# Rejection criteria for open-path Fourier transform infrared spectrometry during continuous atmospheric monitoring

Limin Shao [a], Matthew J. Pollard [a,1], Peter R. Griffiths [a,*],
Dale T. Westermann [b], David L. Bjorneberg [b]

[a] *Department of Chemistry, University of Idaho Moscow, ID 83844-2343, USA*
[b] *USDA-ARS, NW Irrigation & Soils Research Laboratory, 3793 N 3600 E, Kimberly, ID 83341, USA*

## Abstract

Over 32,000 interferograms measured during open-path Fourier transform infrared (OP/FT-IR) measurements at dairy and hog farms were evaluated for anomalies. Five types of anomalies could be distinguished: a reduction in the interferogram intensity because of weather-related optical misalignment; an increase in the amplitude of interferograms measured with too short a path-length that leads to a non-linear detector response; a periodic interference caused by wind-induced vibrations; the presence of spikes in the interferogram; and an increase in the noise level of the interferogram (and hence of the spectrum) because of the effect of electrical interference. Prior to testing for the presence of anomalous data, each interferogram is subjected to a high-pass filter. A noise level index is then calculated from the wings of the interferogram and interferograms are rejected if the value of this parameter is too high. When the criteria developed in this project are applied, OP/FT-IR spectra may be measured at 1-min intervals over a period of several days.
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## 1. Introduction

With typical detection limits of ∼10 ppb for most volatile compounds [1], open-path Fourier transform infrared (OP/FT-IR) spectrometry is a sensitive, non-invasive technique for atmospheric monitoring. Analytes include hazardous air pollutants [2], airborne toxic industrial chemicals [3], and greenhouse gases [4]. The task of continuous, automated monitoring at high temporal resolution and over fairly long periods of time by OP/FT-IR spectrometry has been facilitated by the development of fast personal computers with large storage capacity.

In principle, OP/FT-IR measurements can be made continuously over periods of several hours or even days at intervals of ∼1 min. There are certain practical drawbacks to this technique, however. OP/FT-IR measurements may be affected by uncontrolled or unpredicted ambient factors such as wind, rain, snow, and dust; for example, wind can cause the optics to become misaligned and may enhance the concentration of airborne dust, while rain and snow attenuate the beam and increase the water content of the atmosphere, potentially decreasing the usable OP/FT-IR windows. Furthermore, the infrared beam may occasionally be interrupted by traffic or birds that completely or partially block the beam. Even though quality control (QC) or quality assurance (QA) procedures have been developed for OP/FT-IR spectrometry [5–7] these procedures may be quite difficult to implement when the instrumentation is unattended for extended periods of time. Depending on how the interferograms are affected, some may still contain useful analytical information, while others must be rejected or else they may potentially yield erroneous concentrations for the target molecules. In this paper, we distinguish between several categories of interference in OP/FT-IR spectrometry and propose ways in which those anomalous interferograms that contain useful data are retained while the others are rejected.

Several important issues for QC or QA protocols during continuous OP/FT-IR spectrometry can be cited. Firstly, the amount of data generated is large; continuous monitoring with interferograms measured once every ∼70 s (the condition under

* Corresponding author. Tel.: +1 208 885 5807; fax: +1 208 885 6173.
  *E-mail address:* pgriff@uidaho.edu (P.R. Griffiths).
[1] Present address: Department of Chemistry, Washington State University, Pullman, WA 99164-4630, USA.

which we run our instrument) generates over 1000 interferograms per day, or ~250 Mbytes in spc format (Thermo Galactic, Madison, WI). When the meteorological or environmental conditions are poor (high winds, dust, rain, snow, or fog), the percentage of invalid interferograms may be larger than 10%. Thus sometimes over 100 interferograms per day may have to be recognized as invalid and rejected when the measurements are made under conditions of inclement weather. Secondly, the ambient factors mentioned above could affect the true path-integrated concentration of the target molecules; for example a high wind could rapidly remove pollutants from the infrared beam. Thus simply rejecting an anomalous result because it appears to be out-of-line with the predicted concentrations determined immediately beforehand could lead to important atmospheric changes being missed. Thirdly, even for invalid measurements, the quantitative method could result in apparently normal, but nonetheless incorrect, concentrations being calculated. Thus distinguishing between "good" and "bad" results based solely on whether the predicted concentrations "appear" to be logical is, therefore, fraught with risk.

We have made a detailed investigation of over 32,000 OP/FT-IR interferograms measured in and around dairy and hog farms in Southern Idaho, USA, in conditions that ranged from calm, summer weather to cold, snowy, windy winter weather and we report the results in this paper. We found that interferences could be classified into five types based on how the interferogram or the resulting single-beam spectrum had been affected. From this study, an automatic exclusion procedure was developed to identify those interferograms that should be rejected. Our results have shown that most invalid OP/FT-IR interferograms could be identified and prevented from entering further process steps, even though the inteferogram may provide analytical data that appear to be correct. As a result of this process, data analysis of OP/FT-IR measurements and the interpretation of these results have been effectively and efficiently improved. After exclusion of the false results, the burden on the practical QC or QA is lessened considerably.

## 2. Experimental

OP/FT-IR measurements were carried out in June and July 2004, and January, March, and June 2005 on and around a dairy farm in southern Idaho in a cooperative project for monitoring gaseous emissions with the Northwest Irrigation and Soil Research Laboratory (NWISL) of the United States Department of Agriculture (USDA). The OP/FT-IR spectrometer was manufactured by MDA Corporation (Atlanta, GA), and incorporated a Bomem Michelson 100 interferometer, a 31.5-cm telescope, a cube-corner array retroreflector and a Sterling-engine-cooled mercury cadmium telluride (MCT) detector. Instrument control and data acquisition were done with GRAMS 7.00 (Thermo Galactic, Salem, NH). The distance between the telescope and retroreflector usually ranged between 50 and 150 m, but occasionally longer path-lengths were necessary. Every OP/FT-IR interferogram was measured at a nominal resolution of 1 cm$^{-1}$ by co-adding 16 interferograms. For simplicity, only those interferograms measured in the "forward"

direction were co-added; interferograms generated in the "reverse" direction were discarded. The data acquisition frequency, i.e., the frequency of the HeNe laser reference interferogram, was 20 kHz. All spectra for the analysis were computed with a zero-filling factor of 8 and Norton–Beer "medium" apodization. These measurement conditions were found to give an acceptable tradeoff between the signal-to-noise ratio (SNR) and time resolution for continuous monitoring.

The transmittance at wavenumber $\tilde{v}$, cm$^{-1}$, $T(\tilde{v})$, was measured by calculating the ratio of a long-path spectrum to a short-path background spectrum measured with the retro-reflector located one or two meters from the telescope and converting to absorbance, $A(\tilde{v})$, i.e., $-\log_{10} T(\tilde{v})$. For the short-path background spectrum, a metallic screen was placed over the entrance aperture of the telescope to attenuate the signal so that the response of the MCT detector varied linearly with the intensity of the interferogram. Absorbance spectra measured in this way showed many strong lines from the vibration–rotation spectrum of water and often had less than perfect baselines. Even so, provided that the variation in the intensity of the water lines, the air temperature and the baselines of the spectra in the calibration set covered the range of the these parameters in spectra measured in the field, good analytical data could be obtained by the partial least squares (PLS) regression technique described below.

The most commonly used algorithm to obtain quantitative data from OP/FT-IR spectra is classical least squares regression (CLS). However, for CLS to be applied accurately, only the information from one molecule should contribute to the spectrum in the region of interest [5]. Previous workers have developed a variety of ways to compensate for atmospheric water vapor lines in the spectrum so that they do not interfere with the absorption spectrum of the analyte(s) [5–7]. Unfortunately, none of these approaches is readily implemented to give automated removal of water lines from the spectrum and we have found that CLS regression is inappropriate for automated OP/FT-IR spectra measured under anything other than calm, clear conditions. We have shown that PLS regression overcomes many of the drawbacks of CLS for OP/FT-IR spectrometry [8]. Calibration spectra are synthesized by measuring single-beam OP/FT-IR spectra in a pristine environment (i.e., where no analytes other than atmospheric $H_2O$, $CO_2$, $CH_4$, and $N_2O$ are present in the infrared beam). These spectra are measured over different path-lengths, at different temperatures and relative humidities so that they represent the full range of conditions under which subsequent OP/FT-IR spectra are expected to be measured. Each long-path spectrum is then ratioed against a short-path single-beam spectrum of the type described in the previous paragraph and converted to absorbance. Reference spectra of each analyte are randomly scaled and added to the absorbance spectrum of the background and used as the calibration set for PLS regression.

Many factors contribute to the variance of the background, including the path-integrated concentration of atmospheric $H_2O$ and $CO_2$, the fact that all strong lines in the vibration–rotation spectrum vary with the path-integrated concentration of the analytes in non-linear fashion, the effect of temperature