Quantitative Electron Probe Microanalysis

The recognition and understanding of the role of the microstructure in controlling the macroscopic behavior of a material has been a major theme of science and technology throughout the history of NBS/NIST. In materials science, the late 19th century saw the development of the sample preparation procedures we know today as "metallography" and "materialography," and the emergence of optical microscopes with resolution performance at the physically defined optical limit. Applied to practical technological issues such as understanding the thermomechanical processing of steel to control its strength and ductility, the new microstructural science revealed a vast array of microstructural features, many of which were obviously compositional in nature. By 1912, the noted Harvard scientist Prof. Albert Sauveur could remark "To realize the practical importance of metallography, it should be borne in mind that the physical properties of metals and alloys—that is, those properties to which those substances owe their exceptional industrial importance—are much more closely related to their proximate than to their ultimate composition, and that microscopical examination reveals, in part at least, the proximate composition of metals and alloys, whereas chemical analysis seldom does more than reveal their ultimate composition" (Here the "ultimate composition" is what we today would refer to as the bulk composition, while the "proximate composition" refers to the local microstructural composition.) Sauveur continued in his enthusiastic and colorful prose: "Unfortunately the chemist too often is able to give us positive information in regard to the proportion of the ultimate constituents only, his reference to proximate analysis being of the nature of speculation. Ultimate analysis has reached a high degree of perfection in regard to accuracy as well as to speed of methods and analytical chemists have built up a marvelous structure calling for the greatest admiration, their searching methods never failing to lay bare the ultimate composition of substances. But how much darkness still surrounds the proximate composition of bodies and how great the reward awaiting the lifting of the veil!"

The beginning of the solution to Sauveur's dream came in 1949 with the first results from the electron probe x-ray microanalyzer (EPMA) by Raymond Castaing, a student of A. Guinier at the University of Paris. Castaing presented an extraordinary thesis that described both the complete development of a unique measurement tool for microstructural characterization and a detailed treatment of the underlying physics of electron/x-ray interaction with matter that would provide the framework for developing the new technique into a rigorous quantitative analysis tool. The first stage of this task took nearly 20 years and the contributions of many scientists from Europe, Japan, and the United States, including those of Kurt F. J. Heinrich and his colleagues at NBS. To evaluate the state of the development of quantitative analysis and to stimulate further progress in the measurement science of electron probe microanalysis, Heinrich organized a special workshop in June of 1967 that brought together the leaders of the field. The document of this gathering, NBS Special Publication 298, *Quantitative Electron Probe Microanalysis* [1], edited by Heinrich, became the "bible" of the rapidly developing field. It was understood from Castaing's thesis work that a quantification scheme should proceed from the measurement of the x-ray intensities emitted by the unknown and, under the same beam conditions, from a simple standard suite consisting of pure elements and/or binary compounds. What was needed were correction factors based upon physical calculations of electron penetration and scattering, x-ray absorption, and consequent secondary x-ray fluorescence to convert relative measured x-ray intensities into relative concentrations. Extensive work to develop practical expressions for these factors and obtain the physical data (e.g., x-ray mass absorption coefficients, electron backscatter coefficients, etc.) was being done by researchers organized essentially along national lines. NBS Special Publication 298 brought together the various camps to present their work and the critical details on just how they proposed to implement these complex calculations. Most importantly, SP 298 contained the first robust tests based upon critical data sets that provided a rigorous comparison of the performance of different implementations of correction factors. Thus, the strengths and weaknesses of the algorithms under development could be accurately assessed, and future directions for continuing research could be sensibly planned, propelling the field forward. SP 298 also surveyed newly emerging areas of application, such as biological materials, where a solution was provided to the problem that radiation damage to the specimen limited the utility of the results. Changes in the electron bombarded region could be compensated through measurements of the high energy x-ray continuum.

Kurt Heinrich came to NIST in 1963 from the Dupont Research Station to initiate a competence for NBS in the area of electron beam microanalysis, which had grown slowly through the 1950s until the great acceleration of scientific and technological efforts in the post-Sputnik era led to the development of several commercial EPMA instruments. Heinrich assembled an electron beam group initially including Robert Myklebust, Charles Fiori, Donald Vieth, and Stanley Rasberry, with the close collaboration of Harvey Yakowitz from the Metallurgy Division. Visitors included Jean Henoc of Centre National d'Etudes de Telecommunication (France) and Carol Swyt of the National Institutes of Health. Fig. 1 shows an example of an early EPMA instrument at NBS. Later, Ryna Marinenko, John Small, Eric Steel, and Dale Newbury joined the effort toward development of the measurement science of elemental microanalysis and its application to a wide variety of problems in materials science, semiconductor technology, environmental chemistry, failure analysis, and forensic analysis.

EPMA involves the use of finely-focused electron beams with incident energies usually selected in the range from 10 keV–25 keV to excite characteristic x rays from a microscopic target. Initially, the lateral spatial resolution of EPMA was limited by the electron-optical performance to the minimum beam size that could be focused with sufficient current for practical x-ray spectrometry by wavelength dispersive spectrometry (crystal diffractometry). The micrometer spatial resolution that Castaing reported in his thesis stood for nearly 20 years because microampere currents were needed to excite a sufficient x-ray flux to overcome the low efficiency of diffraction spectrometers. Large current demanded large beam size. This problem was substantially solved with the development of the semiconductor energy dispersive spectrometer (Si-EDS) with geometric and quantum efficiencies that permitted practical x-ray spectrometry with beam currents in the nanoampere range. Heinrich collaborated on the watershed paper introducing the semiconductor EDS to the electron probe field [2]. With semiconductor EDS, microanalysts could take advantage of the rapid, parallel developments in imaging that took place in the late-1960s with the advent of high resolution scanning electron microscopes (SEM). The EPMA quickly evolved into an SEM electron-optical platform capable of imaging with beam diameters of 50 nm and smaller,

Fig. 1. Kurt Heinrich with his EMPA apparatus.

equipped with both crystal diffractometers (for high spectral resolution) and semiconductor EDS (for continuous viewing of the complete x-ray spectrum). Moreover, with submicrometer beam diameters, the EPMA could achieve spatial resolutions limited only by the physics of electron scattering. For intermediate and high atomic number specimens ($Z > 20$), lateral and depth spatial resolutions below 1 μm became possible. The modern EPMA/EDS/WDS can thus image and then selectively analyze discrete sample masses of the order of 1 pg (10^{-12} g), e.g., an isolated particle, with fractional detection limits of 1 fg (10^{-15} g) or less within this picogram sample. This extremely small sample mass was six or more orders of magnitude below the minimum mass that could be studied with contemporary "conventional" chemical analysis [3].

Despite the small mass of the sample selected by the beam interaction, the EPMA measurement can be performed quantitatively with a relative accuracy of ±0.5 % or better and precision of ±0.5 %. The framework for quantification that was laid down by Castaing was refined and enhanced by numerous workers, and the Heinrich group made many important contributions to the success of the method. The x-ray spectrum is affected by a wide range of physical phenomena. The incident electron beam undergoes elastic and inelastic scattering (energy loss) leading to a complex distribution in depth of electron density and ionization power as well as the loss of electrons from the target due to backscattering through the cumulative effects of elastic scattering. The characteristic x rays produced through inner shell ionization must propagate through the specimen, often over a distance of micrometers, to escape through the surface in the direction of the x-ray detector. Along this path, the x rays are subject to photoelectric absorption which attenuates the intensity. Photoelectric absorption leads to secondary fluorescence through ionization of inner shells of the absorbing specimen atoms, which subsequently emit their characteristic x rays. This secondary emission is an additional source of intensity beyond that due to direct electron excitation of those same atoms. The great complication is that each of these radiation interactions, (1) electron scattering, retardation, and ionization power, (2) x-ray absorption, and (3) secondary x-ray fluorescence, is a function of composition, which is unknown. Finally, absorption in the components of the spectrometer and the spectrometer response (efficiency) modify the emitted spectrum to yield the final observed spectrum. Determination of these interelement or "matrix effects" and instrumental effects form the basis for quantitative analysis. NBS/NIST scientists employed a three-pronged approach for this research: (1) studies of the parameters of electron beam/x-ray interactions that form the physical basis of matrix corrections; (2) development of computer software incorporating the physical corrections for efficient calculations; and (3) development of microanalysis standard reference materials.

The study of the interaction of electrons and x rays with matter was an area of intense interest to physics in the first half of the 20th century. By the time EPMA had arisen in the 1950s, physics had moved on to much higher and much lower energies, and interest in measuring data for the EPMA energy range had waned. Those who were interested in developing accurate corrections for electron/x-ray matrix effects in EPMA needed accurate values of key parameters such as electron backscattering coefficients, loss of x-ray production due to backscattering, x-ray mass absorption coefficients, etc. Whenever possible, literature values were utilized, but many critical values were simply unavailable, so extensive measurements and simulations were undertaken by the EPMA community, including the NBS/NIST group [4-8].

Consistent with the mission of NBS/NIST, matrix correction methods for quantitative analysis have been made accessible to U.S. industry and academia through the development of state of the art software that incorporated the laboratory measurement advances in a form that could be readily implemented elsewhere. The development of quantitative EPMA closely follows the remarkable evolution of computing power that is the major theme of the second half of the 20th century. As each advance took place in central computing power in the early years, and then in personal computing power in later years, NBS/NIST quantitative microanalysis software was developed to take full advantage of the improving speed and capacity of computers. Thus there are two parallel series of publications, one set of scientific papers that detail the NBS/NIST contributions to the basic understanding of electron beam/x-ray interactions and matrix corrections for quantitative EPMA analysis, and a second set of papers documenting the software implementation of the mathematical algorithms for these corrections. The open description of this software code enabled U.S. manufacturers of x-ray spectrometry to incorporate NBS/NIST developments into their products [9-13].

The third component of the NBS/NIST program in microanalysis research has been the development of NBS/NIST Standard Reference Materials (SRM) appropriate to the electron probe microanalysis case, which places an unusually great demand on sample homogeneity. The EPMA beam selects a region with micrometer dimensions, so for measurement reproducibility, we must require that our sample be homogeneous down to a much finer scale, ideally approaching the atomic scale. While NIST offers a great many SRMs,

Nature seems generally to abhor homogeneity on the microstructural scale, so that most SRMs created for "bulk" applications do not satisfy the stringent requirements for microstructural homogeneity necessary for EPMA. Most arbitrarily selected groupings of elements when properly synthesized together do not form a uniform material on the micrometer scale. Careful selection and rigorous homogeneity testing of metallic alloys and glasses has resulted in a series of microanalysis SRMs which serve the community in the important role of test materials [14-16].

Finally, these techniques for quantitative EPMA were developed in an environment in which problem solving was encouraged and promoted. Collaborations throughout NBS/NIST and with other federal agencies brought many challenging applications for EPMA, including materials science, failure analysis, electronic technology, biological science, and forensic analysis.

Prepared by Dale E. Newbury.

Bibliography

[1] K. F. J. Heinrich (ed.), *Quantitative Electron Probe Microanalysis,* NBS Special Publication 298, National Bureau of Standards, Washington, DC (1968).

[2] R. Fitzgerald, K. Keil, and K. F. J. Heinrich, Solid-State Energy-Dispersion Spectrometer for Electron-Microprobe X-ray Analysis, *Science* **159**, 528-530 (1968).

[3] K. F. J. Heinrich, D. E. Newbury, R. L. Myklebust, and C. E. Fiori (eds.), *Energy Dispersive X-ray Spectrometry,* NBS Special Publication 604, National Bureau of Standards, Washington, DC (1981).

[4] K. F. J. Heinrich, Electron Probe Microanalysis by Specimen Current Measurement, in *Fourth International Symposium on X-ray Optics and X-ray Microanalysis, Orsay, France, 1965,* Hermann, Paris (1966) pp. 159-167.

[5] K. F. J. Heinrich, X-ray absorption uncertainty, in *The Electron Microprobe,* T. D. McKinley, H. F. J. Heinrich, and D. B. Wittry (eds.), John Wiley and Sons, New York (1966) pp. 296-377.

[6] Kurt F. J. Heinrich, Errors in theoretical correction systems in quantitative electron probe microanalysis—a synopsis, *Anal. Chem.* **44**, 350-354 (1972).

[7] Kurt F. J. Heinrich, Dale E. Newbury, and Harvey Yakowitz (eds.), *Use of Monte Carlo Calculations in Electron Probe Microanalysis and Scanning Electron Microscopy,* NBS Special Publication 460, National Bureau of Standards, Washington, DC (1976).

[8] J. A. Small, D. E. Newbury, and R. L. Myklebust, *X-Ray Bremsstrahlung Intensities from Elemental Targets,* NBS Technical Note 1245, National Bureau of Standards, Gaithersburg, MD (1988).

[9] Kurt F. J. Heinrich, Robert L. Myklebust, Harvey Yakowitz, Stanley D. Rasberry, *A Simple Correction Procedure for Quantitative Electron Probe Microanalysis,* NBS Technical Note 719, National Bureau of Standards, Washington, DC (1972).

[10] H. Yakowitz, R. L. Myklebust, and K. F. J. Heinrich, *FRAME: An On-Line Correction Procedure for Quantitative Electron Probe Microanalysis,* NBS Technical Note 796, National Bureau of Standards, Washington, DC (1973).

[11] Jean Henoc, Kurt F. J. Heinrich, and Robert L. Myklebust, *A Rigorous Correction Procedure for Quantitative Electron Probe Microanalysis (COR 2),* NBS Technical Note 769, National Bureau of Standards, Washington, DC (1973).

[12] R. L. Myklebust, C. E. Fiori, and K. F. J. Heinrich, *FRAME C: A Compact Procedure for Quantitative Energy-Dispersive Electron Probe X-ray Analysis,* NBS Technical Note 1106, National Bureau of Standards, Washington, DC (1979).

[13] Charles E. Fiori and Carol R. Swyt, *Desk Top Spectrum Analyzer,* United States Patent 5,299,138, March 29, 1994.

[14] Kurt F. J. Heinrich, Robert L. Myklebust, Stanley D. Rasberry, and Robert E. Michaelis, *Preparation and Evaluation of SRMs 481 and 482: Gold-Silver and Gold-Copper Alloys for Microanalysis,* NBS Special Publication 260-28, National Bureau of Standards, Washington, DC (1971).

[15] R. B. Marinenko, F. Biancaniello, L. DeRobertis, P. A. Boyer, and A. W. Ruff, *Preparation and Characterization of an Iron-Chromium-Nickel Alloy for Microanalysis: SRM 479a,* NBS Special Publication 260-70, National Bureau of Standards, Washington, DC (1981).

[16] R. B. Marinenko, *Preparation and Characterization of K-411 and K-412 Mineral Glasses for Microanalysis: SRM 470,* NBS Special Publication 260-74, National Bureau of Standards, Washington, DC (1982).