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Calibration of Raman Spectrometer for Gas Phase Measurements

Patrick E. O'Rourke
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REVIEWS AND APPROVALS

AUTHORS:

_____
Patrick E. O'Rourke, Analytical Development   Date

TECHNICAL REVIEW:

_____
Robert Lascola, Analytical Development   Date

APPROVAL:

_____
Clinton Gregory, Manager   Date
Analytical Development

EXECUTIVE SUMMARY

Raman spectroscopy is currently used at SRNL to measure the concentration of gaseous species evolved from chemical reactions. This report documents the methods used to calibrate the spectroscopic systems in both frequency and intensity spaces.

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Introduction

Raman spectroscopy is currently used at SRNL to measure the concentration of gaseous species evolved from chemical reactions. The Raman spectrometers used for this work are manufactured by TSI Inc., model GasRaman NOCH-1. This model instrument incorporates a 532 nm diode pumped solid state laser and fiber optic sampling probe. This memo details the methods used to calibrate Raman spectrometers.

Calibration of spectroscopic instruments is usually accomplished by measuring the response of known standard substances and using these responses to model the quantity of substance through a mathematical equation. For Raman spectroscopic instruments, the measured response is the intensity of light inelastically scattered from molecules by the Raman process, and the mathematical equation is a linear expression:

[Concentration(i)] = Ω * Raman_Line_Intensity(i)

Where [Concentration] has units of pressure, Raman_Line_Intensity has units of counts, and Ω is a proportionality constant determined by measuring the counts of a known pressure of gas under fixed spectrometer conditions. In this work, Ω is expressed as a product of three factors: the Raman scattering cross-section of each measured species i (RSC_i), the spectrometer response function at the measured frequencies of species i (SRF_i), and a Laser energy correction factor (PCF), which is the ratio of a reference power and time to the actual laser power and time used in the experiment. This factoring of Ω allows for correction of short-term laser power drift, long-term spectrometer response drift, and sample integration time adjustment.

[Concentration(i)] = PCF * SRF(i) * RCS(i) * Raman_Line_Intensity(i)

The RCS values were taken from literature values [2]. The PCF is calculated by (300mw * 5 sec) / (Laser-Power * Integration-Time). The SRF values are determined from measurements of gas standards with the NOCH-1:

SRF(i) = [Concentration(i)] / PCF / RCS(i) / Raman_Line_Intensity(i)

Gas compositions used in the spectrometer calibration are listed in Table 1.

Name	Formula	CAS	MW	Target Conc	Stabilizer	Balance Gas
Nitrogen	N_2	7727-37-9	28.01	100.00%		
Oxygen (Air)	O_2	7782-44-7	32.00	20.95%		(Air)
Carbon dioxide	CO_2	124-38-9	44.01	100.00%		
Nitrous oxide	N_2O	10024-97-2	44.01	20.00%	5% N_2	Ar
Nitric oxide	NO	10102-43-9	30.01	20.00%	5% N_2	Ar
Nitrogen dioxide	NO_2	10102-44-0	46.01	5.00%	20% O_2	Ar
Hydrogen_High	H_2	1333-74-0	2.02	10.00%	5% N_2	Ar
Hydrogen_Low	H_2	1333-74-0	2.02	2.67%		Ar

Table 1: Standard Gas Compositions

This calibration technique works well for gases which remain chemically stable during the sampling and measuring process. Ideal gas behavior is assumed; specifically, the RSC values are assumed to be invariant with respect to the consitution of other gases in the sample. This assumption is validated by

observations. The reference laser power is 300 mw, and the reference detector integration time is 5 seconds. Longer integration times are useful provided the concentration of NO_2 gas is low enough so that its fluorescence did not saturate the detector.

Raman Line Intensity Measurement

Accurate determination of SRF values relies on reproducible extraction of Raman line intensities from Raman spectra. For these instruments and conditions, gas phase Raman spectra exhibit the characteristics of fixed Raman shifts and narrow line widths. The value of the Raman line shift for gases is determined by the vibrational/rotational energy levels of the molecule and is typically unaffected by chemical or environmental conditions near STP. The line width is typically narrower than the spectrometer instrument response function and so can be reliably modeled by the instrument shape function.

Raman lines in general are superimposed on a broad fluorescence background. This background must be removed to accurately measure line intensity. Figure 1 shows a typical Raman spectrum of air using a fiber optic Raman probe optimized for laser excitation at 532nm. The sharp line at 1555 cm^{-1} is from oxygen and the line at 2331 cm^{-1} is nitrogen.
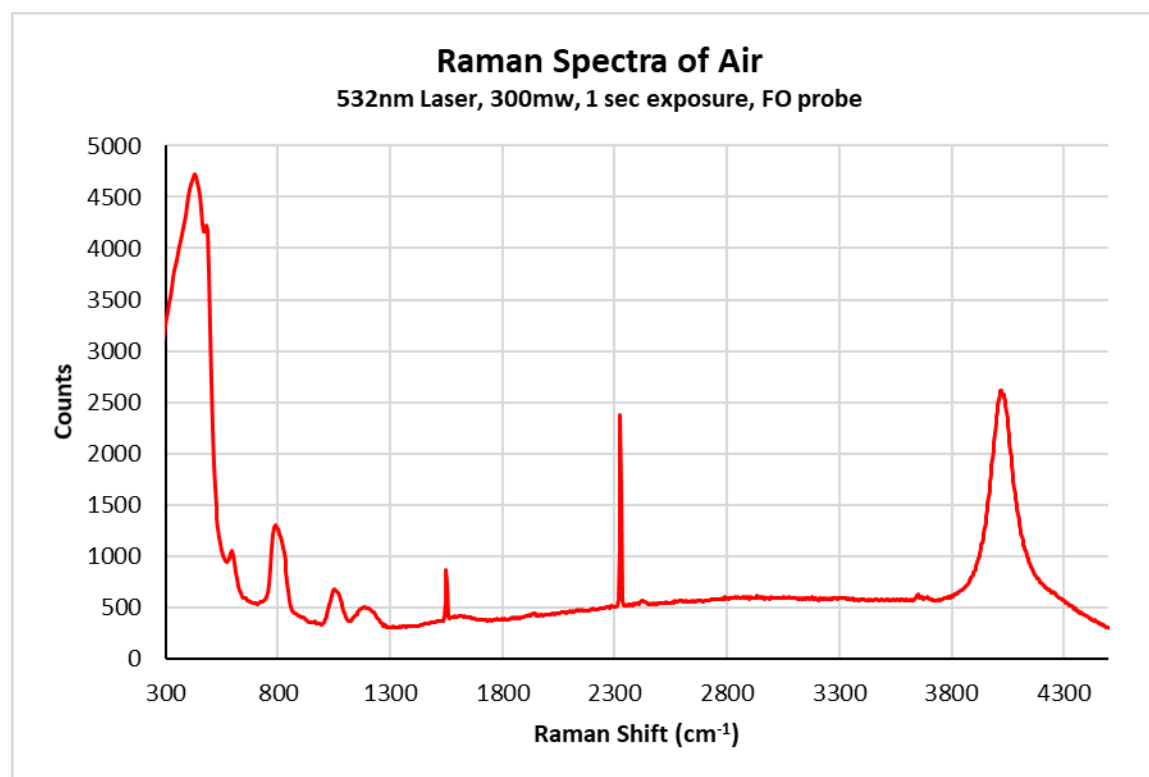

Figure 1: Raw Raman Spectrum of Air

Other broader features in the spectrum are characteristic of the fiber optic probe and sample cell. Identification and quantification of the sharp Raman lines can be enhanced with respect to the broad background by digital processing of the spectrum using Gaussian derivative filters.

$$PS(v) = \sum_{(\rho:\ -N\ to\ N)} G_d DF(\rho) * RS(v+\rho)$$

$G_0DF(\rho) = (1/(Sqr(2\pi)*\sigma))*EXP(-0.5*(\rho/\sigma)^2)$

$G_1DF(\rho) = (\rho/\sigma^2)*G_0DF(\rho)$

$G_2DF(\rho) = ((\rho^2-\sigma^2)/\sigma^4)*G_0DF(\rho)$

Where $PS(\nu)$ is the processed spectrum, $RS(\nu)$ is the Raw spectrum and $G_dDF(\rho)$ is the derivative Gaussian filter (d is derivative order = 0, 1, or 2). σ is a filter parameter specifying the signal line width, and N is the range of the filter, typically greater than 4σ. Sigma is assumed to be the half-width of the instrument function, typically 2 channels for this work, and N = 12. Table 2 lists the values for the zero order, first derivative and second derivative Gaussian filter function. Figure 2 shows the processed Raman spectrum of air. The second derivative Gaussian filter preserves a linear relationship to intensity among peaks with similar widths, but effectively eliminates broad background.

Gaussian Filter Coefficients

Sigma = 2   Range = 12

⬚	Smooth	1st derivative	2nd derivative
-12	0.000000003	-0.000000009	0.000000027
-11	0.000000054	-0.000000148	0.000000394
-10	0.000000743	-0.000001858	0.000004460
-9	0.000007992	-0.000017982	0.000038461
-8	0.000066915	-0.000133830	0.000250932
-7	0.000436341	-0.000763597	0.001227210
-6	0.002215924	-0.003323886	0.004431848
-5	0.008764150	-0.010955188	0.011502947
-4	0.026995483	-0.026995483	0.020246612
-3	0.064758798	-0.048569098	0.020237124
-2	0.120985362	-0.060492681	0.000000000
-1	0.176032663	-0.044008166	-0.033006124
0	0.199471140	0.000000000	-0.049867785
1	0.176032663	0.044008166	-0.033006124
2	0.120985362	0.060492681	0.000000000
3	0.064758798	0.048569098	0.020237124
4	0.026995483	0.026995483	0.020246612
5	0.008764150	0.010955188	0.011502947
6	0.002215924	0.003323886	0.004431848
7	0.000436341	0.000763597	0.001227210
8	0.000066915	0.000133830	0.000250932
9	0.000007992	0.000017982	0.000038461
10	0.000000743	0.000001858	0.000004460
11	0.000000054	0.000000148	0.000000394
12	0.000000003	0.000000009	0.000000027

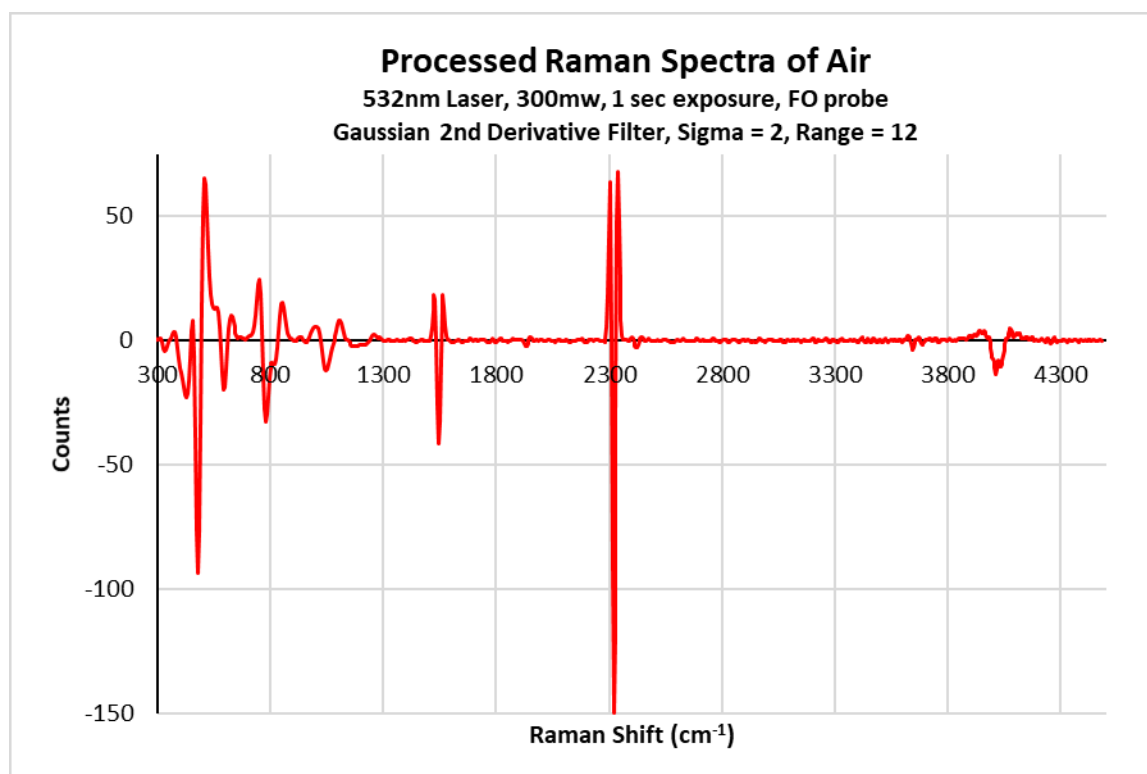Table2. Gaussian filter coefficients

Figure 2: Second Derivative Processed Raman Spectrum of Air

Raman Response Functions

The second derivative signal intensity from each molecule can be accurately determined by comparing the processed spectrum with normalized molecular response functions unique to the molecules of interest. The molecular response functions are calculated by assuming Gaussian peak shapes at the characteristic Raman shifts, relative intensities and line widths as verified from measurements of standard gas mixtures. Tables 3a-3c list characteristic peak features used to calculate molecular response functions. For those gases where a standard was not available, literature values for the peak position was used (in red).

Table 3a Raman Peak Shift

	Cell	NO2	N2	O2	N2O	NO	H2	CO2	CO	H2O	NH3	CH4
Peak1	422.0	752.0	2331.0	1555.0	1285.0	1876.0	352.0	1285.0	2143.0	3654.0	3334.0	2914.0
Peak2	490.0	1321.0			2225.0		587.0	1388.0				
Peak3	590.0	1500.0					815.0					
Peak4	784.0	2068.0					1036.0					
Peak5	1942.0	2288.0					4155.0					
Peak6	2430.0	2632.0										
Peak7	4012.0	2816.0										
Peak8	4354.0	3182.0										
Peak9	4384.0	3554.0										
Peak10		3928.0										

Table	3b	Raman	Peak	Intensity							
Inten1	0.0000	0.3761	1.0000	1.0000	0.9701	1.0000	0.1800	0.0000	1.0000	1.0000	1.0000	1.0000
Inten2	0.9806	0.6268	0.0000	0.0000	0.2425	0.0000	0.7202	1.0000	0.0000	0.0000	0.0000	0.0000
Inten3	0.0000	0.3761	0.0000	0.0000	0.0000	0.0000	0.1440	0.0000	0.0000	0.0000	0.0000	0.0000
Inten4	0.0000	0.4513	0.0000	0.0000	0.0000	0.0000	0.0900	0.0000	0.0000	0.0000	0.0000	0.0000
Inten5	0.0000	0.1504	0.0000	0.0000	0.0000	0.0000	0.6481	0.0000	0.0000	0.0000	0.0000	0.0000
Inten6	0.0000	0.2256	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Inten7	0.1961	0.1254	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Inten8	0.0000	0.1003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Inten9	0.0000	0.0752	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Inten10	0.0000	0.1254	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table	3c	Raman	Peak	Width							
Width1	12.00	8.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00
Width2	8.00	8.00			7.00		7.00	7.00				
Width3	12.00	8.00					7.00					
Width4	12.00	8.00					7.00					
Width5	12.00	8.00					7.00					
Width6	12.00	8.00										
Width7	30.00	8.00										
Width8	12.00	8.00										
Width9	12.00	8.00										
Width10		8.00										

Molecular response functions are calculated from the equation:

$$MRF_i(\nu) = \sum_{(\iota:\ 1\ to\ 10)} Inten_\iota (((\nu-\upsilon_\iota)^2-\sigma_\iota^2)/\sigma_\iota^4)*EXP(-0.5*((\nu-\upsilon_\iota)/\sigma_\iota)^2)$$

$Inten_\iota$ are intensities from table 3b, υ_ι are peak shifts from table 3a, and σ_ι are line widths from table 3c. Molecular response functions are calculated using the Excel macro MakePeak. Figure 3 shows the calculated response functions for the fiber optic cell, nitric oxide (NO_2), nitrogen (N_2) and oxygen (O_2). The response functions are calculated using a common-frequency pixel density of 2 cm^{-1} / point from 200cm^{-1} to 4200 cm^{-1}. Note that the raw pixel density from the Raman spectrometer is approximately 5.8 cm^{-1} / point. Native Raman spectra are interpolated to provide the 2 cm^{-1}/point data density, as described below.

Spectrometer Frequency Calibration

In order to carry out the intensity calculation, the molecular response functions and the processed spectrum must be properly aligned with respect to Raman shift frequency (ν). The Raman shift calibration for the spectrometer depends on its calibration with respect to absolute frequency and on the absolute frequency of the exciting laser. Since the Raman shift arises from the difference of the two absolute values, the spectrometer can be accurately calibrated in for Raman shift by fitting known Raman peak shift positions to detector pixel values using a cubic polynomial function, bypassing measurement of the individual absolute values. Table 4 lists Raman shift values and detector pixels used

in the frequency calibration. These shift values were determined from measurements of samples with known composition.
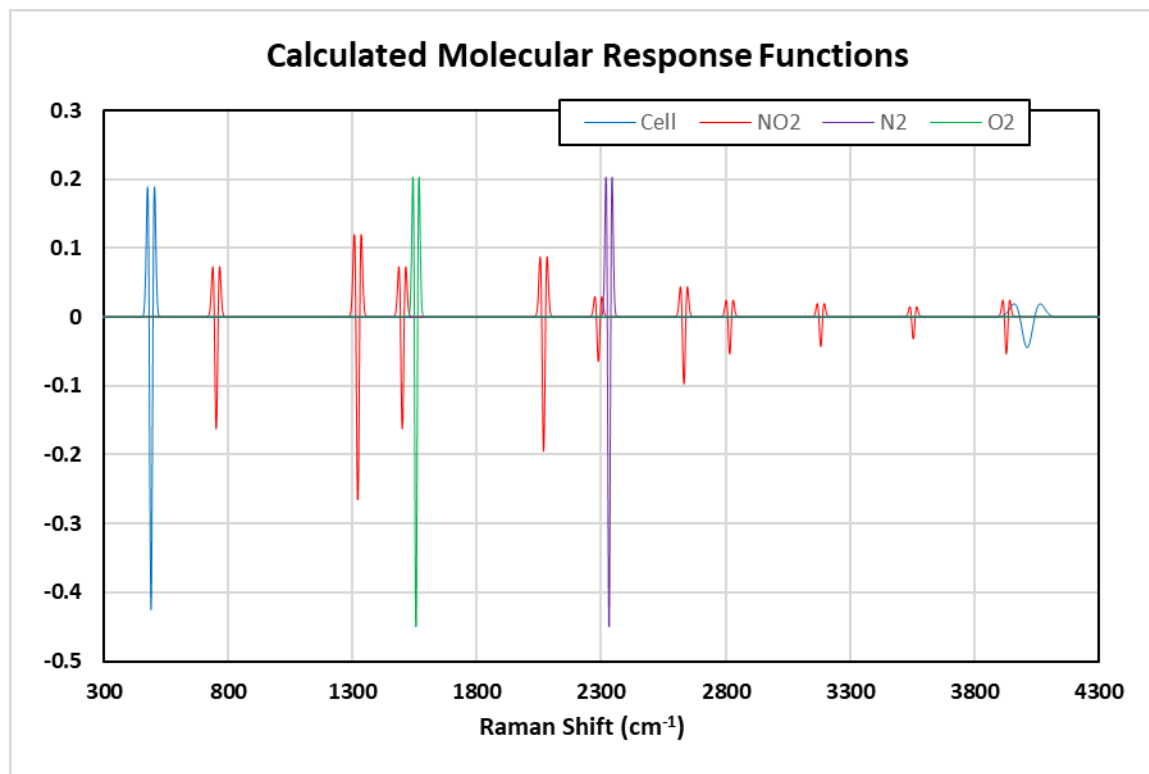

Figure 3: Calculated Raman Response Functions

Molecule	Pixel	Frequency
H2	55.0	352
H2	96.9	587
H2	138.3	815
H2	179.4	1036
N2O	226.9	1285
CO2	226.9	1285
CO2	246.9	1388
O2	279.9	1555
NO	345.3	1876
CO	401.8	2143
N2O	419.8	2226
N2	442.9	2331
CH4	577.6	2914
NH3	682.3	3334
Water	766.3	3654
H2	908.2	4155

Table 4: Raman Lines and Estimated Channel Values Used for Wavelength Calibration

Raman Spectrometer # ELI0000442769:

$\nu = 30.422812 + 5.9192776 * pixel - 0.0017691785 * pixel^2 + 0.0000002781689 * pixel^3$

Raman Spectrometer # ELI0000441972:

$\nu = 120.33317 + 5.7724094 * pixel - 0.0015226275 * pixel^2 + 0.00000011613817 * pixel^3$

Given an accurate pixel to frequency equation, the processed spectrum can be interpolated to a common frequency scale as used for the molecular response functions. The interpolation is executed using the Excel Macros SplineFit and Interpolate. SplineFit is a method to convert the discrete digital data of the processed spectrum to a piece-wise continuous spectrum. Each discrete data value in the processed spectrum (PS) (pixel) is represented by a quadratic polynomial equation calculated by a least-squares fit to points on each side of the pixel. For each pixel in the derivative-processed-raw-spectrum there are three values, the quadratic polynomial coefficients.

$PS(pixel) = a_0 + a_1 * (\varepsilon - pixel) + a_2 * (\varepsilon - pixel)^2$ for $\{\varepsilon: -1 < \varepsilon < 1\}$

The a_i 's are the solution to the matrix equation:

$$\begin{vmatrix} 2N+1 & 0 & \sum_{(n: -N \text{ to } N)} n^2 \\ 0 & \sum_{(n: -N \text{ to } N)} n^2 & 0 \\ \sum_{(n: -N \text{ to } N)} n^2 & 0 & \sum_{(n: -N \text{ to } N)} n^4 \end{vmatrix} \begin{vmatrix} a_0 \\ a_1 \\ a_2 \end{vmatrix} = \begin{vmatrix} \sum_{(n: -N \text{ to } N)} PS(pixel + n) \\ \sum_{(n: -N \text{ to } N)} n * PS(pixel + n) \\ \sum_{(n: -N \text{ to } N)} n^2 * PS(pixel + n) \end{vmatrix}$$

For any given value of N, which defines how many points on each side of the pixel to use in the least squares fit, the inverse matrix of sums is easily calculated once for all pixels. Typically N = 2, and the solution for N=2 is:

$$\begin{vmatrix} 34/70 & 0 & -1/7 \\ 0 & 1/10 & 0 \\ -1/7 & 0 & 1/14 \end{vmatrix} \times \begin{vmatrix} \sum_{(n: -N \text{ to } N)} PS(pixel + n) \\ \sum_{(n: -N \text{ to } N)} n * PS(pixel + n) \\ \sum_{(n: -N \text{ to } N)} n^2 * PS(pixel + n) \end{vmatrix} = \begin{vmatrix} a_0 \\ a_1 \\ a_2 \end{vmatrix}$$

The spline fit coefficients for each pixel can be quickly calculated by construction the sums of the products of derivative-processed-raw-spectrum values with power integer values between -N and N.

With the piece-wise continuous polynomial functions, it is a simple matter to interpolate the derivative-processed-raw-spectrum to the common-frequency array as found in the molecular response functions.

$IPS(\nu_j) = a_0(\nu_i) + a_1(\nu_i) * [(\nu_J - \nu_i) / \nu_i] + a_2(\nu_i) * [(\nu_J - \nu_i) / \nu_i]^2$ for $\{\nu_j: \nu_{i-1} < \nu_j < \nu_{i+1}\}$ and for $\{\nu_j: (\nu_j - \nu_{i-1}) > Abs(\nu_j - \nu_i)\}$ and for $\{\nu_j: (\nu_{i+1} - \nu_j) > Abs(\nu_j - \nu_i)\}$

Where $IPS(\nu_j)$ is the interpolated-derivative-processed-raw-spectrum at the discrete common frequency values used in the molecular response functions.

Inputs for SplineFit and Interpolate are the order of the spline-fit polynomial (typically=2), the number of pixels used in the spline fits (typically 2N+1 = 5), the derivative-processed-raw-spectrum, the pixel-to-frequency polynomial calibration coefficients, and the molecular response function common-frequency array. The accuracy of the Raman line intensity determination is sensitive to the pixel-to-frequency calibration, so it is important to verify the calibration by measuring air composition before

and after a Raman experiment. The frequencies of the oxygen and nitrogen peaks should be at 1555 cm^{-1} and 2331 cm^{-1}, respectively. The composition of air should measure 78.1% nitrogen and 20.9% oxygen (+/-2%). Raman intensities for each molecule of interest are calculated from the processed Raman spectrum as:

$$RLI(i) = \sum\nolimits_{(v:\ 200\ to\ 4200)} MRF_i(v) * PS(v)$$

Spectrometer Response Function Determination

Molecular concentrations are calculated from Raman intensities by multiplying by proportionality constants. The proportional constant values are determined by absolute molecular cross-sections, laser power, integration time and the spectrometer intensity response function. The proportionality constants for each analyte of interest are modeled as a product of the molecular Raman-cross-section and the spectrometer-response-function to allow easier correction to the calibration should the spectrometer-response-function change. In Table 5, the Raman-cross-sections, entered as diagonal elements in the calibration matrix, are taken from literature values, referenced to the nitrogen cross-section.

In general, where spectral overlaps occur, interferences can be accounted for by off-diagonal matrix elements which are the negative product of the relative intensity of the interferent times the cross-section of the analyte. For example, the interference of the 1285 cm^{-1} CO_2 line on primary N_2O line is $-(0.61 * 0.51) = -.311$. In the case of NO_2 interference, the off diagonal elements were determined experimentally because of the complexity of the NO_2 spectrum. Figure 4 shows a nitrogen dioxide spectrum overlaid with MRF's for NO_2, N_2O, and CO_2. Figure 5 shows the calculated concentrations of

RCS	Cell	NO_2	N_2	O_2	N_2O	NO	H_2	CO_2	CO	H_2O	NH_3	CH_4	SRF$_{442769}$
Cell	0.14	0	0	0	0	0	0	0	0	0	0	0	0.2
NO_2	0	0.015	0	0	0	0	0	0	0	0	0	0	0.26
N_2	0	0.08	1	0	0	0	0	0	0	0	0	0	0.17
O_2	0	0.1	0	0.96	0	0	0	0	0	0	0	0	0.185
N_2O	0	-0.02	0	0	0.51	0	0	-.31	0	0	0	0	0.21
NO	0	0.12	0	0	0	2.63	0	0	0	0	0	0	0.17
H_2	0.0230	0.0012	0	0	0	0	0.26	0	0	0	0	0	0.38
CO_2	0	0.0135	0	0	0	0	0	0.88	0	0	0	0	0.24
CO	0	-0.003	0	0	0	0	0	0	1.07	0	0	0	0.2
H_2O	0	-0.005	0	0	0	0	0	0	0	0.28	0	0	0.4
NH_3	0	-0.0014	0	0	0	0	0	0	0	0	0.17	0	0.38
CH_4	0	-0.0018	0	0	0	0	0	0	0	0	0	0.11	0.4

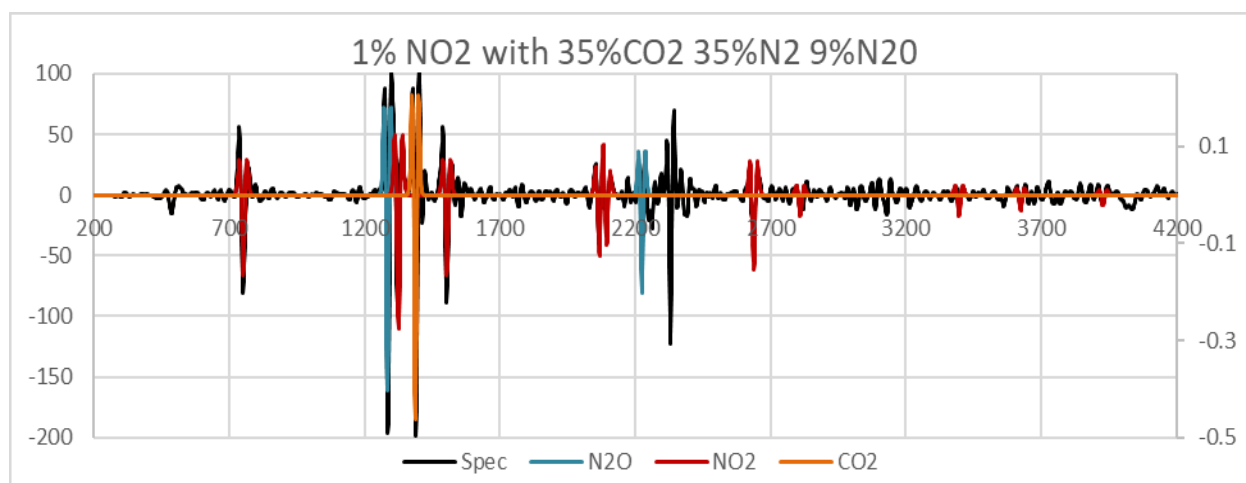Table 5: Raman Cross-section Matrix and Spectrometer Response Values

Figure 4. Spectrum with 1% NO$_2$ with N$_2$O, CO$_2$, and NO$_2$ Molecular Response Functions
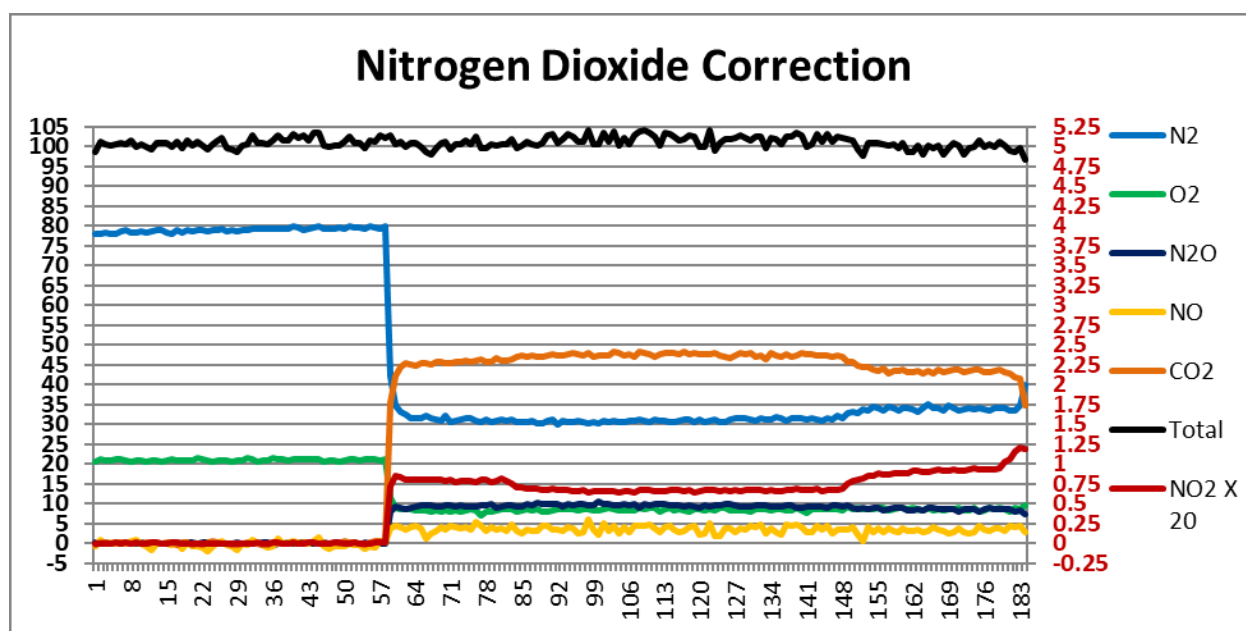

Figure 5. Mixed Gas Concentrations

The Spectrometer-response-functions in Table 5 are determined experimentally from known gas standards where possible. Figure 6 shows data from experiment 7 conducted on 23June2016. The test starts with 100% nitrogen in the cell which is displaced by Hydrogen over 75 minutes. The PCF is set to 0.874 to give 100% Total reading when averaged over the first 10 data points. As time progresses the nitrogen reading drops to 33% and the hydrogen reading increases to 65% with the balance being water at 2%. The average Total pressure is 100% +/-1.5% (1 sigma).
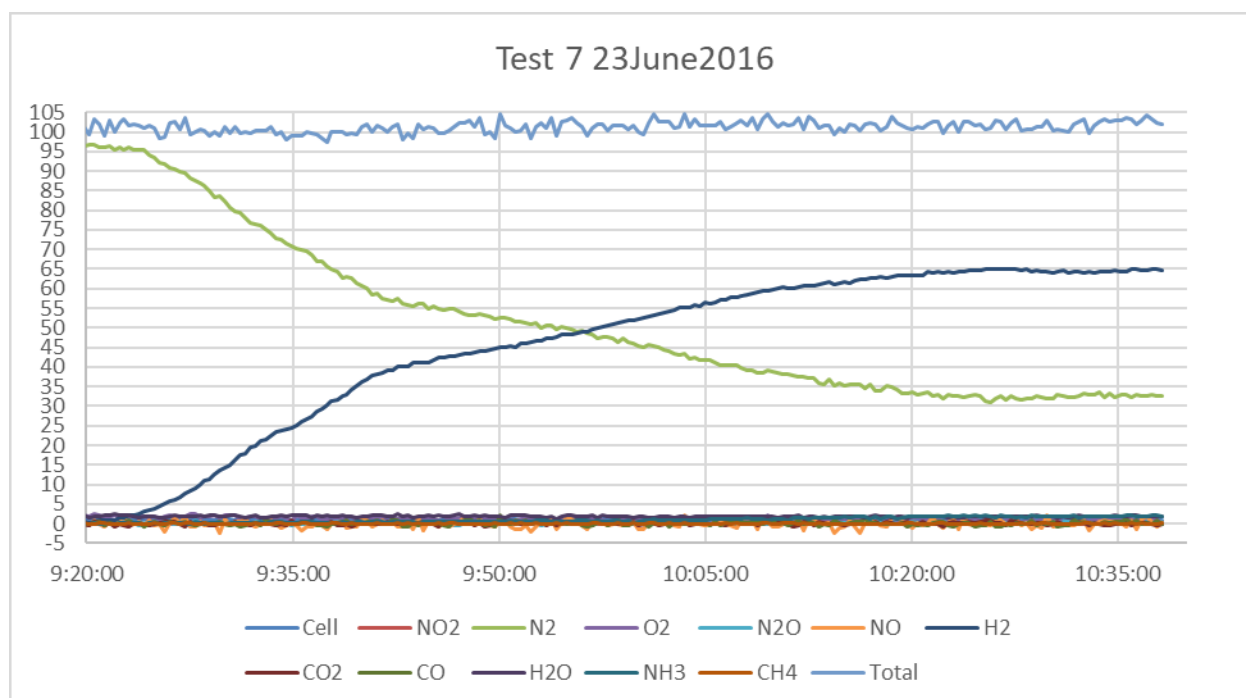
Figure 6: Isobaric effect of hydrogen displacing nitrogen

Molecular and Spectrometer Response by Difference

The Species concentrations can be modeled by straight-forward calibration using measured intensities of gas standards with known composition. The assumption of fixed laser power, integration time and spectrometer configuration should be verified before and after experiments by measuring room air as a check standard. In the case of laser power drift, the PCF should be applied. In the case of instrument modification, a new set of SRF's should be applied. Analyte gas concentration is determined by:

[Concentration(i)] = PCF * SRF_i * ($\sum_{(j)} RCS_{ij}$ * RLI(j))

There are cases when gas standards are not available for some species. Ammonia is one species that is difficult to characterize because a stable high concentration standard is difficult to obtain. It is possible to estimate the SRF for ammonia by difference. Figure 7, experiment Test_6A_Check again shows nitrogen in the Raman cell being displaced by hydrogen. The nitrogen SRF = 0.185 was established by measurements on 100% nitrogen gas at 1 atmosphere pressure. The hydrogen SRF = 0.38 was established by measurements of a 10% H2 standard gas at 1 atmosphere pressure. During the course of the test, the sum of nitrogen and hydrogen remain constant.
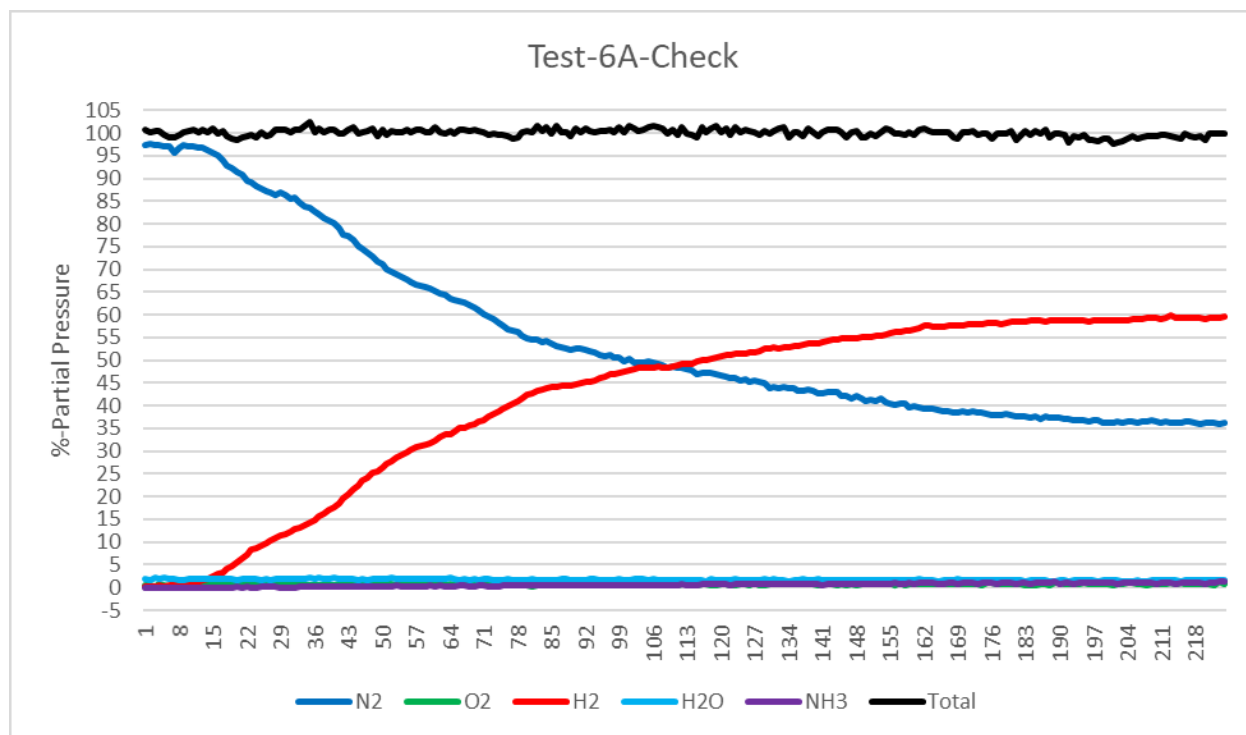
Figure 7. Hydrogen and Nitrogen SRF stability

Figure 8, experiment CDISS-6B shows a mixture of nitrogen, hydrogen and ammonia. The measured values of the gases are constant with the nitrogen concentration = 12.6% (+/- 0.5%), hydrogen = 52.3% (+/- 0.7%), water = 1.2% (+/-0.2%) and N_2O = 0.9% (+/-0.3%). If the balance of concentration = 33.0 (+/-0.9) was assigned to ammonia, the SRF for ammonia = 0.38.
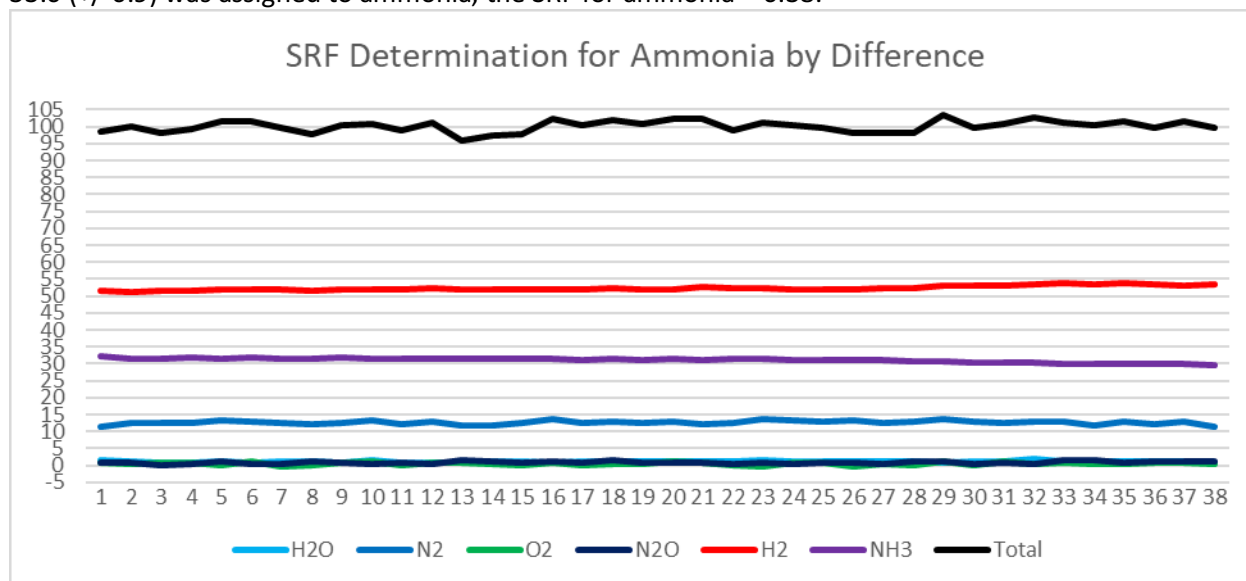

Figure 8: Hydrogen, Ammonia and Nitrogen in Raman Cell

Figure 9, experiment CDISS-6A shows mixtures of hydrogen and ammonia displacing nitrogen. In this experiment the flow cell was partically plugged causing pressure buildup. The cell was vented near measurements 28, 77 and 135. The effect of pressure increase is evident in the total pressure value trending above 100%.
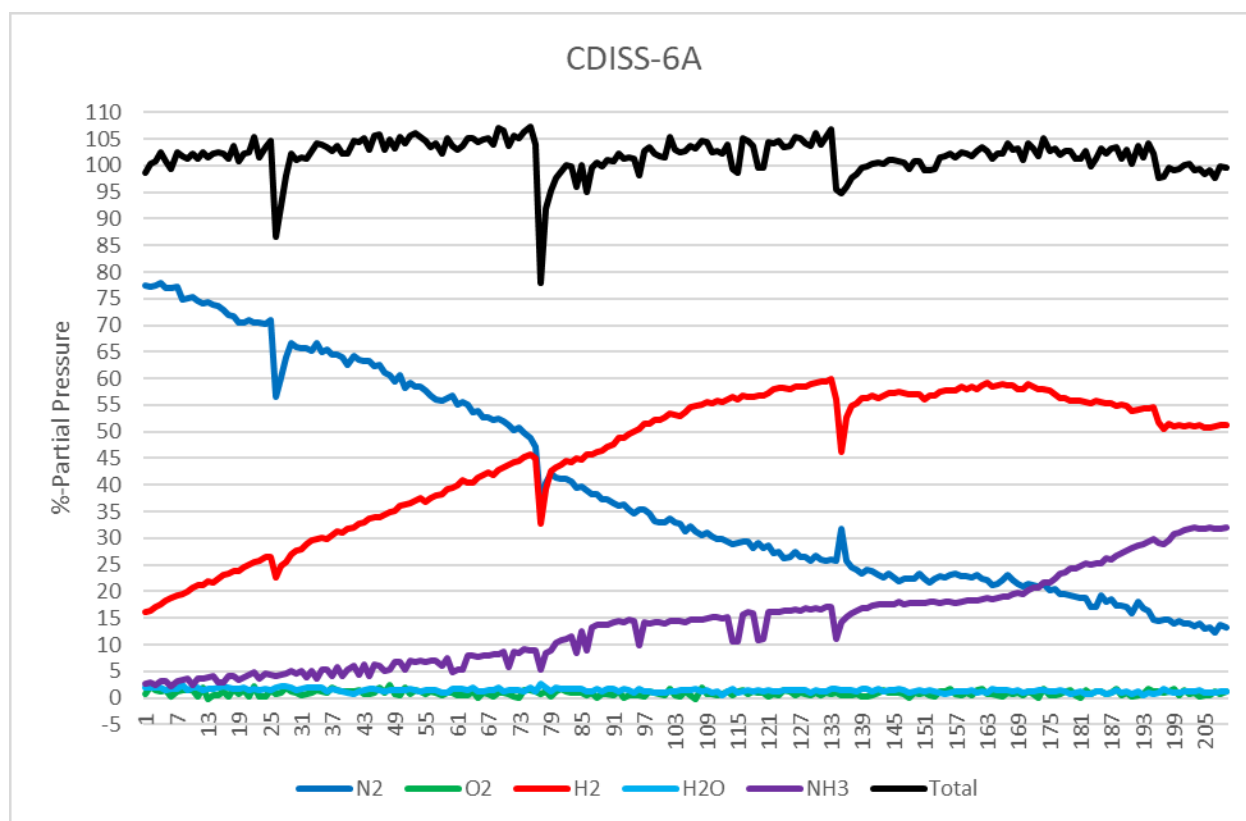
Figure 9. Effect of back pressure in Raman Cell (Spikes are from manual pressure resets)


Appendix: Calibration Procedure Outline

Summary of Instrument Calibration Procedure:
1. Power up instrument and allow to stabilize for at least 20 minutes.
2. Start Raman control software and set to:
   a. Raw pixel output
   b. 5 second exposure
   c. 10 exposure average
   d. 300 mw laser power
   e. 25 micron entrance slit
3. Fill gas cell with air
4. Begin data collection into Excel spreadsheet
5. Open data processing spreadsheet and verify link to data collection sheet.
   The data processing sheet automatically:
   a. Reads frequency calibration from Model sheet
   b. Reads Molecular-Response-functions from Model sheet
   c. Reads common-frequency array from Model sheet
   d. Reads Intensity-calibration constants from Model sheet
   e. Reads spline fit parameters from Model sheet
   f. When available from instrument, load Raw-Raman-spectrum from RawData Sheet
   g. Process Raw-Raman-spectrum
   h. Spline fit
   i. Interpolate
   j. Calculate Raman Intensities
   k. Calculate Molecular Concentration

l. Write processed data to Results sheet
m. Go to f

CO_2 Raman Calibration

N_2O Raman Calibration
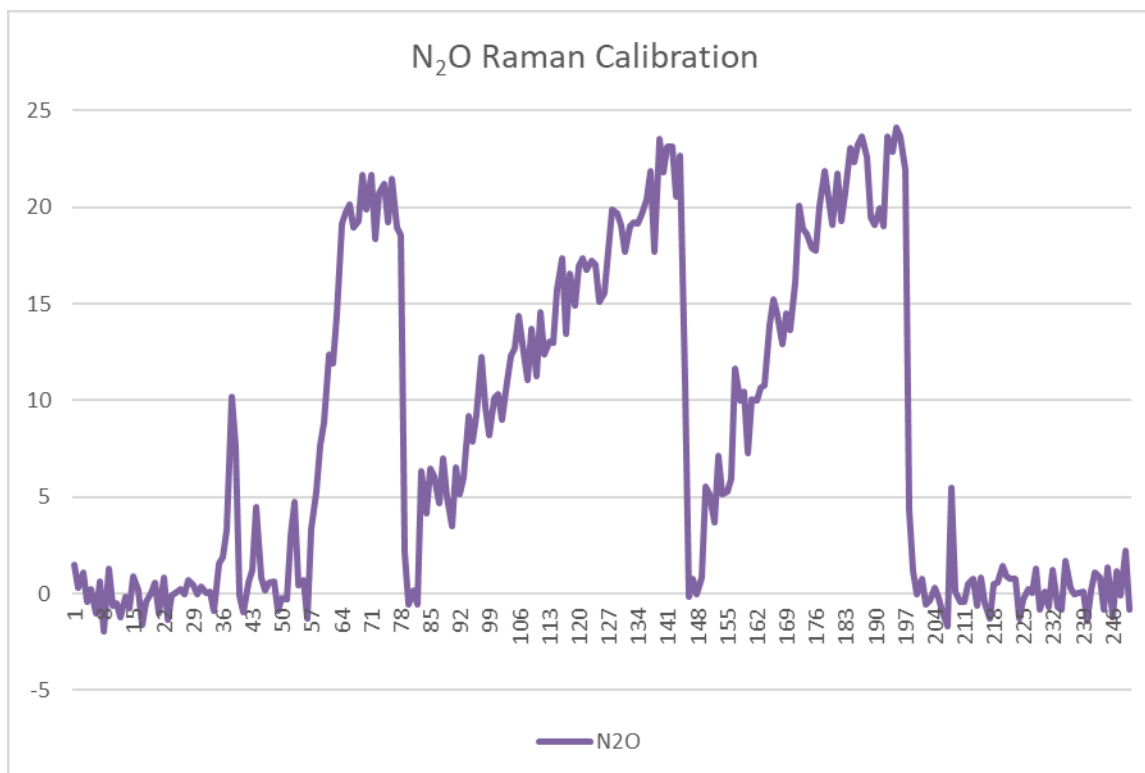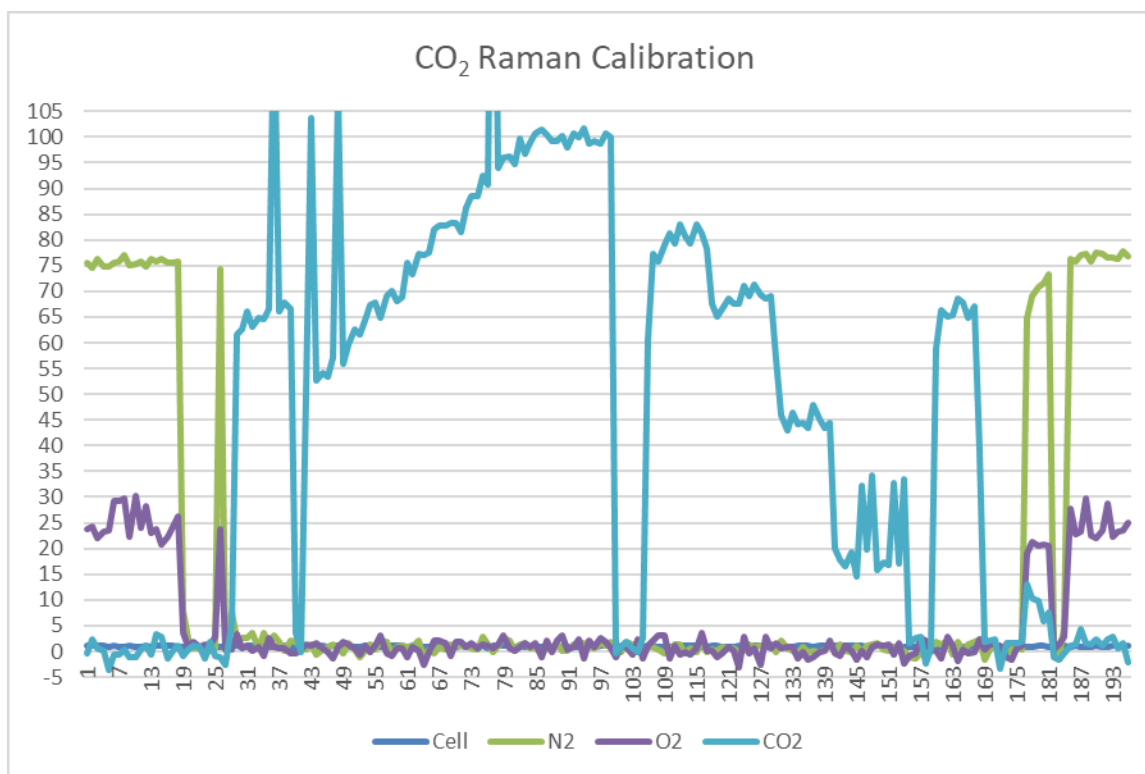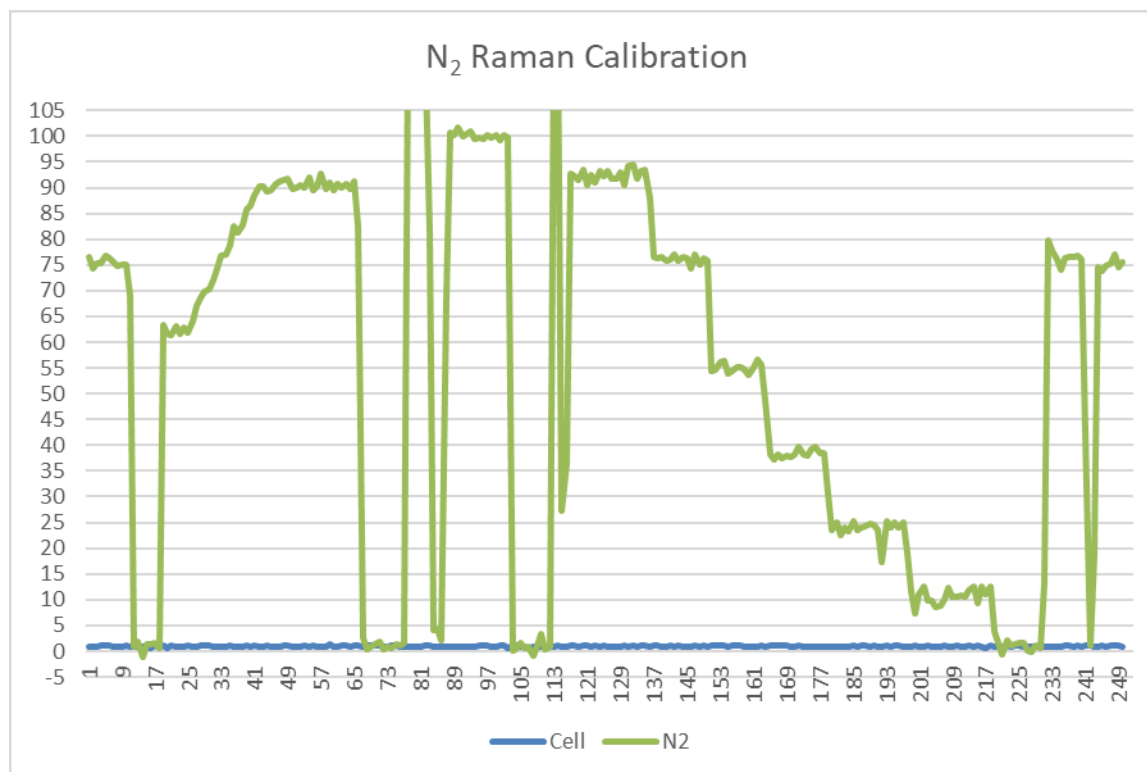
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