

APPLICATIONS IN CONTINUOUS MONITORING OF ATMOSPHERIC POLLUTANTS BY REMOTE SENSING

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ABSTRACT

The development of Open Path FTIR for use in industrial settings has necessitated techniques for obtaining valid background spectra. Measurements over extended path lengths have resulted in greater problems with handling atmospheric moisture correction. Some industrial environments may even have almost continuous levels of chemical species present. Background correction techniques to address these problems employing a near-field source, a fixed reference, or a "rolling" reference, are presented and compared. Field experience obtained at several major plant sites over a year and a half of operation is reviewed.

INTRODUCTION

In the past few years continuous Open-Path FTIR monitoring of fugitive emissions at several industrial plant sites has been implemented successfully. These installations provide fugitive emission monitoring within production units, and fence-line monitoring around multiple production units and plant boundaries. Optical path lengths up to 450 m have been shown to be practical and give path-averaged limits of detection values (LOD) in the tens of ppbs for many organic vapors of industrial hygiene concern. Numerous papers in the past have addressed the use of least squares regression for quantitative analysis of multicomponent gas mixtures [1,2]. Most of these studies have reported on method development with gas mixtures measured in 10 meter gas cells where variables could be controlled, or in field studies where the spectra were processed off-line. These studies have shown that Open-Path FTIR can provide LODs acceptable for fugitive emission monitoring. To apply classical least squares regression (CLS), it is necessary to have a reasonably flat baseline; even a CLS method using first derivative spectra requires a negligible baseline shift between data points [1]. Thus, the ability to collect a valid reference spectrum will help assure a reasonably flat baseline and allow minimal residual errors in calculating concentrations. A universal method for obtaining a suitable background or reference spectrum has not been found. Also, the technique for obtaining a valid clean air reference spectrum to correct for water vapor and instrument response has not been fully addressed. The focus of this paper is to report on various methods for background correction that have been implemented and tested at a number of plant sites for real-time analysis of fugitive emissions.

BACKGROUND CORRECTION TECHNIQUES

Two methods of background correction were implemented for on-line data processing of spectra: the fixed reference and "rolling" reference. In addition to these two methods, this study compares data from a near-field source used as a reference. The best type of background correction depends upon the plant site to be monitored, the amount of contaminants normally present in the

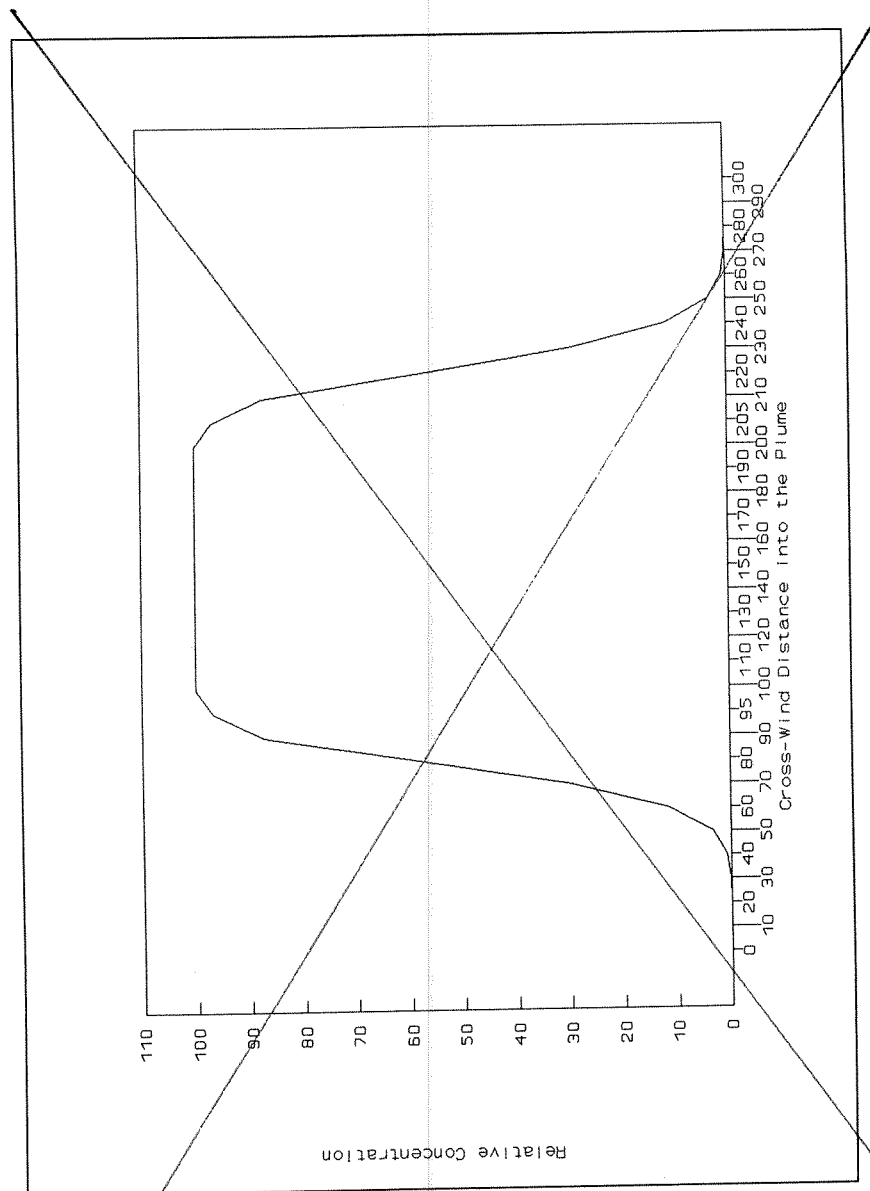


Figure 5. Cross-Plume Concentration Profile of a Typical Emission Plume from a Large Area Source

environment, and the frequency with which clean reference spectra can be obtained. Each of the reference techniques is discussed below.

Near-Field Source

The near-field source is an infrared source with the same temperature and emission characteristics as a corresponding far-field source. It is located no further than 2 m from the analyzer and provides for the collection of reference spectra that characterize the combined instrument and detector response. A reference spectrum is taken periodically from the near-field source and used to process the data from the far-field source. One advantage of this technique is the ability to correct for instrument and detector response. Also, there is little possibility of any target analytes being incorporated into the reference, due to the short path length. A disadvantage of this method is that all absorption peaks must be accounted for by the gas libraries used in the CLS algorithm. Due to the nonlinear response of the water vapor, multiple water library spectra at different concentrations are needed. Changes in water peak position and width due to changes in temperature and pressure will increase the residual error. Additional sources are also required to implement the near-field reference. The near-field source will work well in an application where there is little possibility of obtaining a clean reference from a far-field source.

Fixed Reference

A reference spectrum is collected from each source and examined visually for the presence of any target analytes before being saved as a fixed reference. The fixed reference corrects for detector and instrument response, as does the near-field source. However, this fixed reference also provides good correction for water vapor. The absorbance spectrum generated with this reference may contain positive or negative peaks due to changes in water vapor concentration over time; but, generally, water vapor influence is greatly reduced. The water vapor lines in the absorbance spectrum are reduced, and the remaining water vapor is accounted for with the library spectra. Seasonal changes or variation in instrument response will generally require a new fixed reference to be generated. In the proper environment, updating of the fixed reference once a month has been found to be acceptable. The main advantage of this method is that the reference is pure, without any contaminants.

After a fixed reference is acquired, changes in water vapor or instrument response will degrade the measurements. Also, new references must be updated manually, which requires analyzing the spectra to look for possible contaminants. This technique generally results in lower 3σ values than the near-field method and works well in environments where the air is moderately contaminated. This method is presently being used at only one plant site with the Miles FTIR.

Rolling Reference

The "rolling" reference method collects a reference from each source. After verifying that no contaminating gas peaks are present, the spectrum will be added in a weighted fashion to a "rolling" average spectrum for each source. The advantage of the "rolling" reference over the other methods is that it will have the best correction for water vapor, detector and instrument response, and the lowest residual error.

The main disadvantage is that it is possible that low levels of contaminants can work their way into the "rolling" reference over a long period of time and build up to high levels without alarming. The "rolling" reference is best suited to an environment where: 1) there is generally clean air, and 2) minimum detection limits are needed for alarming.

EXPERIMENTAL METHODS

The instrumentation consisted of Miles remote-sensing gas analyzers operating continuously at a number of plant sites. Data were collected with 1 cm^{-1} resolution at a scan rate of one interferogram per second using an MCT detector cryogenically cooled to about 77 K (operating in the 8-14 μm region). Both 16 and 64 co-added interferograms were used. The analyzer was operating in the bi-static mode using remote infrared sources of various configurations, which are summarized in Table 1. The path lengths of these sources varied from about 20m - 450m. The data presented are a result of approximately one-and-a-half years of in-field continuous monitoring of industrial plant sites.

Table 1. Infrared Source / Reference Type Summary

Number Installed	Reference	Distance (m)	Beam Steering Mirror	Temp. (C)	Source Mirror Dia. (inches)	COCl_2 3σ ppm - m
3	Rolling	60-80	Yes	450	14	0.5-1.5
1	Rolling	100	Yes	900	14	0.5-1.0
3	Fixed	170-310	No	900	14	2.0-6.0
21	Rolling	20-170	No	450	14	0.5-2.0
1	Near-Field	120	No	900	14	5.5
1	Rolling	450	No	900	20	2.0-4.0
1	Fixed	450	No	900	20	4.5-5.0
1	Near-Field	450	No	900	20	4.7-5.2

The main constituent of interest was phosgene (COCl_2). Data were processed using first derivative absorbance spectra with a CLS algorithm. To account for interfering gases, a library of 16 spectra was used. Table 2 lists these spectra and the corresponding typical 3σ for one installation using a 450 C source and a 100 m optical path with 16 co-added interferograms. The relative 3σ levels between gases will remain the same for the different combinations of source temperature, size, and optical path. The library spectra were generated on one instrument and used for all other units in the field.

Table 2. Library Spectra and Typical 3σ Values from a 100m Path with a 450 C Source.

Library Gas Name	3σ
1,1,1-trichloroethane	9.8
acetone	61.1
ethylene	4.0
carbon-tetrachloride	5.5
Freon-11	1.1
Freon-12	1.5
Freon-141B	5.2
Freon-22	2.6
phosgene	1.5
ethyl acetate	11.8
ethanol	29.6
water vapor	0.4
chlorobenzene	7.4
methanol	0.7
ammonia	3.8
vinyl chloride	4.1

EXPERIMENTAL RESULTS

Typical transmission spectra collected from a source at 450 m and 120 m are shown in Fig.1. The low frequency variation in the baseline is a result of the polyethylene windows used in the sample cell. These spectra represent typical data that are to be processed using the various reference techniques. The spectra contain water vapor and ammonia peaks where the ammonia is most pronounced in the 450 m source spectrum. The relative strength of the water peaks is strongest in the 450 m spectrum.

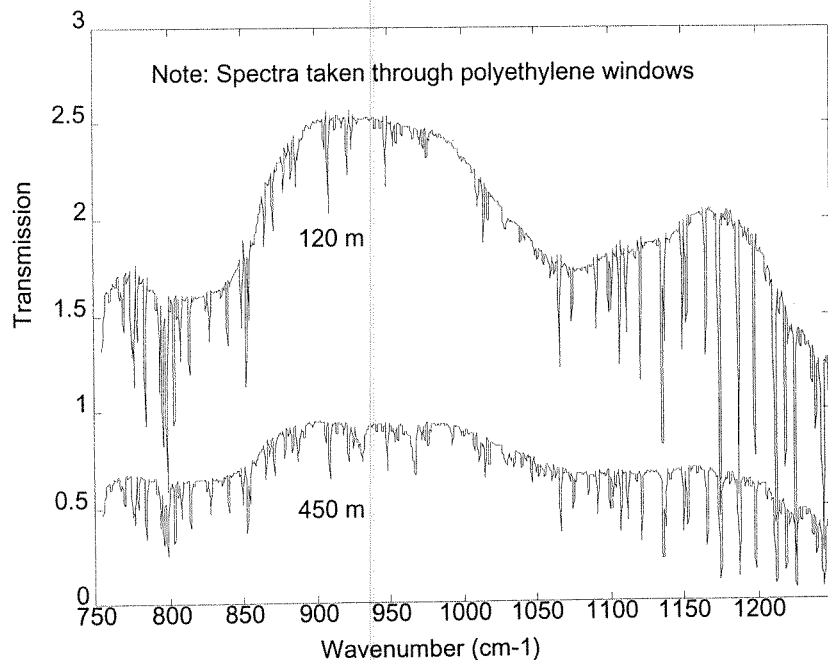


Fig. 1. Infrared Source - Transmission Spectra

Figure 2 shows a near-field reference for a spectrum taken over a 450 m path. The corresponding absorbance spectrum is also shown. This figure illustrates the ability of the near-field reference to correct for instrument response, such as detector fringing. This fringing, present in both the reference and incoming spectrum, is not seen in the absorbance spectrum.

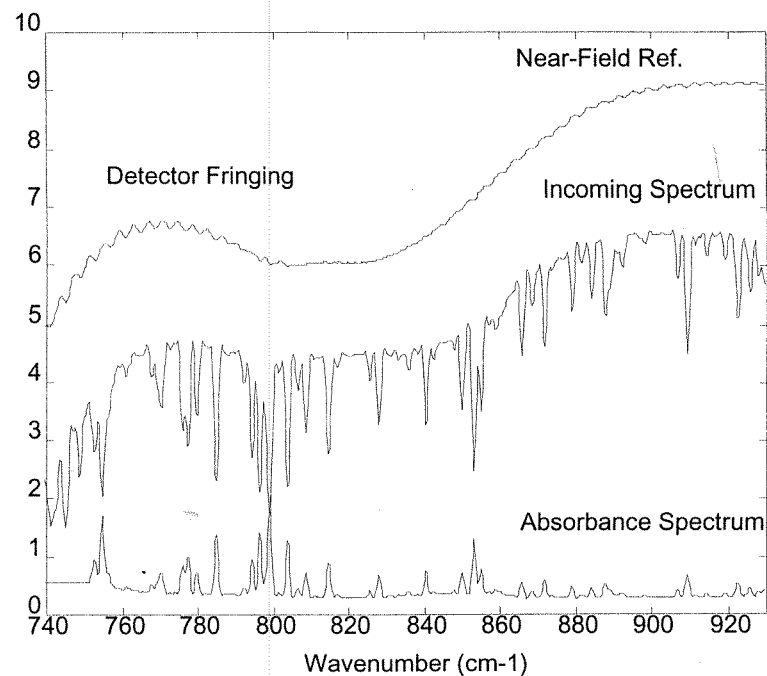


Fig. 2. Near-Field Reference / 450 m Path Incoming and Absorbance Spectra

The spectra in Fig. 3-6 represent phosgene samples prepared with standard gases and are not fugitive emissions. They are used to illustrate the effectiveness of the various reference techniques. Figure 3 shows a typical spectrum processed with the near-field reference. Water vapor and NH_3 have been subtracted from the original spectrum to produce a phosgene peak. The phosgene has then been subtracted from the original spectrum resulting in the residual error of the measurement. Data were collected over a 450 m path and, in this particular case, provided good results. The calculated concentration of the phosgene was 15.7 ppm-m with a 3σ of 5.23 ppm-m, produced from a gas sample measured to be 15.4 ppm-m with a secondary technique. Path-averaged over 450 m, this results in an LOD of 11.62 ppb.

If the incoming spectrum does not match well with the water vapor libraries, the results can be poor when using the near-field reference. Figure 4 shows the phosgene peak after water vapor and NH_3 have been subtracted. The residual error still contains water vapor and NH_3 . The measured value of phosgene was 4.83 ppm-m with a 3σ of 6.74 ppm-m. The chemical analysis produced a value of 7.7 ppm-m. Path-averaged over 450 m, this results in a lower detection limit of 14.98 ppb.

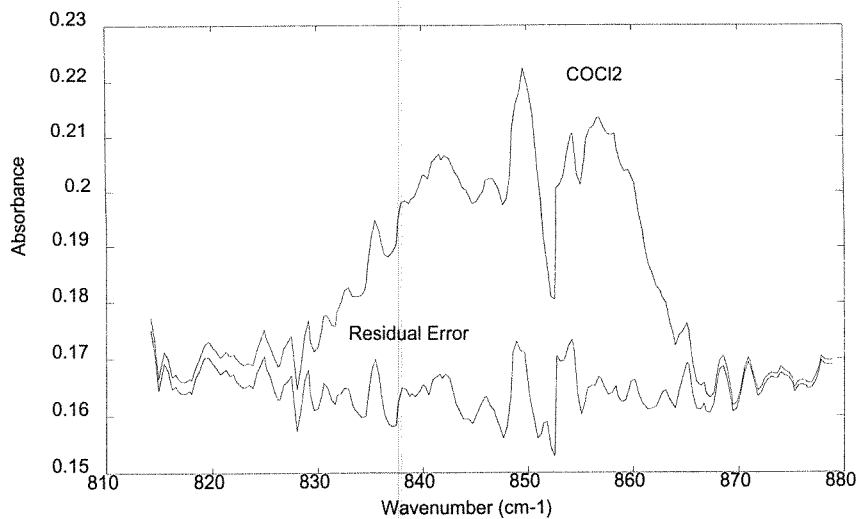


Fig. 3. 15.4 ppm-m Phosgene Spectrum and Residual Error / Near-Field Reference / 450 m Path

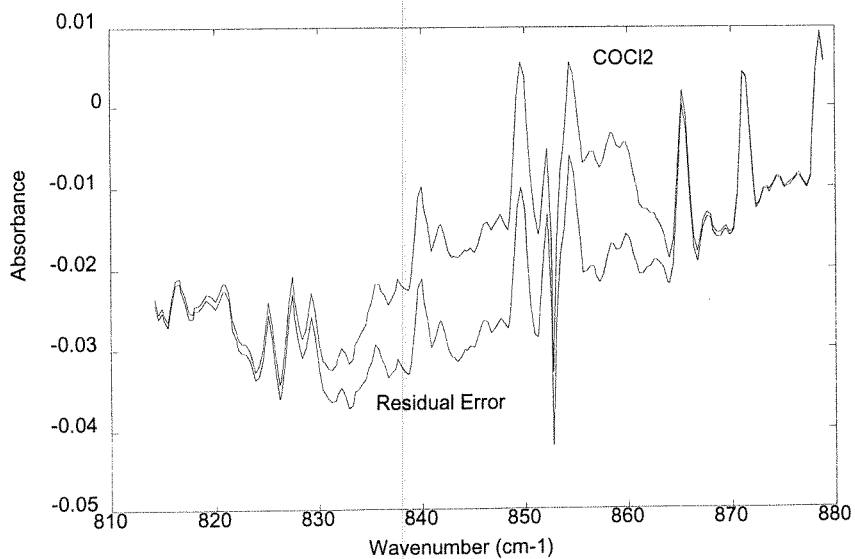


Fig. 4. 7.7 ppm-m Phosgene Spectrum and Residual Error / Near-Field Reference / 450 m Path

The following spectrum was produced with the "rolling" reference, which in general gives the best results. The phosgene peak with water vapor and NH_3 subtracted is shown in Fig. 5. The "rolling" reference accounts well for the water vapor, which is evident by the well-defined structure of the phosgene peak. The calculated values were 7.97 ppm-m with a 3σ of 2.63 ppm-m. Chemical analysis produced a concentration of 7.7 ppm-m. Path-averaged over 450 m, this results in an LOD of 5.84 ppb.

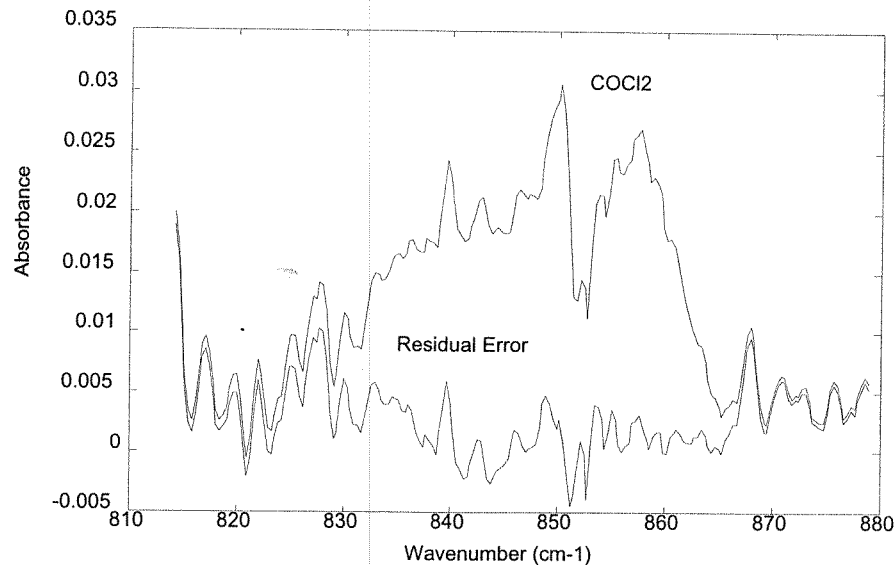


Fig. 5. 7.7 ppm-m Phosgene Spectrum and Residual Error / Rolling Reference / 450 m Path

A disadvantage of the "rolling" reference is the possibility of averaging low-level gases into the reference. This is shown in Fig. 6, where NH_3 peaks are present in the reference, and a lower concentration of NH_3 is present in the incoming spectrum, resulting in negative-going absorbance peaks. In this case, only the measurement of phosgene is important; therefore, the presence of negative peaks can be accounted for by the CLS algorithm and are not a factor in the phosgene concentration calculation.

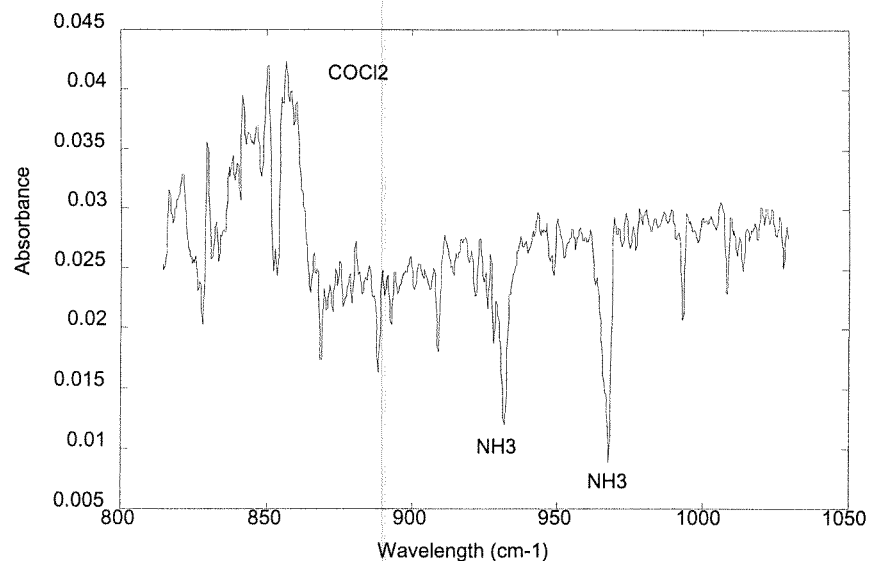


Fig. 6. Over-Subtraction of NH_3 in Spectrum with Rolling Reference / 450 m Path

CONCLUSION

The choice of reference type depends on the particular application. In general, the best results were obtained from the "rolling" reference. The fixed reference gave the second best results, followed by the near-field source. Both the fixed reference and near-field reference would benefit from the application of multiple water vapor libraries at various concentrations.

The "rolling" reference technique could be improved by having a robust qualitative gas detection algorithm, to eliminate the possibility of gases being averaged into the reference. Also, detection limits would be improved by having segmented "rolling" references for each gas band that would be updated individually if the incoming spectrum in each band was free of any absorption peaks. Altogether, these three techniques can provide adequate detection of fugitive emissions for the majority of industrial plant environments.

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Open-Path FTIR and UV DOAS Performance and Regulatory Acceptance Standards I