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Adventures with Oxides: Utilizing Commercial and Internal Reference Materials for Geological and Materials Science Samples

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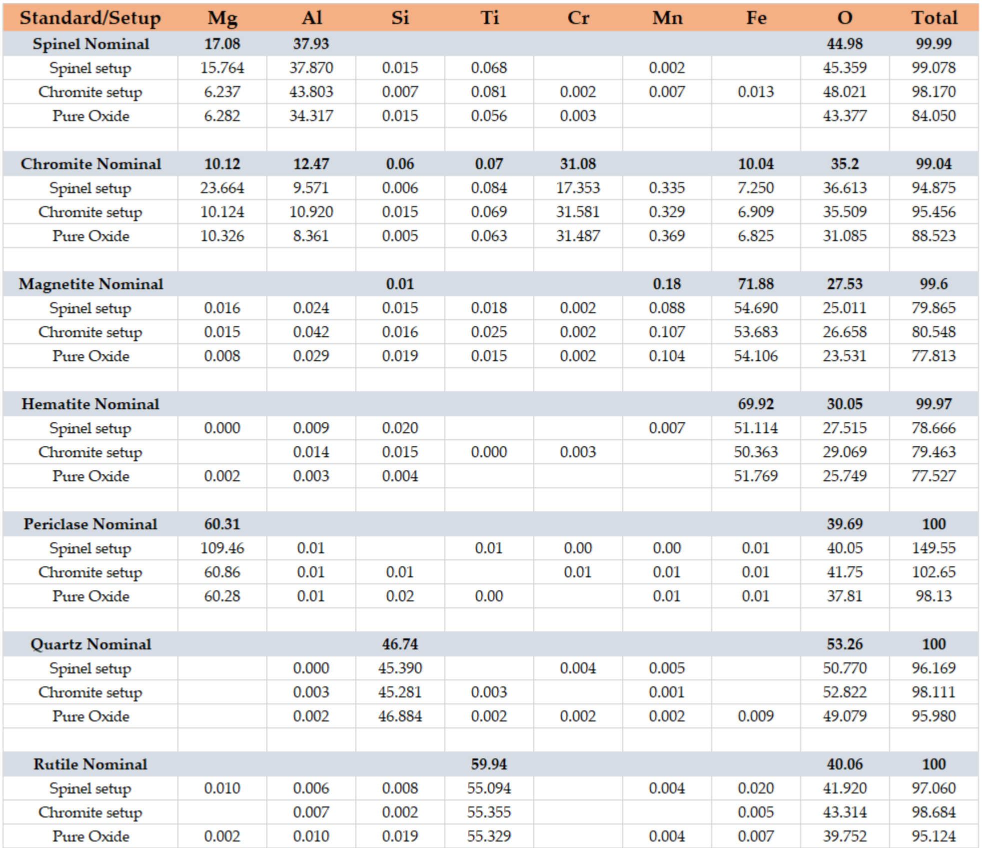
Traditional mineral analysis relies on stoichiometric calculation of oxygen, which works well for many minerals but assumes that the mineral adheres to normal stoichiometry. This is not always a valid assumption. Although direct analysis of oxygen in the electron microprobe is possible, it remains challenging to ensure accuracy. Development of LDE (JEOL) and PC (CAMECA) crystals provide high count rates and high peak-to-background ratios, but traditional matrix corrections often give erroneous values (e.g. Armstrong, 1988). Over the past two decades, several papers have addressed these problems (e.g. Bastin and Heijligers, 1989), but it remains difficult to achieve reliable precision and repeatability. Adding to the complication is the wide variety of reference materials used in different labs; the same mineral can vary from different sources and even have inhomogeneity within an individual specimen. A few papers have attempted to benchmark reference materials for use in mineral analyses with some success (e.g. McGuire et al., 1992).

The situation for pure oxides is also difficult as matrix corrections do not calculate oxygen stoichiometry effectively, leading to the need for direct measurement of oxygen. Results are sensitive to the reference materials used in the analysis setup, resulting in vastly different (inaccurate) variation from the nominal composition (Table 1). Disparities in carbon coat thickness can also influence the absorption of O Kα x-rays, so it is critical to apply a carbon coat simultaneously to both the sample and reference.

With the advent of LaB-6 and field-emission microprobes, researchers are starting to examine small oxide inclusions in minerals and fine-scale ilmenite-magnetite intergrowths for thermobarometry, petrogenic indicators and partitioning coefficients. Another crucial application is in the ceramic industry, where high-performance piezoelectric single-crystal substrates, such as PMN-PT, are grown for various applications. The chemistry of these substrates is critical to the electromechanical coupling of devices, where even a small variance in the stoichiometry can cause performance issues. EPMA is utilized to capture the exact chemistry of both the starting materials and the finished crystals to determine uniformity between batches. Ferroelectric materials such as barium titanate (BT) can be modified to exhibit different properties with simple substitution of other cations into the material. For example, substitution of Sr shifts the Curie temperature while retaining permittivity. Cutting-edge unique optical glasses are also highly dependent on the proper chemistry dictating their properties. In each of these applications, it becomes important to have confidence in the exact chemistry determined by EPMA.

This study examines the complexity and challenge of choosing the correct reference materials to ensure accuracy, precision and repeatability. A wide range of reference materials are sourced from both commercial entities, such as Astimex, and trusted microprobe community sources, such as the Smithsonian. For some applications, internal reference standards are used to provide a baseline for comparison, especially in the ceramic community where they have a batch that performs to their needs and desire to see future batches match the performance. It is not ideal to use their internal standard for all analyses in the future, so this study also addresses benchmarking external standards to give the most consistent results.



Standard/Setup	Mg	Al	Si	Ti	Cr	Mn	Fe	O	Total
Spinel Nominal	**17.08**	**37.93**						**44.98**	**99.99**
Spinel setup	15.764	37.870	0.015	0.068		0.002		45.359	99.078
Chromite setup	6.237	43.803	0.007	0.081	0.002	0.007	0.013	48.021	98.170
Pure Oxide	6.282	34.317	0.015	0.056	0.003			43.377	84.050
Chromite Nominal	**10.12**	**12.47**	**0.06**	**0.07**	**31.08**		**10.04**	**35.2**	**99.04**
Spinel setup	23.664	9.571	0.006	0.084	17.353	0.335	7.250	36.613	94.875
Chromite setup	10.124	10.920	0.015	0.069	31.581	0.329	6.909	35.509	95.456
Pure Oxide	10.326	8.361	0.005	0.063	31.487	0.369	6.825	31.085	88.523
Magnetite Nominal			**0.01**			**0.18**	**71.88**	**27.53**	**99.6**
Spinel setup	0.016	0.024	0.015	0.018	0.002	0.088	54.690	25.011	79.865
Chromite setup	0.015	0.042	0.016	0.025	0.002	0.107	53.683	26.658	80.548
Pure Oxide	0.008	0.029	0.019	0.015	0.002	0.104	54.106	23.531	77.813
Hematite Nominal							**69.92**	**30.05**	**99.97**
Spinel setup	0.000	0.009	0.020			0.007	51.114	27.515	78.666
Chromite setup		0.014	0.015	0.000	0.003		50.363	29.069	79.463
Pure Oxide	0.002	0.003	0.004				51.769	25.749	77.527
Periclase Nominal	**60.31**							**39.69**	**100**
Spinel setup	109.46	0.01		0.01	0.00	0.00	0.01	40.05	149.55
Chromite setup	60.86	0.01	0.01		0.01	0.01	0.01	41.75	102.65
Pure Oxide	60.28	0.01	0.02	0.00		0.01	0.01	37.81	98.13
Quartz Nominal			**46.74**					**53.26**	**100**
Spinel setup		0.000	45.390		0.004	0.005		50.770	96.169
Chromite setup		0.003	45.281	0.003		0.001		52.822	98.111
Pure Oxide		0.002	46.884	0.002	0.002	0.002	0.009	49.079	95.980
Rutile Nominal				**59.94**				**40.06**	**100**
Spinel setup	0.010	0.006	0.008	55.094		0.004	0.020	41.920	97.060
Chromite setup		0.007	0.002	55.355			0.005	43.314	98.684
Pure Oxide	0.002	0.010	0.019	55.329		0.004	0.007	39.752	95.124

Figure 1. Table 1: Comparison of various oxide setups to nominal compositions of reference materials. [Spinel setup: Mg, Al, O on spinel; Si, Ca, Cr on pyrope;Ti on rutile; Mn on almandine; Fe on magnetite][Chromite setup: Mg, Al, Cr, O on chromite; Si, Ca on pyrope; Ti on rutile; Mn on almandine; Fe on magnetite][Pure oxide setup: Mg on periclase; Al on corundum; Si on quartz; Ca on sphene; Ti, O on rutile; Cr on Cr2O3; Mn on Mn metal; Fe on magnetite].

References

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