

**Use of an Internal Mercury-Argon Lamp for the Calibration of Raman Frequency in Large Raman Images of Astromaterials.** Ryan S. Jakubek<sup>1</sup> and Marc D. Fries<sup>2</sup>, <sup>1</sup>Jacobs JETS Contract, NASA-JSC, Houston, Texas 77058, USA, <sup>2</sup>NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058, USA.

**Introduction:** Raman imaging is an emerging tool for the analysis of meteorites, as it is capable of describing mineralogy,<sup>1-5</sup> carbon composition/speciation,<sup>6-8</sup> and crystal orientation<sup>3,9</sup> all within a petrographic context. Adequately examining the heterogeneous composition of a meteorite, while maintaining low laser powers needed to prevent damage to meteorite mineralogy and organics, often requires the collection of large Raman images with long collection times on the timescale of days. However, the frequency calibration of the Raman instrument/spectrometer drifts on long timescales<sup>10,11</sup> resulting in low frequency precision for the Raman spectra comprising a large Raman image.

This decrease in frequency precision can compromise the analysis of geological markers that can provide important information on a meteorite sample. We examine, in detail, the change in bandwidth and frequency of the Raman bands and Hg-Ar emission lines in our Raman images as a function of time and laboratory temperature.

To overcome the drift in calibration, we utilize a commercial WITec Raman instrument with an internal Hg-Ar calibration lamp to individually calibrate each spectrum in the Raman image. Our instrument, known as “Ratatoskr”, uses a beam splitter in place of the customary mirror to facilitate collection of Hg-Ar calibration lines concurrent with Raman spectra. We show that using the internal calibration we can improve the frequency precision for the spectra in our Raman images from  $\sim\pm 0.15\text{ cm}^{-1}$  to  $\sim\pm 0.05\text{ cm}^{-1}$  for Raman spectra collected over multiple days. This is important as it improves measurements of mineral chemistry, latent strain, and other features that are dependent upon accurate peak position determination. We also examine the spectral signal-to-noise ratio needed to minimize the frequency error when fitting bands to Gaussian/Lorentzian profiles. We then use our results to suggest a general method for calibrating the frequency of Raman spectra in large Raman images.

**Instrumentation:** Our Raman internal calibration is performed using the “Ratatoskr” WITec  $\alpha 300R$  confocal Raman microscope (XMB3000-3003). The instrument contains a Hg-Ar emission lamp that is integrated into the optical path of the collected Raman scattering using a beam splitter. The Hg-Ar calibration

lines and Raman scattered light are simultaneously sent to the spectrometer along the same optical path. This configuration allows for the Hg-Ar calibration lines to be observed in every spectrum when collecting Raman microscopy images over long periods of time. Figure 1 shows an optical diagram of the instrumentation.

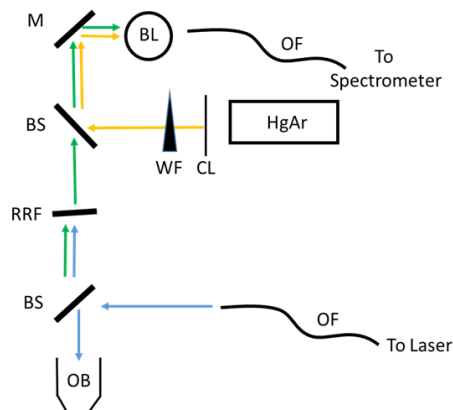


Figure 1: Optical diagram of Raman microscope with internal calibration lamp. The labels in the figure are as follows: M = mirror, BS = beam splitter, RRF = Rayleigh rejection filter, OB = objective, WF= wedge filter, CL= collimating lens, Hg-Ar = mercury argon lamp, BL = ball lens, and OF = optical fiber. The blue arrows, green arrows, and orange arrows indicate the optical path of the incident laser light, the Raman scattered light, and the Hg-Ar lamp light, respectively.

**Calibration Technique:** The standard calibration technique used for the collection of Raman images calibrates the spectrometer once at the beginning of image collection. However, changes in environmental and instrumental conditions cause the calibration to drift with time.<sup>11,12</sup> This results in a shift in observed Raman band frequencies throughout the collection of a Raman image with longer image collection times resulting in more significant frequency drifts.

Using the Hg-Ar calibration lamp we are able to independently calibrate each spectrum within a Raman image eliminating the observed drift in frequency with time. This calibration method improved the frequency precision of our Raman image from  $\sim\pm 0.15\text{ cm}^{-1}$  to  $\sim\pm 0.05\text{ cm}^{-1}$ .

We then extend our calibration to account for changes in the slope of the spectrometer calibration with time. We find that changes in the calibration slope also contribute to drift in the Raman frequency. By accounting for the change in calibration slope, we were able to improve the frequency precision of our Raman images by an additional  $\sim\pm 0.01\text{ cm}^{-1}$ .

**Comparison to Other Techniques:** The most common technique for calibrating a Raman spectrometer involves the use of a Raman frequency standard or emission lamp at the sample position.<sup>13</sup> This requires replacing the sample with the standard to calibrate the spectrometer. This technique cannot be used during the collection of a Raman image because the sample cannot be moved from its position on the microscope stage. Therefore, while this technique is reasonable for typical Raman analyses, is inadequate for long Raman image scans, where data collection can extend for days or even weeks. The method described here resolves this problem and improves upon it, as spectral drift is eliminated and every single spectrum is calibrated in post-processing to the highest possible precision.

The use of calibration standards incorporated into Raman instrumentation have previously been used to calibrate the Raman spectra within Raman images.<sup>12</sup> Our work reports a new technique for the calibration of Raman images and examines the calibration technique in detail.

**Calibration Improves Geological Marker Precision:** The improvement of the frequency precision in our Raman images improves the precision of quantitative measurements calculated from the Raman band frequencies. To demonstrate this, we determined the expected error in the calculation of olivine forsterite number from the frequency shift of the DB2 Raman band.<sup>14–16</sup> We show that calibrating each Raman spectrum individually in our Raman images decreases the error in the calculated forsterite number by  $\sim 59\%$ . Thus, our calibration technique can significantly decrease the error in the quantitative analysis of Raman Geological markers.

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