

## PHYSICS AND ANALYSIS INSTRUMENTS

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Instrumental analysis is the science of identifying or resolving mixtures or complex substances into their component parts, through determination of specific physical properties. Most methods of instrumental analysis are based on the principles of classical general physics, but probably most of their applications are in chemistry, biology, and medicine.

Any instrument for determining any physical property might be used as an analysis instrument, but in practice the term is usually reserved for a group of instruments whose principal use is in determining specific physical properties for analytical purposes.

### METHODS OF OPTICAL ANALYSIS

Perhaps no better example of a specific physical property determination can be cited than flame photometry. The spectator on July 4th will admire the rich red flame from the flares without realizing that the color is produced by the element strontium. The student of physics or chemistry may recognize the more brilliant but less vivid green as produced by barium, and the white stars from the rockets as such less active materials as iron or clay. Even the student chemist is familiar with flame tests, but perhaps without realizing entirely what they mean.

To the spectroscopist, the color of the radiation produced by an incandescent material is an indication of the molecular activity produced by exciting (through heat) the components of that material. Figure 1 portrays the emission characteristics of a few elements excited in a flame. Barium, for example, displays a continuous spectrum, most intense in the green; to the eye, therefore, it is brilliant and greenish. Strontium shows only a short section, in the red; it appears more vivid in color (less admixed with white) but less brilliant than barium. Sodium, with a visible spectrum concentrated in two lines very close together, is a distinctive yellow to the eye, and conspicuous in a spectrogram. Materials which are less easily excited by the relatively low temperature of the flame (clay, for example) emit a continuous spectrum and appear yellowish white.

The flame photometer can be made to give quantitative as well as quali-

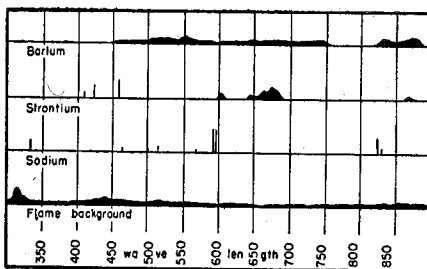


FIG. 1.

tative information, using comparative methods. That is, the intensity of radiation at appropriate wave lengths indicates relative quantities of material being excited into radiation. The instrument is "calibrated" with solutions of known concentrations; then, if both the flame and the rate of addition of sample are uniform, quantitative analysis is possible.

A flame photometer, therefore, comprises a burner to activate samples, a spectrum-analyzing device such as a prism, diffraction-grating or interference-filter assembly, and a device for measuring the intensity of the selected spectrum range.

Where extremely high temperatures are required to excite molecular activity, spark or arc excitation is used, and the spectral intensities are often recorded on a photographic plate.

Activity can also be induced in many molecules by applying light; at certain frequencies (colors) energy will be absorbed by the sample, indicating that corresponding molecular activity is taking place. The optical transmission of the specimen is ordinarily plotted against frequency; this is spectrophotometry—a very powerful method of analysis.

Colorimetry, involving low rather than high spectral resolution, differs from spectrophotometry in that white light is applied to the specimen, with color filters used to isolate certain portions of the spectrum; typically, a set of tri-color filters, each permitting roughly one-third of the visible spectrum to pass, is used. The data is expressed in terms of these filter characteristics. Such measurements are more used in de-

scribing appearance (as in matching pigments, paints, etc.) than in determining composition; they do not usually attain the sensitivity of spectrophotometric instruments—largely because their measurement is that of a small difference in a relatively large quantity. The use of monochromatic light (in the spectrophotometer) greatly increases sensitivity, resolution, and accuracy.

Another group of optical methods is based on other than spectral characteristics. Polarimetry (or saccharimetry) is a standard method for determining the concentration of sirups or sugar solutions (and the type of sugar) by the rotation of the plane of polarization of the light passing through the sample.

Nephelometric or light-scattering methods are valuable for quantitative chemical analysis, measurement of size of small solid particles (for example, Portland cement) and turbidity of solutions, and detection of contaminants in suspension in solutions; a special application is in the determination of actual size and shape of molecules. Related methods are used for analyzing suspensions, making blood-cell counts; and the like.

Measurement of refractive index, reflection characteristics, and other optical characteristics are useful in the study of both solid and liquid samples.

The history of these methods may be of interest. Nephelometry originated in the work of John Tyndall, 90 years ago, in his study of suspended particles in the atmosphere. Spectrophotometry was born, probably, in the early 1800's, with Wollaston's observation and Fraun-

hofer's classification of the absorption lines in the sun's spectrum. The polarimeter was used in sugar refineries in 1842, by sugar growers in 1863, and in 1883 received governmental sanction in tariff assessment. But it is only in the last 20 to 30 years that methods of instrumental analysis have been highly developed.

Another method based on optical concepts (involving absorption of radiant energy) is fluorimetric analysis. In this technique, a sample is irradiated with ultraviolet, exciting certain of its molecules and producing visible light. The intensity of the light is measured, and perhaps analyzed, with the spectrophotometer. The method is especially valuable in detecting very small amounts of radioactive material in biological samples, as it is extremely sensitive. It can easily detect impurities in all except the best grades of reagent chemicals.

Other optical methods include: the electron microscope, which not only permits observation at extreme magnification but also actual analysis in some instances; X-ray and electron diffraction methods, which measure intercrystalline lattice dimensions by using the crystalline material as a diffraction grating traversed by radiation of known wave-length; and the field emission microscope, which produces actual images of molecular structures.

Microscopic techniques in general are highly developed; for example, spectrophotometric analysis can be made on single cells, permitting study of cell structure and growth in a manner beyond the imagination a generation ago.

#### METHODS FOR THERMAL ANALYSIS

These are many and varied. Vapor pressure of microsamples of solutions is determined by minute differences in temperature between sample and standard solutions. Mechanical properties may be studied through coefficients of thermal expansion, transmission, etc. Mixtures of crystalline materials may be resolved by thermal analysis—change of state being indicated by differential temperature measurements over wide ranges. Gas analysis by thermal conductivity is standard in many fields.

#### MECHANICAL ANALYSIS METHODS

Variations in hardness over a wide area or within a single crystal can be measured. The absorption of vibrational energy in an elastically loaded specimen may disclose defects, or it may be used to determine the mechanical properties of the material. One primary advantage of most instrumental analysis methods is that they do not destroy the sample. Measurements of viscosity can show the behavior of a liquid in its handling and normal use, and combined with other measurements can provide information as to essential molecular structure. Particle-size classification may be made by sedimentation and elutriation.

#### ULTRASONIC METHODS

The relatively new group of methods employing high-frequency sound transmission, though mechanical in nature, deserves a classification of its own. In addition to their use in preparation and treatment of materials, high-frequency sound meth-

ods are used to determine viscosity of liquids, composition of gases, concentration of vapors, and the soundness or strength properties of solids. They are of special value since they can produce a continuous indication of the property, rather than intermittent values from individual samples.

Already listed, then, are methods based on light, heat, mechanics, and sound; the other classical fields of physics are electricity and magnetism—and they include many such methods.

#### METHODS OF ELECTRO-ANALYSIS

The chemist has an entire series of electrometric and magnetometric methods, many of them combined with other techniques. The magneto-optic and electro-optic effects (rotation of the plane of polarization of light when an electric or magnetic field is applied) are not much used in laboratory instrumental analysis, but are of great value in pure research, especially in the structure of matter. (Historically, the Zeeman effect was of the greatest importance in the formation of the electron theory of matter.)

Magnetometric analysis—analysis based on the magnetic properties of matter—involves several different phenomena. Magnetic susceptibility, magnetic permeability, coercivity, and para- and dia-magnetism are the properties perhaps most important. (Ferromagnetic materials are usually placed in a class alone.)

Magnetochemistry is based on the fact that all materials are magnetic to some degree, although in general very much less so than the ferromag-

netic materials commonly termed "magnetic." Gases as well as liquids and solids display the property; there are available commercial instruments for oxygen analysis based on this fact. Concentrations of solutions can often be measured by their magnetic susceptibility, correcting for the contained water.

For the rare earths, the customary quantitative analysis procedures are not satisfactory. Determinations by magnetic susceptibility measurements are practical; measurements are made at different temperatures and pressures, and at various field strengths.

Also employing magnetic principles is the mass-spectrometer, in which a beam of atoms is accelerated by an electric field through a transverse magnetic field. Since their deflection by the magnetic field is in inverse proportion to their mass, the different atoms are separately collected. The mass-spectrometer has been used to prepare extremely pure material, as in separating isotopes.

Among the methods of electroanalysis, polarography and amperometric analysis are most widely used. These methods employ a cell containing the test solution and fitted with suitable electrodes, a source of current, and a recording or indicating device by which the current is plotted against the potential. Frequently a dropping-mercury electrode is used, with a current such that complete polarization of the mercury drop occurs as each drop is formed, and a fresh surface appears as each drop falls. In this condition, the electrode potential alternates between that of the polarized and the unpolarized condition,

and as the applied voltage is varied the electrode potential record displays a series of steps. From the shape of these steps, the solution composition may be determined. Extremely dilute solutions can be used; thus microsamples can be analyzed.

Determination of conductance, dielectric constant, and loss-factor of chemical solutions are measurements of electrical parameters and are accomplished by the usual laboratory methods, with any modifications required by the application. They are used for determining the essential characteristics of compounds, for quantitative analysis, and for industrial control. For example, in many steam power plants the conductance of the boiler water is continually measured to insure that scale will not form, and in ocean-going vessels the surrounding seawater may be continually measured to control the evaporators. In biological research, measurements can be made on suspensions of living cells, and by using high-frequency current for the measurement, the conductance of the interior of the cells may be found, without the insulating effect of the cell walls.

One of the most widely-used instruments for electroanalysis is the "pH meter," an instrument for determining the acidity or basicity of solutions. A classic method uses "indicators," which are usually weak organic acids having distinctive colors changing in the salt form. While there are one or two indicators having extremely wide ranges of operation, usable in a wide variety of conditions, most careful work employs electrical methods for determining the hydrogen-ion concentration.

TABLE 1.—Principal Methods of Instrumental Analysis.

1. Optical methods
  - A. Involving high spectral resolution:
    - Spectrophotometry, spectrography, etc.
  - B. Involving low spectral resolution:
    - Colorimetry, etc.
  - C. Involving other operating characteristics:
    - Refractometry, polarimetry, fluorimetry, nephelometry, etc.
  - D. Related methods:
    - Electron microscopy, X-ray and electron diffraction, field emission microscopy.
2. Thermal methods
  - A. Differential thermal analysis:
    - Vapor pressure, change of state, etc.
  - B. Thermal conductivity (analysis of gases, liquids, solids).
3. Mechanical methods
  - A. Static mechanical methods:
    - Hardness, etc.
    - Strength properties.
    - Density, etc.
  - B. Dynamic mechanical methods:
    - Sonic methods.
    - Viscosimetry.
    - Sedimentation, elutriation, etc. (Stokes' Law).
    - Centrifugation.
    - Solvent chromatography.
4. Electrical and magnetic methods
  - A. Magneto-optic and electro-optic effects.
  - B. Magnetometric analysis:
    - Magnetic susceptibility.
    - Magnetic permeability.
    - Coercivity.
    - Para- and dia-magnetism.
  - C. Mass-spectrometry.
  - D. Polarography and amperometric analysis.
  - E. Conductance, dielectric constant.
  - F. Gyromagnetic phenomena.
  - G. Electrometric pH measurement.
  - H. Radiation measurement.
5. Chromatography, electrophoresis, ion exchange, and differential migration methods.

Available instruments permit making continuous pH measurements (even flowing in pipelines) for controlling value and for determining reaction end-points.

Measurement of radiation itself is more strictly electrical in nature. Any penetrating radiation—whether of the high-energy particles emitted by radioactive materials, visible light, ultraviolet, or infrared—can be measured by electrical means.

Radioactive particles are usually detected by their effect in ionization chambers, or in proportional or Geiger-Mueller counters. They may actually be counted or their effect (their rate of arrival) displayed as a meter indication. Since their behavior varies from type to type, instruments may be made to establish their type as well as their number.

The use of such devices for detecting radioactive material is well known, but some of the subsidiary uses are less well known—for example, determination of age of archeological finds by measuring contained radioactivity. Objects several thousand years old are dated with fair accuracy.

One other technique for instrumental analysis should be mentioned before closing a necessarily incomplete list—electrophoresis and chromatographic analysis. Chromatography is not especially new; it originated with Day in 1900 and Tswett

in 1902. But it is still one of the most active fields for research, with its various modifications.

Simply stated, chromatography is the separation of a solution or mixture into its constituents by passing it through an absorbent column of some sort, so that by differential migration and absorption the various components become segregated at different locations. There are many different methods, suited to different materials and degrees of separation. Instead of solvent flow to cause migration, electric potential may be used; this is especially suited to separation of certain proteins, and is called electrophoresis. An analogous method is centrifugation, by which components differing slightly in density can be separated. These methods of separation are often combined with other analytical methods to determine the characteristics of the segregated material.

Many of the methods of instrumental analysis depend upon concepts which receive no emphasis in undergraduate courses in physics and are perhaps unfamiliar to the student. Without attempting to discuss these concepts in detail, it might be possible to add some leavening to the physics curriculum—even in high school—and add interest to it, as well as to present a more detailed picture of what is one of our most active fields of physical science.