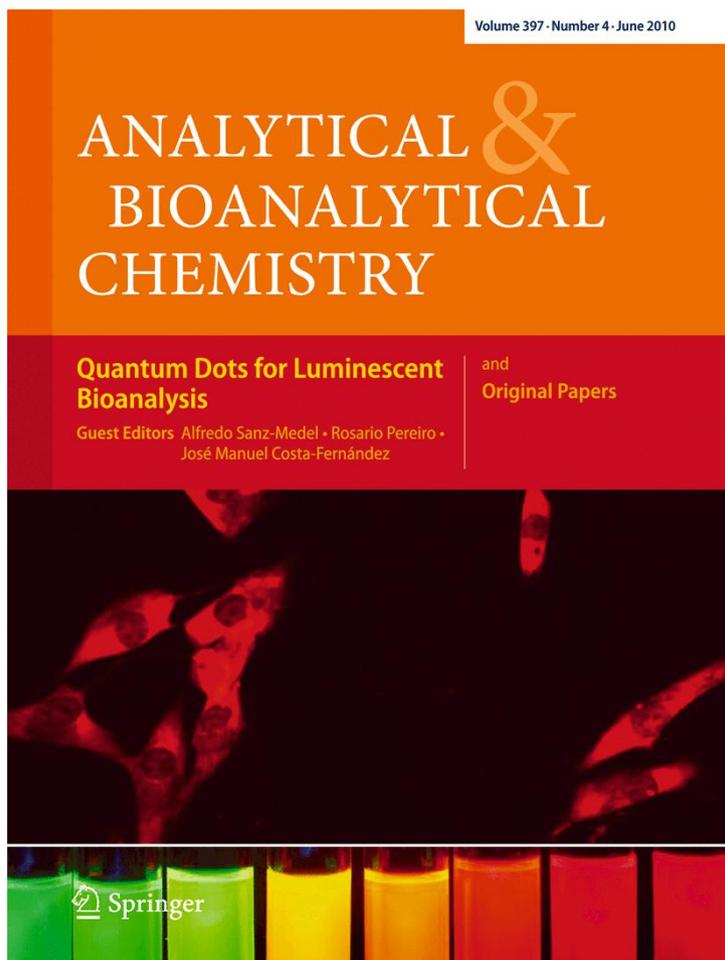


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Detection of chemical agents in the atmosphere by open-path FT-IR spectroscopy under conditions of background interference: II. Fog and rain

Limin Shao · Christopher W. Roske · Peter R. Griffiths

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Abstract Open-path FT-IR spectra of low-concentration releases of diethyl ether were measured both when a glycol fog was passed into the infrared beam and when large water droplets from a lawn sprinkler were sprayed into the beam. It was shown that the glycol fog, for which the droplet size was much less than the wavelength of the infrared radiation, gave rise to a significant interference such that partial least squares (PLS) regression would only yield reasonable values for the ether concentration if background spectra in which the glycol fog was present were included in the calibration set. On the other hand, target factor analysis (TFA) allowed the presence of the ether to be recognized without precalibration. When large water droplets were present in the beam, any infrared radiation entering the droplet was completely absorbed, so that both PLS and TFA would yield accurate results.

Keywords Open-path FT-IR spectrometry · Fog · Rain · Diethyl ether · Target factor analysis · PLS regression

Introduction

In the first paper in this series [1], we showed how target factor analysis could be used to detect the presence of a chemical warfare agent simulant, diethyl ether, even when

fireworks were set off in the beam path giving rise to a severe high-frequency interference. In this paper, we report the results of analogous experiments that were made when a glycol fog (which has strong absorption bands at approximately the same wavelength as the diethyl ether analyte) was allowed to drift into the infrared beam. Previous workers have demonstrated that fogs of condensed atmospheric water vapor both scatter and distort the spectrum and that a different background spectrum should be used when open-path (OP) FT-IR spectra are measured under foggy conditions and processed using classical least squares regression [2, 3]. In this paper, we report that similar data processing techniques to those used in our previous paper [1] can be used to detect the analyte when open-path OP/FT-IR spectra are readily measured through a foggy atmosphere. We also report the result when OP/FT-IR spectra are measured under simulated rainy conditions, where the size of the water droplets is much greater than the size of the aerosol fog.

Experimental

The instrument that was used for these measurements was the same as the one used for our previous work, although the location was different. A small volume of liquid diethyl ether in a Petri dish was either mounted immediately beneath the IR beam or removed, so that the release of the analyte into the beam was controlled. A light cross wind was blowing when these measurements were being taken so that the concentration of the analyte varied significantly from 1 min to the next.

Since it was not possible to achieve a uniform distribution of glycol fog or water droplets from the sprinkler throughout the entire beam, we set up our

L. Shao
Department of Chemistry,
University of Science and Technology of China,
Hefei, Anhui 230026, China

C. W. Roske · P. R. Griffiths (✉)
Department of Chemistry, University of Idaho,
Moscow, ID 83844-2343, USA
e-mail: pgriff@uidaho.edu

equipment with a fairly short path (about 30 m from the telescope to the retroreflector for a “round-trip” pathlength of 60 m) and allowed the fog to drift into the infrared beam, as shown in Fig. 1. The glycol fog was produced by spraying a mixture of triethylene glycol, propylene glycol, 1,3-butylene glycol and water (Rosco Clear Fog Fluid, Rosco Laboratories, Inc., Stamford, CT) from a Rosco Model 1700 smoke machine. After measurements involving the glycol fog were completed, we set up a lawn sprinkler that sprayed fairly large water droplets into the beam.

The timing of the releases of diethyl ether, the glycol fog and the spray of water droplets is summarized in the lower part of Fig. 2. The first fog release was from measurement #217 to #370; the second release was from measurement #422 to #526. For measurement #597 to #772, a lawn sprinkler was mounted immediately beneath the IR beam so that water droplets were sprayed into the IR beam, albeit over a shorter pathlength than would be encountered during a rainstorm. The analyte, diethyl ether, was released twice, first from measurement #104 to #370 and then from measurement #673 to #772. A contour plot of the absorbance spectra that were measured during this experiment is shown in the upper part of Fig. 2. Spectra were only analyzed in the atmospheric window from 1,250 to 888 cm^{-1} .

Seven data sets were constructed to evaluate the detection of diethyl ether in the presence of a glycol fog or water spray as shown in Table 1.

Results and discussion

Overview of the data

Single-beam spectra were measured over the 60-m path and ratioed against a spectrum measured with the retroreflector located very close to the telescope. All interferograms were corrected to compensate for the non-linear response of the MCT detector [4]. The baseline was found to be very close

to zero absorbance units, demonstrating that, for the relatively short (60 m total) pathlength used in this experiment, essentially all the light that leaves the telescope hits the retroreflector and is returned to the telescope. Representative examples of the absorbance spectra measured during this experiment are shown in Figs. 3 and 4.

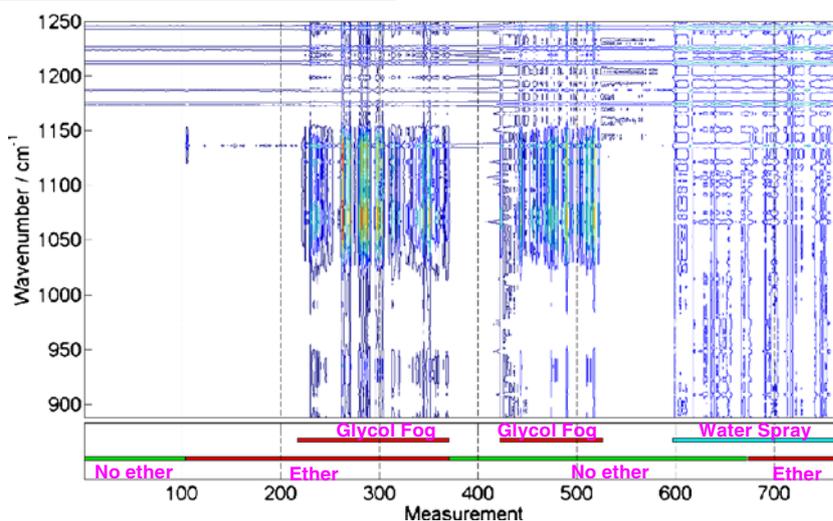
A Petri dish was placed under the beam and a small volume of diethyl ether was poured into it between the measurement of Spectra 103 and 105. Figure 3a shows Spectra 103 and 104 and Fig. 3b shows the difference between these two spectra. Even though the relative humidity in northern Idaho is very low at the time of year when these measurements were taken, weak lines in the vibration–rotation spectrum of water vapor dominate much of the spectrum in the region being studied. The path-integrated concentration of ether in the spectrum shown in Fig. 3 was calculated to be 4 ppm m, corresponding to an average concentration over the entire beam of about 67 ppb. The concentration of ether in the atmosphere during the acquisition of Spectrum 105 was far higher than for any other spectrum measured in Data Sets #2, #3, or #7, presumably because of ether that evaporated into the air while it was being poured into the Petri dish. For all other measurements in which the Petri dish of ether was located under the beam, the concentration is known to be less than 100 ppb. Thus the signal-to-noise ratio (SNR) at the peak of the strongest band in the ether spectra for Spectra 107–200 is always low and is often less than one.

The spectra measured by ratioing a long path (60 m “round trip”) spectrum to a short path spectrum in the absence and presence of the glycol fog are shown in Fig. 4a and b, respectively. For the spectrum shown in Fig. 4a, a few weak lines due to atmospheric water vapor of the same intensity as those in Fig. 3 are seen. The intense broad bands between 1,200 cm^{-1} to 1,000 cm^{-1} in Fig. 4b are due to absorption by the glycol droplets present in the IR beam. The result of subtracting the spectrum shown in Fig. 4a from the one shown in Fig. 4b is shown in blue in Fig. 5. The difference spectrum is similar, but not identical, to the

Fig. 1 (Left) The instrument set-up. (Right) Passing the glycol fog into the beam



Fig. 2 Contour plot of 772 OP/FT-IR absorbance spectra from 1,250 to 888 cm^{-1} arranged in order of time. The lower axes indicate the controls of the glycol fog and water spray and the release of diethyl ether. Note that the absorbance of the fog was far greater than that of the analyte, the strongest band of which was at $\sim 1,014 \text{ cm}^{-1}$



reference spectrum of liquid ethylene glycol, which is shown in red in Fig. 5. This result is not surprising since the fog is composed of a mixture of three glycols (see above) of differing volatility. Because one component may be more volatile than the others, the relative concentration of each constituent may vary on release of the fog. Despite the fact that the glycol fog was opaque to visible light, the spectral baseline is only shifted to about 0.02 absorbance units (AU), demonstrating that minimal scattering occurred at infrared wavelengths. The fact that the spectrum is not distorted by the Christiansen effect shows that the diameter of the glycol droplets is significantly less than the wavelength [5].

Partial least squares regression

The presence of diethyl ether in the beam was detected through the application of partial least squares (PLS) regression, using the same approach that we described previously [1, 6]. Two years before the spectra reported in this paper were measured, 54 background spectra were measured over a nine-month period in pristine air over pathlengths from 50 to 500 m and under conditions such that the temperature and relative humidity of the atmo-

sphere varied over as wide a range as possible. Each of these background spectra was ratioed against a short-pathlength background in the way described above, and converted to absorbance. In this way, we obtained a series of spectra of the atmosphere in which the absolute intensities of the lines in the rotation-vibration spectrum of water vapor varied greatly because of the range of pathlengths covered. In addition, because these background spectra were measured throughout the year so that the temperature varied by over 30 °C, the relative intensities of the lines in the vibration-rotation spectrum of water vapor also showed small but significant variations. Furthermore, because the spectra were measured over total pathlengths as long as 500 m, the baseline of these spectra also showed considerable variation. To each of these background spectra a reference spectrum of diethyl ether was added, and the path-integrated concentration of the ether was calculated from the factor by which each spectrum was scaled. This set of spectra was used as Calibration Set #1 for the PLS regression.

When the concentration of ether in the atmosphere within the IR beam was calculated using Calibration Set #1, the results shown in the upper trace of Fig. 6 were obtained. Neglecting Spectra #104–106 (when the Petri dish was being filled), the average concentration of diethyl ether in Data Set #2 was 54 ppb. The concentration calculated for Spectra 107–200 varied considerably because of changes in the wind speed while the spectral data were being acquired.

For Data Set #3, when the glycol fog was present in the beam, it can be seen that the concentration of diethyl ether calculated using Calibration Set #1 increased to 0.15 ppm (see Fig. 6a). Because the Petri dish of ether was not moved between the acquisition of Data Sets 2 and 3, the average concentration of ether should have remained at approximately the same level before the glycol fog was released,

Table 1 Data sets investigated in this project

Data Set	Interference	Diethyl ether
#1 (1 to 103)	None	NO
#2 (104 to 200)	None	YES
#3 (217 to 370)	Glycol fog	YES
#4 (422 to 526)	Glycol fog	NO
#5 (527 to 597)	None	NO
#6 (598 to 672)	Water spray	NO
#7 (673 to 772)	Water spray	YES

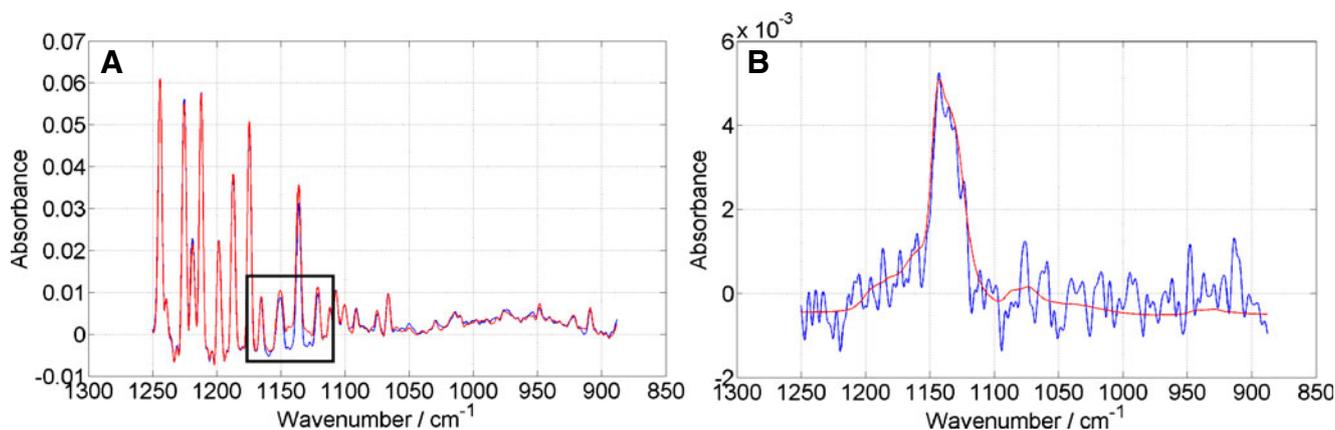


Fig. 3 **a** Spectra 103 and 104; the region in which ether absorbs is highlighted. **b** The difference between Spectra 104 and 103 is shown in *blue*; the reference spectrum of diethyl ether at a path-integrated concentration of 4 ppm m is shown in *red*

whereas the average calculated concentration increased by a factor of three. Obviously there is significant interference by the C–O stretching bands of the three glycols, each of which absorbs at a similar wavenumber to the corresponding band of diethyl ether.

When the calibration set was augmented with spectra measured with Spectra #422–526 that were measured in the presence of the glycol fog but with no ether in the beam (Calibration Set #2), the results were much closer to what was expected, as shown in Fig. 6b. We had no way of confirming whether these results were accurate but the fact that maximum concentration and standard deviation of the calculated concentrations were approximately the same for Data Sets #2 and #3 lends credence to the validity of the results for Data Set #3. The clear lesson to be learned from this result is well known to practitioners of PLS, namely that all sources of variance must be included in the calibration data. This result also demonstrates the difficulty in developing a good calibration set for atmospheric analysis under conditions of background clutter. Our work

was funded by the US Army's Edgewood Chemical Biological Center with the ultimate goal of developing a technique for detecting the onset of chemical agents under conditions of "battlefield clutter". Since the atmosphere in the battlefield can contain many different unmodeled components, it is clear that PLS regression will not be applicable under these conditions.

The spectra measured when the sprinkler was turned on (Data Set #7) were calculated using three different calibration sets. The first two were the same as the ones used to calculate the results shown in Fig. 6. The variation of the concentration of ether with time that was predicted using calibration sets #1 and 2 is shown in green and red, respectively. The results were very close, which suggests that the effect of the increased humidity in the beam while the sprinkler was turned on was negligible, presumably because the training set contained many spectra measured at long (>100 m) pathlength such that the amount of water vapor in the beam was high. When calibration set #2 was used to predict the ether concentration of Data Sets #6 and

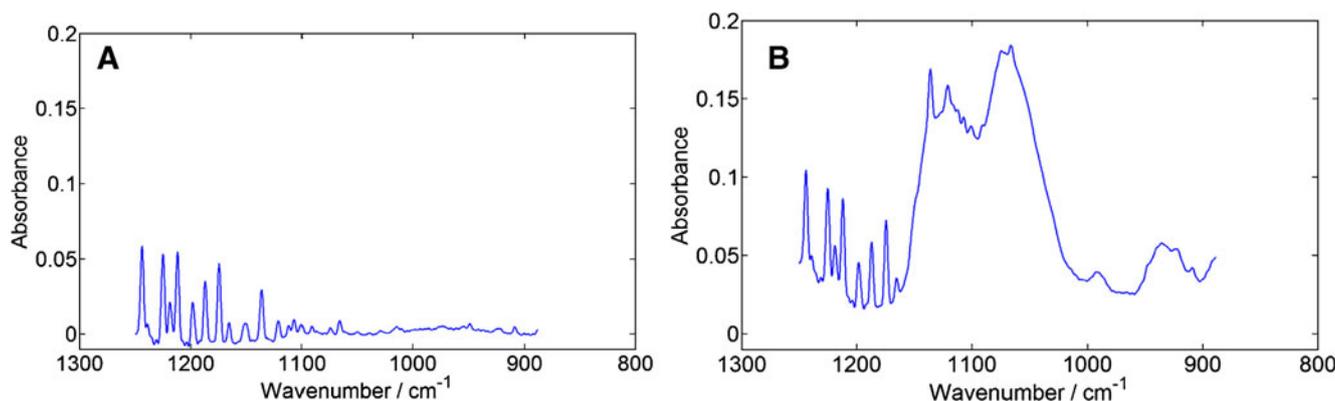
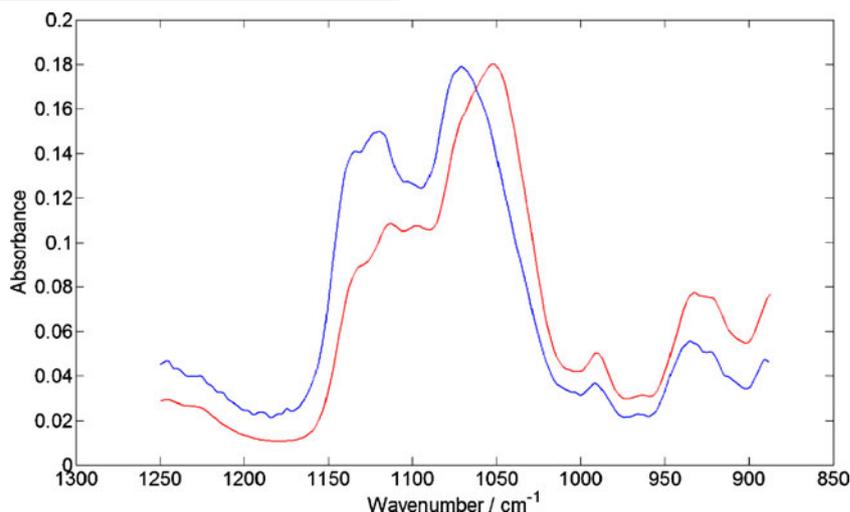


Fig. 4 Absorbance spectra measured by ratioing a long path (60 m) spectrum to a short path spectrum **a** in the absence and **b** in the presence of the glycol fog

Fig. 5 (Blue) Difference between the spectra shown in Fig. 4a and b. (Red) Reference spectrum of ethylene glycol (after scaling)



7, the only effect that was seen was a small shift in the baseline towards zero. This result suggests that the augmentation of calibration set #1, which had been measured 2 years before these measurements, by spectra that had been measured within a few minutes of the time that the sprinkler was turned on slightly improved the accuracy. When some of the spectra in Data Set #6 were added to the calibration set spectra, no change in the result was observed for Data Set #7 (see blue trace in Fig. 7.)

The main cause of the difference between the effect of the glycol fog and the water sprinkler is the size of the droplets. For many compounds, a film that is about 10 μm in diameter will yield a spectrum for which the strongest band has an absorbance of 1 AU. Thus, if the droplets are much less than 10 μm in diameter (as they are for the glycol fog), infrared radiation that enters the droplet will not be completely absorbed even at the wavelengths where the absorptivity is high. For the drops produced by the

water sprinkler, which were several *millimeters* in diameter, infrared radiation that enters the drop will be completely absorbed and will not contribute to the signal that is measured at the MCT detector. Thus, the only effect that would be expected on turning on the sprinkler would be a shift in the spectral baseline, as shown in Fig. 8. OP/FT-IR measurements through foggy and smoky atmospheres are, therefore, much more difficult than measurements made during a rain storm.

Target factor analysis

An alternative technique for detecting the presence of a given compound under conditions of background clutter is target factor analysis (TFA) [7]. A detailed discussion of TFA and its application to OP/FT-IR spectroscopy may be found in Refs. [6] and [7]. Suffice it to say at this point, that in TFA, a principal components analysis is carried out on a

Fig. 6 Concentration of diethyl ether in the 772 OP/FT-IR measurements processed by PLS using **a** calibration set #1 and **b** calibration set #2. The times when the glycol fog (*red*) and the water sprinkler were turned on (*aqua*) are shown below as the *upper horizontal bar*, along with the times that diethyl ether was absent (*green*) or present (*red*) in the beam

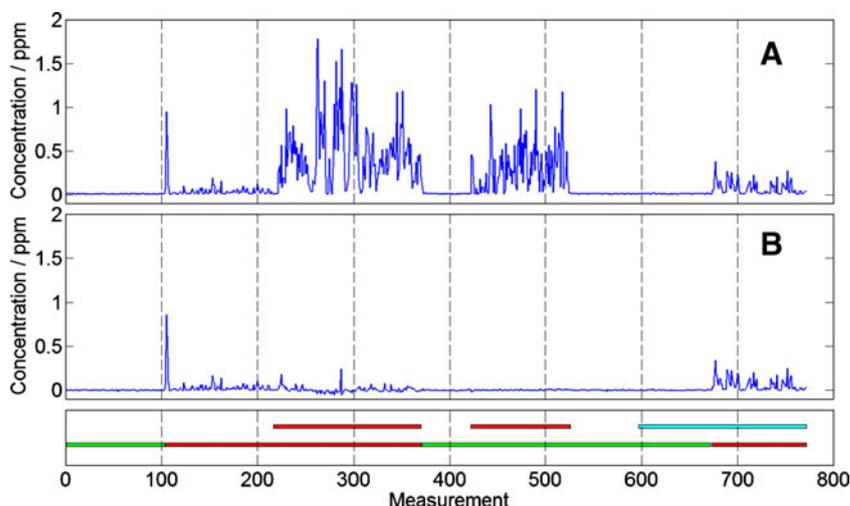
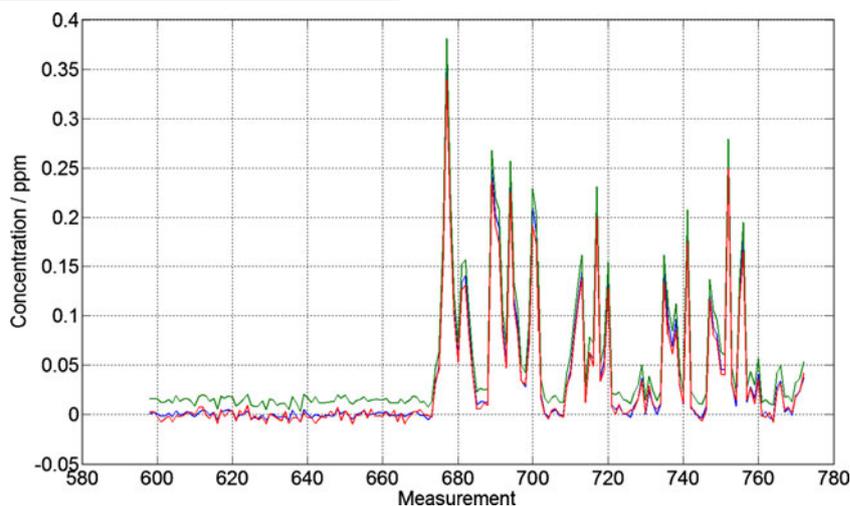


Fig. 7 Concentration of diethyl ether calculated from Data Set #6 (Spectra 592 to 672) and #7 (spectra 672 to 772.) using (green) calibration set #1, (red) calibration set #2 (calibration set #1 augmented with some spectra from Data Set #4) and (blue) calibration set #3 (calibration set #1 augmented with a few spectra from Data Set #6)



data set and the presence of the target molecule is detected by rotating the eigenvectors in order to match one to the spectrum of the target molecule in a least squares manner. We have found that the best way of matching the result of TFA to the spectrum of the target molecule (diethyl ether in this case) is to calculate the weighted correlation coefficient (wcc) between the eigenvectors and the reference spectrum of the target [8]. The weighted correlation coefficient is similar to the conventional correlation coefficient except that larger weights are assigned to those wavelengths that have relatively high absorbance in the reference spectrum. The similarity of the calculated target spectrum and the reference spectrum of diethyl ether is estimated by the calculated value of wcc: the target molecule is deemed to be absent if $wcc < 0.90$ and present if $wcc > 0.90$ [9, 10].

The result of target factor analysis of the first four data sets is shown in Fig. 9, along with the wcc value in each case. The first two results are not surprising, as ether is clearly shown to be absent for data set #1 and present for data set #2. It is interesting to look at the result of

performing TFA for the first 103 spectra and then for the first 104 spectra, i.e., including just one spectrum in the data set in which ether is known to be present at a fairly high concentration. This result is shown in Fig. 10. In the absence of any spectrum measured when diethyl ether is present in the beam $wcc = 0.82$. Using the criterion used in our previous report [9], i.e., that the target molecule is absent if $wcc < 0.90$ and present if $wcc > 0.90$, we can clearly conclude that diethyl ether is present below the detection limit in all spectra up to #103. As we have noted in a recent paper, TFA is effective when the concentration of the analyte changes. Thus, when we included spectrum #104 in the data matrix and then performed TFA, diethyl ether was found unequivocally ($wcc = 0.99$).

The result for data set #3 shown in Fig. 9c demonstrates the feasibility of applying TFA even when an interferent that absorbs in a similar wavenumber range is present in the infrared beam and illustrates the power of this type of data processing. Finally, the result for data set #4 suggests the presence of trace amounts of ether in the beam in the

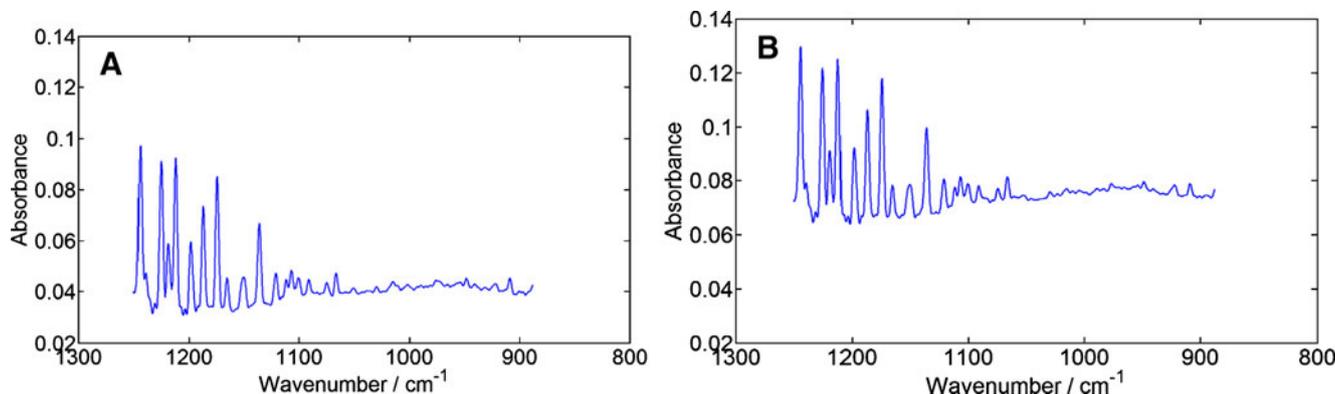


Fig. 8 **a** Spectrum of the atmosphere measured before the sprinkler was turned on; **b** corresponding spectrum after the sprinkler was turned on. The main difference is a simple shift in the baseline

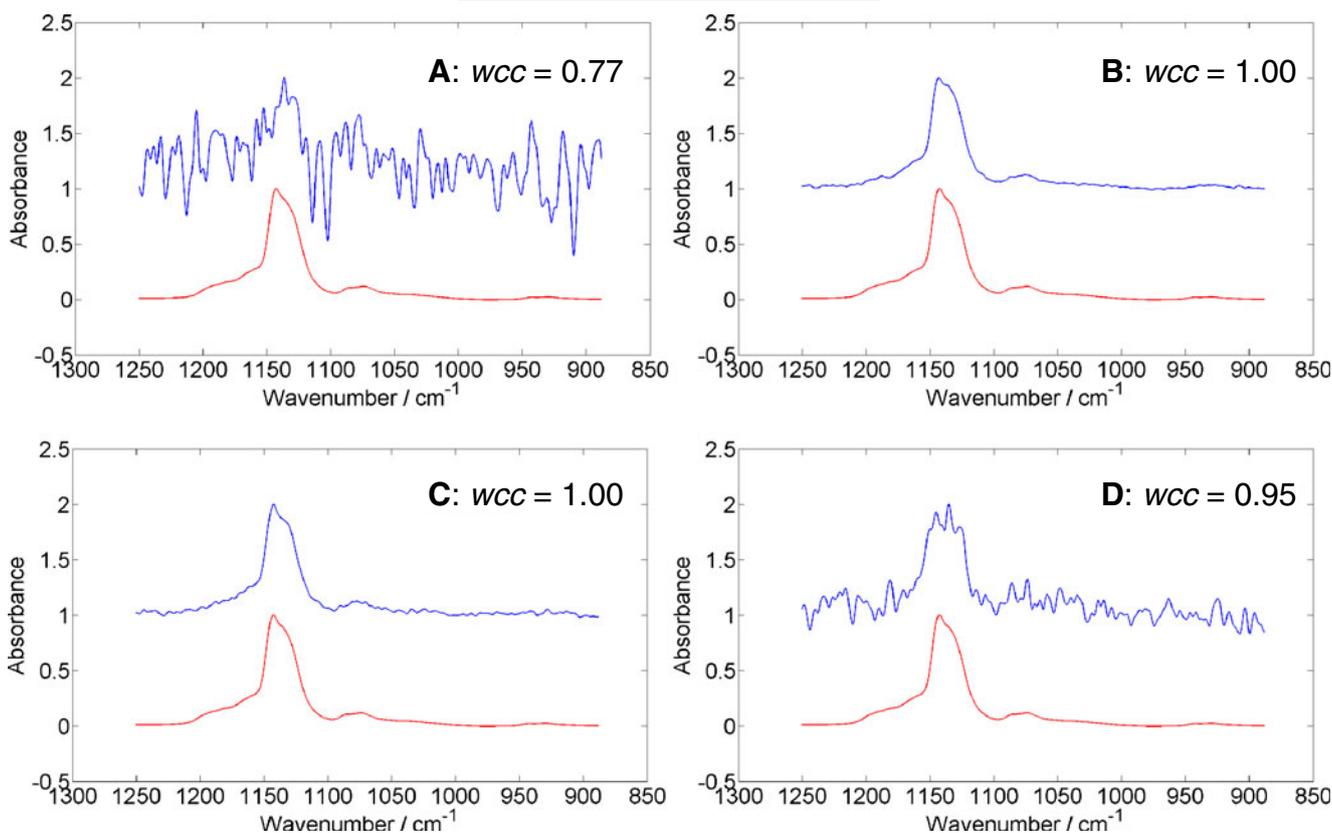


Fig. 9 (Blue) The results of TFA for **a** data set #1 (no ether, no glycol fog), **b** data set #2 (ether, no glycol fog), **c** data set #3 (ether, glycol fog), and **d** data set #4 (no ether, glycol fog). In each case, the reference spectrum of diethyl ether is shown in red

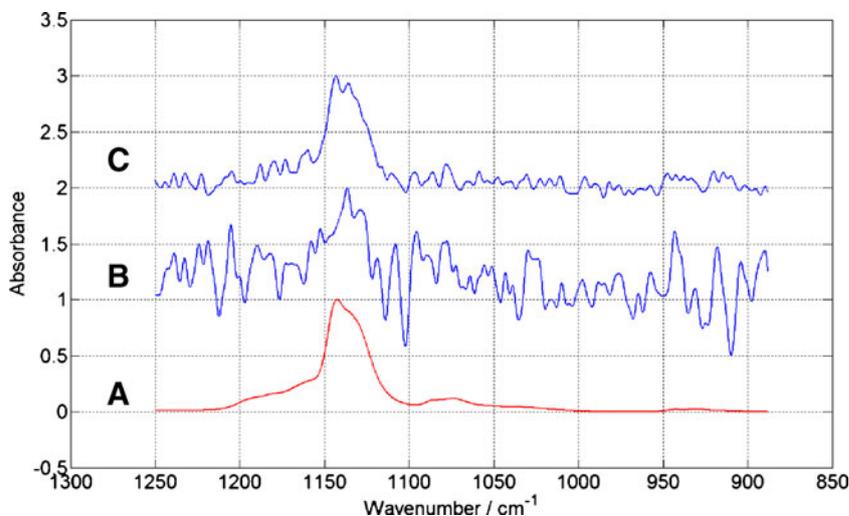
presence of a glycol fog; this result is possibly caused by residual ether remaining in the beam for the early spectra in this set.

We then investigated whether it is possible to obtain any quantitative data after applying TFA. Following the procedure described in our recent paper [10], we performed TFA on the data matrix composed of spectra from #1 to

#104, and obtained the limit of standard deviation to be 0.018 ppm. By definition, the standard deviation of the concentrations of diethyl ether is

$$SD = \sqrt{\frac{\sum_{i=1}^{104} (c_i - \bar{c})^2}{103}} \tag{1}$$

Fig. 10 **a** Reference spectrum of diethyl ether; **b** result of TFA for spectra 1–103 (wcc=0.82); **c** result of TFA for spectra 1–104 (wcc=0.99)



Since $(c_i - \bar{c}) = 0$ for all spectra from $i=1$ to 103, the standard deviation is $SD = c_{104}/\sqrt{103}$. Since the upper limit of SD is 0.018 ppm, the upper limit of c_{104} should be $0.018 \times \sqrt{103} = 0.18$ ppm. Earlier, we estimated c_{104} to be 0.066 ppm. Since the estimated concentration is lower than the upper limit, the theory developed in Ref. [10] is validated, and we are able to obtain not only the upper limit of standard deviation of the concentration distribution, but also the upper limit of the concentration.

Conclusions

The results obtained in this study show that even though partial least squares regression is a powerful technique for detecting the presence of components in OP/FT-IR spectra, it fails when unmodeled constituents are present in the infrared beam. One of the strengths of PLS is that the concentration of the analyte can be obtained for each individual spectrum within a second of the end of the data acquisition, even when the SNR of the strongest band in the spectrum is less than unity. When unmodeled interferents are present in the beam, however, PLS can give grossly erroneous predictions. In this case, target factor analysis can detect the presence of the analyte from a single scan, although a somewhat higher SNR is required than is needed

for PLS. When the target is present at very low concentration, it may be necessary to include several spectra in the data matrix used for TFA [9, 10].

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