

**INSTRUMENTAL  
METHODS  
OF ANALYSIS**

**Fifth Edition**

**HOBART H. WILLARD**

**LYNNE L. MERRITT, JR**

**JOHN A. DEAN**

# INSTRUMENTAL METHODS OF ANALYSIS

**Fifth Edition**

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# Atomic Weights

(Based on Carbon-12)

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Actinium	Ac	89	(227)
Aluminum	Al	13	26.98154
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	(210)
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01218
Bismuth	Bi	83	208.9804
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.011
Cerium	Ce	58	140.12
Cesium	Cs	55	132.9054
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(254)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257)
Fluorine	F	9	18.99840
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.9665
Hafnium	Hf	72	178.49
Helium	He	2	4.00260
Holmium	Ho	67	164.9304
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.9045
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	(255)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.9380
Mendelevium	Md	101	(258)

## Atomic Weights (*Continued*)

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.179
Neptunium	Np	93	237.0482
Nickel	Ni	28	58.71
Niobium	Nb	41	92.9064
Nitrogen	N	7	14.0067
Nobelium	No	102	(255)
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97376
Platinum	Pt	78	195.09
Plutonium	Pu	94	(242)
Polonium	Po	84	(210)
Potassium	K	19	39.098
Praseodymium	Pr	59	140.9077
Promethium	Pm	61	(147)
Protactinium	Pa	91	231.0359
Radium	Ra	88	226.0254
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9055
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.4
Scandium	Sc	21	44.9559
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.868
Sodium	Na	11	22.98977
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.9479
Technetium	Tc	43	98.9062
Tellurium	Te	52	127.60
Terbium	Tb	65	158.9254
Thallium	Tl	81	204.37
Thorium	Th	90	232.0381
Thulium	Tm	69	168.9342
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.029
Vanadium	V	23	50.9414
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.9059
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

Numbers in parentheses are mass numbers of most stable or most common isotope.

# Preface

The Fifth Edition continues to survey modern instrumental methods of chemical analysis. Most of the chapters have been extensively revised and some have been completely rewritten.

Changes in order of presentation now place molecular fluorescence and phosphorescence methods after ultraviolet and visible absorption methods, Raman spectroscopy after infrared spectroscopy, and flame emission and atomic absorption spectrometry before emission spectroscopy. This arrangement is more logical than the order of presentation in the earlier editions.

Among the new topics treated in this edition are: turbidimetry and nephelometry, the vacuum ultraviolet, reflectance measurements, Fourier transform infrared, laser-Raman spectroscopy, Mössbauer spectroscopy, interfacing gas chromatography with mass spectrometry, and all classes of selective ion electrodes. Atomic absorption has been expanded and integrated with flame emission methods. Classical polarography has been absorbed within an enlarged chapter on voltammetry, polarography, and related techniques. Emphasis continues to be placed on structural identification of compounds through infrared and Raman spectra, nuclear magnetic resonance and electron spin resonance spectroscopy, ultraviolet absorption spectra, and mass spectrometry.

Individual chapters are designed, in general, to stand alone. Consequently, the order of presentation is not critical. Instructors will be able to select material for several levels of achievement. References to the literature and collateral readings are included in each chapter. The book should also be suitable as a reference manual.

Numerous examples are incorporated within the text, including those illustrating mathematical operations. These introduce the student to the unit of measurement and reduce, and possibly eliminate, the dependence upon additional problem books. There are 390 numerical problems; answers to virtually all are given separately at the end of the text. Many of these problems contain data that would be obtained in the laboratory experiments and are thus of particular value for schools unable to furnish equipment for specific areas of instrumentation, for supplementing experiments when laboratory periods are limited in number, or for self-study.

Experiments have been selected to illustrate the principles discussed in the theoretical portions of each chapter. Some experiments are described in considerable detail and thus are suitable for use by less experienced undergraduate students. Others are merely sketched outlines or suggestions for work to give instructors in advanced courses flexi-

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## (vi) Preface

bility in eliciting from students a degree of independence and originality in the outline and execution of experimental work.

Because some confusion may arise over the meanings of abbreviations and the uses of symbols, particularly the overlapping uses of certain symbols in the diverse techniques covered in this book, separate listings of abbreviations and symbols are included in pages xii to xix. Whenever available, recommendations of concerned nomenclature commissions have been followed. In addition, the Appendices provide a fairly comprehensive tabulation of standard-reduction potentials in aqueous solution, polarographic half-wave potentials and diffusion-current constants, acid dissociation constants, formation constants of some metal complexes, flame emission and atomic absorption spectra, and a conversion table involving values of absorbance for percent absorption. A four-place table of common logarithms, a table of 1971 atomic weights, and a periodic chart of the elements facilitate computations and provide ready reference data.

The authors remain greatly indebted to the manufacturers who have so generously furnished schematic diagrams, photographs, and technical information of their instruments. Thanks are expressed also to many colleagues who have kindly helped with suggestions and improvements.

HOBART H. WILLARD  
LYNNE L. MERRITT, JR.  
JOHN A. DEAN

# Abbreviations

absorption	Abs
alpha particle	$\alpha$
alternating current (adj.)	ac
ampere	A
angstrom	Å
atmosphere	atm
atomic weight	at. wt
attenuated total reflectance	ATR
barn	b
beta particle	$\beta$
boiling point	bp
calorie	cal
capacitance	C
conductance	1/R
coulomb	C, Q
counts per minute (second)	c/m 1, cpm (c/s)
cubic centimeter	cm <sup>3</sup>
curie	Ci
cycles per second (hertz)	Hz
day	d
decibel	db
degree Celsius	°C
degree Kelvin	°K
deuteron	d
diameter	diam
differential scanning calorimeter	DSC
differential thermal analysis	DTA
direct current (adj.)	dc
disintegrations per minute (second)	dpm, d/m; dps, d/s
dropping mercury electrode	dme
dyne	dyn
electromotive force	emf
electron	e <sup>-</sup> , e
electron paramagnetic resonance	epr



electron spin resonance	esr
electron volt	eV
equivalent weight	equiv wt
ethyl	Et
ethylenediamine	en
ethylenediamine- <i>N, N, N', N'</i> -tetraacetic acid (the anion)	EDTA Y <sup>4-</sup>
<i>exempli gratia</i> (for example)	e.g.
exponential	exp
farad	F, f
formal (concentration)	<i>F</i>
frequency	f
gamma radiation	$\gamma$
gas (physical state)	<i>g</i>
gauss	G
gram	g
hertz	Hz
hour	hr, h
<i>ibidem</i> (in the same place)	Ibid.
<i>id est</i> (that is)	i.e.
inch.	in.
indicator	ind
inductance	<i>L</i>
infrared	ir
inside diameter	i.d.
joule	J
kilo- (prefix)	k-
kilocalorie	kcal
liquid (physical state)	liq, <i>l</i>
liter	liter (alone), l (with prefixes)
logarithm (common)	log
logarithm (natural)	ln
maximum	max
meg- (prefix)	M-
melting point	mp
meter	m
methyl	Me
micro- (prefix)	$\mu$ -
micrometer (micron)	$\mu$ m
milli- (prefix)	m-
milliequivalent	mequiv
milliliter	ml
millimole	mM
minimum	min

#### (xiv) Abbreviations

minute	min, m
molar	<i>M</i>
mole	mol
molecular weight	mol wt
nano- (prefix)	n-
nanometer (millimicron)	nm
Naperian base	<i>e</i>
negative	neg
neutron	<i>n</i>
normal (concentration)	<i>N</i>
normal hydrogen electrode	NHE, SHE
nuclear magnetic resonance	nmr
ohm	$\Omega$
optical speed	<i>f</i> /number
outside diameter	o.d.
oxidant	ox
page(s)	p. (pp.)
parts per billion, volume	ng/ml
parts per billion, weight	ng/g
parts per million, volume	$\mu\text{g/ml}$
parts per million, weight	$\mu\text{g/g}$
percent	%
phenyl	$\phi$ , Ph
pico- (prefix)	p-
positive	pos
potential	<i>E</i>
positron	$\beta^+$
proton	<i>p</i>
proton magnetic resonance	pmr
quantum (energy)	$h\nu$
radiofrequency	rf
reciprocal ohm	mho ( $\Omega^{-1}$ )
reductant	red
reference	ref
resistance	<i>R</i>
revolutions per minute	rpm
saturated calomel electrode	SCE
second	sec, s
solid (physical state)	<i>s</i>
specific gravity	sp gr
standard hydrogen electrode	SHE, NHE
standard temperature and pressure	STP
temperature	temp, <i>T</i>
thermal gravimetric analysis	TGA

torr (mm of mercury)

tritium

ultraviolet

vacuum

vacuum tube voltmeter

versus

volt

volume

volume per volume

volume per weight

watt

wavenumber

wavenumber difference (Raman)

year

torr

t,  $^3\text{H}$ 

uv

vac

VTVM

vs.

V

vol,  $V$ ,  $v$ 

v/v

v/w

W

 $\text{cm}^{-1}$  $\Delta\text{cm}^{-1}$ 

yr, y

# Symbols

$A$	absorbance; activity (radiochemistry); area; atomic weight
$A_{nm}$	transition probability of spontaneous emission ( $m \rightarrow n$ energy level)
$a$	specific absorptivity
$a_i$	hyperfine coupling constant (esr)
$a_x$	activity of species $x$
$B$	source brightness
$B_{mr}$	transition probability of absorption ( $n \rightarrow m$ energy level)
$B_{nm}$	transition probability of induced or stimulated emission ( $m \rightarrow n$ energy level)
$b$	distance, optical path length, thickness
$C$	concentration; capacitance
$C_M$	concentration of solute in mobile phase
$C_S$	concentration of solute in stationary phase
$c$	velocity of light
$D$	dielectric constant; diffusion coefficient
$D_{MO}$	dissociation energy (of metal oxide)
$d$	diameter, distance, or spacing
$d_f$	thickness of liquid film
$d_p$	particle diameter
$E$	electrode potential; potential of a half-reaction; energy
$E^\circ$	standard electrode potential
$E_{1/2}$	half-wave potential
$E_i$	ionization potential; energy of electronic state
$E_j$	junction potential; energy of electronic state
$e$	electronic charge; Napierian base (logarithms)
$F$	faraday; fluorescence
$F_c$	volume flow rate of gas
$F_T$	total flux transmitting power
$f$	focal length; fractional abundance
$f_{nm}$	oscillator strength ( $n \rightarrow m$ energy level)
$f_x$	activity coefficient of species $x$
$f/\text{number}$	effective aperture ratio
$G$	high-frequency conductance
$\Delta G^\circ$	Gibbs free energy

$g$	spectroscopic splitting factor; statistical weights of particular energy levels
$H$	magnetic field strength, plate height (chromatography)
$\Delta H$	enthalpy change; peak-to-peak separation (esr)
$h$	height; Planck constant
$I$	radiant intensity; spin quantum number
$I_d$	diffusion current constant
$I_\nu$	emission line intensity
$i$	angle of incidence; current
$i_d$	diffusion current
$i_{lim}$	limiting current
$i_r$	residual current
$J$	spin-spin coupling constant
$j$	compressibility factor (gas chromatography)
$K_a$	acid dissociation constant
$K_d$	partition coefficient
$K_f$	formation constant
$K_i$	ionization constant (gaseous state)
$K_{sp}$	solubility product
$K_w$	ion product of water
$k$	Boltzmann constant; partition ratio and capacity factor (chromatography); force constant (ir); general constant
$k_\nu$	absorption coefficient (optical)
$L$	length or distance; lightness (color), inductance
$M_s$	angular momentum quantum number
$m$	mass of mercury (dme); order number (optical); metastable
$m^+$	ionized mass fragment
$m/e$	mass-to-charge ratio
$N$	noise; plate number (chromatography); total number of something
$N_A$	Avogadro number
$N_j, N_m$	number of species in excited energy state
$N_n, N_0$	number of species in ground energy state
$n, n_D$	refractive index (at $D$ sodium line)
$n$	number of electrons transferred in an electrode reaction; unshared $p$ -electrons
$P$	pressure; radiant power
$P_M$	parent mass peak
$P_0$	incident radiant power
$p$	pressure; type of electron; depolarization ratio (Raman)
$p$	(prefix) negative logarithm of, pico-
$Q$	flow rate; heat capacity
$R$	gas constant; resolving power
$R.I.$	retention index (Kovats)
$r$	radius; counting rate; resolution (recorders); angle of diffraction
$r_D$	specific refraction

(xviii) Symbols

$S$	electron spin; saturation factor (radiochemistry)
$S_1$	first excited singlet state
$S_0$	ground electronic state
$\Delta S$	entropy
$S/N$	signal-to-noise ratio
$T$	temperature; transmittance
$T_1$	spin-lattice relaxation; first excited triplet state
$T_c$	column temperature
$t$	time; prism base length
$t_{1/2}$	half-life
$t_R$	retention time
$V$	volume; voltage
$V_g^\circ$	specific retention volume at 0°C
$V_M$	volume of mobile phase
$V_N$	net retention volume
$V_R$	retention volume
$V'_R$	adjusted retention volume
$v$	volume; velocity
$W$	weight; zone width at base line (chromatography)
$W_{1/2}$	zone width at $\frac{1}{2}$ peak height
$W_f$	flux
$W_L$	weight of liquid phase
$w$	effective aperture width
$X_C$	capacitive reactance
$X_L$	inductive reactance
$Z$	atomic number
$z$	valence
$z_+, z_-$	ionic charge
$\alpha$	degree of ionization; relative retention ratio
$[\alpha]$	specific rotation
$\beta$	blaze angle; buffer value; volumetric phase ratio
$\beta_N$	Bohr magneton
$\gamma$	activity coefficient; emulsion characteristic (photography); ratio of specific heats at constant pressure and constant volume; surface tension
$\Delta$	(prefix) symbol for finite change
$\delta$	chemical shift (nmr); thickness of diffusion layer
$\partial$	(prefix) partial derivative
$\epsilon$	molar absorptivity
$\epsilon_{\max}$	molar absorptivity at wavelength of an absorption maximum
$\eta$	viscosity
$\eta_D$	refractive index ( $D$ line of sodium)
$\theta$	cell constant (conductance)
$[\theta]$	molecular ellipticity
$\kappa$	specific conductance

$\Lambda$	equivalent conductance
$\Lambda_{\infty}$	equivalent conductance at infinite dilution
$\lambda$	decay constant (radioactivity); wavelength
$\lambda_+, \lambda_-$	ionic conductance
$\lambda_{\max}$	wavelength of an absorption maximum
$\mu$	ionic strength; linear absorption coefficient; magnetic moment
$\mu_m$	mass absorption coefficient
$\mu/\rho$	mass absorption coefficient
$\nu$	frequency; designation of vibrational levels
$\bar{\nu}$	wavenumber
$\Delta\nu_D$	Doppler broadening
$\Delta\nu_L$	Lorentz broadening
$\pi$	pi (3.1416 . . . ); type of electron or bond
$\rho$	density; resistivity
$\sigma$	capture cross section; shielding constant (nmr); standard deviation
$\sigma_{hkl}$	reciprocal lattice vectors
$\tau$	chemical shift (nmr); mean emission lifetime; resolving time; time constant
$v$	velocity
$\Phi$	neutron flux
$\phi$	quantum efficiency
$\chi$	Pauling electronegativity
$\omega$	chopping frequency; overpotential
$\omega_c$	angular velocity
[ ]	molar concentration of

# Periodic Chart

IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII		
1 <b>H</b> 1.0079									
3 <b>Li</b> 6.941	4 <b>Be</b> 9.01218								
11 <b>Na</b> 22.98977	12 <b>Mg</b> 24.305								
19 <b>K</b> 39.098	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.9559	22 <b>Ti</b> 47.90	23 <b>V</b> 50.9414	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.9380	26 <b>Fe</b> 55.847	27 <b>Co</b> 58.9332	28 <b>Ni</b> 58.71
37 <b>Rb</b> 85.4678	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.9059	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.9064	42 <b>Mo</b> 95.94	43 <b>Tc</b> 98.9062	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.9055	46 <b>Pd</b> 106.4
55 <b>Cs</b> 132.9054	56 <b>Ba</b> 137.34	57 <b>*La</b> 138.9055	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.9479	74 <b>W</b> 183.85	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.09
87 <b>Fr</b> (223)	88 <b>Ra</b> 226.0254	89 <b>†Ac</b> (227)	104 <b>§</b> (260)	105 <b>§</b> (260)					

## \*Lanthanum Series

( ) Numbers in parentheses are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1971 values of the Commission on Atomic Weights.

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58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.9077	60 <b>Nd</b> 144.2	61 <b>Pm</b> (147)	62 <b>Sm</b> 150.4	63 <b>Eu</b> 151.96
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## \*Actinium Series

90 <b>Th</b> 232.0381	91 <b>Pa</b> 231.0359	92 <b>U</b> 238.029	93 <b>Np</b> 237.0482	94 <b>Pu</b> (244)	95 <b>Am</b> (243)
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of the Elements

IB		II B	IIIA		IVA	VA	VIA	VIIA	INERT GASES	
								1	2	2
								H	He	
								1.0079	4.00260	
			5	6	7	8	9	10		2
			B	C	N	O	F	Ne		8
			10.81	12.011	14.0067	15.9994	18.99840	20.179		
			13	14	15	16	17	18		2
			Al	Si	P	S	Cl	Ar		8
			26.98154	28.086	30.97376	32.06	35.453	39.948		
29	30	31	32	33	34	35	36			2
Cu	Zn	Ga	Ge	As	Se	Br	Kr			8
63.546	65.38	69.72	72.59	74.9216	78.96	79.904	83.80			
47	48	49	50	51	52	53	54			2
Ag	Cd	In	Sn	Sb	Te	I	Xe			8
107.868	112.40	114.82	118.69	121.75	127.60	126.9045	131.30			
79	80	81	82	83	84	85	86			2
Au	Hg	Tl	Pb	Bi	Po	At	Rn			8
196.9665	200.59	204.37	207.2	208.9804	(210)	(210)	(222)			

64	65	66	67	68	69	70	71	
Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	2
157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.97	8

96	97	98	99	100	101	102	103	
Cm	Bk	Cf	Es	Fm	Md	No	Lr	2
(247)	(247)	(251)	(254)	(257)	(258)	(255)	(255)	8