

INTRODUCTION TO CHEMICAL INSTRUMENTAL ANALYSIS

The purposes of Chapter 1 are to review the definitions of some of the terms that are used in the study of analytical chemistry and to present a brief overview of the instrumental methods of chemical analysis. It is hoped that the introduction can provide insight into the organization of both the remainder of the text and the field of analytical instrumentation. No attempt is made in Chapter 1 to provide a detailed description of the analytical methods.

Some analysts distinguish between a chemical analysis and an assay. Those analysts define a chemical analysis as the entire process that leads to determining the identity or amount of a substance in a sample. The chemical analysis consists of collecting a sample, possibly treating the sample either physically or chemically, performing a laboratory or nonlaboratory measurement on the sample, mathematically manipulating the data as required to obtain a meaningful result, and reporting the result. The chemical assay consists only of the laboratory or nonlaboratory measurement. Other analysts use analysis and assay interchangeably. Most analysts define assay as the laboratory or nonlaboratory measurement, and analysis as either the entire process described previously or as the measurement. The latter definitions are used in the text.

Chemical analysis is concerned with determining either the identity of the chemical substances or the amount of a particular substance in a sample. The former type of analysis is a qualitative chemical analysis. The latter type is a quantitative chemical analysis.

Sometimes chemical analysis is divided into classical and instrumental analysis. Although the division probably is not as important as it once was, many analysts continue to distinguish between the two categories. Classical or

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non-instrumental analysis is the group of analytical methods that only requires the use of chemicals, a balance, calibrated glassware, and other commonplace laboratory apparatus, such as funnels, burners or hot plates, flasks, and beakers. Instrumental analysis requires the use of an analytical instrument in addition to the apparatus that is used for classical analyses. Classical and instrumental methods can be used for qualitative and quantitative analysis. An analytical instrument is a physical, often electrically operated, device that is used to determine the identity or amount of one or more components in the analyzed substance (the analyte).

Regardless of whether classical or instrumental analysis is used, many quantitative analyses can be classified as being gravimetric or volumetric. A gravimetric analysis relies upon a critical mass measurement of the product of a chemical reaction, or a measurement of a mass change during a chemical reaction to determine the amount of a chemical reactant in the sample. The mass measurement is made with an accurate balance. A classical gravimetric analysis usually consists of a precipitation of a salt of the assayed substance. The precipitate is collected by filtration, dried, and weighed. Instrumental gravimetric analysis normally consists of heating the sample on a balance pan in an oven while observing the mass change. The temperature of the sample is increased during the heating and the readout from the device is a plot of mass as a function of sample temperature. That technique is thermogravimetric analysis (Chapter 27).

A volumetric analysis relies upon a critical measurement of the volume of a chemical reactant to determine the concentration of the sample. Volumetric analyses are titrations in which a solution of one of the chemical reactants in a buret is added to a solution of a second chemical reactant. The solution in the buret is the titrant, and the solution in the reaction vessel is the titrand. The sample can be either the titrant or the titrand. The volume of titrant added at the endpoint of the titration is measured and used to calculate the concentration of the sample. A classical volumetric analysis uses a chemical indicator to locate the endpoint of those titrations in which no natural color change is observed. An instrumental volumetric analysis uses a laboratory instrument to determine the endpoint.

INSTRUMENTAL ANALYSIS

Essentially all analytical instruments are electrically operated. An understanding of the operation of the electrical components of an instrument can aid in locating a malfunctioning portion of the instrument and can make it possible for the analyst to obtain maximal use and information from the instrument. In addition, some research analytical chemists design and develop new instruments that can be used for chemical analysis. Consequently, Chapters 2 through 4 are an introductory description of electrical circuits.

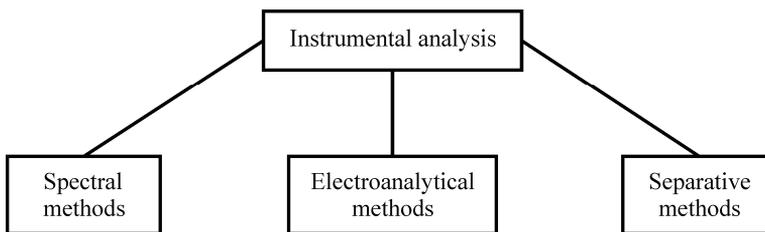


Fig. 1-1 The three major categories of instrumental methods of chemical analysis.

Analytical instruments are devices that measure a physical or chemical property of the assayed substance or that measure some factor that enables determination of a property of the substance. Traditionally, instrumental analyses are divided into three categories (Fig. 1-1) according to the type of property of the assayed substance that is measured or used during the assay. The *spectral methods* use or measure some form of radiation during the assay. The *electroanalytical methods* apply an electrical signal to the sample and/or monitor an electrical property of the sample. The *separative methods* rely upon separation of the components of a sample prior to measuring a property of the components. In the following sections the more important instrumental techniques are mentioned. Because numerous techniques exist, no attempt is made to be comprehensive.

SPECTRAL METHODS

The spectral methods of analysis use an instrument to measure the amount of radiation that is absorbed, emitted, or scattered by the sample. If the amount of absorbed radiation is measured, the technique is absorptiometry or absorption spectrophotometry. Except for naturally occurring radioactive materials, radiation can be emitted from a sample only after the sample has absorbed energy from an outside source. If the absorbed energy is electromagnetic radiation in the x-ray, ultraviolet, or visible region of the spectrum, the subsequently emitted electromagnetic radiation is a form of luminescence termed either fluorescence or phosphorescence depending upon the manner in which the deexcitation takes place. A description of the difference between fluorescence and phosphorescence is included in Chapter 5. Absorption of ultraviolet and visible radiation by atoms and polyatomic species is described in Chapters 6 and 9 respectively. Fluorescence from atoms is described in Chapter 8, and fluorescence and phosphorescence from molecules are described in Chapter 11. A description of the absorption and fluorescence of x-rays is given in Chapter 18. Generally a laboratory instrument that is designed to provide the energy required to excite the sample (if necessary) and to monitor the emitted radiation or particles is a spectrometer.

It is not necessary for the energy that is absorbed by a sample prior to emission to be in the form of electromagnetic radiation. During assays in which chemiluminescence and electrochemiluminescence (Chapter 10) are measured,

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energy emitted from a chemical reaction or electrical energy is absorbed. Sometimes thermal energy from a flame or electrical energy from an electrical discharge (Chapter 7) can be used to initiate emission. Similarly, the energy required to cause emission of radiation or particles from the sample can come from collisions between the sample and electrons (Chapter 19), or ions (Chapter 18).

During assays using the radiochemical methods (Chapter 20), the radioactive products that have decayed from a sample are measured. If the decay follows energy absorption from neutrons that have bombarded the sample, the technique is neutron activation analysis. A radiometric analysis uses a radioactive reagent to chemically react with the assayed substance. The radioactivity of the product of the reaction is either directly measured and related to concentration or the endpoint of a titration with the radioactive reagent is determined by measuring the radioactivity of the titrand during the titration.

Radiation that is scattered from sample particles can be used for analyses. Nephelometry, turbidimetry, and Raman scattering (Chapter 14) are examples of analytical techniques that rely upon scattered radiation. The wavelength of the scattered radiation is identical to that of the incident radiation in nephelometry and turbidimetry. The wavelengths are not identical during Raman scattering.

The ratio of the speed of electromagnetic radiation in a vacuum to the speed of radiation of the same wavelength in a sample is the refractive index of the sample. The refractive index is usually determined by measuring the extent to which the direction of travel of the radiation is altered as it enters the sample. Because the refractive index is a characteristic of a substance, refractometry (Chapter 15) can be used for analysis.

During analyses that use photoacoustic spectroscopy (Chapter 13) chopped incident radiation in the infrared, visible, or ultraviolet region is absorbed by a sample in an enclosed space. A portion of the absorbed radiation is converted to heat that warms the gas adjacent to the sample. The resulting pressure waves in the gas are monitored with a microphone or other device. The incident radiation is chopped at a frequency that is characteristic of the measured sound waves.

The remaining spectral methods of analysis are divided according to the energy of the radiation that is used for the assay. Assays can be performed using radiation in the ultraviolet-visible (Chapters 6 to 11 and 13 to 15), the infrared (Chapter 12), the radiofrequency (Chapter 16), the microwave (Chapter 17), and the thermal (Chapter 27) regions. Absorbance measurements can be made in each of the regions. Fluorescent measurements are usually restricted to excitation in the x-ray and ultraviolet-visible regions. Phosphorescent measurements normally are used to assay polyatomic species after excitation in the ultraviolet-visible region. Nephelometry and turbidimetry generally involve measurements in the visible region. Raman scattering occurs in the ultraviolet-visible region.

Electron spin resonance spectroscopy uses electromagnetic radiation that is in the microwave region of the spectrum. Nuclear magnetic resonance spectroscopy uses electromagnetic radiation in the radiofrequency region. Any

of several methods using thermal radiation can be utilized. The energy, wavelength, and frequency ranges for each type of electromagnetic radiation are listed in Chapter 5. The spectral methods of analysis and the chapter in which each method is described are listed in Table 1-1.

Table 1-1 A list of the major spectral methods of chemical analysis and the chapter in which each method is described

Method	Chapter
Atomic absorption n	6
Atomic fluorescence and ionization	7
Flame and atomic emission	8
Ultraviolet-visible absorption by polyatomic species	9
Chemiluminescence and electrochemiluminescence	10
Fluorescence and phosphorescence	11
Infrared absorption	12
Photoacoustic spectrometry	13
Scattering	14
Refractometry	15
Nuclear magnetic resonance	16
Electron spin resonance	17
X-ray methods	18
Electron spectroscopy	19
Radiochemical methods	20
Thermal analysis	27

ELECTROANALYTICAL METHODS

Those instrumental methods of chemical analysis in which either an electrical signal is applied to one of the electrodes dipping into the sample solution or an electrical property of the solution is measured are the electroanalytical methods. Most electroanalytical techniques apply an electrical signal while a different electrical parameter of the solution is monitored. The electroanalytical methods are divided into categories, as shown in Fig. 1-2, according to the type of electrical measurement that is made and type of applied electrical signal.

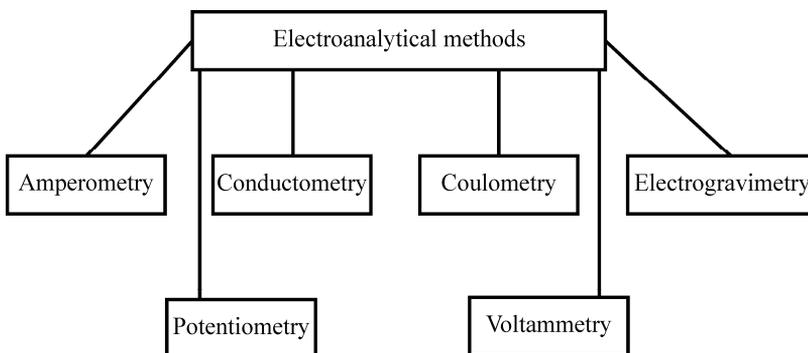


Figure 1-2 The major categories of electroanalytical methods.

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During analysis with most of the electroanalytical methods, electrical contact with the sample is completed by dipping at least two electrodes into the solution. Amperometry is the method in which the potential between the two electrodes is controlled and the current is measured. When the current between the electrodes is controlled (usually at nearly zero) and the potential is measured, the technique is potentiometry.

During electroanalytical studies using coulometry and electrogravimetry, either a potential or a current can be applied to the electrodes in the solution. When the quantity Q of electricity that is consumed during an electrochemical reaction is measured, the technique is coulometry. When the mass of a reaction product (often a metal) after an exhaustive electrolysis is measured, the method is electrogravimetry. Because a separation occurs when the assayed metal plates onto one of the electrodes, electrogravimetry also can be classified as a separative method of chemical analysis.

Conductometry is the electroanalytical method in which the electrical conductance G of the sample solution is measured. Conductance is defined as the inverse of the electrical resistance. Normally an alternating electrical potential is applied to the electrodes during the measurement.

Voltammetry is the technique in which a potential is applied to one of the electrodes by a potentiostat while the current flowing through the electrode is measured. During the current measurement the potential is varied in some predetermined manner. The many types of voltammetry differ in the way in which the applied potential varies. All of the electroanalytical methods with the exception of potentiometry are described in Chapter 23. Potentiometry is described in Chapter 22.

SEPARATIVE METHODS

The separative methods take advantage of physical or chemical properties of the components of a mixture to separate the components. After the separation, the components can be individually assayed either qualitatively or quantitatively.

Sometimes the separating instrument simultaneously performs the separation and the assay. In other cases the separation is done prior to an assay by another method.

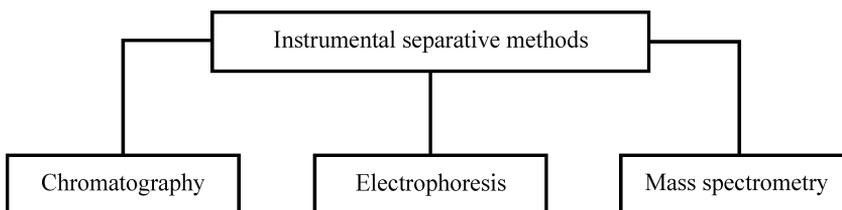


Figure 1-3 The major categories of separative methods of chemical analysis.

Among the noninstrumental separative methods are distillation, extraction, precipitation, filtration, osmosis, and reverse osmosis. Because descriptions of those methods normally are included in other courses, they are not described in the text. The instrumental separative techniques are divided into categories, as shown in Fig. 1-3, according to the method used to effect the separation.

Chromatography is the method by which a mixture is separated into its components as a result of the relative ability of each component to be flushed along or through a stationary phase by a mobile phase. The sample is placed on the edge of the stationary phase (a solid or liquid) and a mobile phase (a liquid or gas) is allowed to flow over the stationary phase and to sweep the sample along the length of the stationary phase. Components which more strongly adhere to the stationary phase are swept less rapidly along the length of the stationary phase than are those components that less strongly adhere to the stationary phase. The result is a separation of sample components in space at a fixed time after the start of the separation, or a separation in time at a fixed distance along the length of the stationary phase. Chromatography is divided into liquid chromatography and gas chromatography, depending upon the state or nature of the mobile phase. Further subdivisions of liquid and gas chromatography are commonly used and are described in Chapters 24 through 26.

Electrophoresis is the separative method that takes advantage of the relative mobility of ions toward an electrode of opposite charge (to the ion) and away from an electrode of similar charge. The buffered solution through which the ions normally travel is either supported by porous paper or is in a gel. Because highly mobile ions move farther toward the electrode of opposite charge than less mobile ions, a separation occurs. Electrophoresis is described in Chapter 25. Because electrophoresis requires application of an electrical signal, it is sometimes classified as an electroanalytical method.

Separations using mass spectrometry are based upon the relative motion in an electrical or magnetic field of the components of a gaseous mixture of sample ions. The electrical or magnetic field causes the ions to move in different paths or at different velocities. The relative motion of each ion is dependent upon the mass-charge ratio of the ion. Mass spectrometry can be used either alone or in combination with some other analytical technique, such as gas or liquid chromatography. Mass spectrometry is described in Chapter 21.

COMPUTERIZATION AND AUTOMATION

Computers that are interfaced to or a component of analytical instruments are commonly used for data treatment and to control operation of the instrument. The use of computers in the analytical laboratory has significantly reduced the time that must be spent on each analysis by the analyst. An introduction to the use of computers for chemical analysis is included in Chapter 28.

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In many instances routine analyses can be performed more accurately and more rapidly by automating the apparatus that are used for the analyses. The results from automated analyses of an industrial process can be used to automatically control the process. Process-control apparatus usually operate in one of two fashions. Either the apparatus automatically samples a product of the industrial process and adjusts one or more of the variables in the process, so as to keep the product within specifications, or it samples one variable of the process while controlling a second variable. Process-control apparatus is especially useful when judgments must be made rapidly or when the sampling or control process is unsafe.

In addition to automating analytical instruments, laboratory robots can be used to perform many of the tasks that have traditionally been performed by human analysts. Regardless of the method of automation, modern automated laboratories are often controlled by computers. Laboratory automation and process control are described in Chapter 28.

CHOOSING AN ANALYTICAL METHOD

A wide array of analytical methods are available to the analyst. In most cases more than one instrumental method can be used for a particular assay. Among the factors that should be considered when choosing an analytical method are:

1. The type of readily available instrument
2. The experience of the analyst in using a particular instrument
3. The expected concentration range within which the sample falls
4. The required precision and accuracy of the assays
5. Potential interferences in the assays
6. The number of samples that must be assayed with the instrument
7. The rate at which the results must be obtained
8. The expense of each assay and the entire analysis

While reading the text it is useful to keep in mind the preceding eight points.