

THE FUTURE OF ANALYTICAL CHEMISTRY

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The future of analytical chemistry is directed by current developments in materials research toward four general objectives. These four objectives, (1) increased precision, (2) lower limits of detectability, (3) finer detail in structural analysis, and (4) generalization and instrumentation of analytical techniques, are not qualitatively different from the requirements imposed on the analyst in the past. The magnitude of the effort needed in these four areas is, however, growing rapidly with the more stringent requirements being placed on materials behavior. The space environment, for instance, imposes a wide variety of conditions on materials used in the fabrication of vehicles and equipment.

To understand more fully the interactions of materials with their environments, it is essential that both the structure and composition of these materials be known. The mechanical behavior of bulk material may be dependent on components present in very small amounts or perhaps on very small differences in the quantities of the major components. Other properties may depend on microscopic and macroscopic arrangement of the various components. These questions of composition and structure are the problem of the analytical chemist, and it is essential that methods and techniques be developed to fulfill the current need.

Increased Precision

To increase the reproducibility of the results of any materials investigation, precision in composition must be achieved. The best methods of analysis in use today offer a precision of the order of one part in 10^4 while the current requirements in some cases are at least two orders of magnitude greater. In presently used instrumental techniques, such as emission and absorption spectroscopy, analysis with precisions of the order of one part in 10^3 are considered good.

Increasing the precision of absorption spectrometers can be accomplished by improving the signal to noise ratio and photometric accuracy of the overall instrument. To do this, one needs to study new, more efficient methods of converting the radiant energy signal into analytical information and more efficient, stable sources of radiant energy.

The problems associated with emission spectroscopy today are essentially problems of source instability. The dc arc source has the desirable characteristic of sensitivity but suffers from instabilities of many types. High voltage ac spark sources show greater precision than dc arcs, but suffer from loss in sensitivity and high continuous backgrounds. Various modifications of these two sources have been studied and some show promise for improved precision and reproducibility. Flame spectroscopy has perhaps the highest precision of any emission technique but still falls short of the requirements, one part in 10^6 . Extensive research on stabilization of emission sources together with continuous background reduction is necessary before this sensitive tool can be used in really precise work.

In designing equipment and developing new techniques for very precise analytical measurements consideration should be given to the analytical quantity from which the information is to be derived. Measurements involving the fundamental physical quantities, mass, length, and time, can be made with precisions of the order of 1 in 10^{6-7} , 1 in 10^8 , and 1 in 10^{8-9} respectively. Analyses based on these quantities can therefore be refined to high precisions. Analyses involving such derived quantities as volume, velocity, and voltage, will be inherently less precise. Consider the measurement of volume: if a length, L, can be measured with a precision of one part in 10^6 , the measurement of a volume derived from this length will be precise to only one part in $1/3 \times 10^6$. In general, derived quantities can be measured to an ultimate precision of $1/n$ of the precision of the quantities from which it is derived where n is the order of the derived constant with respect to these fundamental quantities.

Lower Limits of Detectability

In the fields of electrical and mechanical properties of materials and in biochemistry, the determination of extremely small amounts of impurities in large amounts of substrate is often required. To date, emission spectroscopy of trace metals has achieved perhaps the most general success and, in some cases, can detect and analyse traces of metals as low as one part in 10^{10} in solution.

Analysis of traces of impurities in ultra pure metals by emission spectroscopy is not as successful as we would like, particularly in materials of high atomic weight. Improvements in sources, particularly sources with low continuous background intensity, will allow lower limits of detectability. Application of fiber optics to emission spectrographs will allow large intensity gains by virtue of increased geometrical efficiency, but this will be useful only if the reduction in background intensity is first achieved so that the additional energy can be used.

Newer methods such as the high voltage ac spark source mass spectrometer show great promise in trace analysis. In contrast to emission spectroscopy, the mass spectrometer detection system is as sensitive for the detection of nonmetals as for metals. Although the spectra of elements of higher mass are somewhat more complex than those of lower mass, the great complexity of emission spectra is not observed, giving fewer interference problems and, consequently, greater ease in interpretation. The production of a continuous background in the mass spectrometer is more amenable to reduction methods than it is in conventional emission spectrography. The method is, however, applicable only to solids of relatively low vapor pressures that are either conductors or can be pelletized with conducting materials.

Atomic absorption spectroscopy, a relatively new tool for trace elements analysis, shows promise of increased sensitivity over emission techniques. Estimates of the ratio of emitting to nonemitting atoms in flame and arc sources give a value in the range of 1 to 500. Since atomic absorption spectroscopy views these nonemitting atoms in the source rather than view the relatively small number of emitting atoms, a gain in ultimate sensitivity of about 500 is expected. In practice, however, since some of the nonemitters may exist in the form of molecules the sensitivity increase may not be realized. The greatest gains should be with atoms that do not tend to form strong covalent bonds.

These methods, emission spectroscopy and high voltage spark mass spectrometry, are jointly capable of trace analyses to very low limits, but they are destructive in nature and give information about elemental composition only. Analyses of trace molecular components are possible by these techniques only by inference. Techniques of equivalent sensitivity are needed for trace analyses of molecular entities.

Absorption and mass spectrophotometry combined with gas chromatographic separations have applications to analysis of trace quantities of molecular materials and are in some cases useful with sample sizes as low as 10^{-7} grams. They are, however, not directly applicable to trace analyses in large quantities of substrate without some prior separation. Extension of these standard techniques to lower limits of detectability is essentially a problem in development of new techniques of separation of the trace materials from the large quantity of substrate. Many specific procedures have been advised for these separations but are for the most part not useful as general techniques.

Research along the lines of general separation methods possible with quantitative interpretation such as is possible with vapor phase chromatography is desirable.

Structural Analysis

Perhaps the objective of greatest importance is the extension of analytical chemistry to the field of structural analysis. More and more frequently the analytical chemist is required to decide between a number of possible molecular structures for new synthetic materials. Combined application of such powerful new techniques as Nuclear Magnetic Resonance Spectroscopy and Electron Paramagnetic Resonance Spectroscopy with absorption spectroscopy can and will lead to greater understanding of the behavior of materials.

Extension of the readily accessible region of the electromagnetic spectrum of longer wavelengths into the infrared and microwave regions is desirable for study of secondary structural features of molecules such as chain conformation in elastomeric materials. High resolution long wavelength x-ray absorption and emission spectrometers, although not now routine tools, are capable of giving information about atomic position and, orientation in solids, liquids, and gases. Development of sources, detectors, and dispersing elements is particularly important to place these regions of the spectrum in routine use. In addition, extensive spectra-structure correlation work is essential before the spectra can be interpreted on an analytical basis.

Nuclear Quadripole Resonance Spectroscopy has been applied recently to problems of structural analysis in the solid state but has not been used as an analytical tool. Its disadvantage is that a single piece of equipment is applicable to only a few of the observable resonances because of the wide frequency range (50 kc to 3000 mc). The equipment needed to observe the resonance is not extremely complex and may well be very useful for particular analytical problems. A large number of resonances occur in the .5 to 150 mc range which may be covered by two or three units of more or less conventional radio communications equipment. Extension of this technique to analytical chemistry may prove quite profitable.

Many physical properties of matter have been used in general analytical methods. Among the more important are density, viscosity refractive index, and electric constant, and surface tension. These properties may be correlated with chemical structure and

used in structural analysis. There are many other physical properties, the Faraday Effect, the Kerr Effect, sonic velocity and transmission, to name only a few, which may be the basis for structural analytical techniques.

These measurements will, by their nature, have wide applicability once the basic correlations have been fully explored.

Generalization and Instrumentation

The increased demand for analytical services today places emphasis on rapid, accurate qualitative and quantitative analyses. New methods and modifications of standard procedures to reduce operator time in routine determinations are needed to meet this demand. Instrumentation and automation of determinations now accomplished by wet chemical means will allow the analytical chemist to devote more of his time to problems of a more complex nature.

Studies devoted to new methods with wide application to routine problems and which offer gains in speed and accuracy should not be neglected. Recent advances in instrumentation of elemental organic analysis by combining vapor phase chromatography and coulometric detectors with rapid combustion devices have cut down routine carbon-hydrogen analyses time to approximately 10 minutes, allowing 3 to 4 determinations in the time previously required for a single run.

Investigations of methods for other elemental constituents such as nitrogen and the halogens may offer equivalent gains. Perhaps polarographic analysis of combustion products absorbed in a suitable fluid may be rewarding.

Elemental organic analysis is only one area where instrumentation of analytical methods is needed. Ultimately, generalized instrumental methods should replace all types of routine analysis both organic and inorganic so that the aims of greater speed and increased accuracy can be realized.