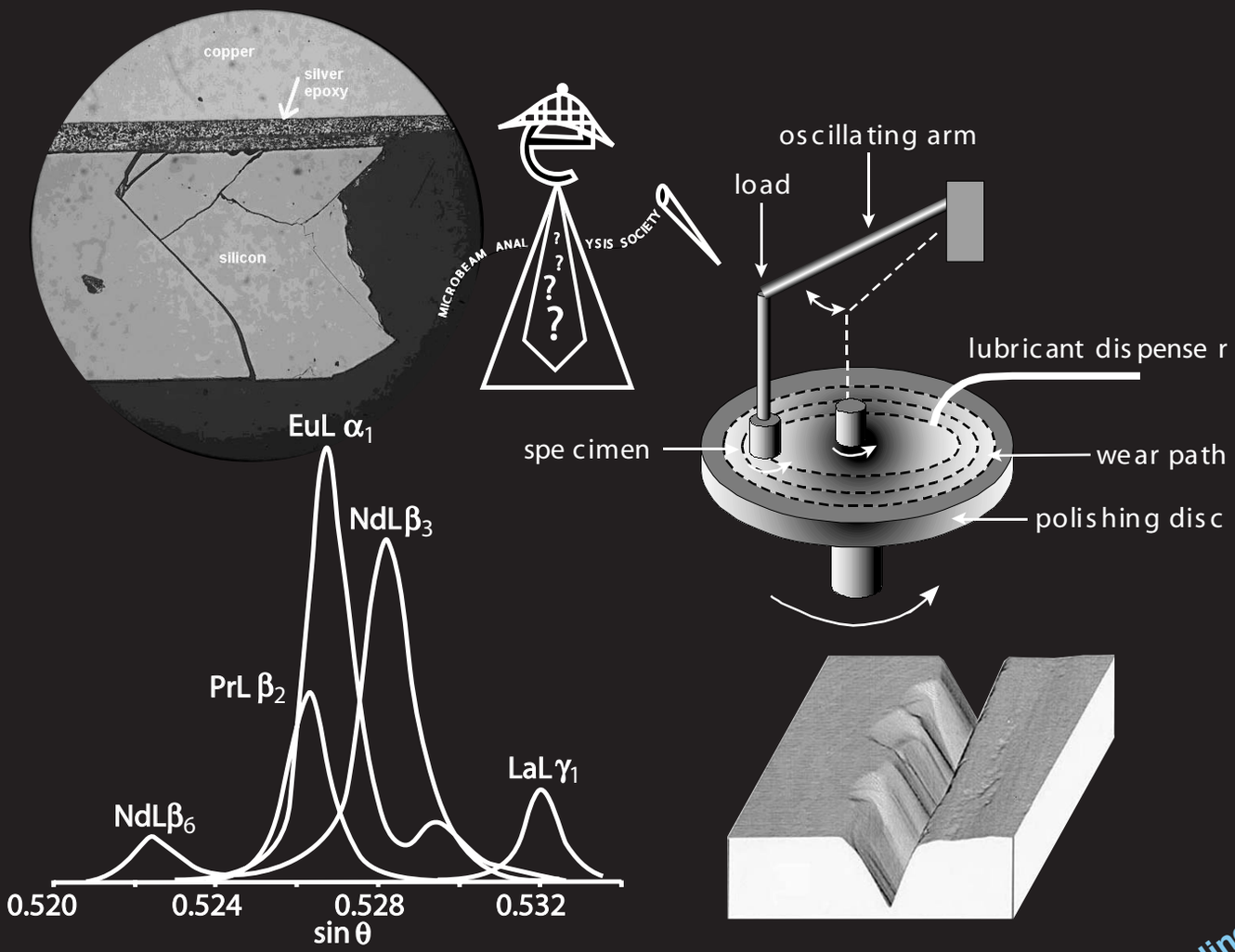
Journal of Research of the National Institute of Standards and Technology

November - December 2002, Vol. 107, No. 6 ISSN 1044-677X

Special Issue: Accuracy Barriers of Quantitative Electron Beam X-Ray Microanalysis



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Technology Administration, U.S. Department of Commerce

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NIST, originally founded as the National Bureau of Standards in 1901, works to strengthen U.S. industry's competitiveness; advance science and engineering; and improve public health, safety, and the environment. One of the agency's basic functions is to develop, maintain, and retain custody of the national standards of measurement, and provide the means and methods for comparing standards used in science, engineering, manufacturing, commerce, industry, and education with the standards adopted or recognized by the Federal Government.

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- Statistical Engineering

[1] At Boulder, CO 80303.
[2] Some elements at Boulder, CO.

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The *Journal of Research of the National Institute of Standards and Technology,* the flagship periodic publication of the national metrology institute of the United States, features advances in metrology and related fields of physical science, engineering, applied mathematics, statistics, biotechnology, and information technology that reflect the scientific and technical programs of the Institute. The *Journal* publishes papers on instrumentation for making accurate measurements, mathematical models of physical phenomena, including computational models, critical data, calibration techniques, well-characterized reference materials, and quality assurance programs that report the results of current NIST work in these areas. Occasionally, a Special Issue of the *Journal* is devoted to papers on a single topic. Also appearing on occasion are review articles and reports on conferences and workshops sponsored in whole or in part by NIST.

ISSN 1044-677X **Coden: JRITEF** **Library of Congress Catalog Card No.: 89-656121**

United States Government Printing Office, Washington: 2002

Kurt Francis Joseph Heinrich

We are dedicating this workshop to Kurt F. J. Heinrich at a most appropriate time; it honors Kurt's many contributions to the field of x-ray microanalysis made during the past 40 plus years, and it also honors him, though somewhat delayed, on his 80th birthday. With his family, Kurt emigrated from Austria (before World War II, he likes to note!) to Argentina where he received his PhD degree in Chemistry in 1949. In 1956 he emigrated to the United States to work at the E. I. DuPont de Nemours Experimental Station in Wilmington, DE where he became involved in x-ray fluorescence (XRF) but soon developed an interest in Electron Probe Microanalysis (EPMA) when DuPont purchased one of the first commercial Applied Research Laboratories (ARL) scanning electron microprobes.

Having set a foothold as a national and international leader in the development of the field of electron probe microanalysis, Kurt was lured in 1964 to the then National Bureau of Standards (NBS) in Washington, DC, to continue working in XRF and EPMA in the Spectroanalysis Section. (One of us, RBM, remembers visiting Kurt in 1964 at the old NBS site on Van Ness Street where he sat in front of a brand new ARL electron microprobe collecting data.) Kurt later became Chief of the Microanalysis Section, a position that he held for many years until 1980 when he became Chief of the Office of International Relations. This was a position for which he was ideally suited with his international scientific experience and fluency in six languages. During his career at NBS Kurt received the Department of Commerce Silver and Gold Medal Awards. Kurt also was one of the founders and second

President of The Electron Probe Analysis Society of America (now called the Microbeam Analysis Society, MAS), and he is now an honorary member of MAS and the Deutsche Verband für Materialforschung. In 1988 Kurt retired from the newly renamed NIST but has remained in contact with the Microanalysis Research Group, continuing to improve upon matrix correction procedures and providing sage advice when needed. Today, Kurt still enjoys participating in a lively, rational argument, and he continues to demonstrate his superb memory, ingenuity, and sense of humor.

Kurt's contributions extend to all aspects of the field of electron probe microanalysis. He authored a book of major importance on the theory and practice in EPMA (*Electron Probe Microanalysis,* Van Nostrand, NY, 1981) and was editor of several other publications, including proceedings of meetings and workshops that he organized (in particular, NBS Special Publication 298, *Quantitative Electron Probe Microanalysis,* 1968, and *Electron Probe Quantitation,* Plenum, NY, 1991). He has published more than 100 archival papers concerned with developments of EPMA instrumentation, improvements in microanalysis techniques, metallurgical and geological applications (including lunar samples and asbestos), characterization of microanalysis standards, uncertainties in quantitative EPMA and correction procedures, bibliographies of EPMA publications, tables of mass absorption coefficients and x-ray lines, development of matrix correction procedures, the early use of color in wavelength dispersive x-ray dot mapping, energy dispersive qualitative and quantitative analysis, and the use of Monte Carlo techniques in quantitative EPMA. This list is not all-inclusive; it demonstrates the diversity of problems Kurt has been concerned with throughout his long, successful career. One of his most significant and lasting contributions to EPMA is his work on mass absorption coefficients that entailed a novel set of empirical equations used to minimize the uncertainties in experimental data. He developed and published the first version while at DuPont and the second, which is still being used, at NIST.

In addition, Kurt has always been in demand (locally, nationally, and internationally) for his research presentations and courses on EPMA. He gives generously of his time and has always spattered his unique humor among descriptions of his scientific accomplishments.

We extend our heartfelt thanks to Kurt for sharing with us his knowledge and zest for learning and improving—not only in the field of EPMA but in all aspects of life.

Dale E. Newbury
Ryna B. Marinenko

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Foreword

Electron probe x-ray microanalysis (EPMA) is one of the oldest yet still one of the most widely applied methods of spatially-resolved elemental analysis. Implemented as electron-excited x-ray spectrometry performed in the scanning electron microscope (SEM), EPMA achieves spatial resolution both laterally and in-depth, typically at the micrometer scale in bulk specimens, and, under special circumstances, spatial resolution can be reduced to the range of nanometers. The popularity of EPMA arises from the extraordinarily broad range of applications: What other technique can solve problems as diverse as determining the nature of the microscopic white crystals that form under certain conditions on the surface of Wisconsin cheese (calcium phosphate, apatite) or elucidating the time-dependent behavior of phase-stabilizing, dimension-preserving gallium in the microstructure of plutonium to preserve the safety and efficacy of the Nation's arsenal of nuclear weapons?

Leading experts in EPMA from industry, academia, and government, from the U.S., Canada, Mexico, and Europe met at the National Institute of Standards and Technology, April 8-11, 2002, to participate in a workshop on "The Accuracy Barrier in Quantitative EPMA and the Role of Standards" co-sponsored by the Surface and Microanalysis Science Division of the Chemical Science and Technology Laboratory and the Microbeam Analysis Society (U.S.). The workshop sought to reach an understanding of the present state of quantitative EPMA, especially to identify those factors that limit the accuracy of the method at the current level of approximately 2 % relative uncertainty. A second task sought to develop a roadmap for future progress. Speakers considered the limitations of current EPMA instrumentation, the theoretical basis of EPMA physical correction procedures, the extension of EPMA into new classes of electron beam instrumentation such as variable pressure/environmental scanning electron microscopes and low voltage SEMs, and the critical role of standards to extend quantitative measurements for specific applications such as protective coatings for high performance materials used in aerospace applications. An industry panel discussion identified vital needs to which NIST might respond, such as new measurements of the relative weights of x-ray peaks from low energy (< 2 keV) L- and M-shell x rays.

The Workshop is dedicated in honor of the keynote speaker, Kurt Heinrich (NIST, retired), who devoted a major portion of his long NIST career to understanding the EPMA measurement process and promulgating robust analytical methods and standards to the international scientific community. Kurt is internationally recognized as one of the "founding fathers" of the EPMA technique, and we are pleased to have had his participation in this Workshop.

With more than 100 attendees filling the lecture room, the meeting was broadcast on the Web to accommodate those who could not attend or were turned away due to space limitations. The 4 day workshop was a gratifying success with excellent presentations by the speakers (several submitted papers for this publication) and the ensuing discussions. We want to thank the speakers again for their superb efforts. We'd also like to thank the many NIST staff members, from the Conference Program Office, the Information Services and Computing Division, and the Microanalysis Research Group (Surface and Microanalysis Science Division) who helped to make this a successful workshop.

When reading these proceedings papers, readers may encounter measurement terms that are not conventionally used in the microanalysis community. On the next page is an explanation by Theodore Vorburger, Chief Editor of the *Journal of Research of the National Institute of Standards and Technology*, for colleagues in microanalysis who may be reading the *Journal* for the first time.

Dale E. Newbury
Ryna B. Marinenko

Special Issue Editors

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Note: Terminology in This Special Issue

NIST's policy is to closely follow international guidelines in terminology for expressing both the uncertainties of measured quantities and the units of physical quantities. You might notice that policy at work in the terms that are emphasized and terms that are avoided in the articles in this collection. During the editing process, a number of terms have been changed from those submitted by the authors in order to make the expression of uncertainty and the use of physical quantities consistent from one article to the next and consistent with the policy of the *Journal*.

For example, the term "uncertainty" is used to characterize "the dispersion of values that could reasonably be attributed" to a measured quantity (quotation from the International Vocabulary of Basic and General Terms in Metrology, published by the International Organization for Standardization). By contrast, the qualitative terms "accuracy" and "error" are generally used to characterize the closeness of the agreement between the result of a measurement and the value of the measurand and are not used to indicate uncertainty itself. The term "precision" is avoided mainly because its meaning is ambiguous. That is, a "precision" measurement could indicate that the overall uncertainty for the measured result is small or it could indicate that individual measured values of a quantity are closely clustered about the mean value.

Regarding units, the International System of Units (SI) is mandated in this and all NIST publications, so you will of course see units of the SI system such as the meter (m), kilogram (kg), second (s), etc. Perhaps the most significant change from practice elsewhere in microanalysis is the expression of relative concentrations. The term ppm, for "parts per million," is avoided because it is English-language specific and not a unit of the SI. Rather, you will see relative concentrations expressed primarily as mass fractions, such as "the mass fraction of species x in the sample is approximately 4×10^{-6}" or "the mass fraction of species x in the sample is 0.05 %," meaning simply 0.05×10^{-2}. The guidelines used at NIST are summarized in Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, by B. N. Taylor and C. E. Kuyatt, Technical Note 1297 (NIST, Gaithersburg MD, September 1994) and Guide for the Use of the International System of Units (SI), by B. N. Taylor, Special Publication 811 (NIST, Gaithersburg MD, April 1995).

Theodore Vorburger

Chief Editor

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