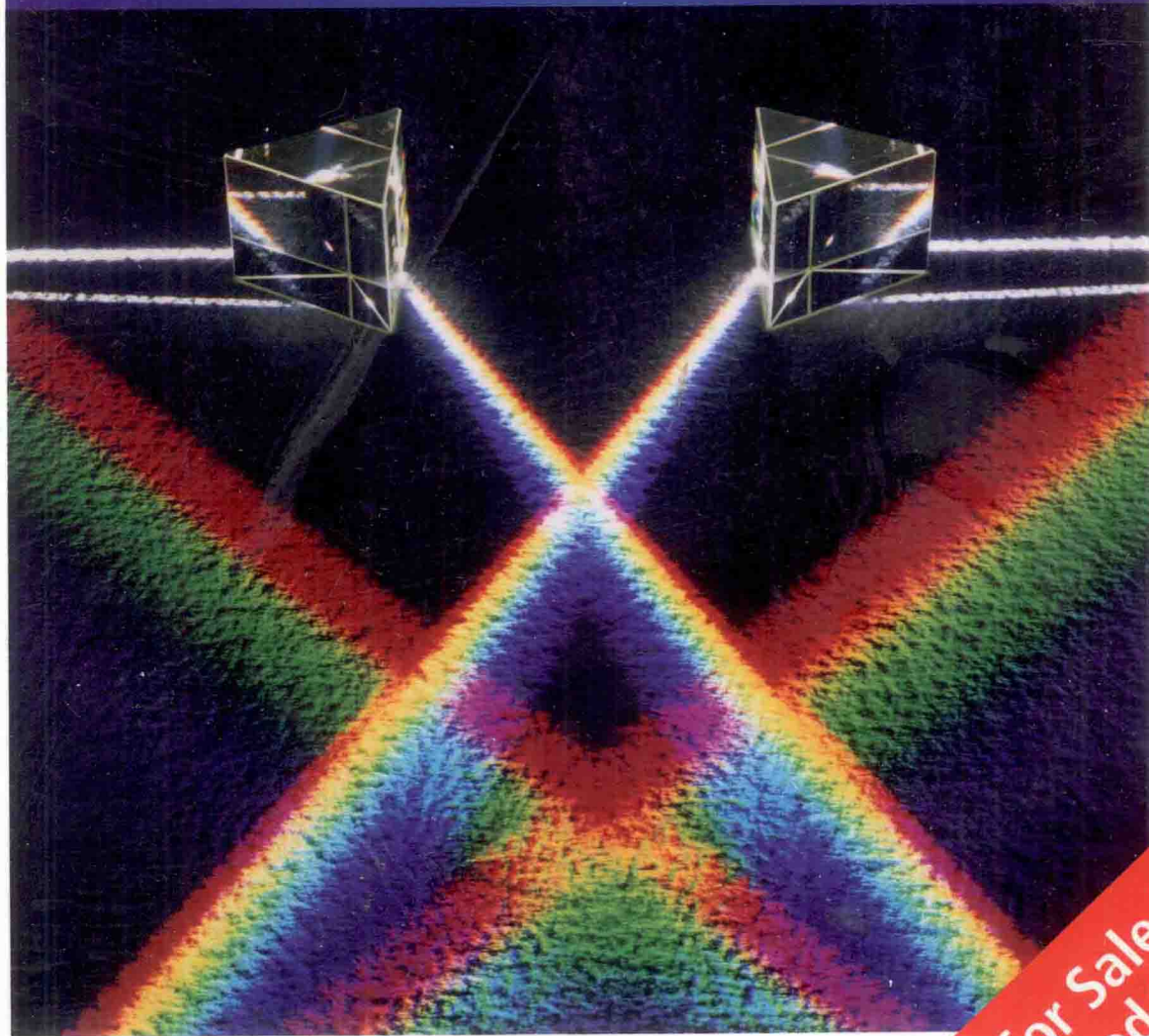


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# Principles of Instrumental Analysis

*6th Edition*



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United States

**SIXTH EDITION**

# Principles of Instrumental Analysis

Douglas A. Skoog  
*Stanford University*

F. James Holler  
*University of Kentucky*

Stanley R. Crouch  
*Michigan State University*



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# Preface

Today, there is a wide and impressive array of powerful and elegant tools for obtaining 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 must develop an understanding of these instrumental tools and their applications to solve important analytical problems in these fields. This book is addressed to meet the needs of these students and other users of analytical instruments.

When instrument users are familiar with the fundamental principles of operation of modern analytical instrumentation, they then will make appropriate choices and efficient use of these measurement tools. There are often a bewildering number of alternative methods for solving any given analytical problem, but by understanding the advantages and limitations of the various tools, users can choose the most appropriate instrumental method and be attuned to its limitations in sensitivity, precision, and accuracy. In addition, knowledge of measurement principles is necessary for calibration, standardization, and validation of instrumental methods. 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 available and their strengths and limitations.

## ORGANIZATION OF THIS EDITION



This text is organized in sections similar to the fifth 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 such analytical separation methods as 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 that follow in any order desired. To assist students in using this book, the answers to most numerical problems are provided at the end of the book.



## NEW TO THIS EDITION

- We have included a new chapter on particle size determination (Chapter 34). The physical and chemical properties of many research materials and consumer and industrial products are intimately related to their particle size distributions. As a result, particle size analysis has become an important technique in many research and industrial laboratories.
- Exciting new *Instrumental Analysis in Action* features have been added at the end of each of the six sections. These case studies describe how some of the methods introduced in each section can be applied to a specific analytical problem. These stimulating examples have been selected from the forensic, environmental, and biomedical areas.
-  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, *Applications of Microsoft® Excel in Analytical Chemistry* (Belmont, CA: Brooks/Cole, 2004), for assistance in understanding these applications.
- The book is now printed in two colors. This particularly 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 chap-

ter and requires reading the original literature of analytical chemistry, derivations, extensive analysis of real experimental data, and creative problem solving.

- 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 mass spectrometry (Chapters 11 and 20), surface characterization (Chapter 21), voltammetry (Chapter 25), chromatography (Chapters 26 and 27), and thermal analysis (Chapter 31). 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 plasma 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.
- 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.thomsonedu.com/chemistry/skoog](http://www.thomsonedu.com/chemistry/skoog) 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.thomsonedu.com/chemistry/skoog](http://www.thomsonedu.com/chemistry/skoog).



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Numerous manufacturers of analytical instruments and other products and services related to analytical chemistry have contributed by providing diagrams, application notes, and photos of their products. We are particularly grateful to Agilent Technologies, Bioanalytical Systems, Beckman Coulter, Inc., Brinkman Instruments, Caliper Life Sciences, Hach Co., Hamamatsu Photonics, InPhotonics, Inc., Kaiser Optical Systems, Leeman Labs, LifeScan, Inc., Mettler-Toledo, Inc., National Instruments Corp., Ocean Optics, Inc., Perkin-Elmer Corp., Postnova Analytics, Spectro Analytical Instruments, T. A. Instruments, Thermo-Electron Corp., and Varian, Inc. for providing photos.

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Douglas A. Skoog  
 F. James Holler  
 Stanley R. Crouch

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# Introduction

**A** *nalytical 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.*



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## 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. The extent of their general application is, however, decreasing with the passage of time and with 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 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 most 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. Some 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.

**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

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 absorption, refractive index, and electrical conductance are 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.

## 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.

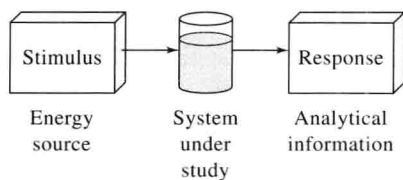
### 1C-1 Data Domains

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.<sup>1</sup> 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

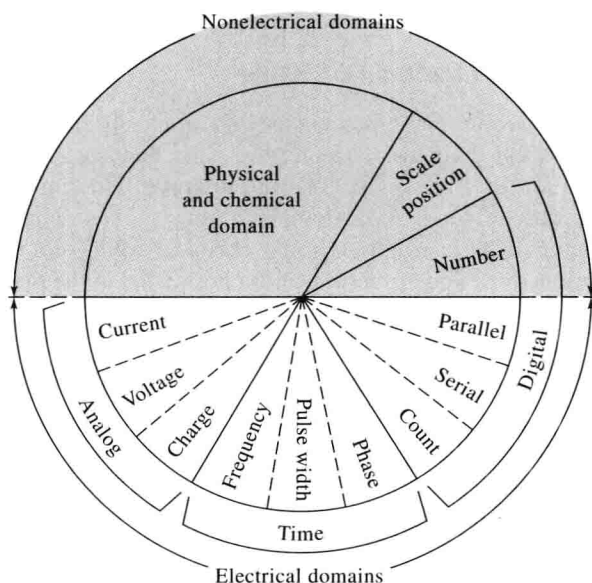


**FIGURE 1-1** Block diagram showing the overall process of an instrumental measurement.

<sup>1</sup>C. G. Enke, *Anal. Chem.*, **1971**, 43, 69A.

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.

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, 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 nonelectrical 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 and so-



**Tutorial:** Learn more about **data domains**.