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Comparing the Intensities and Spectral Resolution Achieved by Wavelength-Dispersive Spectrometers on Microprobes and SEMs.

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Recently, there has been much discussion regarding whether quantitative X-ray microanalysis by EDS has achieved the accuracy and precision yielded by traditional EPMA (e.g., [1]). In the most recent of these comparative studies [2], WDS analysis was done using an electron microprobe and EDS analysis was done using an SDD-EDS on an SEM. Here, we compare the accuracy and precision achieved by quantitative microanalysis using concurrently acquired WDS and EDS measurements.

Quantitative compositions were determined using the Cameca SX100 at the University of Oregon, which has five Rowland circle wavelength-dispersive spectrometers—three contain low-pressure P10 flow-though detectors and two contain high-pressure P10 flow-though detectors—and a Thermo Scientific UltraDry EDS, and the Probe for EPMA software [3]. All measurements were made using a 15 kV accelerating voltage, a 30 nA beam current, and a beam diameter of 10 µm. Standardization was done using synthetic MgO for Mg Kα, labradorite (Lake Co.) for Al Kα, synthetic SiO_2 for Si Kα, diopside (Chesterman) for Ca Kα, and magnetite (Port Henry, U.C. #3380) for Fe Kα. The following standards were analyzed as unknown samples for Mg Kα, Al Kα, Si Kα, Ca Kα, and Fe Kα: synthetic TiO_2, synthetic MnO, synthetic NiO, synthetic Mg_2SiO_4 (forsterite), NBS K-411, NBS K-412, VG-A99 USNM 113498/1, and orthoclase (MAD-10). Standard (primary and secondary) intensities were corrected for deadtime. Standard intensities were corrected for standard drift over time. In cases in which "unknown" samples contain unanalyzed elements, these elemental concentrations were entered as fixed concentrations for the matrix corrections. The synthetic TiO_2, MnO, and NiO standards were analyzed to determine the ability of EDS and WDS to measure 0 wt%. For WDS measurements, all elements were counted on peak for 60 s. A TAP crystal was used for counting Mg Kα and Al Kα, a LPET crystal was used for counting Si Kα and Ca Kα, and an LiF diffractor was used for counting Fe Kα. For EDS measurements, spectra were collected with the time constant set to "auto", and deadtimes were typically kept below 30%, in order to minimize the magnitude of the corrections made by peak deconvolution and sum peak removal algorithms. EDS spectra were acquired for 40 s of livetime. The K-lines were used for quantitative analysis by EDS. For calculating concentrations from WDS measurements, the backgrounds were calculated using both off peak and mean atomic number (MAN, [4]) methods. Off peak intensities were counted for 10 s. The off peak correction method was linear for Mg Kα, Si Kα, Ca Kα, and Fe Kα and exponential for Al Kα. We used ZAF or Phi-Rho-Z (Armstrong/Love-Scott [5]) for the matrix correction method and Henke (LINEMU.DAT) [6,7,8] for the mass absorption coefficients dataset for calculating concentrations from EDS and WDS data.

Results are summarized in Table 1. The results are the averages of ten analyses, and the 99% CI WDS detection limits ranged from 0.012 wt% for Si Kα to 0.050 wt% for Fe Kα.

In most cases, modern SDD-EDS is now closely rivaling the accuracy and precision achievable by WDS. However, WDS analysis is better, certainly more practical, for trace analysis (see the Al concentrations measured in the TiO_2 standard in Table 1). The combination of integrated and concurrent EDS and WDS for quantitative analysis is now an appealing option in which major and minor elements could be analyzed by EDS and minor and trace elements could be analyzed by WDS.

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Table 1. WDS and EDS analyses

	TiO_2				MnO				NiO			
	Publ.	MAN	Off-Pk	EDS	Publ.	MAN	Off-Pk	EDS	Publ.	MAN	Off-Pk	EDS
O	40.05	*40.05*	*40.05*	*40.05*	22.55	*22.55*	*22.55*	*22.55*	21.42	*21.42*	*21.42*	*21.42*
Mg	0	-0.001	-0.002	0.004	0	0.000	0.002	0.000	0	0.000	0.001	0.000
Al	0.01	0.016	0.010	0.025	0	-0.001	0.003	0.028	0	0.000	0.008	0.000
Si	0	0.002	0.009	0.101	0	-0.004	0.011	0.123	0	0.002	0.025	0.216
Ca	0	0.001	0.000	0.000	0	-0.001	-0.002	0.001	0	0.000	-0.001	0.006
Ti	59.94	*59.94*	*59.94*	*59.94*	0	-	-	-	0	-	-	-
Mn	0	-	-	-	77.45	77.45	77.45	77.45	0	-	-	-
Fe	0	0.000	0.005	0.014	0	0.098	0.024	1.530	0	0.000	0.010	0.030
Ni	0	-	-	-	0	-	-	-	78.58	*78.58*	*78.58*	*78.58*
Sum	100	100.01	100.01	100.13	100	100.09	100.04	101.68	100	100.00	100.04	100.25

	Mg_2SiO_4				NBS K-411				NBS K-412			
	Publ.	MAN	Off-Pk	EDS	Publ.	MAN	Off-Pk	EDS	Publ.	MAN	Off-Pk	EDS
O	45.49	*45.49*	*45.49*	*45.49*	43.60	*43.60*	*43.60*	*43.60*	43.60	*43.60*	*43.60*	*43.60*
Mg	34.55	34.72	34.71	34.71	8.85	8.88	8.87	8.80	11.66	11.77	11.76	11.55
Al	0	-0.002	0.003	0.000	0.053	0.025	0.022	0.081	4.91	4.90	4.90	5.00
Si	19.96	19.85	19.83	20.39	25.38	25.32	25.30	24.66	21.20	21.10	21.09	21.14
Ca	0	0.004	0.007	0.000	11.06	10.80	10.79	10.86	10.90	10.68	10.68	10.78
Mn	0	-	-	-	0.077	*0.077*	*0.077*	*0.077*	0.062	*0.062*	*0.062*	*0.062*
Fe	0	0.001	0.007	0.017	11.21	11.11	11.10	11.22	7.74	7.72	7.73	7.80
Sum	100	100.06	100.04	100.59	100.2	99.81	99.76	99.30	100	99.83	99.82	99.93

	VG-A99 USNM 113498/1				Orthoclase (MAD-10)			
	Publ.	MAN	Off-Pk	EDS	Publ.	MAN	Off-Pk	EDS
O	43.34	*43.34*	*43.34*	*43.34*	45.80	*45.80*	*45.80*	*45.80*
Na	1.97	*1.97*	*1.97*	*1.97*	0.675	*0.675*	*0.675*	*0.675*
Mg	3.06	3.03	3.03	3.00	0	0.001	-0.001	0.036
Al	6.61	6.47	6.46	6.61	8.85	8.77	8.77	8.81
Si	23.81	23.57	23.55	23.51	30.29	30.26	30.23	30.16
P	0.166	*0.166*	*0.166*	*0.166*	0	-	-	-
K	0.681	*0.681*	*0.681*	*0.681*	12.86	*12.86*	*12.86*	*12.86*
Ca	6.65	6.41	6.41	6.42	0	0.000	-0.015	0.000
Ti	2.43	*2.43*	*2.43*	*2.43*	0	-	-	-
Mn	0.116	*0.116*	*0.116*	*0.116*	0	-	-	-
Fe	10.34	10.17	10.17	10.28	1.46	1.36	1.36	1.28
Ba	0	-	-	-	0.054	*0.054*	*0.054*	*0.054*
Sum	99.17	98.35	98.32	98.52	99.99	99.78	99.73	99.68

All values are in wt% and are averages of 10 analyses. "Publ." refers to the actual standard composition. "MAN" refers to WDS analyses calculated using the MAN background method. "Off-Pk" refers to WDS analyses calculated using an off-peak background method. *Italicized values* are fixed. The standard deviation of the WDS analyses ranged from 0.001 to 0.079. The standard deviation of the EDS analyses ranged from 0.001 to 1.182.

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