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Wavelength Dispersive Spectrometer and Energy Dispersive Spectrometer Automation: Past and Future Development

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Abstract: As part of the Microbeam Analysis Society (MAS) symposium marking 50 years of electron microprobe analysis, this article reviews the important advances made over the decades to the automation of data collection and computerized analysis of data from the electron microprobe. Out of many innovations that contributed to the advance of microprobe automation, we have chosen to focus on a few developments that the authors feel represent the major trends in advancement of the "state of the art" of this instrumentation. After providing brief summaries of the three generations of advances in the hardware and software of automation systems, several key applications developments are described, followed by our prediction of which current developments may impact the future automation of the microprobe.

Key words: electron microprobe analysis, automation, quantitative analysis, energy dispersive spectroscopy, wavelength dispersive spectroscopy, light element analysis, area analysis

INTRODUCTION

Automation of electron probe analysis began to accelerate rapidly in the early 1970s. This acceleration was primarily based on advances in computer technology. These advances included the availability of low cost laboratory computers and the availability of new operating systems and programming languages that the individual researcher could afford to dedicate to a single instrument. The minicomputer was the ideal device to take on the repetitive and very tedious task of scanning the wavelength dispersive spectrometer (WDS) over the entire range of possible X-ray energies, finding the peaks, and measuring the peak and background intensities. By the end of the decade, most researchers and instrument manufacturers in the microanalysis field had adopted the PDP-11 minicomputer, and programming languages such as FOCAL, FORTRAN, and BASIC that ran on these computers, to build their version of a microprobe automation system. An excellent summary of these early efforts can be found in the review article by Hatfield (1976).

In addition to the advances in computer technology, the application of the energy dispersive spectrometer (EDS), with its required multichannel analyzer (MCA) hardware, to the microprobe in 1968 accelerated the development of on-line software for data reduction. Of particular interest for the microprobe researcher was software which intended to realize the potential for saving analysis time by combined

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WDS and EDS analysis. While the full potential of such a combination has been limited by the vastly different collection efficiencies of the two types of spectrometers, the rapid adoption of the EDS for scanning electron microscopes lead to rapid software advances that also benefited both qualitative and quantitative analysis on the automated microprobe. It is from this point in time that we take up our review of progress in EDS and WDS automation of the microprobe. The next section of this review describes the developments in instrumentation systems from the late 1970s to the present, followed by a section about key applications that have been enabled by the instrumental development. The final section lists some current day innovations and the impact these technologies may have on WDS and EDS automation.

INSTRUMENT DEVELOPMENTS

The first use of the energy dispersive detector on the electron probe in 1968 added the need to control the acquisition, display, and processing of EDS spectra (Fitzgerald et al., 1968). What followed this innovation was a period of time when much effort was focused on development of hardware and software for on-line data reduction and analysis. These efforts produced systems that we shall denote as the "first generation" EDS/WDS automation system.

First Generation WDS/EDS Automation System

These systems were characterized by the use of dedicated control electronics to collect data. Often each spectrometer was controlled by a set of modules, either NIM or a collection of separate PC boards that functioned as scalar-timers, current integrators, and motor controllers. Each device was interfaced to the computer individually or to a computer "bus" that carried signals and data to and from the host computer. There was little electronic intelligence on a single board. All activities would be started by commands from the host computer. The device would carry out commands and the result transmitted back to the host for processing. A peak scan, for example, could involve lots of such transactions, but would eventually result in obtaining a measured peak intensity stored in the host computer memory. Intensities could be processed on off-line mainframes with program written in FORTRAN or APL. The result was that it could take hours to do a quantitative analysis of a few points on the sample. Soon, however, computer memory became cheap enough, and languages compact enough, to run in on-line minicomputers, and the analysis time was reduced to minutes per point. Another result of this transition to on-line processing was the creation of a suite of programs to provide on-line matrix corrections and spectral processing, and automation of WDS and EDS analysis (Chodos and Albee, 1971; Colby, 1971; Yakowitz et al., 1973; Schamber, 1977).

The culmination of these development efforts was first reported in 1977 with the analysis of a lunar whitlockite (phosphate mineral) and a common chromite specimen by simultaneous EDS/WDS measurement (McCarthy et al., 1977; Friel et al., 1977). The concentrations of 23 elements were determined in the whitlockite analysis, eight by EDS. The analysis took a total of 37 min for data collection and analysis. A block diagram of the automation system hardware is shown in Figure 1. Note that each block represents an entire PC board dedicated to the particular function described in that block. The entire system including EDS MCA, computer, and automation hardware occupied a 6-foot tall 19-inch equipment rack! In that article, the authors noted the complementary sensitivity of the EDS and WDS, and suggested the use of WDS for trace elements and severe peak overlaps, and EDS for other elements and rapid qualitative analysis, a convention that remains common on the electron microprobe even today. Toward the end of the decade, the analytical accuracy and precision achieved by automated analysis of bulk samples approached the limits of accuracy and precision imposed by the instrumental stability of the microprobe and electronics, with the exception of analysis of light element concentrations.

Benchmark Analysis for Automation Progress

The results of the chromite analysis are given in Table 1. Note that using this system in 1976, the analysis took a total of 3.6 min. We will use this analysis to summarize the progress made over the next two decades. We asked skilled researchers with the later generations of automated microprobes to reproduce the chromite analysis under the same conditions on their newer instruments. We will present the results for comparison below after a discussion of the advances in system design in the last 20 years.

Improvements: 1978–1998

The explosive growth in digital electronics and microprocessors for data processing and control functions during the

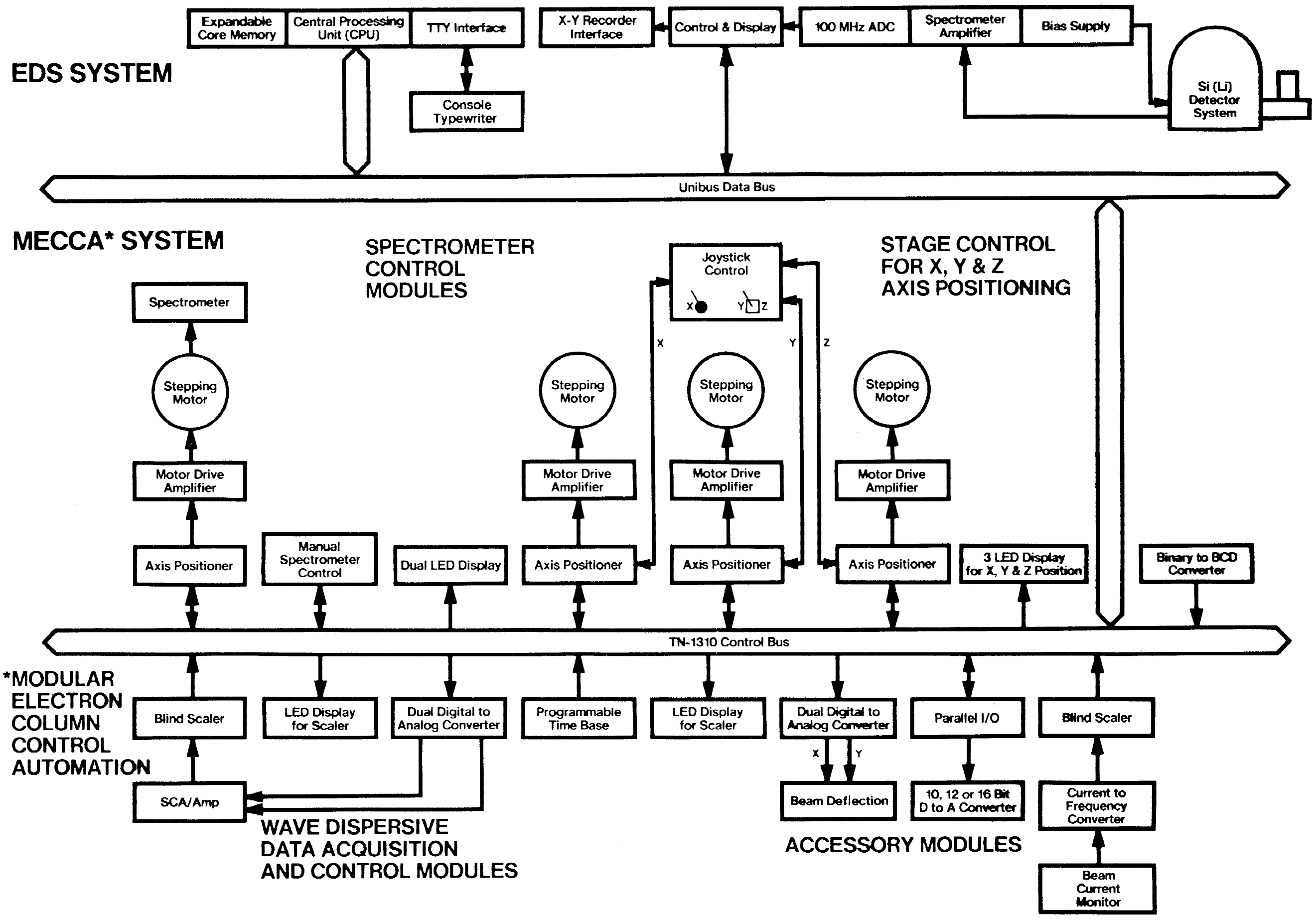


Figure 1. Block diagram of an early wavelength dispersive spectrometer (WDS) and energy dispersive spectrometer (EDS) automation system from 1977. Each block includes one or more logic boards dedicated to the function described in the block.

1980s was rapidly applied to electron probe automation. Second- and third-generation automation systems included direct digital control of many microscope functions, beam position, and imaging conditions. This was accomplished primarily by using microprocessors to make two advances in system design. First, intelligence was distributed from the host computer into a number of dedicated microprocessors plus the host computer. This allows many more operations to occur in parallel, increasing the speed of the entire system. Second, each microprocessor board can integrate a number of functions that previously required a number of separate control boards. A major improvement of this integration was that spectrometer and stage motion became more accurate and precise, very much faster, and motions could be coordinated in complex ways. For example, systems can scan the spectrometers as the beam is scanned across the sample surface in order to acquire a low-magnification, X-ray elemental image. Likewise, crystals can be changed during motion and at any point in the travel. On the host computer side, faster computers, cheap solid-state memory, and mass storage devices have allowed software developers to make even more dramatic advances. As an example, in an EDS system today, identification of 10 elements from the spectrum will take about 200 msec and the quantitative analysis can take as little as 20 msec. As a result of all these advances, the data collection and analysis of 23 elements of the lunar mineral reported in 1977 can be accomplished at least three times faster on a modern instrument.

One example of a modern combined WDS/EDS automated microprobe is shown in Figure 2. This particular system has three spectrometers and an EDS detector. A block diagram of a similar instrument is shown in Figure 3. Notice the simplification of the system hardware compared to the system described in Figure 1. The probe control system has been simplified to a single dedicated control unit that controls three intelligent controllers for the stage, spectrometers, and electron optical column. The EDS unit has a

Table 1. Chromite Analysis Results from Early WDS/EDS System in 1977[a]

WDS					EDS			Combined WDS/EDS		Classical analyses (wet chemistry)
Oxide	XTAL[e]	Conc[f] (wt%)	ΔC[g]	C_{DL}[h]	Conc (wt%)	ΔC	C_{DL}	Conc (wt%)	ΔC	Conc (wt%)
FeO	LiF	21.84	0.57	0.05	21.60	0.52	0.23	22.85 E[b]	0.52	22.09
TiO_2	LiF	0.41	0.06	0.02	0.45	0.15	0.15	0.39 E	0.15	0.46
MnO	LiF	0.38	0.06	0.01	0		0.31	0.39 W[c]	0.06	0.21
Al_2O_3	RAP	20.52	0.50	0.07	20.18	0.32	0.07	20.80 E	0.32	19.40
MgO	RAP	13.25	0.36	0.03	13.83	0.38	0.06	13.36 W	0.36	12.21
Cr_2O_3	LiF	44.43	0.53	0.03	44.28	0.74	0.19	43.94 E	0.74	44.55
NiO	LiF	0.05	0.07	0.05	0		0.28	0.01 W	0.05	0.14
V_2O_3		na[d]			na			na		0.25
CoO		na			na			na		0.04
Total		100.89			100.34			101.73		99.35
Counting time/element		30 sec			100 sec			30/100		
Data acquisition time		3.5 min			1.7 min			1.7 min		
Data reduction time		0.5 min			2.0 min			1.9 min		
Total time		4.0 min			3.7 min			3.6 min		

[a] First reported results of an automated energy dispersive spectrometer (EDS) and wavelength dispersive spectometer (WDS) analysis of a chromite sample, reprinted from McCarthy et al. (1972). Copyright 1977 by International Scientific Communications, Inc.

[b] E = EDS.

[c] W = WDS.

[d] na = not analyzed.

[e] XTAL = diffractor.

[f] Conc = concentration.

[g] ΔC = concentration uncertainty.

[h] C_{DL} = detection limit.

controller board, but both controllers interface to a single host workstation (EWS) that provides integrated printing, mass storage, control and graphical user interface for the entire system.

Chromite Analysis Comparison

A comparison of the impact of all these improvements in hardware and software has been made in a crude manner, by asking several expert microprobe users to recreate the chromite analysis of the 1977 publication. The results for the original automation system and two later systems, one from the 1985 era, the final from the 1995 time frame is given in Table 2. The conditions for each analysis were 15 kV accelerating voltage, 50 nA beam current, and 50 sec count time or 0.5% statistics on each peak. Three spectrometers were used with background measured at each point of a multiple point analysis; the time per point listed is the average time from a multiple point run of 10 or 25 points. The result is fairly impressive. The analysis time for a single analysis has been reduced by about a factor of four in the last two decades.

KEY APPLICATIONS DEVELOPMENT

The decades of the 1980s and 1990s also included efforts that extended both the analytical results and the application of the automated instrument to specific applications. Two applications, in particular, that have required the use of WDS and the microprobe, have benefited from improved automation. These applications are accurate and precise analysis of light elements and area analysis. Area analysis is commonly done to determine the homogeneity of concentrations in a specimen, or to detect flaws or inclusions. Refinement of each of these applications played a role in shaping the further development of automated equipment. Likewise, automated systems enabled researchers to refine

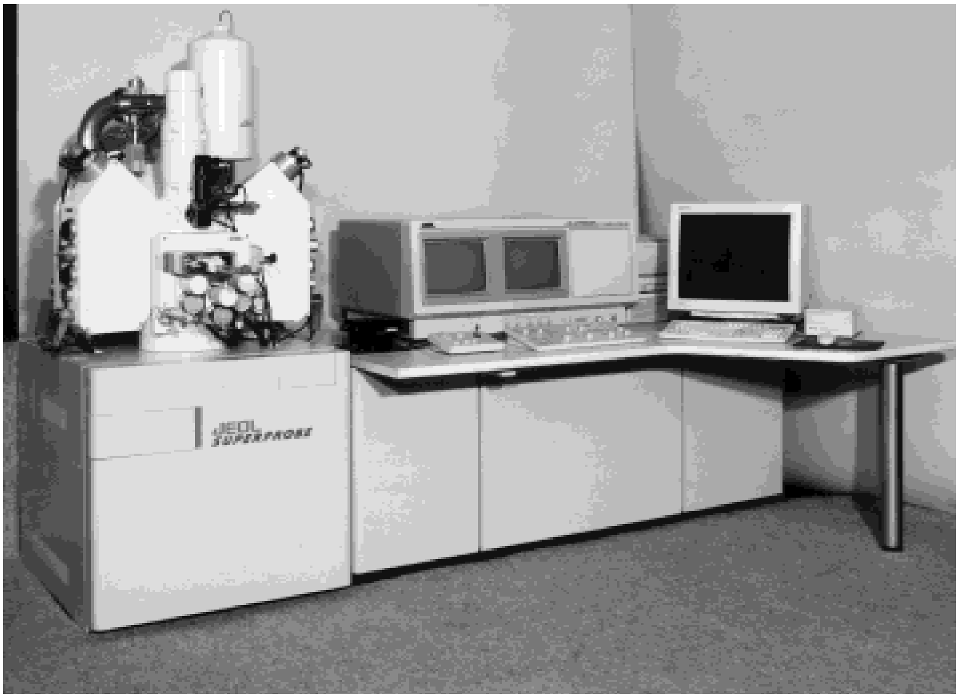


Figure 2. Photo of a modern WDS and EDS automation system. The entire automation system has been integrated into the electronics console of the microprobe itself. Control of the analytical system is via the workstation pictured on the far right-hand side.

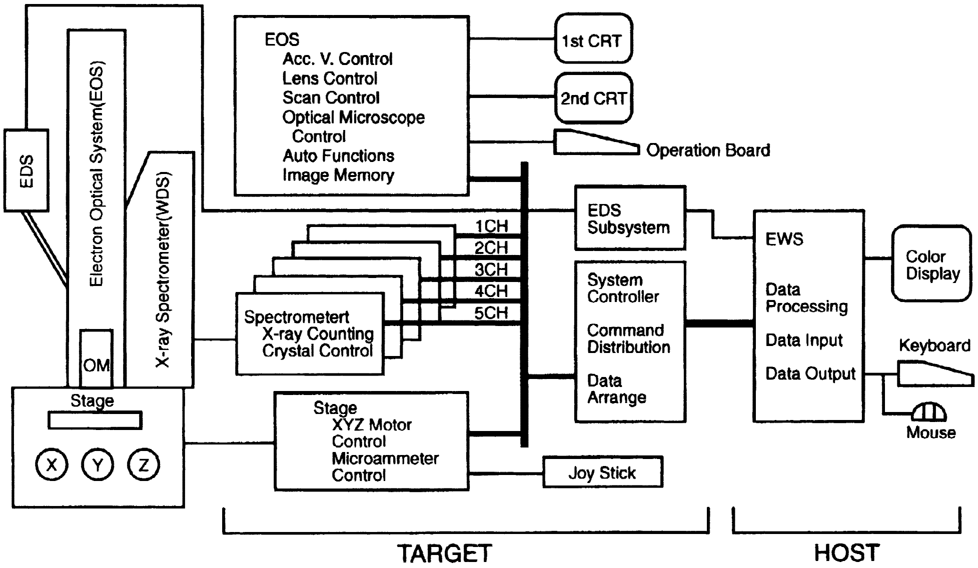


Figure 3. Block diagram of the automation system shown in Figure 2. Note that automation has been highly integrated into three or four intelligent subsystems that can coordinate via a system control bus to the microscope controller and the host workstation (EWS). Image data are displayed on the normal scanning electron microscope cathode ray tube (CRT) display or the color display.

the accuracy and scope of these key applications. We will discuss the contribution and impact improved WDS and EDS automation to each of these applications in this section.

Light Element Analysis

The refinement of Φ(ρz) methods has been a major effort since the early 1980s. The need for accurate microanalysis of

Table 2. Comparison of Chromite Analysis Results from Three Generations of Automated Systems

System date	Microprobe	WDS analysis time (min)	Automation system and software
1977	ARL-EMX	4	Tracor/Tracor
1985	Cameca MBX	2.7	Tracor/Sandia
1995	JEOL 8900	1.2	JEOL

Table 3. Illustration of the Improvement in Precision of the Second Generation of Phi-Rho-Z Corrections for Ultra-light Elements[a]

Element	PROZA96		ZAF	
(# analysis)	*k*′/*k*	rms (%)[b]	*k*′/*k*	rms (%)
B (192)	1.0022	3.3114	1.0019	12.8484
C (114)	1.0001	3.2092	.9986	15.4000
O (144)	0.9989	3.6820	1.0291	12.0841
N (294)	1.0004	2.0090	0.9913	9.3734

[a] Computed *k*-ratios and variance of the results are compared to the same results from a modern ZAF correction program.

[b] rms = root mean square error.

light elements is a direct result of the interest in developing new classes of materials with extremes in properties like hardness, wear-resistance and high temperatures. Often such properties are obtained by incorporation of compounds containing the light elements B, C, N, and O. Since the properties of materials are linked to microstructure, accurate microanalysis of the microstructure is required. Much of the analytical data that led to the improvement in light element analysis embodied in the current Phi-Rho-Z correction software was collected by automated electron probe analysis, a process far too tedious to have been done manually. In a series of studies ranging over more than a decade, Bastin and Heijligers (1998), used an automated WDS/EDS system to study the practical problems in the quantitative analysis of the light elements, and used the data to greatly improve the ability of the $\Phi(\rho z)$ matrix correction program. The result of this hard and patient work is given in Table 3. Compared to the usual ZAF correction procedure, the analysis procedure developed provides better than a factor of four improvement in the root mean square error (rms) of the analysis of B, C, N, and O. The program used is called PROZA96.

Area Analysis

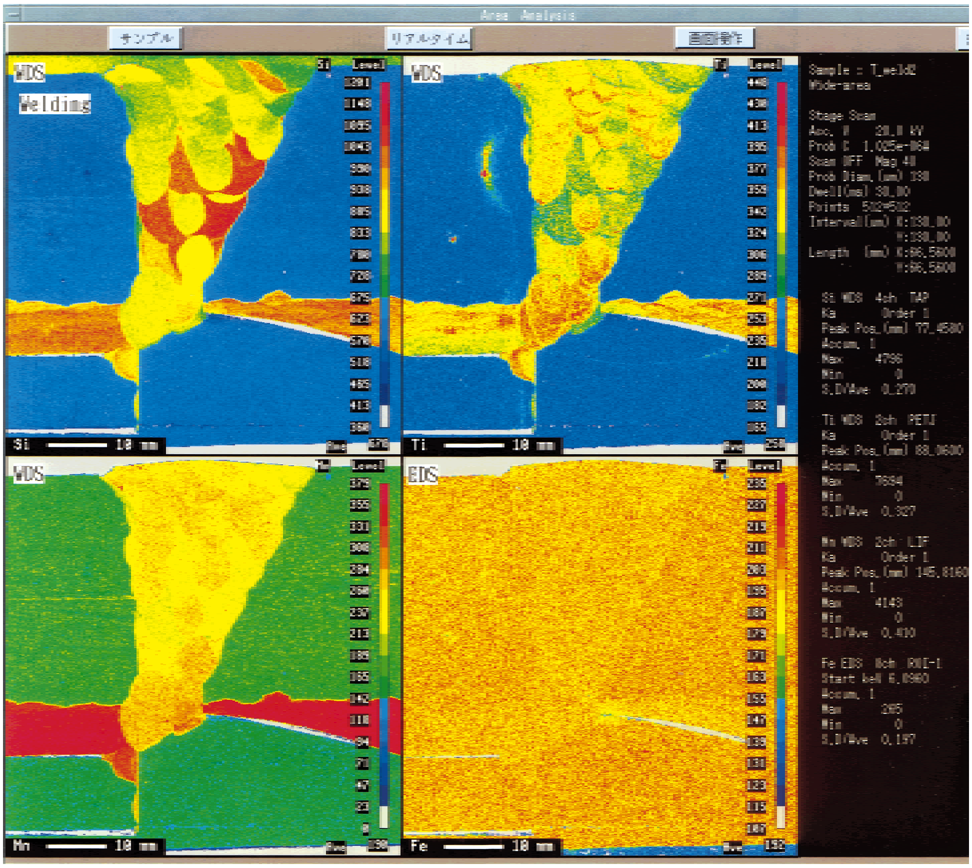
Area analysis has been used to determine the spatial distribution of elemental composition of minerals or trace elements in steels for decades. When the variation of composition on the scale of microns is required, the instrument of choice is the electron microprobe. The most common approach to area analysis involves measuring the concentrations at each point in a regular array of points on the sample, and determining the statistical variations of the results or somehow visualizing the quantitative elemental distribution (particularly of trace elements) as an image. Many approaches have been used to perform an area analysis. Area analysis may be performed over fairly small areas with random assignment of the spots or of large areas scanned in a regular array. In the 1970s, the procedure for area analysis in the microprobe was manual and tedious. The sample was observed via the optical microscope attachment and manually positioned to each spot in an array on the sample. Typical analysis involved 100 × 100 points and required tuning multiple spectrometers. Data reduction was done off-line. Such a procedure could take many hours, if not days, to complete.

WDS/EDS automation has greatly reduced the time to do area analysis and improved the interpretation of the results. The most common methods to perform automated area analysis are by stage scanning, or by beam scanning, with or without spectrometer scanning. The hardware and software advances that improve both methods will be described next.

Large Area Analysis

The first improvement resulted from major advances in stage scanning speeds and data processing speeds. The use of advanced motor controllers driving DC motors allows the stage to be rastered over areas as large as tens of millimeters while intensity data is collected from each spectrometer and the EDS. Such a system has been described by several authors (Buskes and Baughman, 1988; Nagatsuka et al., 1988). For maximum speed, the spectrometers cannot move, and average background intensities per element must be predetermined. If all elements are measured, or calibration factors obtained for each element, the elemental concentration at each point can be computed as the intensity data is collected. Images of the intensity, or concentration, can be displayed live, on-line, or stored for later inspection. Typical performance is a total collection time of 3 hr for 512 × 512 points (pixels), counting time 30 msec/pixel, 1 μA of beam current, at 20 kV accelerating voltage. Figure 4 is an example of an area analysis taken by the microprobe described in Figure 3. The image is of a weld in a Fe-based material, which covers an area of 66 mm × 66 mm. The intensity variation and average intensity for four elements are shown: three elements, Si, Ti, and Mn are monitored by WDS, and the Fe in the base alloy by EDS.

The drawback with this type of system was the inability to store unprocessed data, measure backgrounds accurately, or collect data for all elements without sacrificing analysis



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Sample : T_weld2
Wide-area

Stage Scan
Acc. V     20.0 kV
Prob C  1.025e-06A
Scan OFF  Mag 40
Prob Diam.(um) 130
Dwell(ms) 30.00
Points  512*512
Interval(um) X:130.00
             Y:130.00
Length  (mm) X:66.5600
             Y:66.5600

  Si WDS  4ch  TAP
  Ka        Order 1
  Peak Pos.(mm) 77.4580
  Accum. 1
  Max      4796
  Min         0
  S.D/Ave  0.270

  Ti WDS  2ch  PETJ
  Ka        Order 1
  Peak Pos.(mm) 88.0600
  Accum. 1
  Max      7694
  Min         0
  S.D/Ave  0.327

  Mn WDS  2ch  LIF
  Ka        Order 1
  Peak Pos.(mm) 146.8160
  Accum. 1
  Max      4143
  Min         0
  S.D/Ave  0.410

  Fe EDS  0ch  ROI-1
  Start keV 6.0960
  Accum. 1
  Max       265
  Min         0
  S.D/Ave  0.197
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Figure 4. An example of an automated area analysis of a 66 mm × 66 mm area of a weld in a metal sample. The analysis was performed on a system similar to that shown in Figure 2. Both EDS and WDS data were collected and displayed as intensity maps.

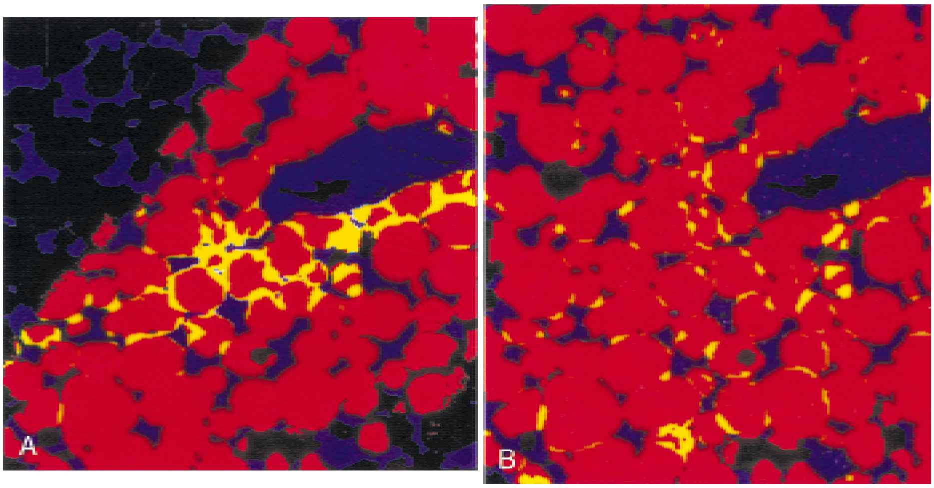

Figure 5. An example of an area analysis using the technique of compositional mapping. The data were collected at low magnification (field width is 500 μm) using three WDS spectrometers, and the composition at each point was calculated. **A:** The distortion due to defocus is shown. **B:** This distortion can be corrected by processing after data collection in this method, and the result is shown.

speed. This prevents later reanalysis of the data, such as adding elements to the analysis at a later time, or using image processing to enhance the data interpretation.

Low-magnification Area Analysis and Compositional Imaging

Many of the limitations of large area analysis were addressed as part of the effort to improve low-magnification mapping and analysis by beam scanning. Low-magnification area analysis can be performed by stage scanning, but this may not be the most time efficient due to the large stage movements involved. Beam scanning would be more efficient but is more difficult to do with WDS because of severe effects of defocusing on the WDS intensities. While defocusing can be eliminated by spectrometer scanning, the beam scan needs to be aligned with a single spectrometer in most cases, so this is not efficient either. A method to address these problems was explored and described in detail by a team at the National Institute of Standards and Technology (NIST) over the decade from mid-1980 to mid-1990 (Marinenko et al., 1987; Newbury et al., 1990). The solution is a result of faster computers, and much cheaper memory and storage media. At each point in the area analysis, the collected intensities are stored and quantification is done on each pixel, either when collected or in post-processing. In all cases, the raw data for each point is stored and saved for later correction or other processing. Operations that may be carried out on each pixel include dead time correction, peak overlap correction (if required), background correction, defocusing and collimation effects corrected, standardization, matrix correction, and image processing and display. An example of the result of this approach to area analysis is shown in Figure 5A, B. The sample is a ceramic with cobalt, vanadium, and magnesium present in the phases. The field width is 500 μm. Each image is a quantitative map of the magnesium concentration. A vanadium-rich inclusion is visible in the upper right-hand corner. In Figure 5A, the map is greatly distorted by the effect of spectrometer defocusing at the edges of the image. Figure 5B shows the accurate magnesium concentration after the data has been processed to remove the defocus effects. The NIST group called this method digital compositional mapping. It has recently been extended dramatically by collecting and storing complete EDS spectra at each point in an area analysis. This allows the researcher to construct images of elements that were not originally thought to be in the sample but were discovered by further processing of the data set. This new form of area analysis commonly has been called compositional imaging.

FUTURE DEVELOPMENT

Significant improvements in instrumentation provide benefits to the researcher by reducing the time to perform an analysis, improving the sensitivity or accuracy of measurements or lowering the cost of the instrument. As instrumentation specialists, we will leave the issue of improving the accuracy of quantitative analysis to others, and address the prospects for improvements in measurement time and sensitivity. Two emerging technologies show the promise of having a significant impact on the measurement times required for an analysis. The first technology is the microcalorimeter EDS. The second is compact X-ray optics that can be used with WDS or EDS to improve collection efficiency (Agnello et al., 1997; McCarthy and McMillan, 1998). Taken together, these technologies may change the complementary roles of these spectrometers to one of near parity. The microcalorimeter EDS (Wollman et al., 1997) coupled with an X-ray optic possesses resolution on the order of 10 eV over a broad energy range (200 eV to 10 keV) and has the parallel collection property of a current EDS. With a slight improvement (2×) in its current count rate capability, the microcalorimeter EDS can be equal in sensitivity to the WDS except for trace elements <0.1 wt%. If so, the analysis of lunar whitlockite could be accomplished within several hundred seconds, which represents an improvement of an order of magnitude in analysis time! This improvement leads us to imagine a future automated electron probe instrument where the primary spectrometer is a microcalorimeter EDS equipped with a single WDS for the occasional determination of minor trace elements.

SUMMARY

Out of many innovations that contributed to the advance of microprobe automation, we have reviewed a few key developments in this article that the authors feel represent the major trends in advancement of the "state of the art" of this instrumentation. In this brief summary of the nearly three decades of development of the hardware and software of automation systems, we have surely left out many contributions that should have been mentioned. We apologize for these omissions. However, it is clear from this review that impressive progress has been made, which we can summarize quite briefly as follows:

- Single point data collection improved by factor of 4
  e.g., chromite analysis: 1978—4 min; 1999—1 min
- Quantitative analysis speed improved by factor of 10,000
- Area scans fully quantitative in 3 h vs. 2 days. Factor of >8
- Light element quantitative accuracy improved by a factor of 4

We also are convinced that with the introduction of exciting new technologies, such as X-ray optical devices and the microcalorimeter, the future will hold advances as dramatic as those of the past.

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