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

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Abstract

Performance standard specifications for point chemical vapor detectors are established in ASTM E 2885-13 and ASTM E 2933-13. The performance evaluation of the detectors requires the accurate delivery of known concentrations of the chemical target to the system under 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 extends the capability of a previously demonstrated method for using Fourier transform infrared (FT-IR) absorption spectroscopy for quantitatively evaluating the composition of vapor streams containing hazardous materials at Acute Exposure Guideline Levels (AEGL) to include test conditions colder than laboratory ambient temperatures. 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 additional reference spectra and spectral profile strategies to mitigate the uncertainties due to impurities and water condensation within the low-temperature (7 °C, -5 °C) test cell. 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.

Keywords

test method independent referee; Fourier transform infrared (FT-IR) absorption spectroscopy; toxic industrial chemicals (TICs); quantitative analysis

Introduction

This report continues a demonstration of a referee test method for the evaluation of the performance of toxic chemical vapor detectors [1]. The method employs an optical absorption measurement to provide an absolute quantitative measure of a toxic analyte vapor concentration introduced into a challenge air stream that is presented to detectors under test.

Toxic chemical vapor detectors must demonstrate capabilities that meet baseline performance requirements, such as those recently published in the standard specifications for chemical vapor detectors for homeland security applications, ASTM E 2885-13 [2] and ASTM E 2933-13 [3]. For testing the responses of the chemical vapor detectors, the concentration of the toxic test analyte must be known to within a stated uncertainty. Because of the potential reactivity of the toxic analytes under test conditions, the analyte concentration is best determined by independent methods (a “referee”) at the measurement point of the detector under test. The referee method employed in these studies makes an optical absorption measurement of the gas using a commercial Fourier transform infrared (FT-IR) absorption spectrometer and relies upon the use of primary reference spectra from available spectral libraries, thus providing traceable quantitative concentration measurements with defined levels of uncertainty. The previous study showed that this protocol is capable of verifying test streams at temperatures of 33 °C and 45 °C with a relative uncertainty of 5 % ($2u_c$) in the analyte concentration, a marked improvement over the estimated 20 % ($1u_c$) reported for test methods in current use [4]. This work extends those studies to 7 °C and –5 °C, and expands upon the analysis methods used for quantification of the analyte gases in the challenge streams.

The testing parameters for validation of chemical detectors include temperature and humidity parameters for challenge streams that have been established by recently published chemical vapor detector standard specifications [2, 3]. These specifications give targeted concentrations for testing that are based upon each chemical’s Acute Exposure Guideline Levels (AEGL) [5, 6]. For the demonstration of our FT-IR-based approach, low-temperature tests were conducted under the specified 7 °C and –5 °C environmental conditions for target analyte concentrations just above that of the 30-min exposure AEGL-2 and AEGL-3 concentrations. For the general population, these airborne concentration thresholds correspond to potential irreversible or longlasting adverse effects (AEGL-2), and to potential life-threatening effects or death (AEGL-3) for susceptible individuals in the general public [5]. The testing conditions, with acceptable range limits, are shown in Table 1 [2].

Experimental

Challenge Stream Generation

This work continued the study of three gas-phase TIC (Toxic Industrial Chemicals) analytes: acrylonitrile, ethylene oxide and formaldehyde. These were generated from analyte permeation tubes, as described previously [1]. Dilution of the analyte streams to specified concentrations was then done with either purge air (hydrocarbons, water vapor and CO₂ removed) or with filtered air (hydrocarbons and most water vapor removed, CO₂ unaffected) to which water vapor could be added using a dew-point generator, depending upon test conditions.

The standard specifications for point chemical vapor detectors require the vapor concentration of the challenge stream to be above the 30-min-exposure AEGL value threshold by an amount equal to the expanded measurement uncertainty [2, 3]. We established target concentrations for the analytes based upon our goals for the expanded uncertainties, U , derived from our previous work in this area [1]. For these demonstrations,

$U = ku_c$, with the combined standard uncertainty u_c determined from experimental standard uncertainties and the coverage factor of $k = 2$ corresponding to 97.5 % certainty of meeting or exceeding the test target [7]. In our prior efforts, we established target expanded uncertainties for all analytes at 5 %, which corresponds to target concentrations of 5 % higher than the AEGL being tested against. We maintain that same level for the acrylonitrile and ethylene oxide analytes, but increase the target concentration for formaldehyde to 10 % above the AEGL owing to the larger uncertainty associated with the formaldehyde primary reference spectrum. The list of target analytes, their 30-min-exposure AEGL-2 and AEGL-3 concentrations, and the infrared spectral fit ranges are shown in Table 2. The ranges were selected to fit a reasonably strong absorption band for the analyte of interest, while minimizing overlap with water or carbon dioxide.

FT-IR Measurements and Spectral Analysis

FT-IR data sets were obtained as described in detail previously [1]. Briefly, spectra were obtained at 0.5 cm^{-1} resolution and averaged over 512 scans using a Bruker IFS66v [8]. Cell pressure and temperature were measured throughout the spectral acquisition. The path length of the cell was verified with toluene measurements (described in [1]) as $(2.00 \pm 0.01)\text{ m}$ and was used in the calculations here. Background spectra were collected as before of either the purge air or air matched to the environmental test conditions (humidity and carbon dioxide). Typically sets of 8 to 12 analyte spectra were generated at each test condition to aid in assessing the measurement uncertainty.

For environmental testing at $7\text{ }^{\circ}\text{C}$ and $-5\text{ }^{\circ}\text{C}$, the apparatus was modified to chill the gas transport lines and the optical cell. A coil of copper tubing was brazed tightly around the optical cell body and a form-fitting brass end cap containing a serpentine channel for coolant flow was attached to the cell body such that it covered the mirror plate. These modifications assured that all surfaces of the optical cell excepting the infrared beam line windows were in thermal contact with flowing coolant. In order to give the flowing gas more time to equilibrate to the target temperature, an air-coolant heat exchanger was made by enclosing a 14 cm diameter coil of 0.432 cm diameter electropolished stainless steel tubing inside a steel cylinder. An inner cylinder of plastic was used to fill the remainder of the heat exchanger volume in order to reduce the volume of coolant required and its recirculation time. The coolant flow was directed from the recirculating chiller to the optical cell tubing, then to the heat exchanger coil enclosure, before returning to the refrigerated bath, so that the apparatus operated approximately as two double-pipe heat exchangers in series under countercurrent flow. A thermocouple attached to the optical cell body was used to confirm that the coolant temperature at the optical cell was within the experimental range of the target temperature. The entire heat exchange apparatus was insulated and housed inside an extended compartment of the infrared spectrometer purged volume to prevent condensation. The gas delivery tubing length inside the heat exchanger was $\approx 450\text{ cm}$, with an approximate volume and interior surface area of 66 cm^3 and 610 cm^2 , respectively, while the optical cell had a volume of 200 cm^3 and interior surface area of $\approx 250\text{ cm}^2$. While the total cooled volume of the coil is only 1/3 that of the optical cell, it has nearly 2.5 times the interior surface area; the high surface area-to-volume ratios accelerated heat transfer. Estimates computed using heat transfer equations [9] and handbook values for the thermophysical properties of air [10]

suggest that even at the highest flow rate used for the present demonstration ($10.8 \text{ cm}^3/\text{s}$ at 0°C and 101.325 kPa), the air temperature was reduced to the target condition in much less time ($\approx 0.04 \text{ s}$) than was required to travel the length of the heat exchange coil ($\approx 6 \text{ s}$). To confirm the calculated estimates, the heat exchanger was tested prior to integration with the optical cell by inserting a thermocouple into the gas outlet of the heat exchange coil and measuring the gas temperature under operating conditions. As a final confirmation, the intensity distributions of the rotational sidebands of the test gas spectra, which are temperature dependent, were within the fitting error of the distributions found in the reference spectra (detailed in the Results and Discussion). A complete schematic of the integration of the gas flow metering, mixing, temperature control, delivery, infrared spectra measurement, and exhaust is shown in Fig. 1.

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. TIC analyte concentrations were evaluated by least squares (LS) minimization fitting of reference spectra to the data [1, 11–13]. For the spectrum of a toxic analyte in wet air, reference spectra for the analyte, water and, if needed, CO_2 were included in the fit. In fitting formaldehyde, it was necessary to add a reference spectrum for formic acid to the fit (see Results and Discussion for further details). Parameters of the fit were a shift of the wavenumber of the data so that the positions of the peak maxima best matched those of the analyte reference spectrum, a baseline that could have both an offset and a slope, and the amplitudes of the reference spectra required to fit the data. The LS fit utilized Stepit from the Quantum Chemistry Program Exchange, a method for determining the most probable values of the fit parameters [12]. Fitting routines such as this permit the independent variable, the wavenumber, to also become a parameter of the fit, which can be important for fitting spectral bands containing narrow transitions. 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.

Reference spectra at 5°C from the Pacific Northwest National Laboratory (PNNL) library for CO_2 were used in fitting the data at either 7°C or -5°C [14, 15]. Low-temperature reference spectra for water and formic acid were not available, and therefore 25°C PNNL reference spectra were used. While these reference spectra did not exactly match the spectral profiles at the test temperatures, they were sufficient to provide adequate fits since accurate quantitative measurements of only the target analyte 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.

Analyte Reference Spectra

Primary reference spectra were obtained from the National Institute of Standards and Technology (NIST) Quantitative Infrared Database for acrylonitrile and ethylene oxide and from the Northwest-Infrared vapor phase infrared spectral library maintained by PNNL for formaldehyde [14–18]. Reference spectra for the analytes are available at only a few selected temperatures (23°C from the NIST database and typically 5°C , 25°C and 50°C from the

PNNL library) and for the standard FT-IR resolutions. Unless the reference data temperature is equal to that of the laboratory data, generally their respective line shapes will not match. Secondary reference spectra that can be used for analysis, obtained from measurements at the temperatures of the tests, feature line shapes free of temperature-dependence effects. Acquiring these secondary spectra requires that the measurements be made with gas streams containing verified analyte concentrations. This condition can be accomplished if spectra of the test gas streams are first obtained at 23 °C or 25 °C, which then can be quantitatively analyzed using the standard library spectral reference spectra. The secondary reference spectra were normalized for concentration, path length, temperature of 23 °C, and pressure of 101.325 kPa.

In the determination of these gas stream analyte concentrations, reference spectra obtained at a FT-IR resolution of 0.125 cm^{-1} from the NIST database or the PNNL library were used. The spectral data for this study were obtained at an FT-IR resolution of 0.5 cm^{-1} , requiring deresolution of the standard references. Any real FT-IR spectrometer will have a larger resolution than the ideal value [19], so for each analyte we optimized the reference resolution to best fit the observed spectral line shapes. The best fit deresolutions were 0.54 cm^{-1} for acrylonitrile, 0.55 cm^{-1} for ethylene oxide, and 0.59 cm^{-1} for formaldehyde. Deresolution was accomplished by using the DERESOLVE software utility from the Environmental Protection Agency [20], which employed a Blackman-Harris 3-term apodization. Interfering spectra, such as H_2O and CO_2 , were deresolved to the same value used for the analytes of interest.

Table 3 shows the contributions to the analyte concentration uncertainty. Global spectral fitting contains uncertainty contributions from such factors as the stability of the system and from variability associated with the analysis of the spectra, which includes baseline determination and the observed repeatability uncertainty. We assigned a higher uncertainty for the analysis of formaldehyde since we directly observed impurities in the formaldehyde spectra [1]. 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, and multiplying by the coverage factor, 2. The expanded uncertainties of the primary reference spectra are 2.0 % (acrylonitrile), 2.1 % (ethylene oxide) and 10.0 % (formaldehyde). These yield expanded uncertainties for the secondary reference spectra of 2.5 % (acrylonitrile), 2.6 % (ethylene oxide) and 10.5 % (formaldehyde). To calculate the expanded uncertainties associated with our final environmental tests, we add in a second contribution from the uncertainties attributed to the temperature and pressure measurements and the global spectral fitting. These calculations yield U for the measurements here of 2.7 % (acrylonitrile), 2.8 % (ethylene oxide) and 10.7 % (formaldehyde). We note that the same detector used in these experiments was also used to acquire the data from which the primary reference spectra were generated for acrylonitrile and ethylene oxide. These primary reference spectra contain the uncertainty for the non-linearity of the detector, which was not included again in the calculations for the expanded uncertainties of the secondary reference spectra. For all analyte concentrations, the $2u_c$ expanded uncertainty will be reported, unless otherwise stated.

Results and Discussion

Temperature plays a role in the shape of absorption bands, and therefore, in how well reference spectra may be fit to data. In Fig. 2, we show an FT-IR absorption spectrum from acrylonitrile at -5°C in a purge air background. This spectrum was fit using a least squares approach with three different reference spectra. Overlaid on the spectrum is the fit using a primary reference spectrum at 25°C . The deviations between the data and fit are expanded below the main plot. Fit deviations are shown for two other spectra: a primary reference spectrum at 5°C from the PNNL library, and a -5°C secondary reference spectrum generated for this study. As expected, as the reference spectrum gets closer to the acquisition temperature of the data, the deviations decrease until a nearly flat line is observed. Using the secondary reference spectrum at -5°C yields an acrylonitrile concentration of (189 ± 5) $\mu\text{mol/mol}$. While the fit differences may seem small, using the 25°C reference in the analysis introduces a systematic error of $+2.5\%$, as determined from the difference in the fit concentration from that using the secondary reference. (Using the NIST 23°C primary reference in the fit, this error is essentially the same, at $+2.4\%$.) Using the 5°C reference for analysis, the error is reduced to $+0.4\%$. Acrylonitrile spectra at this same concentration in purge air but at 7°C showed reduced but still significant errors of $+1.4\%$ when fit to the 25°C reference and -0.5% when fit to the 5°C reference.

Application of Secondary Reference Spectra

The creation and use of the secondary reference spectra is consistent with the goal of minimizing the measurement uncertainty budget, but has the additional advantage in that high-quality fits free of spectral baseline uncertainties that bias the fitting process can more easily be obtained. Therefore, all TIC spectra at 7°C and -5°C were analyzed using secondary reference spectra.

Environmental tests at 7°C were done using the filtered air stream containing 6 g/m^3 of H_2O . Ethylene oxide at (382 ± 11) $\mu\text{mol/mol}$ in humidified air at 7°C is shown in Fig. 3. The fit used the 7°C ethylene oxide secondary reference, a 5°C PNNL CO_2 reference, and a 25°C PNNL H_2O reference. Shown is the fit in red overlaying the data in blue. The contributions of CO_2 (in green) and of H_2O vapor (in navy), and the deviation of the data from the fit (in purple), are shown expanded by a factor of 3 and offset. While small, the exclusion of either CO_2 or H_2O from the fit changes the ethylene oxide concentration computed from the fit by 0.1% . Again, the flat residual deviation trace demonstrates reliability of the fit.

At 7°C with 6 g/m^3 water vapor, a broad absorbance band centered at approximately 3400 cm^{-1} becomes evident. We speculate that a thin film of water may be condensing on the cooled mirrors of the cell to give this observed absorbance [21, 22]. For acrylonitrile or ethylene oxide, this coating caused no spectroscopic analysis problems since the condensed water absorbance bands are well removed from the bands employed in the fits. However, for formaldehyde, the long tail of the band overlaps the formaldehyde transitions of interest (Fig. 4). For this spectrum, acquired in filtered air at 7°C with 6 g/m^3 of water vapor, a background that matched the water concentration was used to subtract out the water vapor-phase absorption contributions. However, the condensed water layer thickness was time-

dependent, and its growth with time results in the broad featureless contribution that is seen in this formaldehyde spectrum. In order to compensate for the effects of this absorption band, we included a term equal to the sum of two Lorentzian line shapes in the fitting program. For the fitting process, the constants of each Lorentzian (amplitude, HWHM, and position) were independent parameters. The results of such a fitting approach are shown in Fig. 4 with the contribution from condensed water (green trace). The fit deviation (in purple), shown in the expanded scale, is flat within the noise, indicating that the long tail of the two-Lorentzian term adequately describes the condensed water spectral contribution. The concentration of formaldehyde calculated from this fit was $(82 \pm 9) \mu\text{mol/mol}$, or approximately AEGL-3 + 10 % for formaldehyde. We note that spectral contributions from formic acid have been previously observed in formaldehyde spectra [1]. In this case, the use of formic acid in the fit does not significantly change the results, and further analyses, discussed below, suggest that discrete formic acid is not present in the gas stream.

To corroborate the validity of using Lorentzian terms to model the shape of the condensed water spectrum, we examined the spectrum of water without the presence of formaldehyde (inset, Fig. 4). The absorbance of an air stream containing $6 \text{ g/m}^3 \text{ H}_2\text{O}$ at 7°C (in blue) shows contributions from both water vapor and condensed water. This absorbance spectrum was obtained using a background of purge air. These spectra were part of the same data set that provided the formaldehyde spectrum shown in Fig. 4. The two-Lorentzian term spectrum describing the condensed water, shown in the inset in green and overlaying the water spectrum, was obtained from the formaldehyde fit shown in Fig. 4. The long tail of the term fits the water spectrum very well, independently of an interfering formaldehyde spectrum.

The water condensate layer could vary with time and in some cases was not at a near-steady-state when the spectral data were obtained. For example, in Fig. 5a, the Lorentzian fits of the spectral amplitude for the condensed water film for one set of data were nearly constant, increasing a small amount with each succeeding data set. For another data set, shown in Fig. 5b, the amplitudes of the Lorentzian terms varied, increasing then resetting to a lower value before increasing again, and then repeating. In spite of these variations, the quality of the fit as measured by χ^2 was essentially the same for each fit using these models to compensate for condensed water.

Similarly, for the -5°C data, a broad absorbance band was observed in the same region of the spectrum, which was attributed to the presence of a thin film of ice [23]. The filtered-air water content in the FT-IR cell was calculated to be $\approx 0.5 \text{ g/m}^3$ based upon the measured water content in the dilution air flow and the mixing ratio with the analyte flow stream. While this is low enough to be considered dry air in the context of these tests, it evidently was enough to permit some ice formation in the cell. From our sequence of measurements, the possibility of ice on the FT-IR detector sensor could be ruled out. The shape of the absorbance spectrum of ice, while distinct from the condensed water spectrum in amplitude, position and width, is similar enough that the data could also be fit well with the inclusion of the two-Lorentzian term.

Other Confounding Factors

Formic acid is present in the secondary reference spectra; however, in this work its presence was not subtracted out. Formic acid is an impurity (degradation product) in the generation of the formaldehyde air stream, as noted in previous work [1]. The concentration of the formic acid was verified and tracked by fits in the range from 950 cm^{-1} to 1350 cm^{-1} where its absorption profile is stronger, employing the $5\text{ }^{\circ}\text{C}$ PNNL formaldehyde and formic acid primary references. Note that the PNNL reference spectrum is free of formic acid. A fit to the $-5\text{ }^{\circ}\text{C}$ secondary reference spectrum for formaldehyde that was multiplied to 200 $\mu\text{mol/mol}$ concentration, is shown in Fig. 6. The formic acid concentration is $1.25\text{ }\mu\text{mol/mol}$. Formic acid concentrations down to the level of $0.1\text{ }\mu\text{mol/mol}$ can clearly be detected in these fits. At AEGL-3 + 10 % concentration of formaldehyde ($77\text{ }\mu\text{mol/mol}$), this is equivalent to $0.5\text{ }\mu\text{mol/mol}$ formic acid, a level that was observed in much of our data. At this concentration, the presence of the formic acid spectrum affects the value of the formaldehyde concentration derived from the fits by 0.1 % or less.

The formic acid concentration was tracked in all fits. For the environmental tests at $7\text{ }^{\circ}\text{C}$ with 6 g/m^3 water, the spectral signature of the formic acid is not observed, resulting in an apparent concentration of $0\text{ }\mu\text{mol/mol}$. In its place, as shown in Fig. 7, is an unknown spectral contribution in the region 1000 cm^{-1} to 1090 cm^{-1} (and to a lesser extent, 1100 cm^{-1} to 1200 cm^{-1}). An inset in Fig. 7 shows the fit to formaldehyde in a purge air stream at $7\text{ }^{\circ}\text{C}$ obtained on the same day, with the formic acid contribution at a concentration of $\approx 0.25\text{ }\mu\text{mol/mol}$ clearly visible. The presence of this unknown spectral component implies that the formic acid does not necessarily dissociate or decompose in the presence of water (it does not match the spectral profile of common formaldehyde or formic acid reaction products such as methanol, carbon monoxide, carbon dioxide, methyl formate, or formic acid dimers), with the suggestion that a complex of some sort is formed in the presence of water vapor. We also note that this unknown spectral contribution was observed under other conditions. In addition to observing it at $7\text{ }^{\circ}\text{C}$ with $6\text{ g/m}^3\text{ H}_2\text{O}$, we also observed similar spectral features in spectra acquired at $45\text{ }^{\circ}\text{C}$ with 29 g/m^3 water and $33\text{ }^{\circ}\text{C}$ with 29 g/m^3 water. However, it was not observed in spectra obtained at $-5\text{ }^{\circ}\text{C}$ or at $33\text{ }^{\circ}\text{C}$ with 6 g/m^3 water [1].

The fitting program provided for shifting the x-axis of the data to best match the x-axis of the reference spectrum. This only affects fits for spectra with narrow features, as occurs with formaldehyde. Fig. 8 displays a fit that does not allow a shifting of the x-axis for formaldehyde at $(81 \pm 9)\text{ }\mu\text{mol/mol}$ and $25\text{ }^{\circ}\text{C}$, when fit to the $25\text{ }^{\circ}\text{C}$ PNNL reference spectrum. The inset shows an expansion of the fit. The deviation of the fit, (data-fit), is shown offset (in purple). The deviation for a fit allowing x-axis shifting is also shown (in blue). For this fit, the data were shifted on the x-axis by -0.044 cm^{-1} . The concentration obtained in the two fits changes by 0.33 %.

Lastly, we note that for all three analytes at all temperatures measured, including $33\text{ }^{\circ}\text{C}$ and $45\text{ }^{\circ}\text{C}$ reported earlier [1], the spectral line shapes of the analytes did not change in the presence of water vapor, and therefore high quality fits could be obtained with reference spectra that were developed in dry air. It should be noted that this is not necessarily always the case, as spectral linewidths are dependent upon the nature of the intermolecular interactions of the compounds in a bi-molecular collision. For example, panel (a) in Fig. 9

shows a fit to the CO₂ spectrum that exists in a test stream acquired during a formaldehyde test at 7 °C with 6 g/m³ water. The data (blue) can be seen to be broadened from the fit to the PNNL CO₂ primary reference spectrum in dry nitrogen [14] (red). The poor quality of the fit results in a predicted concentration that is high by about 20 %. Note that if the analyte transitions of interest were intermingled with the CO₂ absorption bands, fits to data containing water vapor would need a CO₂ reference spectrum with the proper width. The broadening of the CO₂ spectrum was essentially the same for both 6 g/m³ and 29 g/m³ H₂O at 33 °C, as can be seen in Fig. 9b. If the analyte under test exhibits line broadening as well, primary reference spectra that properly describe the broadening under varying conditions of temperature and water concentration would be needed.

Modification of Analysis Uncertainty

The determination of analyte concentration in this paper has employed measurement and analysis techniques designed to minimize the major sources of error, with the constraint of reliance upon existing reference spectral databases and libraries for the basis of determining analyte concentration. Some users employing this quantification approach may desire to introduce simplifying modifications of the procedures used here, since the resulting increase in the uncertainty of the analyte concentration may be acceptable for their purposes. Given here are typical consequences of modifications to the approach, as applied to the three analytes treated here, to serve as a general guide. The ranges given in concentration change reflect the variation of the concentration and of the test temperature of the data in the fits. The modifications will increase the χ^2 of the fit since the spectral profiles of the data then are not fit as well, increasing the measurement uncertainty. As this is a general guide to the effects, we also note that the observations below are specific to the analytes being studied, and the uncertainties introduced by simplifying the approach would need to be quantified on a case-by-case basis for application to other analytes and background conditions.

Inclusion of the CO₂ reference spectra was required for the fits as demonstrated with the ethylene oxide data (Fig. 3). Not including CO₂ in the fitting resulted in changes in the ethylene oxide concentration ranging from 0.1 % to 0.7 %. Changing the fit to a range from 970 cm⁻¹ to 1000 cm⁻¹ avoids most of the CO₂ and will reduce this bias to less than 0.1 %. This is to be compared to approximately 0.3 % uncertainty in the ethylene oxide concentration that results from the variation in the baseline between different fits that employed different wavenumber ranges for fitting. Inclusion of CO₂ is not needed in fitting acrylonitrile and formaldehyde, since in the fit ranges for these analytes any of the CO₂ transitions are very weak and are well below the noise level of the data.

The water vapor spectral lines appear only in the wings of the analyte spectra for the data ranges used in fitting the three analytes. These lines are usually small and are residual, since most of any water line is subtracted from the spectral data in the ratio process of forming the absorption spectrum. Ignoring the water lines in fitting these data results in a small shift in the baseline, with a change in the analyte concentration typically between 0.1 % and 0.7 %. In some of the ethylene oxide spectra that were acquired, the water line peak heights approximated that of the analyte itself, and the baseline shift was large enough to change the apparent analyte concentration by 2 % to 4 %. The reference spectrum for water at 25 °C

was adequate for fitting the data, particularly since it was not needed to calculate a quantitative result.

Inclusion in the fitting of the ability to vary the x-position of the data in the fitting process was needed here only for the formaldehyde spectrum due to its individually resolvable rotational sidebands (Fig.8), and remediated a systematic error of less than 0.5 % (in most cases, 0.3 % or less).

Instead of developing the secondary reference spectra as was employed in treating the data here, library reference spectra could be used for the fitting. Because of the temperature dependence of an analyte's spectral side bands, library reference spectra at temperatures as close to test temperature as possible will give the best fits to these bands. While the NIST database currently provides spectra only at 23 °C, the PNNL reference library provides 25 °C data for all of its listed chemicals, and 5 °C and 50 °C for many of the others [14].

Table 5 gives the fractional change in the analyte concentration for data at (−5, 7, 33 and 45) °C, when fit using PNNL reference spectra at (5, 25 and 50) °C, as appropriate. These reference spectra were deresolved as shown in order to provide the best possible fit to the line shape of the data. The fractional change comparison is to fits using the analyte secondary reference spectrum that was developed in this and the preceding paper [1]. The fractional change in concentration varied from less than 0.1 % to 2 %, with no consistent pattern. The χ^2 quality of the fit does not track well with the concentration differences and so is not included in the table. Increases in χ^2 by a factor of 40 were not unusual, and could be as large as 300 in an extreme case.

As expected, fits using analyte reference spectra at either 23 °C or 25 °C to fit the data results in larger systematic concentration errors. For the temperature span of the data shown in Table 5, differences could range from 0.5 % to as much as 4 %, for reference functions deresolved as shown in the table. Deresolving the reference spectra to the standard 0.4821 cm^{-1} sharpens the peak structures of the band which therefore allows fits to more closely follow the band envelope, and the result is that this decreases the concentration discrepancies by about 20 %.

While all of these effects produce a bias, in general they are not additive. For example, changes from ignoring water or CO₂ separately do not sum to the change seen if both are ignored. This result is typical for systems featuring independent sources of uncertainty.

Conclusion

This work extends the use of FT-IR absorption spectroscopy to evaluate the concentrations of toxic chemicals in vapor streams for use in testing at temperatures below laboratory ambient. Point chemical vapor detectors under test, to meet the requirements in ASTM standard specifications [2, 3], shall alarm for certain target analyte concentrations. Referee approaches, such as the one described in this paper, serve as an independent verification method for the quantification of analyte delivered to chemical detectors under test. Ultimately, the use of standard measurement approaches with documented uncertainties will facilitate the comparison of results between laboratories.

We have shown that for the test conditions (temperatures, humidities and toxic chemical compositions) specified in recent ASTM standard specifications, the measured spectra are not ideally matched to published reference spectra. For minimized measurement uncertainty, then, secondary reference spectra should be collected under controlled conditions using the same instrumentation, with the resultant measurements at the test conditions traceable to the standard reference spectra. In this work, published reference spectra at 23 °C or 25 °C were used to evaluate the concentration of single-component vapor streams that could then provide vapor streams of known concentrations at the required measurement temperature for the generation of secondary reference spectra. In those circumstances in which impurities are introduced into or produced by the generation of the target condition, such as the formic acid vapor found in the formaldehyde tests, reference spectra for the impurities may be employed to reduce the contribution of these spurious spectral features to the fit uncertainty and thus the overall measurement uncertainty of the target condition. Additionally, the low-temperature work resulted in spectra that included intensity due to condensed water or ice. The spectral line shapes of these interferences could be modelled with a sum of two Lorentzian line shapes, resulting in an excellent fit to the displacement of the spectral baseline and residuals that were within the spectral noise level.

This demonstration presents an extensive procedure for producing a reliable test referee for analyte vapor streams under specified environmental conditions with minimal uncertainty in the analyte concentration. We have examined several factors and their quantified effects upon the measurement uncertainty, in the event that the required uncertainty budget allows for the relaxation of certain testing and analysis parameters. Furthermore, while we used only a small subset of the possible toxic chemicals, we also note that this approach may be extended to other chemical analytes that have appropriate infrared absorption cross sections. While we have briefly discussed mitigating the effects of spectral interferences on the measurement uncertainty in the case of formic acid formation in the formaldehyde samples, for other gas mixtures of interest additional complications due to sample contamination may arise. Furthermore, reference spectra of acceptable quality for a given vapor of interest or suspect contaminant may be unavailable at relevant test conditions (e.g., temperature, humidity, background, etc.). In these cases, it may be possible to create secondary reference spectra specific to the complications encountered. Literature specific to gas mixture synthesis and reference spectra measurement could be consulted for additional approaches (e.g. [13, 24–26] and references therein). Following these procedures will ultimately enable an estimation of the uncertainty for quantification of the analyte in a test stream under diverse environmental test conditions.

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Figure 1.

A simplified schematic for the delivery and control of the test stream. The cooling coil and FT-IR cell are temperature-controlled using a liquid cooling/heating system. Other gas-flow lines in the sample chamber are insulated. Purge air (water- and CO₂-free) flows through the FT-IR bench and the sample chamber. DPG ≡ dew-point generator, mfc ≡ mass flow controller.

Figure 2.

An FT-IR spectrum of acrylonitrile at a concentration of $(189 \pm 5) \mu\text{mol/mol}$ in purge air at -5°C , as fit using the 25°C PNNL acrylonitrile reference. The residual deviation of the data from the fit is shown expanded by a factor of 3 and offset for clarity (top of three residuals). The center residual is from a similarly expanded fit using the 5°C PNNL reference data. The bottom residual was determined from a fit using the secondary reference spectrum collected at -5°C .

Figure 3.

An FT-IR spectrum of ethylene oxide at (382 ± 11) $\mu\text{mol/mol}$ in humid air at 7 °C. The fit used the 7 °C secondary reference, a 5 °C PNNL CO₂ reference, and a 25 °C PNNL H₂O reference. The fit is in red, overlaying the data in blue. The contributions of CO₂ in green and of H₂O vapor in navy, and the deviation of the data from the fit in purple, are shown expanded and offset.

Figure 4.

An FT-IR spectrum of formaldehyde at $(82 \pm 9) \mu\text{mol/mol}$, containing $6 \text{ g/m}^3 \text{ H}_2\text{O}$ at 7°C . Shown is the fit in red overlaying the data in blue, with a two-Lorentzian term describing the condensed water spectrum in green. The fit deviation in purple is shown expanded and offset. The inset shows the fit of the Lorentzian model for the spectrum of water without the presence of an analyte.

Figure 5.

The spectral amplitudes of the condensed water film for one set of formaldehyde data (a, AEGL-3 + 10 %) are shown to be nearly constant, increasing a small amount with each succeeding data set. For another data set (b, AEGL-2 + 10 %), the amplitudes of the Lorentzian term varied, increasing and decreasing throughout the data acquisition.

Figure 6.

A fit to the $-5\text{ }^{\circ}\text{C}$ secondary reference spectrum for formaldehyde that was multiplied to 200 $\mu\text{mol/mol}$ concentration. The formic acid contribution to the fit ($1.25\text{ }\mu\text{mol/mol}$) is offset for clarity.

Figure 7.

A spectral fit to determine the formic acid in the presence of the formaldehyde stream at 7 °C containing 6 g/m³ H₂O found no formic acid spectral contribution. An unknown spectral contribution in the region ranging from 1000 cm⁻¹ to 1090 cm⁻¹ (and to a lesser extent, 1100 cm⁻¹ to 1200 cm⁻¹) is shown. The inset shows the fit to formaldehyde in a purge air stream obtained on the same day, with the formic acid spectrum at a concentration of ≈ 0.25 $\mu\text{mol/mol}$ clearly visible.

Figure 8.

A fit that does not allow a shifting of the x-axis of the data, for a formaldehyde stream at $(81 \pm 9) \mu\text{mol/mol}$ and 25°C fit to the 25°C PNNL reference spectrum, with the inset showing an expansion of the fit. The deviation of the fit, (data - fit), is shown offset in purple. The deviation for a fit allowing x-axis shifting is shown in blue. The derived concentration from the two fits changes by 0.33 %.

Figure 9.

(a) A fit to the CO₂ absorption band associated with a formaldehyde spectrum obtained in air with 6 g/m³ H₂O at 7 °C. The data, in blue, are broadened with respect to the PNNL reference spectrum for CO₂ in dry nitrogen at 5 °C, shown in red (expanded in the inset). The deviations from the fit are shown offset below the spectrum. (b) Example of deviations from broadening of acquired CO₂ spectra at a different temperature (33 °C) and the

difference in deviations between two absolute humidities. The fits at 33 °C used the PNNL reference spectrum for CO₂ in dry nitrogen at 25 °C.

Table 1

Testing conditions for handheld point chemical vapor detectors. Reprinted, with permission, from ASTM E 2885-13 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 [2].

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 [5, 6] and fit ranges for the demonstration analytes.

analyte	30 min AEGL-2 ($\mu\text{mol/mol}$)	30 min AEGL-3 ($\mu\text{mol/mol}$)	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 3Additional contributions of uncertainty: $1u$

Source	Estimated uncertainty ($1u$)
Detector non-linearity *	1 %
Path length	0.5 %
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 [16].

Table 4

Final concentrations and fit variations for demonstration laboratory challenge streams. The variability in the fits is given as ± 2 standard deviations for $n = 8$ to 12 spectra.

Analyte	^a Target value ($\mu\text{mol/mol}$)	Concentration ($\mu\text{mol/mol}$), with variability	
		$-5\text{ }^{\circ}\text{C}$, dry	$7\text{ }^{\circ}\text{C}$, $6\text{ g/m}^3\text{ H}_2\text{O}$
Formaldehyde AEGL-3	77	78.4 ± 0.3	80.7 ± 0.2
Formaldehyde AEGL-2	15	16.7 ± 0.1	16.4 ± 0.1
Ethylene Oxide AEGL-3	378	378.6 ± 0.1	382.3 ± 0.8
Ethylene Oxide AEGL-2	84	86.3 ± 0.1	85.6 ± 0.1
Acrylonitrile AEGL-3	189	190.7 ± 0.1	190.1 ± 0.1
Acrylonitrile AEGL-2	116	119.6 ± 0.1	117.2 ± 0.1

^aTarget value calculated at 10 % (formaldehyde) or 5 % (ethylene oxide and acrylonitrile) over the AEGL concentration (see Table 2)

Table 5

The fractional change in the analyte concentration for data at (−5, 7, 33 and 45) °C from ‘Best Fit’, when fit using PNNL primary reference spectra at (5, 25 and 50) °C, as appropriate.

Analyte	Spectral Acquisition Temperature				Deresolution (cm ^{−1})
	−5 °C	7 °C	33 °C	45 °C	
Acrylonitrile	0.4 %	−0.7 %	−0.5 %	1.2 %	0.54
Ethylene Oxide	0.3 %	−0.6 %	1.7 to 2.3 %	1.9 %	0.55
Formaldehyde	0.9 to 1.5%	< 0.1 %	−0.3 %	−0.15 %	0.59