

Seventh Edition

Principles *of* Instrumental Analysis

Skoog | Holler | Crouch

INTERNATIONAL ATOMIC MASSES*

Name	Symbol	Atomic Number	Atomic Mass	Name	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	[227]	Mendelevium	Md	101	[258]
Aluminium	Al	13	26.9815385(7)	Mercury	Hg	80	200.592(3)
Americium	Am	95	[243]	Molybdenum	Mo	42	95.95(1)
Antimony	Sb	51	121.760(1)	Neodymium	Nd	60	144.242(3)
Argon	Ar	18	39.948(1)	Neon	Ne	10	20.1797(6)
Arsenic	As	33	74.921595(6)	Neptunium	Np	93	[237]
Astatine	At	85	[210]	Nickel	Ni	28	58.6934(4)
Barium	Ba	56	137.327(7)	Niobium	Nb	41	92.90637(2)
Berkelium	Bk	97	[247]	Nitrogen	N	7	14.007
Beryllium	Be	4	9.0121831(5)	Nobelium	No	102	[259]
Bismuth	Bi	83	208.98040(1)	Osmium	Os	76	190.23(3)
Bohrium	Bh	107	[270]	Oxygen	O	8	15.999
Boron	B	5	10.81	Palladium	Pd	46	106.42(1)
Bromine	Br	35	79.904	Phosphorus	P	15	30.973761998(5)
Cadmium	Cd	48	112.414(4)	Platinum	Pt	78	195.084(9)
Calcium	Ca	20	40.078(4)	Plutonium	Pu	94	[244]
Californium	Cf	98	[251]	Polonium	Po	84	[209]
Carbon	C	6	12.011	Potassium	K	19	39.0983(1)
Cerium	Ce	58	140.116(1)	Praseodymium	Pr	59	140.90766(2)
Cesium	Cs	55	132.90545196(6)	Promethium	Pm	61	[145]
Chlorine	Cl	17	35.45	Protactinium	Pa	91	231.03588(2)
Chromium	Cr	24	51.9961(6)	Radium	Ra	88	[226]
Cobalt	Co	27	58.933194(4)	Radon	Rn	86	[222]
Copernicium	Cn	112	[285]	Rhenium	Re	75	186.207(1)
Copper	Cu	29	63.546(3)	Rhodium	Rh	45	102.90550(2)
Curium	Cm	96	[247]	Roentgenium	Rg	111	[281]
Darmstadtium	Ds	110	[281]	Rubidium	Rb	37	85.4678(3)
Dubnium	Db	105	[270]	Ruthenium	Ru	44	101.07(2)
Dysprosium	Dy	66	162.500(1)	Rutherfordium	Rf	104	[267]
Einsteinium	Es	99	[252]	Samarium	Sm	62	150.36(2)
Erbium	Er	68	167.259(3)	Scandium	Sc	21	44.955908(5)
Europium	Eu	63	151.964(1)	Seaborgium	Sg	106	[269]
Fermium	Fm	100	[257]	Selenium	Se	34	78.971(8)
Flerovium	Fl	114	[289]	Silicon	Si	14	28.085
Fluorine	F	9	18.998403163(6)	Silver	Ag	47	107.8682(2)
Francium	Fr	87	[223]	Sodium	Na	11	22.98976928(2)
Gadolinium	Gd	64	157.25(3)	Strontium	Sr	38	87.62(1)
Gallium	Ga	31	69.723(1)	Sulfur	S	16	32.06
Germanium	Ge	32	72.630(8)	Tantalum	Ta	73	180.94788(2)
Gold	Au	79	196.966569(5)	Technetium	Tc	43	[97]
Hafnium	Hf	72	178.49(2)	Tellurium	Te	52	127.60(3)
Hassium	Hs	108	[270]	Terbium	Tb	65	158.92535(2)
Helium	He	2	4.002602(2)	Thallium	Tl	81	204.38
Holmium	Ho	67	164.93033(2)	Thorium	Th	90	232.0377(4)
Hydrogen	H	1	1.008	Thulium	Tm	69	168.93422(2)
Indium	In	49	114.818(1)	Tin	Sn	50	118.710(7)
Iodine	I	53	126.90447(3)	Titanium	Ti	22	47.867(1)
Iridium	Ir	77	192.217(3)	Tungsten	W	74	183.84(1)
Iron	Fe	26	55.845(2)	Ununocium	Uuo	118	[294]
Krypton	Kr	36	83.798(2)	Ununpentium	Uup	115	[289]
Lanthanum	La	57	138.90547(7)	Ununtrium	Uut	113	[285]
Lawrencium	Lr	103	[262]	Uranium	U	92	238.02891(3)
Lead	Pb	82	207.2(1)	Vanadium	V	23	50.9415(1)
Lithium	Li	3	6.94	Xenon	Xe	54	131.293(6)
Livermorium	Lv	116	[293]	Ytterbium	Yb	70	173.045(10)
Lutetium	Lu	71	174.9668(1)	Yttrium	Y	39	88.90584(2)
Magnesium	Mg	12	24.305	Zinc	Zn	30	65.38(2)
Manganese	Mn	25	54.938044(3)	Zirconium	Zr	40	91.224(2)
Meitnerium	Mt	109	[278]				

*The 2013 values from the IUPAC website at <http://www.chem.qmul.ac.uk/iupac/AtWt/>

Numbers in parentheses indicate the uncertainty in the last digit of the atomic masses. Values enclosed in brackets, for example, [209], indicate the mass number of the longest-lived isotope of the element. From J. Meija, et al., *Pure Appl. Chem.*, 2016, 88, 265, DOI: 10.1515/pac-2015-0305.

IMPORTANT PHYSICAL CONSTANTS

Constant	Symbol	Value
Speed of light (<i>in vacuo</i>)	c	$2.99792 \times 10^8 \text{ ms}^{-1}$
Planck's constant	h	$6.62607 \times 10^{-34} \text{ J s}$
Avogadro's number	N	$6.022140 \times 10^{23} \text{ particles mol}^{-1}$
Faraday constant	F	$96485.33 \text{ C mol}^{-1}$
Gas constant	R	$8.31446 \text{ J K}^{-1} \text{ mol}^{-1}$
		$0.0820578 \text{ L atm K}^{-1} \text{ mol}^{-1}$
Boltzmann's constant	k	$1.38065 \times 10^{-23} \text{ J K}^{-1}$
Rest mass of the electron	m_e	$9.10938 \times 10^{-31} \text{ kg}$
Electronic charge	e	$1.602177 \times 10^{-19} \text{ C}$

ENERGY CONVERSION FACTORS

	Joules	Ergs	Calories	Liter Atmosphere	Electron Volts
1 joule =	1	10^7	2.3901×10^{-1}	9.8692×10^{-3}	6.2415×10^{18}
1 erg =	10^{-7}	1	2.3901×10^{-8}	9.8692×10^{-10}	6.2415×10^{11}
1 calorie =	4.1840	4.1840×10^7	1	4.1293×10^{-2}	2.6114×10^{19}
1 liter atmosphere =	1.0133×10^2	1.0133×10^9	24.217	1	6.3242×10^{20}
1 electron volt =	1.6022×10^{-19}	1.6022×10^{-12}	3.8293×10^{-20}	1.5812×10^{-21}	1

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We dedicate this book to Veronica Crouch (Nicky), who passed away July 11, 2016 due to metastatic pancreatic cancer. She was a valuable part of our team and will be greatly missed.

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Preface

Today, there is a wide and impressive array of powerful and elegant tools for collecting qualitative and quantitative information about the composition and structure of matter. Students of chemistry, biochemistry, physics, geology, the life sciences, forensic science, and environmental science need to develop an understanding of these instrumental tools and their applications to relevant analytical problems in these fields. This book is designed to meet the needs of these students and other users of analytical instruments.

When instrument users are familiar with the fundamental principles underlying modern analytical instrumentation, they can make appropriate choices and efficient use of these measurement tools. For any given analytical problem, a seemingly bewildering number of alternative methods exist for obtaining the desired information. By understanding the advantages and limitations of the various tools, suitable choices can be made, and the user can be attuned to limitations in sensitivity, precision, and accuracy. In addition, users of instrumental methods should be aware of the various techniques for calibrating and standardizing instruments, and validating the measurements made. It is therefore our objective to give readers a thorough introduction to the principles of instrumental analysis, including spectroscopic, electrochemical, chromatographic, radiochemical, thermal, and surface analytical methods. By carefully studying this text, readers will discover the types of instruments that are available and their strengths and limitations.

ORGANIZATION OF THIS EDITION

This text is organized in sections similar to the sixth edition. After the brief introductory chapter, the book is divided into six sections.

- »» Section 1 contains four chapters on basic electrical circuits, operational amplifiers, digital electronics and computers, signals, noise, and signal-to-noise enhancement.
- »» Section 2 comprises seven chapters devoted to various atomic spectrometric methods, including an introduction to spectroscopy and spectroscopic instrumentation, atomic absorption, atomic emission, atomic mass spectrometry, and X-ray spectrometry.
- »» Section 3 treats molecular spectroscopy in nine chapters that describe absorption, emission, luminescence, infrared, Raman, nuclear magnetic resonance, mass spectrometry, and surface analytical methods.
- »» Section 4 consists of four chapters that treat electroanalytical chemistry, including potentiometry, coulometry, and voltammetry.
- »» Section 5 contains five chapters that discuss analytical separation methods including gas and liquid chromatography, supercritical fluid chromatography, electrophoresis, and field-flow fractionation.
- »» Section 6 consists of four chapters devoted to miscellaneous instrumental methods with emphasis on thermal, radiochemical, and automated methods. A chapter on particle size analysis is also included in this final section.

Since the first edition of this text appeared in 1971, the field of instrumental analysis has grown so large and diverse that it is impossible to treat all of the modern instrumental techniques in a one- or even two-semester course. Also, instructors have differing opinions on which techniques to discuss and which to omit in their courses. Because of this, we have included more material in this text than can be covered

in a single instrumental analysis course, and as a result, this comprehensive text will also be a valuable reference for years to come. An important advantage of organizing the material into sections is that instructors have flexibility in picking and choosing topics to be included in reading assignments. Thus, as in the previous edition, the sections on atomic and molecular spectroscopy, electrochemistry, and chromatography begin with introductory chapters that precede the chapters devoted to specific methods of each type. After assigning the introductory chapter in a section, an instructor can select the chapters to follow in any order desired. To assist students in using this book, the answers to about half of the problems are provided at the end of the book.



NEW TO THIS EDITION

- » Because many instrumental techniques have been or are being used in NASA's exploration of Mars, we have attempted to present the principles and applications of these methods where appropriate.
- » We have included in this book new or updated *Instrumental Analysis in Action* features at the end of each section. One of the new case studies discusses the *bisphenol A* controversy and the role of chromatography in this environmental problem. The second covers the role of neutron activation analysis in the many investigations of the John F. Kennedy assassination. The case studies expand on the methods introduced in each section and show how they can be applied to specific analytical problems. These stimulating examples have been selected from the forensic, environmental, and biomedical areas.
- » *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 from the website **www.doi.org**. A DOI may be typed into a form on the website home page, and when the identifier is submitted, the browser transfers directly to the article on the publisher's website. For example, the DOI 10.1351/goldbook.S05812 can be typed into the form, and the browser is directed to the IUPAC article on *spectral bandwidth error*. Alternatively, DOIs may be entered directly into the address bar (also called location bar or URL bar) of any browser after adding the prefix *http://dx.doi.org/* to the DOI as follows: *http://dx.doi.org/10.1351/goldbook.S05812*. Please note that students or instructors must have authorized access to the publication of interest to retrieve articles. Many journals permit unauthorized users to access abstracts of articles without a subscription. Thus, preliminary research may be accomplished without full authorization.
- » All chapters have been revised and updated with recent references to the literature of analytical

chemistry. Among the chapters that have been changed extensively are those on optical instrument components (Chapter 7), plasma atomic emission spectrometry (Chapter 10), atomic mass spectrometry (Chapter 11), X-ray spectrometry (Chapter 12), molecular mass spectrometry (Chapter 20), and supercritical fluid chromatography (Chapter 29). Throughout the book, new and updated methods and techniques are described, and photos of specific commercial instruments have been added where appropriate. Some of these modern topics include laser-based spectrometry, fluorescence quenching and lifetime measurements, tandem mass spectrometry, and biosensors.


- » Many new and revised charts, diagrams, and plots contain data, curves, and waveforms calculated from theory or obtained from the original literature to provide an accurate and realistic representation.


KEY FEATURES FOR THIS EDITION

- »  Spreadsheet applications have been included throughout to illustrate how these powerful programs can be applied to instrumental methods. Problems accompanied by this icon  encourage the use of spreadsheets. When a more detailed approach is required or supplemental reading is appropriate, readers are referred to our companion book, S. R. Crouch and F. J. Holler, *Applications of Microsoft Excel in Analytical Chemistry*, 3rd ed., Belmont, CA: Cengage Learning, 2017. Those who purchase this text or our other texts have full access to this companion text at www.tinyurl.com/skoogpia7. This companion provides assistance in understanding these applications.
- » The book is printed in two colors. This feature aids in understanding the many figures and diagrams in the text. The second color clarifies graphs; aids in following the data flow in diagrams; provides keys for correlating data that appear in multiple charts, graphs, and diagrams; and makes for a more pleasing overall appearance.
- » An open-ended *Challenge Problem* provides a capstone research-oriented experience for each chapter. 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 they may require library or web searches to find information. We hope that these challenge problems stimulate discussion and extend the topics of the chapters into new areas. We encourage students and 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.

- »» Throughout the text, we have attempted to present material in a student-friendly style that is active and engaging. Examples are sprinkled throughout each chapter to aid in solving relevant and interesting problems. The solutions to the problems in each example are indicated so that students can easily separate the problem setup from the problem solution.

ANCILLARIES

- »»  The book's companion website at www.tinyurl.com/skoogpia7 includes more than 100 interactive tutorials on instrumental methods,

simulations of analytical techniques, exercises, and animations to help students visualize important concepts. In addition, Excel files containing data and sample spreadsheets are available for download. Selected papers from the chemical literature are also available as PDF files to engage student interest and to provide background information for study. Throughout the book, this icon  alerts and encourages students to incorporate the website into their studies.

- »» An Instructor's Manual containing the solutions to all the text problems and online images from the text can be found at www.tinyurl.com/skoogpia7.

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throughout the world over the past six decades learned much of what they know of analytical chemistry from Doug Skoog. We are privileged and proud to have worked by his side.

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F. James Holler
Stanley R. Crouch

Introduction

Analytical chemistry deals with methods for determining the chemical composition of samples of matter. A **qualitative method** yields information about the identity of atomic or molecular species or the functional groups in the sample. A **quantitative method**, in contrast, provides numerical information as to the relative amount of one or more of these components.



Throughout the book, this logo indicates an opportunity for online self-study. Visit the book's companion website at www.tinyurl.com/skoogpia7 to view interactive tutorials, guided simulations, and exercises.

1A CLASSIFICATION OF ANALYTICAL METHODS

Analytical methods are often classified as being either *classical* or *instrumental*. Classical methods, sometimes called *wet-chemical methods*, preceded instrumental methods by a century or more.

1A-1 Classical Methods

In the early years of chemistry, most analyses were carried out by separating the components of interest (the *analytes*) in a sample by precipitation, extraction, or distillation. For qualitative analyses, the separated components were then treated with reagents that yielded products that could be recognized by their colors, their boiling or melting points, their solubilities in a series of solvents, their odors, their optical activities, or their refractive indexes. For quantitative analyses, the amount of analyte was determined by *gravimetric* or by *volumetric* measurements.

In gravimetric measurements, the mass of the analyte or some compound produced from the analyte was determined. In volumetric, also called *titrimetric*, procedures, the volume or mass of a standard reagent required to react completely with the analyte was measured.

These classical methods for separating and determining analytes are still used in many laboratories. However, because of the increasing need for determining small amounts of analytes at low concentrations, the use of classical methods has decreased with the passage of time and the advent of instrumental methods to supplant them.

1A-2 Instrumental Methods

Early in the twentieth century, scientists began to exploit phenomena other than those used for classical methods for solving analytical problems. Thus, measurements of such analyte physical properties as conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, and fluorescence began to be used for quantitative analysis. Furthermore, highly efficient chromatographic and electrophoretic techniques began to replace distillation, extraction, and precipitation for the separation of components of complex mixtures prior to their

qualitative or quantitative determination. These newer methods for separating and determining chemical species are known collectively as *instrumental methods of analysis*.

Many of the phenomena underlying instrumental methods have been known for a century or more. Their application by most scientists, however, was delayed by a lack of reliable and simple instrumentation. In fact, the growth of modern instrumental methods of analysis has paralleled the development of the electronics and computer industries.

1B TYPES OF INSTRUMENTAL METHODS

Let us first consider some of the chemical and physical characteristics that are useful for qualitative or quantitative analysis. Table 1-1 lists many of the characteristic properties that are currently used for instrumental analysis. Most of the characteristics listed in the table require a source of energy to stimulate a measurable response from the analyte. For example, in atomic emission an increase in the temperature of the analyte is required first to produce gaseous analyte atoms and then to excite the atoms to higher energy states. The excited-state atoms then emit characteristic electromagnetic radiation, which is the quantity measured by the instrument. Sources of energy may take the form of a rapid thermal change as in the previous example; electromagnetic radiation from a selected region of the spectrum; application of an electrical quantity, such as voltage, current, or charge; or perhaps subtler forms intrinsic to the analyte itself.

Note that the first six entries in Table 1-1 involve interactions of the analyte with electromagnetic radiation. In the first property, radiant energy is produced by the analyte; the next five properties involve changes in electromagnetic radiation brought about by its interaction with the sample. Four electrical properties then follow. Finally, five miscellaneous properties are grouped together: mass, mass-to-charge ratio, reaction rate, thermal characteristics, and radioactivity.

The second column in Table 1-1 lists the instrumental methods that are based on the various physical and chemical properties. Be aware that it is not always easy to select an optimal method from among available instrumental techniques and their classical counterparts. Many instrumental techniques are more sensitive than classical techniques, but others are not. With certain combinations of elements or compounds, an instrumental method may be more selective, but with others, a gravimetric or volumetric approach may suffer less interference. Generalizations on the basis of accuracy, convenience, or expenditure of time are equally difficult to draw. Nor is it necessarily true that instrumental procedures employ more sophisticated or more costly apparatus.

As noted earlier, in addition to the numerous methods listed in the second column of Table 1-1, there is a group of instrumental procedures that are used for separation and resolution of closely related compounds. Most of these procedures are based on chromatography, solvent extraction, or electrophoresis. One of the characteristics listed in Table 1-1 is usually used to complete the analysis following chromatographic separations. Thus, for example, thermal conductivity, ultraviolet and infrared

TABLE 1-1 Chemical and Physical Properties Used in Instrumental Methods

Characteristic Properties	Instrumental Methods
Emission of radiation	Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)
Absorption of radiation	Spectrophotometry and photometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy
Scattering of radiation	Turbidimetry; nephelometry; Raman spectroscopy
Refraction of radiation	Refractometry; interferometry
Diffraction of radiation	X-ray and electron diffraction methods
Rotation of radiation	Polarimetry; optical rotary dispersion; circular dichroism
Electrical potential	Potentiometry; chronopotentiometry
Electrical charge	Coulometry
Electrical current	Amperometry; polarography
Electrical resistance	Conductometry
Mass	Gravimetry (quartz crystal microbalance)
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal characteristics	Thermal gravimetry and titrimetry; differential scanning calorimetry; differential thermal analyses; thermal conductometric methods
Radioactivity	Activation and isotope dilution methods

absorption, refractive index, and electrical conductance are often used for this purpose.

This text deals with the principles, the applications, and the performance characteristics of the instrumental methods listed in Table 1-1 and of chromatographic and electrophoretic separation procedures as well. No space is devoted to the classical methods because we assume that the reader has previously studied these techniques.¹

1C INSTRUMENTS FOR ANALYSIS

An instrument for chemical analysis converts information about the physical or chemical characteristics of the analyte to information that can be manipulated and interpreted by a human. Thus, an analytical instrument can be viewed as a communication device between the system under study and the investigator. To retrieve the desired information from the analyte, it is necessary to provide a stimulus, which is usually in the form of electromagnetic, electrical, mechanical, or nuclear energy, as illustrated in Figure 1-1. The stimulus elicits a response from the system under study whose nature and magnitude are governed by the fundamental laws of chemistry and physics. The resulting information is contained in the phenomena that result from the interaction of the stimulus with the analyte. A familiar example is passing a narrow band of wavelengths of visible light through a sample to measure the extent of its absorption by the analyte. The intensity of the light is determined before and after its interaction with the sample, and the ratio of these intensities provides a measure of the analyte concentration.

Generally, instruments for chemical analysis comprise just a few basic components, some of which are listed in Table 1-2. To understand the relationships among these instrument components and the flow of information from the characteristics of the analyte through the components to the numerical or graphical output produced by the instrument, it is instructive to explore how the information of interest can be represented and transformed.

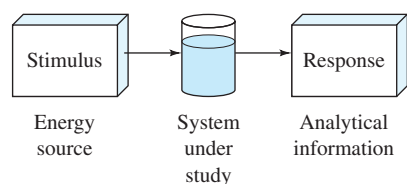


FIGURE 1-1 Block diagram showing the overall process of an instrumental measurement.

1C-1 Data Domains

The measurement process is aided by a wide variety of devices that convert information from one form to another. Before investigating how instruments function, it is important to understand how information can be *encoded* (represented) by physical and chemical characteristics and particularly by *electrical signals*, such as current, voltage, and charge. The various modes of encoding information are called *data domains*. A classification scheme has been developed based on this concept that greatly simplifies the analysis of instrumental systems and promotes understanding of the measurement process.² As shown in the data-domain map of Figure 1-2, data domains may be broadly classified into *nonelectrical domains* and *electrical domains*.

1C-2 Nonelectrical Domains

The measurement process begins and ends in nonelectrical domains. The physical and chemical information that is of interest in a particular experiment resides in these data domains. Among these characteristics are length, density, chemical composition, intensity of light, pressure, and others listed in the first column of Table 1-1.

It is possible to make a measurement by having the information reside entirely in nonelectrical domains. For instance, the determination of the mass of an object using a mechanical equal-arm balance involves a comparison of the mass of the object, which is placed on one balance pan, with standard masses placed on a second pan. The information representing the mass of the object in standard units is encoded directly by the experimenter, who provides information processing by summing the masses to arrive at a number. In certain other mechanical balances, the gravitational force on a mass is amplified mechanically by making one of the balance arms longer than the other, thus increasing the resolution of the measurement.

The determination of the linear dimensions of an object with a ruler and the measurement of the volume of a sample of liquid with a graduated cylinder are other examples of measurements carried out exclusively in nonelectrical domains. Such measurements are often associated with classical analytical methods. The advent of inexpensive electronic signal processors, sensitive transducers (see Section 1C-4), and readout devices has led to the development of a host of electronic instruments, which acquire information from nonelectrical domains, process it in electrical domains, and finally present it in a non-electrical way. Electronic devices process information and transform it from one domain to another in ways analogous to the multiplication of mass in mechanical balances with unequal arms. Because these devices are available and capable of rapid



Tutorial: Learn more about **data domains** at www.tinyurl.com/skoogpia7.

¹For a discussion of classical methods, see D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Fundamentals of Analytical Chemistry*, 9th ed., Belmont, CA: Brooks/Cole, 2014, Chaps. 1–17.

²C. G. Enke, *Anal. Chem.*, **1971**, *43*, 69A, DOI: 10.1021/ac60296a764.

TABLE 1-2 Some Examples of Instrument Components

Instrument	Energy Source (stimulus)	Analytical Information	Information Sorter	Input Transducer	Data Domain of Transduced Information	Signal Processor/Readout
Photometer	Tungsten lamp	Attenuated light beam	Filter	Photodiode	Electrical current	Amplifier, digitizer, LED display
Atomic emission spectrometer	Inductively coupled plasma	UV or visible radiation	Monochromator	Photomultiplier tube	Electrical current	Amplifier, digitizer, digital display
Coulometer	Direct-current source	Charge required to reduce or oxidize analyte	Cell potential	Electrodes	Time	Amplifier, digital timer
pH meter	Sample/glass electrode	Hydrogen ion activity	Glass electrode	Glass-calomel electrodes	Electrical voltage	Amplifier, digitizer, digital display
Mass spectrometer	Ion source	Mass-to-charge ratio	Mass analyzer	Electron multiplier	Electrical current	Amplifier, digitizer, computer system
Gas chromatograph with flame ionization	Flame	Ion concentration vs. time	Chromatographic column	Biased electrodes	Electrical current	Electrometer, digitizer, computer system

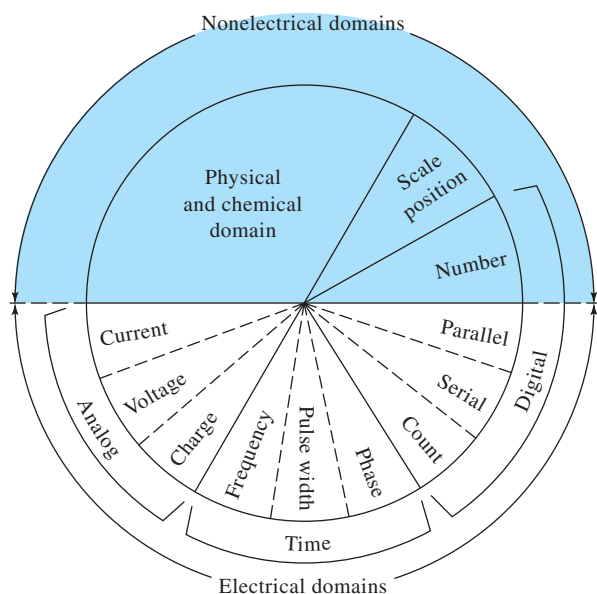


FIGURE 1-2 Data-domain map. The upper (shaded) half of the map consists of nonelectrical domains. The bottom half is made up of electrical domains. Note that the digital domain spans both electrical and nonelectrical domains.

and sophisticated information processing, instruments that rely exclusively on nonelectrical information transfer are rapidly becoming obsolete. Nonetheless, the information we seek begins in the properties of the analyte and ends in a number, both of which are nonelectrical representations. The ultimate objective in an analytical measurement is to obtain a final numerical result that is in some manner proportional to the sought-for chemical or physical characteristic of the analyte.

1C-3 Electrical Domains

The modes of encoding information as electrical quantities can be subdivided into *analog domains*, *time domains*, and the *digital domain*, as illustrated in the bottom half of the circular map in Figure 1-2. Note that the digital domain is not only composed of electrical signals but also includes one nonelectrical representation, because numbers presented on any type of display convey digital information.

Any measurement process can be represented as a series of *interdomain conversions*. For example, Figure 1-3 illustrates the measurement of the molecular fluorescence intensity of a sample of tonic water containing a trace of quinine and, in a general

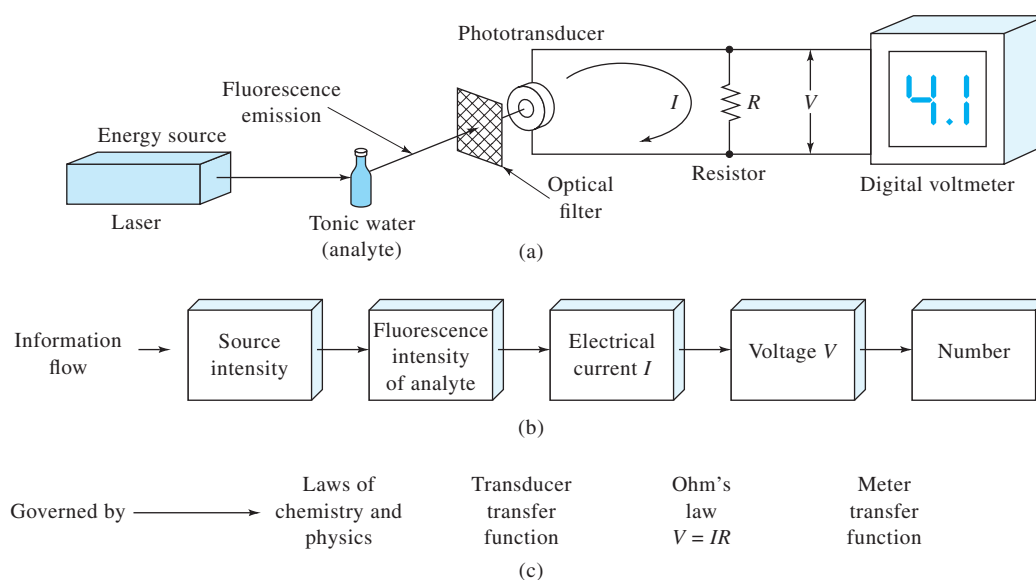


FIGURE 1-3 A block diagram of a fluorometer showing (a) a general diagram of the instrument, (b) a diagrammatic representation of the flow of information through various data domains in the instrument, and (c) the rules governing the data-domain transformations during the measurement process.

way, some of the data-domain conversions that are necessary to arrive at a number related to the intensity. The intensity of the fluorescence is significant in this context because it is proportional to the concentration of the quinine in the tonic water, which is ultimately the information that we desire. The information begins in the solution of tonic water as the concentration of quinine. This information is teased from the sample by applying to it a stimulus in the form of electromagnetic energy from the laser shown in Figure 1-3. The radiation interacts with the quinine molecules in the tonic water to produce fluorescence emission in a region of the spectrum characteristic of quinine and of a magnitude proportional to its concentration. Radiation that is unrelated to the concentration of quinine is removed from the beam of light by an optical filter, as shown in Figure 1-3. The intensity of the fluorescence emission, which is nonelectrical information, is encoded into an electrical signal by a special type of device called an *input transducer*. The particular type of transducer used in this experiment is a phototransducer, of which there are numerous types, some of which are discussed in Chapters 6 and 7. In this example, the input transducer converts the fluorescence from the tonic water to an electrical current I , proportional to the intensity of the radiation. The mathematical relationship between the electrical output and the input radiant power impinging on its surface is called the *transfer function* of the transducer.

The current from the phototransducer is then passed through a resistor R , which according to Ohm's law produces a voltage V that is proportional to I , which is in turn proportional to the intensity of the fluorescence. Finally, V is measured by the digital voltmeter to provide a readout proportional to the concentration of the quinine in the sample.

Voltmeters, alphanumeric displays, electric motors, computer screens, and many other devices that serve to convert data from electrical to nonelectrical domains are called *output transducers*. The digital voltmeter of the fluorometer of Figure 1-3 is a rather complex output transducer that converts the voltage V to a number on a liquid-crystal display so that it may be read and interpreted by the user of the instrument. We shall consider the detailed nature of the digital voltmeter and various other electrical circuits and signals in Chapters 2 through 4.

Analog-Domain Signals

Information in the analog domain is encoded as the *magnitude* of one of the electrical quantities—voltage, current, charge, or power. These quantities are continuous in both amplitude and time, as shown by the typical analog signals of Figure 1-4. Magnitudes of analog quantities can be measured continuously, or they can be sampled at specific points in time dictated by the needs of a particular experiment or instrumental method, as discussed in Chapter 4. Although the data of Figure 1-4 are recorded as a function of time, any variable such as wavelength, magnetic field strength, or temperature may be the independent variable under appropriate circumstances. The correlation of two analog signals that result from corresponding measured physical or chemical properties is important in a wide variety of instrumental techniques, such as nuclear magnetic resonance spectroscopy, infrared spectroscopy, and differential thermal analysis.

Because electrical noise influences the magnitude of electrical signals, analog signals are especially susceptible to electrical noise that results from interactions within measurement circuits or from other electrical devices in the vicinity of the