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COMMENTARY

Analytical Chemistry: Historic and Modern

In assuming the editorship of this journal a few years ago, a selfish objective was to increase the coverage of my own field of analytical chemistry. Using a broad definition of this field, I feel that its current developments are more exciting than at any time I can remember over many decades. An amazing amount and diversity of chemical information can now be obtained by a host of new or improved methods with critical applications in basic research, medical diagnoses,[1] industrial control, and key societal problems. A previous proposal[2] classifies the attributes of analytical methods as follows:

sensitivity
specificity
speed
sampling
simplicity
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In the 18th and 19th centuries, analysis was central to chemistry. Although new capabilities for accurate weighing were critical to this, microscopy was even more promising by the above criteria. Émile M. Chamot began Cornell's tradition in this in 1895 and was joined in 1925 by Clyde W. Mason. Their books on chemical microscopy have been standards in the field, the latest appearing in 1983. In this issue of *Accounts*, their former student W. C. McCrone authors "The Shroud of Turin: Blood or Artist's Pigment?"; this and "The Vinland Map: Still a Forgery" by K. M. Towe are very exciting illustrations of the modern power of this venerable technique, even in competition with sophisticated instruments hundreds of times as expensive. Further, its sensitivity, specificity, and speed are certainly outstanding; McCrone and his colleagues can recognize more than 30 000 types of nanogram-level particles, most of them at sight. This is the technique of choice, for example, for differentiating iron oxides which vary widely in oxidation, hydration, and crystallinity levels, and for identifying specific fibers, starches, pollens, minerals, pigments, and pollutants. Here the critical criterion for present applications may be "simplicity"; although obtaining reliable information using the polarized light microscope requires relatively little training, few chemists receive this, although this is still common in geology. Largely due to McCrone's persuasiveness, persistence, and personal teaching efforts, chemical microscopy has been reintroduced into both the undergraduate and graduate curricula at Cornell.

With such a great heritage, the present status accorded analytical chemistry deserves examination, contrasting its absence from several of the best chemistry departments with the revolutionary developments in the field today. Of exciting new techniques, scanning tunneling microscopy provides direct molecular-level measurements (sensitivity) with surprisingly favorable simplicity and cost. For this, Binnig and Rohrer received the 1986 Nobel Prize in Physics; what we in the field see as analytical chemistry is often pioneered by scientists who classify themselves otherwise. Similarly, compositional analysis plays a critical role in the development of superconductors (Bednorz and Müller, 1987). Biologists Gilbert and Sanger received the 1980 Nobel Prize in Chemistry for their nucleotide sequencing technique that is the key to the highly publicized human genome project. This diversity of professional backgrounds is also represented in other Chemistry Nobel Prizes of analytical importance, such as those in other forms of chromatography (Tiselius, Martin and Synge, Moore and Stein), mass spectrometry (Aston), X-ray diffraction (Debye, Kendrew and Perutz,[3] Hodgkin, Hauptman and Karle[4]), electron microscopy (Klug), and spectroscopy (Herzberg, Herschbach, Lee, and Polanyi). The physical chemist Heyrovský received the 1959 Nobel Prize for "the polarographic method of analysis", while the 1923 Prize for "microanalysis of organic substances" went to Pregl, whose doctorate was awarded in medicine. From this I conclude that we, like Newton, are standing on the shoulders of giants, and that our discipline is unusually demanding in its breadth of scientific skills and interests. A discovery in almost any area of science can be valuable,

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but this must be recognized and made applicable to important relevant problems. This attractiveness has approximately doubled the proportion of U.S. Ph.D.'s in analytical chemistry over the last 20 years, with demand still exceeding supply.

High data rates are a compelling attraction of modern instrumentation. However, we analytical chemists can be overly enamored with the acquisition of data itself. Quoting the philosopher deBono, "data is not information until it has been processed into an idea". A real solution here has been the computer revolution. The gas chromatograph/mass spectrometer produces megabit/second data; even with a compound eluted from the GC every few seconds, probability-based matching against 140 000 reference mass spectra is fast enough for real-time identifications.[5] Similarly, obtaining even more detailed structural information from even larger molecules by multidimensional NMR requires further "automation of the spectral analysis".[6] Within such a broadened definition, analytical chemistry is an important part of many *Accounts* articles of 1988 and 1989.[6,7]

I do not ask that individual experts in such methodologies categorize themselves as analytical chemists. However, the separate discipline of analytical chemistry deserves more consideration for the vital role it can play. Its unusual diversity puts an even greater value on finding common interests, discussing alternative approaches to analytical problems, and utilizing new developments in theory, instrumentation, electronics, and computers. A disproportionate part of the effort for a specific research problem can involve developing special analytical tools; a much smaller additional effort could make these suitable and appealing for important research of others. Analytical chemistry offers a forum for encouraging and evaluating both basic and applied research critical to the acquisition and utilization of chemical information, as I hope is reflected in the pages of this journal.[3,4,6,7]

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High-Speed Cyclic Voltammetry

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The time scale of voltammetric measurements has been decreased by several orders of magnitude in the last decade. Cyclic voltammograms recorded at scan rates in the range of 10^6 V/s have been reported.[1,2] At these scan rates, transient electrogenerated species with a lifetime of $\approx$20 ns can be characterized. Thus, cyclic voltammetry now can be used on a time scale that is unprecedented for electrochemical methods. This reduction in time scale presents new opportunities for applications of voltammetry in the characterization of solution redox behavior as well as chemical analysis.

Cyclic voltammetry is perhaps most widely used by chemists as a method to determine the standard reduction potential of a redox couple, $E°$. Normally this is done by recording the position of the peaks of the voltammetric waves of the voltammograms and using

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