	42 +6,5,4,3,2 4912 2890 10.2 **Mo** Molybdenum 95.96 ±2	43 +7 4538 2473 11.5 **Tc** Technetium (98)	44 +2,3,4,6,8 4423 2523 12.2 **Ru** Ruthenium 101.07 ±2	45 +2,3,4 3970 2236 12.4 **Rh** Rhodium 102.905 50 ±2
55 +1 944 302 1.87 **Cs** Cesium 132.905 451 9 ±2	56 +2 2171 1002 3.5 **Ba** Barium 137.327 ±7	57 +3 3730 1193 6.7 **La** Lanthanum 138.905 47 ±7	72 +4 4876 2500 13.1 **Hf** Hafnium 178.49 ±2	73 +5 5731 3287 16.6 **Ta** Tantalum 180.947 88 ±2	74 +6,5,4,3,2 5828 3680 19.3 **W** Tungsten 183.84	75 +7,6,4,2,-1 5869 3453 21.0 **Re** Rhenium 186.207	76 +2,3,4,6,8 5285 3300 22.4 **Os** Osmium 190.23 ±3	77 +2,3,4,6 4701 2716 22.5 **Ir** Iridium 192.217 ±3
87 +1 950 300 — **Fr** Francium (223)	88 +2 1809 973 5 **Ra** Radium (226)	89 +3 3473 1323 10.07 **Ac** Actinium (227)	104 — — — **Rf** Rutherfordium (267)	105 — — — **Db** Dubnium (268)	106 — — — **Sg** Seaborgium (271)	107 — — — **Bh** Bohrium (270)	108 — — — **Hs** Hassium (277)	109 — — — **Mt** Meitnerium (276)

58 +3,4 3699 1071 6.78 **Ce** Cerium 140.116	59 +3,4 3785 1204 6.77 **Pr** Praseodymium 140.907 65 ±2	60 +3 3341 1289 7.00 **Nd** Neodymium 144.242 ±3	61 +3 3785 1204 6.48 **Pm** Promethium (145)	62 +3,2 2064 1345 7.54 **Sm** Samarium 150.36 ±2	63 +3,2 1870 1090 5.26 **Eu** Europium 151.964
90 +4 5061 2028 11.7 **Th** Thorium 232.038 06 ±2	91 +5,4 — — 15.4 **Pa** Protactinium 231.035 88 ±2	92 +6,5,4,3 4407 1405 18.9 **U** Uranium 238.028 91 ±3	93 +6,5,4,3 — 910 20.4 **Np** Neptunium (237)	94 +6,5,4,3 3503 913 19.8 **Pu** Plutonium (244)	95 +6,5,4,3 2880 1268 13.6 **Am** Americium (243)

of the Elements

	Atomic Mass Interval
H	[1.007 84; 1.008 11]
Li	[6.938; 6.997]
B	[10.806; 10.821]
C	[12.009 6; 12.011 6]
N	[14.006 43; 14.007 28]
O	[15.999 03; 15.999 77]
Si	[28.084; 28.086]
S	[32.059; 32.076]
Cl	[35.446; 35.457]
Tl	[204.382; 204.385]

10	11	12	13	14	15	16	17	18
								2 4.2 0.95 0.176¤ **He** Helium 4.002 602 ±2
			5 +3 4275 2300 2.34 **B** Boron 10.814 ±8	6 ±4,2 4470 4100 2.62 **C** Carbon 12.010 6 ±10	7 ±3,5,4,2 77 63 1.234¤ **N** Nitrogen 14.006 8 ±4	8 -2 90 50 1.410¤ **O** Oxygen 15.999 4 ±4	9 -1 85 53 1.674¤ **F** Fluorine 18.998 403 2 ±5	10 27 25 0.889¤ **Ne** Neon 20.179 7 ±6
			13 +3 2793 933 2.70 **Al** Aluminum 26.981 538 6 ±8	14 +4 3540 1685 2.33 **Si** Silicon 28.085	15 ±3,5,4 550 317 1.82 **P** Phosphorus 30.973 762 ±2	16 ±2,4,6 718 388 2.07 **S** Sulfur 32.068 ±9	17 ±1,3,5,7 239 172 3.12¤ **Cl** Chlorine 35.452 ±6	18 87 84 1.760¤ **Ar** Argon 39.948
28 +2,3 3187 1726 8.90 **Ni** Nickel 58.693 4 ±4	29 +2,1 2836 1358 8.96 **Cu** Copper 63.546 ±3	30 +2 1180 693 7.14 **Zn** Zinc 65.38 ±2	31 +3 2478 303 5.91 **Ga** Gallium 69.723	32 +4 3107 1210 5.32 **Ge** Germanium 72.63	33 ±3,5 876 — 5.72 **As** Arsenic 74.921 60 ±2	34 -2,4,6 958 494 4.80 **Se** Selenium 78.96 ±3	35 ±1,5 332 266 3.12 **Br** Bromine 79.904	36 120 116 3.69¤ **Kr** Krypton 83.798 ±2
46 +2,4 3237 1825 12.0 **Pd** Palladium 106.42	47 +1 2436 1234 10.5 **Ag** Silver 107.868 2 ±2	48 +2 1040 594 8.65 **Cd** Cadmium 112.411 ±8	49 +3 2346 430 7.31 **In** Indium 114.818 ±3	50 +4,2 2876 505 7.30 **Sn** Tin 118.710 ±7	51 ±3,5 1860 904 6.68 **Sb** Antimony 121.760	52 -2,4,6 1261 723 6.24 **Te** Tellurium 127.60 ±3	53 ±1,5,7 458 387 4.92 **I** Iodine 126.904 47 ±3	54 165 161 5.78¤ **Xe** Xenon 131.293 ±6
78 +2,4 4100 2045 21.4 **Pt** Platinum 195.084 ±9	79 +3,1 3130 1338 19.3 **Au** Gold 196.966 569 ±4	80 +2,1 630 234 13.5 **Hg** Mercury 200.59 ±2	81 +3,1 1746 577 11.85 **Tl** Thallium 204.384 ±2	82 +4,2 2023 601 11.4 **Pb** Lead 207.2	83 +3,5 1837 545 9.8 **Bi** Bismuth 208.980 40	84 +4,2 1235 527 9.4 **Po** Polonium (209)	85 ±1,3,5,7 610 575 — **At** Astatine (210)	86 211 202 9.78¤ **Rn** Radon (222)
110 — — — **Ds** Darmstadtium (281)	111 — — — **Rg** Roentgenium (280)	112 — — — **Cn** Copernicium (285)	113 (284)	114 — — — **Fl** Flerovium (289)	115 (288)	116 — — — **Lv** Livermorium (293)	117 (294)	118 (294)

64 +3 3539 1585 7.89 **Gd** Gadolinium 157.25 ±3	65 +3,4 3496 1630 8.27 **Tb** Terbium 158.925 35 ±2	66 +3 2835 1682 8.54 **Dy** Dysprosium 162.500	67 +3 2968 1743 8.80 **Ho** Holmium 164.930 32 ±2	68 +3 3136 1795 9.05 **Er** Erbium 167.259 ±3	69 +3,2 2220 1818 9.33 **Tm** Thulium 168.934 21 ±2	70 +3,2 1467 1097 6.98 **Yb** Ytterbium 173.054 ±5	71 +3 3668 1936 9.84 **Lu** Lutetium 174.966 8
96 +3 — 1340 13.5 **Cm** Curium (247)	97 +4,3 — — — **Bk** Berkelium (247)	98 +3 — 900 — **Cf** Californium (251)	99 — — — **Es** Einsteinium (252)	100 — — — **Fm** Fermium (257)	101 — — — **Md** Mendelevium (260)	102 — — — **No** Nobelium (259)	103 — — — **Lr** Lawrencium (262)

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W. H. Freeman & Company
A Macmillan Education Imprint

Publisher: Kate Parker

Senior Acquisitions Editor: Lauren Schultz

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Illustrations: Network Graphics, Precision Graphics

Illustration Coordinators: Matthew McAdams, Janice Donnola

Production Coordinator: Julia DeRosa

Composition and Text Layout: Aptara®, Inc.

Printing and Binding: RR Donnelley

Front Cover/Title Page Photo Credit: © The Natural History Museum/The Image Works

Back Cover Photo Credit: Pascal Goetgheluck/Science Source

Library of Congress Control Number: 2014950382
ISBN-13: 978-1-4641-3538-5
ISBN-10: 1-4641-3538-X

Printed in the United States of America
First Printing

W. H. Freeman and Company
41 Madison Avenue
New York, NY 10010

www.whfreeman.com

BRIEF CONTENTS

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CONTENTS

EXPERIMENTS

Experiments are found at the website
www.whfreeman.com/qca/

SPREADSHEET TOPICS

SPREADSHEETS AT WEBSITE

CONNECTIONS: Maria Goeppert Mayer

[Emilio Segre Visual Archives/ Science Source.]

Maria Goeppert Mayer (1906–1972) was the second and, so far, last woman (after Marie Curie) to receive the Nobel Prize in Physics. She shared half of the 1963 prize with Hans Jensen for their independent theories of atomic nuclear shell structure published in 1949.

What does she have to do with this book? The back cover shows evidence that the body temperature of certain dinosaurs was similar to that of warm blooded animals. In 1947, she and Jacob Bigeleisen published a paper, "Calculation of Equilibrium Constants for Isotopic Exchange Reactions."* This paper was one of the foundational studies for paleothermometry—the use of isotopes to deduce the temperature at which objects such as dinosaur teeth were formed. From mathematical physics to analytical chemistry to dinosaurs, there is a thread of connection.

Maria was born to a sixth-generation university professor in Göttingen, Germany.† From early childhood, she knew that she would acquire a university education, but there were few avenues for girls' education. She attended a small, private girls' school, which closed before her studies were complete. Against all advice, she took and passed the University of Göttingen entrance examination to be admitted in 1924. Her first exposure to quantum mechanics by Max Born hooked her. She received a Ph.D. in 1930, with three Nobel Prize winners on her committee.

Maria married Joe Mayer, a Caltech- and Berkeley-educated physical chemist who was a postdoctoral boarder in the Goeppert household. They moved to the U.S., where Joe began a distinguished career at Johns Hopkins University, Columbia University, and the University of Chicago. In 1940 they coauthored *Statistical Mechanics*, a textbook used for more than 40 years. Maria was regarded as at least equally gifted, but she was not offered a paid position at any university despite teaching courses, advising graduate students, serving on committees, and writing graduate examinations—all as a volunteer! Her first paid appointment as a professor at the University of California at San Diego came in 1960, four years after her election to the National Academy of Sciences.

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*J. Bigeleisen and M. G. Mayer, *J. Chem. Phys*. **1947,** *15*, 261.

†S. B. McGrayne, *Nobel Prize Women in Science* (Washington DC: Joseph Henry Press, 1998).

PREFACE

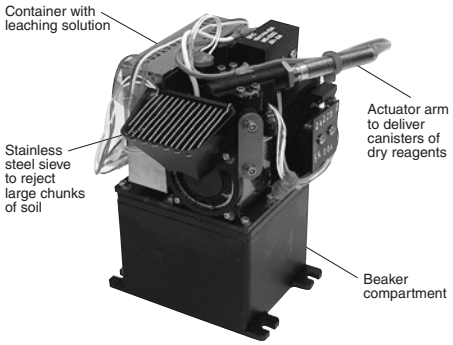
Goals of This Book

My goals are 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 in life sciences and environmental science. I have attempted to present the subject in a rigorous, readable, and interesting manner, lucid enough for nonchemistry majors, but containing the depth required by advanced undergraduates. This book grew out of an introductory analytical chemistry course that I taught mainly for nonmajors at the University of California at Davis and from a course for third-year chemistry students at Franklin and Marshall College in Lancaster, Pennsylvania.

What's New?

Beginning with dinosaur body temperature on the back cover of this book, analytical chemistry addresses interesting questions in the wider world. The facing page draws a connection between the back cover and underlying human achievement in physics that enables us to deduce body temperature from the isotopic composition of teeth. The story of Maria Goeppert Mayer is a lesson for us all in how women in science were so poorly treated not so long ago.

In this edition, the introduction to titrations has been consolidated in Chapter 7. Acid-base, EDTA, redox, and spectrophotometric titrations are still treated in other chapters. The power of the spreadsheet is unleashed in Chapter 8 to reach numerical solutions to equilibrium problems and in Chapter 19 to compute equilibrium constants from spectrophotometric data. Atomic spectroscopy Chapter 21 has a new section on X-ray fluorescence as a routine analytical tool. Mass spectrometry Chapter 22 has been expanded to increase the level of detail and to help keep up with new developments. Chapter 27 has an extraordinary sequence of micrographs showing the onset of crystallization of a precipitate. Three new methods in sample preparation were added to Chapter 28. Appendix B takes a deeper look at propagation of uncertainty and Appendix C treats analysis of variance.



BOX 15-3 Measuring sulfate on Mars by titration with barium [Mars Lander: NASA/JPL-Caltech/University of Arizona/Max Planck Institute.]

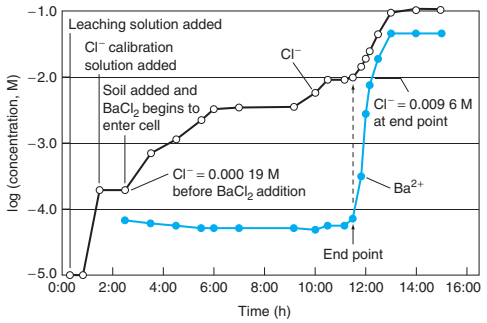


FIGURE FROM PROBLEM 7-21 Barium sulfate precipitation titration from Phoenix Mars Lander [Data courtesy S. Kounaves, Tufts University.]

For the first time since I began work on this book in 1978, I have taken on a contributing author for part of this revision. Professor Chuck Lucy of the University of Alberta shares his expertise and teaching experience with us in Chapters 23–26 on chromatography and capillary electrophoresis. He improved the discussion of the efficiency of separation and mechanisms of band spreading. Emphasis is placed on types of interactions between solutes and the stationary phase. Types of solvent polarity are distinguished in liquid chromatography. Examples are given for the selection of stationary phase and pH for liquid chromatography separations. Electrophoresis has more emphasis on the effects of ion size and pH on mobility. Chuck contributes the views of a specialist in separation science to these chapters.

New boxed applications include a home pregnancy test (Chapter 0 opener), observing the addition of one base to DNA with a quartz crystal microbalance (Chapter 2 opener), medical implications of false positive results (Box 5-1), a titration on Mars (Chapter 7 opener),

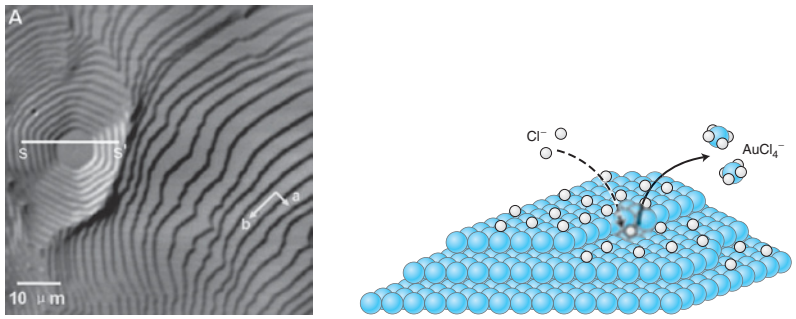
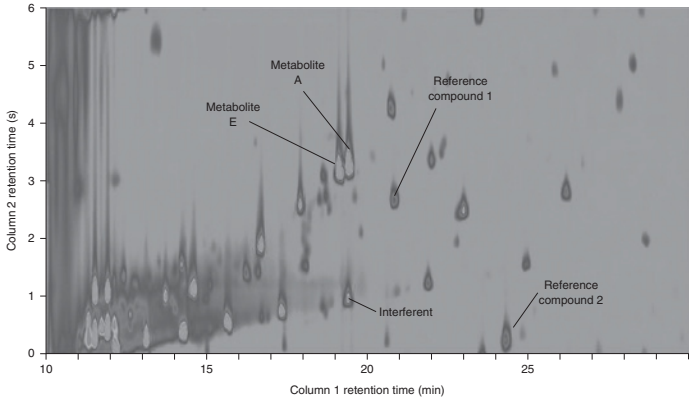


FIGURE FROM BOX 17-1 **Anodic dissolution of gold at atomic steps** [R. Wen, A. Lahiri, M. Azhagurajan, S. Kobayashi, K. Itaya, "A New in situ Optical Microscope with Single Atomic Layer Resolution for Observation of Electrochemical Dissolution of Au (111)," *J Am Chem Soc* **2010,** *132,*13657, Figure 2. Reprinted with permission © 2010, American Chemical Society.]

microequilibrium constants (Box 10-3), acid-base titration of RNA to provide evidence for the mechanism of RNA catalysis (Chapter 11 opener), the hydrogen-oxygen fuel cell and the *Apollo* 13 accident (Box 14-2), the lead-acid battery (Box 14-3), high-throughput DNA sequencing by counting protons (Chapter 15 opener), how perchlorate was discovered on Mars (Box 15-3), ion-selective electrode with a conductive polymer for a sandwich immunoassay (Box 15-4), metal reaction at atomic steps (Box 17-1), an aptamer biosensor for clinical use (Box 17-5), Bunsen burner flame photometer (Box 21-2), atomic emission spectroscopy on Mars (Box 21-3), making elephants fly (mechanism of protein electrospray, Box 22-5), chromatographic analysis of breast milk (Chapter 23 opener), doping in sports (Chapter 24 opener), two-dimensional gas chromatography (Box 24-3), million-plate separation by slip flow chromatography (Box 25-1), forensic DNA profiling (Chapter 26 opener and Section 26-8), and measuring van der Waals attraction (Box 27-1). New Color Plates illustrate the effect of ionic strength on ion dissociation (Color Plate 4), the mechanism of chromatography by partitioning of analyte between phases (Color Plate 30), and separation of dyes by solid-phase extraction (Color Plate 36).



CHAPTER 24 OPENING IMAGE **Two-dimensional gas chromatography–combustion isotope ratio mass spectrometry to detect doping in athletes** [H. J. Tobias, Y. Zhang, R. J. Auchus, J. T. Brenna, "Detection of Synthetic Testosterone Use by Novel Comprehensive Two-Dimensional Gas Chromatography Combustion Isotope Ratio Mass Spectrometry," *Anal Chem* **2011,** *83,* 7158, Figure 4A. Reprinted with permission © 2011, American Chemical Society.]

Pedagogical changes in this edition include more discussion of serial dilution to prepare standards in Chapters 2, 3, and 18, distinction between standard uncertainty and standard deviation in statistics, more discussion of hypothesis testing in statistics, employing the *F* test before the *t* test for comparison of means, using a graphical treatment for internal standards, emphasis on electron flow toward the more positive electrode in electrochemical cells, using nanoscale observations to probe phenomena such as van der Waals forces and

the amorphous structure of glass in a pH electrode, polynomial smoothing of noisy data, expanded discussion of the time-of-flight mass spectrometer and ion mobility separations, enhanced discussion of intermolecular forces in chromatography, enhanced discussion of method development in liquid chromatography, use of a free, online liquid chromatography simulator, introduction of two literature search questions in chromatography, and taking more advantage of the power of Excel for numerical analysis. Box 3-3 explains how I have chosen to handle atomic weight intervals in the latest periodic table of the elements.

Features

Topics are introduced and illustrated with concrete, interesting examples. In addition to their pedagogic value, Chapter Openers, Boxes, Demonstrations, and Color Plates are intended to help lighten the load of a very dense subject. **Chapter Openers** show the relevance of analytical chemistry to the real world and to other disciplines of science. I can't come to your classroom to present **Chemical Demonstrations,** but I can tell you about some of my favorites and show how they look with the **Color Plates** located near the center of the book. **Boxes** discuss interesting topics related to what you are studying or amplify points in the text.

Problem Solving

Nobody can do your learning for you. The two most important ways to master this course are to work problems and to gain experience in the laboratory. **Worked Examples** are a principal pedagogic tool to teach problem solving and to illustrate how to apply what you have just read. Each worked example ends with a **Test Yourself** question that you are encouraged to answer to apply what you learned in the example. There are Exercises and Problems at the end of each chapter. **Exercises** are the minimum set of problems that apply most major concepts of each chapter. Please struggle mightily with an Exercise before consulting the solution at the back of the book. **Problems** at the end of the chapter cover the entire content of the book. **Short Answers** are at the back of the book and complete solutions appear in the **Solutions Manual.**

Spreadsheets are indispensable for science and engineering and uses far beyond this course. You can cover this book without using spreadsheets, but you will never regret taking the time to learn to use them. A few of the powerful features of Microsoft Excel are described as they are needed, including graphing in Chapters 2 and 4, statistical functions and regression in Chapter 4, solving equations with Goal Seek, Solver, and circular definitions in Chapters 7, 8, 13, and 19, and some matrix operations in Chapter 19. The text teaches you how to construct spreadsheets to simulate many types of titrations, to solve chemical equilibrium problems, and to simulate chromatographic separations.

Other Features of This Book

Terms to Understand Essential vocabulary, highlighted in **bold** in the text, is collected at the end of the chapter. Other unfamiliar or new terms are *italic* in the text.

Glossary **Bold** vocabulary terms and many of the italic terms are defined in the glossary.

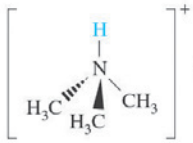
Appendixes Tables of solubility products, acid dissociation constants, redox potentials, and formation constants appear at the back of the book. You will also find discussions of logarithms and exponents, propagation of error, analysis of variance, balancing redox equations, normality, analytical standards, and a little bit about DNA.

Notes and References Citations in the chapters appear at the end of the book.

Inside Cover Here is your trusty periodic table, as well as tables of physical constants and other information.

EXAMPLE **A Weak-Acid Problem**

Find the pH of 0.050 M trimethylammonium chloride.



Cl^- Trimethylammonium chloride

Solution We assume that ammonium halide salts are completely dissociated to give $(CH_3)_3NH^+$ and Cl^-.* We then recognize that trimethylammonium ion is a weak acid, being the conjugate acid of trimethylamine, $(CH_3)_3N$, a weak base. Cl^- has no basic or

CHAPTER 9 EXAMPLE PAGE 193

	A	B	C	D	E	F
1	Thallium azide equilibria					
2	1. *Estimate* values of pC = –log[C] for N_3^- and OH^- in cells B6 and B7					
3	2. Use Solver to adjust the values of pC to minimize the sum in cell F8					
4						
5	Species	pC	C (= 10^-pC)		Mass and charge balances	b_i
6	N_3^-	2	0.01	C6 = 10^-B6	$b_1 = 0 = [Tl^+] - [N_3^-] - [HN_3] =$	1.19E-02
7	OH^-	4	0.0001	C7 = 10^-B7	$b_2 = 0 = [Tl^+] + [H^+] - [N_3^-] - [OH^-] =$	1.18E-02
8	Tl^+		0.021877616	C8 = D12/C6	$\Sigma b_i^2 =$	2.80E-04
9	HN_3		4.46684E-08	C9 = D13*C6/C7	F6 = C8-C6-C9	
10	H^+		1E-10	C10 = D14/C7	F7 = C8+C10-C6-C7	
11					F8 = F6^2+F7^2	
12	$pK_{sp} =$	3.66	$K_{sp} =$	0.000218776	= 10^-B12	
13	$pK_b =$	9.35	$K_b =$	4.46684E-10	= 10^-B13	
14	$pK_w =$	14.00	$K_W =$	1E-14	= 10^-B14	

FIGURE 8-9 Thallium azide solubility spreadsheet without activity coefficients. Initial estimates $pN_3^- = 2$ and $pOH^- = 4$ appear in cells B6 and B7. From these two numbers, the spreadsheet computes concentrations in cells C6:C10. Solver then varies pN_3^- and pOH^- in cells B6 and B7 until the charge and mass balances in cell F8 are satisfied.

Media and Supplements

The ***Solutions Manual for Quantitative Chemical Analysis*** contains complete solutions to all problems.

New Clicker Questions allow instructors to integrate active learning in the classroom and to assess students' understanding of key concepts during lectures. Available in Microsoft Word and PowerPoint (PPT).

New Lecture PowerPoints have been developed to minimize preparation time for new users of the book. These files offer suggested lectures including key illustrations and summaries that instructors can adapt to their teaching styles.

New Test Bank offers questions in editable Microsoft Word format.

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The **student website** www.whfreeman.com/qca has **directions for experiments** which may be reproduced for your use. You will also find **lists of experiments** from the *Journal of Chemical Education*. **Supplementary topics** at the website include spreadsheets for precipitation and redox titrations, discussion of microequilibrium constants, a spreadsheet simulation of gradient liquid chromatography, and Fourier transformation of an interferogram into an infrared spectrum. You will also find 24 **selected Excel spreadsheets** from the textbook ready to use at the student website.

The **instructors' website**, www.whfreeman.com/qca, has all **artwork** and **tables** from the book in preformatted PowerPoint slides.

The People

My wife Sally works on every aspect of this book and the Solutions Manual. She contributes mightily to whatever clarity and accuracy we have achieved.

Solutions to problems and exercises were meticulously checked by Heather Audesirk, a graduate student at Caltech, and by Julia Lee, a senior at Harvey Mudd College.

A book of this size and complexity is the work of many people. Brittany Murphy, Anna Bristow, and Lauren Schultz provided editorial and market guidance. Jennifer Carey was the Project Editor responsible for making sure that all pieces of this book fell into the right place. Marjorie Anderson attended to the challenging details of copyediting. Photo research and permissions were ably handled by Cecilia Varas and Richard Fox. Matthew McAdams, Janice Donnola, and Tracey Kuehn coordinated the illustration program. Anna Skiba-Crafts was the courageous proofreader.

In Closing

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 in or out of chemistry. I truly relish your comments, criticisms, suggestions, and corrections. Please address correspondence to me at the Chemistry Division (Mail Stop 6303), Research Department, Michelson Laboratory, China Lake, CA 93555.

Dan Harris
March 2015

Acknowledgements

I am indebted to many people who provided new information for this edition, asked probing questions, and made good suggestions. Pete Palmer of San Francisco State University graciously shared his instructional material for X-ray fluorescence and provided a detailed critique of my draft, as well as suggestions for mass spectrometry. Karyn Usher of Metropolitan State University, Saint Paul, Minnesota, photographed her solid-phase extraction experiment that appears in Color Plate 36. Martin Mirenda of the Universidad de Buenos Aires provided Color Plate 4 showing the instructive effect of ionic strength on the color of bromocresol green. Jim De Yoreo and Mike Nielsen of Battelle Pacific Northwest National Laboratory provided the exquisite time-lapse calcium carbonate nucleation transmission electron micrographs in Figure 27-2.

Barbara Belmont of California State University, Dominguez Hills asked a seemingly simple question in 2011 about the propagation of uncertainty that required the knowledge of my statistician colleague, Dr. Ding Huang, to answer. This question led to the expanded Appendix B. D. Brynn Hibbert of the University of New South Wales, Australia, was also a resource for statistics. Jürgen Gross of Heidelberg University and David Sparkman of the University of the Pacific in California were resources for mass spectrometry. Dale Lecaptain of Central Michigan University requested more emphasis on serial dilutions, which has been added. Brian K. Niece of Assumption College, Worcester, Massachusetts, corrected my procedure for using hydroxynaphthol blue indicator for EDTA titrations. Micha Enevoldsen of Frederiksberg, Denmark, taught me that Kjeldahl was a Danish chemist, not a Dutch chemist. He also taught me that Kjeldahl was one of the "three great pH's," who also include S. P. L. Sørensen and K. U. Linderstrøm-Lang. Chan Kang of Chonbuk National University, Korea, pointed out that I had been using the letter *n* to mean more than one thing in electrochemistry, which I have attempted to correct in this edition. Alena Kubatova of the University of North Dakota provided some of her teaching materials for mass spectrometry. Other helpful corrections and suggestions came from Richard Gregor (Rollins College, Florida), Franco Basile (University of Wyoming), Jeffrey Smith (Carleton University, Ottawa), Kris Varazo (Francis Marion University, Florence, South Carolina), Doo Soo Chung (Seoul National University), Ron Cooke (California State University, Chico), David D. Weiss (Kansas University), Steven Brown (University of Delaware), Athula Attygalle (Stevens Institute of Technology, Hoboken, New Jersey), and Peter Liddel (Glass Expansion, West Melbourne, Australia).

People who reviewed the 8th edition of Quantitative Chemical Analysis and parts of the manuscript for the 9th edition include Truis Smith-Palmer (St. Francis Xavier University), William Lammela (Nazareth College), Nelly Mateeva (Florida A&M University), Alena Kubatova (University of North Dakota), Barry Ryan (Emory University), Neil Jespersen (St. John's University), David Kreller (Georgia Southern University), Darcey Wayment (Nicholls State University), Karla McCain (Austin College), Grant Wangila (University of Arkansas), James Rybarczyk (Ball State University), Frederick Northrup (Northwestern University), Mark Even (Kent State University), Jill Robinson (Indiana University), Pete Palmer (San Francisco State University), Cindy Burkhardt (Radford University), Nathanael Fackler (Nebraska Weslyan University), Stuart Chalk (University of North Florida), Reynaldo Barreto (Purdue University North Central), Susan Varnum (Temple University), Wendy Cory (College of Charleston), Eric D. Dodds (University of Nebraska, Lincoln), Troy D. Wood (University of Buffalo), Roy Cohen (Xavier University), Christopher Easley (Auburn University), Leslie Sombers (North Carolina State University), Victor Hugo Vilchiz (Virginia State University), Yehia Mechref (Texas Tech University), Lenuta Cires Gonzales (California State University, San Marcos), Wendell Griffith (University of Toledo), Anahita Izadyar (Arkansas State University), Leslie Hiatt (Austin Peay State University), David Carter (Angelo State University), Andre Venter (Western Michigan University), Rosemarie Chinni (Alvernia University), Mary Sohn (Florida Technical College), Christopher Babayco (Columbia College), Razi Hassan (Alabama A&M University), Chris Milojevich (University of Tampa), Steven Brown (University of Delaware), Anne Falke (Worcester State University), Julio Alvarez (Virginia Commonwealth University), Keith Kuwata (Macalaster College), Levi Mielke (University of Indianapolis), Simon Mwongela (Georgia Gwinnett College), Omowunmi Sadik (State University of New York at Binghamton), Jingdong Mao (Old Dominion University), Jani Ingram (Northern Arizona University), Matthew Mongelli (Kean University), Vince Cammarata (Auburn University), Ed Segstro (University of Winnipeg), Tiffany Mathews (Villanova University), Andrea Matti (Wayne State University), Rebecca Barlag (Ohio University), Barbara Munk (Wayne State University), John Berry (Florida International University), Patricia Cleary (University of Wisconsin, Eau Claire), and Sandra Barnes (Alcorn State University).

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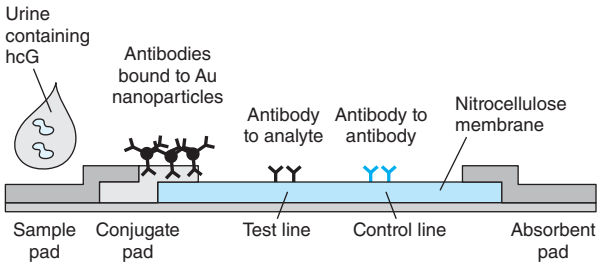
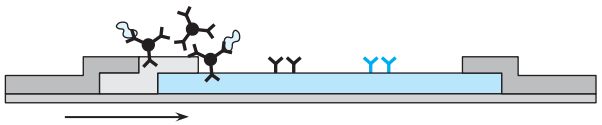
0 The Analytical Process

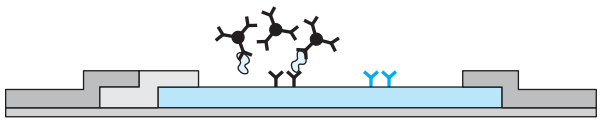
HOW DOES A HOME PREGNANCY TEST WORK?



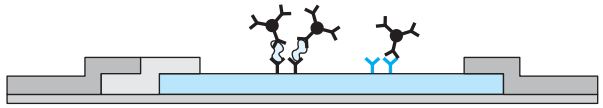
(*a*) Apply drop of urine to sample pad



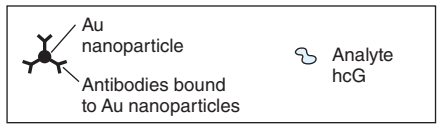
(*b*) hcG binds to antibody as liquid wicks past conjugate pad

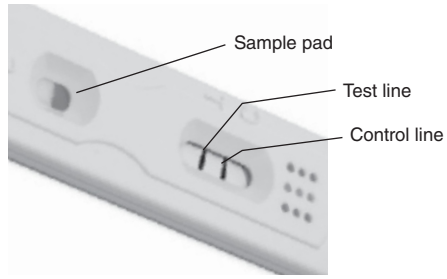


(*c*) Another part of hcG binds to antibody at test line



(*d*) Conjugate reagent not attached to hcG binds to antibody at control line





(*e*) Home pregnancy test [Rob Byron/Shutterstock.]

A common home pregnancy test detects a hormone called hcG in urine. This hormone begins to be secreted shortly after conception.

An *antibody* is a protein secreted by white blood cells to bind to a foreign molecule called an *antigen*. Antibody-antigen binding is the first step in the immune response that eventually removes a foreign substance or an invading cell from your body. Antibodies to human proteins such as hcG can be cultivated in animals.

In the *lateral flow home pregnancy immunoassay* shown in the diagram, urine is applied to the sample pad at the left end of a horizontal test strip made of nitrocellulose that serves as a wick. Liquid flows from left to right by capillary action. Liquid first encounters detection reagent on the conjugate pad. The reagent is called a conjugate because it consists of hcG antibody attached to red-colored gold nanoparticles. The antibody binds to one site on hcG.

As liquid flows to the right, hcG bound to the conjugate is trapped at the test line, which contains an antibody that binds to another site on hcG. Gold nanoparticles trapped with hcG at the test line create a visible red line. As liquid continues to the right, it encounters the control line with antibodies that bind to the conjugate reagent. A second red line forms at the control line. At the far right is an absorbent pad that soaks up liquid containing anything that was not retained at the test or control lines.

In a positive pregnancy test, both lines turn red. The test is negative if only the control line turns red. If the control line fails to turn red, the test is invalid.

Bold terms should be learned. *Italicized* terms are less important. A glossary of terms is found at the back of the book.

Quantitative analysis: How much is present?
Qualitative analysis: What is present?

Quantitative chemical analysis is the measurement of *how much* of a chemical substance is present. The purpose of quantitative analysis is usually to answer a question such as "Does this mineral contain enough copper to be an economical source of copper?" The home pregnancy test above is a **qualitative chemical analysis,** which looks for the presence of a hormone that is produced during pregnancy. This test answers the even more important question, "Am I pregnant?" Qualitative analysis tells us *what* is present and quantitative

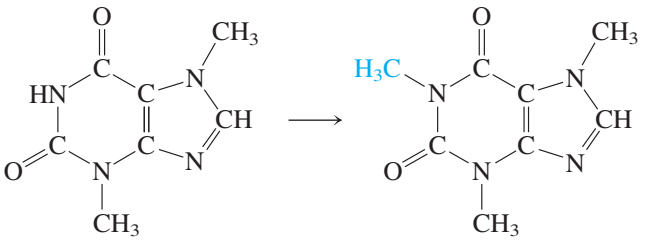
analysis tells us *how much* is present. In quantitative analysis, the chemical measurement is only part of a process that includes asking a meaningful question, collecting a relevant sample, treating the sample so that the chemical of interest can be measured, making the measurement, interpreting the results, and providing a report.

0-1 The Analytical Chemist's Job

Notes and references appear after the last chapter of the book.

My favorite chocolate bar,[1] jammed with 33% fat and 47% sugar, propels me over mountains in California's Sierra Nevada. In addition to its high energy content, chocolate packs an extra punch with the stimulant caffeine and its biochemical precursor, theobromine.

Chocolate is great to eat, but not so easy to analyze. [Dima Sobko/Shutterstock.]



Theobromine (from Greek "food of the gods")
A diuretic, smooth muscle relaxant, cardiac stimulant, and vasodilator

Caffeine
A central nervous system stimulant

A **diuretic** makes you urinate.
A **vasodilator** enlarges blood vessels.

Too much caffeine is harmful for many people, and some unlucky individuals cannot tolerate even small amounts. How much caffeine is in a chocolate bar? How does that amount compare with the quantity in coffee or soft drinks? At Bates College in Maine, Professor Tom Wenzel teaches his students chemical problem solving through questions such as these.[2]

Chemical Abstracts is the most comprehensive source for locating articles published in chemistry journals. *SciFinder* is software that accesses *Chemical Abstracts.*

But, how *do* you measure the caffeine content of a chocolate bar? Two students, Denby and Scott, began their quest with a search of *Chemical Abstracts* for analytical methods. Looking for the key words "caffeine" and "chocolate," they uncovered numerous articles in chemistry journals. Two reports, both entitled "High-Pressure Liquid Chromatographic Determination of Theobromine and Caffeine in Cocoa and Chocolate Products,"[3] described a procedure suitable for the equipment in their laboratory.[4]

Sampling

The first step in any chemical analysis is procuring a representative sample to measure—a process called **sampling.** Is all chocolate the same? Of course not. Denby and Scott bought one chocolate bar and analyzed pieces of it. If you wanted to make broad statements about "caffeine in chocolate," you would need to analyze a variety of chocolates. You would also need to measure multiple samples of each type to determine the range of caffeine in each kind of chocolate.

Homogeneous: same throughout
Heterogeneous: differs from region to region

A pure chocolate bar is fairly **homogeneous,** which means that its composition is the same everywhere. It might be safe to assume that a piece from one end has the same caffeine content as a piece from the other end. Chocolate with a macadamia nut in the middle is an example of a **heterogeneous** material—one whose composition differs from place to place. The nut is different from the chocolate. To sample a heterogeneous material, you need to use a strategy different from that used to sample a homogeneous material. You would need to know the average mass of chocolate and the average mass of nuts in many candies. You would need to know the average caffeine content of the chocolate and of the macadamia nut (if it has any caffeine). Only then could you make a statement about the average caffeine content of macadamia chocolate.

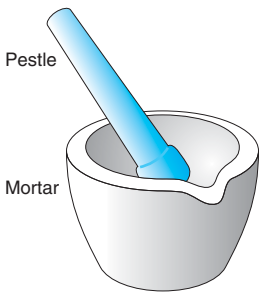


FIGURE 0-1 Ceramic mortar and pestle used to grind solids into fine powders.

Sample Preparation

The first step in the procedure calls for weighing out some chocolate and extracting fat from it by dissolving the fat in a hydrocarbon solvent. Fat needs to be removed because it would interfere with chromatography later in the analysis. Unfortunately, if you just shake a chunk of chocolate with solvent, extraction is not very effective because the solvent has no access to the inside of the chocolate. So, our resourceful students sliced the chocolate into small bits and placed the pieces into a mortar and pestle (Figure 0-1), thinking they would grind the solid into small particles.

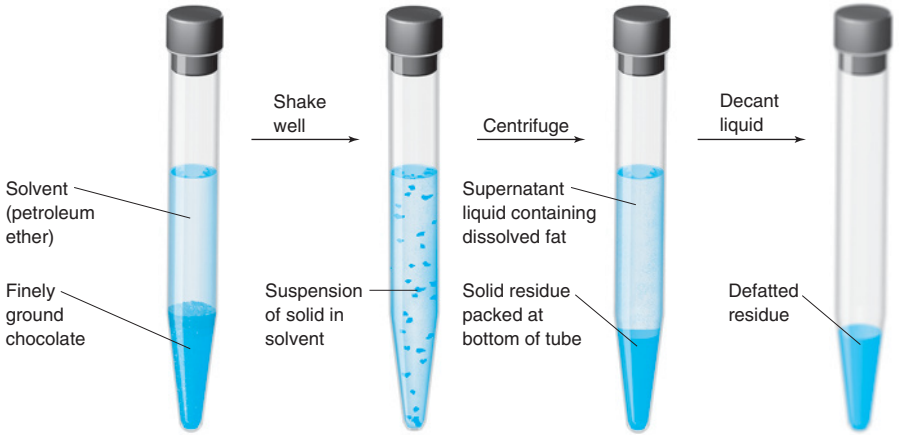


FIGURE 0-2 Extracting fat from chocolate to leave defatted solid residue for analysis.

Imagine trying to grind chocolate! The solid is too soft to grind. So Denby and Scott froze the mortar and pestle with its load of sliced chocolate. Once the chocolate was cold, it was brittle enough to grind. Small pieces were placed in a preweighed 15-milliliter (mL) centrifuge tube, and their mass was noted.

Figure 0-2 shows the next part of the procedure, which is to remove fat that would interfere with subsequent chromatography. A 10-mL portion of the solvent, petroleum ether, was added to the tube, and the top was capped with a stopper. The tube was shaken vigorously to dissolve fat from the solid chocolate into the solvent. Caffeine and theobromine are insoluble in this solvent. The mixture of liquid and fine particles was then spun in a centrifuge to pack the chocolate at the bottom of the tube. The clear liquid, containing dissolved fat, could now be **decanted** (poured off) and discarded. Extraction with fresh portions of solvent was repeated twice more to remove more fat from the chocolate. Residual solvent in the chocolate was then removed by heating the centrifuge tube in a beaker of boiling water. The mass of chocolate residue could be calculated by weighing the tube plus its content of defatted chocolate residue and subtracting the known mass of the empty tube.

Substances being measured—caffeine and theobromine in this case—are called **analytes.** The next step in the sample preparation procedure was to make a **quantitative transfer** (a complete transfer) of the fat-free chocolate residue to an Erlenmeyer flask and to dissolve the analytes in water for the chemical analysis. If any residue were not transferred from the tube to the flask, then the final analysis would be in error because not all of the analyte would be present. To perform the quantitative transfer, Denby and Scott added a few milliliters of pure water to the centrifuge tube and used stirring and heating to dissolve or suspend as much of the chocolate as possible. Then they poured the **slurry** (a suspension of solid in a liquid) into a 50-mL flask. They repeated the procedure several times with fresh portions of water to ensure that every bit of chocolate was transferred from the centrifuge tube to the flask.

A solution of anything in water is called an **aqueous** solution.

To complete the dissolution of analytes, Denby and Scott added water to bring the volume up to about 30 mL. They heated the flask in a boiling water bath to extract all the caffeine and theobromine from the chocolate into the water. To compute the quantity of analyte later, the total mass of water must be known. Denby and Scott knew the mass of chocolate residue in the centrifuge tube and they knew the mass of the empty Erlenmeyer flask. So they put the flask on a balance and added water drop by drop until there were 33.3 g of water in the flask. Later, they would compare known solutions of pure analyte in water with the unknown solution containing 33.3 g of water.

Before Denby and Scott could inject the unknown solution into a chromatograph for the chemical analysis, they had to clean up the unknown even further (Figure 0-3). The chocolate residue in water contained tiny solid particles that would surely clog their expensive chromatography column and ruin it. So they transferred a portion of the slurry to a centrifuge tube and centrifuged the mixture to pack as much of the solid as possible at the bottom of the tube. The cloudy, tan, **supernatant liquid** (liquid above the packed solid) was then filtered in a further attempt to remove tiny particles of solid from the liquid.

It is critical to avoid injecting solids into a chromatography column, but the tan liquid still looked cloudy. So Denby and Scott took turns between classes to repeat the centrifugation and filtration five times. After each cycle in which the supernatant liquid was filtered and centrifuged, it became a little cleaner. But the liquid was never completely clear. Given enough time, more solid always seemed to precipitate from the filtered solution.

Real-life samples rarely cooperate with you!

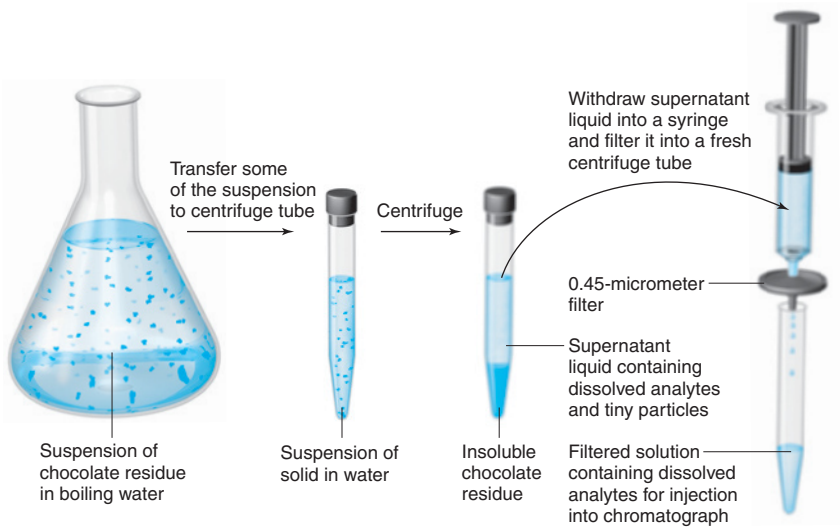


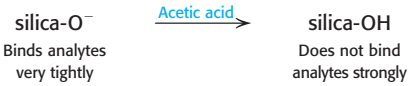
FIGURE 0-3 Centrifugation and filtration are used to separate undesired solid residue from the aqueous solution of analytes.

The tedious procedure described so far is called **sample preparation**—transforming a sample into a state that is suitable for analysis. In this case, fat had to be removed from the chocolate, analytes had to be extracted into water, and residual solid had to be separated from the water.

Chemical Analysis (At Last!)

Denby and Scott finally decided that the solution of analytes was as clean as they could make it in the time available. The next step was to inject solution into a *chromatography* column, which would separate the analytes and measure the quantity of each. The column in Figure 0-4a is packed with tiny particles of silica (SiO_2) to which are attached long hydrocarbon molecules. Twenty microliters (20.0×10^{-6} liters) of the chocolate extract were injected into the column and washed through with a solvent made by mixing 79 mL of pure water, 20 mL of methanol, and 1 mL of acetic acid. Caffeine has greater affinity

Chromatography solvent is selected by a systematic trial-and-error process described in Chapter 25. Acetic acid reacts with negative oxygen atoms on the silica surface. When not neutralized, these oxygen atoms tightly bind a small fraction of caffeine and theobromine.



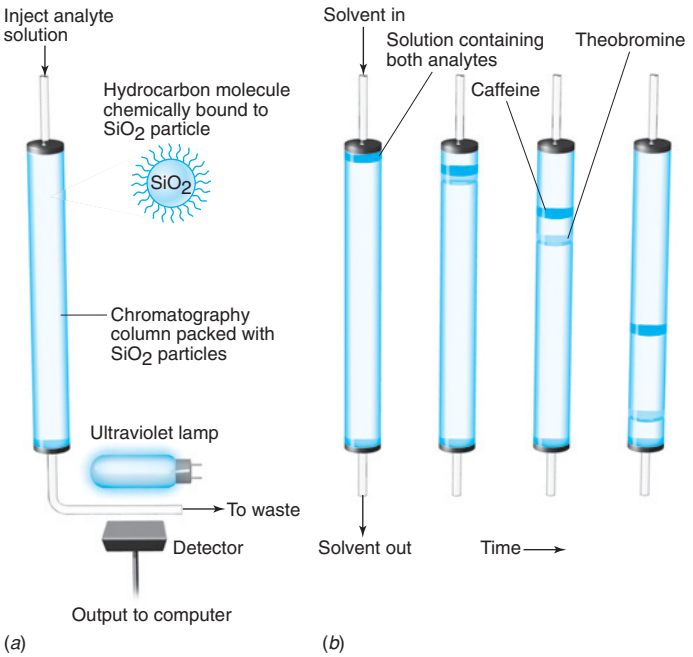


FIGURE 0-4 Principle of liquid chromatography. (*a*) Chromatography apparatus with an ultraviolet absorbance monitor to detect analytes at the column outlet. (*b*) Separation of caffeine and theobromine by chromatography. Caffeine has greater affinity than theobromine for the hydrocarbon layer on the particles in the column. Therefore, caffeine is retained more strongly and moves through the column more slowly than theobromine.

than theobromine for the hydrocarbon on the silica surface. Therefore, caffeine "sticks" to the coated silica particles in the column more strongly than theobromine does. When both analytes are flushed through the column by solvent, theobromine reaches the outlet before caffeine (Figure 0-4b).

Analytes are detected at the outlet by their ability to absorb ultraviolet radiation from the lamp in Figure 0-4a. The graph of detector response versus time in Figure 0-5 is called a *chromatogram.* Theobromine and caffeine are the major peaks in the chromatogram. Small peaks arise from other substances extracted from the chocolate.

Only substances that absorb ultraviolet radiation at a wavelength of 254 nanometers are observed in Figure 0-5. The major components in the aqueous extract are sugars, but they are not detected in this experiment.

The chromatogram alone does not tell us what compounds are present. One way to identify individual peaks is to measure spectral characteristics of each one as it emerges from the column. Another way is to add an authentic sample of either caffeine or theobromine to the unknown and see whether one of the peaks grows in magnitude.

In Figure 0-5, the *area* under each peak is proportional to the quantity of compound passing through the detector. The best way to measure area is with a computer attached to the chromatography detector. Denby and Scott did not have a computer linked to their chromatograph, so they measured the *height* of each peak instead.

Calibration Curves

In general, analytes with equal concentrations give different detector responses. Therefore, the response must be measured for known concentrations of each analyte. A graph of detector response as a function of analyte concentration is called a **calibration curve** or a *standard curve.* To construct such a curve, **standard solutions** containing known concentrations of pure theobromine or caffeine were prepared and injected into the column, and the resulting peak heights were measured. Figure 0-6 is a chromatogram of one of the standard solutions, and Figure 0-7 shows calibration curves made by injecting solutions containing 10.0, 25.0, 50.0, or 100.0 micrograms of each analyte per gram of solution.

Straight lines drawn through the calibration points could then be used to find the concentrations of theobromine and caffeine in an unknown. From the equation of the theobromine

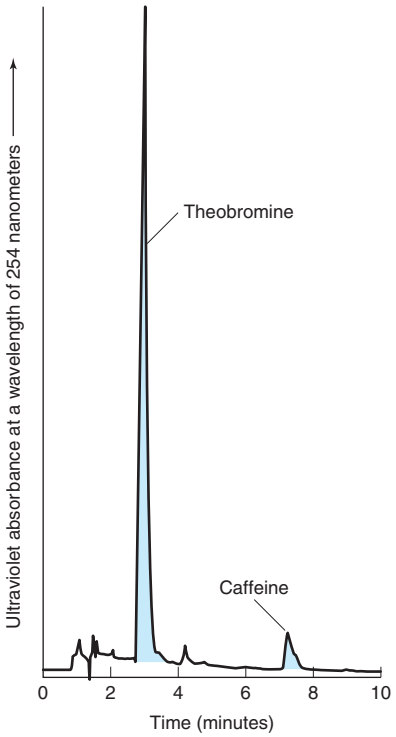


FIGURE 0-5 Chromatogram of 20.0 microliters of dark chocolate extract. A 150-mm-long × 4.6-mm-diameter column, packed with 5-micrometer-diameter particles of Hypersil ODS, was eluted (washed) with water:methanol:acetic acid (79:20:1 by volume) at a rate of 1.0 mL per minute.

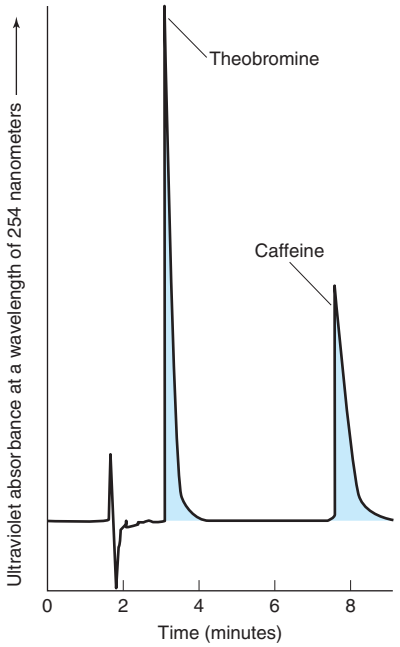


FIGURE 0-6 Chromatogram of 20.0 microliters of a standard solution containing 50.0 micrograms of theobromine and 50.0 micrograms of caffeine per gram of solution.

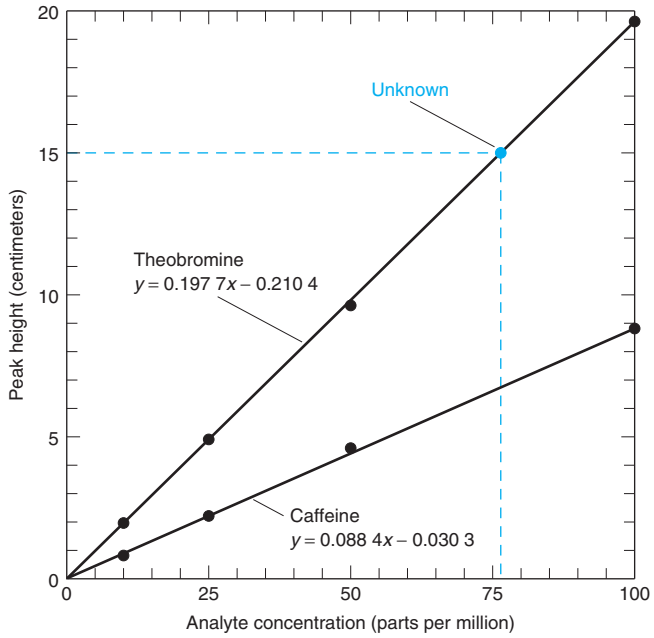


FIGURE 0-7 Calibration curves show observed peak heights for known concentrations of pure compounds. One *part per million* is one microgram of analyte per gram of solution. Equations of the straight lines drawn through the experimental data points were determined by the *method of least squares* described in Chapter 4.

line in Figure 0-7, we can say that, if the observed peak height of theobromine from an unknown solution is 15.0 cm, then the concentration is 76.9 micrograms per gram of solution.

Interpreting the Results

Knowing how much analyte is in the aqueous extract of the chocolate, Denby and Scott could calculate how much theobromine and caffeine were in the original chocolate. Results for dark and white chocolates are shown in Table 0-1. The quantities found in white chocolate are only about 2% as great as the quantities in dark chocolate.

The table also reports the *standard deviation* of three replicate measurements for each sample. Standard deviation, discussed in Chapter 4, is a measure of the reproducibility of the results. If three samples were to give identical results, the standard deviation would be 0. If results are not very reproducible, then the standard deviation is large. For theobromine in dark chocolate, the standard deviation (0.002) is less than 1% of the average (0.392), so we say the measurement is reproducible. For theobromine in white chocolate, the standard deviation (0.007) is nearly as great as the average (0.010), so the measurement is poorly reproducible.

TABLE 0-1 Analyses of dark and white chocolate

	Grams of analyte per 100 grams of chocolate	
Analyte	**Dark chocolate**	**White chocolate**
Theobromine	0.392 ± 0.002	0.010 ± 0.007
Caffeine	0.050 ± 0.003	0.000 9 ± 0.001 4

Average ± standard deviation of three replicate injections of each extract.

The purpose of an analysis is to reach a conclusion. The questions posed earlier were "How much caffeine is in a chocolate bar?" and "How does it compare with the quantity in coffee or soft drinks?" After all this work, Denby and Scott discovered how much caffeine was in *one* particular chocolate bar that they analyzed. It would take a great deal more work to sample many chocolate bars of the same type and many different types of chocolate to gain a broad view. Table 0-2 compares results from analyses of different sources of caffeine. A can of soft drink or a cup of tea contains less than one-half of the caffeine in a small cup of coffee. Chocolate contains even less caffeine, but a hungry backpacker eating enough baking chocolate can get a pretty good jolt!

TABLE 0-2 Caffeine content of beverages and foods

Source	Caffeine (milligrams per serving)	Serving size[a] (ounces)
Regular coffee	106–164	5
Decaffeinated coffee	2–5	5
Tea	21–50	5
Cocoa beverage	2–8	6
Baking chocolate	35	1
Sweet chocolate	20	1
Milk chocolate	6	1
Caffeinated soft drinks	36–57	12
Red Bull	80	8.2

a. 1 ounce = 28.35 grams
DATA SOURCES: http://www.holymtn.com/tea/caffeine_content.htm. Red Bull from http://wilstar.com/caffeine.htm.

Simplifying Sample Preparation with Solid-Phase Extraction

The procedure followed by Denby and Scott in the mid-1990s was developed before *solid-phase extraction* (page 785) came into use. Today, solid-phase extraction simplifies sample preparation by separating some major interfering components of the mixture from the desired analytes.[5] The procedure shown in Figure 0-8 features a short, disposable column containing a chromatography solid phase that can clean the sample enough prior to performing chromatography on an expensive analytical column.

Denby and Scott extracted fat with organic solvent. Then they extracted caffeine and theobromine with hot water and laboriously removed fine particles by repeated centrifugation and filtration. Solid-phase extraction in Figure 0-8 removes sugars, fats, and fine

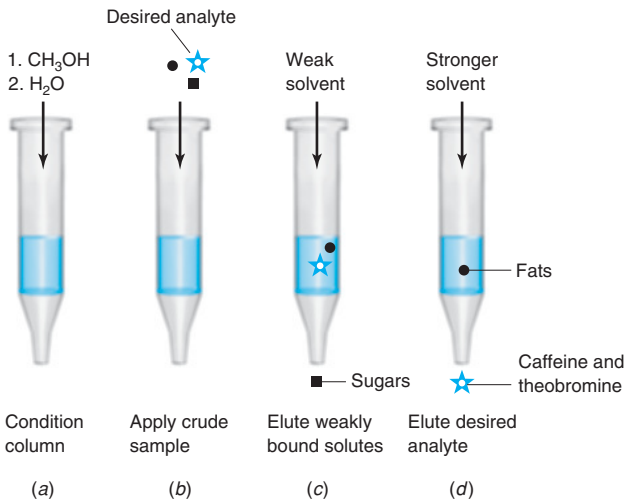


FIGURE 0-8 Solid-phase extraction separates caffeine and theobromine from sugars and fats found in chocolate. Sugars wash right through the column because they are not attracted to the hydrocarbon that is covalently attached to the particles on the column. Fats are so soluble in the hydrocarbon that they are not washed off the column by methanol. Caffeine and theobromine are soluble in the hydrocarbon but are washed off the column with methanol.

particles from the aqueous sample, replacing the extraction with organic solvent, centrifugation, and filtration. Crushed whole chocolate (0.5 gram) is suspended in 20 mL of water at 80°C for 15 minutes to extract caffeine, theobromine, and other water-soluble components. A solid-phase extraction column containing 0.5 gram of silica particles with covalently attached hydrocarbons (like the particles on the column in Figure 0-4) is cleaned with 1 mL of methanol followed by 1 mL of water. When 0.5 mL of aqueous extract is applied to the column, theobromine and caffeine adhere to the hydrocarbon on the silica particles in the column. Many water-soluble components such as sugars are washed through with 1 mL of water. Caffeine and theobromine are then washed from the column with 2.5 mL of methanol. Fats remain on the column. After evaporating the methanol to dryness, the residue is dissolved in 1 mL of water and is ready for chromatography. See Color Plate 36 near the center of this book for an example of solid-phase extraction.

0-2 General Steps in a Chemical Analysis

The analytical process often begins with a question that is not phrased in terms of a chemical analysis. The question could be "Is this water safe to drink?" or "Does emission testing of automobiles reduce air pollution?" A scientist translates such questions into the need for particular measurements. An analytical chemist then chooses or invents a procedure to carry out those measurements.

When the analysis is complete, the analyst must translate the results into terms that can be understood by others—preferably by the general public. A critical feature of any result is its reliability. What is the statistical uncertainty in reported results? If you took samples in a different manner, would you obtain the same results? Is a tiny amount (a *trace*) of analyte found in a sample really there or is it contamination from the analytical procedure? Only after we understand the results and their limitations can we draw conclusions.

Here are the general steps in the analytical process:

Formulating the question — Translate general questions into specific questions to be answered through chemical measurements.

Selecting analytical procedures — Search the chemical literature to find appropriate procedures or, if necessary, devise new procedures to make the required measurements.

Sampling — *Sampling* is the process of selecting representative material to analyze. Box 0-1 provides some ideas on how to do so. If you begin with a poorly chosen sample or if the sample changes between the time it is collected and the time it is analyzed, results are meaningless. "Garbage in—garbage out!"

Sample preparation — Converting a representative sample into a form suitable for analysis is called *sample preparation,* which usually means dissolving the sample. Samples with a low concentration of analyte may need to be concentrated prior to analysis. It may be necessary to remove or *mask* species that interfere with the chemical analysis. For a chocolate bar, sample preparation consisted of removing fat and dissolving the desired analytes. Fat was removed because it would interfere with chromatography.

Chemists use the term **species** to refer to any chemical of interest. Species is both singular and plural.

Interference occurs when a species other than analyte increases or decreases the response of the analytical method and makes it appear that there is more or less analyte than is actually present.

Masking is the transformation of an interfering species into a form that is not detected. For example, Ca^{2+} in lake water can be measured with a reagent called EDTA. Al^{3+} interferes with this analysis because it also reacts with EDTA. Al^{3+} can be masked with excess F^- to form AlF_6^{3-}, which does not react with EDTA.

Analysis — Measure the concentration of analyte in several identical **aliquots** (portions). The purpose of *replicate measurements* (repeated measurements) is to assess the variability (uncertainty) in the analysis and to guard against a gross error in the analysis of a single aliquot. *The uncertainty of a measurement is as important as the measurement itself* because it tells us how reliable the measurement is. If necessary, use different analytical methods on similar samples to show that the choice of analytical method is not biasing the result. You may also wish to construct several different samples to see what variations arise from your sampling and sample preparation procedure.

Reporting and interpretation — Deliver a clearly written, complete report of your results, highlighting any limitations that you attach to them. Your report might be written to be read only by a specialist (such as your instructor), or it might be written for a general audience (such as a legislator or newspaper reporter). Be sure the report is appropriate for its intended audience.

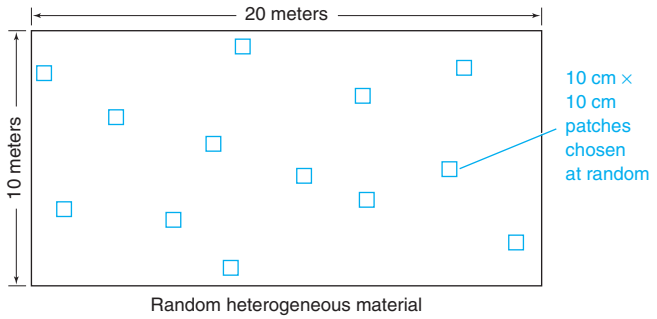
Drawing conclusions — Once a report is written, the analyst might not be involved in what is done with the information, such as modifying the raw material supply for a factory or creating new laws to regulate food additives. The more clearly a report is written, the less likely it is to be misinterpreted by those who use it.

Most of this book deals with measuring chemical concentrations in homogeneous aliquots of an unknown. Analysis is meaningless unless you have collected the sample properly, you have taken measures to ensure the reliability of the analytical method, and you communicate your results clearly and completely. The chemical analysis is only the middle portion of a process that begins with a question and ends with a conclusion.

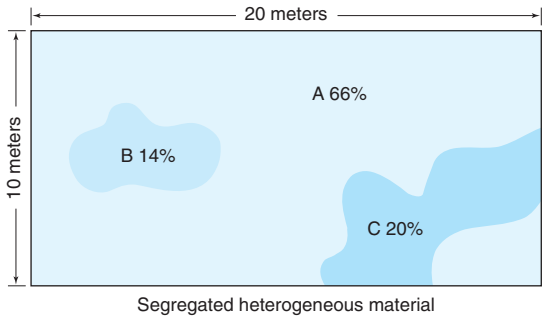
BOX 0-1 Constructing a Representative Sample

In a **random heterogeneous material,** differences in composition occur randomly and on a fine scale. When you collect a portion of the material for analysis, you obtain some of each of the different compositions. To construct a representative sample from a heterogeneous material, you can first visually divide the material into segments. A **random sample** is collected by taking portions from the desired number of segments chosen at random. If you wanted to measure the magnesium content of the grass in the 10-meter × 20-meter field in panel *a,* you could divide the field into 20 000 small patches that are 10 centimeters on a side. After assigning a number to each small patch, you could use a computer program to pick 100 numbers at random from 1 to 20 000. Then harvest and combine the grass from each of these 100 patches to construct a representative bulk sample for analysis.

For a **segregated heterogeneous material** (in which large regions have obviously different compositions), a representative **composite sample** must be constructed. For example, the field in panel *b* has three different types of grass segregated into regions A, B, and C. You could draw a map of the field on graph paper and measure the area in each region. In this case, 66% of the area lies in region A, 14% lies in region B, and 20% lies in region C. To construct a representative bulk sample from this segregated material, take 66 of the small patches from region A, 14 from region B, and 20 from region C. You could do so by drawing random numbers from 1 to 20 000 to select patches until you have the desired number from each region.



(*a*)



(*b*)

Terms to Understand

Terms are introduced in **bold** type in the chapter and are also defined in the Glossary.

aliquot
analyte
aqueous
calibration curve
composite sample
decant
heterogeneous
homogeneous
interference
masking
qualitative chemical analysis
quantitative chemical analysis
quantitative transfer
random heterogeneous material
random sample
sample preparation
sampling
segregated heterogeneous material
slurry
species
standard solution
supernatant liquid

Problems

Complete solutions to Problems can be found in the *Solutions Manual.* Short answers to numerical problems are at the back of the book.

0-1. What is the difference between *qualitative* and *quantitative* analysis?

0-2. List the steps in a chemical analysis.

0-3. What does it mean to *mask* an interfering species?

0-4. What is the purpose of a calibration curve?

0-5. (a) What is the difference between a homogeneous material and a heterogeneous material?

(b) After reading Box 0-1, state the difference between a segregated heterogeneous material and a random heterogeneous material.

(c) How would you construct a representative sample from each type of material?

0-6. The iodide (I^-) content of a commercial mineral water was measured by two methods that produced wildly different results.[6] Method A found 0.23 milligrams of I^- per liter (mg/L) and method B found 0.009 mg/L. When Mn^{2+} was added to the water, the I^- content found by method A increased each time that more Mn^{2+} was added, but results from method B were unchanged. Which of the *Terms to Understand* describes what is occurring in these measurements? Explain your answer. Which result is more reliable?