Increasing the Quantitative Credibility of Open-Path Fourier Transform Infrared (FT-IR) Spectroscopic Data, with Focus on Several Properties of the Background Spectrum

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The choice of the type of background spectrum affects the credibility of open-path Fourier transform infrared spectroscopy (OP/FT-IR) data, and consequently, the quality of data analysis. We systematically investigated several properties of the background spectrum. The results show that a short-path background measured with the lowest amplifier gain could significantly reduce noise in the calculated absorbance spectrum, by at least 30% in our case. We demonstrated that by using a short-path background, data analysis is more resistant to interferences such as wavenumber shift or resolution alteration that occurs as a consequence of aging hardware or misalignment. We discussed a systematic error introduced into quantitative analyses by the short-path background and developed a procedure to correct that error. With this correction approach, a short-path background established five years ago was still found to be valid. By incorporating these findings into the protocol for quantitative analysis, we processed the measurements with two OP/FT-IR instruments set up side by side in the vicinity of a large dairy farm, to monitor NH₃, CH₄, and N₂O. The two sets of calculated concentrations showed high agreement with each other. The findings of our investigations are helpful to atmospheric monitoring practitioners of OP/FT-IR spectroscopy and could also be a reference for future amendments to the protocols outlined in the guidelines of the U.S. Environmental Protection Agency, the American Society for Testing and Materials, and the European Committee for Standardization.

Index Headings: Open-path FT-IR spectrometry; OP/FT-IR; Background spectrum; Quantitative analysis; Credibility.

INTRODUCTION

In the field of atmospheric measurement of greenhouse and other gases, open-path Fourier transform infrared spectroscopy (OP/FT-IR) is an effective and convenient technique, with advantages including field monitoring and in situ data acquisition without sample handling. OP/FT-IR measurements are fast (seconds), so when run in the continuous mode, OP/FT-IR yields information with high temporal resolution, which could provide quick responses to atmospheric events. These advantages make OP/FT-IR an almost ideal technique to monitor different types of air molecules including hazardous air pollutants, threat chemicals, and greenhouse gases. More than just identifying air molecules, OP/FT-IR spectrometry also features quantitative accuracy, as evaluated in several investigations. However, obtaining quantitative accuracy in OP/FT-IR measurements is challenging. Since they are measured in open air, OP/FT-IR spectra contain information from multiple components and are often complicated by unpredictable interferences. Under well controlled conditions, e.g., with a gas cell filled with the analyte of interest, the quantitative accuracy of IR spectroscopy is good, but in field tests, the accuracy of OP/FT-IR is degraded when compared with the results of other atmospheric monitoring techniques. Therefore, effective data processing techniques are necessary in order to obtain reliable results from OP/FT-IR measurements.

Several methods of data analysis have been applied to OP/FT-IR measurements. These include classical least-squares regression (which is recommended by the U.S. Environmental Protection Agency [USEPA] and by the European Committee for Standardization [ECS]), the multi-atmospheric layer transmission forward, nonlinear least-squares fitting procedure, and partial least-squares regression (PLS). With the integration of multiple chemometric methods, an expert system was found effective in the quantitative analysis of OP/FT-IR measurements. It should be noted that in the data processing of OP/FT-IR measurements, however advanced the algorithm, it cannot yield better results than what the experimental data, specifically the absorbance spectrum, can provide. Therefore, the credibility of the absorbance spectrum is a necessary condition for the quality of data analysis.

Several factors affect the information of OP/FT-IR spectra, including spectral resolution and apodization function. Another important factor is the type of background spectrum that is used to calculate the absorbance spectrum. A desirable background spectrum contains all other information except that of the molecule(s) of interest. To this end, it has commonly been believed that the background should be measured under the same conditions as those for the sample spectrum but without the molecule(s) of interest. This requirement is readily satisfied in laboratories, but it is not the case for OP/FT-IR spectrometry. There are three types of backgrounds in OP/FT-IR, as found in the guidelines of the USEPA, the ECS, and the American Society for Testing and Materials (ASTM). By analogy with laboratory measurements, one type of background spectrum is supposedly measured under the same conditions (path length, humidity, temperature resolution, etc.) as those for the sample spectrum without the molecule(s) of interest. We call such a background spectrum a long path. The fact that OP/FT-IR spectra are measured in open air makes it very difficult, if not impossible, for the experimental conditions controlled to be the same as those during the measurement of the sample spectrum. In addition, the longer the path, the more likely it is that interfering compounds will enter the IR beam while measuring the background. Due to these facts, it takes

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APPLIED SPECTROSCOPY 335
The findings of our investigations should be helpful to practitioners of OP/FT-IR spectroscopy; they could also serve as a reference for future amendment to the protocols outlined in the guidelines of the USEPA, the ECS, and the ASTM.

EXPERIMENTAL

OP/FT-IR spectra were measured in 2005 and 2010, on and around animal farms in southern Idaho in two cooperative projects for monitoring gaseous emissions, with the Northwest Irrigation and Soil Research Laboratory of the United States Department of Agriculture, Agriculture Research Service. Two OP/FT-IR spectrometers were used. One instrument (Air-Sentry, Crex Monitoring Solutions, Atlanta, GA) was purchased in 2010, and the other (donated to the University of Idaho by DuPont after more than 10 years of perimeter monitoring operation) was older than 25 years. Each contained a Globar source, a cube-corner interferometer of the type incorporated in the ABB-Bomem MB-100 FT-IR spectrometer, and a 25 cm telescope to expand the IR beam being passed to the retroreflector. The cube-corner array retroreflector was positioned on the distal end of monitoring path to return the beam to a mercury–cadmium–telluride (MCT) detector. Other experimental details are given in the work by Shao et al.4,24

The spectra used to investigate the effect of amplifier gain on noise level were measured with the old instrument by setting the retroreflector 10 m away from the telescope. On the instrument, a five-position rotary switch controls the amplifier gain from the lowest (gain A) to the highest (gain E). Each amplifier setting gave an approximately twofold change in the gain from its neighbor. When short-path background spectra were measured with gains C through E, it was necessary to insert one, two, or three metallic screens in the beam for each increase in gain to attenuate the beam, as recommended in the guidelines of the USEPA, the ECS, and the ASTM.

Every OP/FT-IR interferogram was measured by co-adding 16 double-sided interferograms at a nominal resolution of 1 cm⁻¹, and then correcting for the nonlinear response of the MCT detector.25 All spectra for the analysis were computed with a zero-filling factor of 8 and Norton–Beern medium apodization; the Mertz phase-correction method was used with 512 points around centerburst. All manipulation of spectra and data processing was done with MATLAB 7.0.1 software (The MathWorks, Inc., Natick, MA) on the Windows XP (Microsoft, Redman, WA) operating system.

RESULTS AND DISCUSSION

Effect of the Background Noise on Absorbance. The noise in OP/FT-IR spectrum arises from various components including the IR source, the detector, and the amplifier. Manufacturers of commercially available OP/FT-IR instruments usually make the IR source and the detector inaccessible to the experimenter, so the noise from the two sources under a given set of conditions generally remains at a constant level. The experimenter can usually adjust the amplifier gain to avoid extraordinarily weak or intense signal strength, common in OP/FT-IR measurement due to an excessively long or short path length. A high amplifier gain is necessary for long-path measurements, so the accompanying high noise level in the recorded signal, i.e., the interferogram, is inevitable and is eventually introduced into the absorbance spectrum, which is the object of data analysis. The noise in the absorbance spectrum has another contributor, namely, the background spectrum. The relationship between these types of noise can be derived from the definition of absorbance, \( A = \log(SBS_{bk}/SBS) \), where SBS and SBS_bk denote the single-beam spectra of the sample and the background, respectively. Let \( \sigma_r \) and \( \sigma_b \) denote the root-mean-square (RMS) noise levels of SBS and SBS_bk, then the RMS noise level of the corresponding absorbance spectrum, \( \sigma_A \), can be derived as

\[
\sigma_A^2 = \left( \frac{1}{(\ln 10)\text{SBS}} \right)^2 \sigma_r^2 + \left( \frac{1}{(\ln 10)\text{SBS}_{-bk}} \right)^2 \sigma_b^2
\]  

Equation 1 shows that the noise level of the absorbance spectrum is determined by the noise of the single-beam spectra of the sample and the background, and by the intensities of the two spectra. While there is not much that can be done to decrease \( \sigma_r \), it is possible to have relatively small \( \sigma_b \) by using a short-path background measured with the lowest amplifier gain in the absence of metallic screens. The accompanying advantage is the low-level noise in the short-path background.
spectrum. This advantage is not found if the short-path background is measured with a screen in the beam, as recommended in the guidelines of the USEPA, the ECS, and the ASTM, because the amplifier gain is high.

In order to test the above analysis, OP/FT-IR interferograms were measured with the amplifier gain set at A (the lowest), B, C, D, and E (the highest). At each amplifier gain, two interferograms were measured so that one was the sample and the other is the background. From the five samples and the five backgrounds, 25 absorbance spectra in total were obtained. RMS noise levels were calculated between 2520 and 2480 cm\(^{-1}\) in those absorbance spectra and plotted against the amplifier gains (Fig. 1). Figure 1 clearly shows that the noise level of the absorbance spectrum increases with high amplifier gain, whether it is for the measurement of the sample or the background. The three-dimensional plot exhibits a symmetric pattern along the line from point AA to point EE, which means the noise in the background has the same weight as the noise in the sample in determining the noise level of corresponding absorbance spectrum. Eq. 1 and the fact that SBS approximates SBS\(_{bk}\), since the sample spectrum was measured at the same distance as the background can explain the symmetry. This conclusion can be further corroborated by absorbance spectra b and c in Fig. 2. In Fig. 2, spectrum b is computed from a sample and a background interferogram measured with the amplifier gains being A and E, respectively; in the case of spectrum c, the amplifier gains were E and A, respectively. According to Eq. 1, the noise levels of two spectra should be the same. The calculated RMS noise levels of spectra b and c were \(5.68 \times 10^{-4}\) and \(5.61 \times 10^{-4}\), very close to each other.

Note that in Fig. 1, the noise levels for points AA, AB, BA, and BB are essentially identical, as these spectra were measured with no screen in the beam, and the increase in the signal at the centerburst when the gain was switched from A to B was not enough to overfill the analog-to-digital converter (ADC).

In Fig. 2, spectra a and b are from the same sample interferogram (lowest amplifier gain, A), with two background interferograms measured with the lowest and the highest amplifier gains. The RMS noise levels were calculated at \(1.49 \times 10^{-4}\) and \(5.68 \times 10^{-4}\), so using a background measured with the lowest amplifier gain could decrease the noise in absorbance by more than 70%. Spectra c and d are from the same sample interferogram (highest amplifier gain, E, with three screens in the beam), with two background interferograms measured with the lowest and the highest amplifier gains. The RMS noise levels were calculated at \(5.61 \times 10^{-4}\) and \(8.03 \times 10^{-4}\). In this case, using a background measured with the lowest amplifier gain could decrease the noise in absorbance by more than 30%. The noise reduction is not attainable with a long-path background, as it cannot be measured with the lowest amplifier gain. If the short-path background spectrum were noise free, the advantage would have been 41%, since the noise level of the spectrum that is equivalent to the spectrum d in Fig. 2 would have been reduced by \(\sqrt{2}\).

**Lifespan of the Background.** An ideal background would counteract the background spectral features in the sample spectrum due to the IR source, optical components, and detector. This requires that the background spectral features be the same as those in the sample spectrum. Any background has a finite lifespan; when significant differences occur, the background is no longer valid. Thus, it is advised that a new background be acquired whenever the IR source or the alignment of any optical component (mirror, beam splitter,
In OP/FT-IR spectroscopy, a background also contains the absorption of omnipresent air molecules such as H₂O, CO₂, CH₄, and N₂O. The absorption of such molecules is path integrated, so the longer the path length, the higher the absorption, even if the concentration of the molecule is more or less constant. For a long-path background, the high absorption of these molecules would cancel out most of the counterpart in the sample spectrum, and thus make the interference less serious (provided that those molecules are not the analyte). However, if some changes occur, e.g., wavenumber shift or resolution alteration, the high absorption of these molecules in the long-path background would be changed in either position or shape and thus have serious impact on the absorbance, so the background is no longer valid.

In order to evaluate the effect of wavenumber shift in the background on absorbance, a long- and a short-path background were measured in pristine air. The measurements were one day before the sample spectrum, without disassembling the equipment, so that the wavenumber shift due to the instrument is negligible. To simulate a wavenumber shift, we changed the value of the He–Ne laser wavenumber in the software by 2 cm⁻¹ in computing the single-beam spectra of the backgrounds. This would lead to a wavenumber shift of ~0.5 cm⁻¹ at 4000 cm⁻¹ and ~0.12 cm⁻¹ at 400 cm⁻¹. The absorbance spectra computed without and with the simulated wavenumber shift in the long-path background are shown on the top and in the middle in Fig. 3a. The two spectra are clearly different; the difference occurs where H₂O absorbs strongly (3150–3000 cm⁻¹ and 1250–1100 cm⁻¹ in the spectra shown in Fig. 3) and exhibits the characteristic shape of the first derivative of absorption peak, as indicated by the difference spectrum at the bottom of Fig. 3a. This is because the shifted absorption bands of H₂O in the long-path background interact with unshifted absorption bands in the sample spectrum, giving rise to the first-derivative features. With respect to NH₃, the absorbance (within 1000–900 cm⁻¹) in the two spectra is nearly the same, and this is because NH₃ was absent in the background and unaffected by wavenumber shift.

The same study was conducted with a short-path background. The absorbance spectra computed without and with the simulated wavenumber shift in the short-path background are shown on the top and in the middle in Fig. 3b. Contrary to the case of the long-path background, the two spectra were found very close, indicative of a slight, even negligible impact of the wavenumber shift in the short-path background on the absorbance spectrum.

From the above analysis, it can be concluded that a wavenumber shift in the background affects the absorbance of the molecules that are present both in the sample and in the background, such as CH₄, H₂O, N₂O, and CO₂. The longer the path, the higher the path-integrated absorption of those molecules in the background and eventually, the more marked the effect will be. For the molecules that are absent in pristine air where the background is supposed to be measured, e.g., NH₃, a wavenumber shift in the long-path background does not affect their absorbance. However, quantitative accuracy is attainable only when the absorption bands of the molecule of interest are well separated from the deformed absorption peaks of CH₄, H₂O, N₂O, or CO₂, which is a severe constraint for most methods of data analysis. Therefore, a long-path background is only valid within the time in which the instrument does not age so much as to give rise to a significant wavenumber shift. Such a problem does not exist when a short-path background is used. Due to the short path, the path-integrated absorption of any molecule is much lower than that in the sample spectrum (measured over a relatively long path), and thus the wavenumber shift has a negligible effect on the absorbance.

The effect of background on absorbance naturally raises the question of how long a background remains valid. For this question, we compared the absorbance spectra computed with two long-path backgrounds, respectively, as shown on the top and in the middle of Fig. 4a. The two backgrounds were measured in 2010 and 2005, one day and five years before the sample, respectively. Clearly, the long-path background of 2005 seriously affected the absorbance of H₂O. In the affected spectrum, both first- and second-derivative characteristics were found in the rotational lines of H₂O, indicative of wavenumber shift and spectral resolution alteration that were probably due to the hardware aging over five years. Those problems are trivial in the case of a short-path background measured with the same instrument in 2005, as shown in Fig. 4b. From the difference spectrum, shown at the bottom of Fig. 4b, the short-path background measured five years before the sample primarily brings a slowly varying baseline to the absorbance spectrum. If an effective baseline correction method is applied, the absorbance spectrum is still valid for analysis. In this sense, the short-path background has a much longer lifespan than the long-path background. A background with long lifespan not only expedites the analysis, but also significantly decreases the frequency of background measurements. In open air, frequent measurements of backgrounds significantly increase the risk of having unpredictable interferences.

**Systematic Error when Using Short-Path Backgrounds.**

We demonstrated several advantages of using short-path backgrounds in OP/FT-IR spectrometry. However, a valid
short-path background is not an ideal one, which generates an error. Let $SBS_{\text{sample}}$ and $SBS_{\text{background, ideal}}$ denote the single-beam spectra of the sample and the ideal short-path background, and the ideal absorbance is computed as:

$$A_{\text{ideal}} = \log (SBS_{\text{background, ideal}}) - \log (SBS_{\text{sample}})$$ (2)

While $A_{\text{ideal}}$ is unavailable, it is the actual absorbance, $A_{\text{actual}}$, that is analyzed. The actual absorbance is computed with an actual short-path background in the following manner:

$$A_{\text{actual}} = \log (SBS_{\text{background, actual}}) - \log (SBS_{\text{sample}})$$ (3)

Combining Eqs. 2 and 3 gives

$$A_{\text{actual}} = A_{\text{ideal}} - A_{\text{background, actual}}$$ (4)

where

$$A_{\text{background, actual}} = \log (SBS_{\text{background, ideal}}) - \log (SBS_{\text{background, actual}})$$

is the absorbance of the actual short-path background against the ideal background. Equation 4 indicates that using an actual short-path background results in an absorbance spectrum with error (denoted by $A_{\text{background, actual}}$), and the error is a systematic one bearing no relationship to either $A_{\text{ideal}}$ or $A_{\text{actual}}$.

Using a quantitative method to process the absorbance $A_{\text{actual}}$, we could obtain the concentration of the molecule of interest, denoted as $c_{\text{calculated}}$. If the quantification is performed on the ideal absorbance $A_{\text{ideal}}$, the true concentration could be obtained, denoted as $c_{\text{true}}$. Although $c_{\text{true}}$ is unknown, it relates to $c_{\text{calculated}}$ in the following way according to Eq. 4:

$$c_{\text{calculated}} = c_{\text{true}} - \Delta$$ (5)

where $\Delta$ is the response of the same quantitative method to the systematic error in the absorbance spectrum, i.e., $A_{\text{background, actual}}$ in Eq. 4. Since the systematic error bears no relationship to $A_{\text{ideal}}$ or $A_{\text{actual}}$, $\Delta$ is independent of $c_{\text{true}}$ or $c_{\text{calculated}}$ and only relates to the very short-path background and the quantitative method. This exclusive relation makes the error correctable. It should be noticed that these concentrations are path-integrated ones.

The correction of the systematic error in $c_{\text{calculated}}$ needs the bias, shown as $\Delta$ in Eq. 5. The bias can be readily determined by measuring a standard sample with known concentration, $c_{\text{true}}$. After the measurement of the standard sample, its absorbance spectrum is computed with the actual short-path background, and then processed with the quantitative method, so as to obtain $c_{\text{calculated}}$. With $c_{\text{true}}$ and $c_{\text{calculated}}$, the bias could be determined, and then used to correct the error in the concentrations calculated by the same quantitative method in processing the absorbance spectra computed with the same short-path background. The standard sample might be unnecessary if the molecule of interest is absent in pristine air, e.g., NH$_3$. In this case, the experimenter first conducts a series of OP/FT-IR measurements of pristine air in an area where no sources of other gases are within proximity and the meteorological conditions remain stable, and then compute the absorbance spectra with the same short-path background and finally, use the same quantitative method to calculate the concentrations of the molecule of interest. Due to its absence in pristine air, the true concentration of the analyte is zero, so the biases are readily obtained through Eq. 5, and the average is taken. A merit of this approach is the equivalence to multiple standard samples, so the average of the determined biases is more reliable than the bias determined from using a single standard sample. For the molecules present in pristine air, e.g., CH$_4$, the determination of the bias requires standard samples. Apparently, whenever a different short-path background or another quantitative method is used, the bias should be reevaluated, following the same procedure.

In order to test the above analysis, we processed 332 OP/FT-IR measurements from a continuous monitoring session in 2005. Two short-path backgrounds measured in 2005 and 2010 were used to compute two sets of absorbance spectra. PLS is the quantitative method to calculate the concentrations of NH$_3$ in air, and the results are given in Fig. 5. From Fig. 5, it can be seen that the two sets of concentrations are very similar, but an obvious offset exists and exhibits no relationship to the calculated concentrations, which is consistent with the above discussion of bias. In order to determine the biases, 100 continuous OP/FT-IR measurements in pristine air were used. Since NH$_3$ was absent in the pristine air, the true concentration of NH$_3$ in these measurements is zero. After computing 100 absorbance spectra with the short-path background of 2005, PLS was applied to calculate the concentrations of NH$_3$, and the average of the biases determined through Eq. 5 was $-0.0044$ parts per million (ppm). In the case of the short-path background of 2010, the average bias was calculated at 0.013 ppm. The systematic errors were corrected by applying the two biases to the two sets of calculated concentrations, respectively, which in Fig. 5 is equivalent to moving the red curve downward by 0.0044 ppm and the black curve upward by 0.013 ppm. We could readily infer that after the correction, the
two curves are almost superimposed on each other, which means the error was mostly removed.

Quantitative Reconciliation. As analyzed in the above sections, using short-path backgrounds could rid OP/FT-IR absorbance spectra of several uncertainties with respect to high-level noise, wavenumber shift, resolution alteration, and unpredictable molecules in air. As a result, the credibility of OP/FT-IR spectroscopic data was improved. In order to give this conclusion a rigorous test, it is desirable to use the measurements of the same sample by two instruments and test if the calculated concentrations reconcile with each other. However, in field measurement of open air, it is practically impossible to have identical samples for the two instruments, so we set up two instruments as close to each other as possible, with parallel monitoring paths (<1 m apart) in order that they measured very similar but not identical samples. The monitoring was run continuously, so we could compare not only single concentrations, but also the patterns of concentration variation versus time between the two instruments. PLS regression was used to calculate the concentrations of NH$_3$, CH$_4$, and N$_2$O.

Two continuous monitoring sessions were conducted, in each of which the two instruments were operated simultaneously. Two sets of absorbance spectra were computed with corresponding short-path backgrounds. It was found that many spectra measured by the two instruments at the same time show the same peak absorbance of NH$_3$, N$_2$O and CH$_4$, but the spectra are different with respect to baseline and absorbance of water vapor. The averages of the calculated concentrations of those molecules are listed in Table I. It is found that the average concentration from the old instrument is very close to that from the new instrument, for any molecule, in each monitoring session. Figure 6 shows the comparison between the concentrations of NH$_3$ from the old instrument and those from the new instrument in session 1, revealing very good agreement. Therefore, both the credibility of the OP/FT-IR spectroscopic data and the effectiveness of PLS regression were demonstrated for quantitative analysis. It should be noted that in the atmosphere around dairy farms, molecules of NH$_3$ and CH$_4$ are spatially and temporally heterogeneous, since a majority of them are released from the cows. As a result, the two OP/FT-IR instruments did not measure the exact same samples, even having been set up side by side. Among the pairs of spectra that were measured simultaneously, we found most showed equal absorbance for NH$_3$ and CH$_4$, but a few did not, which reasonably accounts for part of the small discrepancy in the concentrations in Table I and Fig. 6. In previous research in which three OP/FT-IR instruments were set up along parallel paths 3 m apart, it was found that the concentrations obtained with a long-path background from each instrument were different from another, even with well-controlled release of the target molecules into the monitored area.\textsuperscript{26}

### Table I. Averages of the concentrations of three molecules (in parts per million by volume) from measurements by two instruments in continuous monitoring mode (a/b), where (a) is the old instrument, and (b) is the new instrument.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Session no. 1</th>
<th>Session no. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>0.410/0.399</td>
<td>0.125/0.140</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.15/3.18</td>
<td>2.41/2.46</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>0.388/0.385</td>
<td>0.374/0.362</td>
</tr>
</tbody>
</table>

CONCLUSION

Apart from the wavenumber shift or the spectral resolution alteration due to instrument aging or misalignment, OP/FT-IR measurements suffer from more uncertainties than the bench measurements in laboratories, including unexpected interferences and meteorological factors. Using a short-path background significantly reduces those side effects on absorbance, thereby increasing the credibility of data for quantitative analysis.

Short-path backgrounds have the advantage of long lifespans, which eliminate the need to transport the OP/FT-IR instrument to multiple locations to obtain backgrounds and also decreases the possibility of measuring unexpected molecules.

In measuring a short-path background, the experimenter should first decrease the amplifier gain rather than use a metallic screen to avoid ADC overflow. However, the lowest gain should be set (usually by the manufacturer) so that detector noise is approximately equal to the least-significant bit.
of the ADC. If a still lower gain is called for, then a metallic screen should be inserted into the beam.

The use of a short-path background introduces a systematic error into the absorbance, and the error can be corrected either with a standard of the molecule of interest or OP/FT-IR measurements of pristine air in which the molecule of interest is absent.

Even though short-path backgrounds show strong resistance to interferences, careful inspection is required. In one experiment, we noticed some abnormal concentrations of \( \text{N}_2\text{O} \) calculated with PLS. It turned out that the short-path background contained an abnormally high level of \( \text{CO} \), even though we believed that we had measured it in pristine air. We speculated that the excessive \( \text{CO} \) could have been from the generator when the wind direction changed or passing vehicles.

\( \text{CO} \) absorbs in the wavenumber region in which we calculated the concentration of \( \text{N}_2\text{O} \), i.e., \( 2260-2160 \text{ cm}^{-1} \). After we used another short-path background having been carefully inspected to be free of \( \text{CO} \), the calculated concentrations of \( \text{N}_2\text{O} \) were normal.

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