

Fourier transform infrared optical remote sensing for monitoring airborne gas and vapor contaminants in the field

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Open path Fourier transform infrared spectrometric instrumentation, data analysis strategies and software, and field application strategies have been tested and applied to the identification and quantitation of gas and vapor air contaminants. These strategies and methods are described, along with descriptions of applications and areas requiring additional work.

1. Introduction

The Clean Air Act Amendments of 1990 indicate that the best available technology may be used in order to monitor for the presence of various atmospheric gaseous pollutants. This is a performance standard in contrast with the previous specification standard mandate to use the technology that is rigorously detailed in the Federal Register. The Clean Air Act Amendments also require that as many as 189 compounds may have to be monitored in the future.

In addition, there is a growing need to be able to determine the presence in real time of a potentially large number of compounds in the workplace. A related interest in rapid measurements has arisen from the requirement to monitor the remediation of hazardous waste sites. These unmet needs have created a renewed interest in the use of remote [or open path (OP)] sensors because they can generally measure many compounds simultaneously and quickly. Remote sensors are generally spectroscopic instruments that can use either dispersive or non-dispersive optics. This article presents an overview of the current use of one such instrument: the

Fourier transform infrared (FTIR) spectrometer. More specifically the technique discussed here uses a long open air path for the light beam, without the use of a fixed optical bench.

OP-FTIR instruments used to monitor atmospheric pollutant gases were originally discussed in the 1970's and early 80's [1-3]. Although these efforts were remarkably successful given the limitations of the instruments and their computers, the results were largely overlooked by the vast majority of the investigators concerned with air pollution monitoring. Then, in the late 1980's, because of improvements in instrumentation, use of the technique regained momentum, and today it is being vigorously pursued [4-6]. Over the past five years, more than 175 articles and presentations have been published in journals and proceedings. These cover almost every aspect of the use of closed gas cell and OP-FTIR instruments. Comprehensive review articles with extensive bibliographies have been, or will soon be published [7,8]. A guidance document concerning the use of OP-FTIR instruments has also been published [9]. This document contains an extensive bibliography and a glossary of terms, and is intended to be used as the foundation for the application of OP-FTIR systems.

In the USA, there are two commercially available instruments and more prototype instruments being developed. There is also one additional OP-FTIR that is available in Europe. These instruments all transmit a light beam across a long open path and use one of two primary optical configurations. The bistatic mode has the light source at one end of the path and the detector at the other. The monostatic configuration has the source and the detector at the same end of the path. When the monostatic mode is used, a reflector of some sort is used at the physical end of the path to return the beam to the detector. The return mirror can be one of several designs: a flat mirror, a 'cat's eye' design, a retro-reflector made up of 'corner cubes' and a retro-reflector that actually translates the beam a bit before it is returned to the detector.

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2. OP-FTIR principles

Internally, the heart of the FTIR sensor is a Michelson interferometer. A full description of this optical device is well beyond the scope of this article but many good descriptions are available [10,11]. The simplest interferometer design has two orthogonal mirrors, one of which moves. As the mirror moves each wavelength is at some point in constructive interference and at some point in destructive interference. Thus all wavelength intensities are modulated at a frequency that is dependent on the mirror velocity and on the wavelength itself. All monostatic configurations transmit the beam through the interferometer before it traverses the open air path. Thus, any black body radiation entering the system from the surroundings is suppressed by the modulation of the signal. The quantity that is actually recorded is the intensity as a function of the moving mirror position. This is called the interferogram. A Fourier transform performed on this interferogram results in the so-called single beam spectrum or the intensity as a function of frequency. Generally, the single beam spectrum is used for all further data processing.

The fundamental physical law that underlies the analysis is Beer's law, which states that the intensity of light traversing an absorbing medium decreases exponentially with the absorbance. The absorbance is defined as the product of the optical absorption coefficient, the gas concentration and the path length. Mathematically this is written as

$$I(\nu) = I_o(\nu) e^{-\alpha CL}$$

Beer's law indicates that a background I_o must somehow be measured if the concentration C is to be calculated. The background is the light intensity obtained when the absorbing gas is not present. The acquisition of the background spectrum represents a severe problem for the users of this technique since it is not possible to simply remove the pollutant gas from the atmosphere. Several schemes for obtaining this spectrum have been devised and all are potential sources of error. A common practice is to create a synthetic spectrum from a real atmospheric one. This is done by fitting a high order polynomial to the original spectrum in such a way that all the absorbance due to the particular gas of interest is removed. If data is taken at a small area source such as a small waste site or workplace, it may or may not be possible to take one spectrum on the upwind side of the site and use it for the background.

In order to actually calculate the concentration of the unknown gas, a reference spectrum is used. This reference spectrum is produced by measuring the absorbance of a known quantity of gas (usually at fairly high concentrations) in a cell that is short compared to the path length, or by filling a room with the gas standard of a known concentration [12]. The production of these spectra is not a simple chore and great attention must be paid to the details of the experimental setup. Once this reference is obtained it is used repeatedly any time that gas is measured in the atmosphere. The analysis procedure most commonly used is to perform a classical least squares analysis using the reference absorbance as the independent quantity. This analysis is done over a wavelength region that is selected by the operator [13,14]. The selection of the wavelength region tries to account for all known possible spectral interferences. The iterative least squares (ILSF) analysis has been developed to identify and quantify mixtures of unknown air contaminants [15]. However, as of this date, the ILSF method has neither been field tested nor generally adopted.

A limited set of reference spectra is commercially available for use with available commercial instruments. It should be noted that there are presently no prescribed procedures for the production of reference spectra. All the commercially available reference spectra have been taken at a single concentration and in a short cell. This puts two restrictions on the analysis. First, reciprocity must exist between the terms (concentration/path length) in the exponent of Beer's law and second, the system must be operating in a linear response region. These requirements seem to be fulfilled at the concentrations normally encountered in atmospheric measurements. Further discussion of this point can be found in the literature [16].

As the instruments are presently used there is no requirement to calibrate them on a routine basis. The one requirement is that the operator somehow must ensure that the instrument is responding properly to a known absorbance. At the present time, quality control and quality assurance procedures are only in the development stages. No consensus has been reached about how quantities such as accuracy or precision should be measured or reported. These questions are by no means trivial. For example, if the measurement is to be of polar or labile compounds, how does one prepare a standard sample that can be used repeatedly to determine the instrument precision? If the operator

wants to measure 15 compounds and each has to be prepared separately, will the precision and accuracy checks require so much time that only half the day can be spent acquiring actual data? The current effort seems to be an attempt to find a small, well-behaved subset of compounds that can be used for these purposes. Hopefully, measurement of these compounds will provide the end user of the data with sufficient information about the quality of the data.

The current state of the art of this technique is such that the detection limit for many compounds is in the 10–30 parts per billion range when using a path length of about 100 m and a 5-min data acquisition time. It is reasonable to claim that the overall instrument accuracy is in the 15–25% range, again depending on the compound. The instrument precision is quite good (about 5%) for single compounds that are free of spectral interferences [17].

3. Field applications of OP-FTIR

There are many potential uses of OP-FTIR. Currently there seem to be three areas that are receiving most attention. There is interest in developing the technique so that the emission rates of pollutant gases from area and stack sources can be measured. There is an interest in using the technique to make measurements of fugitive (spills or leaks) emissions in order to alert inhabitants of neighborhoods in the vicinity of waste sites or other producers of toxic gases (Fig. 1) [18]. Finally there is an interest in developing the technique for use in work areas to determine whether the workers are being exposed to unduly high levels of gases [19].

The OP-FTIR technique has both an advantage and a disadvantage over conventional point monitors because it makes a path integrated measurement. As applied to the determination of emission rates from area or point sources, this means a simplification of the mathematics required for the calculation [20,21]. As environmental control strategies are introduced it will be necessary to determine their effectiveness and one way to do that is to measure the emission rates from sources. Although the OP-FTIR can readily make a path integrated measurement, a cursory examination of the Gaussian plume model shows that air concentration measurements based on path integrated data may not be satisfactory for prediction of concentrations of those contaminants at receptor sites.



Fig. 1. Preparation of a Summa canister to collect air sample along an open path infrared beam at an industrial site fenceline in Delaware in 1988. The canister was transported along the beam path at a constant speed using the bicycle, thus obtaining a beam path averaged concentration sample. Shown are R. d'Simone (left) of MDA Corporation and Dr. G. Russwurm of ManTech Environmental. Dr. Russwurm was the cyclist. The instrument telescope is visible in the center.

What is needed is a measurement of the pollutant isopleths in the entire plane. Some inroads to accomplishing this are being made with the development of a tomographic technique using the OP-FTIR (Fig. 2) [22,23].

A large percentage of the publications that deal with OP-FTIR concern measurements at landfills, waste sites, and in the vicinity of industrial chemical areas [4,24–26]. Two peer-reviewed publications have shown the applicability of this method to the workplace [18,27].

These publications taken together show another advantage of the FTIR technique in that overall a large number of gases have been measured, albeit not simultaneously. During many of the studies described in the literature point monitors were used as a comparison technique. This comparison clearly shows that when the monitor is close to the source there can be a great variation of the pollutant concentration along the path. It is also clear that the concentration can change very rapidly as the wind shifts. These conditions make it imperative that measurements be made over a carefully chosen path and in a short period of time. Both of these requirements can be satisfied by the OP-FTIR instrument.



Fig. 2. Open path FTIR instrument from MDA, Inc. (now Environmental Technologies Group, Inc.). The instrument was equipped with a rotating turret for rapid beam movement, aiming and spectral acquisition. The instrument was set up for a room-sized computed tomography experiment using 56 mirrors and retro-reflectors. The experiment was performed at the University of California (Berkeley) Richmond Field Station in the summer of 1993. Pictured is Dooyong Park, doctoral student at the University of Michigan. Funding for this project is from NIOSH and the US DOE.

4. Future improvements

One of the difficulties of the FTIR technique is the impact of water vapor on the analysis. There is generally quite a bit of water vapor (percent levels) in the atmosphere and it is a spectrally interfering species that is present throughout the entire wavelength region. To overcome this, higher spectral resolution may be desirable, depending on the analyte and the concentration domain. This is being addressed by the manufacturers. There should shortly be moderately priced, small and rugged instruments available in the USA that have better than 0.5 cm^{-1} resolution.

The conditions under which reference spectra are produced need to be carefully examined and a production protocol needs to be written. This effort is being addressed along with a set of instrument performance specifications by a committee of the International Organization of Legal Metrology which is chaired by Dr. S. Chappell of the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

The Atmospheric Research and Exposure Assessment Laboratory of the US Environmental

Protection Agency is preparing an operational protocol for the production of OP-FTIR data with known quality. This document will, of necessity, cover the measurement of only a small number of gases. It will become part of the EPA compendium of methods on toxic organics.

Future trends, made possible through the availability of faster, lighter, higher throughput, more rugged instruments include the use of these systems for computed tomography of air contaminant concentration profiles, in the field, in real time. Issues that need to be resolved to accomplish this, not including the requirement for improved instruments, are PC-compatible software for tomography, faster PC's, the solution of the I(O) and the unknown analyte problems, incorporation of time-series and meteorological information into the software strategy, and the availability of self-training, self-diagnosing software for use by non-spectroscopists. In addition, a tool that can also be handheld is a worthy goal for the arsenal of air monitoring instruments.

5. Conclusions

The main advantage of the OP-FTIR technique is that there is no need for sampling lines, pumps and manifolds. Also, if software is available for the specific application, this is a true real time measurement method. It can provide the same accurate monitoring results as can be obtained from point measurement methods.

Furthermore, beam space sampling integrates sampling in both time and path. The method has great potential for saving manpower and reducing repetition of analysis, since the beam measurement integrates all spatial sampling points along the beam path. However, one of the principal challenges remains the assessment of the OP-FTIR information for its utility in assessment of worker and community exposure.

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