

## Op-FTIR Quality Assurance

This document presents the Quality Assurance protocol used for the measurement of broad spectrum Op-FTIR spectra according to the guidelines given by the United States Environmental Protection Agency and other agencies that certify the calibration, operation and maintenance of broadband spectroscopy related to the sampling of the atmosphere. It should be noted that TO-16 is a generic document that covers the operation of Op-FTIRs and is not instrument specific. Therefore the protocol is based on the key elements of the document as they are applied to the CEREX Op-FTIR monitoring system and the application of a long-term fenceline monitoring system at an industrial facility. The following items as they pertain to the operation of the Op-FTIR fenceline monitoring systems:

- Evaluation of optimal detection limits for chemicals of interest
- Measurement of the impact of stray light and detector non-linearity
- Measurement of Root Mean Square (RMS) noise
- Measurement of gas concentration of ambient gases (N<sub>2</sub>O, Methane, and CO)
- Measurement of gas concentration of QA test gas (SF<sub>6</sub>)

Further information as to the relevant portions of the EPA's TO-16 Reference method are included as Appendix A.

### **Evaluation of optimal detection limits for chemical of interest**

TO-16 states that one method of determining the detection limits of chemical is to take 17 single beam spectra and ratio them sequentially to obtain 16 absorbance spectra. Then each gas should be quantified with the absorbance spectra. The detection limits for each gas are obtained by taking the average of the 16 results. Although this method will yield a detection limit result, CEREX has traditionally used the statistical analysis information yielded by its quantification software. The rationale behind this is it is consistent with the real-time and post-analysis software.

The procedure to evaluate the detection limits using this method is as following:

- Create an absorbance spectra using two back to back single beam spectra
- Perform a linear regression analysis using the absorbance spectra as the dependent variable and the quantitative reference spectra as the independent variable
- Record the 95% confidence interval of the resulting analysis
- Multiply the confidence interval by the concentration pathlength of the reference spectra to obtain the detection limits

If the detection limits do not include 0 in the 95% confidence band, a different reference region should be selected.

## Results of Detection limit Evaluation

### North Fenceline Results

Gas	Ref Conc (ppm-m)	-0.95	ppm	0.95
Phenol	100	-8.9E-05	-0.0383	0.000617
Butadiene	100	-0.00018	-0.00058	0.000814
Ethylene	100	-0.00171	0.00557	0.012850
MTBE	100	-0.00408	-0.00024	0.003596
Carbonyl				
Sulfide	100	-0.00156	0.00177	0.005098
Ethanol	100	-0.00983	-0.00625	-0.00267
Napthalene	100	-0.02154	-0.01038	0.000788
NH3	100	-0.00105	0.000852	0.002754
Mercaptin	100	-0.07130	0.312387	0.696079
MEA	100	-0.00407	-0.00183	0.000403
Pentane	100	-0.17353	0.064041	0.301615
Hexane	100	-0.14471	0.02105	0.186813
Octane	100	-0.07883	-0.02903	0.020771
Butane	100	-0.24485	-0.07026	0.104323
Ethane	100	-0.05164	-0.00889	0.03385
Propane	100	-0.07375	-0.00264	0.068476

### South Fenceline Results

Gas	Ref Conc (ppm-m)	-95%	ppm	95%
Phenol	100	-0.36938	-0.0357	0.297984
Butadiene	100	-0.00258	0.015685	0.033948
Ethylene	100	-0.01152	-0.0021	0.007325
MTBE	100	-0.016	-0.01006	0.00371
Carbonyl				
Sulfide	100	-0.00162	-0.00016	0.001304
Ethanol	100	-0.0008	0.005588	0.011978
Napthalene	100	-0.02404	-0.00866	0.006707
NH3	100	-0.00336	-0.00106	0.001244
Mercaptin	100	-0.37368	0.06559	0.504881
MEA	100	-0.00032	0.003165	0.006652
Pentane	100	0.000138	-0.05287	0.000954
Hexane	100	-0.05287	-0.20261	0.308847
Octane	100	-0.20261	-0.03499	0.04977
Butane	100	-0.03499	-0.18961	0.040836
Ethane	100	-0.18961	-0.07001	0.076204
Propane	100	-0.07001	-0.05139	0.00493

## **Measurement of the impact of stray light and detector non-linearity**

The effects of stray light and detector non-linearity will result in inconsistencies with data quantification. This being the case it is important to evaluate the magnitude of these sources of light as they relate to the overall light spectra of a single beam. In the CEREX Op-FTIR air monitor, stray light is minimized by inserting light absorbing material (echosorb) inside the body of the air monitor. In addition, stray light from external sources (black body radiation) is minimized because the IR beam is modulated before it is sent out into the open air. Finally detection non-linearity (which is measured at the elbow of the single beam spectra around 600 wavenumbers) only becomes prevalent when the signal is 60% of the full spectra intensity of the detector. At the ConocoPhillips refinery, the signal has never been more than 20% of the full scale. Thus there is no impact of detector non-linearity.

## Root Mean Square Noise

Site Location: Conoco South  
Collection Time and Date: 03/16/2005 11:20 am  
Sample Spectra Name #1: QA March 1  
Sample Spectra Name #2: QA March 2  
Absorbance Spectra Name: ABS March 2

		<u>RMS Noise</u>
Region of Interest	968-1008	0.010054
	2480-2520	0.017669

Site Location: Conoco North  
Collection Time and Date: 03/16/2005 13:20 pm  
Sample Spectra Name #1: QA March 1  
Sample Spectra Name #2: QA March 2  
Absorbance Spectra Name: ABS March 2

		<u>RMS Noise</u>
Region of Interest	968-1008	0.0102
	2480-2520	0.006126

## Measurement of gas concentration of ambient gases (N<sub>2</sub>O, Methane, and CO)

As part of an on-going measurement program, the atmospheric background gases can be monitored as an on-going check of sampling. The natural atmospheric background level of nitrous oxide and methane is monitored along with the analytes of interest. The atmospheric background level for nitrous oxide is around 0.300 ppm +/- 10%. In the absence of external sources of methane gas, the atmospheric background concentration is around 1.7 ppm. These atmospheric gases should remain relatively constant throughout the entire monitoring period in the absence of other sources. The results of quantification of N<sub>2</sub>O, Methane and CO are presented below:

### Ambient Concentration South Fenceline

Gas	Ref Conc (ppm-m)	Ambient Concentration (ppm)
CO	100	0.379243496
Methane	100	1.799944247
N <sub>2</sub> O	100	0.255048886

### Ambient Concentration North Fenceline

Gas	Ref Conc (ppm-m)	Ambient Concentration (ppm)
CO	100	0.299536419
Methane	100	1.654248186
N <sub>2</sub> O	100	0.241717634

## Measurement of gas concentration of QA test gas (SF6)

CEREX has developed an external cell that can be filled with a test gas. Because of its availability on-site, the test gas used for the calibration was Sulfur. The gas is tested using the FTIR's external gas cell and the small mirror fitted to the telescope window. Results of +/- 10% difference in the gas cell results are acceptable. In the event the results are >+/- 10% the entire system shall be checked out and the test rerun. If sufficient corrective action cannot be taken in the field, the system will be returned to the laboratory and corrective action taken.

Site	Actual Ref Conc (ppm)	Concentration (ppm)
CP-North	10	9.87
CP-South	10	9.62

# Appendix A FTIR Quality Assurance

## Introduction

This appendix presents the key elements of the Quality Assurance (QA) protocol outlined in EPA's Reference Method TO-16. The reference method provides a generic outline of critical elements associated with QA in a general format. Thus this supplemental document is presented to highlight specific elements of TO-16 as they pertain to the operation of a CEREX Op-FTIR air monitoring system.

Broadband spectroscopy refers to the measurement of spectral regions that include a large portion of electromagnetic energy. For the purpose of this document it specifically refers to the measurement of light energy between the range of 600-4200 wavenumbers in the infrared spectral range. The measurement of the spectral regions result in what is typical referred to a single beam measurement. This single beam spectrum contains all the information needed about the absorbing compounds in the light path. However, before quantitative analysis of the spectrum can occur, a few transformations of the single beam spectrum take place. First a single beam background spectrum is generated. This is essentially a single beam spectrum that does not contain the target absorbing gases. Physically this can be taken by taking spectra from upwind of a plume being monitored. By dividing the original single beam spectrum by the background, a transmission spectrum is obtained. The negative logarithm of this spectrum gives an absorption spectrum. This is used for further analysis as all reference spectra available in libraries are in this form.

The specific topics this document are as follows:

- Selection of a target analyte list
- Quantification Methodology
- Background Generation Methodology
- Data Review and Quality Control

## **Selection of a target analyte list**

The development of an analyte list is determined before sampling begins. A list of target analytes are part of the sampling plan. The predetermined analyte list is used to create the analysis script used to compare absorption spectra collected by the air monitor and the reference spectra used to correlate concentration data.

Script file generation begins with examination of the absorption spectrum of the target gases. The entire absorption feature (end points at <1% of peak absorption where possible). In the case of the Op-FTIR, the spectral feature should be chosen with the highest absorption coefficient that is outside of the water vapor and carbon dioxide absorption bands is the most likely to be selected for analysis of that gas. If a known interfering gas has spectral features that overlap the features of interest of a target compound, it should be taken into account during the analysis. This is accomplished by configuring the analysis script to co-test for interference. A different absorption feature should be chosen if the interfering gas(s), absorbance coefficient is >5 times larger than the absorption coefficient of the compound of interest. In the event that another free absorption feature is not available, then the existing feature must be used.

## **Data Quantification Procedure**

The analysis of broadband spectra follows a methodology, which is covered in more detail in the guidance documents mentioned above. An outline of this methodology is as follows:

1. Generate a single beam file that is used as a background.
2. Using the background file, create an absorbance spectra by ratioing the background file to the data file.
3. Compare the residual spectral features to a set of reference library spectra.
4. Based on this comparison, determine the gases in the atmosphere as well as their concentration.

## **Methods of Generating a Background file:**

As explained in EPA's TO-16 Guidance document, there are a number of methods used to generate single beam background files. The method that is chosen should be based on the method that consistently produces the lowest detection limits for the analyte in question. The methods that are commonly used include the following:

- Long path clean air background spectra
- Zero path clean air spectra
- Updated background

### **Background Generation Method #1 – Long Path Clean Air Background**

Depending on the monitoring situation, it is sometimes possible to obtain a single beam spectra using data taken there was no contribution from the source. Examples of this type of scenario include:

- If the monitoring event is a worksite, data taken during work inactivity.
- Monitoring the wind direction and using a single beam spectra at a time when the wind direction was away from the source.
- Using a background that was taken in an area with "clean air"

### **Background Generation Method #2 – Zero Path Clean Air Background**

This technique involves placing a reflective surface such as a mirror or a retroreflector within 1 meter of the output telescope. In order to ensure that any detector non-linearity effects take place, the signal strength be less than 4,000 counts. When using a zero path background, the script file should include a site specific water vapor spectra as an interferent.

### **Background Generation Method #3 – Automatic Updated Background**

The current versions of the CEREX Op-FTIR software has the capability to update the background when the software does not detect the presence of the analyte.

# Data review and Quality Control

## Tracking Atmospheric Gases

The analyte list should also be used for QC and gases that are normally found at natural atmospheric background levels by the instruments. These atmospheric background gases can be monitored as an on-going check of sampling. The natural atmospheric background level of nitrous oxide and methane is monitored along with the analytes of interest. The atmospheric background level for nitrous oxide is around 0.300 ppm +/- 10%. In the absence of external sources of methane gas, the atmospheric background concentration is around 1.7 ppm. These atmospheric gases should remain relatively constant throughout the entire monitoring period in the absence of other sources.

## Noise Equivalent Absorption - Root Mean Square (RMS) Noise

RMS noise is used to determine the inherent noise of the system. This is an important QA element as it determines the detection limits for the gases of interest. The procedure to measure RMS noise is to collect two successive single beam spectra. The spectra should simulate the standard field setup including the following:

- A typical path length for the equipment (100m, 200 m etc.)
- A typical sample time for each spectra

Fixed sample regions should be selected that incorporate the regions where spectral absorption occurs. Each of these regions should include 100 data points. The following procedure should then be followed:

- Open both spectral files in Microsoft Excel™.
- Copy data from one of the files into the other file.
- In Microsoft Excel™, run the regression function, make sure that the software has the Residual Function enabled.
- Run the regression analysis

Results similar to those at right will appear:

	A	B	C
22	RESIDUAL OUTPUT		
23			
24	<i>Observation</i>	<i>Predicted Y</i>	<i>Residuals</i>
25	1	200.5070065	0.415793521
26	2	204.737158	-0.479357984
27	3	207.942696	0.421604046
28	4	211.5949426	-0.134442574
29	5	210.9224241	0.549975944
30	6	214.7462581	0.164741887
31	7	214.2362064	0.637093562
32	8	219.3267051	-0.088905087
33	9	218.0421	0.642000014
34	10	218.5747026	0.034497419
35	11	217.8614922	-0.078292181
36	12	222.6243465	0.155953493
37	13	229.3559462	0.202053822
38	14	229.7937347	-0.396234686
39	15	230.7509961	-1.044396142
40	16	235.6088646	-0.535564554
41	17	238.2589488	-0.354148785
42	18	246.8186763	-0.227476292
43	19	243.3560578	-0.153957844
44	20	245.811903	-0.32440304
45	21	244.6968854	0.266414623
46	22	248.3085403	0.791659658
47	23	248.5795523	0.343247724
48	24	251.3649416	-0.035041568
49	25	253.1484687	-1.104068698



Once the residuals have been generated, they should be copied into the cell next to the actual values. To calculate the RMS values use the following formula

$$\{\text{sum}[(X_{\text{actual}} - X_{\text{predicted}})^2]\}^{.5}/(N-2)$$

with N being the number of points being sampled.

This analysis should be performed in three regions of the UV spectra. For a system with a xenon source, the regions should be near 240, 270, and 300 nanometers.

## **Subtraction of Stray Light or Black Body Radiation**

Since the FTIR is a monostatic modulated source design, black body radiation within the field of view is ignored by the detector. However the interferometer provides an insignificant amount of stray light within itself. The analysis module does not have a provision for automatically subtracting the stray light spectrum from the single-beam.

## **Direct Assay of Test Gas Using the External QA Gas Cell**

After warm up, a zero path background is collected. Instrument QC should be performed before atmospheric data is collected. However if immediate sampling is necessary, QC can be performed on the FTIR at the end of the sampling. Sulfur hexafluoride is used to test the system. The gas is tested using the FTIR's external gas cell and the small mirror fitted to the telescope window. The cell within the FTIR is 0.05 meters. Results of +/- 10% difference in the gas cell results are acceptable. In the event the results are >+/- 10% the entire system shall be checked out and the test rerun. If sufficient corrective action cannot be taken in the field, the system will be returned to the laboratory and corrective action taken.

## **Sulfur Hexafluoride Test**

The gas cylinder is fitted with the appropriate gas regulator and the regulator is adjusted to zero flow. The output connection of the regulator is attached to the Teflon tubing and flow from the cylinder. Allow sulfur hexafluoride to flow into the internal gas cell until five cell volumes of flow has occurred. The gas cylinder valve is closed and the tank and regulator disconnected from the Teflon tubing leading to the rotameter. The results should be reported in ppm-m units and the percent difference from the standard is computed and logged in the FTIR field log.