# INSTRUMENTAL METHODS OF ANALYSIS

Fifth Edition

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**D. VAN NOSTRAND COMPANY**

New York Cincinnati Toronto London Melbourne

D. Van Nostrand Company Regional Offices:
New York Cincinnati Millbrae

D. Van Nostrand Company International Offices:
London Toronto Melbourne


Library of Congress Catalog Card Number: 73-9122
ISBN: 0-442-29479-4



Published by D. Van Nostrand Company
450 West 33rd Street, New York, N.Y. 10001

Published simultaneously in Canada by
Van Nostrand Reinhold Ltd.
10 9 8 7 6 5 4 3

# 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-

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.

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# Contents

# List of Experiments

**Experiment**

# 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 | $cm^3$ |
| 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 | $e^-$, $e$ |
| electron paramagnetic resonance | epr |

| | |
|---|---|
| electron spin resonance | esr |
| electron volt | eV |
| equivalent weight | equiv wt |
| ethyl | Et |
| ethylenediamine | en |
| ethylenediamine-*N*, *N*, *N'*, *N'*-tetraacetic acid | EDTA |
| (the anion) | $Y^{4-}$ |
| *exempli gratia* (for example) | e.g. |
| exponential | exp |
| farad | F, f |
| formal (concentration) | *F* |
| frequency | f |
| gamma radiation | $\gamma$ |
| gas (physical state) | *g* |
| gauss | G |
| gram | g |
| hertz | Hz |
| hour | hr, h |
| *ibidem* (in the same place) | Ibid. |
| *id est* (that is) | i.e. |
| inch. | in. |
| indicator | ind |
| inductance | *L* |
| infrared | ir |
| inside diameter | i.d. |
| joule | J |
| kilo- (prefix) | k- |
| kilocalorie | kcal |
| liquid (physical state) | liq, *l* |
| 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 |

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

| | |
|---|---|
| torr (mm of mercury) | torr |
| tritium | t, $^3H$ |
| ultraviolet | uv |
| vacuum | vac |
| vacuum tube voltmeter | VTVM |
| versus | vs. |
| volt | V |
| volume | vol, $V$, v |
| volume per volume | v/v |
| volume per weight | v/w |
| watt | W |
| wavenumber | $cm^{-1}$ |
| wavenumber difference (Raman) | $\Delta cm^{-1}$ |
| year | 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 |
| $B_{mn}$ | 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 |
| $D_{\mathrm{MO}}$ | 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; Naperian 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 $x$ |
| $f$/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 |
| $i_{\text{lim}}$ | 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) |
| $K_{\text{sp}}$ | 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 |

| | |
|---|---|
| $S$ | 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 |