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RECENT DEVELOPMENTS IN WAVELENGTH AND ENERGY DISPERSIVE SPECTROMETRY

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Abstract - The past few years have seen major developments in the field of X-ray instrumentation and in addition, great progress has been made in the provision of algorithms for the conversion of characteristic X-ray wavelength intensity to concentration.

The energy dispersive spectrometer, which made its impact in X-ray spectrometry in the early 1970's, is now largely established and in many cases can be considered a viable alternative to the wavelength dispersive system. The energy dispersive system offers significant advantages in speed and overall system cost, although lacking somewhat in sensitivity, particularly in the lower atomic number regions. Earlier count rate limitations have been greatly reduced by design of faster counting and scaling electronics, and by the design of secondary emission sources giving selected energy range excitation.

Minicomputer development has continued to influence the design of both wavelength and energy dispersive spectrometers and the most recent development of low cost floppy disc systems is likely to have a significant influence in mathematical correction procedures over the next few years. For many years, the high cost of core space has limited the mathematical capability of integrated computer/spectrometer combinations to the extent that only semi-empirical matrix correction techniques could be employed. It is to be hoped that the availability of low cost core space will allow the use and further development of fundamental type algorithms which allow elemental analysis with the minimum of calibration standards.

The greatest remaining obstacle to rapid and accurate X-ray analysis is the need to obtain a specimen which is homogeneous over the analysed depth, which in the case of the lower atomic number elements may amount to only a few microns. This is of particular importance in the analysis of ore and mineral specimens where small scale heterogeneity is commonplace.

This paper reviews these and other problems and seeks to define the current state of the art in analytical X-ray emission spectrometry.

INTRODUCTION

The past few years have seen major developments in the field of X-ray emission spectrometry and modern machines are capable of high speed replicate analyses giving excellent sensitivity to the low part per million range. Where the specimen being analyzed is reasonably homogeneous, over the tens of microns range, high accuracies can also be obtained with minimum use of calibration standards.

The sensitivity of the wavelength dispersive spectrometer has improved somewhat during the past five years or so, but major advances in this area have mainly involved the method of data acquisition. On the other hand, technology in the area of energy dispersive spectrometers has developed tremendously during the same time period and in a growing number of instances the two techniques are in direct competition with each other.

Taking first the area of instrumentation for energy dispersive spectrometry this technique first made its impact in the early 1970's, and is now largely established, in many cases being considered a viable alternative to the wavelength dispersive system. Although still lacking somewhat in low atomic number region sensitivity, the energy dispersive spectrometer offers significant advantages in speed over the single channel wavelength dispersive system and cost over the multichannel wavelength dispersive system. The ability to acquire the total emission spectrum from the specimen simultaneously, is particularly advantageous in those cases where quantitative or semi-quantitative analysis is required on a specimen whose previous history is unknown. Typical of this situation are applications in exploration and field surveys which may involve large numbers of samples and in which the presence of both expected and unexpected elements may be important.

Further examples include the forensic and pollution monitoring fields where the energy dispersive technique is already making a major contribution. Total counting rates in energy dispersive systems are still limited to around $4\text{x}10^4$ c/s provided reasonable energy resolution characteristics are to be maintained. Since the total photon flux from all elements in the analyzed specimen is incident on the detector at the same time, earlier bremsstrahlung source energy dispersive units suffered both in sensitivity and pulse resolution. Although these count rate limitations have now been greatly reduced by proper design of faster scaling electronics, the modern energy dispersive spectrometer gains its flexibility from a variety of secondary fluorescer/filter combinations, yielding a wide, selectable range of excitation conditions, in turn allowing selective excitation of segments of the total energy region. Although the secondary fluorescer system is slower and somewhat more costly than its bremsstrahlung source counterpart, the sensitivity and accuracy obtainable with the secondary approach compare favourably with those of the wavelength dispersive system, while, of course, retaining most of the inherent advantages of the energy dispersive spectrometer.

Basically five types of excitation sources are used in modern energy dispersive spectrometers and these are listed in table 1. The cheapest source is the low power continuous source which runs typically at 500 watts and offers good general purpose analytical characteristics. When used in the pulsed or continuous mode it gives reasonable performance for wide element range excitation. Both the scatter/diffractor 1) and the regenerative monochromatic filter 2) offer definite advantages in certain portions of the element region but probably the most versatile excitation method is the secondary fluorescer method 3) used with or without additional filtration. The scheme of such a system is shown in fig.1. Careful choice of fluorescer and filter give a wide range of source energy distributions giving in turn selective and efficient excitation over different portions of the atomic number region.

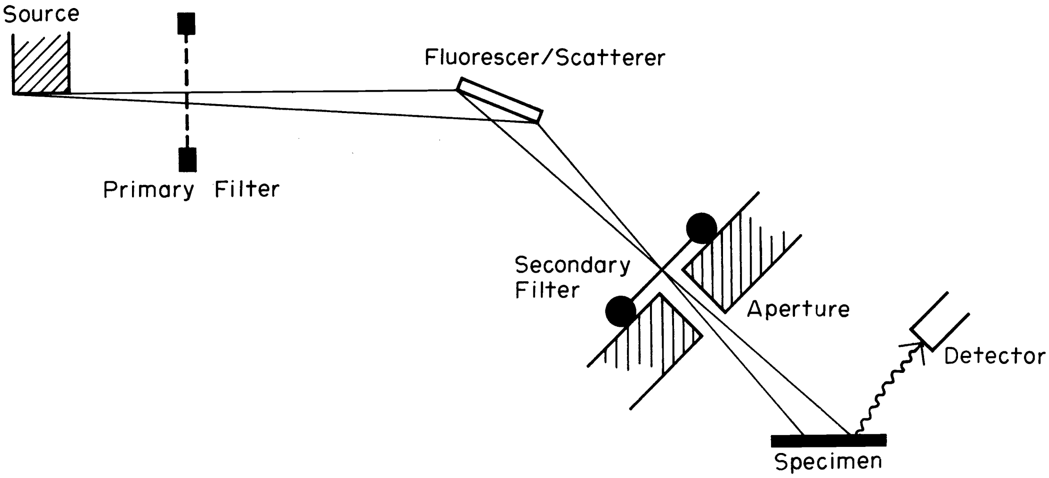


Figure 1. Basic Geometry of Secondary Fluorescer

As an example, the data given in table 2 were obtained on the U.S. Environmental Protection Agency standard filter papers 4). A summary of average peak and backgrounds is given along with detection limits obtained in 100 seconds real time using the EDS secondary fluorescer system and the conventional single channel wavelength dispersive spectrometer.

In general the EDS configuration gives detection limits 2-5 times worse for the heavier elements and an order of magnitude worse for the light elements where the secondary fluorescer technique is least optimal. Table 3 shows a similar comparison for the U.S.G.S. Standard Rock AGV-1. These data give an absolute comparison between the EDS and WDS techniques but it will be appreciated that in the EDS case many elements are determined simultaneously, and a significant time advantage may accrue.

The major advances in the basic instrumentation for wavelength dispersive spectrometry lies in the provision of high intensity, thin window, reverse potential X-ray tubes, and in the use of logarithmically bent analysing crystals. This later development retains the high efficiency of the Johannson arrangement but has the advantage of being easily tunable for different wavelengths. These improvements, when incorporated into the multi-channel spectrometer, allow the simultaneous analysis of nearly thirty elements in less than a minute. As an example the data given in table 4 were obtained on converter slags using a modern multichannel wavelength dispersive spectrometer. Excellent accuracy was obtained on a wide range of elements in a counting time of 20 seconds. The conventional wavelength dispersive spectrometer still lacks somewhat in sensitivity for the longer wavelengths but some of the newer acid phthalate crystals allow sensitivities, for the lower atomic number elements, down to the low ppm region.

Table 1

Excitation methods used in energy dispersive spectrometry

1. Bremsstrahlung Source, Continuous Excitation

   Typical loading 500 watts at 50 kV maximum optimum for energies up to 5 keV. The cheapest excitation source. Probably the best solution for a wide range of Z's at medium/high concentration ranges.

2. Bremsstrahlung Source, Pulsed excitation

   Similar to 1 but pulsing of the source significantly reduces pulse pile-up giving better counting efficiency above 5,000 c/s.

3. Secondary Fluorescer/Filter

   Gives wide range of excitation conditions. Excellent for trace analysis in energy range 5-25 keV. Slow for wide ranges of atomic numbers. Poor for low Z elements.

4. Scatterer/Diffractor

   Gives intense, almost monochromatic excitation. Good for a narrow range of energies. Greatly simplifies matrix effect calculation.

5. Regenerative Monochromator Filter

   Similar to transmission target X-ray tube. Good for medium to high Z elements.

Table 2

Data obtained on Environmental Protection Agency Standard Filters using Energy Dispersive (EDS) and Wavelength Dispersive (WDS) Spectrometers

							EDS	WDS			
Elem	keV	R_p	R_b	C	Unit	M	C_{MDL}	C^*_{MDL}	Target	KV	MA
Na	1.04	6.46	4.78	23.6	$\mu g/cm^2$	0.071	9.21	1.30	Si	25	50
Mg	1.24	7.10	4.57	29.6	"	0.085	7.50	0.40	Si	25	50
K	3.32	517.16	13.20	27.1	"	18.6	0.059	0.0040	Ti	25	35
Ca	3.68	486.77	13.89	19.1	"	24.8	0.045	0.0038	Ti	25	35
V	4.94	463.64	1.63	16.7	"	27.7	0.014	0.0081	Cu	35	35
Co	6.92	292.83	5.22	3.54	"	81.2	0.008	0.014	Cu	35	35
Zn	8.62	128.84	4.13	13.5	"	9.24	0.066	0.018	Mo	45	35
As	10.54	239.93	4.77	17.9	"	13.1	0.05	0.030	Mo	45	35
As	11.72	41.52	3.47	17.9	"	2.13	0.26	0.215	Mo	45	35
Br	11.91	1104.75	3.56	55.4	"	19.9	0.028	0.034	Mo	45	35
Ba	4.47	191.20	1.58	22.9	"	8.28	0.046	0.0048	Cu	35	35
Pb	12.61	241.77	7.32	27.8	"	8.43	0.096	0.106	Mo	45	35
Cd	3.14	219.43	3.32	30.9	"	6.99	0.078	0.014	Ti	25	45
Cd	23.10	175.03	15.90	30.9	"	5.15	0.23	0.264	Sm	60	30
Sn	3.44	361.17	3.81	14.4	"	24.8	0.024	0.116	Ti	25	40
Sn	25.17	226.50	32.57	14.4	"	13.5	0.13		Sm	60	30

Table 3

Data obtained on U.S.G.S. Standard Rock AGV-1

							EDS	WDS			
Elem	kev	R_p	R_b	C	Unit	M	C_{MDL}	C^*_{MDL}	Target	KV	MA
Na	1.04	11.36	9.71	3.21	%	0.51	1.82	0.0107	Ti	20	25
Na	1.04	12.21	10.62	3.21	%	0.50	1.97		Ag	25	30
P	2.00	0.58	5.64	70	ppm	0.056	12.7	0.622	Ag	25	30
Mn	5.90	45.33	7.76	980	ppm	0.038	21.8	11.0	Cu	25	20
Cu	8.04	14.01	4.73	63.7	ppm	0.15	4.5		Ge	30	4

Minicomputer development has continued to greatly influence the design of both wavelength and energy dispersive spectrometers and the most recent development of the low cost floppy disc system is likely to further enhance this trend. Computer controlled X-ray spectrometers have been available since the mid 1950's and there are many hundreds of these systems in use today. The degree of sophistication of these machines has increased gradually over the past several years but in all cases the flexibility of the analytical system is directly relatable to the available computer hardware. Table 5 shows the evolution of the hardware used in these systems and indicates that the early machines typically used 4-8K mini-computers with paper tape as the indirect storage media. Programs were then almost exclusively written in assembler code and nearly all manufacturers offered relatively inflexible "canned" programs. By the early 1970's, a new level was reached with availability of magnetic cassette oriented systems and in many cases, use of real time cassette monitors allowed the use of high level language programs - typically FORTRAN or BASIC. The more recent advent of the floppy disc system now allows us to move to yet another plateau.

The floppy disc essentially gives firm disc performance at a price comparable with tape cassette systems. To the programmer this in turn means large virtual memory capability in a minicomputer environment. Computer costs have continued to drop over the past several years and current core costs in the U.S.A. are around 10 cents/word for direct access core and 1 cent/word for virtual memory. It is now possible to obtain a one µ sec cycle time, 32K computer with twin floppy discs and a sophisticated high-speed graphics terminal, for around U.S. $10,000. Most computer manufacturers now include in their standard software, sophisticated real-time operating system software and newer computer controlled spectrometers run in a highly efficient, interactive, multi-tasking environment. Reduced core costs also allow the use of high level language programming and most computer controlled spectrometer manufacturers are now turning to data handling programs which are written in FORTRAN or BASIC, with assembler language routines to control the spectrometer hardware and data acquisition. This in turn means that inflexible, machine-dependent, software is being replaced by flexible, modular programs which are relatively easy to modify by the average X-ray spectroscopist. A major consequence of this in the near future will be the development of many more approaches to the provision of intensity/concentration algorithms, since the programming development will now lie with the spectroscopist rather than the specialist computer programmer.

In addition to offering great flexibility in terms of routine quantitative analysis, incorporation of a high speed graphics terminal reduces much of the tedium in calibration of the spectrometer. The terminal can be used for the display of spectra, of pulse amplitude distributions from the detectors, or for intensity/concentration calibration data. Easy access to intensity/concentration data bases, along with curve fitting and regression routines allows calibration constants to be obtained with ease.

As far as hardware control is concerned, use of a highly interactive disc operating system allows great flexibility in the control of data acquisition5). As an example, a qualitative analysis using a wavelength dispersive X-ray spectrometer has traditionally

Table 4

Analysis of Converter Slag with the Multichannel Wavelength Dispersive Spectrometer *

Element	Concentration Range (%)	1 sigma wt. (%)
Mg	0.5 - 9	$0.040\sqrt{C+2.9}$
Al	0.5 - 13	$0.017\sqrt{C+0.3}$
Si	0.5 - 60	$0.024\sqrt{C+0.2}$
P	0.01 - 8	$0.011\sqrt{C+0.2}$
Ca	0.1 - 60	$0.011\sqrt{C+0.6}$
Ti	0.1 - 1	$0.011\sqrt{C+0.2}$
V	0.1 - 1	$0.011\sqrt{C+0.2}$
Cr	0.1 - 4	$0.007\sqrt{C+0.3}$
Mn	0.5 - 20	$0.005\sqrt{C+0.2}$
Fe	0.8 - 25	$0.006\sqrt{C+0.3}$

* Samples Fused 1:40 with lithium tetraborate

Table 5

Evolution of Computer Hardware used in the Automatic X-Ray Spectrometer

	Direct Access	Indirect Storage		Programming Languages
Time Period	Core Size	Media	Access Times	
Mid 1960's	4 - 8K	Paper-tape	Minutes	Assembler
Early 1970's	8 - 16K	Cassette	Seconds	Assembler/High Level
Mid 1970's	32K	Floppy-Disc	Milliseconds	High Level

been done by scanning the goniometer over a selected 2θ range, at the same time integrating the pulses from the detector in a rate meter circuit and displaying the resulting analog signal on an X/t recorder. This process is relatively time-consuming, particularly in those cases where data on the whole atomic number range is required. Table 6 gives typical data acquisition time for a wavelength dispersive spectrometer and it will be seen that where the whole range of elememts from fluorine upwards is required, about 2 hours of total scanning time is necessary, with 4 or 5 changes of instrumental conditions.

Table 6

Typical Data Acquisition Times with a Wavelength, Dispersive Spectrometer

Element Range	Crystal	2θ Range and Scanning Time
F plus Na	TAP	$2 \times 3^0 = 6^0$ at 1^0/min = 6 mins.
Mg	ADP	3^0 at 1^0/min = 3 mins.
Al to K	PE	$45\text{-}145^0 = 100^0$ at 2^0/min = 50 mins.
Ca to U	LiF(200)	$10\text{-}120^0 = 110^0$ at 2^0/min = 55 mins.

Total Scanning Time = 114 mins.

Resetting of Conditions = 6 mins.

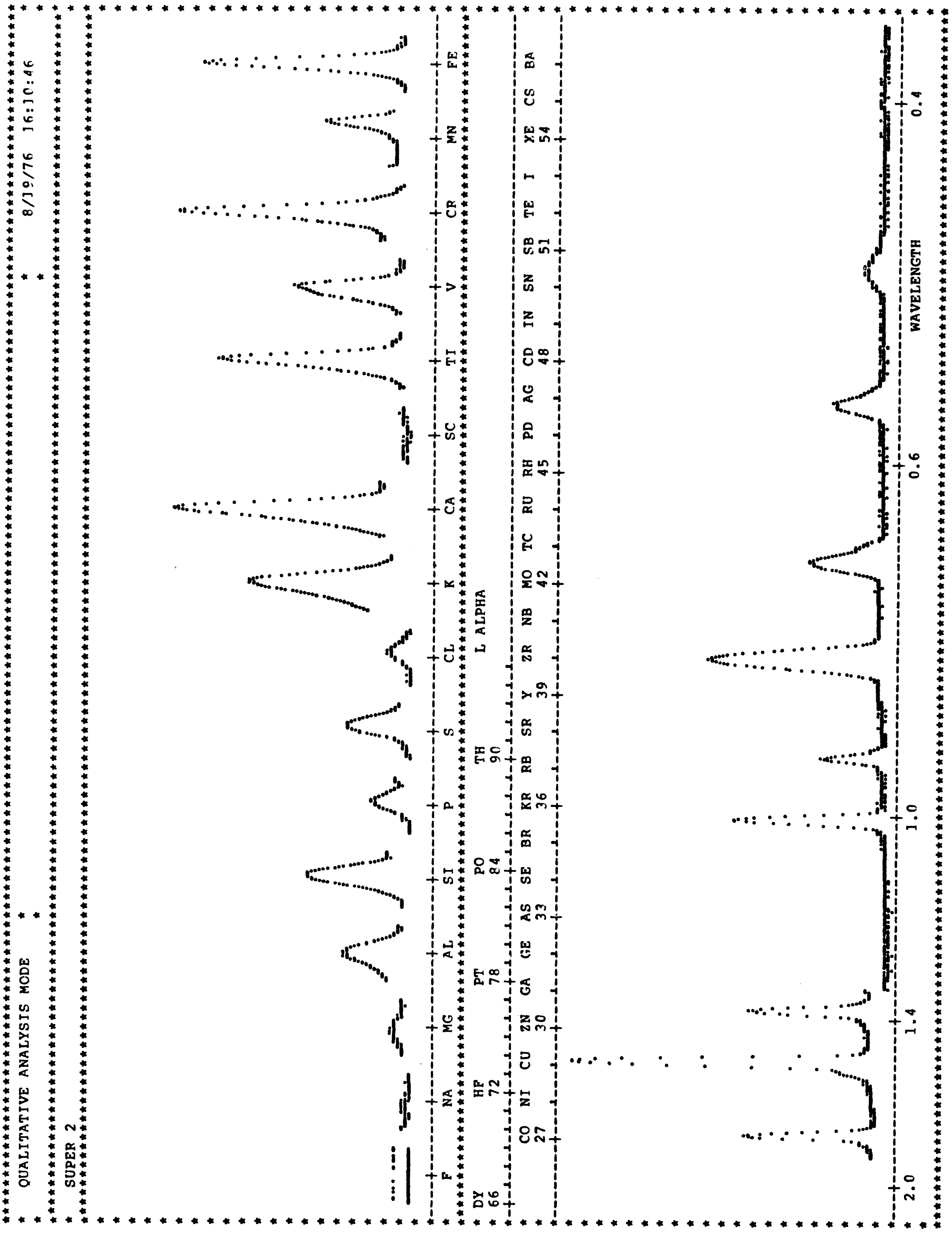
Total 120 mins.

This latter point means, in turn, that the operator must be in the vicinity to make the required parameter changes as required. In addition to the time problem, the automation of such a system is unwieldy, particularly where multiple sample handling is desirable.

The direct synchronisation of the goniometer and X/t recorder, both of which are scanning at a fixed rate, also leads to several major drawbacks. For example, due to the fact that a fixed $d\theta/dt$ rate is being used on the goniometer, a plot is obtained in which λ varies as the Sin of θ. Also, since λ varies as approximately $1/Z^2$, the atomic number scale in the resulting spectrogram is a complex function requiring the use of look-up tables or charts to identify atomic numbers from the diffraction maxima in the spectrogram. A further consequence is that for a fixed spectral series (e.g. $K\alpha$ lines) and a fixed (n/2d), Z varies as $1/\sqrt{\text{Sin}\theta}$, hence spectra will tend to be cluttered at low 2θ values and widely spread at high 2θ values.

In our own laboratory we have taken another look at this problem using a modern interactive spectrometer incorporating an X/Y plotter and we have found that many improvements can be made. In defining an improved qualitative system, it is useful to devote a minimum time to scanning over (generally) irrelevant portions of the spectral region. This is particularly the case in the Low Z region F (9) to Fe (26) where the optimum situation is probably to slew rapidly to the vicinity of the strongest line of the element, step slowly over this line, slew to the next element, and so on. By selecting the optimum measuring conditions for each element during each slew cycle each element can be measured under conditions of maximum sensitivity. Another useful technique is to allow the intensity to be displayed as $\sqrt{I}$ rather than I, which allows reasonable profiles to be obtained for both low and high concentrations.

For the middle and high atomic number range, this slew/step technique is not the best since there are multiple series of lines present which may also be useful in interpretation. In this region, we use a rather novel alternative approach in which the X axis of the plotter is incremented at each goniometer step increment, but in which the goniometer step increment is varied over the 2θ range. This allows us to obtain a spectrogram which is linear in Z, giving the dual advantages of data acquisition at an optimum rate, plus an output which is very easily interpreted. Again, we have the $\sqrt{I}$ option for the Y axis, if required.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8/19/76 16:10:46
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MG
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DY 66
HF 72
PT 78
PO 84
TH 90
L ALPHA
CO 27
NI
CU
ZN 30
GA
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AS 33
SE
BR
KR 36
RB
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Y 39
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MO 42
TC
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RH 45
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AG
CD 48
IN
SN
SB 51
TE
I
XE 54
CS
BA
2.0
1.4
1.0
0.6
0.4
WAVELENGTH

Fig. 2

Fig. 2 shows the actual output of the new qualitative mode. As will be seen, a single page is used for the complete output, this page being divided roughly into two major segments. The top portion records all elements between F (9) and Fe (26) using the slew/step approach, and the lower portion uses the asynchronous scanning technique to cover the remaining elements above Fe in atomic number. The top of the page contains an identification plus date and time of day, the latter being derived from the real-time clock of the computer. As was previously indicated, the operator can pre-enter 20 different sets of analytical conditions, 16 for the slew/step low Z portion and 4 for the asynchronous scan middle/high Z portion.

This latter facility means that certain operating parameters can also be changed automatically during the course of the asynchronous scan. In addition to the change in the $\Delta 2\theta$ increment, it may be useful to vary the time per step, the collimator, the excitation conditions, or the detector combination, in order to control the sensitivity of the spectrometer over the wavelength range. For example by automatically changing the kV on the X-ray tube from 80kV at Z = 60 to 60kV at Z = 40, and 50kV at Z = 20, almost constant excitation conditions can be obtained. Obviously there are many additional programmable combinations of possibilities. In addition to providing an optimally obtained out-put in a compact and readable form, data acquisition by this means is extremely rapid. For instance the scan shown in Figure 2 was obtained in less than 20 minutes, which is a factor of six faster than conventional means.

In addition to its obvious application in hardware control the floppy disc oriented mini-computer has a great potential in the solution of intensity/concentration algorithms both for energy dispersive and wave-length dispersive methods. Earlier empirical intensity/concentration correction algorithms played a useful role in the late 1960's for quantitative X-ray spectrometry$^{6)}$. These models had limitations, however, many of which were imposed by the restriction in the available core space of the computers used at the time.

Among the earlier spectroscopists to realize the limitations of these models were Claisse and Quintin$^{7)}$. In 1967 these workers pointed out that the traditionally used Lachance/Traill model$^{8)}$ really could not allow for the polychromatic nature of the incident radiation and suggested the use of an expanded form of the original model. Figure 3 shows the forms of the three main alpha-correction models currently in use. Note that these are all concentration correction models since all of the correction terms are made up of products of alpha correction constants and weight fractions of the interfering elements. Rasberry and Heinrich$^{9)}$ also challenged the traditional form of the correction model, pointing out that the curve for enhancement could not be adequately described by a hyperbolic function, and in 1970 they proposed an entirely new model in which predominant absorption, or predominant secondary fluorescence, were treated separately. Here the α coefficients are used when the significant effect of element j on element i is absorption, and the β coefficients are used when the predominant effect of element k on element i is enhancement. The Claisse/Quintin model is also shown in the figure, albeit in a somewhat shortened form. This contains additional higher order terms which allow for the polychromatic nature of the X-ray beam. One of the more important conclusions of the study by Claisse and Quintin was that the coefficients could be calculated where the spectral distribution of the primary beam was known.

The problem in adequately describing the spectral distribution of the primary radiation had, in fact, inhibited the developments of absolute intensity/concentration algorithms until 1968, when Birks' group at the U.S. Naval Research Laboratory published details of their "fundamental parameters" approach$^{10)}$. This method differed from the previously published absolute methods principally in the use of measured primary spectra rather than in calculated data. The value of such an absolute method is inestimable since this virtually eliminates the need for standards. Errors in the application of the method do accrue because of current uncertainties in certain fundamental data such as mass absorption coefficients and fluorescent yields, but as the authors point out, sufficiently accurate data will undoubtedly be eventually forthcoming.

A further question which arises with the fundamental parameter technique is the inaccuracy introduced in the use of published spectral distribution data. Although the original experiment performed by Gilfrich and Birks$^{11)}$ was well conceived to give the required data, such an experiment is beyond the capabilities of the average X-ray laboratory. As evidenced from those who have used the technique over the past several years, the majority of workers has been prepared to accept the original Gilfrich/Birks spectral data.

Stephenson's approach (CORSET)$^{12)}$, in which he uses the effective wavelength concept to get around the difficulty in precisely evaluating the complete integral of the primary spectral distribution, has played a useful part over the past couple of years. This method is particularly applicable to the quantitative analysis of complex specimens such as a rocks and minerals and although not yielding quite the degree of accuracy of the more

Forms of the "Alpha" correction models

Linear model:

$$W_i/R_i = K_i$$

Lachance-Traill:

$$W_i/R_i = K_i + \sum \alpha_{ij} \cdot W_j$$

Rasberry-Heinrich:

$$W_i/R_i = K_i + \sum \alpha_{ij} \cdot W_j + \sum \beta_{ik} \cdot W_k / 1 + W_i$$

Claisse-Quintin:

$$W_i/R_i = K_i + \sum \alpha_{ij} \cdot W_j + \sum \gamma_{ij} \cdot W_j^2$$

Fig. 3

sophisticated methods it is quickly and easily applied. For example, the method has been in use at the Colorado School of Mines for a number of years[13] and has been used extensively for ore body survey work.

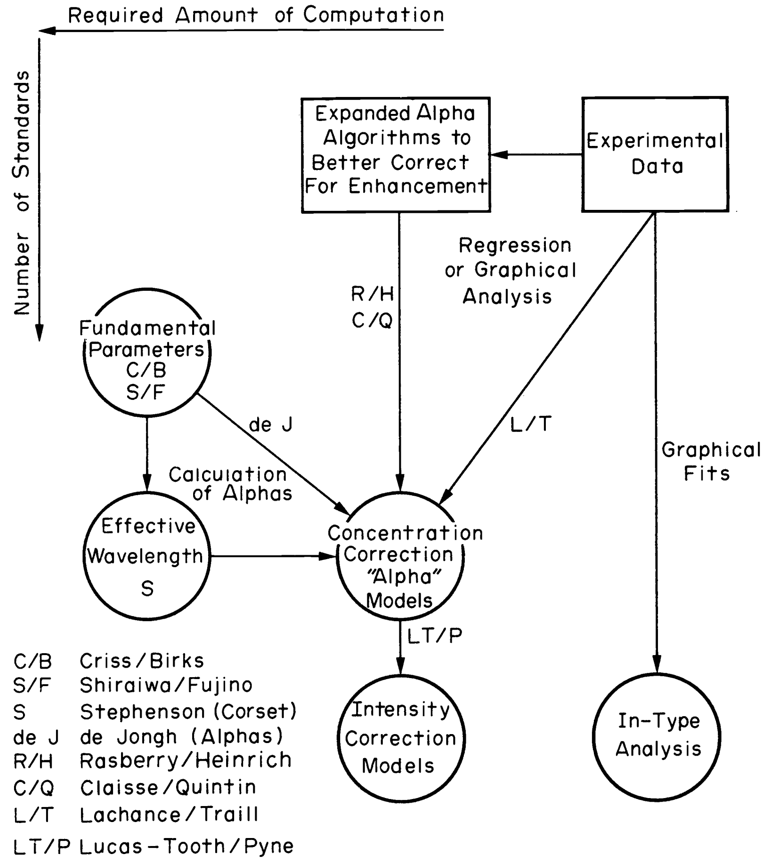
Another useful practical approach is that of de Jongh[14] who, by use of his program "ALPHAS", has used the Shiraiwa/Fujino fundamental equation[15] to calculate the alpha correction factors in the Lachance/Traill equation. This approach is particularly useful in that it allows the correction factors to be applied with the small on-line computers being used to control the spectrometer, where the factors themselves are calculated with a large off-line computer.

In terms of where we stand today Figure 4 summarizes the more important of the models currently in use. The circles represent the actual approaches and if we ignore type-standardization, four basic models exist,

1. Fundamental Parameter methods
2. The Effective Wavelength approach
3. Concentration correction models
4. Intensity correction models

In general terms one can say that as we pass down this list the required amount of computation decreases, but the number of calibration standards required increases. The fundamental type approach is obviously the most desirable but the computer facility required for this type of approach has, until now, been beyond that provided by the conventional minicomputer, mainly because of the requirement for extensive look-up tables. Recent advances in minicomputer technology should allow that the basic facility for applying the fundamental type correction models be within the capability of most moderately sized X-ray laboratories within the next few years, and flexible high level language programs should result. On the other hand, at the present time lack of

accurate fundamental constants, along with lack of readily available data on X-ray tube spectra, results in the production of concentration data which in many cases is barely accurate enough for certain applications. It would appear, therefore, that the so-called empirical approaches will still be used for some time to come, even though there is still some disagreement as to the best form of the concentration correction model to be employed.



Mathematical Correction Methods for Quantitative X-ray Spectrometry

The greatest remaining obstacle to rapid and accurate X-ray analysis is the need to obtain a specimen which is homogeneous over the analysed depth, which in the case of the lower atomic number elements may amount to only a few microns. This is of particular importance in the analysis of ore and mineral specimens where small scale heterogeneity is commonplace. At the present time the only general solution to this problem lies in fusing the specimens with a suitable glass-forming flux. Although this is time-consuming, a number of reasonably low cost fluxing devices have recently become available and many laboratories could afford to have several such devices thus reducing the time required for batch analysis.

REFERENCES

1. C.J. Sparks, Jr., O.R. Cavin, L.A. Harris and J.C. Ogle, in "Trace Substances in Environmental Health - VII". D.D. Hemphill ed., University of Missouri, Columbia (1973) 361.

2. G.R. Dyer, D.A. Gedcke and T.R. Harris, Advances in X-ray Analysis, 16 (1972) 228.

3. D.E. Porter, X-ray Spectrometry, 2 (1973) 85.

4. J.C. Russ, private communication.

5. R. Jenkins, D. Myers, and F.R. Paolini, Advances in X-ray Analysis, 20 (1976) in press.

6. R. Jenkins, Advances in X-ray Analysis, 19 (1975) 1.

7. F. Claisse and M. Quintin, Can. Spectrosc., 12 (1967) 129.

8. G.R. Lachance and R.J. Traill, Can. Spectrosc., 11 (1966) 63.

9. S.D. Rasberry and K.F.J. Heinrich, XVI Colloquim Spectroscopicum Internationale, Heidelberg, Germany (1970).

10. J.W. Criss and L.S. Birks, Anal. Chem., 40 (1968) 1080.

11. J.V. Gilfrich and L.S. Birks, Anal. Chem., 40 (1968) 1077.

12. D.A. Stephenson, Anal. Chem, 43 (1971) 310.

13. M. Slaughter, private communication.

14. W.K. de Jongh, X-ray Spectrometry, 2 (1973) 151

15. T. Shiraiwa and N. Fujino, Jap. J. Appl. Phys., 5 (1966) 886.