A Unifying Description of Modern Analytical Instrumentation within a Course on Instrumental Methods of Analysis

ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · NOVEMBER 2004

Impact Factor: 1.11 · DOI: 10.1021/ed081p1767

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A Unifying Description of Modern Analytical Instrumentation within a Course on Instrumental Methods of Analysis

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The development of curricula presenting modern chemical instrumentation becomes increasingly difficult as new techniques are introduced. This is compounded by a growing trend among instrumentation manufacturers to develop modern instrumentation as various "black boxes" with increased computer control of operation parameters. A description of each technique with its associated theory, instrumentation design, and application becomes increasingly difficult with a one-semester instrumental methods of analysis course. Generally, textbooks for these courses have been organized by technique with sections devoted to atomic and molecular spectroscopies, electroanalytical methods, mass and surface spectrometry, and separation and chromatographic techniques *(1–4)*. Additional sections have also been included pertaining to basic electronics and signal-to-noise enhancement methods used in modern analytical instrumentation *(1–5)*. Alternately, Strobel and Heineman *(5)* have presented a modular approach to chemical instrumentation in which a module is considered as a grouping of components for the performance of a specific function.

A unifying theme has been used at New Mexico State University to present this course material. It involves the description of all analytic instrumentation as comprising five discernable modules in terms of their general function in each technique. These modules have been labeled as (i) the source, (ii) the sample, (iii) the discriminator, (iv) the detector, and (v) the output device. The components of a variety of analytical intruments can be divided among the five modules as seen in Table 1. This modular approach to instrumentation can be further illustrated with schematics of flame atomic absorption, ion chromatography, and mass spectrometry, as seen in Figures 1–4, respectively. It should be noted that the detector and output modules in this approach can be further treated using the concept of data domains (i.e., analog,

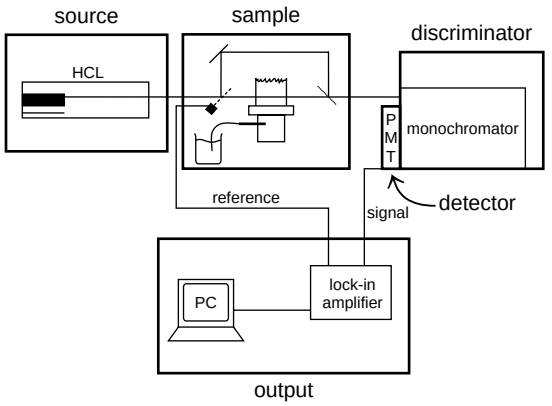

Figure 1. A schematic diagram depicting an atomic absorption spectrometer incorporating a flame atomizer identifying each of the five common modules.

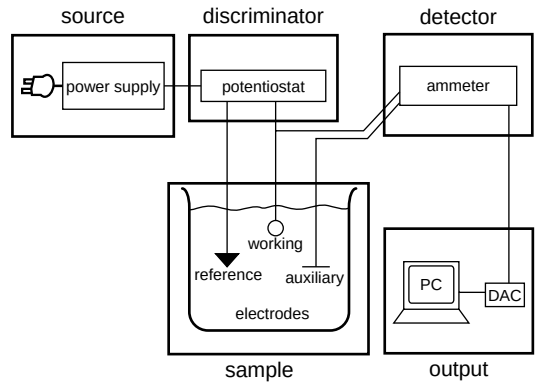

Figure 2. A schematic diagram depicting an electrochemical amperometric detection system showing the five common modules.

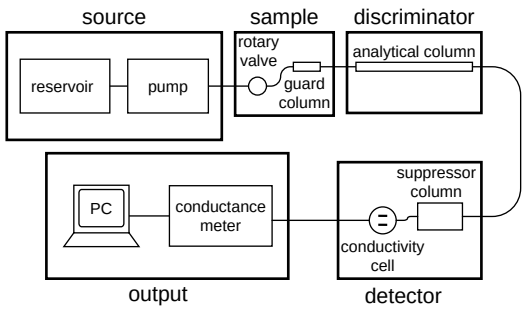

Figure 3. A schematic diagram depicting an ion chromatograph using a conductivity detector illustrating the components of each of the five common modules.

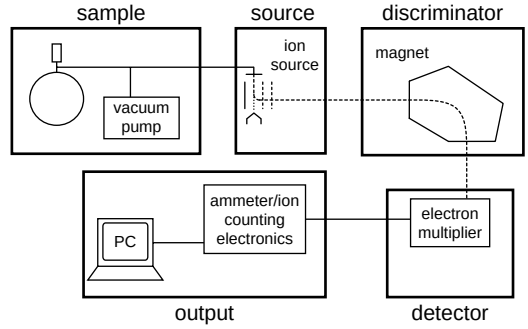

Figure 4. A schematic diagram depicting a magnetic-sector mass spectrometer with electron-impact ionization and an expansion chamber for sample introduction showing the five common modules.

Table 1. Listing of Components in Each Module for a Variety of Analytical Instrumentation

Instrumental Method	Source	Sample	Discriminator	Detector	Output
Molecular absorption	D_2-arc lamp, W-lamp, W/halogen lamp	Solution cuvette, test tube, flow cell, remote	Monochromator, interference filters	Phototube, PMT, photodiode array, CCD array	Strip chart recorder, digital display, computer with DAC
Molecular fluorescence	Xe-arc lamp, laser	Solution cell, remote sample, flow cell	Monochromator, interference filters	PMT PDA, CCD array	Strip chart recorder, digital display, computer with DAC
Atomic absorption	HCL, EDL	Nebulizer/spray chamber, flame, Quartz tube, graphite tube furnace	Monochromator, interference filters	PT, PMT, PDA, CCD array	Strip chart recorder, digital display, computer with DAC
Atomic emission	ICP, flame, DCP, DC-arc, spark, focused laser beam (LIBS), glow discharge	Nebulizers, spray chambers, solution, powders, conducting solids, insulating solids	Monochromator, polychromator, interference filters	PMT, PDA, CCD	Strip chart recorder, digital display, computer with DAC
Infrared absorption	Nernst glower, Globar, Nichrom wire	Neat liquid, solution, Nujol mull, KBr pellet, ATR cell	Monochromator, Interferometer, interference filters	PbS, Golay detector, thermocouple	Strip chart recorder, digital display, computer with DAC
Raman scattering	Laser	Solution cell, solids	Spectrograph, double monochromator, Interferometer	PMT, CCD	Strip chart recorder, digital display, computer with DAC
NMR	RF generator	Solutions, liquids, solids	Magnetic field	RF receiver	Computer
ISE, Potentiometry	Reference electrode	Solutions	Electrode membrane	Voltmeter	Strip chart recorder, digital display, computer with DAC
Voltammetry	Power supply	Solutions	Potentiostat and reference electrode	Auxiliary electrode	*x-y* recorder, digital display, computer with DAC
GC	Pressurized gas cylinders and pressure regulator	Syringe with septum and injection oven	Column and column oven	FID, TCD, ELCD, PID, ECD, etc.	Strip chart recorder, digital display, integrator, computer with DAC
HPLC	Solvent reservoirs and high pressure pump	Rotary injection valve and sample loop	Column	RI, UV, fluorescence, EC, etc.	Strip chart recorder, digital display, integrator, computer with DAC
Ion chromatography	Solution reservoirs and pump	Rotary injection valve and sample loop	Column of ion exchange resin	Suppressor column and conductivity detector, UV, fluorescence, etc.	Strip chart recorder, digital display, integrator, computer with DAC
Capillary electrophesis	Buffer reservoir	Pressure or electroosmotic flow injection	Column, high electric field	UV, fluorescence, potentiometry, voltammetry, etc.	Strip chart recorder, digital display, integrator, computer with DAC
X-ray photoelectron spectroscopy (XPS or ESCA)	X-ray tube	Sample surface in vacuum chamber	Electron energy analyzer	Faraday cup, electron multiplier	Strip chart recorder, digital display, computer with DAC
Auger electron spectroscopy	Electron gun	Sample surface in vacuum chamber	Electron energy analyzer	Faraday cup, electron multiplier	Strip chart recorder, digital display, computer with DAC
Mass spectrometers	Electron impact ionization, chemical ionization, field ionization, field desorption, MALDI, electrospray ionization	Septum with expansion volume and needle valve, direct insertion probe, GC column, LC column	Magnetic field, electric and magnetic fields, accelerating potential, quadrupole electric field	Faraday cup, electron multiplier channeltron, image current	Strip chart recorder, digital display, computer with DAC
ICP–MS	ICP	Nebulizer/spray chamber, graphite tube furnace, laser ablation	Magnetic field, electric and magnetic fields,accelerating potential, drift tube, quadrupole electric field	Faraday cup, electron multiplier channeltron, image current	
GC–MS		Gas chromatography		Mass spectrometer	
LC–MS		Liquid chromatography		Mass spectrometer	

digital, and time) as initially described by Enke *(6)*. In Enke's discussions, instruments were described in terms of data domain conversions and were then illustrated using a domain converter classification map; the chemical or physical information pertaining to a sample (e.g., its composition) was converted to one or more data domains to become a measurable quantity (i.e., a scale position or a number). That same author has more recently extended this approach to use differentiating characteristics to discuss analytical methods *(7)*.

The five module concept is coupled with an understanding of the limited number of quantities that can be measured directly without subsequent calculations. These include (i) voltage (electrical potential), (ii) current, (iii) length, and (iv) time (or frequency). It is therefore a requirement of any analytical instrument to encode the desired analytical information regarding a sample (e.g., the concentrations of one or more analytes) and convert it into one of any combination of these measurable quantities or data domains *(6)*. The reduction of an analytical measurement to some combination of these quantities can assist the students' understanding of the operation of any instrumental technique and the propagation of inherent uncertainties in any determination.

A simple example is often provided regarding the "measurement" of temperature. The use of a mercury thermometer involves the measurement of the *length* of a column of mercury on a calibrated scale that allows its conversion to units of temperature. Alternately, the use of a thermocouple involves the measurement of an *electrical potential* arising from the junction of two dissimilar metals relative to a reference junction. Thus, it is the uncertainties associated with those actually measured quantities (e.g., length) that often determine the accuracy of the desired quantity (i.e., temperature).

Source

The most easily conceptualized examples of this module are found in spectroscopic instrumentation that requires a source of incident radiation (Figure 1). These techniques include the absorption of electromagnetic radiation (γ-rays through radio frequencies in Mössbauer to NMR spectroscopies, respectively). However, techniques involving elastic scattering would involve similar forms of sources (e.g., turbidimetry measurements).

Similar to the techniques that use radiation to promote analytes to an alternate spectroscopic state, amperometric techniques require a "source" of electrons to alter the oxidation states of the targeted analytes (Figure 2). Chromatographic techniques require as a "source" a supply of a mobile phase and a means for its delivery. Thus, the cylinder of pressurized gas and pressure regulators would comprise the source in gas chromatography instrumentation while the reservoirs of liquid mobile phase and pumps would be included in the source for liquid chromatographs (Figure 3).

The identification of the source in mass spectrometry is directed to the methods of ion production. Modes of ion production can be discussed; the similarities emphasized and the unique capabilities of each method highlighted. For example, the involvement of an electron source in both electron impact and chemical ionization ion sources can be presented with descriptions of the differences between "hard" and "soft" ionization mechanisms and their effects on the resulting spectra.

Sample

Within every instrument for chemical analysis, the sample to be analyzed must be presented to the device to elucidate some aspect of its chemical composition. Often this is as simple as a beaker containing the sample solution in the case of potentiometric measurements using an ion selective electrode or as complex as a liquid chromatograph for a mass spectrometer. Table 1 lists many different sample components of several instrumental methods for analysis. These include sample cuvettes used in molecular absorbance or fluorescence measurements to nebulizers, spray chambers, and electrothermal vaporizers (i.e., graphite furnaces) used in atomic spectroscopy.

In conjunction with the sample are the components required for its introduction into the instrument. Thus, a gas chromatograph includes, as components of its sample "module", the syringe used in the withdrawal of a small volume of the sample, the septum assembly, and the injector heater for the rapid volatilization of the sample prior to its introduction to the column. With capillary columns, a sample splitter is added to this list. Instrumentation for differential light detection and ranging (differential LIDAR or DIAL) measurements includes the laser beam projection and return light collection optics in the list of components of the sample module. An HPLC includes a rotary injection valve and sample volume loop as its sample component. The sample component of a mass spectrometer could be as simple as a needle valve outlet from a gas expansion volume or as involved as the interface to a liquid chromatograph.

Discriminator

Once the source has interacted with the sample, the chemical information describing the composition of the sample must be discriminated according to variations in the properties of those interactions and the sample components. This is most easily illustrated for a molecular absorption spectrometer. After the incident radiation of multiple wavelengths is imaged through a volume of sample solution, the wavelengths of light are separated through the use of a spectrometer or monochromator. The use of monochromators for the discrimination of wavelengths of light can then be the basis for discussions of optical imaging, diffraction, and the wavelength dependence of refraction.

Conceptually, a Michelson interferometer used in FT-IR spectrometers is an alternate method for the discrimination of wavelengths of light. With its introduction, the concept of constructive interference can be presented along with the physical processes involved in interference filters. Similarities in the discriminator component in FT-IR and FT-Raman spectrometers illustrates how the same component is used in instruments based on different interactions while providing complementary information about the sample.

The movement of ions within applied fields (or their absence) can then be addressed in discussions of means by which ions can be discriminated based on their mass-to-charge ratio in mass spectrometers and electron spectroscopy techniques. By concentrating on the different separation mechanisms for ions produced in various sources, it is possible for the students to understand the similarities and dif-

ferences in how each system is able to achieve that separation. For example, a comparison of systems based on ions with the same kinetic energy (e.g., time-of-flight and sector instruments) can be contrasted with separation devices not dependent on the initial kinetic energy of the ions (e.g., quadrupole filters and traps).

Interactions of analytes with the stationary phase in chromatographic separations enables these components of a sample to be discriminated as they move through the analytical column in GC, LC, SFC, or IC. Variations in stationary phases and column design can then be addressed in terms of the requirements of the separation undertaken by each technique. This can then be contrasted with the mechanisms of separation occurring in capillary electrophoresis and electroosmotic mobility.

Detectors

A critical component of any analytical instrument is the device that allows for the conversion of the discriminated parameters into measurable quantities (typically, a current, voltage, or string of discrete events). Detectors can be as simple as a conducting wire or plate connected to electrical ground through some load resistor (i.e., a Faraday plate) for the detection of charged particles (as in mass spectrometry or electron spectroscopic techniques) or as involved as a Fourier transform infrared spectrometer (for the detection of species in the effluent of a liquid chromatograph). The characteristics of a detector will be determined by the properties acted on by the discriminator. Thus the separation of light by a monochromator requires the use of a photo-responsive detector (e.g., a photomultiplier tube or a charge injection device) while solutes separated by a gas chromatography column may require either their conversion to an ion (as in a flame ionization detector) or the interruption of the flow of charged species (as in an electron-capture detector).

Output Devices

Once the analytical information has been converted to one or more of the directly measurable quantities, it is necessary to transform it into a visual form. This is accomplished in a similar manner for most, if not all, modern analytical instrumentation. Amplifiers, recorders (strip-chart or *x*-*y*), multimeters, or computers meet the requirements for an output device. As a result of these similarities, a discussion of the various devices can generally suffice for all types of instrumentation. The general utilization of computers as output devices in modern instrumentation requires the description of analog-to-digital converters (ADCs) for the processing of measured currents or voltages. After the discussion of these output devices, their inclusion in descriptions of instrumentation is then often described as "the usual suspects". It is then inferred that once the form of the measured quantity (i.e., length, time, current, or voltage) has been determined for an analytical technique, any of the appropriate output devices could then be employed.

Applications

This approach has been incorporated within the curriculum of an instrumental methods of analysis course for the past seven years. Student responses have been favorable. Instrumentation descriptions have been incorporated based on the five modules (i.e., source, sample, discriminator, detector, and output). This has allowed the students to concentrate on the chemical and physical processes involved in each analytical instrumental method to gain an understanding of how those interactions enable the determinations to be made. Thus, chromatograms, absorbance spectra, electrophoretograms, mass spectra, and NMR spectra can all be considered as results of different types of discriminators acting on the samples using different sources. An understanding of those differences enables the correct interpretation of each type of data, but the similarities become more apparent. Additionally, the coupling of techniques becomes easier to conceptualize using this approach. Each technique in a hyphenated system simply becomes one of the "modules" for another technique (e.g., the gas chromatograph in a GC–MS can be considered as the sample component of a mass spectrometer and the mass spectrometer can be treated as the detector for the gas chromatograph). Discussions of hyphenated techniques then concentrate on the methods used to couple the two (or more) instruments, for example the use of electrospray ionization for coupling a liquid chromatograph with a mass spectrometer.

Often the end of the course allows the discussion of recently developed analytical instrumentation. These discussions have been streamlined through the identification of each of the five modules and the unique characteristics of each module for that technique. Through this approach to understanding the operation and design of analytical instrumentation, the students appear to be better equipped to apply these most recent advances in measurement science.

It should be noted that although the five components have been presented in the order of source, sample, discriminator, detector, and output, the actual components may not be physically present in that order. An example of this is a scanning UV–vis absorption spectrometer where the discriminating monochromator is often placed prior to the sample cell. Alternately, the source can follow the sample module (as illustrated in Figure 4 for a magnetic sector mass spectrometer with electron-impact ionization). Additionally, a single physical component within an instrument may serve as more than one module in this approach as with voltammetric methods where the working electrode is part of both the detector and discriminator modules (in conjunction with the auxiliary and reference electrodes, respectively). Regardless, the functions of the components within each instrument can be categorized using this description.

Summary

The present article describes a unifying modular approach to the description of modern instrumentation used in analytical measurements. Through the identification of the five modules (i.e., the source, sample, discriminator, detector, and output) for any analytical instrument, discussions pertaining to the different physical and chemical interactions can be better directed towards the similarities and differences in the actual methods.

Acknowledgments

The author thanks the many students who have been involved in the development of this approach and the many graduate students who were required to "rethink" many of the instruments used in this course. The helpful suggestions of Frank V. Bright at the State University of New York at Buffalo are also gratefully acknowledged.

Literature Cited

1. Skoog, D. A.; Holler, F. J.; Nieman, T. A. *Principles of Instrumental Analysis,* 5th ed.; Harcourt Brace & Co.: Philadelphia, PA, 1998.
2. Willard, H. H.; Merritt, L. L., Jr.; Dean, J. A.; Settle, F. A., Jr. *Instrumental Methods of Analysis,* 7th ed.; Wadsworth: Belmont, CA, 1988.
3. Settle, F. A. *Handbook of Instrumental Techniques for Analytical Chemistry;* Prentice Hall: Englewood Cliffs, NJ, 1997.
4. Analytical Sciences Digital Library Home Page. *http://www.asdlib.org/* (accessed Sep 2004).
5. Strobel, H. A.; Heineman, W. R. *Chemical Instrumentation: A Systematic Approach,* 3rd ed.; John Wiley and Sons: New York, 1989.
6. Enke, C. G. *Anal. Chem.* **1971,** *43,* 69A–80A.
7. Enke, C. G. *The Art and Science of Chemical Analysis;* John Wiley and Sons: New York, 2001.