

The Golden Age of Microanalysis

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Abstract: The history of electron probe analysis in the USA in its first two decades is reviewed, with reference to the personalities which were involved, the development of instrumentation and theory, and the technical problems and limitations of that era.

Key words: electron probe microanalysis, computers in electron probe microanalysis, early years of electron probe microanalysis, quantitative electron probe microanalysis, matrix correction procedures

INTRODUCTION

In its first 20 years, microprobe research was an exciting experience, under conditions quite different from today. Available instruments were primitive compared with those we have now; theories of quantitation and physical parameters were often unreliable. It was the time of “Microanalysis BC,” i.e., “before computers.” We had to choose the data handling procedures that are now provided with the instruments by the manufacturer, and to perform the calculations by hand. At the same time, electron probe microanalysis (EPMA) offered a wide-open field for theoretical and experimental research as well as for instrumental innovations; bureaucratic management was still, mercifully, in its childhood. What a wonderful time that was!

HOW I GOT INVOLVED

My involvement in EPMA agreed well with my scientific interests. I had the good fortune of being introduced to microscopy and to experimental inorganic chemistry at my

high school in Vienna. When the unsavory political developments in Europe motivated my family to immigrate to Argentina, I there obtained employment in analytical chemistry laboratories. My thesis advisor at the University of Buenos Aires, Dr. Reinaldo Vanossi, was investigating novel procedures of semi-microanalysis, replacing with extraction and distillation the classical analytical methods based on precipitation and filtration. He included in his analytical scheme rarer elements such as beryllium, tungsten, and gallium that had been ignored before. Unfortunately, the efforts of this gifted investigator came to naught with the progress in instrumental and spectroscopic analysis that displaced the traditional “wet methods.”

In search of an interesting research position, I entered the USA in 1957. I worked at the E.I. DuPont Experimental Station in Wilmington, DE, developing procedures for the determination of tantalum in niobium oxide. The “wet” methods resulting from this effort, involving anion exchange resin separation in complex hydrofluoric solutions, were too time- and labor-consuming to be used in practice. Therefore I chose X-ray fluorescence spectrometry of oxide pellets or borate fusion beads to accomplish my goal. At this point, I left classical chemistry and embarked on studies of X-ray physics.

I was fascinated by the techniques and instrumentation of X-ray spectrometry. The problem I tried to resolve was, however, very complex. At the available excitation potentials, and with the extant instrumentation, tantalum could only be detected and determined by the measurement of one of the *L* lines. However, the first-order reflections of the Ta $L\alpha_1$ and $L\beta_1$ lines were interfered with by the second-order reflections of the $K\alpha$ and $K\beta$ lines of niobium. To resolve this interference, I studied the higher-order reflections of X-rays from various types of crystals, as well as counting statistics and dead-time corrections. I found a solution after getting an excellent lecture and demonstration of pulse-height analysis from William Campbell, at the laboratory of the Bureau of Mines at College Park, MD. This learning experience would become very useful to me later when I started working with the electron probe. The group at the Bureau of Mines also built a homemade microprobe, and several well-known microanalysts, including James Brown, James Burkhalter, and Robert L. Myklebust, started their careers in this laboratory.

As soon as I obtained my first X-ray spectra, I started speculating about the use of the new tool for the characterization of microscopic areas on a specimen surface. Investigators had attempted to limit the analyzed area through the collimation of the primary X-rays emitted from the X-ray tube, but I found it more efficient to restrict the path of the fluorescent X-rays to the detector by collimating them through the shaft of a hypodermic needle. The low count rates I obtained required the analyzed area to be as large as 0.1 to 1 mm. I published my results in 1961 at the proceedings of the 5th Denver Conference of X-ray Analysis (Heinrich, 1961). General Electric, who was the manufacturer of the spectrometer, marketed my device that they called the Heinrich probe. I believe that they sold as much as half a dozen. My supervisors, however, thought that DuPont was not the most appropriate place for developing "the poor man's X-ray probe." If I was really interested in microanalysis, I should do it with an electron probe microanalyzer. On the strength of this argument, the Applied Research Laboratory scanning electron probe made its entrance in my laboratory.

In the 1960s, the leader in the USA of electron probe analysis was LaVerne Birks at the Naval Research Laboratory. He had organized a meeting at his institution in February 1958, at which several European scientists, including Raimond Castaing, Peter Duncumb, and Thomas Mulvey, were present. This gathering, which took place before my involvement in the matter, was seminal for the introduction

of microanalysis in the USA. Birks would later become one of the founders, and the first president, of the Electron Probe Analysis Society (EPASA), now called the Microprobe Analysis Society (MAS). The first national meeting with wide attendance was that organized for the American Electrochemical Society at the campus of the University of Maryland in 1964. The Proceedings, edited by T.D. McKinley, myself, and D.B. Wittry, appeared in 1966 (McKinley et al., 1966). They included my first tabulation of X-ray absorption coefficients (Heinrich, 1966a) and a 90-page bibliography on electron probe microanalysis and related subjects. In subsequent years, they would be followed by the proceedings of the national meetings organized by EPASA as a main source of publication in the USA. Several workshops were also organized at the National Bureau of Standards (NBS), Massachusetts Institute of Technology (MIT), and Lehigh University (Fig. 1).

Before the organization of national meetings solely concerned with microanalysis by EPASA, the annual conferences on X-ray analysis organized by Denver University were the preferred forum for presentation of results in this field, with frequent participation by international visitors. The 1960 USA tour of the inventor of the electron probe, Raimond Castaing, brought me together with him and his wife in Denver. I was forced to refresh my rusty high school French, since Mrs. Castaing did not speak English. Castaing, however, felt quite at home. He posed in front of my camera in a Native American outfit he had borrowed, drum and everything, from a "native" on the tourist warpath. On an excursion to Central City, we bought him a fake local newspaper, dated 1885 or so, with the headline, "R. Castaing Elected Mayor of Central City." A year later, I met Castaing again. He told me that this paper had been very effective with his parents, explaining, "When they saw that I had been elected to office in an American city, they realized that their son was a great success."

THE INSTRUMENTS

Before we decided on the instrument our laboratory was to obtain, my supervisor suggested that I visit as many laboratories as possible. Most microprobes I saw had been built by the investigators, since very few establishments thought that they could afford to buy the commercial French model. It was admirable indeed to see how scientists, most of whom had not been previously involved in instrument development, managed this difficult task. Not surprisingly, the



Figure 1. Attendees at the electron probe seminar held at the National Bureau of Standards, June 12–13, 1967. From left to right: (back) S.J.B. Reed, L. Birks, N.E. Weston, G. Dörfler, P. Duncumb, D.B. Wittry, J.D. Brown, T. Hall; (middle) J.W. Criss, D.J. Nagel, I. Adler, M.A. Giles, V.D. Scott, C.J. Powell, W.J. Campbell, D.M. Poole; (front) J. Philibert, S. Sabatani, L.L. Marton, K.F.J. Heinrich, J. Henoc, G. Shinoda, T. Mulvey, J.I. Goldstein, and D.B. Brown.

performance of some of these instruments fell below expectations. However, in the process, the community gained useful experience and would eventually make important contributions to the art of electron probe construction.

Birks' laboratory was one of the first I visited. On a table covered with white cardboard was a rather small (less than 3-foot, if I remember well) electron optical column from which the X-rays exited into the room. On the table surface, several curves had been drawn with pencil, and I was informed that these were the focal circles on which the crystals and detectors were placed manually.

Among the scientists who built their own instruments was also Isidore Adler at the Geological Survey, who later would be a main investigator in the microprobe team to analyze lunar specimens. One of the points of contention at this time was the best X-ray emergence angle (the "take-off angle"). Castaing had started with a modified transmission electron microscope, and the shape of its lenses forced him to use an angle of about 16° (the specimen surface was tilted 10° with respect to the plane normal to the electron beam). In a later prototype, a light optic system with spherical mirrors was used, but the take-off angle was low. Castaing defended this choice, saying that large emergence angles would enhance the unwanted fluorescent (secondary) X-ray emission. Most British and American investigators argued instead that low take-off angles caused problems due to high X-ray absorption in the specimen, and to deviations from flatness or orientation of the specimen. Adler expressed his position on the matter quite diplomatically, say-

ing, "All I know is, my angle is six degrees, and *that* is too low." The other extreme of the angular range was an instrument with a 90° take-off angle (Shirai and Onoguchi, 1963) made possible by bending the electron beam with a magnetic prism. Such an arrangement, of course, did not allow for more than one X-ray spectrometer. Later error propagation studies at NBS [presently the National Institute of Standards and Technology (NIST)] showed that an increase in the X-ray emergence angle beyond 45° did not produce significant advantages.

Opinions also diverged about the use of electron beam area scanning. Castaing had worked with X-ray spectrometers of excellent (if not excessive) resolution, which were very sensitive to spatial alignment. He observed that the displacement of the scanning electron beam would cause intolerable variations in the observed X-ray intensities. The British investigators (mainly V. Cosslett and P. Duncumb, who worked at the Cavendish Laboratory with Cosslett), believed that the advantages of area scanning for orientation on the specimen and for qualitative element distribution studies were too great to be discarded. Cambridge Instruments Ltd., close to Cosslett's lab, produced a commercial scanning microprobe in which they minimized the problems of defocusing by using a semi-focusing X-ray spectrometer. Although the efficiency of this spectrometer was less than optimal in certain wavelength regions, it was used successfully for many years in the United Kingdom.

David Wittry with Pol Duwez (who had translated into English the 1951 doctoral thesis of Castaing), had built an

electron probe at the California Institute of Technology in Pasadena, and was the technical consultant for Applied Research Laboratories (ARL) at that time located in Montrose, CA. This company, which had previously made optical and X-ray fluorescence spectrometers for use in industry, produced a highly successful electron probe which became the most common research instrument in the USA and, for quite some time, the whole world. This instrument was also manufactured under license from ARL by Shimadzu Ltd. in Japan. With its highly original design, due to Wittry, the arguments about take-off angle and scanning were effectively settled. Its salient feature was a highly asymmetrical objective lens, shaped so that the X-rays emerging from the specimen could be observed through the bore of the lens, rather than below it. Three 4" X-ray spectrometers were located within the vacuum enclosure, rendering unnecessary the use of exit windows between the specimen and the spectrometer. This arrangement (with the option of using 11" spectrometers if higher spectral resolution was required) was responsible for the enormous bulk of the vacuum section that gave the device the looks of a pregnant whale. The specimen was raised within the bore of the final lens by an elevator. Good topographic scanning images of the specimen could be obtained by means of a detector for high-energy backscattered electrons, or by amplification and display on the oscilloscope of the current flowing from the specimen to the common ground, that was modulated by the emission of both secondary and backscattered electrons from the specimen surface. The instrument purchased by DuPont de Nemours was the fourth ARL scanning probe. When I moved to NBS in 1964, I continued working with a similar instrument.

Another excellent commercial design was due to Victor Macres. It was based on the fact that the microscopes installed in our instruments were less than optimal. In the instruments of Castaing, as well as in the ARL probe, the magnification could not be changed, and polarizers could not be used. (Only much later, ARL offered a microscope including a low-magnification mode, and the quality of the optical images was less than perfect.) This was particularly disturbing to mineralogists, for whom visual observation is of vital importance. Macres solved this problem by using an arrangement in which the electron beam impacted the specimen obliquely, and installing at a right angle to the specimen surface a high-quality light microscope. Unfortunately, the oblique electron beam complicated the quantitation procedures, since such a configuration had not been used in the experiments of Castaing (Castaing and Des-

camps, 1955; Castaing and Henoc, 1966; Green, 1963), and others on which the corrections of X-ray intensities were based.

Not all homemade instruments were successful. I recall a visit to a laboratory in Pennsylvania where an electron microscope had been converted into a makeshift microprobe. The operator analyzed a specimen I had carried with me and proudly showed me the tungsten spectrum he had obtained. Unfortunately, my specimen was a piece of tantalum. More serious was the case of a commercial enterprise that intended to build a novel type of instrument. The constructor had the mistaken idea that the limitation in the spatial resolution of the instrument was due to space charges at the crossover points of the electron beam, and he hoped to build an instrument in which the beam would be gradually compressed without crossovers. This project was vigorously criticized both by Castaing and by Coslett at the Third International Conference on X-ray Optics and X-ray Analysis at Stanford, CA in 1962, and the company went into bankruptcy at a time when 17 clients had actually ordered this instrument.

It was for a while considered that any commercial instrument should be able to produce Kossel diffraction diagrams. These are caused by diffraction of the X-rays produced by the impact of the electron beam, and are similar to normal X-ray diffraction patterns. The technique is mentioned in Castaing's thesis, and Philibert, in France, did useful investigations on precipitates in steels with it. Although I do not recall having seen any significant investigation using this technique in an electron probe in the USA, a Kossel camera was for some time considered a must for any instrument. This requirement was difficult to fulfill in the ARL probe because the position of the specimen within the bore of the objective lens. Harvey Yakowitz, who had started building a microprobe at the Metallurgy Department of NBS, showed that instead of performing this technique in the electron probe, a simple instrument could be built for this purpose (Yakowitz, 1966). And that was the last I heard about Kossel lines. Harvey later joined efforts with my team, and for many years we cooperated closely in investigating the theory of quantitative analysis.

A company in Europe developed an instrument that could be converted in 1 day from a transmission electron microscope into an electron probe (the Elmisonde). The idea of having two instruments for the price of one may have seemed attractive to the manufacturer, but few investigators found it very practical.

Another curious concept of the time was that of the

atmospheric electron probe in which the beam would emerge through a differentially pumped gate into the air. One investigator in the Boston area explained to me that lunar specimens, which could be as heavy as a ton, would be too valuable to be sectioned. Therefore, he was building an atmospheric microprobe with a specimen stage capable of holding and moving such gigantic objects. By propensity or financial necessity, he constructed every part of his instrument himself, starting with the high voltage generator. He published a method of cleaving crystals for X-ray spectrometers with a razor blade, and then his project ran out of money. B.W. Schumacher at the Ontario Research Institute in Toronto was successful in building such a device, for reasons that escape me. I do not think there are many people who, like myself, have seen an electron beam land in a beaker filled with water.

Safety precautions were not, in the early years of microanalysis, on top of our list. Yet, the safety attitudes in American laboratories, both at DuPont and at NBS, by far exceeded my experience in South America, where I had worked with about all the popular poisons (lead, arsenic, mercury, and beryllium), distilled ethyl ether on an open gas burner, and handled all sorts of acids and lyes without safety goggles, gloves, or any other such devices, pipetting by mouth all poisonous or corrosive liquids. While I am not aware that anybody's health was seriously affected by working with microprobes (including those of us who stuck their hands into the synthetic oil of the high-voltage transformers), I have heard the following story, which I pass on without guaranteeing its authenticity. It is said that a young scientist working on a high-voltage transmission electron microscope noticed strange changes in her toenails. The lady, who was quite tall, had found her space in front of the instrument quite cramped. To stretch her legs, she used to push her feet into the one little space under the instrument that was not sufficiently shielded from the X-rays generated in the column. I am confident that the damage she suffered was not substantial or permanent.

A DETECTIVE STORY

Although I was delighted by the quality of the ARL microprobe at DuPont as a scanning electron microscope, I was less impressed by its handling of the X-ray signal. The photon pulses received in the detectors were integrated by an electrometer. Hence, the count rate remained unknown, and counting statistics could not be applied nor could

pulse-height selection be performed. Having learned my lesson at Campbell's lab, I convinced management that I should replace the original X-ray electronics by a combination of proportional amplifiers, single-channel pulse height analyzers, and pulse-counting scalars, with an oscilloscope constantly monitoring the amplified detector pulses. This system permitted the exact determination of, and correction for, coincidence losses, indispensable if any quantitative treatment of X-ray intensities were to be successful, and soon it became standard.

The electronics I had installed in the DuPont microprobe were all based on vacuum tube technology. As the quality of electronic equipment improved with the arrival of solid-state devices, the virtues of the proportional detector became more evident. With a pulse duration in the microsecond range, i.e., a thousand times shorter than that of the Geiger detector, and with the capability to distinguish different orders of reflection from analyzing crystals by pulse height analysis, it became the detector of choice for analysis with crystal spectrometers until this day. In systems based on vacuum tubes, the long conducting line from the detector to the first amplifier stage often picked up electric noise. In certain buildings, critical microprobe work could not be done while the elevators were working. In another case in the Boston area, intermittent electronic noise appeared whenever it was raining. This interference proved to be due to sparks on the wet power lines of passing streetcars. Such problems disappeared with the arrival of solid state preamplifiers that could be mounted closely coupled to the detectors (and with the disappearance of streetcars). At the time these devices became available, I had moved to NBS, first in Washington, DC and later in Gaithersburg, MD. The equipment modifications on the NBS probe were performed by Charles (Chuck) Fiori, who, coming from the Museum of Natural History of the Smithsonian Institution, had joined our group. I observed, not without misgivings, how Chuck attached ugly blobs of solder and smears of isolating silicone rubber to the innards of the beast. However, there is nothing like success, and eventually I was reassured that Chuck knew very well what he was doing.

My X-ray spectrometers were also a far cry from today's equipment. The lowest atomic number of observable elements was 11 or 12. The extension of microanalysis to the elements five to nine of the periodic table would be the most significant development to follow later, since these elements include some of the most important ones for materials science, mineralogy, and biology. The dearth of natural crystals usable as diffractors was a basic handicap for a

more traditional way of analysis in the region below 1 keV. This problem was solved with the introduction of devices based on multiple layers of barium or lead stearates. The detectors employed in this energy region require very thin windows transparent to soft X-rays, and a continual gas flow compensates for the losses of gas diffusing through the window (flow proportional detector). Quantitative analysis in this energy range, however, presented serious problems that persist until the present.

At the Stanford Symposium in 1962, Ray Dolby, a Californian who did his thesis work at the Cavendish Laboratory in Cambridge, UK, astonished the audience by presenting scanning X-ray images of the spatial distribution of X-ray emissions from beryllium, carbon, and oxygen (Dolby, 1963). He used a network of three single-channel pulse height analyzers, combining and manipulating their output to achieve these spectacular results. His method was not found practical for routine analysis because of the need for massive vacuum tube electronics and cumbersome calibration procedures. But Dolby would become famous and, no doubt, wealthy, because of his invention of a system for audio amplification which is now used wherever music is recorded or replayed. He was among the small group of American scientists honored in 1999 at the White House for their achievements.

The most significant innovation in microprobe detector systems was the introduction of the lithium-drifted silicon detector (Fitzgerald et al., 1968). This energy-dispersive device provided a simple and rapid way to obtain qualitative spectra. It could also be used for scanning images and quantitative analysis. Moreover, scanning and transmission electron microscopes could be converted into analytical tools by this relatively inexpensive addition, and the analytical electron microscope based on the Si(Li) detector opened an entirely new perspective to the analysis of biological specimens. The history of this development was covered in my presentation at last year's MAS meeting (Heinrich, 1998).

STONE AGE QUANTITATION

After 50 years, Castaing's doctoral thesis remains an admirable document of technical genius, well worth its study. One of the amazing aspects of Castaing's early work is his realization that (and how) electron probe analysis could be performed with quantitative accuracy. Quantitation should be based not on the comparison of the lines of the elements in the specimen, but on the ratios of intensities of the same

emission line emitted by the specimen and by standards of known composition. The most frequently used standards were, in fact, pure elements. However, in the earlier years of microanalysis, there were still important limitations to the performance of accurate quantitative analysis:

1. The basic physical laws governing the energy loss of the penetrating electrons and the production and partial absorption of the emerging X-rays were not well established.
2. Important parameters, such as X-ray absorption coefficients, were not known with the accuracy required for quantitative analysis.
3. No computers were available that could perform the calculations that nowadays are done online as a matter of course.
4. Given the novelty of the technique, analyses and corrections were often performed by analysts without any previous training in the subject (including myself).

Castaing was quite aware that the physical events in the specimen were too complex to be described explicitly in quantitative terms. He offered an approach to determining the absorption losses of the X-rays on their way to the surface, based on clever tracer experiments that he and his collaborators performed (Castaing and Descamps, 1955; Castaing and Henoc, 1966). These experiments, and a set of measurements Green performed on elementary specimens in an instrument with variable take-off angles (Green, 1963), were to be the experimental foundation for X-ray absorption corrections for years to come. Castaing also proposed a fairly rigorous correction for the contribution of fluorescent (secondary) X-rays, later further refined by Reed and Long (1963) and by Duncumb and Shields (1963). The problem he did not solve explicitly was the determination of X-ray generation within the specimen. Instead he offered successively three approximations to provide viable solutions to the problem.

Although the proposed algorithms were semi-empirical, the French school, beginning with Castaing, always presented theoretical models to support them. I became painfully aware of my ignorance in this regard when I participated in a summer school course at MIT organized in August 1960 by Prof. Norton and his student, Robert Ogilvie, with participation of Castaing, T. Mulvey, and other European investigators. To educate myself, I collected all literature references I could gather, and this was the starting point for three editions of my microprobe bibliography (Heinrich, 1966b). I studied what was offered in these pub-

lications. What I could not fully understand, I tried to refute, often not without success.

American investigators tended to develop more empirical solutions to the performance of quantitative analysis. Birks, for instance, presented for the absorption correction a single curve for each operating voltage, as well as a very basic approach to the correction for fluorescent X-ray contributions. The most important empirical contribution to quantitation was the hyperbolic approximation, proposed by Ziebold and Ogilvie (1964), and later applied with great success to mineralogical specimens by A.E. Bence and A.L. Albee (Bence and Albee, 1968). The model attaches a factor (α -factor) to the weight concentrations of the elements in the specimen, and expresses the relation of weight concentration to relative emitted X-ray intensity by

$$K_{\alpha} = \frac{\alpha_a C_a}{\sum_i \alpha_i C_i}$$

in which C_a is the mass fraction of element a, and K_{α} is the X-ray intensity emitted by it in the specimen relative to that from a pure element. Each term α_i is an efficiency factor for the element I, (present at concentration C_i). These factors are independent of the specimen composition. Such an expression had been used previously in X-ray fluorescence spectrometry. It is formally identical to the third approximation of Castaing, which, however, was intended to describe generated, instead of emergent, X-ray intensities. Accuracy studies would show that this empirical approach works very well for the absorption correction, moderately well for the atomic number effect, and less so in the presence of significant fluorescent contributions.

My first attempt to apply corrections by hand calculation to X-ray intensity ratios from a binary Nb-Ta alloy (three iterations only) took me 3 days. Worse even, I began to realize that the best models were insufficient unless conditions such as the operating voltage were chosen judiciously, and accurate values of parameters such as the mass absorption coefficients were available. In the years to follow, I studied the propagation of errors in the analytical process, in order to be able to select proper operating procedures. Much of this work was done in cooperation with Yakowitz. I also endeavored to find the best values for parameters such as the X-ray absorption coefficients (Heinrich, 1966a; Heinrich, 1986) and the electron backscatter coefficients that have a bearing on the backscatter correction (Heinrich, 1966c). Contrary to the current assumption, the electron backscatter was found not to be a smooth function of

atomic number. It also varied with the ratio of atomic number and atomic mass. This anomaly vexes some investigators, who still have doubts (quite wrongly, I think) regarding the reality of this effect.

In the course of these studies, I got the idea of using a diamond as a carbon target, and I requested a specimen for my experiments. Soon two sinister-looking men in trench coats appeared in my laboratory and asked me to come along with them. They led me to a bank in the neighborhood, and from the vault they produced an old shoebox containing dozens of plastic containers, all filled with beautiful gem cut white diamonds. They strewed a dozen or so on the table and said, "Take your pick!" I could barely refrain myself from asking, "Can I have two?" The hoard of diamonds turned out to be jewels confiscated by the feds from smugglers.

THE COMPUTERS ARE COMING

When the quantitation theories were established, their developers usually assumed that the physical constants they applied therein were well known, or, at any event, that it was not their task to determine them. Yet, most notably in the case of absorption coefficients, the lack of precise input data frequently affected the accuracy of analysis. Before microanalysis, the exact value of these parameters seems to have been mainly of theoretical interest. In physics, like everywhere else, trends vary with time and, in the 1950s, the measurement of X-ray absorption coefficients was not in the forefront of research. The usual method to determine them is to measure the intensity of monochromatic radiation before and after insertion of a solid absorber of uniform and known thickness. Many of the published values were in error because of flawed techniques of measurement.

In sifting through the data produced by other investigators, it was reasonable to assume that recent data were, in general, more trustworthy, given the progress in the detector development. But the range of elements that could be shaped into thin homogeneous films was limited, and values for other elements had to be interpolated. Often, the coefficients were derived from measurements performed on filtered chemical precipitates, the homogeneity of which had not been tested. Such coefficients were usually too low. Another possibility, i.e., to measure X-ray attenuation in a volume of gas, the pressure of which must be accurately measured, was generally ignored.

The activities in the microprobe field stimulated new

measurements of X-ray absorption coefficients in various laboratories. At DuPont, I measured some of them with the aid of an X-ray fluorescence spectrograph since the experiments could not be performed in the ARL probe.

In the earliest years of my involvement in electron probe microanalysis, we did not have even electronic hand-held or desk calculators. The available tools for calculation were logarithmic tables, slide rules, and the manually driven mechanical desk calculator. When, in the late 1950s or early 1960s, electronic calculation became available, we had to program in FORTRAN, perforate punch cards, and stand in line at the mainframe computers that advanced research institutes had acquired. My first encounter with computers happened at DuPont de Nemours when I prepared my first table of X-ray mass absorption coefficients. Fortunately, the problem I was dealing with did not require much personal interaction with the computer. The equation I used was

$$\frac{\mu}{\rho}(a,E) = C \left(\frac{Z_a^4}{A} \right) E^{-n}$$

in which Z and A are the atomic number and weight of the element a , and C and n are parameters for a region between absorption edges, that vary slowly and continuously with Z . The log-log plot of the coefficient vs. wavelength would therefore be a straight line. Having hand-plotted the available experimental data and estimated the values of C , all there was left was to calculate thousands of points, which the computer service did for me.

Some of the assumptions current at that time limited the accuracy of these tables. One common error was to use in the above equation the term Z^3 instead of Z^4/A . A more serious inaccuracy was due to the belief that the exponential equation postulated for regions between absorption edges was rigorously valid, ignoring deviations from the model close to absorption edges. The recognition of these inadequacies led me later, at NBS, to recalculate the coefficients with a slightly more complicated model that took into account the curvatures of the log-log plot (Heinrich, 1986). This version contains algebraic expressions for all varying coefficients so that it renders actual tables unnecessary. I believe that it still is widely used.

The first on-line computation facility available to me at NBS, a shared-time telephone connection to a computer in Phoenix, AZ, with programming in Basic, was a big advance from card punching. The computer was reached through a clanking Telex typewriter, which, for years to come, would

fill the laboratory with its noise, while covering the floor with perforated paper tapes. Yet, the device was then considered a marvel, and most welcome since it could perform procedures such as the absorption correction of Philibert. The derivation of this correction, presented by Alexis Kirilenko at the Stanford conference (Philibert, 1963), filled three huge blackboards.

Our computer hookup attracted many interested observers, among them Prof. Igor Borovsky from Russia, a very tall, elegant, and dignified gentleman, who would become in time my good friend. Borovsky observed the noisy device and inquired about programming. "What happens if you type in an incorrect command?" was his question. I answered, "Try it yourself!" and he typed, "Professor Igor Borovsky, Baykov Institute of Metallurgy, Moscow, U.S.S.R." The computer promptly answered "ILLEGAL STATEMENT." I must add that the computer treated friend and foe with impartiality; once it dropped a lengthy (but unsaved) program of Harvey Yakowitz, after he, irritated by a temporary but stubborn inaction of the teletype, had entered an insulting remark.

The handling of extensive and complicated operations, and particularly the evaluation of energy-dispersive spectra from the SiLi detector, rendered indispensable the on-line connection of minicomputers such as the PDP-11. The programming needed for this purpose at NBS was mainly done by Fiori and Myklebust. The availability of on-line computers made it also possible to develop more realistic programs for the correction of X-ray intensities. The central element of the classic correction scheme is the "depth distribution model," an algebraic expression of the characteristic X-ray intensities produced at any depth within the specimen. This expression must match the previously mentioned trace experiments, some of which would be further provided by other investigators. The loss of X-rays due to absorption within the specimen could be calculated accurately, provided that the mass absorption coefficients were available. Its calculation, however, required an integration of the distribution of generation and attenuation over depth. An algorithm for this process could only be obtained if the form of the depth distribution model (the $\phi(\rho z)$ model) admitted a mathematical transform called the Laplace transform. This requirement limited the choice of expressions for the $\phi(\rho z)$ model. Furthermore, such a treatment could only be applied to specimens the composition of which was homogeneous within the excited volume. As the speed and power of computers increased, such limitations became unnecessary, and the integration over depth could be performed

numerically, a fact that, however, was ignored for many years. Such a numerical integration would eliminate the need for special treatment of layered specimens. I used numerical integration of $\phi(\rho z)$ expressions in a comparison of several correction procedures (Heinrich, 1992), but I do not know if numerical integration of depth distributions is used by anyone in present day practice.

For working at home on the second model for X-ray absorption coefficients (as well as for playing the amazing *Adventure Game*), I bought a Commodore 64. This computer was a marvel in its time, with a free word processor and a color screen, and, to the amusement of my colleagues, I would present in MAS meetings quite acceptable graphics produced on my “toy.” The computers on the microprobe and those on my desk have since grown much faster and more powerful. A lot of that power is used for fringe benefits such as choosing the color pattern for the desktop, playing a Mozart quartet, and giving me choices for word processing that I will never utilize. The price I paid was three successive desk computers, lots of software I can no longer use, and having to learn new languages such as Comal, Pascal, C⁺ and FutureBasic. I am also disturbed by the fact that some of my old colleagues still active in research spend more and more of their time on the desk computer instead of the microprobe.

A LUNATIC EXPERIENCE

No event in my career has produced more scientific excitement and stimulation of microprobe analysis than the lunar landing and the arrival of the lunar rock specimens. The exhilaration was not, of course, limited to the scientific community. It was, in a century of hot and cold wars and the atomic menace, one adventure that widened our horizons and, for a short time, our expectations for the future.

Shortly after the return of the first lunar landing team, Izzy Adler participated in the annual Denver Conference on X-ray analysis. He was mobbed by questions about the lunar materials, prematurely so because they were still in quarantine, due to a concern (which I did not share) that organisms dangerous to human health could be imported with them. To satisfy his interrogators, he announced, “Preliminary studies show that some specimens are bigger than average, while others are below mean size.” He added that, in his opinion, the lunar team could have spent their limited time on more scientific activities rather than planting the flag on the moon, since the exhaust from the rockets of the

lunar lander would have toppled it on take-off. Adler did not know that a reporter from the Denver Post was in the crowd attending his presentation. Next day he read the headline, “NASA scientist says stars and stripes no longer waving on the moon.” Due to urgent phone calls from Washington, Adler had to cut short his vacation in Colorado.

At NBS, we felt lucky to be asked to participate in the task of investigating the lunar stones. The specimens provided us many hours of exciting investigations, although, not being a geologist, I would be hard pressed to say what we learned from them. On one of our X-ray scans, we came upon an unexpected find—a phase consisting of pure potassium chloride! I called the sponsors at NASA; then I proceeded to look at the specimen in a good optical microscope. Alas, the “lunar phase” was an artifact, a microscopic crystal that somehow had become attached to the polished specimen surface. With my apologies, I explained the error to the NASA geologists. They were not pleased, since they had, meanwhile, found an explanation why potassium chloride would be present in the specimen.

After this gaffe, we worried a lot more about specimen contamination, and rightly so. As soon as the first polished and carbon-coated lunar rock arrived at our laboratory, everybody wanted to see it. But the very first visitor we admitted was not satisfied with only looking at it. Sneaking upon us, he put his finger upon the specimen before I could stop him, commenting innocently, “I almost touched it!” After the excitement had passed, and other duties called our attention, the lunar specimens stayed in our safe for 2 years, until one day we got an urgent call from NASA: Did we still have them? Yes, we did, and, reluctantly, we returned them. And yet, somewhere among the collection of specimens at NIST, there must still be a small cardboard box containing a piece of rock, and labeled: lunar specimen. How come? Well, after several visitors of our lab had “almost touched the lunar rock,” we decided that this nonsense had to stop. So we picked a piece of gravel lying outside our building, polished and carbon-coated it carefully, and presented it to them as the “rock from the moon.” If still preserved, it must by now carry the fingerprints of half the personnel of the chemistry building.

STONES IN MY HEAD

Dr. Anastasios Tousimis once gave a talk about the composition of calcifications in the pineal gland, located at the

base of the brain. He started as follows, "I wanted to know more about the stones in our heads, so I went to see my friend Kurt Heinrich." The analysis of hard tissue such as bones and teeth (and of the calcifications) is not different in principle from that of rocks. Unfortunately, the main interest of biologists and medical researchers was in the characteristics of soft tissue, and the problems arising with such specimens would take many years to solve. It seemed that every aspect of soft tissue analysis was chosen to discourage the microprobers. To begin with, one of the main areas of interest was the ratio of sodium and potassium in certain regions between cells. Sodium was then at the lowest limit of atomic number of the elements that could be detected, and the concentrations of these elements in soft tissue were much lower than those of typical mineral or alloy constituents. The distances within which gradients of these elements were being sought were close to, or below, the resolution of the technique, particularly since the electrons suffered less energy loss in the porous material constituted of low-atomic number elements. But as the means of analysis improved with the SiLi detector and the analytical electron microscope, the real challenge turned out to be the conservation of the local element distribution in the specimen during its preparation and analysis. I later worked for some time, without useful results, in cooperation with a scientist of the National Institutes of Health, on human retinas. Unless controlled by meticulous techniques, the action of the electron beam can destroy such specimens, as I learned painfully by burning retina slices. But soft tissue specimens suffer significant changes in their preparation as well. The components in the living cell are held in place by the forces that govern its functions and, as soon as life ceases, the diffusion of soluble elements begins. Water, the most abundant component of the cell, must be removed before conventional analysis, further disturbing the distribution of dissolved elements. Thus, immobilizing the tissue components before the evidence is destroyed has become one of the main preoccupations of the biological analyst. Unfortunately, after my unsuccessful bout with retinas, I was not involved in further efforts to characterize soft tissue.

EPILOGUE

One of the most gratifying aspects of early microanalysis was the friendly and cooperative spirit among the leading investigators. Their doors were always open, and I always felt welcome on my visits to their laboratories. Their advice

was always useful and their comments encouraging. Although we had spirited discussions about many aspects, they never seemed to affect our personal relations. I felt privileged to be allowed to interact with the scientists leading the research in microanalysis such as Castaing and Cosslett, Shinoda and Borovsky, Birks and Adler. Electron probe microanalysis was for me an exhilarating and gratifying experience. I hope that subsequent generations of researchers will feel the same way.

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