Fourier Transform Infrared Absorption Spectroscopy for Quantitative Analysis of Gas Mixtures for Homeland Security Applications

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This is a preprint of an article published in (K.D. Benkstein, W.S. Hurst, D.C. Meier, P.M. Chu, "Fourier Transform Infrared Absorption Spectroscopy for Quantitative Analysis of Gas Mixtures for Homeland Security Applications," *J. Test. Eval.*, Vol. 44, 2016, pp. 320-328.), located at the following ASTM URL: http://www.astm.org/10.1520/JTE20150019. The author agrees not to update the preprint or replace it with the published version of the Work.

Abstract

Chemical detectors are crucial tools for first responders during emergency-response scenarios and for continuous monitoring of public spaces for general safety. For those who depend upon chemical detectors for safety and security, ensuring that detectors alarm at specified levels is critical. During detector performance evaluation, the accurate delivery of known concentrations of the chemical target to the detector is a key aspect of the test. Referee methods enable the analyte test concentration and associated uncertainties in the analyte test concentration to be validated by independent analysis, which is especially important for reactive analytes. This work demonstrates a method to use Fourier transform infrared (FT-IR) absorption spectroscopy for quantitatively evaluating the composition of vapor streams containing hazardous materials at Acute Exposure Guideline Levels (AEGL) under test conditions defined in recently published standard specifications for chemical vapor detectors. The described method covers the use of primary reference spectra to establish analyte concentrations, the generation of secondary reference spectra suitable for measuring analyte concentrations under specified testing environments, and the use of referee feedback to compensate for depletion of the test analyte. Important benefits of this approach include verification of the test analyte concentration with characterized uncertainties by in situ measurements co-located with the detector under test, near-real-time feedback, and broad applicability to toxic industrial chemicals.

Introduction

Rapid identification and reliable quantification of potentially lethal chemical vapors are required in order to achieve an optimum level of safety for the general public and for first responders during an accidental or intentional atmospheric release of such compounds. If chemical security is to be achieved, chemical vapor detectors employed in these situations must demonstrate capabilities that meet baseline performance requirements, such as the requirements recently published in the standard specifications for chemical vapor detectors for homeland security applications, ASTM E2885-13 [1] and ASTM E2933-13 [2]. Standard testing parameters and methods designed to evaluate a detector's performance must produce widely accepted results for an instrument's risk detection capability, with defined levels of confidence. The verification and validation process relies upon the presentation of a challenge air stream, containing a toxic analyte of interest, to the sampling port of a detector. The concentration of the toxic analyte must be within a well-defined limit of uncertainty and meet target concentrations and target uncertainty criteria. Because of the potential reactivity of the toxic analytes under testing conditions, the analyte concentration is best determined by independent methods (a "referee") at the measurement point of the detector under test. Analyte concentrations based solely on dilution flow calculations can be misleading due to, for example, unquantified analyte degradation and lead to significant errors in the performance evaluation.

This paper presents a demonstration of a referee test method that employs an optical absorption measurement to provide an absolute quantitative measurement of a toxic analyte concentration. Such an optical measurement can be made in the detector testing chamber, so that the efficacy of

gas stream preparation and the assumption that the gas stream is chemically stable during delivery to both the test and referee measurement sites need not be relied upon. In addition, a practical routine method is preferred to minimize the need for special instrumentation and for the development of in-house or commercial reference materials and data for the toxic gases that are of interest. This criterion is met in the present referee method, which makes an absorption measurement of the gas using a commercial Fourier transform infrared (FT-IR) absorption spectrometer. FT-IR spectroscopy has been utilized previously for quantitative analysis of gas-phase components, using a variety of approaches (see, for example, [3-7]). The method that we demonstrate relies upon the use of primary reference spectra from available spectral libraries, thus providing quantitative concentration measurements with defined levels of uncertainty. It is feasible that using an FT-IR absorption measurement, this protocol should be able to verify test streams to an expanded uncertainty of 5 % ($2u_c$). This is a considerable improvement over current standard uncertainty "best guess" estimates of 20 % ($1u_c$) in test methods currently in use [8].

For the present study, the analytes of interest are broadly classified as Toxic Industrial Chemicals (TICs). These chemicals are typically produced in large quantities and can pose hazards when released into the environment, either accidently or intentionally. Formaldehyde, for example, can be inadvertently released into the environment by out-gassing from building materials and methods are being developed to monitor its presence [9]. These analytes are often reactive under typical background atmosphere environments that include varied temperatures and humidity levels. The testing parameters for validation of chemical detectors include temperature and humidity parameters for challenge streams that have been defined by recently published

chemical vapor detector standard specifications [1, 2]. The testing conditions are shown in Table 1 with the acceptable ranges for the temperatures and humidities [1]. Furthermore, the standard specification gives targeted concentrations for testing that are based upon each chemical's Acute Exposure Guideline Limits (AEGL) [10]. For the demonstration of our FT-IR-based approach, tests were conducted under the specified 33 °C and 45 °C environmental conditions for target analyte concentrations just above that of the 30 minute exposure AEGL 2 and AEGL 3 concentrations. The AEGLs represent the airborne concentration thresholds of a chemical at which susceptible individuals in the general population, including infants and children, suffer adverse health effects [11]. AEGL 2 corresponds to irreversible or long-lasting adverse effects, and AEGL 3 corresponds to life-threatening effects or death [2].

Experimental

Challenge Stream Generation

Three gas-phase TIC analytes (acrylonitrile, ethylene oxide and formaldehyde) were generated from analyte permeation tubes in a generator oven supplied by VICI Metronics [12]. Purge air (water vapor and CO_2 removed) was generated from a Whatman 75-45-12VDC FTIR purge gas generator [12]. Purge air constantly flowed through the oven at 50 cm^3/min,[1] as controlled by a mass flow controller (MKS Instruments, Inc.) [12]. The analyte vapor emission from the permeation tubes was allowed to stabilize for at least one day prior to use.

[1] Flow volume rates are specified for gas at 0 °C and 101.325 kPa.

The analyte gas stream was blended in a glass mixing bulb with dilution flow controlled by a mass flow controller to generate gas streams of specific analyte concentrations. For generating the secondary reference spectra, purge air was used for dilution. For the detector tests at environmental conditions, the initial analyte gas stream was diluted using filtered air (hydrocarbons and most water removed, carbon dioxide unaffected) passed through a dew point generator (Li-Cor LI-610 [12]), positioned downstream from the mass flow controller, to control the humidity. The dew point was set to deliver water vapor to the sample cell within the ranges for the test conditions (See Table 1), based upon the cell temperature and the mixing ratio of the analyte flow and the dilution flow. For the environmental tests at elevated temperature, the cell and lines before the cell were heated to the target temperatures using resistive heaters. For safety, all lines and the sample cell itself were maintained in secondary containment, which was continuously flushed with purge air. Chemically passive materials, either electropolished stainless steel or perfluoroalkoxy (PFA) flexible tubing, were used for the analyte delivery lines.

The standard specification for handheld chemical vapor detectors requires the vapor concentration of the challenge stream to be above the 30 minute exposure AEGL value threshold by an amount equal to the expanded measurement uncertainty [1]. The goal of this work was to demonstrate that using the methods given, measurements of the toxic vapor concentration could be made within the expanded uncertainty, U, equal to 5 % of the AEGL target. Here, $U = ku_c$, with the combined standard uncertainty u_c determined from experimental standard uncertainties, and the coverage factor of $k = 2$. Therefore, delivery of analyte concentrations at AEGL + 5 % was targeted. Under these experimental constraints, there is approximately 95 % or greater

confidence that the true test concentration will be between the relevant AEGL value and a concentration 10 % greater than that AEGL value. Of those values that do not fall within the 95 % confidence interval, the probability that the true test concentration will be below the interval rather than above is 50 %, provided that all uncertainties are normally distributed [13]. Therefore, designing the detector test such that the target concentration exceeds the AEGL value by at least $2u_c$ results in a test concentration that exceeds the AEGL value with at least 97.5 % (95 % + 5 %/2) confidence. This target concentration provides a rigorous and relevant test for the procurement evaluator while simultaneously assuring a fair test of capability for the detector vendor. The list of target analytes, their 30 minute exposure AEGL2 and AEGL3 concentrations and the infrared spectral fit ranges are shown in Table 2. The ranges were selected to fit an absorption band for the analyte of interest, while qualitatively minimizing overlap with water or carbon dioxide.

FT-IR Measurements

FT-IR spectra at resolutions of 0.5 cm^{-1} (TICs) or 1 cm^{-1} (toluene) were collected using a Bruker IFS66v [12]. TIC spectra and their corresponding background spectra were averaged over 512 scans each (≈ 7 min). The path length of the sample cell (20-pass cell with an internal volume of 200 cm^3) was previously measured at 2.0114 m with a relative expanded uncertainty of 0.26 % [14]. To confirm that the optical path used all 20 passes through the cell, FT-IR absorption spectra of gravimetrically determined concentrations of toluene vapor from a diffusion tube were acquired and analyzed with reference to primary reference spectra of toluene. The cell temperature and pressure were recorded throughout the spectral acquisitions. Background spectra

were collected of either the purge air or air matched to the environmental test conditions (humidity and carbon dioxide). Sets of at least five analyte spectra (≈ 7 min integration time for each spectrum) were generated for each test condition at the two target concentrations.

FT-IR Spectral Analysis

Interferograms were Fourier transformed with a 3-term Blackman-Harris apodization function (zero-filling factor of 2) and a Bruker proprietary non-linear correction was applied for the MCT (mercury cadmium telluride) detector response [12]. TIC analyte concentrations were evaluated by least squares (LS) fitting of reference spectra to the data. (See [15] for a demonstration of quantitative LS fitting of multi-component gas-phase FT-IR spectra.) For the spectra of a toxic analyte in wet air, reference spectra for the analyte, water and, if needed, CO_2 were included in the fit. Parameters of the fit included a shift of the x-axis of the data so that the positions of the peak maxima matched those of the analyte reference spectrum, a baseline, and the amplitudes of the reference spectra required to fit the data. It has been shown that for non-interacting gases fitting with a baseline represented by an offset and a slope is adequate for obtaining quantitative results [15]. The quality of the fit was determined by χ^2, the sum of the squares of the residuals that are minimized in the LS fit, and by inspection of the fit to the spectral profile of the data. Water and carbon dioxide reference spectra used for the fitting of data at these temperatures were Pacific Northwest National Laboratory (PNNL) reference data spectra at 25 °C and 50 °C [16], which were used for the test data at 33 °C and at 45 °C, respectively. While these two reference spectra did not exactly match the spectral profiles at the test temperatures, these reference spectra were sufficient to provide adequate fits, since accurate quantitative measurements of only the

analyte, not water and carbon dioxide, were the goal of this work. For each fit, the sample spectra were adjusted using the ideal gas law to adjust the sample number densities due to differences in the pressure and temperature of the current spectra versus the reference spectra.

Reference Spectra

Primary reference spectra were obtained from the National Institute of Standards and Technology (NIST) Quantitative Infrared Database for acrylonitrile and ethylene oxide or from the Northwest-Infrared vapor phase infrared spectral library maintained by PNNL for formaldehyde [16-18]. In all cases, the 0.125 cm^{-1} resolution spectra were de-resolved (Blackman-Harris apodization) to 0.5 cm^{-1} resolution spectra using the de-resolution program available from the Environmental Protection Agency [19]. These primary reference spectra were suitable for fitting spectra acquired at room temperature and atmospheric pressure.

To evaluate the environmental test spectra collected at 33 °C and 45 °C, secondary reference spectra for the analytes at these temperatures were generated. The procedure for each analyte and test temperature was similar, and presented here: A secondary reference spectrum was generated by first obtaining spectra of the analyte of interest, typically at a concentration greater than the AEGL 3 value by ≈ 5 %, at a set dilution flow rate and at a temperature that closely matched that of the primary reference spectrum (generally 23 °C). These spectra formed a basis for the determination of the analyte concentration in the stream under this flow rate, as determined from fitting the individual spectra with the primary reference spectrum. Maintaining the same flow

rates (and thus the analyte concentration), spectra were also obtained for the analyte in a system heated to the desired testing temperature (33 °C or 45 °C). The average of these spectra served as secondary reference spectra at these two elevated temperatures for the analyte of interest, with a concentration traceable to the primary reference spectrum, assuming minimal decomposition with the condition change.

Table 3 shows the contributions to the analyte concentration uncertainty. The uncertainty attributed to global spectral fitting includes contributions from such factors as stability, baseline interpretation and analysis (including variability of the results from the spectral fitting process). Because we observe decomposition products in the formaldehyde spectrum, we have used 1 % for analysis of formaldehyde concentrations, rather than 0.5 %, for the uncertainty associated with global spectral fitting. For the secondary reference spectra, the expanded uncertainty, U, ($2u_c$) is estimated by adding in quadrature the appropriate values in Table 3 plus the uncertainty of the primary reference spectra. For the analytes used here, the primary reference expanded uncertainties are 2.0 % (acrylonitrile), 2.1 % (ethylene oxide) and 10.0 % (formaldehyde). These yield expanded uncertainties for the secondary reference spectra of 2.3 % (acrylonitrile), 2.4 % (ethylene oxide) and 10.4 % (formaldehyde).

For the spectra acquired during the environmental tests, the uncertainties associated with the temperature and pressure measurements and the global spectral fitting are added again. The expanded uncertainties, U, in these measurements are then 2.5 % for acrylonitrile, 2.6 % for

ethylene oxide, and 10.6 % for formaldehyde. We note that the primary reference spectra for acrylonitrile and ethylene oxide were acquired using the same MCT detector as was used in these studies. Thus, the primary reference spectra include all uncertainty related to the detector non-linearity [17], and therefore a component for detector non-linearity is not included again when calculating the uncertainty associated with the secondary reference spectra or the environmental tests. From the uncertainty analysis, we observe that the dominant contribution to the uncertainty of the test measurements is the uncertainty of the primary reference spectrum. Unless otherwise stated, analyte concentrations will include the $2u_c$ expanded uncertainty.

Results and Discussion

Published FT-IR reference spectra offer a convenient means to evaluate the concentration of an analyte in a gas-phase sample [17, 18]. This is shown in Fig. 1 for ethylene oxide in purge air at laboratory ambient temperature (RT, ≈ 23.6 °C). The ethylene oxide reference spectrum is well-matched to the shape of the acquired spectrum, with negligible differences, even in the sharp, narrow features in the center of the spectrum. This is seen most clearly in the expanded difference trace. An expanded view of the fit is given in the inset. An LS fit yielded an analyte concentration of (389.8 ± 9.4) µmol/mol.

Under certain testing conditions such as reduced or elevated temperature, a best fit of the reference spectra to the acquired sample spectra can produce a residual spectrum; that is, a simple amplitude correction is insufficient to produce a matched overlay of the two spectra. This

is demonstrated in Fig. 2 for acrylonitrile spectra in purge air acquired at RT, 33 °C and 45 °C, all at the same analyte concentration (an LS fit to the RT spectrum providing a concentration of (191.2 ± 4.4) µmol/mol). The difference spectra in the bottom portion of the plot illustrate the changes that occur in the shape of the absorption bands as temperature increases: the peak amplitudes get smaller, while the band shoulders get broader as higher energy rotational levels are populated [20]. If the higher-temperature spectra (for any of the three analytes used in this demonstration) are fit with reference spectra at 23 °C, the evaluated concentration of the analyte can change by more than 2 %, and the χ^2 for the fit can increase by more than a factor of 15. This demonstrates the need for the collection of secondary reference spectra as described in the Experimental section.

As a demonstration of the general applicability of the use of secondary reference spectra for evaluating analyte concentrations in an environmentally relevant test stream, the protocol was applied to the three analytes of interest. For example, Fig. 3 shows the application of a secondary reference spectrum at 45 °C for ethylene oxide in a fit that also includes reference spectra to account for the presence of both water (≈ 29 g/m^3) and some weak carbon dioxide absorption lines. The 50 °C primary reference spectra for water and CO_2 fit the comparatively weak spectral lines in the data reasonably well and provide an adequate fit for an LS determination of the ethylene oxide concentration. The fit yielded an ethylene oxide concentration of (380.0 ± 9.9) µmol/mol (ca. AEGL3 + 5 %). Similarly, using secondary reference spectra for the analytes, good fits were achieved at the other test conditions and target concentrations for both ethylene oxide and acrylonitrile.

Fig. 4 shows a more difficult evaluation of a formaldehyde spectrum at room temperature using the primary reference spectrum. Note that we have also included the primary reference spectrum for formic acid in the LS model. Deviations between the acquired spectrum and the fit using only the formaldehyde primary reference spectrum (not shown) show broad mismatch from 2825 cm^{-1} to 3050 cm^{-1}. Such mismatches would produce a larger uncertainty in the final evaluated analyte concentrations. However, the inclusion of formic acid (contributions to the fit are shown in Fig. 4) improves the overall fit, which yields a formaldehyde concentration of (75.5 ± 7.9) µmol/mol. Fits in the region 950 cm^{-1} to 1350 cm^{-1} provided the best estimates for the formic acid concentration, which we estimate at ≈ 3 µmol/mol for this data set. We note that formaldehyde is a reactive chemical and can decompose on surfaces and in the gas phase into a variety of products, including formic acid, water, hydrogen, carbon monoxide and carbon dioxide [21, 22]. For this spectrum, we also observed additional carbon dioxide and carbon monoxide beyond the background levels. Based upon these results, consideration must be taken for the presence of decomposition products in the secondary reference spectra.

When water is added to the environmentally relevant challenge stream, the spectral fit shows larger deviations, as shown in Fig. 5a. For this spectrum, the nearby water lines are saturated (the concentration of water is ≈ 6 g/m^3), and interfere with the quality of the fit for formaldehyde. The use of an environmentally matched background spectrum (See Fig. 5b), however, can mitigate the interference of the water lines. Rather than using a conventional purge-air background, we have generated a matched background that has similar levels of water and

carbon dioxide as does the challenge stream. When using this background, the deviations are reduced, and the overall quality of the fit is improved, yielding a formaldehyde concentration of (77.1 ± 8.2) µmol/mol (ca. AEGL3 + 5%). A small negative deviation of the fit from the acquired spectrum can be observed in Fig. 5b from 2890 cm^{-1} to 3000 cm^{-1}. The contributions of formic acid to the secondary reference spectra were not removed when creating those spectra at 45 °C or, with respect to Fig. 5, at 33 °C, partially because primary reference spectra at those temperatures were not available. The spectra in Fig. 5 show less formic acid than the secondary reference spectra, hence the negative deviations. Based upon the overall reactivity of formaldehyde in these testing environments, we have estimated the global spectra fitting uncertainty at 1 % ($1u_c$) for formaldehyde, rather than 0.5 % for the other two case-study analytes.

The results of the approach for quantifying these three analytes under the various environmental conditions are summarized in Table 4. For each test condition, the concentration given is an average of fits to five to ten spectra, and the variability is given as ± 2 standard deviations. In general, the concentrations show little variation within a testing condition (analyte, temperature, humidity), with most tests yielding a deviation over repeated runs from the average value of no more than 0.6 µmol/mol over repeated runs. From our spectral fitting of the formaldehyde spectra, we estimate that the existence of a formaldehyde primary reference spectrum with an uncertainty comparable to that of the other two analytes would result in an expanded uncertainty for the determination of the formaldehyde concentration of approximately 5 %.

After adding water vapor to an ethylene oxide challenge stream, we noted that the analyte concentration was at a lower level than would otherwise be predicted from the mixing ratios from the mass flow controllers. To follow this trend, we systematically varied the water concentration while maintaining a constant mixing ratio between the dilution air stream and the ethylene oxide-in-air stream. The concentration of ethylene oxide in the FT-IR cell, as determined from LS fits, is shown in Fig. 6. The plot shows that the depletion of ethylene oxide, initially at AEGL3, is linear with water concentrations in the gas stream up to 29 g/m^3 at 33 °C. The amount of analyte depletion was time-independent, even to 1 hour under stopped-flow conditions, although it should be noted that with the flow conditions of these measurements the time scale for detecting changes was typically several minutes. The magnitude of the change tracks with added water content in the air stream, that is, the depletion is likely due to increased dilution by the water molecules. Similar effects were seen for the other analytes: for formaldehyde and acrylonitrile at approximately AEGL3 +5 % concentration and 33 °C, changes in concentration of -6.6 % and of a -4.5 %, respectively, were observed with water addition to the test stream at a concentration of 29 g/m^3. Furthermore, we cannot rule out other depletion mechanisms for the various analytes, e.g., reaction with the water vapor. Since direct measurement of the humidified air streams using mass flow controllers would be challenging, owing to the mixed and varying levels of components in the gas stream, the reductions in analyte concentrations with these tests demonstrate the need for real-time feedback to adjust analyte concentrations under the environmental test conditions to ensure that the target analyte concentration is being delivered to the detector under test.

Conclusions

Fourier-transform infrared (FT-IR) absorption spectroscopy using multivariate analysis and published reference spectra to evaluate measured spectra is becoming a common tool for quantitative gas analysis. One major advantage of this approach, which is based on the direct measurement of molecular properties, is that the measurements can be analyzed using reference spectra rather than consumable gas cylinder standards. Through the use of standard measurement protocols and standard reference spectra for data analysis, measurements across laboratories can be easily compared and the associated uncertainties in the measurements can be documented.

This work examines the use of FT-IR absorption spectroscopy for quantitatively evaluating the composition of vapor streams containing hazardous materials at AEGL under test conditions defined in a recently published standard specification for chemical vapor detectors, ASTM E2885-13 and E2933-13 [1, 2]. In this case, the vapor samples of interest are under conditions, i.e., temperature, relative humidity, and composition, which are relevant for the application, but not ideal for matching the measured spectra to published reference spectra. For example, differences in the line and band shapes due to differences in the sample temperatures can produce significant errors in the value assignments. In this work, published reference spectra at 23 °C or 25 °C were used to evaluate the concentration of vapor streams with single components using an intermediate step to generate secondary reference spectra of the chemicals of interest at the measurement temperature. Addition of water vapor to the toxic gas/air stream resulted in a

significant but stable decrease in the toxic gas concentration for all three of the toxic analytes tested.

This demonstration covers a relatively small subset of the possible chemicals that could be monitored in this way. In principle, the referee method described here would be suitable for confirming the detection capabilities of a point sensor for qualitative and quantitative analysis of any target TIC with an infrared absorption cross section sufficiently large to have a measureable spectrum at the AEGL or other application-relevant value. In an ideal case, the analyte spectrum is free of overlapping features from spectra of different components in the gas stream. Even competing features, if not too congested, should allow LS fitting techniques to provide high quality quantitative results.

Acknowledgements

We would like to thank the Department of Homeland Security Science and Technology Directorate for funding this work under agreement # HSHQPM-13-X-00191. We also acknowledge the technical assistance of W. Ausherman in assembling the testing equipment.

References

[1] ASTM E2885-13: Standard Specification for Handheld Point Chemical Vapor Detectors (HPCVD) for Homeland Security Applications, ASTM International, West Conshohocken, PA, 2013.

[2] ASTM E2933 -13: Standard Specification for Stationary Point Chemical Vapor Detectors (SPCVD) for Homeland Security Applications, ASTM International, West Conshohocken, PA, 2013.
[3] D.W.T. Griffith, "Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra," *Appl. Spectrosc.*, Vol. 50, 1996, pp. 59-70.
[4] D.M. Martin, P.J. Medvecz, K.M. Nichols, "Application of FT-IR Absorption Spectroscopy for *in Situ* Gas Concentration and Temperature Measurements in Laboratory- and Pilot-Scale Combustion Environments," *Appl. Spectrosc.*, Vol. 47, 1993, pp. 1898-1906.
[5] D.R. Qin, G. Cadet, "Quantitative analysis of process streams by on-line FT-IR spectrometry," *Anal. Chem.*, Vol. 69, 1997, pp. 1942-1945.
[6] A.V. Sepman, R. den Blanken, R. Schepers, L.P.H. de Goey, "Quantitative Fourier Transform Infrared Diagnostics of the Gas-Phase Composition Using the HITRAN Database and the Equivalent Width of the Spectral Features," *Appl. Spectrosc.*, Vol. 63, 2009, pp. 1211-1222.
[7] C. Cailteau, J. Pironon, P. de Donato, A. Vinsot, T. Fierz, C. Garnier, O. Barres, "FT-IR metrology aspects for on-line monitoring of CO_2 and CH_4 in underground laboratory conditions," *Analytical Methods*, Vol. 3, 2011, pp. 877-887.
[8] C.E. Laljer, in, Personal communication, 2014.
[9] J.H. Phillips, J.E. Patterson, "Determination of formaldehyde evolved during the curing of melamine-formaldehyde-based coatings," *J. Test. Eval.*, Vol. 33, 2005, pp. 73-80.
[10] Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volumes 1 to 15, The National Academies Press, 2013.
[11] Acute Exposure Guideline Levels (AEGLs), http://www.epa.gov/oppt/aegl/pubs/define.htm, last accessed: 01/20/2015.
[12] Commercial equipment and materials are identified in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
[13] B.N. Taylor, C.E. Kuyatt, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, 1994, NIST Technical Note 1297.
[14] P.M. Chu, G.C. Rhoderick, P.A. Johnson, Infrared Absorptivity Temperature Dependence of Gas Phase Methanol and Sulfur Dioxide, U.S. Dept. of Commerce, 2001, NISTIR 6773.
[15] D.M. Haaland, R.G. Easterling, "Application of New Least-Squares Methods for the Quantitative Infrared-analysis of Multicomponent Samples," *Appl. Spectrosc.*, Vol. 36, 1982, pp. 665-673.
[16] T.J. Johnson, R.L. Sams, S.W. Sharpe, The PNNL quantitative infrared database for gas-phase sensing: A spectral library for environmental, hazmat and public safety standoff detection, A.J. Sedlacek, S.D. Cjristesen, R. Colton, T. VoDinh (Eds.) in: Chemical and Biological Point Sensors for Homeland Defense, 2004, pp. 159-167.
[17] P.M. Chu, F.R. Guenther, G.C. Rhoderick, W.J. Lafferty, "The NIST Quantitative Infrared Database," *J. Res. Natl. Inst. Stand. Tech.*, Vol. 104, 1999, pp. 59-81.
[18] S.W. Sharpe, T.J. Johnson, R.L. Sams, P.M. Chu, G.C. Rhoderick, P.A. Johnson, "Gas-Phase Databases for Quantitative Infrared Spectroscopy," *Appl. Spectrosc.*, Vol. 58, 2004, pp. 1452-1461.
[19] U.S. Environmetnal Protection Agency, DERESOLVE, http://www.epa.gov/ttnemc01/ftir/deresolv.html, last accessed: 01/20/2015.

[20] B. Smith, Quantitative Spectroscopy: Theory and Practice, 1st ed., Academic Press, San Diego, California USA, 2002.
[21] T. Salthammer, S. Mentese, R. Marutzky, "Formaldehyde in the Indoor Environment," *Chem. Rev.*, Vol. 110, 2010, pp. 2536-2572.
[22] R.E. Mueller, U. Schurath, "Generation of formaldehyde in test atmospheres with low concentrations of hydrogen and carbon monoxide," *Anal. Chem.*, Vol. 55, 1983, pp. 1440-1442.

Table 1. Testing conditions for handheld point chemical vapor detectors. Reprinted, with permission, from *E2885-13 Standard Specification for Handheld Point Chemical Vapor Detectors (HPCVD) for Homeland Security Applications*, copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. A copy of the complete standard may be obtained from ASTM International, www.astm.org [1].

Manufacturer Documented Climate Ranges	Temperature (°C)	% Relative Humidity	Water Vapor Content (g/m^3)
Temperate	7 ± 2	77 ± 25	6 ± 2
	33 ± 2	17 ± 6	6 ± 2
	33 ± 2	78 ± 6	29 ± 2
Low Temperature	-5 ± 2		0
High Temperature	45 ± 2	43 ± 3	29 ± 2

Table 2. 30 minute exposure Acute Exposure Guideline Levels [10] and fit ranges for the demonstration analytes.

analyte	30 min AEGL2 (µmol/mol)	30 min AEGL3 (µmol/mol)	fit range, lower limit (cm^{-1})	fit range, upper limit (cm^{-1})
acrylonitrile	110	180	815	1170
ethylene oxide	80	360	730	1000
formaldehyde	14	70	2410	3300

Table 3. Additional contributions of uncertainty: $1u_c$.

Source	Estimated uncertainty ($1u_c$)
Detector non-linearity*	1 %
Pathlength	0.013 %
Cell temperature	0.1 %
Cell pressure	0.2 %
Global spectra interpretation	0.5 % (1 % for formaldehyde)

*The same detector was used to prepare the acrylonitrile and ethylene oxide primary reference spectra at NIST [17]

Table 4. Final concentrations and fit variations for demonstration laboratory challenge streams. The variability in the fits is given as ± 2 standard deviations for n = 5 to 10 spectra.

Analyte	[a]Target value (µmol/mol)	Concentration (µmol/mol), with variability		
		33 ˚C, 6 g/m^3 H_2O	33 ˚C, 29 g/m^3 H_2O	45 ˚C, 29 g/m^3 H_2O
Formaldehyde AEGL 3	74	76.9 ± 0.1	76.2 ± 0.1	78.1 ± 0.1
Formaldehyde AEGL 2	15	16.0 ± 0.1	15.2 ± 0.1	15.6 ± 0.1
Ethylene Oxide AEGL 3	378	385.7 ± 0.2	387.2 ± 0.5	388.2 ± 0.6
Ethylene Oxide AEGL 2	84	88.2 ± 0.1	85.3 ± 0.1	85.0 ± 0.2
Acrylonitrile AEGL 3	189	190.7 ± 0.1	193.8 ± 0.4	191.6 ± 0.1
Acrylonitrile AEGL 2	116	117.3 ± 0.1	120.9 ± 0.1	120.7 ± 0.4

[a]Target value calculated at 5 % over the AEGL value (see Table 2)

Figure Captions.

Figure 1. Absorption spectrum for ethylene oxide in purge air at room temperature (RT, black) and the fit of the primary reference spectrum (red) are shown in the top panel. The baseline (dashed line) is also shown. The inset shows an expanded section of the spectrum and the fit. The deviation between spectrum and model across the full region analyzed is shown in green in the top panel and expanded in the bottom panel.

Figure 2. Absorption spectra for acrylonitrile in a purge air background at room temperature RT, 33 °C and 45 °C are shown in the top panel. The concentration of acrylonitrile is (191.2 ± 4.4) µmol/mol by LS fitting. The difference spectra (subtracting the RT spectrum from the elevated temperature spectra) are shown in the bottom panel and are offset for clarity.

Figure 3. An absorption spectrum for ethylene oxide in humid air at 45 °C (black) and the fit of the secondary reference spectrum (red) are shown in the top panel. The contributions from water (blue) and carbon dioxide (gray) are also shown and are offset for clarity. The deviation between spectrum and model across the full region analyzed is shown in the bottom panel.

Figure 4. An absorption spectrum for formaldehyde in purge air at RT (black) and the LS fit of primary reference spectra (red, including spectra for formaldehyde and formic acid) are shown in the top panel. Also included are the contributions to the LS model from the formic acid primary reference spectrum, which is offset for clarity. The deviation (green) between spectrum and model across the region shown is plotted in the bottom panel.

Figure 5. Absorption spectrum for formaldehyde in humid air (≈ 6 g/m^3) at 33 °C, using (a) a purge air background and (b) a matched background with water in filtered air. For each plot, the acquired spectra are shown in black and the LS fit of the secondary reference spectrum to the data are shown in red. The deviations (green) between spectrum and model for each figure is shown in the bottom panel. Also included in (a) are the contributions to the model from the primary reference spectrum of water (blue), which is offset for clarity.

Figure 6. The concentration from the LS fits of ethylene oxide in the test streams at 33 °C as a function of the water content. The y-error bars represent the 0.5 % global fitting uncertainty (See Table 3) and the x-error bars represent the standard uncertainty ($1u_c$) for the concentration of the water for these relative comparisons.

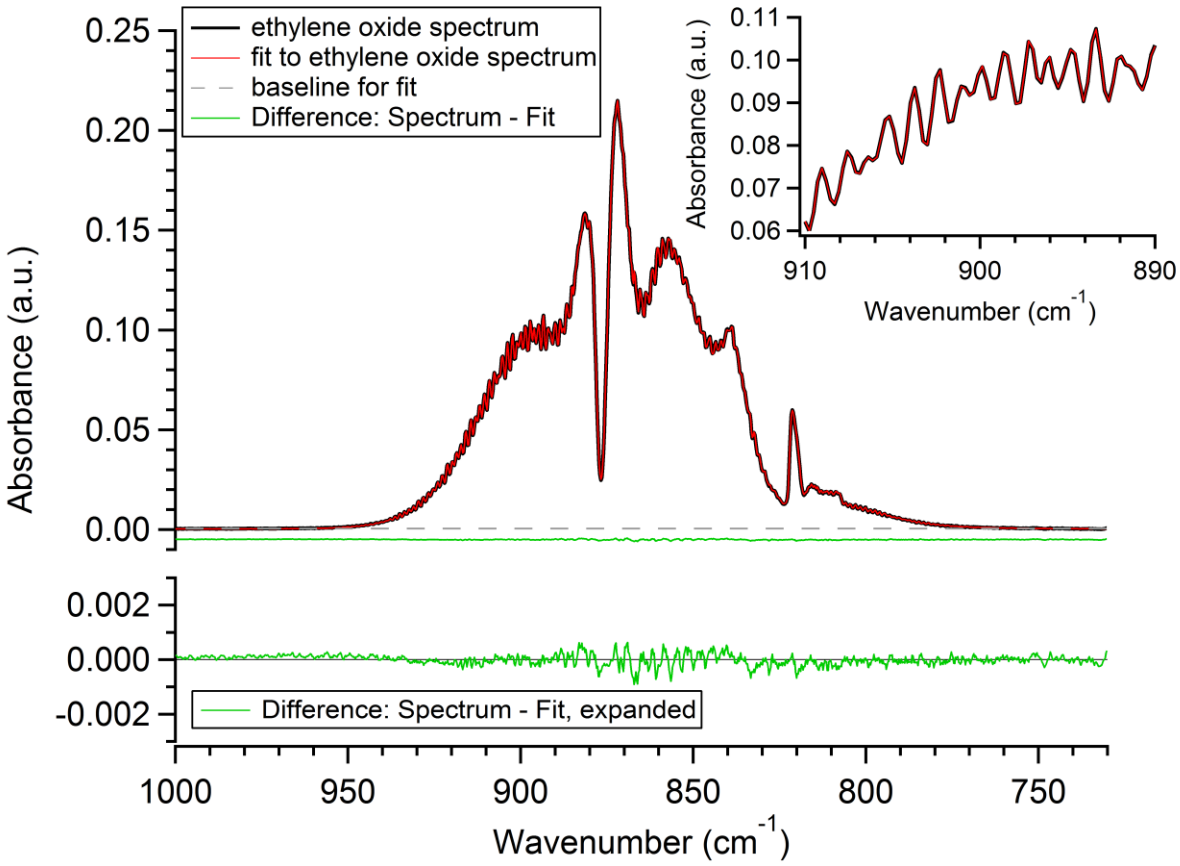

ethylene oxide spectrum
fit to ethylene oxide spectrum
baseline for fit
Difference: Spectrum - Fit
Absorbance (a.u.)
0.25
0.20
0.15
0.10
0.05
0.00
0.11
0.10
0.09
0.08
0.07
0.06
910
900
890
Wavenumber (cm-1)
0.002
0.000
-0.002
Difference: Spectrum - Fit, expanded
1000
950
900
850
800
750
Wavenumber (cm-1)

Figure 1.

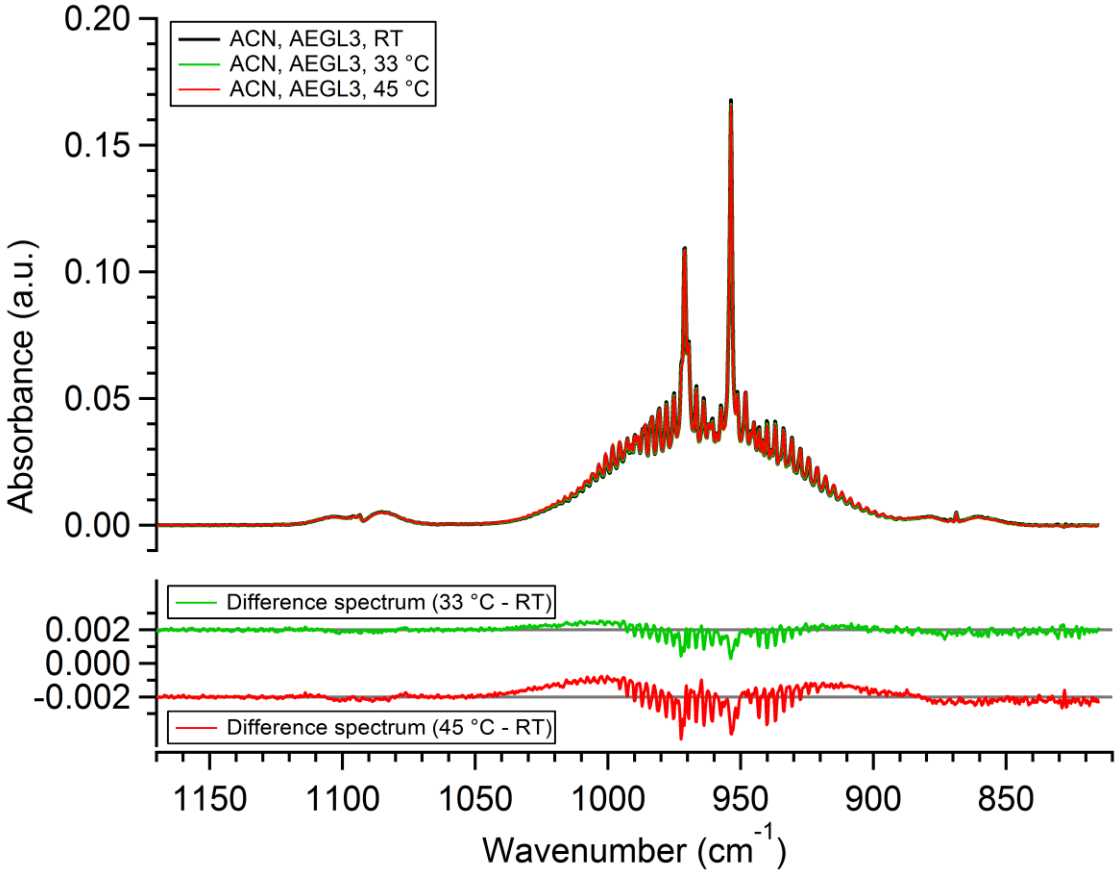

ACN, AEGL3, RT
ACN, AEGL3, 33 °C
ACN, AEGL3, 45 °C
Absorbance (a.u.)
0.20
0.15
0.10
0.05
0.00
Difference spectrum (33 °C - RT)
Difference spectrum (45 °C - RT)
0.002
0.000
-0.002
1150
1100
1050
1000
950
900
850
Wavenumber (cm-1)

Figure 2.

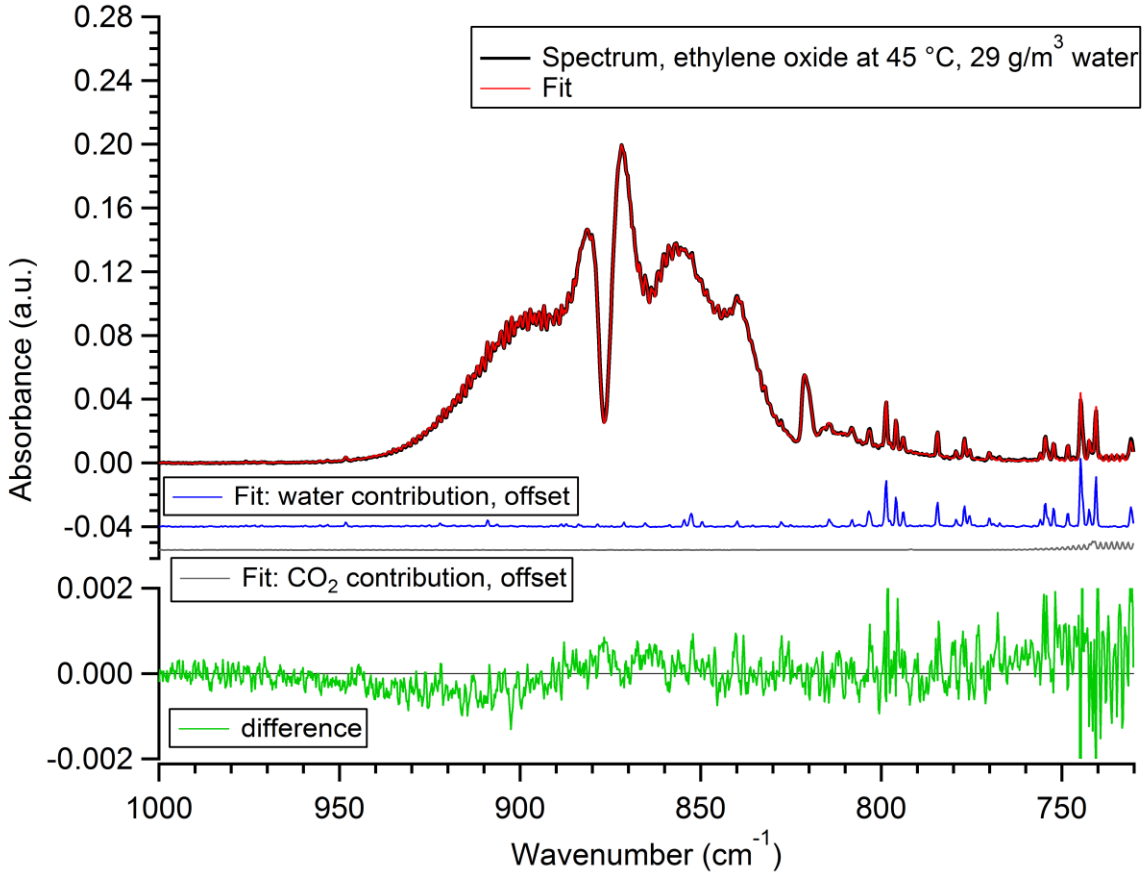

Spectrum, ethylene oxide at 45 °C, 29 g/m3 water
Fit
Fit: water contribution, offset
Fit: CO2 contribution, offset
difference
Absorbance (a.u.)
Wavenumber (cm-1)
0.28
0.24
0.20
0.16
0.12
0.08
0.04
0.00
-0.04
0.002
0.000
-0.002
1000
950
900
850
800
750

Figure 3.

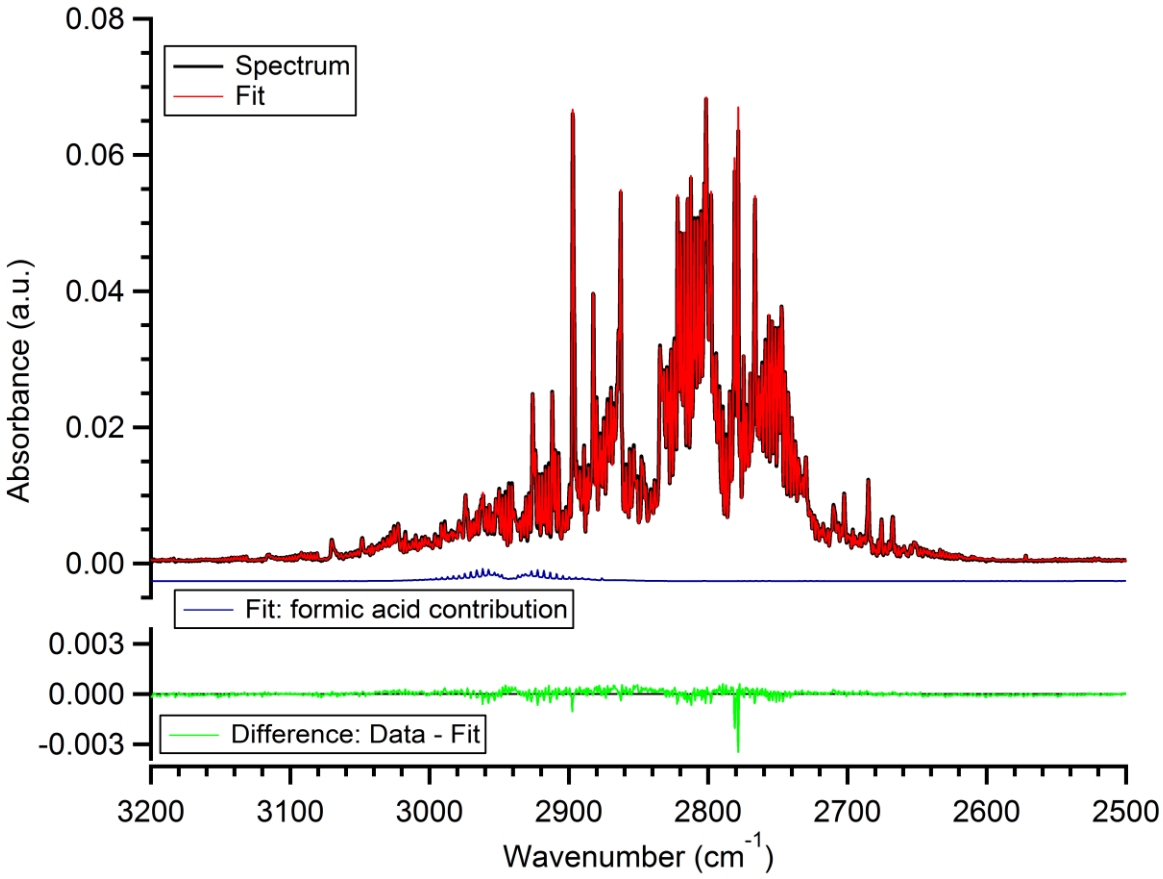

0.08
0.06
0.04
0.02
0.00
Absorbance (a.u.)
Spectrum
Fit
Fit: formic acid contribution
0.003
0.000
-0.003
Difference: Data - Fit
3200
3100
3000
2900
2800
2700
2600
2500
Wavenumber (cm-1)

Figure 4.

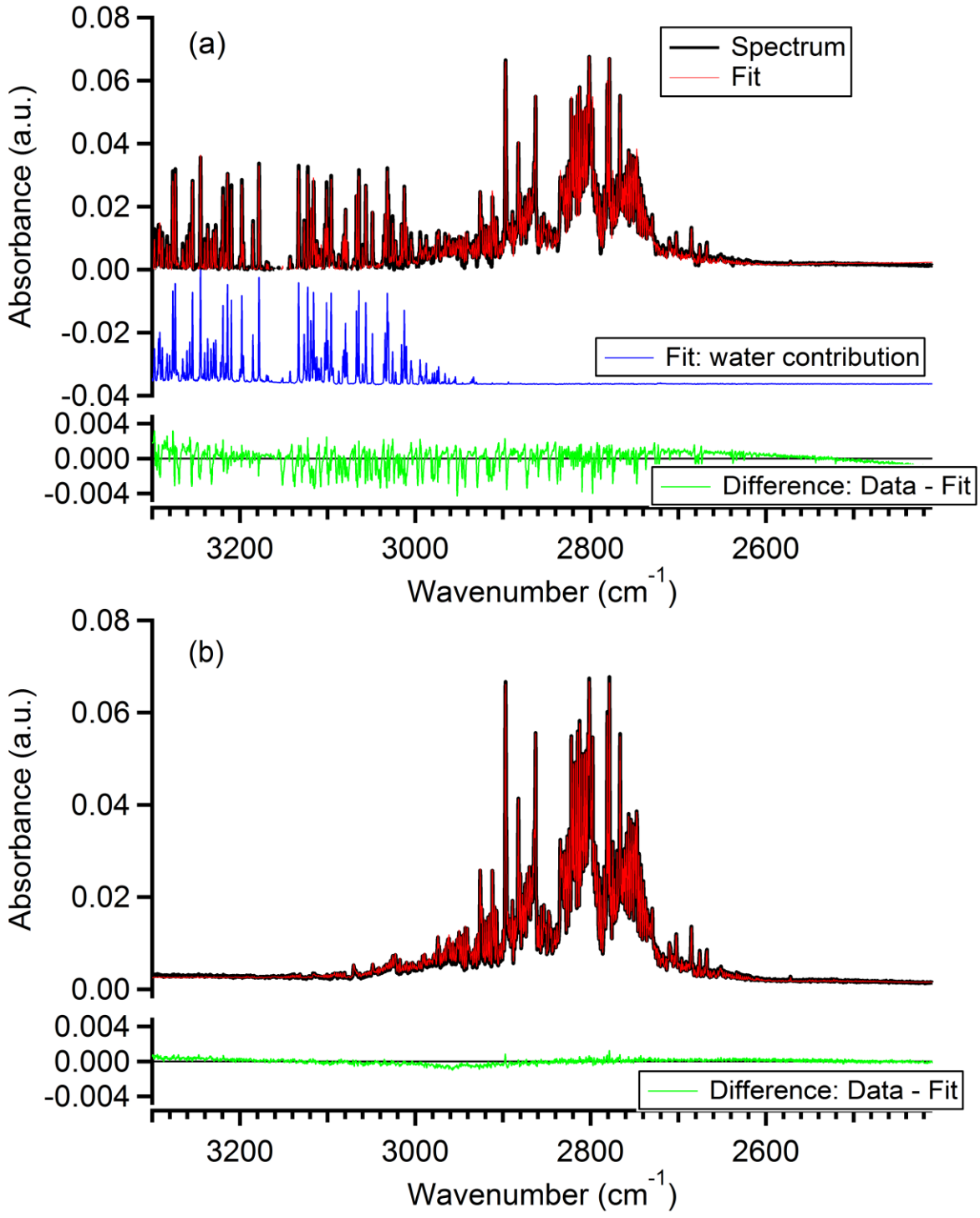

(a)
Spectrum
Fit
Fit: water contribution
Difference: Data - Fit
Absorbance (a.u.)
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
0.004
0.000
-0.004
3200
3000
2800
2600
Wavenumber (cm-1)
(b)
Difference: Data - Fit
Absorbance (a.u.)
Wavenumber (cm-1)

Figure 5.

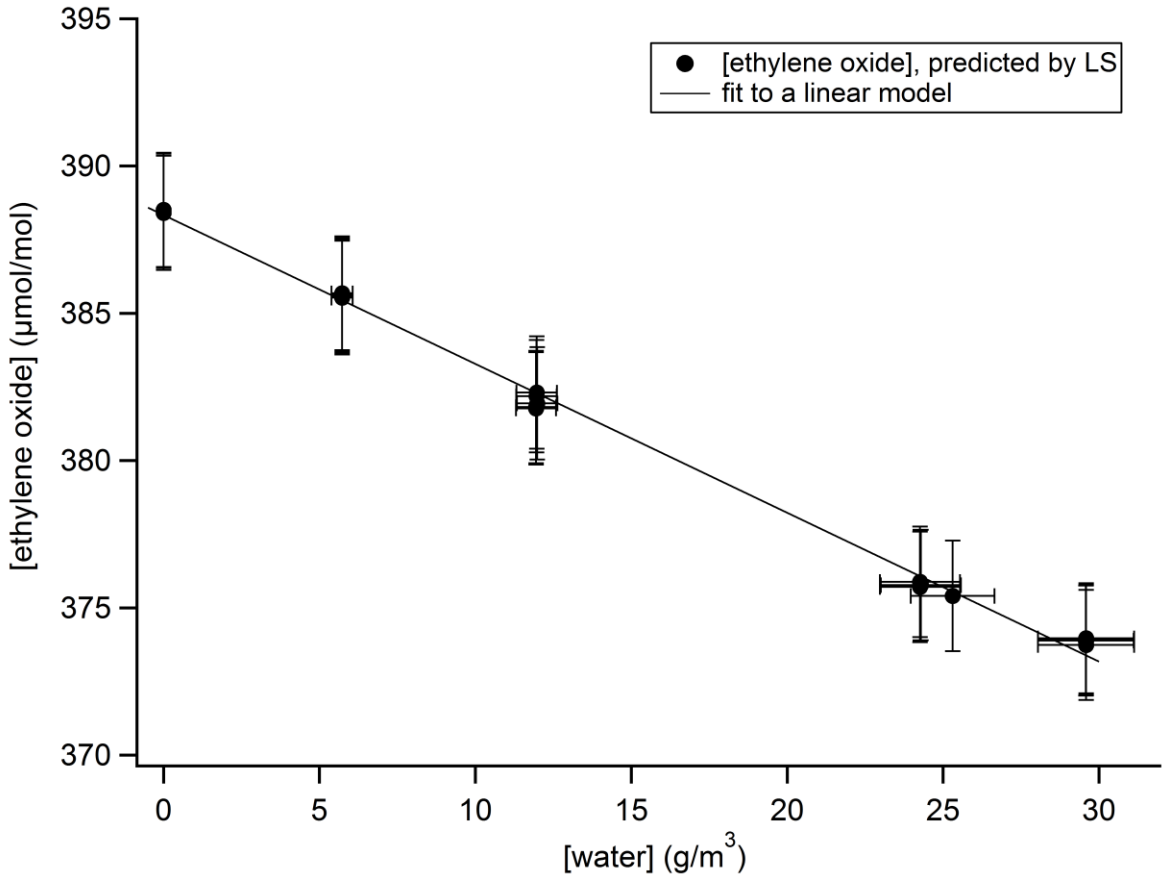

[ethylene oxide], predicted by LS
fit to a linear model
[ethylene oxide] (µmol/mol)
395
390
385
380
375
370
0
5
10
15
20
25
30
[water] (g/m3)

Figure 6.