SIMPLE METHOD FOR SENSITIVITY COMPARISON OF RAMAN SPECTROSCOPIC INSTRUMENTS

Author: A.J.R. Bauer, Ph.D.

Abstract

There is a need for a simple method that can be used to compare sensitivities of commercially available Raman instruments, especially in the demonstration and evaluation process. This short application note will address this need, with an easy method and non-toxic materials, so that those in search of instrumentation can more easily compare and contrast the performance of devices.

Introduction

Sensitivity of Raman spectroscopy is a hard factor to pin down, as it is a function of laser wavelength, excitation cross section of the analyte, laser power on target and acquisition time. In this brief application note, one easily-applied recipe for comparing measurement characteristics of different Raman spectrometers will be described. It is based upon the presentation of a $CaCO_3$/NaCl solid mixture in a vial to an instrument using a 785 nm laser with 290 mW on target at the sample.

This method uses four samples from 0-5% $CaCO_3$ in finely ground NaCl powder to acquire spectra dominated by the carbonate ν_1 stretching feature at 1082 cm^{-1}. The background corrected peak height of this feature is used to generate a calibration curve that is used to establish both sensitivity (counts per %$CaCO_3$ in NaCl) and the limit of detection of the carbonate peak (LOD).

Figure 1. Prepared samples of $CaCO_3$ in NaCl.

Sample Preparation

Acros Organic $CaCO_3$ (calcium carbonate, CAS 471-24-1) was used without additional preparation. Sigma-Aldrich ACS grade NaCl (sodium chloride, CAS 7647-14-5)) was ground with a mortar and pestle to a fine powder that was used as a non-Raman active support for the $CaCO_3$. Both components were weighed on an analytical balance and combined, then mixed again thoroughly with the mortar and pestle. These samples were then introduced to small glass vials and submitted to Raman analysis.

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Experimental Conditions and Calculations:

This work was performed using a TSI ChemLogix ProRaman-L instrument. This device has an excitation laser operating at 785 nm, and is capable of delivering nearly 300 mW to the sample. 10 spectra of each sample were collected at 290 mW with an acquisition time of 60 seconds. No averaging was performed.

An example raw spectrum (4.8% $CaCO_3$ in NaCl) is shown in Figure 2, along with a background corrected version of the spectrum. The background removal was performed with the automated baseline correction function. Peak heights of the spectra with the background removed were used to create a calibration curve (background corrected counts vs. $CaCO_3$ wt% in NaCl) that was fit to a line (R^2=0.9999). These features are shown in Figure 3.

The calibration curve is shown in Figure 4. The linear fit provided by Microsoft® Excel® spreadsheet program was used to model each data point, and then residuals, squared residuals and root mean square error (RMSE) were calculated (*see Calculation Details*). The limit of detection is defined for these purposes as 3.3*RMSE/slope, and for this method described above, LOD=0.07 wt % $CaCO_3$ in NaCl. The sensitivity of this analysis is then 757 background corrected counts per 1 wt % $CaCO_3$ in NaCl.
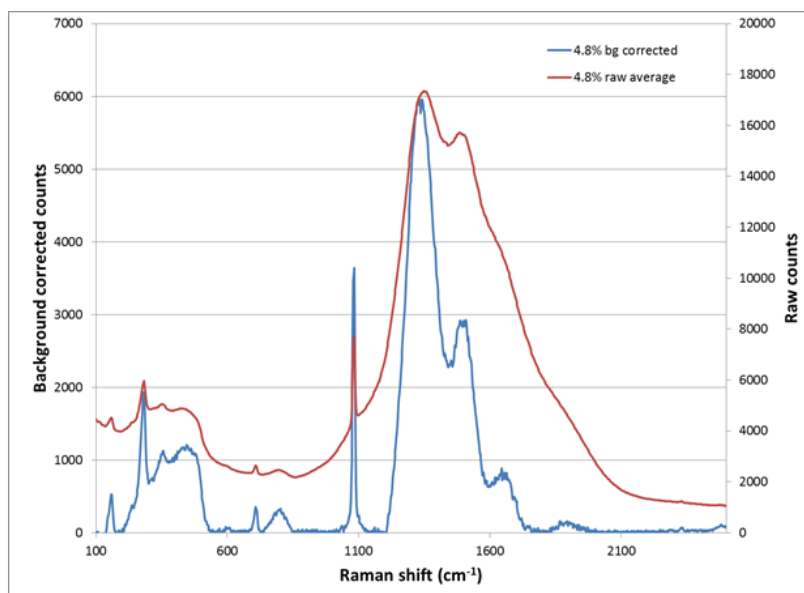

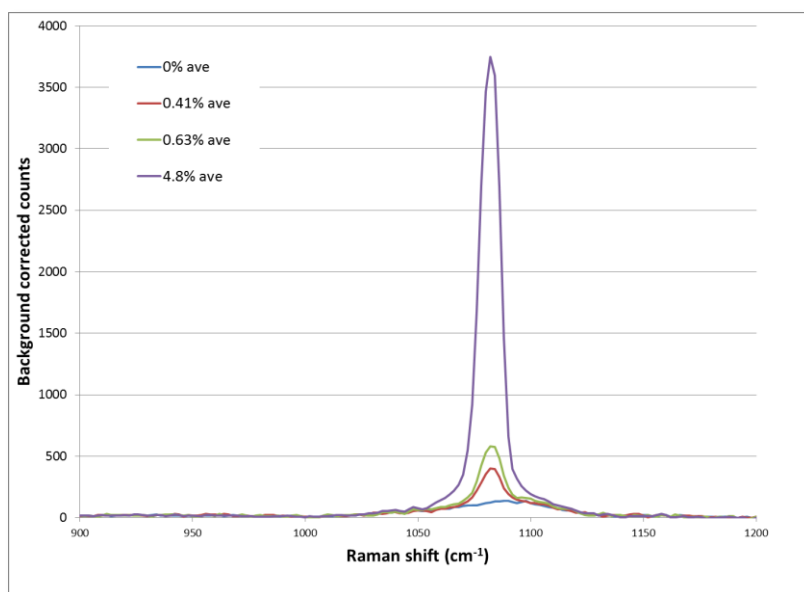**Figure 2**. Raw and background corrected Raman spectra of 4.8 wt% $CaCO_3$ in NaCl

Figure 3. Background corrected spectra of a range $CaCO_3$ concentrations in NaCl. These peak heights were used to generate the calibration curve in Figure 4.

Calculation Details

In this example, the line of best fit has been calculated by Excel® program and is displayed on the graph (y=757.04x+78.513). This equation is used to calculate the y values associated with the model (given the known concentration, x, values). The residuals are found by subtracting the real data from the modeled set. The root mean square of the error (RMSE) is found by squaring the residuals, adding them together, dividing by the number of measurements and then taking the square root of the sum. The Excel® command line for this process is =SQRT(SUM(range)/N). RMSE is then used to finally calculate the LOD by multiplying it by 3.3 and dividing the result by the slope of the best fit line.
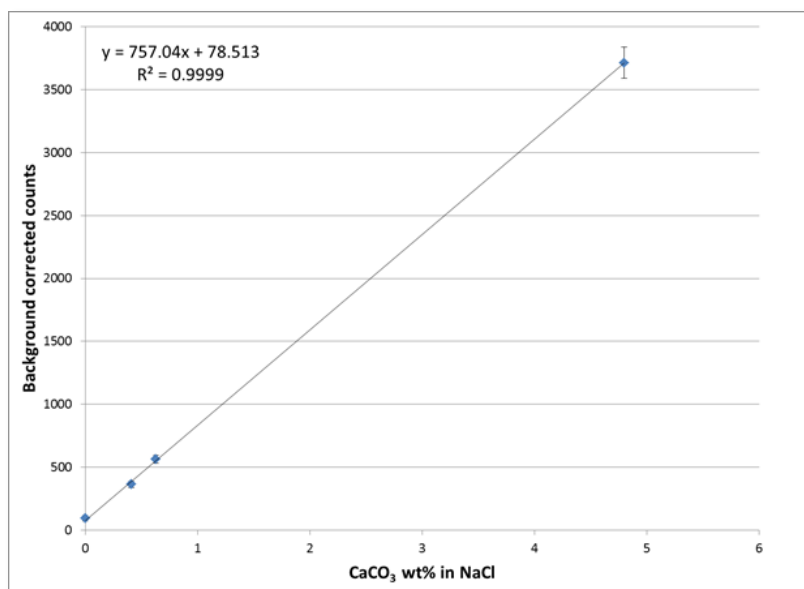

Figure 4. Calibration curve of $CaCO_3$ in NaCl.

As discussed in the opening paragraphs, sensitivity and LOD of Raman methods and instrumentation are a function of acquisition time, among other factors. When this method is performed using a 10 s acquisition time, the calculated LOD is 0.30% $CaCO_3$ in NaCl, and the sensitivity is 164 background corrected counts per 1% $CaCO_3$.

Conclusion

This simple, safe and convenient technique can be used to compare sensitivities of Raman instruments, especially useful in helping decide in the process of purchasing new hardware. Use of this technique should make clear the measurement performance differences between similar instruments, and enable the purchaser to make informed decisions. No more guessing about relative performance in Raman spectrometers is needed.