

Completely automated open-path FT-IR spectrometry

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Abstract Atmospheric analysis by open-path Fourier-transform infrared (OP/FT-IR) spectrometry has been possible for over two decades but has not been widely used because of the limitations of the software of commercial instruments. In this paper, we describe the current state-of-the-art of the hardware and software that constitutes a contemporary OP/FT-IR spectrometer. We then describe advances that have been made in our laboratory that have enabled many of the limitations of this type of instrument to be overcome. These include not having to acquire a single-beam background spectrum that compensates for absorption features in the spectra of atmospheric water vapor and carbon dioxide. Instead, an easily measured “short path-length” background spectrum is used for calculation of each absorbance spectrum that is measured over a long path-length. To accomplish this goal, the algorithm used to calculate the concentrations of trace atmospheric molecules was changed from classical least-squares regression (CLS) to partial least-squares regression (PLS). For calibration, OP/FT-IR spectra are measured in pristine air over a wide variety of path-lengths, temperatures, and humidities,

ratioed against a short-path background, and converted to absorbance; the reference spectrum of each analyte is then multiplied by randomly selected coefficients and added to these background spectra. Automatic baseline correction for small molecules with resolved rotational fine structure, such as ammonia and methane, is effected using wavelet transforms. A novel method of correcting for the effect of the nonlinear response of mercury cadmium telluride detectors is also incorporated. Finally, target factor analysis may be used to detect the onset of a given pollutant when its concentration exceeds a certain threshold. In this way, the concentration of atmospheric species has been obtained from OP/FT-IR spectra measured at intervals of 1 min over a period of many hours with no operator intervention.

Keywords Atmospheric monitoring · Open-path · Fourier-transform infrared · Automatic operation · Baseline correction · Wavelet transforms · Nonlinear response correction · Target factor analysis

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Introduction

Monitoring trace components in the atmosphere by open-path Fourier-transform infrared (OP/FT-IR) spectroscopy [1–3] has several advantages over competitive point-monitoring techniques. For example, because there is no need to collect the sample, the possibility of adsorption on to the walls of the container is precluded. No matter where the pollutant plume is located in the beam, it will still be observed. Furthermore, the instrumentation is transportable, so can be used to detect the presence of pollutants that were released during industrial accidents or the clean-up of toxic waste sites. Finally, since all species except monatomic or homonuclear diatomic molecules have absorption bands in

the mid-infrared spectrum, it is possible to monitor the concentration of any molecule that is believed to be present in the atmosphere; this is not the case for a technique like ultraviolet differential optical absorption spectroscopy (UV-DOAS). Even the presence of a molecule that is not expected to be present will be indicated in the OP/FT-IR spectrum. The first important example of this was shown in 1969 by Stephens, who observed the presence of peroxyacetyl nitrate (PAN) in the atmosphere of the Los Angeles basin by use of open-path infrared spectroscopy in 1969 (just before the development of commercial FT-IR spectrometers) [4]. PAN was subsequently shown to be an important intermediate in the formation of photochemical smog [5–7]. In light of its many advantages for atmospheric monitoring, it is valid to inquire why OP/FT-IR is so rarely used today.

The first drawback is the limit of detection (LOD), which for most molecules is between 1 and 100 parts per billion by volume (ppbv), whereas parts-per-trillion sensitivity is required in several instances. (For example, the use of OP/FT-IR to monitor accidental release of chemical warfare agents near incineration plants is of little use because the LOD required is in the parts-per-trillion range.) Second, much of the infrared spectrum is inaccessible because of absorption by water vapor and carbon dioxide. Even in the so-called atmospheric windows, weak lines in the vibration–rotation spectrum of water and CO₂ can present a significant interference. Of even greater importance, in our opinion, is the fact that the software of most commercial FT-IR instruments is by no means user-friendly and considerable spectroscopic expertise is needed in order to obtain accurate results. As a result, unattended operation in which the concentration of all species of interest is provided at intervals of, say, one minute has not been possible. In this article, we will give an overview of the existing hardware and software for OP/FT-IR spectrometry and show how unattended operation is possible.

Spectrometer configuration

There are two fundamentally different approaches to the measurement of OP/FT-IR spectra. In *bistatic* operation, the source is located on one side of the region to be monitored and a collimated beam of radiation is passed to a collecting telescope on the other side of this region (typically 100 to 500 m away). The collected radiation is passed into a two-beam interferometer from which it is focused onto a detector. Although this approach is efficient from an optical standpoint, electrical power is needed at both ends of the path, which can be quite inconvenient. Furthermore, when the path-length is long, unmodulated radiation from the surroundings may be measured along with the radiation

emitted by the source, giving rise to stray light and reducing the photometric accuracy of the measured spectra.

In the *monostatic* mode of operation, all equipment that requires electrical power is located in the same place. The radiation emitted by the source is collimated to a diameter of 3–5 cm and modulated by a two-beam interferometer. The modulated radiation that emerges from the interferometer is passed on to a beamsplitter where half the light is reflected into a telescope, which expands the beam so that it has a diameter of 20 to 25 cm (approximately the same diameter as for the bistatic instrumentation.) The reason for expanding the beam is to increase the collimation so that, even when the beam has traveled 100–200 m, it has not expanded by more than a factor of two. A retroreflector that is composed of an array of cube corner mirrors is located at the distal end of the optical path. This retroreflector reflects the beam back to the telescope that reduces its diameter back to 3–5 cm. This beam is then passed to the beamsplitter, where half the light is passed to the detector.

The detector for most OP/FT-IR spectrometers is a photoconductive mercury cadmium telluride (MCT) detector that is cooled to about 80 K either with liquid nitrogen (LN₂) or by a closed-cycle cooler. For unattended operation for periods of greater than 4 h, the latter option is greatly preferable. We have operated such an instrument for up to 24 h with spectra measured at a resolution of 1 cm⁻¹ at intervals of approximately one minute. Such measurements were made at a variety of ambient temperatures from below freezing to almost 40 °C. The number of spectra actually acquired was limited by the size of the computer hardware. Had we set up a telemetry system, there was no reason why measurements could have been taken for several days or even weeks. This type of hardware has been commercially available for over 25 years. In fact the instrument that we were using was well over 20 years old, although the data system was updated five years ago.

Software

The real advances in OP/FT-IR spectrometry have been in the software. The output of any FT-IR spectrometer is a single-beam spectrum that must be ratioed against a suitable background spectrum to yield the transmittance spectrum of the sample, $T(\nu)$. For quantitative spectrometry, the transmittance is converted to absorbance, $A(\nu)$, i.e. $-\log_{10}\{T(\nu)\}$. Until recently, the concentration of each pollutant was found using classical least-squares regression (CLS). For the best results with CLS, the background spectrum should be identical to the sample spectrum (i.e., be measured over the same path-length, with the air at the same humidity and temperature) but

with all pollutants absent. Several ways of achieving this goal have been described in the guidance document for OP/FT-IR monitoring [8] and Compendium Method TO-16 [9] published by the US Environmental Protection Agency (USEPA). However, none of these methods works well in practice and each requires considerable time to implement. To get around the problems imposed by the presence of atmospheric absorption lines, the USEPA recommends either the use of short spectral regions in which no lines caused by atmospheric water vapor absorb or that a single-beam background spectrum is used in which the intensity of the water lines is exactly the same as the single-beam sample spectrum. Several techniques for achieving this goal are outlined in the USEPA Guidance Document but, because the relative intensity of the H₂O and CO₂ lines is temperature dependent and because the humidity varies through the day, none of these approaches has been shown to be easily implemented in practice. Indeed, despite the fact that wide spectral regions are measured in FT-IR spectrometry, the USEPA Guidance Document states that OP/FT-IR is only useful for measuring one pollutant at a time using a short spectral region where no other molecule interferes. Furthermore, the actual region that is used for a particular pollutant can vary with the interferents that are present. This type of protocol makes it very difficult to set up an automated analysis procedure.

Hart et al. have shown that, in most circumstances, it is far better to calculate OP/FT-IR spectra by ratioing the single-beam spectrum measured over a long path to a background spectrum measured with the retroreflector only one or two meters from the telescope and converting this transmittance spectrum to absorbance [10–12]. In such spectra, features caused by atmospheric H₂O, CO₂, and CH₄ are still seen in the spectrum. Hong and Cho [13] reported a technique in which absorption by all atmospheric species except water were matched using the QASOFT library of vapor-phase reference spectra [14]. The water spectrum was calculated from the HITRAN database in the way reported by Müller et al. [15] assuming a Lorentzian line shape. The temperature and pressure were set to 298 K and 101,325 Pa, respectively, (although it should be noted that the ambient temperature can vary significantly, which will have a large effect on lines in the water spectrum due to transitions between energy states with high rotational quantum numbers, i.e. those lines most likely to interfere with OP/FT-IR measurements). Hong and Cho modified the software for conventional CLS regression so that the concentrations of all analytes were constrained to lie within reasonable values. Although this approach yielded better results than the protocols recommended by the USEPA, its implementation is still quite time-consuming.

Recent advances in OP/FT-IR software

The approach that we are using also uses spectra calculated using a short-path background spectrum but uses partial least-squares regression (PLS) rather than CLS, as recommended by Hart et al. [10–12], so that the presence of atmospheric interferences is taken into account. For the calibration set, a large number (>50) of single-beam spectra are measured in a pristine atmosphere under as wide a range of path-length, temperature, and humidity as possible. Each of these spectra is ratioed to a single short-path background spectrum and converted to absorbance to give a set of “atmospheric absorbance spectra”. Because the background spectra are measured with a very short path-length, it was always necessary to screen down the beam to ensure that the interferogram centerburst did not exceed the dynamic range of the analog-to-digital converter (ADC). The baseline of the atmospheric absorbance spectra is never at zero absorbance units (AU) and is often not completely flat. These spectra show strong features caused by atmospheric H₂O and CO₂ and weaker features caused by CH₄, for which the global average is about 1.8 ppm. The highest and lowest values of the product of path-length and concentration (subsequently referred to as the “pL product”) for atmospheric H₂O, CO₂, and CH₄ in the calibration set are such that they bracket the values found in all subsequently measured spectra. The effect of a varying baseline and varying intensities of the spectral features of H₂O, CO₂, and CH₄ caused by variations in their pL product and temperature is taken care of by the use of an adequate number of factors in the PLS calibration.

Calibration spectra are then synthesized from the set of atmospheric absorbance spectra by adding the reference spectra of each analyte of interest. The pL product of each analyte is varied randomly prior to adding its spectrum to a given atmospheric absorbance spectrum. Since the pL product of the reference spectra of each analyte is very accurately known, the amount of each analyte represented in each spectrum in the calibration set is known equally accurately. The fact that all the reference spectra were measured with the sample at a single temperature does not appear to significantly affect the accuracy by which concentrations can be predicted by PLS. Typically about 10 factors (eigenvectors) are required to model the background with an additional factor for each analyte [10, 12].

In practice, the best results in OP/FT-IR spectrometry are found when:

- interferograms exhibiting significant interference are rejected,
- interferograms are measured with an MCT detector with a linear response, and
- spectra have a flat baseline.

We have developed algorithms for ensuring that all these criteria are met. Each algorithm can be applied directly to the spectrum or the interferogram so that no operator intervention is required. Let us consider each in turn.

Several types of interference have been noticed during field measurements, ranging from electrical interference, to misalignment of the optics under very windy conditions, to interruption of the beam by a vehicle or a bird. The application of a high-pass filter to the spectral data eliminates the most common of these errors sources. In a few cases high-frequency, high-amplitude noise is introduced into the interferogram, presumably by some sort of electrical interference. Any interferogram for which the ratio of the signal at the centerburst to the root-mean-square noise level in the wings of the interferogram is less than a certain threshold value is rejected. The percentage of interferograms that are rejected is usually small except under very adverse weather conditions but the confidence in the analytical data in those interferograms that are retained is significantly increased [16].

It is well known that the response of MCT detectors can vary nonlinearly with photon flux in the region of the

interferogram centerburst. The effect of this nonlinearity is to offset the baseline of the corresponding single-beam spectra and hence to introduce a severe error in the absorbance of strong spectral features [17, 18]. When an error in the absorbance of strong water lines is introduced in this way, the quantitative accuracy of OP/FT-IR measurements can be severely degraded. The effect of a nonlinear response is seen primarily in the three most intense points at the interferogram centerburst. By adjusting the values of these points in a non-iterative manner, the effect of the nonlinear detector response can be compensated and the photometric accuracy is dramatically improved [19]. The effect of correcting the interferogram with a high-pass filter and correcting the values of the three most intense data points is shown in Fig. 1a through d.

OP/FT-IR spectra for which the interferograms have passed the rejection test and the effect of a nonlinear detector response has been corrected are then ratioed against a short-path background spectrum and the transmittance spectrum is converted to absorbance. As noted above, the baseline of OP/FT-IR spectra is never found exactly at 0 AU. We have found that if the baseline is corrected prior to

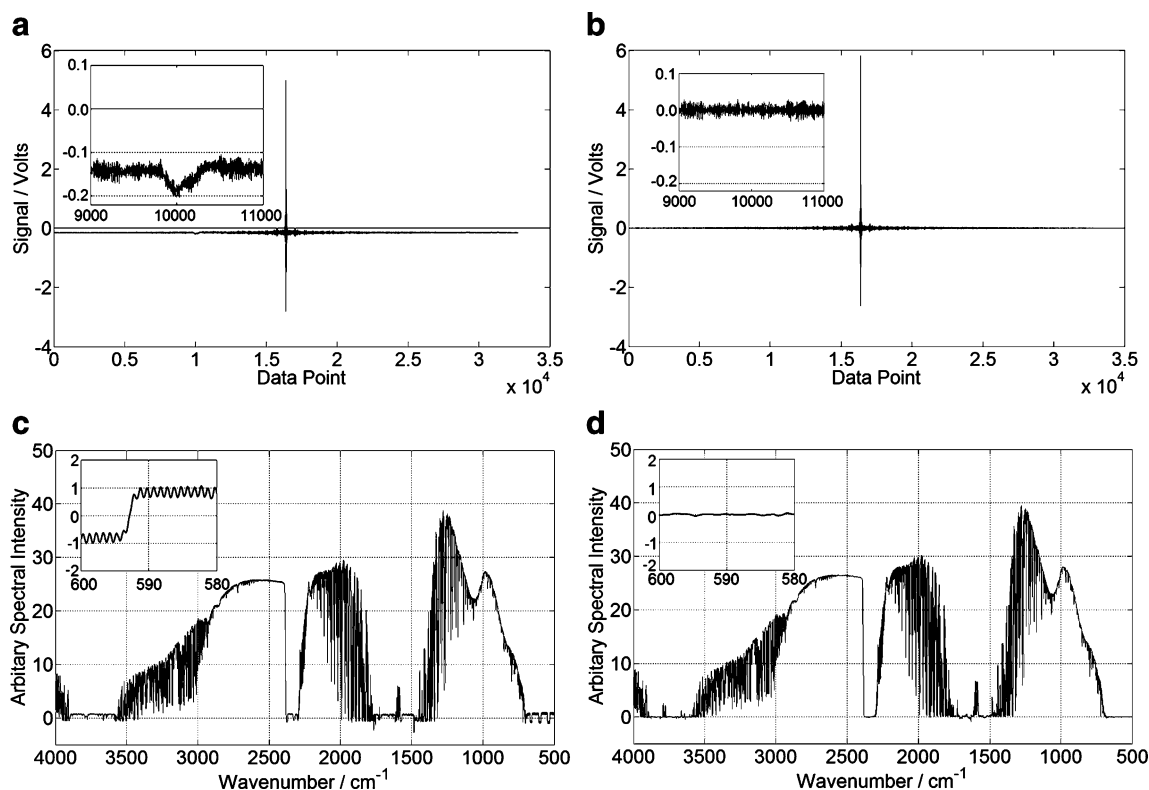


Fig. 1 (a) Experimental OP/FT-IR interferogram with obvious DC offset. Also seen (expanded in the *inset*) is an anomaly around data point 10,000 where the beam was interrupted, possibly by a bird, during one of the co-added scans. (b) Interferogram after high pass filtering and nonlinear detector response correction. The anomaly and dc offset have both been removed. (c) Single-beam spectrum calculated from the raw interferogram in Fig. 1a. The sinusoidal

interference seen in the *inset* arises both from the DC offset and the effect of interrupting the beam. The nonzero baseline due to detector nonlinearity is about -2.5% of the maximum intensity of the spectrum. (d) Single-beam spectrum calculated from the corrected interferogram in Fig. 1b, in which the sinusoidal interference and the nonzero baseline have been removed

quantification by PLS regression, more accurate results are obtained. Many algorithms for baseline correction have been reported but the one that we have found to be most suitable for automatic baseline correction of OP/FT-IR spectra of low molecular-weight analytes with resolvable rotational fine structure (e.g., CH_4 and NH_3) involves the application of wavelet transforms [20]. An example of automated baseline correction of an OP/FT-IR spectrum effected using wavelet transforms is shown in Fig. 2a and b.

Application of OP/FT-IR to agriculture

To illustrate the type of measurements that have been made by OP/FT-IR spectrometry using the software described above, our instrument was set up so that it observed the atmosphere above a field on to which liquefied manure (called “the product” by the farmer performing the application) was being sprayed. On the first day, the product was applied twice in quick succession and the field was not disturbed after the application. The variation of the concentration of ammonia over a period of about 14 h is shown in Fig. 3a; each individual measurement took about 70 s. Clearly a significant amount of the nitrogen content of the product is lost to the atmosphere. The same procedure was carried out four days later, but this time the product was

applied several times, with the field being ploughed by discing after each application; the result is shown in Fig. 3b. This time it is obvious that most of the nitrogen was incorporated into the soil.

Outlook

In 2000, we wrote an article entitled “Open-path FT-IR Spectroscopy: Is completely unattended operation possible?” [21] The developments described above show that this goal has now been reached. Whether or not this technique will achieve the popularity that was once believed to be possible is still an open question. Nevertheless, it is clear that many of

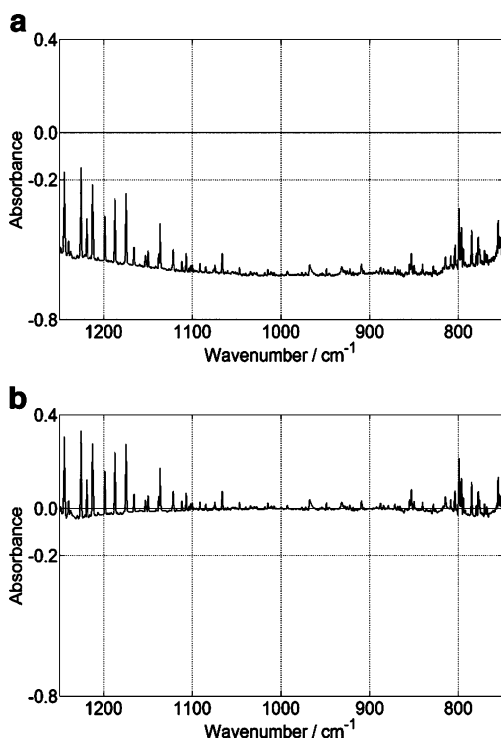


Fig. 2 (a) Absorbance spectrum obtained by ratioing the single-beam spectrum in Fig. 1c against a short path-length background spectrum. (b) Corresponding spectrum to the one shown in Fig. 2a after automatic baseline correction using wavelet transformation

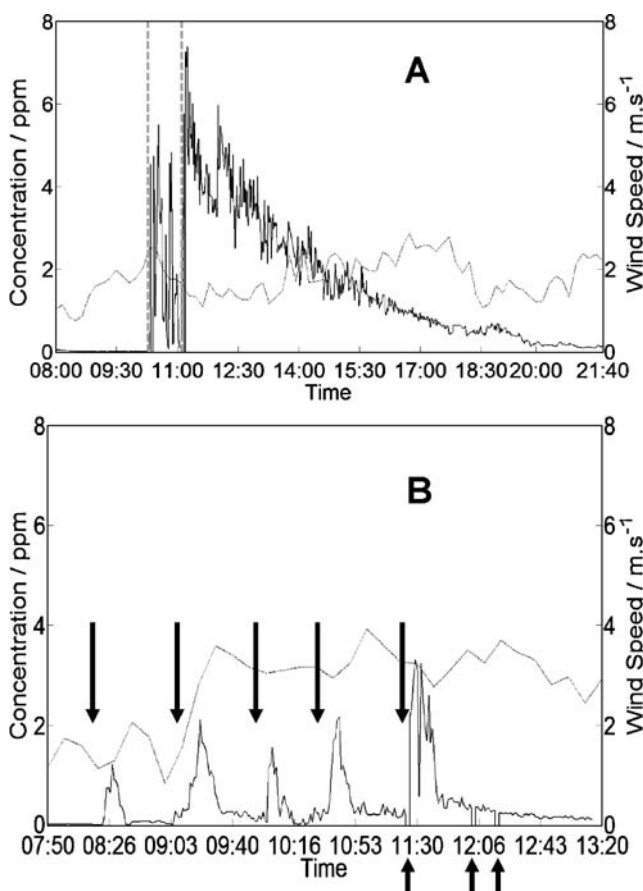


Fig. 3 (A) Variation of the average concentration of ammonia over a field to which liquefied manure was applied twice. (The broken lines in gray indicate starting time for the two applications.) The field was not ploughed after either application. Wind speed is also shown on this plot as the solid grey line. Six hundred sixty eight spectra were measured between 08:00 and 21:40. (B) Corresponding data taken four days later, where the field was ploughed immediately after the product was applied. The application and discing operation was done five times during the monitoring period, as shown by the downward-pointing arrows. For this plot, 276 spectra were measured between 07:50 and 13:15. Three spectra, shown by the upward-pointing arrows, were automatically rejected

the obstacles that caused its relatively low popularity have now been overcome.

Clearly OP/FT-IR spectroscopy is a powerful technique for atmospheric monitoring. It is our opinion that it has not been widely used for several reasons. The first is the software that was installed on commercial OP/FT-IR spectrometers, which required too much knowledge of advanced spectroscopy on the part of the operator. In practice, this type of instrument is only going to become widely accepted if it can be operated by a technician rather than a Ph.D. spectroscopist. Second, a background spectrum that could directly remove not only the instrument response spectrum but also the spectral features due to atmospheric species such as water and carbon dioxide was required, e.g., in the FTIR Open-path Monitoring Guidance Document disseminated by the USEPA [8]. Such spectra could rarely if ever be measured. Both of these drawbacks have been ameliorated in the software that we have developed and that is currently being used in our instrument. Finally, the hardware is bulky and heavy and typically requires at least two people to set it up. However, a reduction in size and weight would probably lead to a reduction in the optical throughput and hence a degradation in performance. We know of no simple solution to this problem. Provided that users are prepared to tolerate this drawback, we believe that OP/FT-IR spectrometry is a powerful and highly underutilized technique for atmospheric analysis.

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