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Combined X-ray Wavelength and Energy-Dispersive Analysis to Increase Microprobe Efficiency

By

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Introduction

Combined operation of x-ray energy-dispersive and automated wavelength--dispersive systems can increase the productivity of a heavily utilized microprobe. Previous automation of the U.S. Geological Survey microprobe in Reston, VA, resulted in growth of the user population to 30 operators whose use exceeded 320 hours a month (i.e. full utilization). Continued high demand for analyses necessitated a further increase in the system's productivity. The addition of a quantitative x-ray energy-dispersive analysis system allowed us to evaluate the results of combined x-ray energy and wavelength-dispersive analysis. We reduced spectrometer motion and obtained faster and easier standardization, decreased analysis time, and, as a bonus, decreased mechanical wear of the spectrometers.

The elements most commonly analyzed in rock-forming silicate and oxide minerals are Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, and Fe. Wavelength standardization for these 10 elements on our wavelength dispersive spectrometers commonly took approximately two hours and a single routine 10 element analysis required about five minutes (including 2.7 minutes used for crystal positioning). The spectrometer collecting data for the largest number of elements usually determined the analytical time; typically that spectrometer had a LIF crystal and measures 5 elements, Ca (atomic number 20) through Fe (atomic number 26). Our initial intention was simply to use the energy--dispersive analyzer as a fourth spectrometer, for some of the elements normally analyzed with LiF, thereby tending to equalize the times necessary for the spectrometers to perform their assigned tasks. We found energy-dispersive analysis to be so successful that we now assign it the majority of the elements.

Instrumentation

The Reston microprobe now comprises three interconnected subsystems: 1) an Applied Research Laboratories (ARL) electron beam microanalyzer (EMX-SM) with three wavelength-dispersive (WD) x-ray spectrometers augmented by a Nuclear Semi-Conductor energy-dispersive (ED) x-ray spectrometer, 2) Krisel Control hardware and software for WD automation, and 3) a Tracor Northern model 1710 multi-channel analyzer (MCA). The first subsystem detects x-rays for all elements with the WD and/or ED spectrometers. Each WD spectrometer has a proportional counter and two diffracting crystals, manually selected by the operator as follows: spectrometer 1, ADP or LiF; spectrometer 2, LiF or PET; spectrometer 3, RAP or TAP. The energy-dispersive spectrometer has a solid-state, lithium-drifted silicon detector with 142 electron volts resolution for Mn K radiation (5.97 Kev). Using externally selectable apertures we can control the count rate of the ED spectrometer to minimize ED count time and maintain resolution while operating at our routine WD condition of 15 KV beam potential and 100 nanoamperes beam current. Krisel Control automation (the second subsystem) positions the WD spectrometers, corrects for short-term drift by reading the beam current before and after focussing and defocussing the beam, collects WD count data for the assigned elements, corrects for WD detector dead time, and, utilizing reference standard data and intensities, produces elemental concentrations uncorrected for matrix effects ((C1 = standard concentrations x (unknown intensities/standard intensities)). Although the Krisel Control software alone has the capability to correct C1 values for matrix effects by either the empirical scheme of Bence and Albee (1968) or the MAGIC IV theoretical procedure of Colby (1971), this feature is not used when the WD system is combined with the ED system. Rather, the WD system passes the C1 values on to the MCA. The third subsystem, the MCA, relies on a microprocessor (the DEC LSI-11) for pulse height analysis of the energies in a spectrum. The microprocessor also supports Flextran (a Tracor Northern interpreter-based language) programs which quantitatively evaluate unknown spectra by means of a digital frequency filter (to remove background mathematically) and a multiple-least-squares routine (to fit standard spectra to the unknown sample spectrum). The ratios of intensities obtained from the sample relative to intensities obtained from the stored standard spectra (K-ratios) are then corrected for matrix effects by either the Bence and Albee (1968) method or the Tracor Northern Inc. version of ZAF, a correction procedure similar to MAGIC IV in that it makes atomic number (Z), atomic absorption (A), and fluorescence (F) corrections. It is not necessary to produce a complete analysis, but if the ED and WD systems operate in combination, Cl data from the WD system are used in the correction routine instead of the corresponding ED data. The programs controlling the combined ED-WD system are written in Flextran and imbedded in the Tracor Northern Super Multiple-Least-Squares (XML) program.

The user performs the set-up and analytical sequences (Figure 1A and 1B respectively) using the XML executive. Our program includes an option to acquire data from the ED and WD systems either simultaneously or in the sequence, ED acquisition before WD acquisition (fig. 1B). When the WD spectrometers are rate-limiting with respect to the time necessary to perform a complete analysis, simultaneous acquisition is more efficient. If the FIT routine is the rate-limiting factor, sequential acquisition is more efficient because the ED spectrum can be stripped during WD data acquisition. That this is the case is in part due to the fact that whenever a WD motor is driven, ED acquisition is suspended to avoid picking up the microphonic noise caused by mechanical vibrations. Temporary suspension of ED data acquisition delays the initiation of spectrum stripping (by the FIT routine), thus lengthening the time for a complete analysis. The analytical sequence (Figure 1B) terminates with the printing of an analysis corrected for matrix effects according to either the Bence-Albee or ZAF scheme. We consider analyses as blocks of information which may be summarized by an average (fig. 1B). A single set-up serves for several successive analyses. This approach allows economy in set-up time not available in the standard XML and matrix correction routines.

Combined operation of the ED and WD systems required modification of both the Tracor Northern and Krisel Control programs. At our request Krisel Control divided its standard operating system (Finger and Hadidiacos, 1972), into software modules to perform the following functions as directed by the MCA:

1) receive the WD spectrometer set-up parameters;
2) standardize for elements to be analyzed on the WD system;
3) perform a WD analysis (position spectrometer, collect data, correct for dead time, and calculate C1 values) and send the results to the MCA;
4) measure beam current and send the result to the MCA; and
5) focus and defocus the beam (the beam is focused only when count data are being acquired).

Our modifications of the Tracor Northern software include:

1) Creation of routines to send data and commands to, and to receive results and responses from, the Krisel system;
2) Correction of errors in the XML and Bence-Albee routines; and
3) Separation of the Tracor Northern XML FIT routine into two parts:

Part one establishes and stores the fitting parameters, the number of channels present in each unknown spectrum, and the analysis time. Rather than perform Part one before each analysis, it is now performed just before the beginning of a sequence of similar analyses. Part two, which actually performs the fitting of the references to the unknown spectrum, must still be done for each analysis. The removal of part one from FIT reduces the time required for fitting by about 40%.

4) Alteration of the Bence-Albee correction program to retain the oxide headings when once set up and to skip elements with K ratios of zero.

5) Restructuring of the Bence-Albee output to print in a horizontal format in which oxide titles are printed on one line, K ratios on the second, uncorrected concentrations on the third, corrected concentrations on the fourth and, if required, formula units on the fifth line.

In addition to program modifications, several new routines were written to standardize and recalibrate the multichannel analyzer, making it possible to use a set of standard spectra for an indefinite period. The resulting routines calculate values for drift, zero shift, and gain ratio by comparing old and current peak locations and intensities from the same mineral or material standard. The recalibrate portion of our routine shifts the reference spectra to the current conditons, rather than altering the unknown spectrum (as in the Tracor Northern recalibrate routine), producing a small time savings as it is performed only once per standardization rather than for each analysis.

Table 1. Analysis of Pyroxene DL-6 by Different Techniques

	Microprobe Analysis (Bence-Albee Correction)							Classical Wet Chemical Analysis	
	W.D.	(S.D.)	E.D.	(S.D.)	ED+WD		(S.D.)		
SiO_2	46.6	(.5)	45.8	(.5)	WD	46.4	(.8)	46.26	
Al_2O_3	8.3	(.2)	9.66	(.09)	WD	8.1	(.1)	8.14	
TiO_2	1.81	(.07)	2.0	(.06)	ED	1.8	(.1)	1.42	
Cr_2O_3	NA		.06	(.05)	ED	0.03	(.03)	NA	
Fe_2O_3	--		--			--		5.21	10.29 as FeO
FeO	10.2	(.1)	9.9	(.1)	ED	9.6	(.3)	5.60	
MgO	10.0	(.2)	10.6	(.1)	ED	10.5	(.4)	10.54	
MnO	0.22	(.03)	0.18	(.09)	ED	0.25	(.03)	0.40	
CaO	20.4	(.3)	21.5	(.2)	ED	21.0	(.1)	21.44	
Na_2O	1.62	(.04)	0.7	(.1)	WD	1.55	(.05)	1.20	
K_2O	.05	(.02)	0.11	(.12)	ED	0.04	(.06)	.02	
Total	99.10		100.51			99.30		100.24	

	Cations	Cations	Cations	Cations
Si	1.77	1.72	1.77	1.737
Al	.37	.42	.34	.360
Ti	.05	.06	.05	.040
Cr	--	.00	.00	--
Fe^{+3}		--		.147
Fe^{+2}	.32	.31	.31	.176
Mg	.57	.59	.59	.590
Mn	.01	.01	.01	.013
Ca	.83	.86	.86	.864
Na	.12	.05	.11	.088
K	.00	.01	.00	.001
	4.04	4.03	4.04	4.015
Time	4.9 minutes for each of 9 analyses included in the average	3.1 minutes for each of 3 analyses included in the average	2.6 minutes for each of 3 analyses included in the average	

Performance

McCarthy et al. (1977) determined the time required for WD, ED, and combined ED and WD analyses. For the 7-element analysis of a chromite, they report very little difference in the time required for completing WD (4.0 min.), ED (3.7 min.), and combined ED and WD (3.6 min.) analyses. We show in Figure 2 that combined ED and WD 10-element analyses of silicates permit considerable time savings over the all-WD analysis. The silicate analysis (Table 1 and Fig. 2) required 4.9 minutes on the WD system (measuring each element for 20 seconds or 20000 counts, whichever occurs first) and 2.6 minutes on the integrated ED and WD system, using 60 seconds ED live-time. The combined system saves additional time by decreasing the time necessary for standardization from 1 1/2 hours to perhaps 15 minutes. (After this report was first written, Tracor Northern made available a separate Flextran compiler for the 1710 MCA. Use of the compiled version of our programs speeds the analyses slightly; for instance, when using configuration 2 (fig. 2), an analysis needs 2.6 minutes using uncompiled software, but only 2.3 minutes using our compiled version.)

We compare WD, ED, combined, and wet-chemical analyses of an aluminous augite (pyroxene) in Table 1. In the combined analysis, Na, Al, and Si were analyzed by the WD portion of the system and the ED system was used for Mg, K, Ca, Ti, Cr, Mn, and Fe (Fig. 2, col. 2). The WD analysis and the combined ED and WD analysis compare well with each other and with the wet chemistry, illustrating that good analytical quality can be obtained when using the combined ED and WD system. The all-ED analysis shows anticipated difficulties with the lighter elements (Na, Al, Si).

Figure 2 clearly illustrates the flexibility available to the user in the arrangement of elements to optimize analytical quality and time. A general strategy in the selection of the WD or ED spectrometer for an element would be to analyze the lighter elements (Na-Si) and those minor elements that require better precision or that are present in lower concentration (<<1%) with the wavelength spectrometers and to analyze the remaining elements with the energy-dispersive spectrometer. When present as major elements (>10wt%), we can also routinely analyze Na and Mg with the energy-dispersive system.

Integration of an ED spectrometer with a mechanical WD system reduces mechanical spectrometer wear as well as analytical time. With operating configurations 4 and 6 of Figure 2, spectrometers 1 and 2 are driven through a great range, each requiring 30 seconds to travel approximately 17400 LiF units (2). In our 10-element all-WD example (configuration 6) almost half of the 5 minutes required for an analysis is used in spectrometer motion. Repeated trips between Al and K on spectrometer 1 and Ca and Fe on spectrometer 2 have caused severe wear of our spectrometer plates, leadscrews, and followers. By analyzing Ca, Fe, and K with the ED spectrometer, the maximum spectrometer travel decreases to 8130 LiF units, reducing wear and prolonging spectrometer life. When a spectrometer does malfunction we can still obtain good analyses by analyzing more elements on the ED spectrometer while repairing the WD spectrometer.

Conclusion

Implementation of a combined ED-WD system can increase the analytical productivity of a microprobe laboratory by reducing the time required for standardization and analysis. The time savings can be significant (47%) even though analytical quality is maintained. In addition, the reliable lifetime of the spectrometers is extended by decreasing their motion. When a wavelength spectrometer does fail, the system can continue functioning with only minor impact on the analytical capability.

References

1. Bence, A.E. and Albee, A.L., 1968, Empirical correction factors for the electron microanalysis of silicates and oxides: Journal of Geology, v. 76, no. 4, p. 382-403

2. Colby, J.W., 1968, Quantitative microprobe analysis of thin insulating films: Advances in X-ray Analysis, v. 11, p. 287-305.

3. Finger, L.W., and Hadidiacos, C.G., 1972, Electron microprobe automation: Carnegie Institute of Washington Yearbook, v. 71, p. 598-603.

4. McCarthy, J.J., Christenson, J.J., and Friel, J.F., 1977, Automated X-ray microanalysis with the electron microprobe and scanning electron microscope: American Laboratory, v. 9, no. 9, p. 67-70, 72-4, 76-7.

Figure 1. Flow charts for microprobe operating system. New routines, written by L.B. Wiggins of the U.S. Geological Survey, are enclosed by heavy solid lines. Tracor Northern routines, unaltered or only slightly modified by us, are enclosed by light-weight lines. Krisel Control routines are enclosed in dashed lines. The flow of information and control signals within the MCA are indicated with solid lines; flow between the MCA and the Krisel System with dashed lines. A) Set-up and standardization sequence. B) Analysis sequence.

Figure 2. A "diagram" showing how the time required for an analysis depends upon the number of elements sought and their distribution between 3 wavelength-dispersive (WD) spectrometers and one energy-dispersive (ED) spectrometer. Elements analyzed by the ED method are indicated by E; for WD elements, the spectrometer number (and crystal) for the USGS system are indicated.

Figure 1A

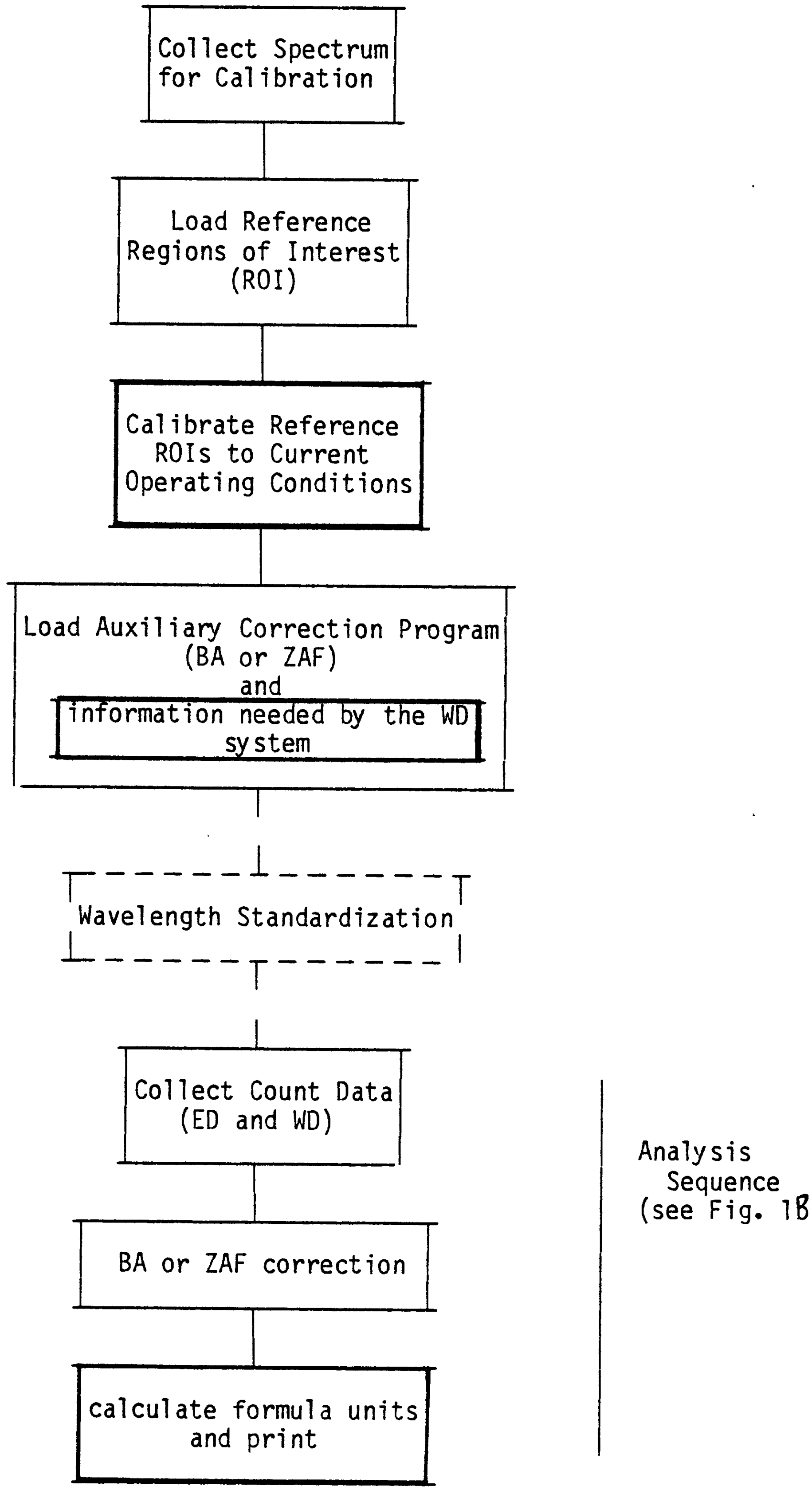
Collect Spectrum for Calibration
Load Reference Regions of Interest (ROI)
Calibrate Reference ROIs to Current Operating Conditions
Load Auxiliary Correction Program (BA or ZAF) and
information needed by the WD system
Wavelength Standardization
Collect Count Data (ED and WD)
BA or ZAF correction
calculate formula units and print
Analysis Sequence (see Fig. 1B)

Figure 1B

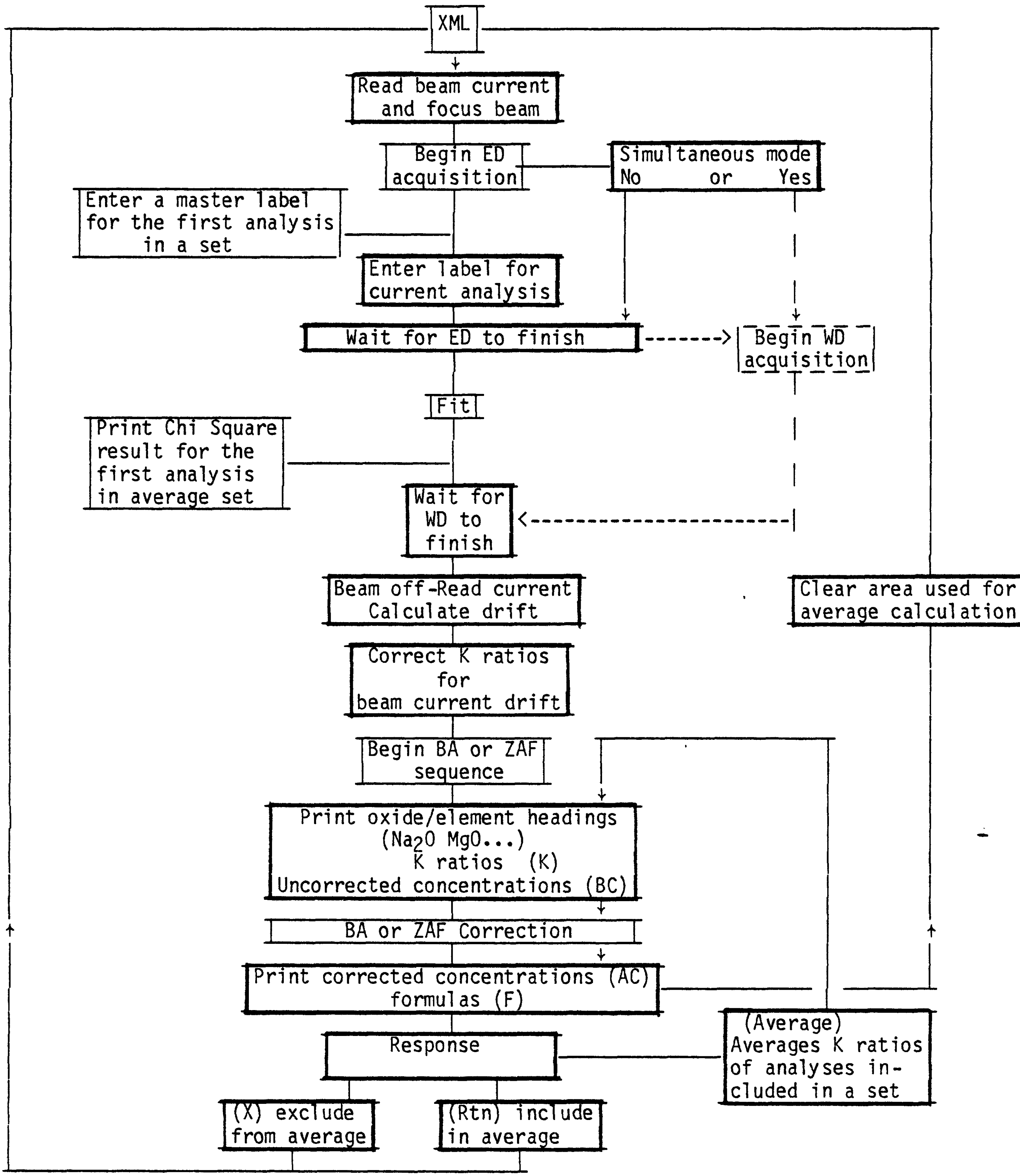
XML
Read beam current and focus beam
Begin ED acquisition
Simultaneous mode No or Yes
Enter a master label for the first analysis in a set
Enter label for current analysis
Wait for ED to finish
Begin WD acquisition
Fit
Print Chi Square result for the first analysis in average set
Wait for WD to finish
Beam off-Read current Calculate drift
Clear area used for average calculation
Correct K ratios for beam current drift
Begin BA or ZAF sequence
Print oxide/element headings (Na_2O MgO...) K ratios (K) Uncorrected concentrations (BC)
BA or ZAF Correction
Print corrected concentrations (AC) formulas (F)
(Average) Averages K ratios of analyses included in a set
Response
(X) exclude from average
(Rtn) include in average

Figure 2. Spectrometer and crystal configurations

	1	2	3	4	5	6
Na	E*	3	3	3	3	3
Mg	E	E	3	3	3	3
Al	E	1	1	1	1	1
Si	E	2	2	2	1	1
K	E	E	E	1	E	1
Ca	E	E	E	2	E	2
Ti	E	E	E	E	2	2
Cr	E	E	E	E	2	2
Mn	E	E	E	E	2	2
Fe	E	E	E	E	E	2

Crystal Arrangement

Spectrometer 1		ADP	ADP	ADP	ADP	ADP	
Spectrometer 2		PET	PET	PET	LiF	LiF	
Spectrometer 3		TAP	TAP	TAP	TAP	TAP	
						4.9	All-WD
Time, Min.		2.6	3.4	4.3	4.0		Sequential Mode
Time, Min.		3.0	3.1	3.8	3.4	4.9	Integrated Mode
	3.1						All-WD

*Energy-dispersive count time 60 seconds.