

Supplementary Materials: New Approach for Direct Determination of Manganese Valence State in Ferromanganese Nodules by X-ray Fluorescence Spectrometry

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Table S1. Calibration curves.

Equation Number	Analytical Parameter	Spectral Overlap	Equation
Equation 3.2	$MnK\beta_5/Mn\beta_{1,3}$	$FeK\alpha_{1,2}$	$N^{Mn} = -2.2044 + 161.6282 \cdot (I(MnK\beta_5)/I(Mn\beta_{1,3})) - 0.00197 \cdot I(FeK\alpha_{1,2})$
Equation 3.4	$MnK\beta'/Mn\beta_{1,3}$	$FeK\alpha_{1,2}$	$N^{Mn} = 27.6222 - 50.8719 \cdot (I(MnK\beta')/I(Mn\beta_{1,3})) + 0.0015 \cdot I(FeK\alpha_{1,2})$
Equation 3.5	$MnK\beta_5/Mn\beta_{1,3}$	-	$N^{Mn} = 15.2209 - 30.3495 \cdot (I(MnK\beta')/I(Mn\beta_{1,3})) + 75.2641 \cdot (I(MnK\beta_5)/I(Mn\beta_{1,3})) - 0.00197 \cdot I(FeK\alpha_{1,2})$
Equation 3.6	$MnK\beta'/Mn\beta_{1,3}$	$FeK\alpha_{1,2}$	$N^{Mn} = 9.5541 + 106.7648 \cdot (I(MnK\beta_5)/I(Mn\beta_{1,3})) - 20.7224 \cdot (I(MnK\beta')/I(Mn\beta_{1,3})) - 0.0007 \cdot I(FeK\alpha_{1,2})$

Table S2. Results of volumetric (vt) and XRF determination of average manganese valence state (N^{Mn}) and recalculation to MnO_2 content.

Sample	N^{Mn}					MnO_2 Content, wt. %				
	vt	Analytical Parameter (Spectral Overlap)				vt	Analytical Parameter			
		$MnK\beta_5/Mn\beta_{1,3}$ (FeKa)	$MnK\beta'/Mn\beta_{1,3}$ (FeKa)	$MnK\beta_5/Mn\beta_{1,3}$ $MnK\beta'/Mn\beta_{1,3}$	$MnK\beta_5/Mn\beta_{1,3}$ $MnK\beta'/Mn\beta_{1,3}$ (FeKa)		$MnK\beta_5/Mn\beta_{1,3}$ (FeKa)	$MnK\beta'/Mn\beta_{1,3}$ (FeKa)	$MnK\beta_5/Mn\beta_{1,3}$ $MnK\beta'/Mn\beta_{1,3}$ (FeKa)	$MnK\beta_5/Mn\beta_{1,3}$ $MnK\beta'/Mn\beta_{1,3}$ (FeKa)
1	3.80	3.82	3.84	3.84	3.83	29.76	30.01	30.29	30.42	30.16
2	3.86	3.89	3.70	3.82	3.77	37.46	38.02	34.23	36.68	35.59
3	3.59	3.74	3.61	3.69	3.65	37.46	41.21	38.10	40.03	39.03
4	3.89	3.77	3.87	3.82	3.84	43.17	40.42	42.84	41.75	42.06
5	3.89	3.88	4.06	3.98	4.01	46.03	45.79	50.25	48.21	49.04
6	3.86	3.91	3.89	3.92	3.91	41.19	42.37	41.92	42.56	42.34
7	3.99	3.87	3.76	3.84	3.80	48.48	45.39	42.88	44.66	43.83
8	3.87	3.82	3.78	3.82	3.79	32.23	31.36	30.69	31.34	30.88
9	3.91	3.73	3.77	3.76	3.75	34.64	31.44	32.20	32.00	31.80
10	3.93	3.93	3.77	3.88	3.83	38.81	38.81	35.59	37.79	36.80
11	3.96	3.83	3.65	3.76	3.71	50.91	47.60	42.75	45.75	44.48
12	3.92	3.90	3.66	3.81	3.75	44.97	44.52	38.80	42.34	40.89
13	3.92	3.83	4.06	3.95	3.99	49.15	46.84	52.93	49.94	51.10
14	3.92	3.88	4.06	3.98	4.01	46.95	45.91	50.38	48.33	49.17
15	3.93	3.97	3.87	3.95	3.92	41.01	41.97	39.75	41.42	40.81