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ANALYTICAL INSTRUMENTATION: CAVEAT EMPTOR

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Twenty years ago instrumentation in chemistry laboratories consisted of a balance, bunsen burner, and perhaps a colorimeter. A really well equipped laboratory might also possess a Beckman DU Spectrophotometer. That description is a far cry from today's situation where the analytical chemist has a large number of techniques available to him (see Table I). The cost of instrumentation that is based on these techniques ranges from a few tens of dollars for such things as indicating columns, to a few hundreds of dollars for such things as pH meters and specific ion meters, to tens of thousands of dollars for such things as atomic absorption and x-ray fluorescence instruments, to over 100,000 dollars for such things as spark source mass spectrographs, electron spectrometers for chemical analysis and combination gas chromatograph mass spectrographs. It is even possible to spend more than a million dollars on such techniques as neutron activation analysis, since a nuclear reactor is required, or on techniques that utilize the beam from an accelerator. It is hard to find any other commodity that covers such a large price range.

Not only is there a large variety of instrumentation covering a large price range, but in addition instruments that depend on the same operating principle are undergoing rapid evolution. Comparison of the early instrumentation for flame photometry with the automated inductively coupled plasma of today that tabulates concentrations of 20 or more elements in a few minutes is no less dramatic than the comparison of the Wright Brothers first airplane with the present Boeing 747. The makers of analytical instruments should be complimented on the rapid progress that has been made in this field. However, exciting as these developments are, they make the purchase of the right instrument a more difficult job for the analyst.

Unlike the airplane, it is not always easy to tell if the analytical instrument is functioning properly. In many cases the instrument prints out a number that does not truly represent a measure of the parameter that the analyst wanted to determine. One of the challenges in purchasing an instrument is to be aware of such problems, before the deal is closed. The best way to meet this challenge is to be as familiar as possible with the limitations of the technique that forms the basis of operation of the instrument.

Take atomic absorption spectrometers as an example. The basis of operation of this instrument depends on the change in light intensity that results when atoms of the analyte absorb light that corresponds to the energy of ground state transitions. Naturally this means that anything that diminishes the light intensity while the analyte atoms are being injected into the optical path will be read by the instrument as additional atoms of the analyte. This includes such things as molecules that absorb the light in the same spectral region as the analyte and particles that scatter the light. Various manufacturers have various methods of correcting for this effect which are more or less effective. In order to purchase the best instrument for the job the analyst must know how to evaluate the importance of these effects to his particular problem and the effectiveness of instrumental corrections.

The first step then is to define the analytical problem. This is much easier to do if the need is to analyze the same sample type repeatedly (i.e., the quality control of drinking water) than it is if the laboratory is presented a large variety of sample types (i.e., ocean water, industrial effluents and waste water from sewage treatment). No instrument is completely free of sample matrix effects. In fact, the most effective approach may be to carry out extensive chemical pretreatment in order to assure that samples of the same matrix are introduced into the instrument.

The next step is to become aware of the instrumentation that is available to solve the problem. This may be a two way street in that the analytical problem may be defined in different terms depending on the instrumentation available (i.e. it may be advantageous to develop matrix modification methods that will allow utilization of a particular instrument).

One excellent way to quickly become aware of instrumental techniques is to look into a book titled "Instrumentation for Environmental Monitoring," that describes instruments that incorporate almost all of the techniques listed in Table I.[1] In the text of this four-volume work are detailed descriptions of these techniques, and an attempt is made to describe the ultimate detection capabilities and the limitations based on publications in scientific journals. In addition, some promising techniques that have not yet been incorporated into commercial instruments are described.

Commercially available instruments whose operation is based on the techniques discussed in the text are described in detail in the Instrument Notes sections. At the beginning of each section is a table that contains brief instrument descriptions (i.e., model, principle of operation, operating range, cost, etc.). These tables are a type of index for a more detailed description of each specific instrument with one or two pages devoted to each. The information on these pages comes primarily from the product literature. In some cases, performance data on specific instruments are available from other sources. This is also included. These detailed descriptions are of value both to the buyer and seller of instruments. The buyer has a ready source of information concerning the many different techniques and the commercially available instrumentation. The seller has an additional mechanism to bring his product to the attention of the buyer as well as a quick way to compare his product with that of the competition.

Of course, the usual way to decide on the purchase of an instrument is to talk to others who have similar analytical problems, notice advertisements that appear in various journals, obtain product literature from the producers of the instruments and perhaps even see a demonstration of the instrument that seems best suited to the job. The book, "Instrumentation for Environmental Monitoring", can make a valuable contribution to each of these procedures. Discussion with others can be much more fruitful if detailed information is at hand on the principle of operation of the instrument and some of the inherent weaknesses in the technique. The search of the advertisements is less haphazard and less time consuming since the information in the instrumentation survey was compiled from producers listed in the annual directories published by Science, Analytical Chemistry, Environmental Science and Technology, Nuclear News and American Laboratory. In addition, data from these producers is arranged so that corresponding features of different instruments can be readily compared. Familiarity with this material can result in more meaningful instrument demonstrations since sample types can be chosen that reveal the limitations of the instrument.

In the past few years a new consideration has been added to the choice of an analytical instrument. For many applications the sensitivity and precision of the analysis must conform to government regulations. The "reference methods" for water analysis are listed in Table II.[2] Notice that almost all of the approved methods are instrumental methods. As a result of a court settlement known as the "EPA Consent Decree," the EPA is establishing effluent guidelines for 114 organics, 13 metals, cyanide and asbestos.[3] Approved methods have not yet been promulgated, but it seems certain that the reference method for organics will be gas chromatography/mass spectrometry, and the reference method for asbestos will be electron microscopy. It is important to be familiar with this information if instrumentation is being chosen to monitor industrial effluents.

In searching for an analytical instrument, one should avoid any certainty that there is one instrument superior to all others. Each situation is different, and more often than not the best instrument for one situation will not be the best for another.

For example, in the case of UV-vis spectrometers one might think the best instrument would be the one which has the greatest flexibility in terms of scale expansion, choice of readout and wavelength range. However, this flexibility means that the occasional user will spend more time reading the instrument manual to recall the proper operation procedure. Generally, the more flexible the instrument the more complicated it is and the more breakdowns that can occur. Also, more flexible instruments generally require more space; a commodity that always seems to be in short supply. Of course, more flexible instruments always cost more. Other considerations that are specific to the situation are the response of the manufacturer to breakdown (if a service representative is nearby, you will likely get quicker repair service); the presence of others in the vicinity who use the same instrument (they may be valuable in the discussion of problems or they may be able to lend a needed part); how long the instrument had been in production (manufacturers tend to correct problems that become manifest only after the instrument has been used for some time); and attitude of the operator (if he feels some other instrument is much better, he is not likely to get the best performance out of this one).

There is a high degree of competition between instrument manufacturers. Because of this, development of new instruments and improvements of existing instruments has been rapid. Development in many fields of analytical chemistry speed up, not when a new technique is first discovered, but rather when commercial instruments become available so that large numbers of workers can adapt these instruments to many different problems. Instrument manufacturers should feel proud of the rapid instrumental development they have achieved. A disadvantage of this highly competitive situation is that frequently salesmen are under enough pressure that they tend to overstate the usefulness of their instrument and understate its shortcomings.

This situation has its good and bad sides for the analytical chemist. It means he can now purchase equipment that will allow him to greatly improve his analytical capabilities over what it was a few years ago. However, it also means he must be much more aware of the instruments available and the limitations of this instrumentation in order that he not spend his money for performance far below his expectations.

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References

1) Environmental Instrumentation Group, "Instrumentation for Environmental Monitoring", available from Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

2) Code of Federal Regulations 40 CFR 136.3 Jul 78, available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

3) L. H. Keith, W. A. Telliard, "Priority Pollutants: a Perspective View", Environ. Sci. Technol. 13(4) 416 (1979).

TABLE I: Techniques for Chemical Analysis

Inorganic
- Emission spectrographic
  - inductively coupled plasma
  - argon plasma arc
  - atomic fluorescence
  - fluorimitry
- Absorption spectrographic
  - flame atomic absorption
  - flameless atomic absorption
  - cold vapor absorption (Hg)
  - hydride generation (As, Se)
  - ultra violet-visible absorption
- Electrochemical
  - voltametric
  - amperometric
  - anodic stripping voltammetry
  - specific ion electrodes
- Activation
  - neutron
  - proton
  - helium-3
- Others
  - x-ray fluorescence
  - x-ray diffraction
  - electron spectroscopy for chemical analysis
  - spark source mass spectroscopy
  - ion chromatography

Organic
- Chromatographic
  - gas
  - gas chromatography-mass spectroscopy
  - thin layer
  - liquid
  - high pressure liquid
- Spectrographic
  - infrared
  - Fourier transform
  - Raman
  - ultra violet fluorescence
  - nuclear magnetic resonance

TABLE I: continued

Air Pollutants
- Spectrographic
  - correlation
  - derivative
  - ultra violet-visible absorption
  - ultra violet fluorescence
  - non-dispersive infrared
  - non-dispersive ultra violet
  - flame photometric
  - chemiluminescence
  - Fourier transform
- Electrochemical
  - amperometric (coulometric)
  - conductometric
  - voltammetric (electrochemical transducers)
- Other
  - condensation nuclei
  - flame ionization
  - catalytic oxidation flame ionization
  - gas chromatography flame ionization

TABLE II: List of EPA "reference methods" for water analysis[2]

Atomic absorption

Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Au, Ir, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Os, Pd, Pt, K, Rh, Se, Ag, Na, Tl, Sn, Ti, V, Zn, hardness (Ca+Mg)

Colorimetric

B, Si, Benzidine, Cl^-, Cl_2, Color, CN, Hardness, Nitrate, Nitrite, Phenols, Sulfate, Sulfide, Surfactants, Kjeldahl nitrogen, Phosphorous, Orthophosphate

Combustion - Infrared

Total Organic Carbon

Electrometric

Acidity, Alkalinity, Ammonia, BOD, Cl_2, DO, F^-, pH, Kjeldahl nitrogen, conductance

Gas Chromatographic

Chlorinated organic compounds, Pentachlorophenol, Phosphorous

Nephelometric

Sulphate, Turbidity

Radiological

Alpha, Beta, Radium

Non-Instrumental

Coliform, Fecal streptococci, Oil and Grease, Solids

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