PRINCIPLES OF INSTRUMENTAL ANALYSIS

SECOND EDITION

PRINCIPLES OF INSTRUMENTAL ANALYSIS

SECOND EDITION

Douglas A. Skoog *Stanford University*

Donald M. West *San Jose State University*

SAUNDERS GOLDEN SUNBURST SERIES

1980 SAUNDERS COLLEGE

PHILADELPHIA

Saunders College
West Washington Square
Philadelphia, PA 19105

Library of Congress Cataloging in Publication Data

Skoog, Douglas Arvid, 1918–
Principles of instrumental analysis.

Bibliography: p.
Includes index.
1. Instrumental analysis. I. West, Donald M.,
joint author. II. Title.
QD79.I5S58 1980 543'.08 79-26284
ISBN 0-03-021161-1

Printed in the United States of America

1 2 3 144 9 8 7 6 5 4 3

PREFACE

Physical and biological scientists currently have available to them an amazing array of powerful tools for obtaining qualitative and quantitative information about the properties and composition of matter. For this reason it is our belief that students of chemistry, biochemistry, the health-related sciences, and mineral sciences should, very early in their careers develop an appreciation for these tools and a knowledge of how they can be employed to solve analytical problems.

We believe that the efficient use of analytical instruments requires that the scientist have an understanding of the fundamental principles upon which modern measuring devices are based. Only then can he make intelligent choices among the many possible ways of solving an analytical problem; only then can he appreciate the pitfalls that accompany any physical measurement; and only then can he develop a feel for the probable limitations of his measurements in terms of sensitivity and accuracy. It is the goal of this second edition of *Principles of Instrumental Analysis*, as it was the goal of the first, to provide the student with an introduction to these principles as well as to generate an appreciation of the kinds of instruments that are currently available from commercial sources and their strengths and limitations.

During the nine years that have elapsed since the appearance of the first edition of this book, major changes in instrumental design have occurred. Among these has been the nearly total displacement of the vacuum tube by the transistor. Second has been the appearance of tiny, inexpensive, operational amplifiers based on transistors. Such amplifiers have permitted scientists having a minimal understanding of electronics to design and build a vast array of useful circuits for measurement and computation. A third major development has been the introduction of the microprocessor—a self-contained and inexpensive computer etched on a tiny silicon chip. Microprocessors are found in ever-increasing numbers in modern instruments, where they serve to control instrument variables, to monitor signals, and to process data. Because of these electronic developments, two entirely new chapters have been added in this edition to present elementary treatments of electrical circuits, transistors, operational amplifiers, microprocessors, and computers. In addition, throughout the text, sections have been added that describe the applications of these devices, particularly to automation of various kinds of instruments.

Other new chapters include one dealing with thermal methods, another with components of instruments for optical spectroscopy, still another with general theoretical aspects of atomic and molecular absorption spectroscopy, and finally a chapter treating the general theory of chromatographic separations. Parts of the material for the latter three chapters are found scattered throughout several chapters in the first edition; other parts are entirely new. In the latter category is a section that treats the effects of instrumental and environmental noise on the precision and accuracy of spectroscopic absorption measurements. Also largely new is the development of general chromatographic theory from kinetic considerations. The chapter on optical instruments brings together information that was formerly found in chapters on infrared, ultraviolet and visible, and atomic absorption spectroscopy; flame and emission spectroscopy; and fluorescence and Raman spectroscopy.

Since the publication of the first edition, a host of modifications of well-established instrumental methods have emerged and are now included. Among these new developments are Fourier transform nuclear magnetic resonance and infrared methods, infrared photometers for pollutant measurements, laser modifications of spectroscopic measurements, nuclear magnetic resonance measurements on nuclei other than hydrogen, electron spin resonance spectroscopy, photon counting, inductively coupled plasma sources for emission spectroscopy, semiconductor detectors for X-rays and gamma rays, energy dispersive X-ray systems, the electron microprobe, X-ray photoelectric spectrometry, chemical, field ionization, and spark sources for mass spectrometry, gas electrodes, potentiostatic controls for polarography, differential pulsed and rapid scan polarography, cyclic and ac voltammetry, high performance liquid chromatography, new packings for gas-liquid chromatography, interfacing of chromatography with mass, infrared, and fluorescence detectors, instruments for simultaneous, multielement analysis, and automated instruments for spectroscopy, electroanalysis, titrimetry, and chromatography.

In addition to the foregoing, the new edition contains, as an appendix, a brief treatment of the propagation of random errors in analytical measurements.

It is worth noting that selected portions of the material found in this text have also appeared in the authors' two other titles.[1] The principal overlap of the material in this book with that in the earlier two occurs in the chapters on potentiometry, coulometry, and voltammetry. Duplication will be found to a lesser extent in the chapters on ultraviolet and visible absorption spectroscopy and atomic emission spectroscopy.

The authors wish to acknowledge with thanks the considerable contributions of Professor Alfred R. Armstrong, College of William and Mary, and Dr. James LuValle, Stanford University, who have read the entire manuscript in detail and offered many useful suggestions. We are also grateful to Professor R. deLevie of Georgetown University for his comprehensive review and numerous suggestions for Chapters 2 and 3, to Professor H. S. Mosher of Stanford University for his helpful comments on the chapter on optical activity, and to Professors S. R. Crouch of Michigan State University and J. D. Ingle, Jr., of Oregon State University for their detailed criticisms on and suggestions for the section on precision of spectral measurements. Finally, we offer our thanks to several others who have taken the time to comment, often in some detail, on portions

[1] D. A. Skoog and D. M. West, *Fundamentals of Analytical Chemistry*, 3d ed., 1976, and *Analytical Chemistry*, 3d ed., 1979, Holt, Rinehart and Winston, New York.

or all of the manuscript. Included are Professors R. R. Bessette, Southeastern Massachusetts University; M. F. Bryant, University of Georgia; J. F. Coetzee, University of Pittsburgh; P. Dumas, Trenton State College; E. T. Gray, Jr., University of Hartford; D. M. King, Western Washington University; P. F. Lott, University of Missouri, Kansas City; C. H. Lochmuller, Duke University; F. W. Smith, Youngstown State University; M. Thompson, University of Toronto; A. Timnick, Michigan State University; W. H. Smith, Texas Tech University; J. E. Byrd, California State College—Stanislaus; A. M. Olivares, Texas A & I University; and E. J. Billo, Boston College.

We also wish to thank Dr. Natalie McClure, now of Syntex Corporation, for preparing problem sets and their solutions for Chapters 8, 14, and 17, and Professor Daniel C. Harris, of University of California—Davis, for preparing problem sets and solutions for Chapters 5, 9–13, 23, and 25.

Stanford, California
San Jose, California
September, 1979

DOUGLAS A. SKOOG
DONALD M. WEST

PRINCIPLES OF INSTRUMENTAL ANALYSIS

International Atomic Weights

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	(227)	Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	(243)	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	(237)
Arsenic	As	33	74.9216	Nickel	Ni	28	58.70
Astatine	At	85	(210)	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	(247)	Nobelium	No	102	(254)
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	106.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	(244)
Californium	Cf	98	(249)	Polonium	Po	84	(210)
Carbon	C	6	12.01115	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.907
Cesium	Cs	55	132.905	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.453	Protactinium	Pa	91	(231)
Chromium	Cr	24	51.996	Radium	Ra	88	(226)
Cobalt	Co	27	58.9332	Radon	Rn	86	(222)
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96	(245)	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100	(252)	Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	(223)	Silver	Ag	47	107.870
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	(99)
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lw	103	(257)	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.942	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Mv	101	(256)				

Numbers in parentheses indicate mass number of most stable known isotope.

Important Physical Constants

Constant	Symbol	Value
Velocity of light (*vacuo*)	c	2.9979×10^{10} cm sec^{-1}
Planck constant	h	6.6256×10^{-27} erg sec
Avogadro number	N	6.0226×10^{23} particles mol^{-1}
Faraday constant	F	96491 C mol^{-1}
Gas constant	R	8.3143×10^{7} erg deg^{-1} mol^{-1}
		1.9872 cal deg^{-1} mol^{-1}
		8.2054×10^{-2} liter atm deg^{-1} mol^{-1}
Boltzmann constant	k	1.3805×10^{-16} erg deg^{-1}
Rest mass of the electron	m_e	9.1090×10^{-28} g
Electronic charge	e	-4.8033×10^{-10} esu -1.6021×10^{-19} C

Energy Conversion Factors

	Ergs	Joules	Calories	Liter atmospheres	Electron volts
1 erg =	1	10^{-7}	2.3901×10^{-8}	9.8687×10^{-10}	6.2418×10^{11}
1 joule =	10^{7}	1	2.3901×10^{-1}	9.8687×10^{-3}	6.2418×10^{18}
1 calorie =	4.1840×10^{7}	4.1840	1	4.1291×10^{-2}	2.6116×10^{19}
1 liter atmosphere =	1.0133×10^{9}	1.0133×10^{2}	24.218	1	6.3248×10^{20}
1 electron volt =	1.6021×10^{-12}	1.6021×10^{-19}	3.8291×10^{-20}	1.5811×10^{-21}	1

Conversion Factors for Electromagnetic Radiation

(To convert data in units of *x* shown in the first column to the units indicated in the remaining columns, multiply or divide as shown.)

Units of x	Frequency, Hz	Wave-number, cm^{-1}	Energy: kcal/mol	Energy: erg	Energy: eV	Wave-length, cm
Hz	$1.00\,x$	$3.34 \times 10^{-11}\,x$	$9.54 \times 10^{-14}\,x$	$6.63 \times 10^{-27}\,x$	$4.14 \times 10^{-15}\,x$	$\frac{3.00 \times 10^{10}}{x}$
cm^{-1}	$3.00 \times 10^{10}\,x$	$1.00\,x$	$2.86 \times 10^{-3}\,x$	$1.99 \times 10^{-16}\,x$	$1.24 \times 10^{-4}\,x$	$\frac{1.00}{x}$
kcal/mol	$1.05 \times 10^{13}\,x$	$3.50 \times 10^{2}\,x$	$1.00\,x$	$6.95 \times 10^{-14}\,x$	$4.34 \times 10^{-2}\,x$	$\frac{2.86 \times 10^{-3}}{x}$
erg	$1.51 \times 10^{26}\,x$	$5.04 \times 10^{15}\,x$	$1.44 \times 10^{13}\,x$	$1.00\,x$	$6.24 \times 10^{11}\,x$	$\frac{1.99 \times 10^{-16}}{x}$
eV	$2.42 \times 10^{14}\,x$	$8.07 \times 10^{3}\,x$	$2.31 \times 10^{1}\,x$	$1.60 \times 10^{-12}\,x$	$1.00\,x$	$\frac{1.24 \times 10^{-4}}{x}$
cm	$\frac{3.00 \times 10^{10}}{x}$	$\frac{1.00}{x}$	$\frac{2.86 \times 10^{-3}}{x}$	$\frac{1.99 \times 10^{-16}}{x}$	$\frac{1.24 \times 10^{-4}}{x}$	$1.00\,x$
nm	$\frac{3.00 \times 10^{17}}{x}$	$\frac{1.00 \times 10^{7}}{x}$	$\frac{2.86 \times 10^{4}}{x}$	$\frac{1.99 \times 10^{-9}}{x}$	$\frac{1.24 \times 10^{3}}{x}$	$1.00 \times 10^{-7}\,x$

Symbols for Units

A	ampere	hr	hour
Å	ångström	Hz	herz
atm	atmosphere	J	joule
C	coulomb	°K	degree Kelvin
°C	degree Celsius	*M*	mole/liter
eV	electron volt	*m*	meter
F	farad	min	minute
F	faraday	*N*	equivalent/liter
F	formula weight/liter	s	second
G	gauss	V	volt
g	gram	W	watt
H	henry	Ω	(omega) ohm

Multiplicative Prefixes

Prefix	Symbol	Factor
pico	p	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
deci	d	10^{-1}
kilo	k	10^{3}
mega	M	10^{6}
giga	G	10^{9}

Symbols for Common Physical and Chemical Quantities

A	absorbance, area	*S/N*	signal to noise
a	absorptivity, amplifier gain, activity	*T*	transmittance, temperature
C	capacitance, concentration	*t*	time
D	diffusion coefficient	*V*	dc voltage
d	diameter, spacing	*V*	volume
deg	angular degree	*v*	ac voltage
E	electrical potential, energy	v	velocity
e	electron	*X*	reactance
f	frequency, activity coefficient	$\bar{x}$	mean
G	conductance, free energy	*Z*	impedance
H	magnetic field, enthalpy		
I	dc current		
i	ac current		
K	equilibrium constant		
L	inductance	ε	(epsilon) molar absorptivity
n	refractive index, number of equivalents	λ	(lambda) wavelength
n	spectral order	μ	(mu) mean
P	radiant or electrical power	ν	(nu) frequency
Q	quantity of dc electricity	ρ	(rho) density
q	quantity of ac electricity	σ	(sigma) standard deviation, wavenumber
R	electrical resistance, gas constant	τ	(tau) period
s	standard deviation	ϕ	(phi) phase angle
		ω	(omega) angular velocity

内 部 交 流

F 174 ／122

仪器分析原理　第 2 版
（英 2 － 4 ／1855）

C —00620

CONTENTS

PREFACE iii

1 **INTRODUCTION** 1
Types of Analytical Methods 1
Instruments for Analysis 3

2 **ELECTRICITY AND ELECTRIC CIRCUITS** 6
Introduction 7
Reactance in Electrical Circuits 14
Simple Electrical Measurements 27

3 **ELEMENTARY ELECTRONICS** 41
Semiconductors 42
Amplifiers Employing Transistors 48
Power Supplies and Regulators Employing Transistors 52
Operational Amplifiers 55
Noise 68
Readout Devices 77
Interfacing of Instruments with Computers 79

4 **ELECTROMAGNETIC RADIATION AND ITS INTERACTIONS WITH MATTER** 91
Properties of Electromagnetic Radiation 92
The Interaction of Radiation with Matter 101
Emission of Radiation 109

5 **COMPONENTS OF INSTRUMENTS FOR OPTICAL SPECTROSCOPY** 113
Components and Configurations of Instruments for Optical Spectroscopy 114
Radiation Sources 115
Wavelength Selection; Monochromators 123
Wavelength Selection; Filters 136
Sample Containers 137
Radiation Detection 137
Signal Processors and Readouts 145

6 **AN INTRODUCTION TO ABSORPTION SPECTROSCOPY** 148
Terms Employed in Absorption Spectroscopy 149
Quantitative Aspects of Absorption Measurements 151

7 APPLICATIONS OF ULTRAVIOLET AND VISIBLE ABSORPTION MEASUREMENTS 168
Absorbing Species 169
Some Typical Instruments 180
Application of Absorption Measurement to Qualitative Analysis 187
Quantitative Analysis by Absorption Measurements 188
Photometric Titrations 197
Automatic Photometric and Spectrophotometric Analysis 199
Photoacoustic Spectroscopy 202

8 INFRARED ABSORPTION SPECTROSCOPY 209
Theory of Infrared Absorption 210
Infrared Instrument Components 219
Some Typical Instruments 221
Sample Handling Techniques 226
Qualitative Applications of Infrared Absorption 230
Quantitative Applications 237
Infrared Fourier Transform Spectroscopy 241
Hadamard Transform Spectroscopy 254

9 RAMAN SPECTROSCOPY 262
Theory of Raman Spectroscopy 263
Instrumentation 268
Applications of Raman Spectroscopy 270

10 MOLECULAR FLUORESCENCE SPECTROSCOPY 279
Theory of Fluorescence 280
Instruments for Fluorescence Analysis 289
Applications of Fluoremetry 293
Nephelometry and Turbidimetry 294

11 ATOMIC SPECTROSCOPY 301
Theory of Flame Spectroscopy 303
Flame Characteristics 308
Atomizers for Atomic Spectroscopy 312
Atomic Absorption Spectroscopy 315
Atomic Emission Spectroscopy 326
Atomic Fluorescence Spectroscopy 332

12 EMISSION SPECTROSCOPY 335
Emission Spectra 337
Arc and Spark Sources 337
Argon Plasma Sources 340
Instruments for Emission Spectroscopy 342
Applications of Emission Spectroscopy 347

13 MISCELLANEOUS OPTICAL METHODS 352
Refractometry 353
Polarimetry 357
Optical Rotatory Dispersion and Circular Dichroism 370

14 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY 376
Theory of Nuclear Magnetic Resonance 377
Experimental Methods of NMR Spectroscopy 386
Environmental Effects on Proton NMR Spectra 390
Applications of Proton NMR 404
Application of Proton NMR to Quantitative Analysis 407
Fourier Transform NMR 409
Electron Spin Resonance Spectroscopy 412

15 X-RAY METHODS 426
Fundamental Principles 427
Instrument Components 434
X-Ray Fluorescence Methods 444
X-Ray Diffraction Methods 450
The Electron Microprobe Method 452
X-Ray Photoelectron Spectroscopy 453

16 RADIOCHEMICAL METHODS 458
The Radioactive Decay Process 459
Neutron Activation Analysis 467
Isotopic Dilution Methods 471
Radiometric Methods 473

17 MASS SPECTROMETRY 476
The Mass Spectrometer 477
Mass Spectra 488
Qualitative Applications of Mass Spectrometry 491
Quantitative Applications of Mass Spectrometry 496

18 AN INTRODUCTION TO ELECTROANALYTICAL CHEMISTRY 500
Electrochemical Cells 501
Cell Potentials 507
Half-Cell or Electrode Potentials 512
Calculation of Cell Potentials from Electrode Potentials 524
Effect of Current on Cell Potentials 527
Reference Electrodes 531
Standard Weston Cells 534

19 POTENTIOMETRIC METHODS 538
Indicator Electrodes 539
Instruments for Cell Potential Measurement 554
Direct Potentiometric Measurements 555
Potentiometric Titrations 559

20 ELECTROGRAVIMETRIC AND COULOMETRIC METHODS 580
Current-Voltage Relationship During an Electrolysis 581
Electrogravimetric Methods of Analysis 587
Coulometric Methods of Analysis 590

21 VOLTAMMETRY AND POLAROGRAPHY 605
Polarography 606
Applications of Polarography 617
Voltammetry at Solid Electrodes 622
Polarography with Potentiostatic Control 625
Modified Voltammetric Methods 627
Amperometric Titrations 635
Amperometric Titrations with Two Polarized Microelectrodes 637

22 CONDUCTOMETRIC METHODS 643
Electrolytic Conductance 644
The Measurement of Conductance 647
Conductometric Titrations 648
Applications of Direct Conductance Measurements 651
Oscillometry 652

23 THERMAL METHODS 654
Thermogravimetric Methods 655
Differential Thermal Analysis and Differential Scanning Calorimetry 657
Thermometric Titrations 662

24 AN INTRODUCTION TO CHROMATOGRAPHY 666
A General Description of Chromatography 667
The Rate Theory of Chromatography 671
Separations on Columns 676
Summary of Important Relationships for Chromatography 681
Qualitative and Quantitative Analysis by Chromatography 681

25 LIQUID CHROMATOGRAPHY 689
Column Chromatography 690
Planar Chromatography 705
Electrophoresis and Electrochromatography 709

26 GAS-LIQUID CHROMATOGRAPHY 715
Principles of Gas-Liquid Chromatography 716
Apparatus 717
Applications of Gas-Liquid Chromatography 722
Gas-Solid Chromatography 731
Examples of Applications of Gas Chromatography 731

APPENDIX 1 PROPAGATION OF UNCERTAINTIES IN PHYSICAL MEASUREMENTS 737

APPENDIX 2 SOME STANDARD AND FORMAL ELECTRODE POTENTIALS 745

INDEX 749