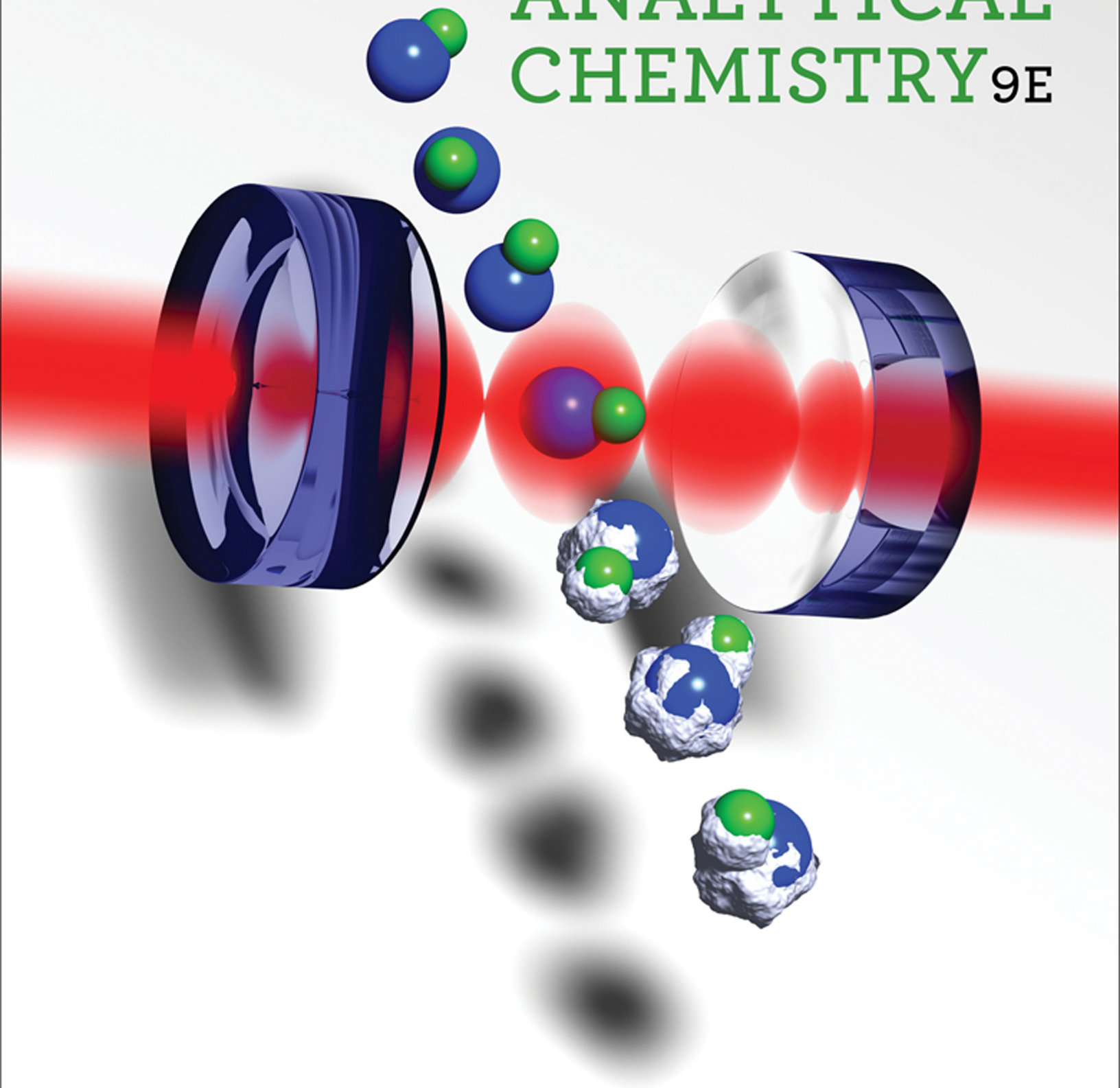
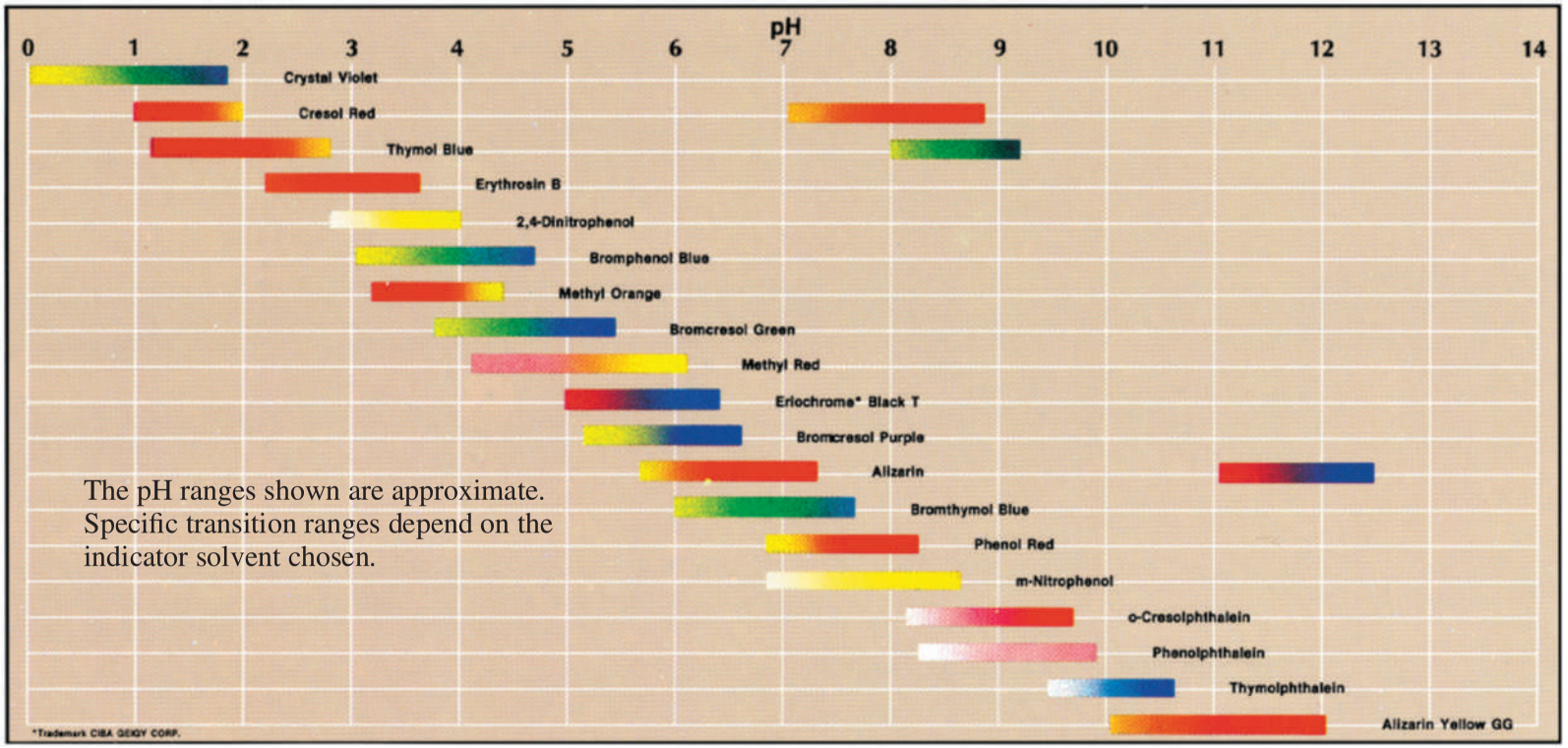
SKOOG | WEST

FUNDAMENTALS OF ANALYTICAL CHEMISTRY 9E



F. JAMES HOLLER | STANLEY R. CROUCH

Some Acid/Base Indicators and Their Color Changes



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PERIODIC TABLE OF THE ELEMENTS

Metals
Nonmetals
Metalloids

	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIIIB 8	VIIIB 9	VIIIB 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	0 18
1	1 H 1.008																1 H 1.008	2 He 4.0026
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.9984	10 Ne 20.1797
3	11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.085	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.845	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9058	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.9045	54 Xe 131.293
6	55 Cs 132.9055	56 Ba 137.327	57 La 138.9055 *	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.084	79 Au 196.9666	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227) **	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

*Lanthanide Series

58 Ce 140.116	59 Pr 140.9076	60 Nd 144.242	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.500	67 Ho 164.9303	68 Er 167.259	69 Tm 168.9342	70 Yb 173.054	71 Lu 174.9668

** Actinide Series

90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.

INTERNATIONAL ATOMIC MASSES

Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)
Aluminum	Al	13	26.9815386
Americium	Am	95	(243)
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	(210)
Barium	Ba	56	137.327
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98040
Bohrium	Bh	107	(270)
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Calcium	Ca	20	40.078
Californium	Cf	98	(251)
Carbon	C	6	12.011
Cerium	Ce	58	140.116
Cesium	Cs	55	132.90545
Chlorine	Cl	17	35.45
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copernicium	Cn	112	(285)
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Darmstadtium	Ds	110	(281)
Dubnium	Db	105	(268)
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	(252)
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	(257)
Flerovium	Fl	114	(289)
Fluorine	F	9	18.9984032
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.63
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	(277)
Helium	He	2	4.002602
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.008
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.90547
Lawrencium	Lr	103	(262)
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Livermorium	Lv	116	(293)
Lutetium	Lu	71	174.9668
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	(276)
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.96
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	(237)
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.007
Nobelium	No	102	(259)
Osmium	Os	76	190.23
Oxygen	O	8	15.999
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.084
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.03588
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	(280)
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(265)
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	(271)
Selenium	Se	34	78.96
Silicon	Si	14	28.085
Silver	Ag	47	107.8682
Sodium	Na	11	22.98976928
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.94788
Technetium	Tc	43	(98)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.38
Thorium	Th	90	232.03806
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Ununoctium	Uuo	118	(294)
Ununpentium	Uup	115	(288)
Ununseptium	Uus	117	(294)
Ununtrium	Uut	113	(284)
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.054
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.224

The values given in parentheses are the atomic mass numbers of the isotopes of the longest known half-life. From M. E. Wieser and T. B. Coplen, *Pure Appl. Chem.,* **2011**, *83*(2), 359–96, **DOI**: 10.1351/PAC-REP-10-09-14.

MOLAR MASSES OF SOME COMPOUNDS

Compound	Molar Mass	Compound	Molar Mass
AgBr	187.772	$K_3Fe(CN)_6$	329.248
AgCl	143.32	$K_4Fe(CN)_6$	368.346
Ag_2CrO_4	331.729	$KHC_8H_4O_4$ (phthalate)	204.222
AgI	234.7727	$KH(IO_3)_2$	389.909
$AgNO_3$	169.872	K_2HPO_4	174.174
AgSCN	165.95	KH_2PO_4	136.084
Al_2O_3	101.960	$KHSO_4$	136.16
$Al_2(SO_4)_3$	342.13	KI	166.0028
As_2O_3	197.840	KIO_3	214.000
B_2O_3	69.62	KIO_4	229.999
$BaCO_3$	197.335	$KMnO_4$	158.032
$BaCl_2 \cdot 2H_2O$	244.26	KNO_3	101.102
$BaCrO_4$	253.319	KOH	56.105
$Ba(IO_3)_2$	487.130	KSCN	97.18
$Ba(OH)_2$	171.341	K_2SO_4	174.25
$BaSO_4$	233.38	$La(IO_3)_3$	663.610
Bi_2O_3	465.958	$Mg(C_9H_6NO)_2$ (8-hydroxyquinolate)	312.611
CO_2	44.009		
$CaCO_3$	100.086	$MgCO_3$	84.313
CaC_2O_4	128.096	$MgNH_4PO_4$	137.314
CaF_2	78.075	MgO	40.304
CaO	56.077	$Mg_2P_2O_7$	222.551
$CaSO_4$	136.13	$MgSO_4$	120.36
$Ce(HSO_4)_4$	528.37	MnO_2	86.936
CeO_2	172.114	Mn_2O_3	157.873
$Ce(SO_4)_2$	332.23	Mn_3O_4	228.810
$(NH_4)_2Ce(NO_3)_6$	548.22	$Na_2B_4O_7 \cdot 10H_2O$	381.36
$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$	632.53	NaBr	102.894
Cr_2O_3	151.989	$NaC_2H_3O_2$	82.034
CuO	79.545	$Na_2C_2O_4$	133.998
Cu_2O	143.091	NaCl	58.44
$CuSO_4$	159.60	NaCN	49.008
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	392.13	Na_2CO_3	105.988
FeO	71.844	$NaHCO_3$	84.006
Fe_2O_3	159.687	$Na_2H_2EDTA \cdot 2H_2O$	372.238
Fe_3O_4	231.531	Na_2O_2	77.978
HBr	80.912	NaOH	39.997
$HC_2H_3O_2$ (acetic acid)	60.052	NaSCN	81.07
$HC_7H_5O_2$ (benzoic acid)	122.123	Na_2SO_4	142.04
$(HOCH_2)_3CNH_2$ (TRIS)	121.135	$Na_2S_2O_3 \cdot 5H_2O$	248.17
HCl	36.46	NH_4Cl	53.49
$HClO_4$	100.45	$(NH_4)_2C_2O_4 \cdot H_2O$	142.111
$H_2C_2O_4 \cdot 2H_2O$	126.064	NH_4NO_3	80.043
H_5IO_6	227.938	$(NH_4)_2SO_4$	132.13
HNO_3	63.012	$(NH_4)_2S_2O_8$	228.19
H_2O	18.015	NH_4VO_3	116.978
H_2O_2	34.014	$Ni(C_4H_7O_2N_2)_2$ (dimethylglyoximate)	288.917
H_3PO_4	97.994		
H_2S	34.08	$PbCrO_4$	323.2
H_2SO_3	82.07	PbO	223.2
H_2SO_4	98.07	PbO_2	239.2
HgO	216.59	$PbSO_4$	303.3
Hg_2Cl_2	472.08	P_2O_5	141.943
$HgCl_2$	271.49	Sb_2S_3	339.70
KBr	119.002	SiO_2	60.083
$KBrO_3$	166.999	$SnCl_2$	189.61
KCl	74.55	SnO_2	150.71
$KClO_3$	122.55	SO_2	64.06
KCN	65.116	SO_3	80.06
K_2CrO_4	194.189	$Zn_2P_2O_7$	304.70
$K_2Cr_2O_7$	294.182		

*Excel Shortcut Keystrokes for the PC**

**Macintosh equivalents, if different, appear in square brackets*

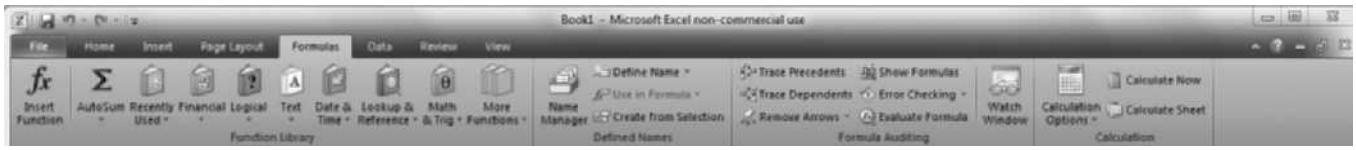
TO ACCOMPLISH THIS TASK	TYPE THESE KEYSTROKES
Alternate between displaying cell values and displaying cell formulas	**Ctrl+` [⌘+`]**
Calculate all sheets in all open workbooks	**F9**
Calculate the active worksheet	**Shift+F9**
Cancel an entry in a cell or formula bar	**Esc**
Complete a cell entry and move down in the selection	**Enter [Return]**
Complete a cell entry and move to the left in the selection	**Shift+Tab**
Complete a cell entry and move to the right in the selection	**Tab**
Complete a cell entry and move up in the selection	**Shift+Enter**
Copy a formula from the cell above the active cell into the cell or the formula bar	**Ctrl+'** (Apostrophe) **[⌘+']**
Copy a selection	**Ctrl+C[⌘+C]**
Copy the value from the cell above the active cell into the cell or the formula bar	**Ctrl+Shift+"** (Quotation Mark) **[⌘+Shift+"]**
Cut a selection	**Ctrl+X [⌘+X]**
Define a name	**Ctrl+F3 [⌘+F3]**
Delete the character to the left of the insertion point, or delete the selection	**Backspace [Delete]**
Delete the character to the right of the insertion point, or delete the selection	**Delete [Del]**
Displays the Insert Function dialog box	**Shift+F3**
Displays Key Tips for ribbon shortcuts	**ALT**
Edit a cell comment	**Shift+F2**
Edit the active cell	**F2 [None]**
Edit the active cell and then clear it, or delete the preceding character in the active cell as you edit the cell contents	**Backspace [Delete]**
Enter a formula as an array formula	**Ctrl+Shift+Enter**
Fill down	**Ctrl+D[⌘+D]**
Fill the selected cell range with the current entry	**Ctrl+Enter [None]**
Fill to the right	**Ctrl+R [⌘+R]**
Format cells dialog box	**Ctrl+1 [⌘+1]**
Insert the AutoSum formula	**Alt+=** (Equal Sign) **[⌘+Shift+T]**
Move one character up, down, left, or right	**Arrow Keys**
Move to the beginning of the line	**Home**
Paste a name into a formula	**F3 [None]**
Paste a selection	**Ctrl+V [⌘+V]**
Repeat the last action	**F4 Or Ctrl+Y [⌘+Y]**
Selects the entire worksheet	**Ctrl+A**
Start a formula	= (Equal Sign)
Start a new line in the same cell	**Alt+Enter [⌘+Option+Enter]**
Undo	**Ctrl+Z[⌘+Z]**

Microsoft® Excel Ribbon and Tabs for Excel 2010

Home Ribbon Wide View

Home Ribbon Narrow View

Insert Tab



Formulas Tab

Data Tab

Not shown are Page Layout, Review and View Tabs

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$H_2O + I_3^-(aq) + H_3AsO_3(aq) \rightarrow \quad \leftarrow 3I^-(aq) + H_3AsO_4(aq) + H^+(aq)$

(a) (b)

Color Plate 1 Chemical Equilibrium 1: Reaction between iodine and arsenic(III) at pH 1. (a) One mmol I_3^- added to one mmol H_3AsO_3. (b) Three mmol I^- added to one mmol H_3AsO_4. Both combinations of solutions produce the same final equilibrium state (see Section 9B-1, page 202).

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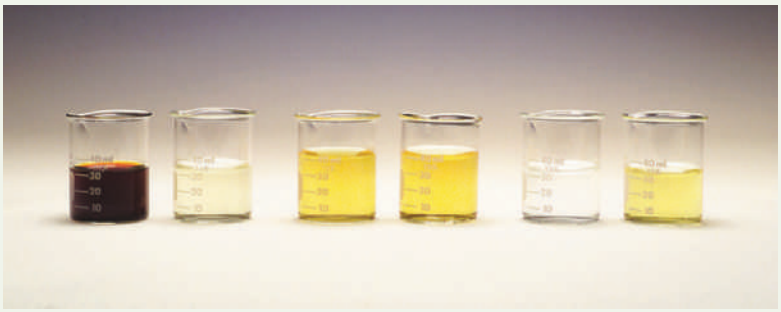
$H_2O + I_3^-(aq) + H_3AsO_3(aq) \rightarrow \quad \leftarrow 3I^-(aq) + H_3AsO_4(aq) + H^+(aq)$

(a) (b)

Color Plate 2 Chemical Equilibrium 2: The same reaction as in color plate 1 carried out at pH 7, producing a different equilibrium state than that in Color Plate 1, and although similar to the situation in Color Plate 1, the same state is produced from either the forward (a) or the reverse (b) direction (see Section 9B-1, page 202).



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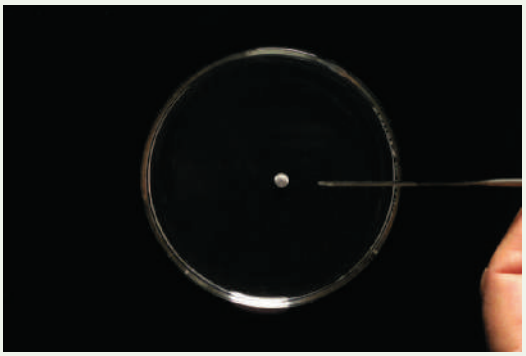
$I_3^-(aq) + 2Fe(CN)_6^{4-}(aq) \rightarrow \quad \leftarrow 3I^-(aq) + 2Fe(CN)_6^{3-}(aq)$

(a) (b)

Color Plate 3 Chemical Equilibrium 3: Reaction between iodine and ferrocyanide. (a) One mmol I_3^- added to two mmol $Fe(CN)_6^{4-}$. (b) Three mmol I^- added to two mmol $Fe(CN)_6^{3-}$. Both combinations of solutions produce the same final equilibrium state. (see Section 9B-1, page 202).



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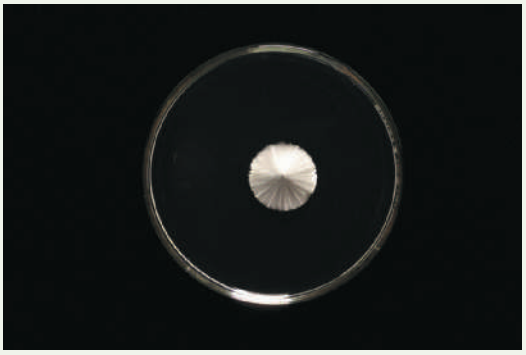

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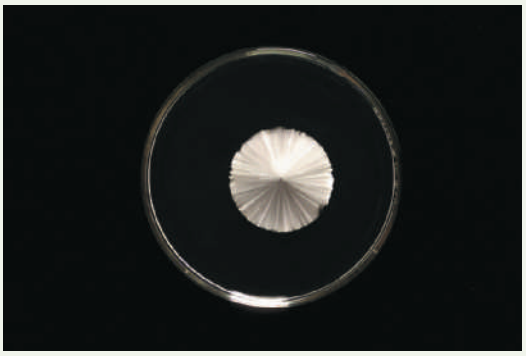

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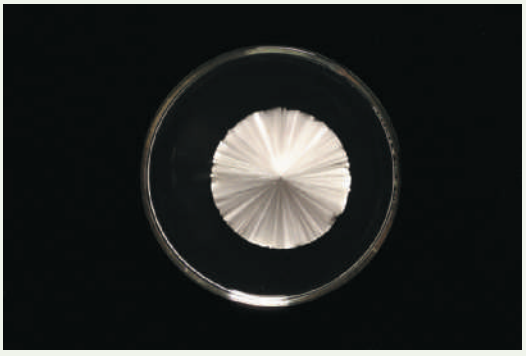

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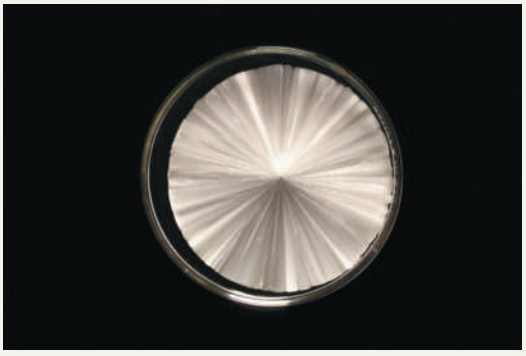

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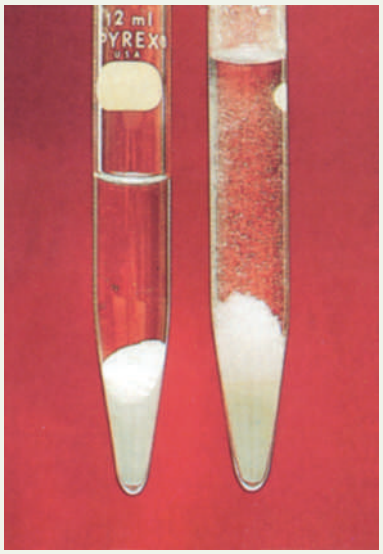
Color Plate 5 Crystallization of sodium acetate from a supersaturated solution (see Section 12A-2, page 280). A tiny seed crystal is dropped into the center of a petri dish containing a supersaturated solution of the compound. The time sequence of photos taken about once per second shows the growth of the beautiful crystals of sodium acetate.



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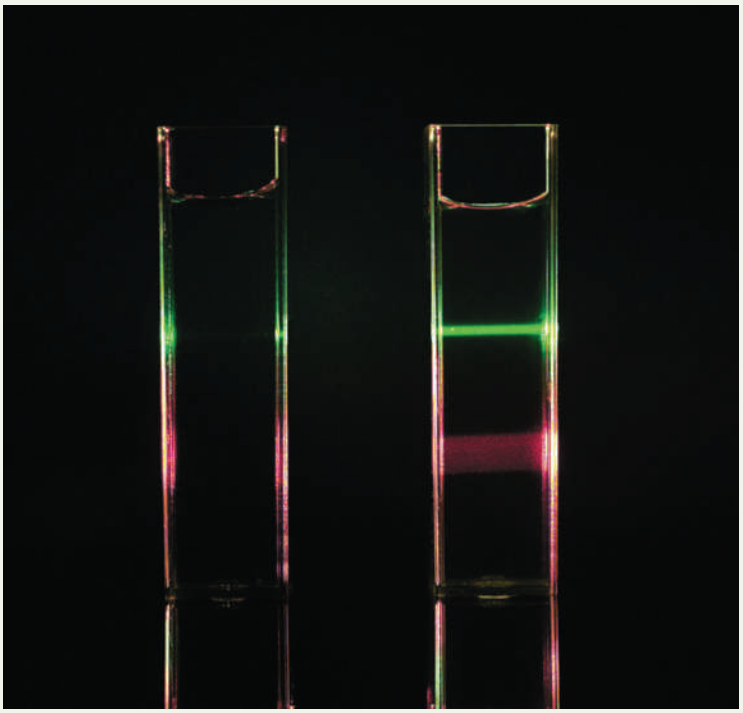
Color Plate 4 The common-ion effect. The test tube on the left contains a saturated solution of silver acetate, AgOAc. The following equilibrium is established in the test tube:

$$AgOAc(s) \rightleftharpoons Ag^{+}(aq) + OAc^{-}(aq)$$

When $AgNO_3$ is added to the test tube, the equilibrium shifts to the left to form more AgOAc, as shown in the test tube on the right (see Section 9B-5, page 209).



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Color Plate 6 The Tyndall effect. The photo shows two cuvettes: the one on the left contains only water while the one on the right contains a solution of starch. As red and green laser beams pass through the water in the left cuvette, they are invisible. Colloidal particles in the starch solution in the right cuvette scatter the light from the two lasers, so the beams become visible (see Section 12A-2, margin note, page 280).

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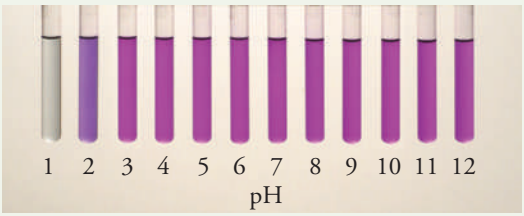
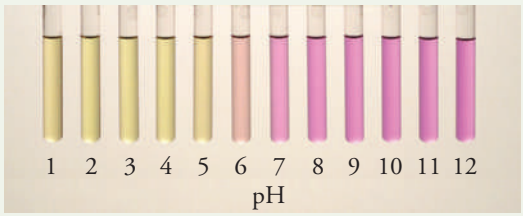
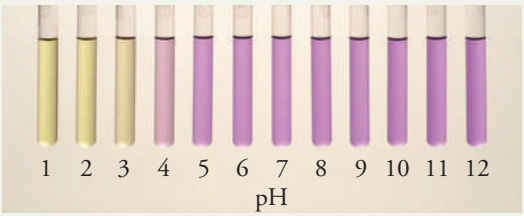
Color Plate 7 When dimethylglyoxime is added to a slightly basic solution of $Ni^{2+}(aq)$, shown on the left, a bright red precipitate of $Ni(C_4H_7N_2O_2)_2$ is formed as seen in the beaker on the right (see Section 12C-3, page 294).



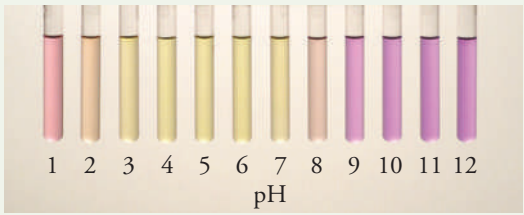
Methyl violet (0.0–1.6)



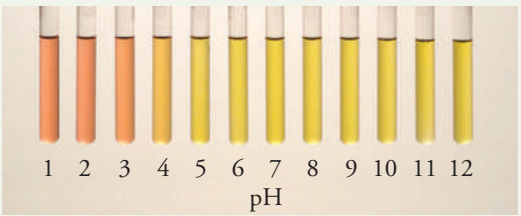
Chlorophenol red (4.8–6.7)



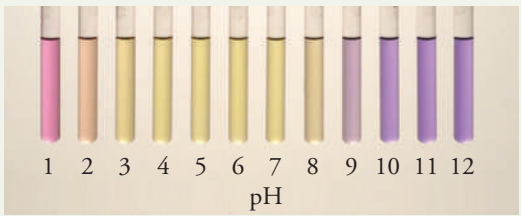
Bromophenol blue (3.0–4.6)



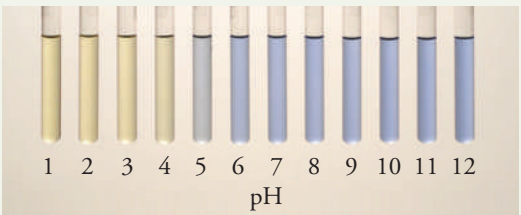
m-Cresol purple (7.4–9.0)



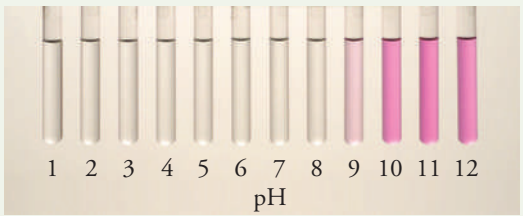
Methyl orange (3.2–4.4)



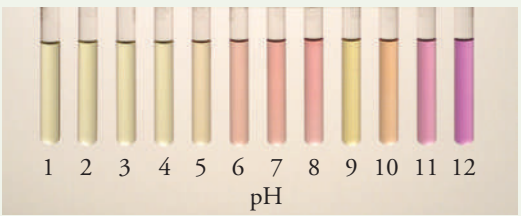
Thymol blue (8.0–9.2)



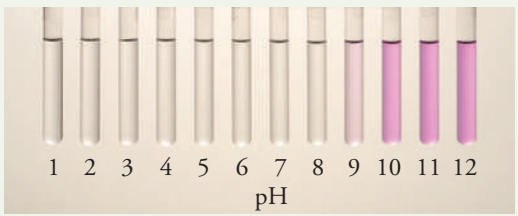
Bromocresol green (3.8–5.4)



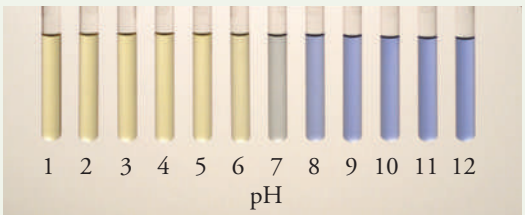
Phenolphthalein (8.0–10.0)



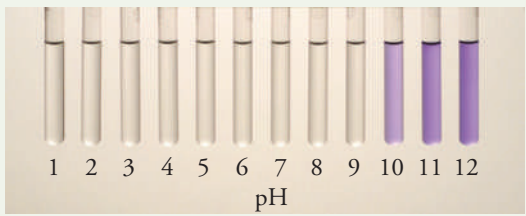
Alizarin red (4.6–6.0)



o-Cresolphthalein (8.2–9.8)



Bromothymol (6.0–7.0)



Thymolphthalein (8.8–10.5)

Charles D. Winters

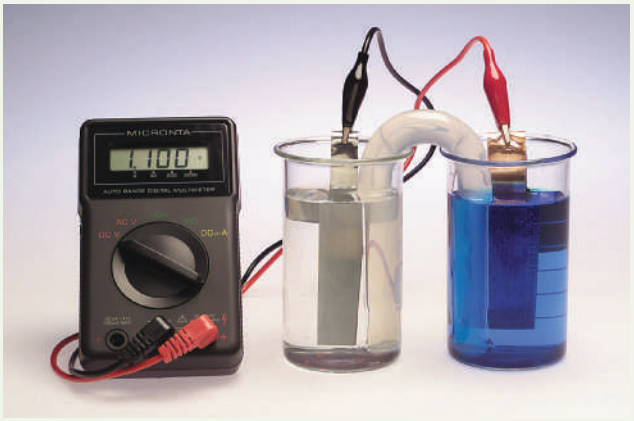
Color Plate 8 Acid/base indicators and their transition pH ranges (see Section 14A-2, page 323).

Charles D. Winters

Color Plate 9 End point in an acid/base titration with phenolphthalein as indicator. The end point is achieved when the barely perceptible pink color of phenolphthalein persists. The flask on the left shows the titration less than half a drop prior to the end point; the middle flask shows the end point. The flask on the right shows what happens when a slight excess of base is added to the titration mixture. The solution turns a deep pink color, and the end point has been exceeded (see Section 13A-1, page 304).

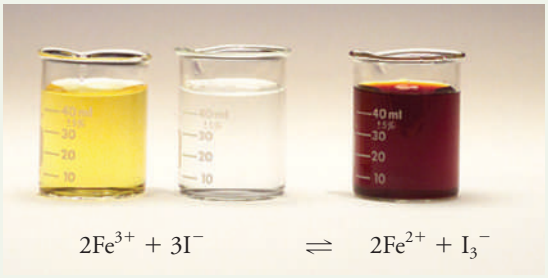
Charles D. Winters

Color Plate 10 Reduction of silver(I) by direct reaction with copper, forming the "silver tree" (see Section 18A-2, page 445).



Charles D. Winters

Color Plate 11 A modern version of the Daniell Cell (see Feature 18-2, page 450).



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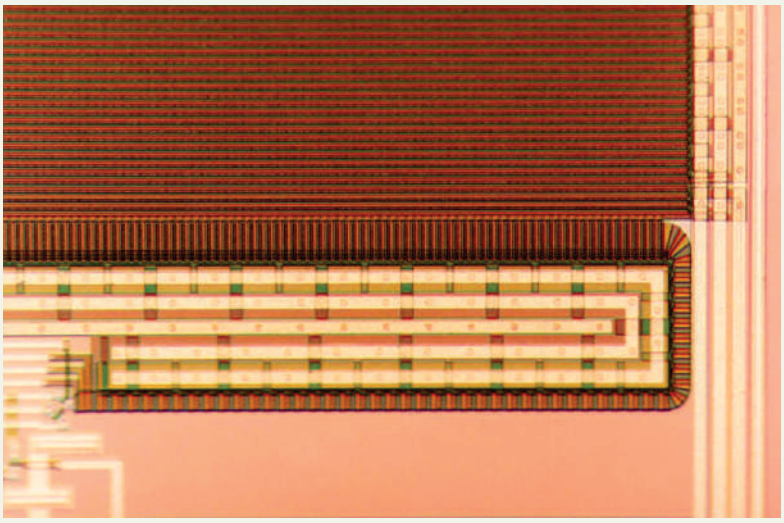
Color Plate 12 Reduction between Iron(III) and iodide. The species in each beaker are indicated by the colors of the solutions. Iron (III) is pale yellow, iodide is colorless, and triiodide is intense red-orange (see margin note, Section 18C-6, page 464).

Charles D. Winters

Color Plate 13 The time dependence of the reaction between permanganate and oxalate (see Section 20C-1, page 515).

© H&H Productions

(a)



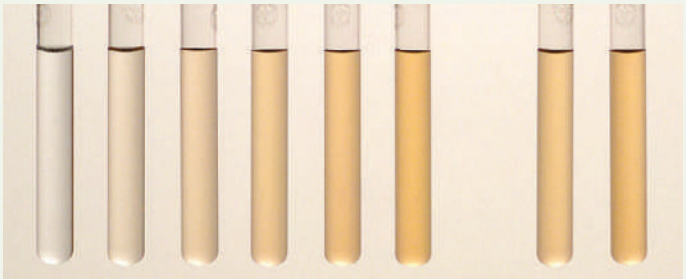
Simon Tulloch

(b)

Simon Tulloch

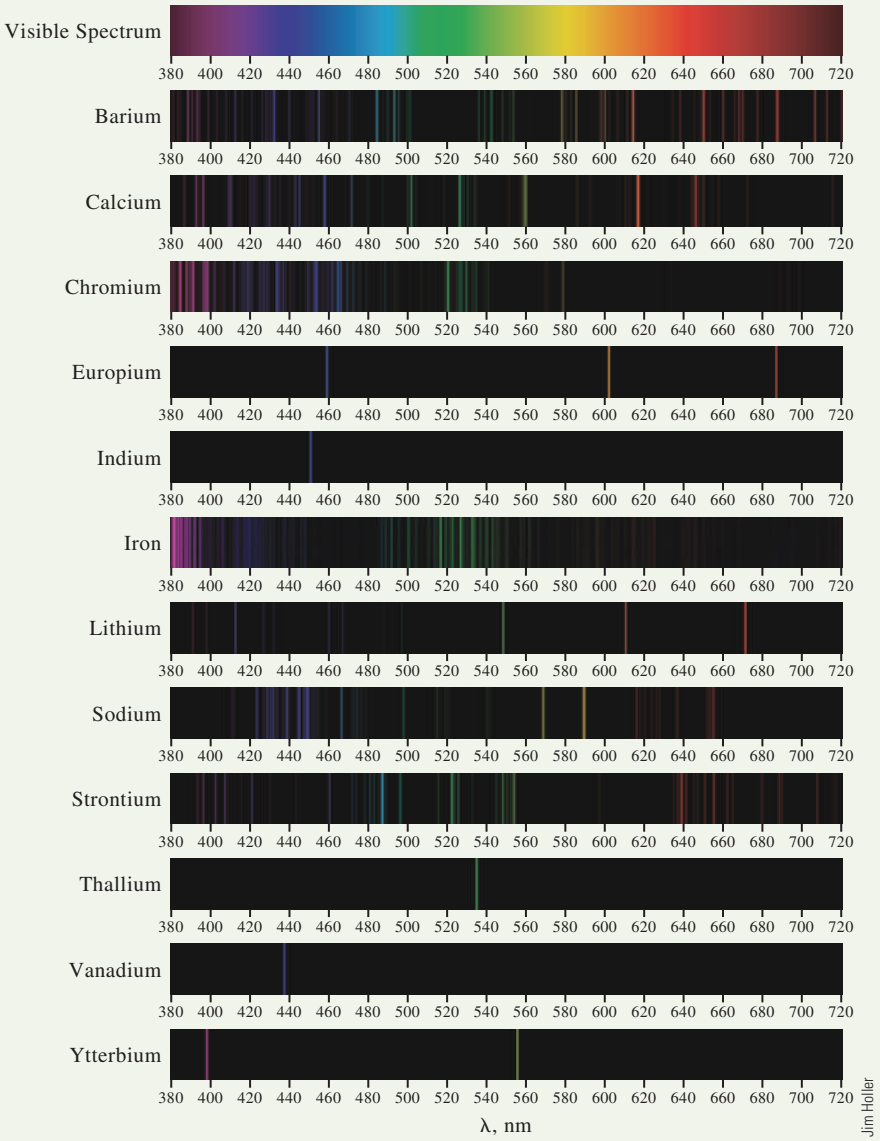
(c)

Color Plate 14 (a) Typical linear CCD arrays for spectrophotometers. The array on the right has 4096 pixels, and the array on the left has 2048 pixels. In both arrays, each pixel has the dimensions of 14 μm × 14 μm. These devices have a spectral range of 200-1000 nm, a dynamic range of 2500:1 (see Section 8E-2), and are available with low-cost glass or UV-enhanced fused silica windows. In addition to the sizes shown, the arrays are available in lengths of 512 and 1024 pixels. (b) Photomicrograph of a section of a two-dimensional CCD array that is used for imaging and spectroscopy. Light falling on the millions of pixels in the upper left of the photo creates charge that is transferred to the vertical channels at the bottom of the photo and shifted from left to right along the string of channels until it reaches the output amplifier section shown in (c). The amplifier provides a voltage proportional to the charge accumulated on each pixel, which is in turn proportional to the intensity of light falling on the pixel (see Section 25A-4, page 705, for a discussion of charge-transfer devices).

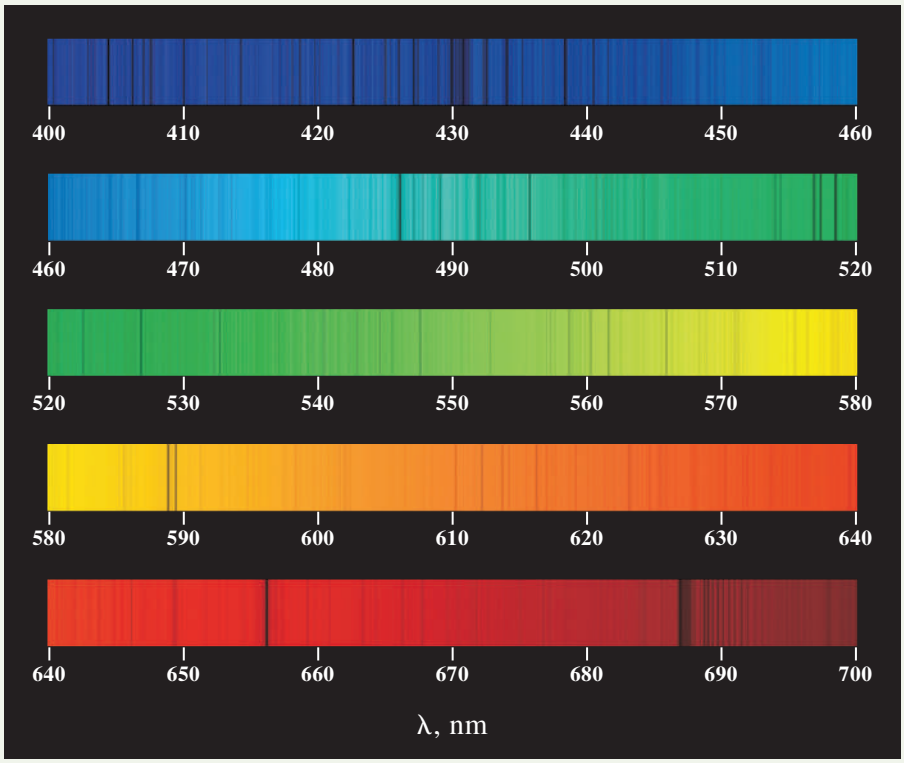


Charles D. Winters

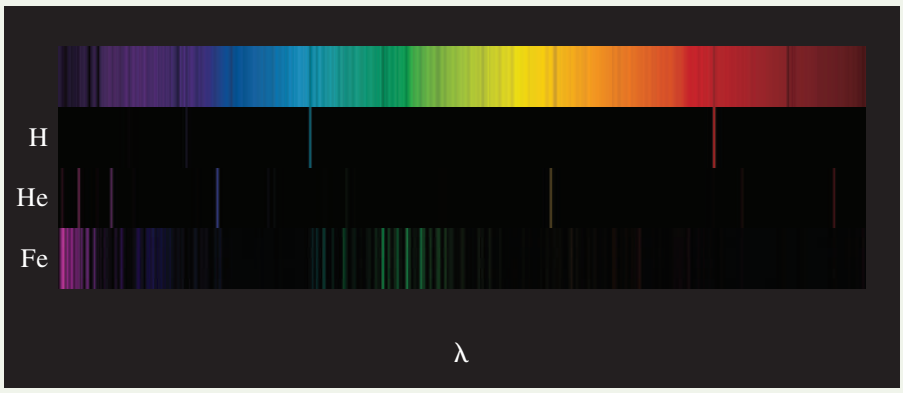
Color Plate 15 Series of standards (left) and two unknowns (right) for the spectrophotometric determination of Fe(II) using 1,10-phenanthroline as reagent (see Section 26A-3 and Problem 26-26, page 757). The color is due to the complex $Fe(phen)_3^{2+}$. The absorbance of the standards is measured, and a working curve is analyzed using linear least-squares (see Section 8C-2, page 172). The equation for the line is then used to determine the concentrations of the unknown solutions from their measured absorbances.



Color Plate 16 Spectrum of white light and emission spectra of selected elements (see Chapter 28).



(a)



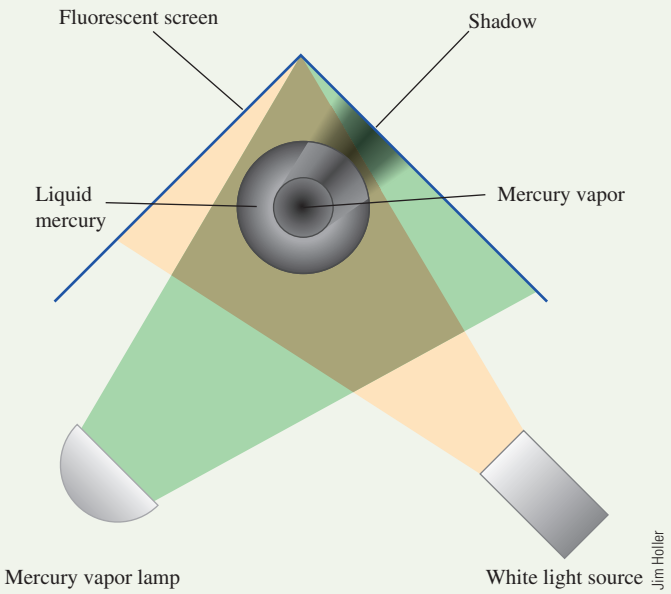
(Dr. Donald Mickey)

(a)

Color Plate 17 The solar spectrum. (a) Expanded color version of the solar spectrum shown in black and white in Feature 24-1 (see Figure 24F-1, page 657). The huge number of dark absorption lines are produced by all of the elements in the sun. See if you can spot some prominent lines like the famous sodium doublet. (b) Compact version of the solar spectrum in (a) compared to the emission spectra of hydrogen, helium, and iron. It is relatively easy to spot lines in the emission spectra of hydrogen and iron that correspond to absorption lines in the solar spectrum, but the lines of helium are quite obscure. In spite of this problem, helium was discovered when these lines were observed in the solar spectrum (see Section 28D). (Images created by Dr. Donald Mickey, University of Hawaii Institute for Astronomy from National Solar Observatory spectral data/NSO/Kitt Peak FTS data by NSF/NOAO.)

Charles D. Winters

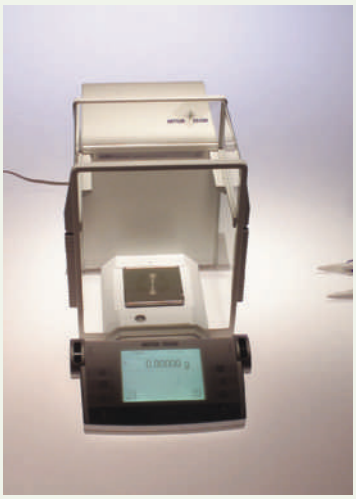
(a)



Jim Holler

(b)

Color Plate 18 (a) Demonstration of atomic absorption by mercury vapor. (b) White light from the source on the right passes through the mercury vapor above the flask and no shadow appears on the fluorescent screen on the left. Light from the mercury lamp on the left containing the characteristic UV lines of the element is absorbed by the vapor in and above the flask, which casts a shadow on the screen on the right of the plume of mercury vapor (see Section 28D-4, page 797).



(a)

(b)

(c)

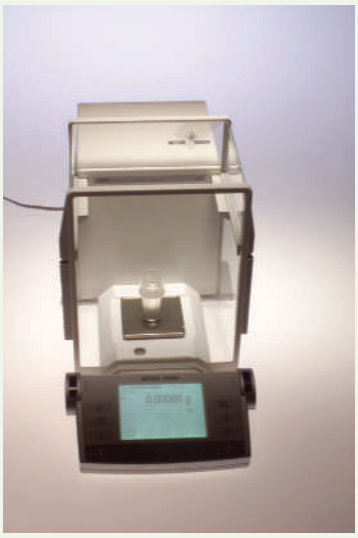
(d)

(e)

Color Plate 19 Weighing by difference the old-fashioned way. (a) Zero the balance. (b) Place a weighing bottle containing the solute on the balance pan. (c) Read the mass (33.2015 g). (d) Transfer the desired amount of solute to a flask. (e) Replace the weighing bottle on the pan and read the mass (33.0832 g). Finally, calculate the mass of the solute transferred to the flask: 33.2015 g − 33.0832 g = 0.1131 g (see Section 2E-4, page 27). (Electronic balance provided by Mettler-Toledo, Inc.)

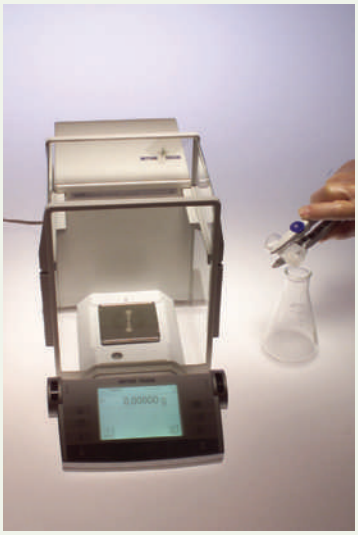
Charles D. Winters

(a)



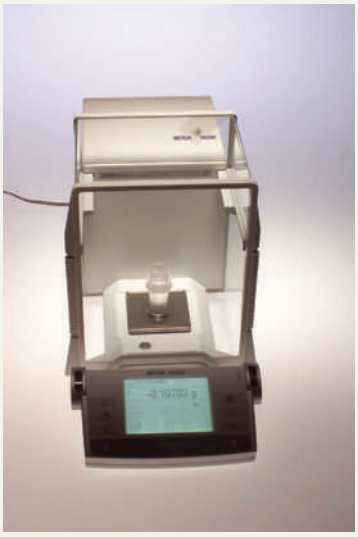
Charles D. Winters

(b)



Charles D. Winters

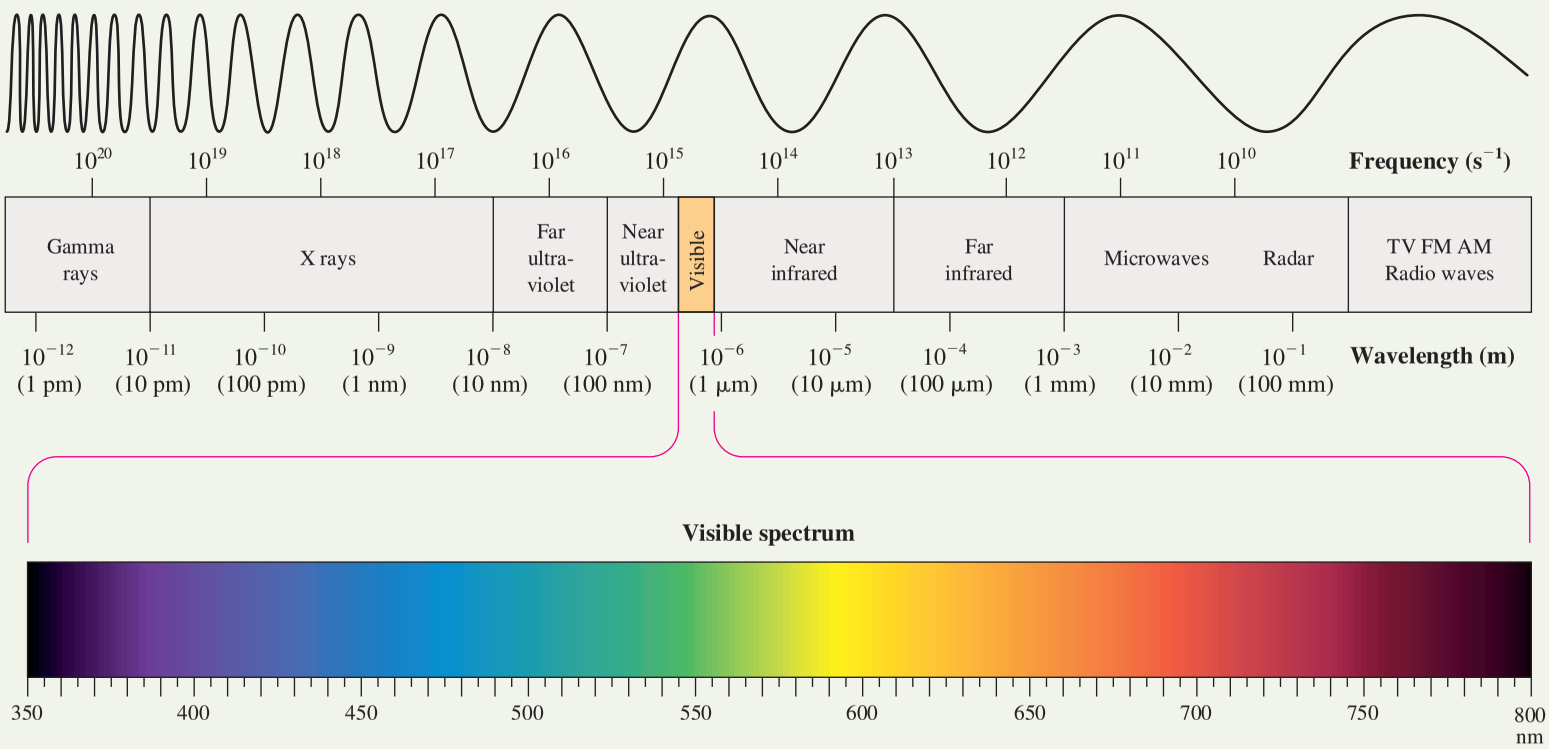
(c)



Charles D. Winters

(d)

Color Plate 20 Weighing by difference the modern way. Place a weighing bottle containing the solute on the balance pan and (a) depress the tare or zero button. The balance should then read 0.0000 g, as shown in (b). (c) Transfer the desired amount of solute to a flask. Replace the weighing bottle on the pan, and (d) the balance reads the decrease in mass directly as −0.1070 g (see Section 2E-4, page 27). Many modern balances have built-in computers with programs to perform a variety of weighing tasks. For example, it is possible to dispense many consecutive quantities of a substance and automatically read out the loss in mass following each dispensing. Many balances also have computer intterfaces so that reading may be logged directly to programs running on the computer. (Electronic balance provided by Mettler-Toledo, Inc.)



Color Plate 21 Electromagnetic spectrum. The spectrum extends from high-energy (frequency) gamma rays to low-energy (frequency) radio waves (see Section 24B-1, page 654). Note that the visible region is only a tiny fraction of the spectrum. The visible region, broken out in the lower portion, extends from the violet (≈380 nm) to the red region (≈800 nm). (Courtesy of Ebbing and Gammon, *General Chemistry*, 10th ed.)

Fundamentals of Analytical Chemistry

NINTH EDITION

Douglas A. Skoog
Stanford University

Donald M. West
San Jose State University

F. James Holler
University of Kentucky

Stanley R. Crouch
Michigan State University

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Contents in Brief

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Preface

The ninth edition of *Fundamentals of Analytical Chemistry* is an introductory textbook designed primarily for a one- or two-semester course for chemistry majors. Since the publication of the eighth edition, the scope of analytical chemistry has continued to evolve, and thus, we have included in this edition many applications to biology, medicine, materials science, ecology, forensic science, and other related fields. As in the previous edition, we have incorporated many spreadsheet applications, examples, and exercises. We have revised some older treatments to incorporate contemporary instrumentation and techniques. In response to the comments of many readers and reviewers, we have added a chapter on mass spectrometry to provide detailed instruction on this vital topic as early as possible in the chemistry curriculum. Our companion book, *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., provides students with a tutorial guide for using spreadsheets in analytical chemistry and introduces many additional spreadsheet operations.

We recognize that courses in analytical chemistry vary from institution to institution and depend on the available facilities and instrumentation, the time allocated to analytical chemistry in the chemistry curriculum, and the unique instructional philosophies of teachers. We have, therefore, designed the ninth edition of *Fundamentals of Analytical Chemistry* so that instructors can tailor the text to meet their needs and students can learn the concepts of analytical chemistry on several levels: in descriptions, in pictorials, in illustrations, in interesting and relevant features, and in using online learning.

Since the production of the eighth edition of this text, the duties and responsibilities for planning and writing a new edition have fallen to two of us (FJH and SRC). While making the many changes and improvements cited above and in the remainder of the preface, we have maintained the basic philosophy and organization of the eight previous editions and endeavored to preserve the same high standards that characterized those texts.

OBJECTIVES

The primary objective of this text is to provide a thorough background in the chemical principles that are particularly important to analytical chemistry. Second, we want students to develop an appreciation for the difficult task of judging the accuracy and precision of experimental data and to show how these judgments can be sharpened by applying statistical methods to analytical data. Third, we aim to introduce a broad range of modern and classic techniques that are useful in analytical chemistry. Fourth, we hope that, with the help of this book, students will develop the skills necessary to solve quantitative analytical problems and, where appropriate, use powerful spreadsheet tools to solve problems, perform calculations, and create simulations of chemical phenomena. Finally, we aim to teach laboratory skills that will give students confidence in their ability to obtain high-quality analytical data and that will highlight the importance of attention to detail in acquiring these data.

COVERAGE AND ORGANIZATION

The material in this text covers both fundamental and practical aspects of chemical analysis. We have organized the chapters into Parts that group together related topics. There are seven major Parts to the text that follow the brief introduction in Chapter 1.

- **Part I** covers the tools of analytical chemistry and comprises seven chapters. Chapter 2 discusses the chemicals and equipment used in analytical laboratories and includes many photographs of analytical operations. Chapter 3 is a tutorial introduction to the use of spreadsheets in analytical chemistry. Chapter 4 reviews the basic calculations of analytical chemistry, including expressions of chemical concentration and stoichiometric relationships. Chapters 5, 6, and 7 present topics in statistics and data analysis that are important in analytical chemistry and incorporate extensive use of spreadsheet calculations. Analysis of variance, ANOVA, is included in Chapter 7, and Chapter 8 provides details about acquiring samples, standardization, and calibration.
- **Part II** covers the principles and application of chemical equilibrium systems in quantitative analysis. Chapter 9 explores the fundamentals of chemical equilibria. Chapter 10 discusses the effect of electrolytes on equilibrium systems. The systematic approach for attacking equilibrium problems in complex systems is the subject of Chapter 11.
- **Part III** brings together several chapters dealing with classical gravimetric and volumetric analytical chemistry. Gravimetric analysis is described in Chapter 12. In Chapters 13 through 17, we consider the theory and practice of titrimetric methods of analysis, including acid/base titrations, precipitation titrations, and complexometric titrations. We take advantage of the systematic approach to equilibria and the use of spreadsheets in the calculations.
- **Part IV** is devoted to electrochemical methods. After an introduction to electrochemistry in Chapter 18, Chapter 19 describes the many uses of electrode potentials. Oxidation/reduction titrations are the subject of Chapter 20, while Chapter 21 presents the use of potentiometric methods to measure concentrations of molecular and ionic species. Chapter 22 considers the bulk electrolytic methods of electrogravimetry and coulometry, and Chapter 23 discusses voltammetric methods, including linear sweep and cyclic voltammetry, anodic stripping voltammetry, and polarography.
- **Part V** presents spectroscopic methods of analysis. The nature of light and its interaction with matter are explored in Chapter 24. Spectroscopic instruments and their components are the topics covered in Chapter 25. The various applications of molecular absorption spectrometric methods are discussed in some detail in Chapter 26, while Chapter 27 is concerned with molecular fluorescence spectroscopy. Chapter 28 covers various atomic spectrometric methods, including plasma and flame emission methods and electrothermal and flame atomic absorption spectroscopy. Chapter 29 on mass spectrometry is new to this edition and provides an introduction to ionization sources, mass analyzers, and ion detectors. Both atomic and molecular mass spectrometry are included.
- **Part VI** includes five chapters dealing with kinetics and analytical separations. We investigate kinetic methods of analysis in Chapter 30. Chapter 31 introduces analytical separations including ion exchange and the various chromatographic methods. Chapter 32 discusses gas chromatography, while high-performance liquid chromatography is covered in Chapter 33. The final chapter in this Part, Chapter 34, introduces some miscellaneous separation methods,

including supercritical fluid chromatography, capillary electrophoresis, and field-flow fractionation.

- The final **Part VII** consists of four chapters dealing with the practical aspects of analytical chemistry. These chapters are published on our website at **www.cengage.com/chemistry/skoog/fac9.** We consider real samples and compare them to ideal samples in Chapter 35. Methods for preparing samples are discussed in Chapter 36, while techniques for decomposing and dissolving samples are covered in Chapter 37. The text ends with Chapter 38, which provides detailed procedures for laboratory experiments that cover many of the principles and applications discussed in previous chapters.

FLEXIBILITY

Because the text is divided into Parts, there is substantial flexibility in the use of the material. Many of the Parts can stand alone or be taken in a different order. For example, some instructors may want to cover spectroscopic methods prior to electrochemical methods or separations prior to spectroscopic methods.

HIGHLIGHTS

This edition incorporates many features and methods intended to enhance the learning experience for the student and to provide a versatile teaching tool for the instructor.

Important Equations. Equations that we feel are the most important have been highlighted with a color screen for emphasis and ease of review.

Mathematical Level. Generally the principles of chemical analysis developed here are based on college algebra. A few of the concepts presented require basic differential and integral calculus.

Worked Examples. A large number of worked examples serve as aids in understanding the concepts of analytical chemistry. In this edition, we title the examples for easier identification. As in the eighth edition, we follow the practice of including units in chemical calculations and using the factor-label method to check correctness. The examples also are models for the solution of problems found at the end of most of the chapters. Many of these use spreadsheet calculations as described next. Where appropriate, solutions to the worked examples are clearly marked with the *word* Solution for ease in identification.

Spreadsheet Calculations. Throughout the book we have introduced spreadsheets for problem solving, graphical analysis, and many other applications. Microsoft Excel® on the PC has been adopted as the standard for these calculations, but the instructions can be easily adapted to other spreadsheet programs and platforms. Many other detailed examples are presented in our companion book, *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed. We have attempted to document each stand-alone spreadsheet with working formulas and entries.

Spreadsheet Summaries. References to our companion book *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., are given as Spreadsheet Summaries in the text. These are intended to direct the user to examples, tutorials, and elaborations of the text topics.

Questions and Problems. An extensive set of questions and problems is included at the end of most chapters. Answers to approximately half of the problems are given at the end of the book. Many of the problems are best solved using spreadsheets. These are identified by a spreadsheet icon  placed in the margin next to the problem.

Challenge Problems. Most of the chapters have a challenge problem at the end of the regular questions and problems. Such problems are intended to be open-ended, research-type problems that are more challenging than normal. These problems may consist of multiple steps, dependent on one another, or may require library or Web searches to find information. We hope that these challenge problems stimulate discussion and extend the topics of the chapter into new areas. We encourage instructors to use them in innovative ways, such as for group projects, inquiry-driven learning assignments, and case study discussions. Because many challenge problems are open-ended and may have multiple solutions, we do not provide answers or explanations for them.

Features. A series of boxed and highlighted Features are found throughout the text. These essays contain interesting applications of analytical chemistry to the modern world, derivation of equations, explanations of more difficult theoretical points, or historical notes. Examples include, W. S. Gosset ("Student") (Chapter 7), Antioxidants (Chapter 20), Fourier Transform Spectroscopy (Chapter 25), LC/MS/MS (Chapter 33), and Capillary Electrophoresis in DNA Sequencing (Chapter 34).

Illustrations and Photos. We feel strongly that photographs, drawings, pictorials, and other visual aids greatly assist the learning process. Hence, we have included new and updated visual materials to aid the student. Most of the drawings are done in two colors to increase the information content and to highlight important aspects of the figures. Photographs and color plates taken exclusively for this book by renowned chemistry photographer Charles Winters are intended to illustrate concepts, equipment, and procedures that are difficult to illustrate with drawings.

Expanded Figure Captions. Where appropriate, we have attempted to make the figure captions quite descriptive so that reading the caption provides a second level of explanation for many of the concepts. In some cases, the figures can stand by themselves much in the manner of a *Scientific American* illustration.

Web Works. In most of the chapters we have included a brief Web Works feature at the end of the chapter. In these features, we ask the student to find information on the web, do online searches, visit the websites of equipment manufacturers, or solve analytical problems. These Web Works and the links given are intended to stimulate student interest in exploring the information available on the World Wide Web. The links will be updated regularly on our website, **www.cengage.com/chemistry/skoog/fac9.**

Glossary. At the end of the book we have placed a glossary that defines the most important terms, phrases, techniques, and operations used in the text. The glossary is intended to provide students with a means for rapidly determining a meaning without having to search through the text.

Appendixes and Endpapers. Included in the appendixes are an updated guide to the literature of analytical chemistry; tables of chemical constants, electrode potentials, and recommended compounds for the preparation of standard materials; sections on the use of logarithms and exponential notation and normality and equivalents (terms that are not used in the text itself); and a derivation of the propagation of error equations. The endpapers of this book provide a full-color chart of chemical indicators, a periodic table, a 2009 IUPAC table of atomic masses, and a table of molar masses of compounds of particular interest in analytical chemistry based on the 2009 atomic masses. In addition, included in the book is a tear-out reference card for the 2010 and 2007 versions of Microsoft Excel.

WHAT'S NEW

Readers of the eighth edition will find numerous changes in the ninth edition in content as well as in style and format.

Content. Several changes in content have been made to strengthen the book.

- Many chapters have been strengthened by adding spreadsheet examples, applications, and problems. Chapter 3 gives tutorials on the construction and use of spreadsheets. Many other tutorials are included in our supplement, *Applications of Microsoft® Excel in Analytical Chemistry*, 2nd ed., and a number of these have been corrected, updated, and augmented.
- The definitions of molar concentration have been updated in Chapter 4 to conform to current IUPAC usage, and the associated terminology including *molar concentration* and *molar analytical concentration* have been infused throughout the text.
- The chapters on statistics (5–7) have been updated and brought into conformity with the terminology of modern statistics. Analysis of variance (ANOVA) has been included in Chapter 7. ANOVA is very easy to perform with modern spreadsheet programs and quite useful in analytical problem solving. These chapters are closely linked to our Excel supplement through Examples, Features, and Summaries.
- In Chapter 8, explanations of external standard, internal standard, and standard additions methods have been clarified, expanded, and described more thoroughly. Special attention is paid to the use of least-squares methods in standardization and calibration.
- A new introduction and explanation of mass balance has been written for Chapter 11.
- An explanation and a marginal note have been added on the gravimetric factor.
- A new feature on the master equation approach was added to Chapter 14.
- Chapter 17 has been rewritten to include both complexation and precipitation titrations.
- Chapters 18, 19, 20, and 21 on electrochemical cells and cell potentials have been revised to clarify and unify the discussion. Chapter 23 has been altered to decrease the emphasis on classical polarography. The chapter now includes a discussion of cyclic voltammetry.
- In Chapter 25, the discussion on thermal IR detectors now puts more emphasis on the DTGS pyroelectric detector.
- Chapter 29 introduces both atomic and molecular mass spectrometry and covers the similarities and differences in these methods. The introduction of mass spectrometry allows the separation chapters (31–34) to place additional emphasis on combined techniques, such as chromatographic methods with mass spectrometric detection.
- The challenge problems have been updated, augmented, and replaced where appropriate.
- References to the analytical chemistry literature have been updated and corrected as necessary.
- *Digital Object Identifiers* (*DOIs*) have been added to most references to the primary literature. These universal identifiers greatly simplify the task of locating articles by a link on the website **www.doi.org.** A DOI may be typed into a form on the home page, and when the identifier is submitted, the browser transfers directly to the article on the publisher's website. For example, 10.1351/goldbook.C01222

can be typed into the form, and the browser is directed to the IUPAC article on concentration. Alternatively, DOIs may be entered directly into the URL blank of any browser as http://dx.doi.org/10.1351/goldbook.C01222. Please note that students or instructors must have authorized access to the publication of interest.

Style and Format. We have continued to make style and format changes to make the text more readable and student friendly.

- We have attempted to use shorter sentences, a more active voice, and a more conversational writing style in each chapter.
- More descriptive figure captions are used whenever appropriate to allow a student to understand the figure and its meaning without alternating between text and caption.
- Molecular models are used liberally in most chapters to stimulate interest in the beauty of molecular structures and to reinforce structural concepts and descriptive chemistry presented in general chemistry and upper-level courses.
- Several new figures have replaced obsolete figures of past editions.
- Photographs, taken specifically for this text, are used whenever appropriate to illustrate important techniques, apparatus, and operations.
- Marginal notes are used throughout to emphasize recently discussed concepts or to reinforce key information.
- Key terms are now defined in the margins throughout the book.
- All examples now delineate the question and its answer or solution.

SUPPORTING MATERIALS

Please visit **www.cengage.com/chemistry/skoog/fac9** for information about student and instructor resources for this text.

ACKNOWLEDGMENTS

We wish to acknowledge with thanks the comments and suggestions of many reviewers who critiqued the eighth edition prior to our writing or who evaluated the current manuscript in various stages.

REVIEWERS

Lane Baker,
Indiana University
Heather Bullen,
Northern Kentucky University
Peter de Boves Harrington,
Ohio University
Jani Ingram,
Northern Arizona University
R. Scott Martin,
St. Louis University
Gary Rice,
College of William and Mary
Kathryn Severin,
Michigan State University
Dana Spence,
Michigan State University
Scott Waite,
University of Nevada, Reno

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We are grateful to the many members of the staff of Cengage, who provided solid support during the production of this text. Acquiring Sponsoring Editor Chris Simpson has provided excellent leadership and encouragement throughout the course of this project. This is our fourth book with Senior Developmental Editor Sandi Kiselica. As always, she has done a marvelous job of overseeing and organizing the project, maintaining continuity, and making many important comments and suggestions. Simply put, she's the best in the business, and we sincerely appreciate her work. We are grateful to our copy editor, James Corrick, for his consistency and attention to detail. His keen eye and excellent editorial skills have contributed significantly to the quality of the text. Alicia Landsberg has done a fine job coordinating the various ancillary materials, and Jeremy Glover, our photo researcher, has handled the many tasks associated with acquiring new photos and securing permissions for graphics. Project Manager Erin Donahue of PreMediaGlobal kept the project moving with daily reminders and frequent schedule updates while coordinating the entire production process. Her counterpart at Cengage was Content Project Manager Jennifer Risden, who coordinated the editorial process. Finally, we thank Rebecca Berardy Schwartz, our Cengage media editor for this edition.

This is the first edition of *Fundamentals of Analytical Chemistry* written without the skill, guidance, and counsel of our senior coauthors Douglas A. Skoog and Donald M. West. Doug died in 2008, and Don followed in 2011. Doug was Don's preceptor while he was a graduate student at Stanford University, and they began writing analytical chemistry textbooks together in the 1950s. They produced twenty editions of three best-selling textbooks over a period of forty-five years. Doug's vast knowledge of analytical chemistry and consummate writing skill coupled with Don's organizational expertise and attention to detail formed an outstanding complement. We aspire to maintain the high standard of excellence of Skoog and West as we continue to build on their legacy. In honor of their manifest contributions to the philosophy, organization, and writing of this book and many others, we have chosen to list their names above the title. Since the publication of the eighth edition, the team lost another partner in Judith B. Skoog, Doug's wife who died in 2010. Judy was a world-class editorial assistant who typed and proofread twenty editions of three books (and most of the instructor's manuals), amounting to well over 100,000 pages. We miss her accuracy, speed, tenacity, good humor, and friendship in producing beautiful manuscripts.

Finally, we are deeply grateful to our wives Vicki Holler and Nicky Crouch for their counsel, patience, and support during the several years of writing this text and preparing it for production.

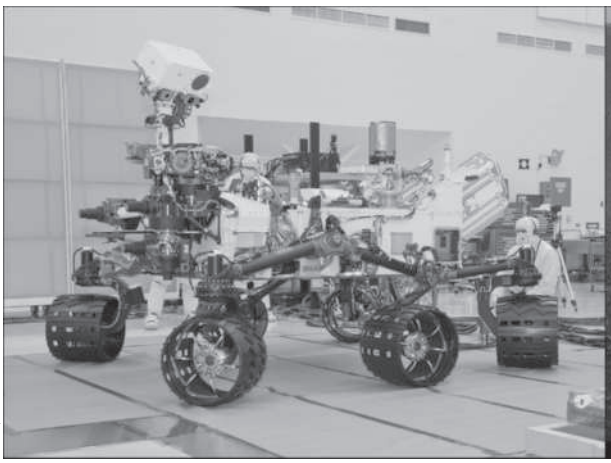
F. James Holler
Stanley R. Crouch

The Nature of Analytical Chemistry

CHAPTER 1

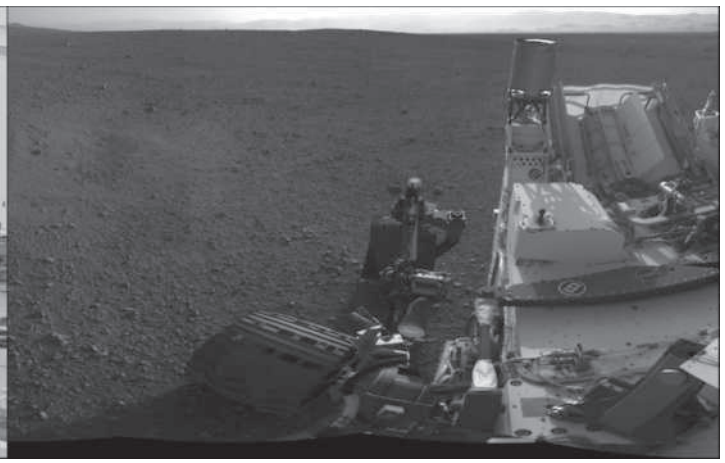
Analytical chemistry is a measurement science consisting of a set of powerful ideas and methods that are useful in all fields of science, engineering, and medicine. Some exciting illustrations of the power and significance of analytical chemistry have occurred, are occurring, and will occur during NASA's rover explorations of the planet Mars. On July 4, 1997, the Pathfinder spacecraft delivered the Sojourner rover to the Martian surface. Analytical instruments returned information on the chemical composition of rocks and soil. Investigations by the lander and rover suggested that Mars was at one time in its past warm and wet with liquid water on the surface and water vapor in the atmosphere. In January 2004, the Mars rovers Spirit and Opportunity arrived on Mars for a three-month mission. A major result from Spirit's alpha particle X-ray spectrometer (APXS) and Mossbauer spectrometer was finding concentrated deposits of silica and, at a different site, high concentrations of carbonate. Spirit continued to explore and transmit data until 2010, outliving even the most optimistic predictions. Even more amazing, Opportunity continues to travel the surface of Mars and, by March, 2012, had covered more than 21 miles exploring and transmitting images of craters, small hills, and other features.

In late 2011, the Mars Science Laboratory aboard the rover Curiosity was launched. It arrived on August 6, 2012 with a host of analytical instruments on board. The Chemistry and Camera package includes a laser-induced breakdown spectrometer (LIBS, see Chapter 28) and a remote microimager. The LIBS instrument will provide determination



NASA/JPL-Caltech

Mars Science Laboratory aboard rover Curiosity



NASA/JPL-Caltech

Curiosity observing Martian landscape from Gale crater, August 2012

of many elements with no sample preparation. It can determine the identity and amounts of major, minor, and trace elements and can detect hydrated minerals. The sample analysis package contains a quadrupole mass spectrometer (Chapter 29), a gas chromatograph (Chapter 32), and a tunable laser spectrometer (Chapter 25). Its goals are to survey carbon compound sources, search for organic compounds important to life, reveal the chemical and isotopic states of several elements, determine the composition of the Martian atmosphere, and search for noble gas and light element isotopes.[1]

Qualitative analysis reveals the *identity* of the elements and compounds in a sample.

Quantitative analysis indicates the *amount* of each substance in a sample.

Analytes are the components of a sample that are determined.

These examples demonstrate that both qualitative and quantitative information are required in an analysis. **Qualitative analysis** establishes the chemical identity of the species in the sample. **Quantitative analysis** determines the relative amounts of these species, or **analytes**, in numerical terms. The data from the various spectrometers on the rovers contain both types of information. As is common with many analytical instruments, the gas chromatograph and mass spectrometer incorporate a separation step as a necessary part of the analytical process. With a few analytical tools, exemplified here by the APXS and LIBS experiments, chemical separation of the various elements contained in the rocks is unnecessary since the methods provide highly selective information. In this text, we will explore quantitative methods of analysis, separation methods, and the principles behind their operation. A qualitative analysis is often an integral part of the separation step, and determining the identity of the analytes is an essential adjunct to quantitative analysis.

1A THE ROLE OF ANALYTICAL CHEMISTRY

Analytical chemistry is applied throughout industry, medicine, and all the sciences. To illustrate, consider a few examples. The concentrations of oxygen and of carbon dioxide are determined in millions of blood samples every day and used to diagnose and treat illnesses. Quantities of hydrocarbons, nitrogen oxides, and carbon monoxide present in automobile exhaust gases are measured to determine the effectiveness of emission-control devices. Quantitative measurements of ionized calcium in blood serum help diagnose parathyroid disease in humans. Quantitative determination of nitrogen in foods establishes their protein content and thus their nutritional value. Analysis of steel during its production permits adjustment in the concentrations of such elements as carbon, nickel, and chromium to achieve a desired strength, hardness, corrosion resistance, and ductility. The mercaptan content of household gas supplies is monitored continually to ensure that the gas has a sufficiently obnoxious odor to warn of dangerous leaks. Farmers tailor fertilization and irrigation schedules to meet changing plant needs during the growing season, gauging these needs from quantitative analyses of plants and soil.

Quantitative analytical measurements also play a vital role in many research areas in chemistry, biochemistry, biology, geology, physics, and the other sciences. For example, quantitative measurements of potassium, calcium, and sodium ions in the body fluids of animals permit physiologists to study the role these ions play in nerve-signal conduction as well as muscle contraction and relaxation. Chemists unravel the mechanisms of chemical reactions through reaction rate studies. The rate of consumption of reactants or formation of products

[1]For details on the Mars Science Laboratory mission and the rover Curiosity, see http://www.nasa.gov.

in a chemical reaction can be calculated from quantitative measurements made at precise time intervals. Materials scientists rely heavily on quantitative analyses of crystalline germanium and silicon in their studies of semiconductor devices whose impurities lie in the concentration range of 1×10^{-6} to 1×10^{-9} percent. Archaeologists identify the sources of volcanic glasses (obsidian) by measuring concentrations of minor elements in samples taken from various locations. This knowledge in turn makes it possible to trace prehistoric trade routes for tools and weapons fashioned from obsidian.

Many chemists, biochemists, and medicinal chemists devote much time in the laboratory gathering quantitative information about systems that are important and interesting to them. The central role of analytical chemistry in this enterprise and many others is illustrated in **Figure 1-1**. All branches of chemistry draw on the ideas and techniques of analytical chemistry. Analytical chemistry has a similar function with respect to the many other scientific fields listed in the diagram. Chemistry is often called *the central science*; its top center position and the central position of analytical chemistry in the figure

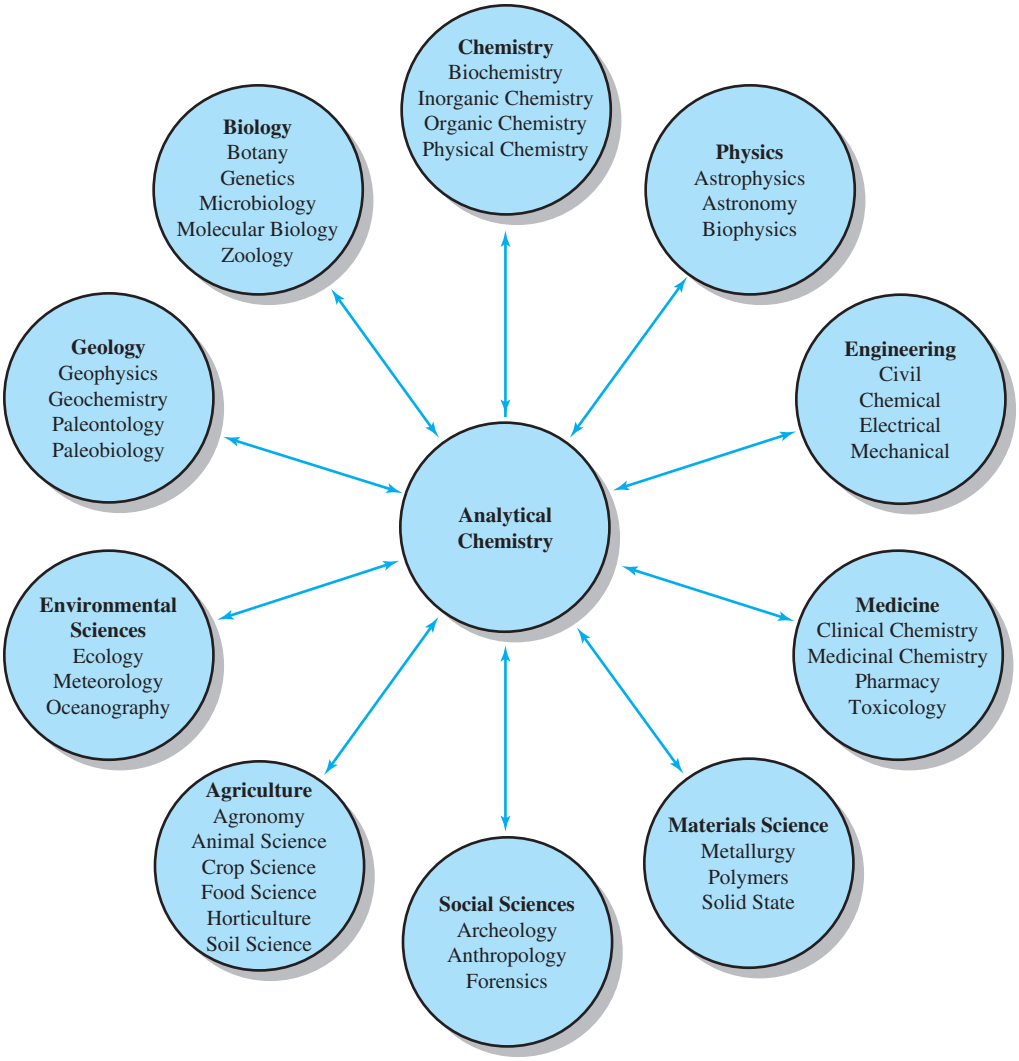


Figure 1-1 The relationship between analytical chemistry, other branches of chemistry, and the other sciences. The central location of analytical chemistry in the diagram signifies its importance and the breadth of its interactions with many other disciplines.

emphasize this importance. The interdisciplinary nature of chemical analysis makes it a vital tool in medical, industrial, government, and academic laboratories throughout the world.

1B QUANTITATIVE ANALYTICAL METHODS

We compute the results of a typical quantitative analysis from two measurements. One is the mass or the volume of sample being analyzed. The second measurement is of some quantity that is proportional to the amount of analyte in the sample such as mass, volume, intensity of light, or electrical charge. This second measurement usually completes the analysis, and we usually classify analytical methods according to the nature of this final measurement. In **gravimetric methods**, we determine the mass of the analyte or some compound chemically related to it. In a **volumetric method**, we measure the volume of a solution containing sufficient reagent to react completely with the analyte. In **electroanalytical methods**, we measure electrical properties such as potential, current, resistance, and quantity of electrical charge. In **spectroscopic methods**, we explore the interaction between electromagnetic radiation and analyte atoms or molecules or the emission of radiation by analytes. Finally, in a group of miscellaneous methods, we measure such quantities as mass-to-charge ratio of ions by mass spectrometry, rate of radioactive decay, heat of reaction, rate of reaction, sample thermal conductivity, optical activity, and refractive index.

1C A TYPICAL QUANTITATIVE ANALYSIS

A typical quantitative analysis includes the sequence of steps shown in the flow diagram of **Figure 1-2**. In some instances, one or more of these steps can be omitted. For example, if the sample is already a liquid, we can avoid the dissolution step. Chapters 1 through 34 focus on the last three steps in Figure 1-2. In the measurement step, we measure one of the physical properties mentioned in Section 1B. In the calculation step, we find the relative amount of the analyte present in the samples. In the final step, we evaluate the quality of the results and estimate their reliability.

In the paragraphs that follow, you will find a brief overview of each of the nine steps shown in Figure 1-2. We then present a case study to illustrate the use of these steps in solving an important and practical analytical problem. The details of this study foreshadow many of the methods and ideas you will explore as you study analytical chemistry.

1C-1 Choosing a Method

The essential first step in any quantitative analysis is the selection of a method as depicted in Figure 1-2. The choice is sometimes difficult and requires experience as well as intuition. One of the first questions that must be considered in the selection process is the level of accuracy required. Unfortunately, high reliability nearly always requires a large investment of time. The selected method usually represents a compromise between the accuracy required and the time and money available for the analysis.

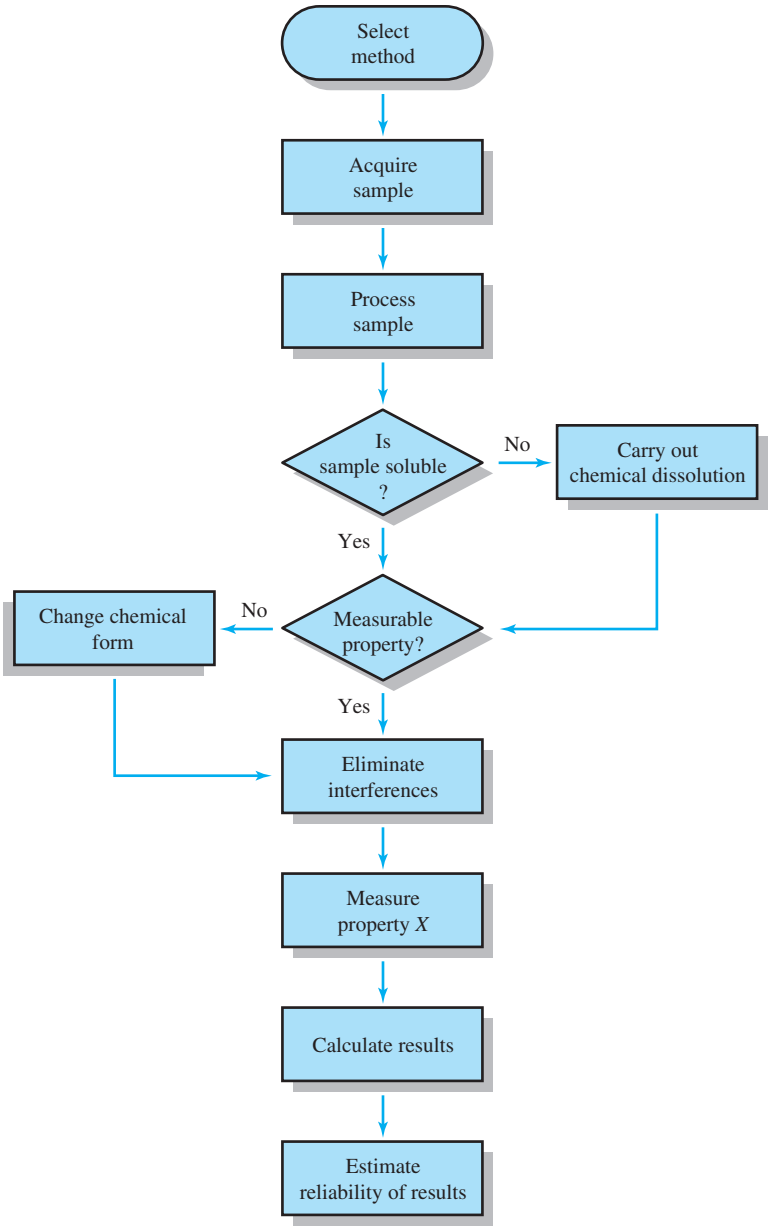


Figure 1-2 Flow diagram showing the steps in a quantitative analysis. There are a number of possible paths through these steps. In the simplest example represented by the central vertical pathway, we select a method, acquire and process the sample, dissolve the sample in a suitable solvent, measure a property of the analyte, calculate the results, and estimate the reliability of the results. Depending on the complexity of the sample and the chosen method, various other pathways may be necessary.

A second consideration related to economic factors is the number of samples that will be analyzed. If there are many samples, we can afford to spend a significant amount of time in preliminary operations such as assembling and calibrating instruments and equipment and preparing standard solutions. If we have only a single sample or a just a few samples, it may be more appropriate to select a procedure that avoids or minimizes such preliminary steps.

Finally, the complexity of the sample and the number of components in the sample always influence the choice of method to some degree.

1C-2 Acquiring the Sample

As illustrated in Figure 1-2, the second step in a quantitative analysis is to acquire the sample. To produce meaningful information, an analysis must be performed on a sample that has the same composition as the bulk of material from which it was

A material is **heterogeneous** if its constituent parts can be distinguished visually or with the aid of a microscope. Coal, animal tissue, and soil are heterogeneous.

An **assay** is the process of determining how much of a given sample is the material by its indicated name. For example, a zinc alloy is assayed for its zinc content, and its assay is a particular numerical value.

We *analyze* samples, and we *determine* substances. For example, a blood sample is analyzed to determine the concentrations of various substances such as blood gases and glucose. We, therefore, speak of the determination of blood gases or glucose, *not* the analysis of blood gases or glucose.

taken. When the bulk is large and **heterogeneous**, great effort is required to get a representative sample. Consider, for example, a railroad car containing 25 tons of silver ore. The buyer and seller of the ore must agree on a price, which will be based primarily on the silver content of the shipment. The ore itself is inherently heterogeneous, consisting of many lumps that vary in size as well as in silver content. The **assay** of this shipment will be performed on a sample that weighs about one gram. For the analysis to have significance, the composition of this small sample must be representative of the 25 tons (or approximately 22,700,000 g) of ore in the shipment. Isolation of one gram of material that accurately represents the average composition of the nearly 23,000,000 g of bulk sample is a difficult undertaking that requires a careful, systematic manipulation of the entire shipment. **Sampling** is the process of collecting a small mass of a material whose composition accurately represents the bulk of the material being sampled. Sampling is discussed in more detail in Chapter 8.

The collection of specimens from biological sources represents a second type of sampling problem. Sampling of human blood for the determination of blood gases illustrates the difficulty of acquiring a representative sample from a complex biological system. The concentration of oxygen and carbon dioxide in blood depends on a variety of physiological and environmental variables. For example, applying a tourniquet incorrectly or hand flexing by the patient may cause the blood oxygen concentration to fluctuate. Because physicians make life-and-death decisions based on results of blood gas analyses, strict procedures have been developed for sampling and transporting specimens to the clinical laboratory. These procedures ensure that the sample is representative of the patient at the time it is collected and that its integrity is preserved until the sample can be analyzed.

Many sampling problems are easier to solve than the two just described. Whether sampling is simple or complex, however, the analyst must be sure that the laboratory sample is representative of the whole before proceeding. Sampling is frequently the most difficult step in an analysis and the source of greatest error. The final analytical result will never be any more reliable than the reliability of the sampling step.

1C-3 Processing the Sample

As shown in Figure 1-2, the third step in an analysis is to process the sample. Under certain circumstances, no sample processing is required prior to the measurement step. For example, once a water sample is withdrawn from a stream, a lake, or an ocean, the pH of the sample can be measured directly. Under most circumstances, we must process the sample in one of several different ways. The first step in processing the sample is often the preparation of a laboratory sample.

Preparing a Laboratory Sample

A solid laboratory sample is ground to decrease particle size, mixed to ensure homogeneity, and stored for various lengths of time before analysis begins. Absorption or desorption of water may occur during each step, depending on the humidity of the environment. Because any loss or gain of water changes the chemical composition of solids, it is a good idea to dry samples just before starting an analysis. Alternatively, the moisture content of the sample can be determined at the time of the analysis in a separate analytical procedure.

Liquid samples present a slightly different but related set of problems during the preparation step. If such samples are allowed to stand in open containers, the solvent may evaporate and change the concentration of the analyte. If the analyte is a gas dissolved in a liquid, as in our blood gas example, the sample container must be kept inside a second sealed container, perhaps during the entire analytical procedure, to prevent contamination by atmospheric gases. Extraordinary measures, including sample manipulation and measurement in an inert atmosphere, may be required to preserve the integrity of the sample.

Defining Replicate Samples

Most chemical analyses are performed on **replicate samples** whose masses or volumes have been determined by careful measurements with an analytical balance or with a precise volumetric device. Replication improves the quality of the results and provides a measure of their reliability. Quantitative measurements on replicates are usually averaged, and various statistical tests are performed on the results to establish their reliability.

Replicate samples, or **replicates**, are portions of a material of approximately the same size that are carried through an analytical procedure at the same time and in the same way.

Preparing Solutions: Physical and Chemical Changes

Most analyses are performed on solutions of the sample made with a suitable solvent. Ideally, the solvent should dissolve the entire sample, including the analyte, rapidly and completely. The conditions of dissolution should be sufficiently mild that loss of the analyte cannot occur. In our flow diagram of Figure 1-2, we ask whether the sample is soluble in the solvent of choice. Unfortunately, many materials that must be analyzed are insoluble in common solvents. Examples include silicate minerals, high-molecular-mass polymers, and specimens of animal tissue. With such substances, we must follow the flow diagram to the box on the right and perform some rather harsh chemistry. Converting the analyte in such materials into a soluble form is often the most difficult and time-consuming task in the analytical process. The sample may require heating with aqueous solutions of strong acids, strong bases, oxidizing agents, reducing agents, or some combination of such reagents. It may be necessary to ignite the sample in air or oxygen or to perform a high-temperature fusion of the sample in the presence of various fluxes. Once the analyte is made soluble, we then ask whether the sample has a property that is proportional to analyte concentration and that we can measure. If it does not, other chemical steps may be necessary, as shown in Figure 1-2, to convert the analyte to a

form that is suitable for the measurement step. For example, in the determination of manganese in steel, the element must be oxidized to MnO_4^- before the absorbance of the colored solution is measured (see Chapter 26). At this point in the analysis, it may be possible to proceed directly to the measurement step, but more often than not, we must eliminate interferences in the sample before making measurements, as illustrated in the flow diagram.

1C-4 Eliminating Interferences

An **interference** or **interferent** is a species that causes an error in an analysis by enhancing or attenuating (making smaller) the quantity being measured.

Once we have the sample in solution and converted the analyte to an appropriate form for measurement, the next step is to eliminate substances from the sample that may interfere with measurement (see Figure 1-2). Few chemical or physical properties of importance in chemical analysis are unique to a single chemical species. Instead, the reactions used and the properties measured are characteristic of a group of elements of compounds. Species other than the analyte that affect the final measurement are called **interferences**, or **interferents**. A scheme must be devised to isolate the analytes from interferences before the final measurement is made. No hard and fast rules can be given for eliminating interference. This problem can certainly be the most demanding aspect of an analysis. Chapters 31 through 34 describe separation methods in detail.

1C-5 Calibrating and Measuring Concentration

The **matrix**, or **sample matrix**, is the collection of all of the components in the sample containing an analyte.

Techniques or reactions that work for only one analyte are said to be **specific**. Techniques or reactions that apply to only a few analytes are **selective**.

All analytical results depend on a final measurement X of a physical or chemical property of the analyte, as shown in Figure 1-2. This property must vary in a known and reproducible way with the concentration c_A of the analyte. Ideally, the measurement of the property is directly proportional to the concentration, that is,

$$c_A = kX$$

where k is a proportionality constant. With a few exceptions, analytical methods require the empirical determination of k with chemical standards for which c_A is known.[2] The process of determining k is thus an important step in most analyses; this step is called a **calibration**. Calibration methods are discussed in some detail in Chapter 8.

Calibration is the process of determining the proportionality between analyte concentration and a measured quantity.

1C-6 Calculating Results

Computing analyte concentrations from experimental data is usually relatively easy, particularly with computers. This step is depicted in the next-to-last block of the flow diagram of Figure 1-2. These computations are based on the raw experimental data collected in the measurement step, the characteristics of the measurement instruments, and the stoichiometry of the analytical reaction. Samples of these calculations appear throughout this book.

1C-7 Evaluating Results by Estimating Reliability

As the final step in Figure 1-2 shows, analytical results are complete only when their reliability has been estimated. The experimenter must provide some measure of the uncertainties associated with computed results if the data are to have any value.

[2]Two exceptions are gravimetric methods, discussed in Chapter 12, and coulometric methods, considered in Chapter 22. In both these methods, k can be computed from known physical constants.

Chapters 5, 6, and 7 present detailed methods for carrying out this important final step in the analytical process.

❮ An analytical result without an estimate of reliability is of no value.

1D AN INTEGRAL ROLE FOR CHEMICAL ANALYSIS: FEEDBACK CONTROL SYSTEMS

Analytical chemistry is usually not an end in itself but is part of a bigger picture in which the analytical results may be used to help control a patient's health, to control the amount of mercury in fish, to control the quality of a product, to determine the status of a synthesis, or to find out whether there is life on Mars. Chemical analysis is the measurement element in all of these examples and in many other cases. Consider the role of quantitative analysis in the determination and control of the concentration of glucose in blood. The system flow diagram of **Figure 1-3** illustrates the process. Patients suffering from insulin-dependent diabetes mellitus develop hyperglycemia, which manifests itself in a blood glucose concentration above the normal concentration range of 65 to 100 mg/dL. We begin our example by determining that the desired state is a blood glucose level below 100 mg/dL. Many patients must monitor their blood glucose levels by periodically submitting samples to a clinical laboratory for analysis or by measuring the levels themselves using a handheld electronic glucose monitor.

The first step in the monitoring process is to determine the actual state by collecting a blood sample from the patient and measuring the blood glucose level. The results are displayed, and then the actual state is compared to the desired state, as shown in Figure 1-3. If the measured blood glucose level is above 100 mg/dL, the patient's insulin level, which is a controllable quantity, is increased by injection or oral administration. After a delay to allow the insulin time to take effect, the glucose level is measured again to determine if the desired state has been achieved. If the level is below the threshold, the insulin level has been maintained, so no insulin is required. After a suitable delay time, the blood glucose level is measured again, and the cycle is repeated. In this way, the insulin level in the patient's blood, and thus the

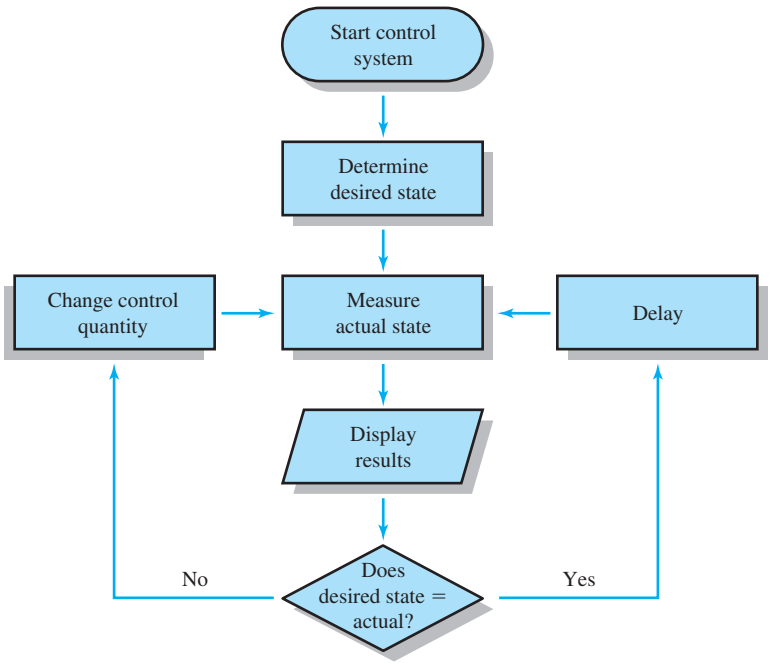


Figure 1-3 Feedback system flow diagram. The desired system state is defined, the actual state of the system is measured, and the two states are compared. The difference between the two states is used to change a controllable quantity that results in a change in the state of the system. Quantitative measurements are again performed on the system, and the comparison is repeated. The new difference between the desired state and the actual state is again used to change the state of the system if necessary. The process provides continuous monitoring and feedback to maintain the controllable quantity, and thus the actual state, at the proper level. The text describes the monitoring and control of blood glucose as an example of a feedback control system.