X-RAY ENERGY SPECTROMETRY FOR ELECTRON-PROBE ANALYSIS*

TAKESHI MORI*** and KEIICHIRO KANEHIRA**

Abstract This article reports a method of quantitative electron-probe analysis using a Si(Li) detector. This method employs the technique of background modeling, and includes, among others, corrections for incomplete charge collection and electronic noise. Improvements in analysis of light elements resulted, which is particularly of advantage for silicate specimens. Pure metals were employed, wherever possible, as analytical standards.

The method has been applied to a variety of geochemical samples including glasses made from the reference rocks of JG-1 and JB-1. Comparison with wet chemical analyses and examination of chemical formula of minerals imply accuracy and precision of the method. The accuracy is not substantially inferior to the conventional wet chemical analysis. This is true even for elements with 0.1–0.2 wt%. The precision can be of the same order with that of the wet chemical analysis. EDS can now cope with a wider range of analytical situations in geochemistry.

Introduction

X-ray intensity spectrum as recorded by an energy-dispersive spectrometer (EDS) fitted to an electron-probe deviates from a sum of characteristic X-ray peaks and a background continuum. The deviation is due to the various artifacts derived from the silicon detector and its environment: silicon-escape peaks, electronic noise, incomplete charge collection, sum peaks and so on (GOLDSTEIN *et al.*, 1981). Thus, extraction of the net peak intensities requires complicated spectrum processing. A variety of data reduction procedures have been proposed, and are currently employed among laboratories.

They fall into two categories. Background modeling first establishes net peak intensities for unknown and standard, then calculates the intensity ratios between the two (e.g. REED & WARE, 1975). This procedure

requires modeling the background continuum, but gives good quantitative results. Background filtering attempts, by mathematical filtration, to obtain the intensity ratios without once extracting net peak intensities (e.g. MCCARTHY & SCHAMBER, 1981). This procedure is simple to use, but slightly sacrifices analytical quality.

The data reduction method we are going to propose employs background modeling, and is designed to improve accuracy in analysis of light elements and minor elements, while retaining excellence in major elements and in heavy elements.

The EDS system consists of a Hitachi S550 scanning electron microscope, Kevex 7000Q-75 analyzer and DEC 11/03-L minicomputer. QANTX, the Kevex-supplied software, has been used throughout. The routine usage of the software for quantitative analysis was reported by FUJIMAKI & AOKI (1980). We added, to the Kevex routine, corrections for a few of the artifacts. The modification was technically trivial but proved essential in high quality EDS analysis.

This paper is to report the results of our attempt to improve quality of EDS analysis. We describe the analytical method with emphasis on the corrections of incomplete charge

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** Department of Earth Sciences, Chiba University 1-33 Yayoi-cho, Chiba, 260 Japan.

*** Present address : Department of Geology and Mineralogy, Faculty of Science, Kyoto University, Kyoto, 606 Japan.

Fig. 1. Spectrum of Ti metal as recorded by EDS. The intensity per channel is in a logarithmic scale so that the intensities except for the characteristic X-rays of Ti (a) can be clearly observed. b : a background X-ray continuum, c : a silicon-escape peak of Ti, d : sum peaks, e : low energy tailing due to incomplete charge collection of Ti X-rays, f : electronic noise

collection and of electronic noise. Presentation of analyses of rock-forming minerals is for the purpose to see accuracy and precision of the method.

Spectrum processing

X-ray spectrum

A raw X-ray spectrum of titanium is shown in Fig. 1. We divided the spectrum into six parts depending how intensities were generated.

The two peaks at 4.51 and 4.93 keV are characteristic X-rays, K_α and K_β , of titanium. Note the two peaks are not well resolved. With lowering X-ray energy, generation of the continuum increases, but absorption by sample itself and the detector periphery becomes effective. These two are the main factors to determine the shape of the continuum.

The small peak at 2.77 keV is a silicon-escape peak. When X-rays from an element heavier than silicon enter the detector, the energy is once used to produce silicon X-rays. These are subsequently reabsorbed by the detector, but a portion at the detector surfaces can escape from the detector. The result is appearance of a small peak shifted downwards by 1.74 keV, the energy of silicon X-ray, from the parent X-ray peak. Probability of the escape is a function of energy at fixed analytical conditions. Correction method for escape peaks is well established (e. g. REED & WARE, 1972), and can be easily

made by transferring the escape peaks back to the parent peaks.

If two X-rays, with or without same energy, simultaneously enter the silicon detector, an X-ray appears at the energy from both X-rays combined, resulting in a spurious peak called sum peak. Fig. 1 shows two sum peaks, one from two K_α rays of Ti, the other from a K_α - K_β pair. In this case, 0.8% of the parent Ti K were lost to the sum peaks. Correction for the sum peaks can be made accordingly. For analysis of silicate and oxide samples, the intensities of parent peaks are much smaller than in this example. As a result, sum peaks become small enough to be corrected for. At our routine analytical conditions, sum peaks derived from simultaneous entry of three X-rays are not observable even for pure metals.

Correction for electronic noise

Fig. 1 also portrays electronic noise at the low energy range. If any characteristic X-rays were not within the range, correction for the noise would not have practically been needed. The trouble is that the range extends over Na K_α line. That is, Na is, in appearance, always detected even for Na-free unknowns, and is overestimated for Na-bearing samples.

We employed a similar line of the correction method as proposed by INOUE & NAKATSUKA (1980). Fig. 2-a illustrates a part of spectrum of wollastonite and the

Fig. 2. a : Spectrum of wollastonite after correction for escape peaks. X-ray continuum is indicated by the shadow. Note the electronic noise (discrepancy) below 1.2 keV. b : a model of the electronic noise used in the correction. Na X-ray is located within the noise range.

background continuum fitted to the spectrum. Aside from the X-ray peaks, the continuum starts deviating at 1.2 keV downwards. This deviation, after smoothing the fluctuation due to X-ray counting statistics, gave rise to a model to be used in the correction for electronic noise (Fig. 2-b). The intensities at almost zero energy are, in fact, infinite, but that is irrelevant for analysis. This model intensities are scaled to each spectrum at the 0.3–0.7 keV range, then subtracted from the spectrum.

Removal of the background continuum

Peak to background ratio measured with EDS systems is much lower than with wavelength-dispersive spectrometer (WDS) systems. Therefore, accurate removal of the background continuum is all the more important. The common practice in WDS is to measure background intensities at both

sides of each peak, then to subtract the average of the two from the peak intensity. This method cannot be employed in EDS, since peaks often overlap and jump-ratios at absorption edges can be high.

The continuum is a function of instru-

Fig. 3. Fit of a background X-ray continuum to spectra after corrections for escape peaks and electronic noise. a : Fe metal, the spurious peak of Si is from the silicon dead-layer and also probably from oil contamination. b : forsterite, c : enstatite; Note the Na peak from 0.1 wt% Na_2O . When peaks overlap, fit can only be judged at both sides of overlapping peaks.

mental parameters, sample geometry, operating conditions, average atomic number and so on. With these all well known, however, theoretical prediction of the background continuum is not satisfactory. This is especially true at low energies. Many geochemical samples are, unfortunately, high in low-energy elements.

Several authors proposed semi-theoretical formulations to calculate the continuum intensities as a function of energy (e.g. WARE & REED, 1973). The Kevex formulation follows the similar line, and contains, as parameters, thicknesses of the Be window, gold layer on the silicon detector and silicon-inactive layer. The maker-supplied nominal thicknesses are respectively 7.5 μm , 20 nm and 100 nm.

The calculated background is scaled to EDS spectra at energies higher than 2 keV excluding peak positions. The background model thus generated always exceeds the spectra at low energies. That is, absorption of the continuum is more effective than those thicknesses imply. Observation of the jump-ratios at absorption edges of Au *M* and Si *K* indicated that the thicknesses of gold and silicon-inactive layers are appropriate. Thus, we use the thickness of Be window as a fitting parameter for the background modeling. 18 μm , the default value, is sufficient for a good range of samples. Accurate analysis, however, requires to choose an optimum value by observing the fit of the calculated models

to spectra (Fig. 3). This process is a nuisance, but with some initial experience we could easily list the optimum values for various specimen matrices.

Correction for incomplete charge collection

Peak distortion due to incomplete charge collection by the detector is observed as low-energy tailing, i.e. excess intensities on the low-energy side of peaks (Fig. 1). These intensities, unless removed, are taken for characteristic X-rays of the adjacent elements.

The intensity within a low-energy tailing is, by its nature, proportional to the intensity of the parent peak. The tail to peak intensity ratio varies from element to element, and also changes with operating conditions.

The method to remove the tailing intensities is depicted in Fig. 4. This example, a spectrum of standard corundum corrected for escape peaks, electronic noise and a background continuum, shows distortion from a Gaussian distribution. The excess intensity above the Gaussian fit represents low-energy tailing of Al-peak. In order to correct for incomplete charge collection, this intensity should be transferred back to the parent Al peak, but we do not normally do that. Instead, we simply subtract this intensity from the spectrum on channel by channel basis. The correction for unknown samples is similarly made, but this time the intensity subtracted is in proportion to the peak height. This simplicity does not cause error in the in-

Fig. 4. Correction for incomplete charge collection. Spectrum of corundum after corrections for escape peaks, electronic noise and X-ray continuum. The shade with vertical lines represents least square fit of a Gaussian model to the spectrum. The excess intensity (stippled) is due to incomplete charge collection. Without correction, Mg is erroneously detected.

tensity ratio between unknown and standard as far as the correction is applied to both. Measurements of the tail intensities have been made for the relevant elements, and the results have been stored in diskettes. The correction must be made for elements in the way of decreasing atomic number. Incomplete charge collection causes analytical error especially for light elements. When necessary, the correction should be made for all existing elements, but for a majority of silicate minerals correction for up to Ca is satisfactory.

Deconvolution of peak overlap

Good examples of peak overlap are clinopyroxenes and amphiboles which exhibit overlap of Na, Mg, Al and Si lines. Deconvolution is for the purpose to extract net peak intensities, and is done subsequently to the corrections mentioned above. The process involves least-square fitting of Gaussians to the peaks of spectra, then extracts net peak intensities under the Gaussians. This procedure is applied to both standard and unknown samples.

Spectrum processing is finally completed, and the intensity data are now ready for ZAF correction.

Analytical method

Energy calibration

X-ray spectrum acquisition is normally made in the 0–10.24 keV range with each 10 eV increments allocated to 1024 channels. Energy calibration is an important setup process for a pulse processor. This is achieved by adjusting zero and gain controls of the pulse processor, so that two known characteristic X-rays are located at the right energies. For this purpose, we use iron and aluminium metals as references, and adjust the energies within 1 eV error. Energy shift of the pulse processor is critically dependent on room temperature. Temperature is controlled within 1°C of a fixed value, though a shift of 2–3°C is still permissible. Energy calibration is made when the room temperature is altered and if shift in peak positions is observed.

Analytical conditions

The electron microscope employs the in-

cident angle of 90°, and 38° for X-ray take-off angle. Electron beam current is monitored by a Faraday cup connected to an ammeter. We normally use 20 kV accelerating potential, and 200 pA beam current. Constancy of the beam current is crucial to the microprobe analysis, but is not so easily accomplished as it appears. This is because the beam current is susceptible to the electromagnetic field in the electron microscope. Adjustments of the focusing and some other knobs should always be the same. Focusing is alternately made by adjusting sample height.

Beam diameter can be focused to 10 nm, but silicate minerals suffer damages by such high density bombardment. Therefore, the beam must be defocused to some extent. Beam size of ca 5 microns is suitable for ordinary unhydrous minerals. Hydrous minerals may require a slightly larger beam. For very weak samples, beam scanning in a restricted region would be more suitable than a stationed beam.

Acquisition of X-ray spectrum over 200 sec live time yields 250,000–300,000 count net peak intensities for typical silicate minerals.

Standards

Choice of standards is of crucial importance in quantitative electron-probe analysis. Standards for WDS are rather limited because of the strict requirements (SWEATMAN & LONG, 1969). By contrast, EDS can command wider variety of standards (MORI,

Table 1. Standards

Na	jadeite (albite)	V	V
Mg	MgO	Cr	Cr
Al	Al ₂ O ₃	Mn	Mn (MnSiO ₃)
Si	Si	Fe	Fe
P	GaP	Co	Co
S	pyrite	Ni	Ni (Ni ₂ SiO ₄)
Cl	NaCl	Cu	Cu
K	K ₂ Cr ₂ O ₇	Zn	Zn
Ca	Calcite (wollastonite)	Ga	GaP
Ti	Ti (TiO ₂)	Ge	Ge

Standards referred to by mineral names are natural, otherwise synthetic.

1983). Our standards are listed in Table 1. Maximum use of metals is characteristic, though simple oxides are used for Mg and Al instead of the soft metals. The low-current beam scanned on specimens enabled to use potassium dichromate as standard for K, and calcite for Ca.

The analytical data in the next chapter were collected in a two-years time span, during which some standards were successively substituted by others. Those standards used only in the early stage are shown in parentheses.

Spectra of standards are processed as was already described, then compositions and net peak intensities are stored in floppy-diskettes and are served at every analysis of unknown samples.

We observed that long-range decrease in detection efficiency is inevitable. The reasons are twofold: contamination of the detector

environment and worsening vacuum within the detector system. The decrease becomes remarkable as the X-ray energy decreases. In a worst period, the rate of decrease calculated for a year was 0.8% for Ti, 2% for Si, 8% for Mg and 15% for Na. As far as the system is well maintained, the decrease is much less, though the standards for light elements better be periodically remeasured.

Analytical sequence

Elements to be analyzed for an unknown sample are determined by observing the X-ray spectrum after the acquisition is completed. The spectrum is sequentially corrected for escape peaks, electronic noise, a background continuum and incomplete charge collection. Then, overlapping peaks are deconvoluted, and the net peak intensities are extracted. The final stage of data reduction is much the same as in the conventional WDS, i.e. ZAF correction converts the intensity data

Table 2. Effects of corrections for electronic noise and incomplete charge collection

	1	2	3	4	5
SiO ₂	40.94	41.23	40.91	n.a.	40.69(24)
TiO ₂	.05	.05	.05	.03	n.d.
Al ₂ O ₃	n.d.	.11	n.d.	.04	.04(2)
Cr ₂ O ₃	n.d.	n.d.	n.d.	.01	.02(1)
FeO	8.19	8.19	8.19	8.05	8.23(7)
MnO	.13	.13	.13	.10	.09(3)
NiO	.47	.47	.47	.43	.41(3)
MgO	50.09	50.80	50.00	50.24	50.77(15)
CaO	n.d.	n.d.	n.d.	.08	.04(1)
Na ₂ O	.11	1.14	n.d.	n.a.	.02(1)
Total	99.98	102.12	99.75	-	100.31(28)

Sample is forsterite (A3). See Table 3.

1 : without correction for electronic noise

2 : without correction for incomplete charge collection

3 : routine analysis

4 : wet chemical analysis (O'Hara and Mercy, 1963)

5 : average of WDS analyses

The numbers in parentheses are standard deviations (1 sigma) and refer to the last decimal places.

n.d. : not detected, n.a. : not analyzed

to chemical compositions. This stage includes corrections for absorption (HEINRICH, 1967), characteristic fluorescence (REED, 1965), back-scatter losses (BISHOP, 1966) and ionization-penetration losses (PHILIBERT & TIXIER, 1968; BERGER & SELTZER, 1964).

Results and discussion

Effects of corrections for electronic noise and incomplete charge collection

Table 2 shows the effects of corrections for electronic noise and incomplete charge col-

lection. The olivine analysis resulted from the routine analytical method is in the column 3. The same raw spectrum without the correction for electronic noise resulted in 0.11 wt% of Na₂O in appearance (column 1), which seems too high for olivines. In fact, the careful WDS analyses indicate presence of only 0.02% in the olivine (column 5). The rest must have come from the noise. This problem could be bypassed by not analyzing Na for Na-free unknowns, but for Na-bearing samples, overestimate in Na is inevi-

Table 3. Samples

forsterite	A3	garnet lherzolite xenolith, South Africa (O'Hara & Mercy, 1963)
enstatite	A3	
diopside	A3	
garnet	A3	
monticellite	MY107	skarn, Crestmore, California
tephroite	MY106	Kamo-cho, Kyoto Pref.
jadeite	MY316	jadeite-albite rock, Oya-machi, Hyogo Pref.
wollastonite	M8-1	synthetic mineral, CaSiO ₃
nepheline	MY522	nepheline-syenite pegmatite, Dungannon, Canada
leucite	MY525	Roccamonfina, Italy
kyanite	M8-2	Sambagawa metabasite, Shikoku
zoisite	M8-2	
kaersutite	M1-3	megacryst in basalt, Australia
piemontite	KK69111801	siliceous sediment, Mineoka, Boso Pen.
sphene	KF1	Sambagawa basic schist, Kii Pen.
chlorite	KF2	
ilmenite	19	Sogndal, Norway
rutile	26	Oaxaco, Mexico
spinel	M4-6	synthetic mineral, MgAl ₂ O ₄
magnetite	21	Labrador, Canada
titanomagnetite	KFJ-1	deoxidized basalt, Mt. Fuji
ulvöspinel	KFJ-1	
pyrrhotite	C12	monoclinic, Fe ₇ S ₈ , 4C type, Chichibu Mine
troilite	TI-5	Bella Roca meteorite
JG-1	U3	glass made from reference rock of Geol. Surv. Jpn.
JB-1	U2	
CrCats4	M4-7	synthetic glass with pyroxene stoichiometry Made by J.F. Schairer
CrCats10	M4-8	

table. This example also shows slight increase in SiO_2 and MgO , which was brought by the higher Na_2O through ZAF correction.

The effect of correction for incomplete charge collection is much more pronounced. The column 2 shows overestimates in Na_2O and Al_2O_3 , which is the result of incomplete charge collection. Note both MgO and SiO_2 were also overestimated as was the case in the analysis of column 1. The correction for incomplete charge collection is essential especially in analysis of light elements.

Samples

We analyzed a variety of samples in order to assess accuracy and precision of the EDS analysis. They include natural minerals, and synthetic minerals and glasses. Table 3 gives brief descriptions for the samples. Assessment of accuracy in an analytical method normally requires samples for which compositions are very accurately known, but such samples are not easily available. Samples with known compositions by the conventional wet chemistry have usually been analyzed

Table 4-a. Analysis of unhydrous silicates

	forster- ite EDS	monticel- lite EDS	tephro- ite EDS	EDS	enstatite		diopside		
					WDS	Wet chem	EDS	WDS	Wet chem
SiO_2	40.92(31)	38.04	30.72	58.03(33)	57.35(11)	n.a.	54.64(41)	53.77(45)	53.90
TiO_2	.02(4)	n.d.	n.d.	.01(2)	.05(2)	.07	.02(4)	.07(1)	.20
Al_2O_3	n.d.	n.d.	n.d.	.60(6)	.76(4)	1.53	2.02(61)	2.43(6)	2.40
Cr_2O_3	.03(5)	n.d.	.29	.21(3)	.21(2)	.17	1.65(4)	1.75(4)	1.55
FeO	8.27(11)	2.66	1.61	5.16(8)	5.06(10)	5.05	2.24(9)	2.36(4)	2.49
MnO	.07(6)	.22	64.51	.11(5)	.11(1)	.11	.06(11)	.05(1)	.08
NiO	.41(5)	.12	.21	n.d.	.12(2)	.10	.04(5)	.06(1)	.05
MgO	49.85(37)	23.03	3.13	35.34(20)	35.77(19)	36.22	15.86(25)	15.81(6)	16.39
CaO	.01(3)	35.89	.44	.23(2)	.27(2)	.24	20.88(91)	20.44(6)	20.57
Na_2O	.02(4)	n.a.	n.d.	.12(7)	.08(1)	n.a.	2.13(40)	2.09(3)	1.80
Total	99.60(57)	99.96	100.91	99.81(56)	99.78(19)	-	99.54(43)	98.83(51)	99.43
Si	1.001(3)	1.005	.998	1.991(2)	1.972(3)		1.989(4)	1.972(5)	1.965
Ti	.001(1)	-	-	-	.001(1)		-	.002(1)	.005
Al	-	-	-	.024(3)	.031(2)		.087(26)	.105(2)	.103
Cr	.001(1)	-	.007	.006(1)	.005(1)		.047(2)	.051(2)	.045
Fe	.169(3)	.059	.044	.148(2)	.145(3)		.068(3)	.072(2)	.076
Mn	.001(1)	.005	1.776	.003(2)	.003(1)		.002(3)	.002(1)	.002
Ni	.008(1)	.003	.005	-	.003(1)		.001(2)	.002(1)	.001
Mg	1.817(4)	.907	.152	1.808(6)	1.834(9)		.861(17)	.865(3)	.891
Ca	-	1.016	.015	.009(1)	.010(1)		.814(40)	.803(4)	.803
Na	.001(2)	-	-	.008(5)	.005(1)		.150(28)	.148(2)	.127
Total	2.999(4)	2.995	2.997	2.997(4)	4.009(3)		4.019(6)	4.022(4)	4.018

only once. In addition, comparison with such compositions of natural minerals may not rigorously make sense, since they are rarely homogeneous. Synthetic minerals and glasses can be reliable references if they were well made. But again the compositions need guarantee from independent sources.

The best reference samples we have are glasses made from the reference rocks (JG-1

and JB-1) of Geological Survey of Japan (ANDO *et al*, 1974). These glasses were already reported by MORI & GREEN (1976). The other samples are of slightly lesser values as reference samples.

EDS data are listed along with, if available, wet chemical analyses, WDS analyses or theoretical compositions in Tables 4 (unhydrous silicates), 5 (hydrous silicates), 6

Table 4-b. Analysis of unhydrous silicates

	jadeite		wollastonite		garnet		nephel- ine	leucite	kyanite
	EDS	EDS	Theor	EDS	WDS	Wet chem	EDS	EDS	EDS
SiO ₂	58.55	51.65	51.71	42.01(35)	41.95(10)	41.78	42.25	54.55	37.13
TiO ₂	.02	n.a.	-	.01(2)	.03(1)	.17	n.d.	n.d.	n.d.
Al ₂ O ₃	25.08	n.a.	-	22.16(20)	21.95(13)	22.26	34.27	22.92	62.16
Cr ₂ O ₃	n.d.	n.a.	-	2.38(13)	2.46(9)	2.32	n.d.	n.d.	n.d.
FeO	n.d.	n.a.	-	8.34(5)	8.49(9)	8.80	n.d.	.26*	.41*
MnO	n.d.	n.a.	-	.42(3)	.45(2)	.45	n.d.	n.d.	n.d.
MgO	n.d.	n.a.	-	20.23(13)	20.42(7)	20.13	n.d.	n.d.	n.d.
CaO	.23	48.64	48.29	4.62(6)	4.64(6)	4.60	.22	.14	n.d.
Na ₂ O	15.29	n.a.	-	n.d.	.01(1)	.04	17.25	.72	n.d.
K ₂ O	n.a.	n.a.	-	n.a.	.02(1)	tr	5.80	20.61	n.d.
Total	99.17	100.29	100.00	100.17(45)	100.42(16)	100.55	99.79	99.20	99.70
Si	1.990	1.994	2.000	2.992(14)	2.986(5)	2.973	1.020	1.997	1.006
Ti	.001	-	-	-	.002(1)	.009	-	-	-
Al	1.005	-	-	1.860(18)	1.841(13)	1.867	.975	.989	1.984
Cr	-	-	-	.134(7)	.138(5)	.131	-	-	-
Fe	-	-	-	.497(5)	.505(5)	.524	-	.007	.008
Mn	-	-	-	.026(2)	.027(1)	.027	-	-	-
Mg	-	-	-	2.148(8)	2.167(7)	2.135	-	-	-
Ca	.009	2.012	2.000	.353(6)	.354(5)	.351	.006	.006	-
Na	1.008	-	-	-	.001(1)	.006	.807	.051	-
K	-	-	-	-	.002(1)	-	.179	.962	-
Total	4.013	4.006	4.000	8.010(7)	8.023(3)	8.023	2.987	4.012	2.998

* : as Fe₂O₃

(oxides), 7 (sulfides), and 8 (glasses). Numbers in parentheses are standard deviations (1 sigma), and refer to the last decimal places. The WDS data were obtained by the Edinburgh University Cambridge microscan 5.

Accuracy and precision

The data in Tables 4–8 indicate levels of analytical quality in various ways. Precision clearly reveals itself as reproducibility expressed in terms of standard deviations. Errors due to counting statistics contribute to the reproducibility. The counting statistics is

Table 5. Analysis of hydrous silicates

	kaersutite		zoisite	piemontite	sphene	chlorite
	EDS	Wet chem	EDS	EDS	EDS	EDS
SiO ₂	39.42	39.51	38.79	37.06	31.11	28.18
TiO ₂	5.68	5.64	n.d.	n.d.	35.83	n.d.
Al ₂ O ₃	14.30	14.26	31.66	17.30	2.44	18.57
Cr ₂ O ₃	n.d.	tr	n.d.	n.d.	.06	n.a.
FeO	11.90	12.49	2.24*	3.79*	.16	18.57
MnO	.17	.09	n.d.	16.02**	n.d.	.52
NiO	n.d.	n.a.	n.d.	n.d.	.10	n.d.
MgO	11.53	11.36	.10	.26	n.d.	21.11
CaO	9.96	10.12	24.43	22.39	28.65	.09
Na ₂ O	2.92	2.80	n.d.	n.d.	n.a.	n.d.
K ₂ O	1.69	1.59	n.a.	n.a.	n.a.	n.d.
Total	97.57	97.86	97.22	96.82	98.35	87.04
Si	5.868	5.873	2.985	3.052	1.027	1.443
Ti	.636	.630	-	-	.890	-
Al	2.509	2.498	2.872	1.680	.095	1.121
Cr	-	-	-	-	.002	-
Fe	1.481	1.553	.130	.235	.004	.795
Mn	.021	.011	-	1.005	-	.023
Ni	-	-	-	-	.003	-
Mg	2.557	2.517	.012	.032	-	1.611
Ca	1.589	1.612	2.014	1.977	1.014	.005
Na	.842	.807	-	-	-	-
K	.321	.301	-	-	-	-
Total	15.824	15.802	8.013	7.984	3.035	4.997

* : as Fe₂O₃** : as MnO₃

related to X-ray detection efficiency, which varies with elements. The efficiency is best for Si, P and S, and drops for both heavier and lighter elements. Si, for example, yields four times as many counts per unit concentration as Na and Ni (MORI, 1983).

This means that the statistical errors for Na and Ni are twice as much as for Si. In many cases in Tables 4-8, roughly a half of the standard deviation originated from the counting statistics.

Accuracy, by contrast, is rather difficult to

Table 6. Analysis of oxides

	ilmenite	rutile	MgAl ₂ O ₄ -spinel		magnetite	Ti-magnetite	ulvöspinel
	EDS*	EDS	EDS	Theor	EDS*	EDS*	EDS*
SiO ₂	.04	n.a.	n.a.	-	n.a.	.49	.32
TiO ₂	47.80	98.96	n.a.	-	.19	21.20	30.98
Al ₂ O ₃	n.d.	n.d.	70.79	71.66	n.d.	1.18	.58
Cr ₂ O ₃	n.d.	n.d.	n.a.	-	n.d.	n.d.	.20
V ₂ O ₃	n.a.	n.a.	n.a.	-	n.a.	1.07	1.10
Fe ₂ O ₃	11.93	.61			68.85	24.62	6.11
FeO	36.49	n.d.	n.a.	-	30.96	48.99	58.19
MnO	.42	n.d.	n.a.	-	.36	.72	.57
ZnO	n.a.	n.a.	n.a.	-	n.a.	n.a.	.41
MgO	3.43	n.d.	28.67	28.34	n.d.	.93	.37
CaO	n.d.	n.d.	n.a.	-	n.d.	.25	.33
Total	100.11	99.57	99.47	100.00	100.36	99.44	99.16
Si	.001	-	-	-	-	.018	.012
Ti	.888	.995	-	-	.005	.594	.870
Al	-	-	1.988	2.000	-	.052	.026
Cr	-	-	-	-	-	-	.006
V	-	-	-	-	-	.032	.033
Fe ³⁺	.222	.006	-	-	1.989	.691	.172
Fe ²⁺	.754	-	-	-	.994	1.528	1.818
Mn	.009	-	-	-	.012	.023	.018
Zn	-	-	-	-	-	-	.011
Mg	.126	-	1.018	1.000	-	.052	.021
Ca	-	-	-	-	-	.010	.013
Total	2.000	1.001	3.006	3.000	3.000	3.000	3.000

* : oxidation state of Fe estimated on the basis of stoichiometry

assess, since true compositions for reference samples are never known. Indications for accuracy now available include the oxide totals for the unhydrous minerals with known state of iron oxidation, the chemical formula of stoichiometric minerals, and comparison with the wet chemical analyses.

The totals of the analyses in Tables 4, 7 and 8 fall in the 98.8–101 range. Even when appreciable amount of iron is present in both the ferrous and ferric states, assumption of stoichiometry gives rise to estimation of oxidation state, which in turn results in a total around 100 (see the magnetite and titanomagnetite in Table 6). We have generally observed that the majority of unhydrous samples have a total, after correction for the oxidation state if necessary, from 98.5 to 101. Totals seem, however, slightly depend on mineral species and specimen matrices, e.g. forsterites and garnets tend to have totals higher than 100, while lower for pyroxenes. This kind of systematics could be caused through the ZAF correction. The totals for the hydrous minerals (Table 5) approach 100 if appropriate contents of water are added, though still the corrected totals may show a little deficiency.

To sum up, accuracy of 1.5 relative % is indicated for elements with concentrations of several tens wt %. No indication is obtained for minor elements.

Chemical formula can also be a clue if iron-oxidation state is known and if samples possess well-defined stoichiometry. Analysis of various forsteritic olivines, for instance, rarely shows Si cations outside 0.995–1.005 per 4 oxygens. The implication is that if SiO_2

Table 7. Analysis of sulfides

	pyrrhotite troilite	
	Fe_7S_8	
Fe	60.23	63.44
S	39.57	36.68
Total	99.80	100.12
Fe	6.993	7.943
S	8.000	8.000

No other elements detected.

Table 8. Analysis of glasses

	JG-1			JB-1			CrCats4		CrCats10	
	EDS	WDS	Wet chem*	EDS	WDS	Wet chem*	EDS	Theor	EDS	Theor
SiO_2	72.17(54)	71.16(43)	72.78(46)	53.06(23)	51.98(30)	53.00(44)	54.20	54.26	52.14	52.40
TiO_2	.25(3)	.29(1)	.26(5)	1.25(4)	1.29(3)	1.37(10)	n.a.	-	n.a.	-
Al_2O_3	14.65(39)	14.84(54)	14.33(21)	14.51(16)	14.45(1)	14.72(20)	.83	.84	2.15	2.10
Cr_2O_3	n.d.	.01(1)	.01(0)	.04(5)	.04(1)	.06(1)	1.27	1.25	2.66	3.13
Fe_2O_3	2.04(7)	2.22(12)	2.20(13)	8.60(11)	9.46(46)	9.14(19)	n.a.	-	n.a.	-
MnO	n.d.	.06(1)	.06(1)	.13(5)	.17(3)	.15(2)	n.a.	-	n.d.	-
NiO	n.d.	.01(1)	-	n.d.	.02(2)	.02(0)	n.a.	-	n.a.	-
MgO	.68(9)	.84(5)	.75(9)	7.67(11)	7.84(2)	7.84(14)	17.54	17.87	16.88	16.76
CaO	2.18(6)	2.28(9)	2.22(11)	9.35(7)	9.23(2)	9.41(18)	25.54	25.78	25.63	25.61
Na_2O	3.20(13)	3.31(12)**	3.40(10)	2.83(20)	2.83(5)	2.84(7)	n.a.	-	n.a.	-
K_2O	4.01(7)	3.86(4)	3.99(10)	1.40(4)	1.33(2)	1.45(10)	n.a.	-	n.a.	-
Total	99.18(66)	98.88(52)	100.00	98.84(52)	98.64(10)	100.00	99.38	100.00	99.46	100.00

* : recalculated to a total of 100 ** : corrected for Na-evaporation

Fig. 5. Relative precision and accuracy vs wt% oxide. Solid circle : precision (inter-laboratory reproducibility) of wet chemical analysis as inferred from analyses of the JG-1 and JB-1 reference rocks (ANDO *et al*, 1974). Open circle and square : respectively for precision and accuracy of EDS. Larger symbol is for the JG-1 and JB-1 glasses, and smaller one for the other samples. Some questionable data are indicated by "?" (see text).

were single source of error, accuracy would be 0.5 wt % for SiO_2 of ca 42 wt %, i. e. a little more than 1% relative error. The diopside and garnet (Table 4) show excess in cation totals, but this could only indicate a portion of iron is in the ferric state. Sulfides are minerals for which both cations and anions were analyzed. The chemical formula of the troilite (Table 7) does not appear good. But if troilite possesses strict FeS stoichiometry as is generally believed, the estimated errors are only 0.1 and 0.2 wt % respectively for Fe and S.

Accuracy is best examined by comparing the EDS and wet chemical data of the JG-1 and JB-1 glasses. The result (Fig. 5) is that the accuracy of EDS is about 1% for 50 wt % level, 3% for 5 wt % and 10% for 0.5 wt %. Added to Fig. 5 is accuracy estimated from the minerals with single wet chemical analysis, and from the synthetic minerals and glasses. The majority of data confirm the accuracy estimated using the JG-1 and JB-1 glasses, but some data show larger deviations from the wet chemical analyses. The problem is that the reference compositions for these samples might be less reliable than for the JG-1 and JB-1 glasses. In fact, when the

accuracy of EDS appears low, the WDS data also tend to deviate from the wet chemical data. An example is the diopside (Table 4-a). Na_2O and MgO contents by the WDS differ from the wet chemical analyses, and are close to the EDS analyses. We do not know which method produced closer data to the true compositions. If the WDS data are employed as the most probable values, the accuracy of EDS is substantially improved. A similar problem is encountered in the case of the CrCats10 glass. The EDS and theoretical values for Cr_2O_3 do not well agree, and alternative use of the CrCats4 glass as standard for Cr does not result in better consistency. This implies that the CrCats10 glass does not possess the composition as intended to be. As far as accuracy is concerned, we can not totally expel this kind of ambiguity. All these questionable data are indicated as such in Fig. 5.

Fig. 5 also depicts precision of EDS and wet chemical analyses. The raw data are in Tables 4-8. Note that the EDS precision is of our laboratory, and that the precision for wet chemical analysis means inter-laboratory reproducibility involving more than 20 laboratories. The precision of wet chemical

analysis has well defined trend in contrast to the diversified nature of the EDS precision. We may conclude that intra-laboratory precision of EDS can be of the same order with inter-laboratory precision of the chemical analysis.

Fig. 5 also shows that as far as the JG-1 and JB-1 glasses are concerned, the EDS data rarely deviate from the wet chemical data by more than the 1-sigma precision of the wet chemical analysis. Therefore, we may conservatively conclude that EDS analysis is not substantially inferior to the conventional wet chemical analysis. This conclusion would be valid even for elements with concentrations down to 0.1 wt %, where accuracy was hitherto considered much worse (e.g. REED & WARE, 1975).

Conclusion

Our efforts in EDS analysis centered on two points. Firstly, we selected standards as reliable as possible. Secondly, we located practical sources of error, analyzed how they worked, and made corrections accordingly. The results are the accuracy not substantially inferior to that of the conventional wet chemical analysis, the precision comparable to the inter-laboratory reproducibility of wet chemical analysis, and improvements of EDS especially in light trace elements.

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エネルギー分散型マイクロプローブ分析のためのスペクトル解析

森 健・兼平慶一郎

(要 旨)

シリコン検出器を用いたエネルギー分散型マイクロプローブ分析のデータ処理法を提案する。この方法は、バックグラウンドの除去に際し、デジタル・フィルター法には依らず、バックグラウンドのモデル・スペクトルを使用する。固体検出器による不完全な電荷捕捉や電子的雑音による分析誤差の補正を行なう点に特徴がある。このことにより、軽元素の分析精度が向上し、珪酸塩鉱物の分析には特に都合が良くなった。分析標準にはできる限り単体金属を採用した。

この方法を用いて JG-1 と JB-1 から作ったガラスをも含めた各種の地球化学的試料を分析した。分析法の正確度や精密度は湿式分析値との比較や、鉱物の化学式を調べることにより判定できる。正確度は伝統的な湿式化学分析に比較しても実質的な見劣りはない。このことは、従来不正確とされていた 0.1~0.2 wt% レベルでもいえることである。一方、精密度も湿式分析法と同程度を実現できる。エネルギー分散法は地球化学の領域で従来より広く各種の問題に対処し得るようになった。