Trace Element Analyses of Micron-Size Particles and Statistical Determination of Minimum Detection Limits

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Savannah River National Laboratory (SRNL) has developed expertise in producing homogeneous, ca. 1 μm-diameter spherical particles of mixed-element components, wherein dopants can be varied from a trace constituent (ppm) to wt.% concentrations. The samples used for this work are nickel-doped cerium oxide microspheres produced by SRNL. They were initially selected as analogs for plutonium-doped uranium oxide particles and analyzed as part of a larger study to evaluate whether electron probe microanalyzers (EPMA) can be used to characterize nuclear materials as an alternative or complementary method to mass spectrometers. The five samples used in this study contained nominal compositions of 0, 0.004, 0.04, 0.4 and 4 wt.% Ni. They were analyzed by both an Agilent 7900 Q-ICP-MS at SRNL and the JEOL JXA-8530F Plus EPMA at the University of Minnesota. In addition to EPMA results (calibrated with high-precision Q-ICP-MS analyses) suggesting that the EPMA could address outstanding nuclear material characterization needs, these samples 1) showcase the ability of the EPMA to quantify not just trace concentrations, but trace concentrations in microparticles (1 μm diameter, Fig. 1), and 2) offer a unique opportunity to evaluate the methodology for assessing the minimum detection limits of EPMA analyses.

Particles were electrostatically deposited on silicon planchets, and for the EPMA analyses no sample preparation work was undertaken. The microspheres were not embedded or polished, nor was a conductive coating applied. They simply adhered to the silicon wafer, even when high beam currents and accelerating voltages were applied. Due to their morphology and size, bulk standards and normal matrix correction routines would not adequately characterize these materials. Instead, a calibration curve was used for quantification. This calibration curve was constructed by using the concentrations (Q-ICP-MS) and average net Ni counts (EPMA) of the 0 and 4 wt.% Ni samples. The results are summarized in Table 1 and plotted in Fig. 2. Given the size of the microspheres, the data show very good agreement between the independently measured Q-ICP-MS values and calibrated EPMA results. However, if trace element EPMA analyses could not be validated by other analytical techniques, how can one determine if the results actually represent true measured concentrations versus just random noise?

Typically, minimum detection limits (MDL) are based solely on the number of counts in the analysis [1], but this method is only valid for one analytical point. When measuring trace elements, many analyses are acquired, with the average of those points used to estimate the composition. In addition, the usual MDL determination does not account for all the other variables that can affect the detection limits, including instability in the electronics, variability in the spectrometers, beam drift, room temperature variations, or even cosmic rays (e.g., the JEOL SXES spectrometer is an excellent cosmic ray detector). An alternative method based on the

approached laid out by Goldstein *et al.* [2] would include all of these variabilities and provide a more realistic estimate.

Student's t-test was designed to compare two sets of data (Fig. 3) and determine the probability that those two datasets in fact represent the same population. If one of those data sets represented a zero concentration of the element in question, then Student's t-test can assess if the measured data is statistically distinct from zero. If it is, then by definition our set of data must be above the minimum detection limit, even if MDL calculations for each analytical point indicates otherwise. If it is not distinguishable from zero, then it is below the MDL. The exact MDL value for these analytical conditions can be determined by shifting our data set closer to or farther from the zero value until it is at the threshold value. The difference is then the MDL. The specific MDL is then a function of the instrument, the analytical conditions, the room environment, and the number of data points collected. These calculations can be readily performed using the Microsoft Excel program. In order to use Student's t-test in this manner, one must decide what threshold will be used for the probability test. Typically, either two- or three-sigma is used as the threshold. However, is there an objective rationale for selecting one over the other, or has it been completely arbitrary? Datasets including the one presented here help us evaluate that question.

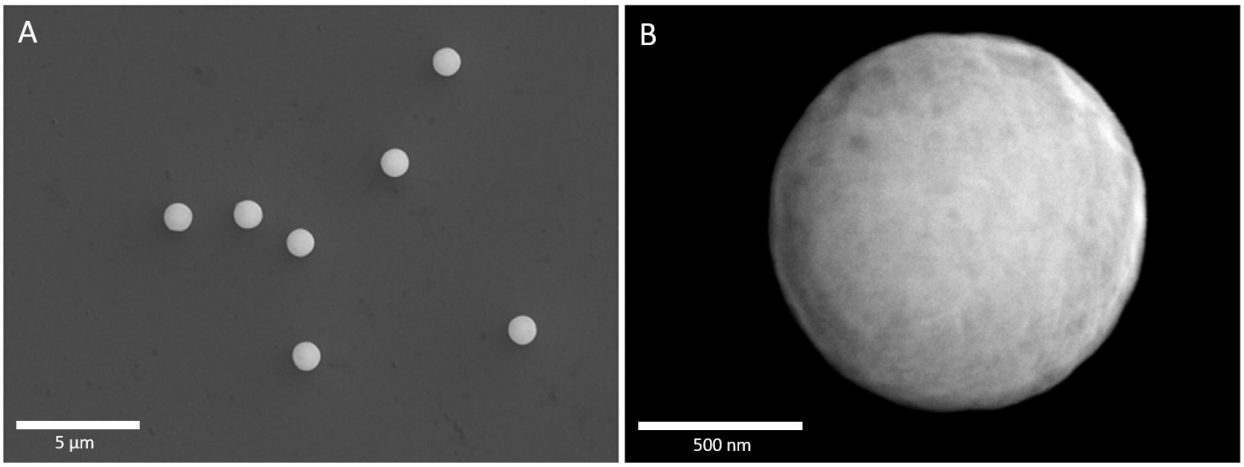

Fig. 1. Secondary electron images of representative microspheres, (A) 5,000x, and (B) 65,000x.

Nominal Ni (wt%)	Meas. Ni (wt.%) ICP-MS	±2SD	Avg Net Ni cps/µA, EPMA	±2SE	Measured Ni (wt%) EPMA	±2SE
0	0.0000795	0.0000078	-30.29 (n=27)	9.0	0.000	0.007
0.004	0.00437	0.00048	-5.8141 (n=32)	8.6	0.0093	0.0094
0.04	0.0498	0.0046	127.02 (n=25)	11.2	0.059	0.011
0.4	0.474	0.044	1327 (n=23)	15.1	0.511	0.036
4	4.63	0.27	12268.2 (n=19)	187.8	4.63	0.14

Table 1. Data for the five samples; the nominal Ni content, ICP-MS measured concentration, EPMA measured net counts and EPMA measured wt.%.

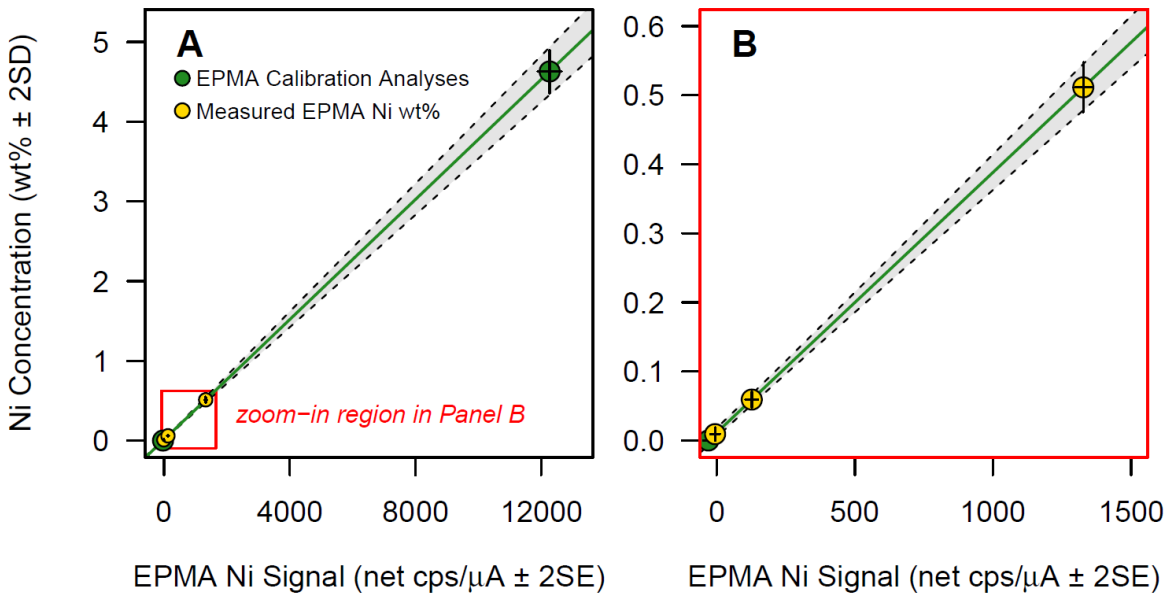

Fig. 2. EPMA net counts from the three unknowns (yellow dots) relative to the two samples used for calibration (0 and 4 wt.% Ni; green dots), plotted against the measured ICP-MS values. Green line is the calibration curve used to quantify the EPMA data. Dashed lines are the error envelope at a 95% confidence level.

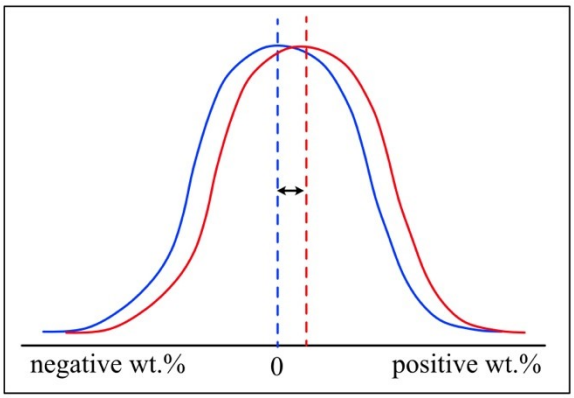

Fig. 3. Student's t-test comparing two data sets. Blue histogram represents a sample with a zero concentration of the element, and the red histogram is the measured data. Student's t-test will provide the probability that these two sets represent two samplings of the same population versus two distinct populations, given the difference in the average, the number of analyses, and the spread in the data. If they represent two populations, then the measured data must be above the MDL.

References:

1. S.J.B Reed, Electron Microprobe Analysis. Cambridge, UK: Cambridge Univ. Press; 1997.
2. J. Goldstein, *et al.*, Scanning Electron Microscopy and X-ray Microanalysis. New York: Plenum Press; 1992.