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Comments to Rules: 1180/1180.1

Presented to :

South Coast AQMD

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"Policymakers have long valued the principle of ***technology neutrality***, which holds that laws and regulations should avoid privileging or penalizing one set of technologies over another."

Conclusion and Recommendations

❑ The Proposed Rule 1180/1180.1 and the supportive documents should be technology-neutral and should avoid privileging or penalizing one set of technologies over another. The current rule guidelines language gives an unjustified advantage to UV DOAS technology over officially proven OP FTIR technology.

❑ No significant superiority of LP-UV DOAS over OP-FTIR was demonstrated in field measurements that justify the new requirement to constrain OP-Fenceline technology of BTEX and Naphthalene to UV DOAS.

❑ UV DOAS has a limitation in quantifying Naphthalene, O-Xylene, and Ethylbenzene.

❑ Acrolein can and should be measured below the OEAHH threshold. If SC AQMD does not think it possible, despite 3 years of reporting acrolein with MDL below 1.1 ppb by the different refineries, new notification level must be determined for all the refineries.

❑ The Guidelines should determine the desired MDL for each compound considering the threshold (if applicable usually at least 30% of the threshold but not higher than the threshold itself).

❑ The Guideline should give one procedure for Detection Limit calculation based on an official method that all refineries must follow.

❑ The Guidelines should be specific in the procedure for calculating Total Alkanes TA.

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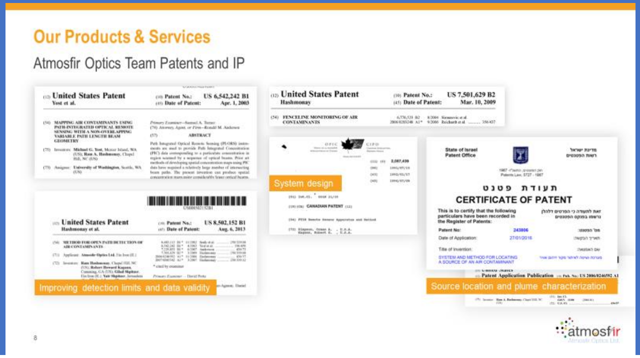
Data & Software R&D, Services, Integration company, providing advanced air monitoring services worldwide based on a SaaS business model .

The company has **extensive experience** in developing methods and technologies for measuring air pollutants.

Atmosfir has performed dozens of projects worldwide.

ISO 17025 Accredited for TO-16



Our Products & Services

Atmosfir Optics Team Patents and IP

(12) United States Patent
Yost et al.
(10) Patent No.: US 6,542,242 B1
(45) Date of Patent: Apr. 1, 2003
(54) MAPPING AIR CONTAMINANTS USING PATH-INTEGRATED OPTICAL REMOTE SENSING WITH A NON-OVERLAPPING VARIABLE PATH LENGTH BEAM GEOMETRY
(75) Inventors: Michael G. Yost, Mercer Island, WA (US); Ram A. Hashmonay, Chapel Hill, NC (US)
(73) Assignee: University of Washington, Seattle, WA (US)

(12) United States Patent
Hashmonay
(10) Patent No.: US 7,501,629 B2
(45) Date of Patent: Mar. 10, 2009
(54) FENCELINE MONITORING OF AIR CONTAMINANTS

System design

CANADIAN PATENT

State of Israel
Patent Office
מדינת ישראל
רשות הפטנטים
תעודת פטנט
CERTIFICATE OF PATENT
This is to certify that the following particulars have been recorded in the Register of Patents:
Patent No: 243806
Date of Application: 27/01/2016
Title of Invention:
SYSTEM AND METHOD FOR LOCATING A SOURCE OF AN AIR CONTAMINANT

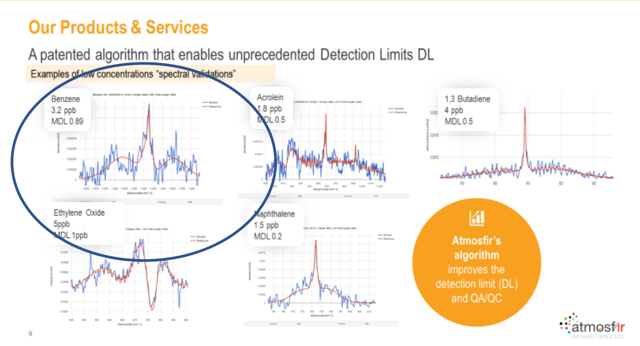
(12) United States Patent
Hashmonay et al.
(10) Patent No.: US 8,502,152 B1
(45) Date of Patent: Aug. 6, 2013
(54) METHOD FOR OPEN PATH DETECTION OF AIR CONTAMINANTS
(71) Applicant: Atmosfir Optics Ltd.

Patent Application Publication

Improving detection limits and data validity

Source location and plume characterization

8



Our Products & Services

A patented algorithm that enables unprecedented Detection Limits DL

Examples of low concentrations "spectral validations"

Atmosfir's algorithm improves the detection limit (DL) and QA/QC

9

הרשות הלאומית להסמכת מעבדות
Israel Laboratory Accreditation Authority

Department: Testing Laboratory ISO/IEC 17025: 2017 Accreditation No. 493

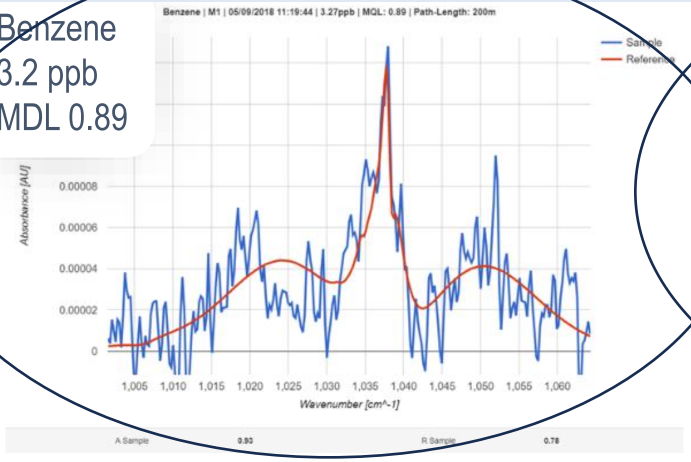
Item	Scope Type	Site	Materials / Products Tested		Types of Test / Properties Measured		Standard / Method	Opinion and Interpretation	Remarks
Group of products: *Environment, Chemical Testing*					משפחת מוצרים: איכות הסביבה, בדיקות כימיות				
Gas Analyser					מדידת ריכוז גזים באוויר				
1	A	T	Ambient air	אוויר פתוח	Atmospheric measurements near ground with FTIR spectroscopy	מדידות אוויר סמוך לקרקע באמצעות ספקטרוסקופיות FTIR	EN 15483	—	EN= European Standard תרכובות גזיות אורגניות ואנאורגניות בולעות קרינת אינפרא אדום Infrared active organic and inorganic compounds in the gaseous state
2	A	T	Ambient air	אוויר פתוח	Long-Path Open-Path Fourier Transform Infrared monitoring of Atmospheric Gases	ניטור גזים באוויר לאורך קו מדידה באמצעות FTIR	US EPA TO-16	—	US EPA=United States Environmental Protection Agency תרכובות גזיות אורגניות ואנאורגניות בולעות קרינת אינפרא אדום Infrared active organic and inorganic compounds in the gaseous state

*confidential and property of Atmosfir

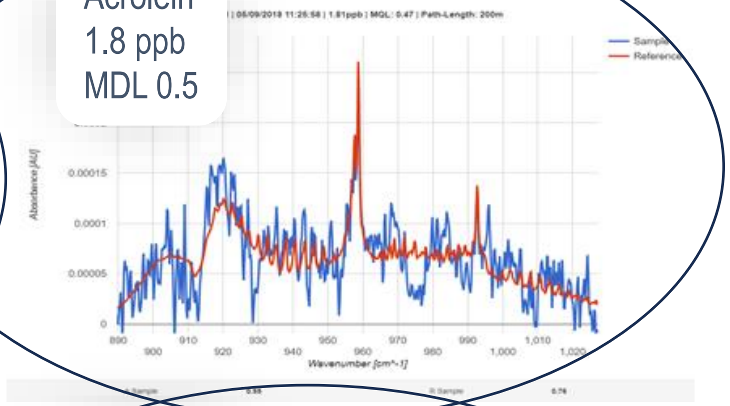
Spectral Validation of Rule 1180 compound of interest using OP FTIR with ppb MDL

OP FTIR: Real Time Detection Limits using a good quality FTIR and good Spectral method

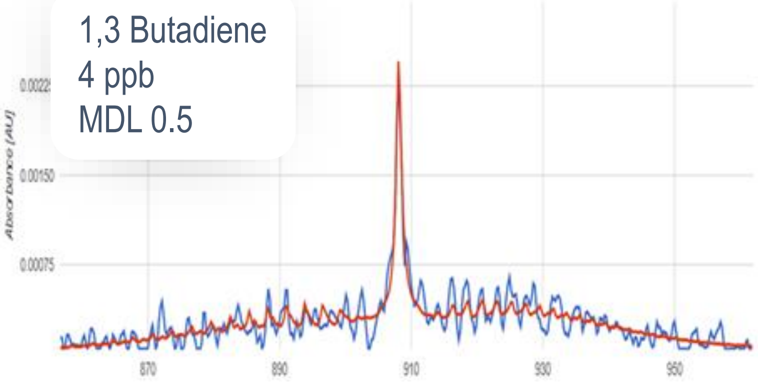
Examples of low concentrations “spectral validations”



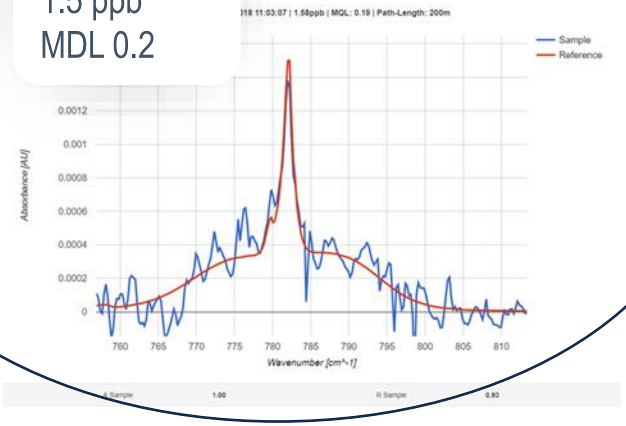
Benzene
3.2 ppb
MDL 0.89



Acrolein
1.8 ppb
MDL 0.5



1,3 Butadiene
4 ppb
MDL 0.5



Naphthalene
1.5 ppb
MDL 0.2

NIST Reference IR Spectrum 🟥
Field IR Spectrum 🟦

Atmosfir’s algorithm improves the detection limit (DL) and QA/QC

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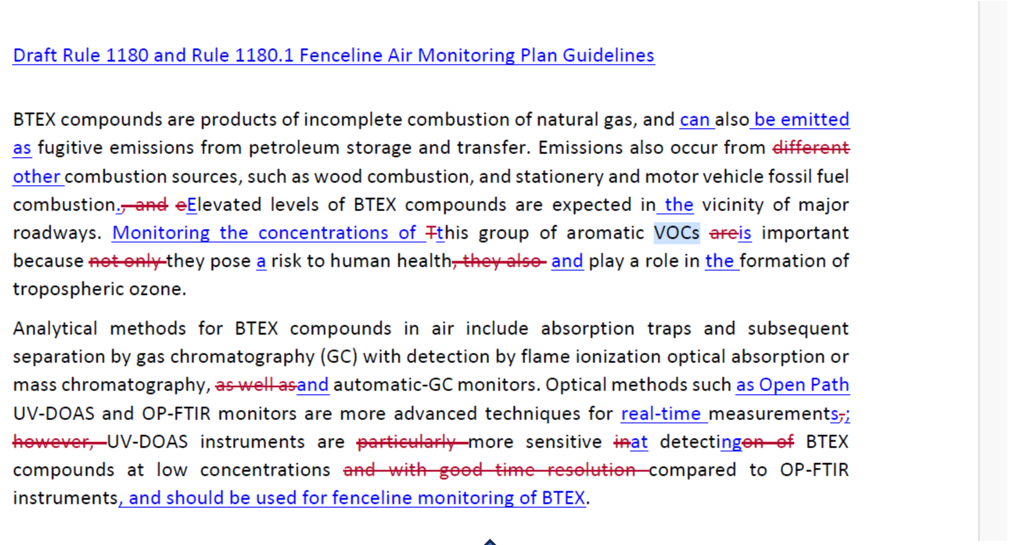
1. No Superiority of UV DOAS over OP-FTIR Considering BTEX Thresholds in Rule 1180. The guideline calling for the use of UV DOAS for BTEX is not technology-neutral and should be changed.

From Rule 1180/1180.1 Guidelines

"methods such as Open Path UV-DOAS and OP-FTIR monitors are more advanced techniques for real-time measurements; UV-DOAS instruments are more sensitive at detecting BTEX compounds at low concentrations compared to OP-FTIR instruments, and should be used for fenceline monitoring of BTEX "



Draft Rule 1180 and Rule 1180.1 Fenceline Air Monitoring Plan Guidelines

BTEX compounds are products of incomplete combustion of natural gas, and can also be emitted as fugitive emissions from petroleum storage and transfer. Emissions also occur from ~~different~~ other combustion sources, such as wood combustion, and stationery and motor vehicle fossil fuel combustion.~~, and~~ ~~e~~Elevated levels of BTEX compounds are expected in the vicinity of major roadways. Monitoring the concentrations of ~~T~~this group of aromatic VOCs ~~are~~is important because ~~not only~~ they pose a risk to human health~~, they also~~ and play a role in the formation of tropospheric ozone.

Analytical methods for BTEX compounds in air include absorption traps and subsequent separation by gas chromatography (GC) with detection by flame ionization optical absorption or mass chromatography, ~~as well as~~and automatic-GC monitors. Optical methods such as Open Path UV-DOAS and OP-FTIR monitors are more advanced techniques for real-time measurements~~,~~; ~~however,~~ UV-DOAS instruments are ~~particularly~~ more sensitive ~~in~~at detecting~~on of~~ BTEX compounds at low concentrations ~~and with good time resolution~~ compared to OP-FTIR instruments, and should be used for fenceline monitoring of BTEX.

****No significant superiority of LP-UV DOAS over OP-FTIR was demonstrated in field measurements that justify the new requirement to constrain OP-Fence line technology of BTEX.***
****O-xylene and Ethylbenzene have a wider and smoother signature and therefore they are problematic to analyze using LP UV DOAS***
****In the staff report both technologies are accepted and that should be the case also in the guideline.***

Suggestion: delete the last sentence that prefers one technology (UV DOAS) over another technology (OP FTIR).

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US EPA Official Method T0-16 is Peer Reviewed.

An official website of the United States government Here's how you know

EPA United States Environmental Protection Agency

Search EPA.gov

Ambient Monitoring Technology Information Center (AMTIC)

CONTACT US

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

This page contains links to EPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. The Compendium contains a set of 17 peer reviewed, standardized methods for the determination of volatile, semi-volatile, and selected toxic organic pollutants in the air. EPA has developed this compendium of methods to assist Federal, State, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date monitoring technology for characterizing organic pollutants in the ambient air.

- Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition (pdf) (201.66 KB, January 1999, EPA/625/R-96/010b)
  Cover page, Foreword, Table of Contents, Method Summaries, and Project Summary
- Addendum to Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition (pdf) (57.64 KB, October 4, 2000)
  Addendum
- Method TO-1 (pdf) (351.65 KB, April, 1984)
  Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)

Trends Sites (NATTS) Technical Assistance Document (TAD) Revision 3 (October 2016)

- Webinar on EPA Method TO-15A for NATTS Participants (pdf) (3.24 MB)
  Important Updates for the NATTS Network and Ambient Air Measurements
- To-15A Webinar Comments Table (pdf) (341.91 KB)
- Method TO-16 (pdf) (246.34 KB, January 1999)
  Long-Path Open-Path Fourier Transform Infrared Monitoring Of Atmospheric Gases
- Method TO-17 (pdf) (344.67 KB)
  Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes

The use of Open Path FTIR is a Peer reviewed method for VOCs including BTEX, Naphthalene and many more compounds.

The Compendium Methods “are **peer reviewed**, standardized methods for the determination of volatile, semi-volatile, and selected toxic organic pollutants in the air.
EPA has developed this compendium of methods to assist Federal, State, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date monitoring technology for characterizing organic pollutants in the ambient air “ .

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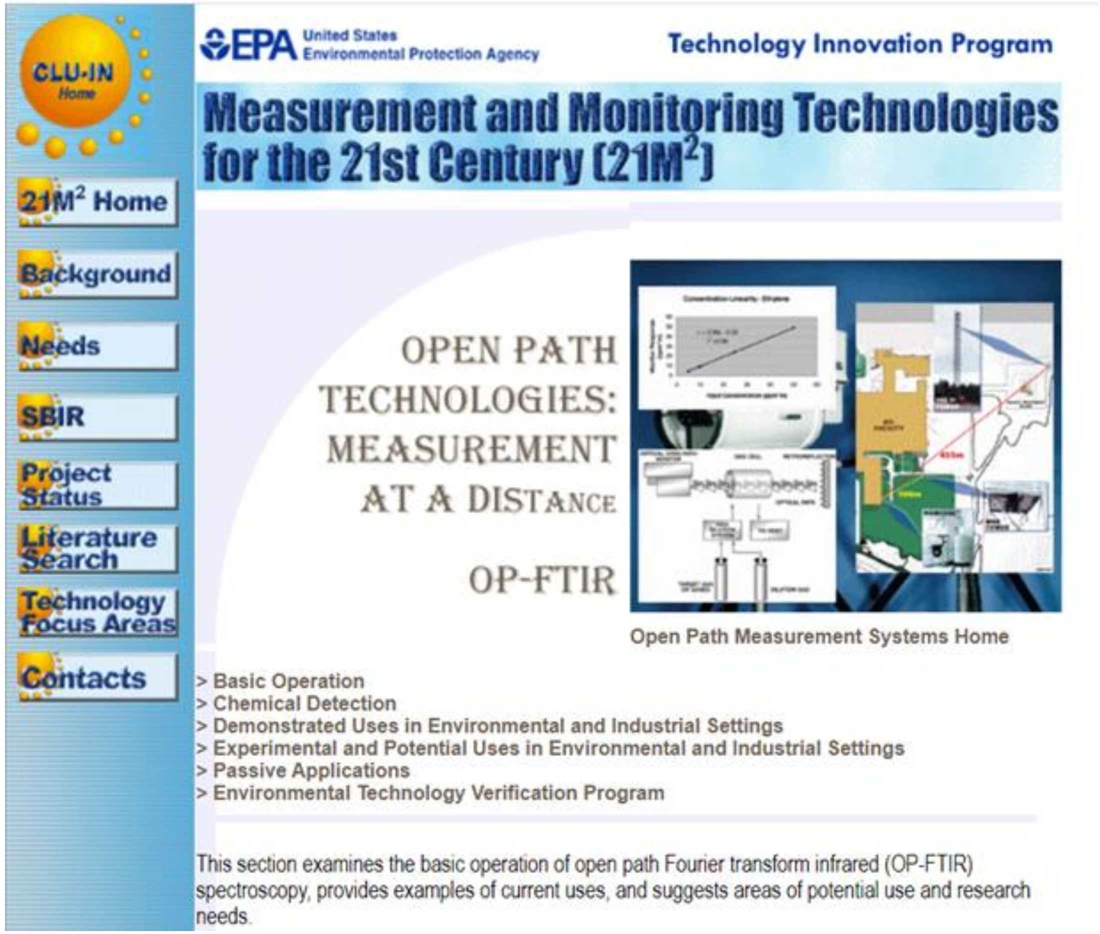
US EPA TO-16 was Designed to Measure VOCs Including BTEX



EPA United States Environmental Protection Agency

Technology Innovation Program

Measurement and Monitoring Technologies for the 21st Century (21M²)

OPEN PATH TECHNOLOGIES: MEASUREMENT AT A DISTANCE

OP-FTIR

Open Path Measurement Systems Home

- > Basic Operation
- > Chemical Detection
- > Demonstrated Uses in Environmental and Industrial Settings
- > Experimental and Potential Uses in Environmental and Industrial Settings
- > Passive Applications
- > Environmental Technology Verification Program

This section examines the basic operation of open path Fourier transform infrared (OP-FTIR) spectroscopy, provides examples of current uses, and suggests areas of potential use and research needs.

squares regression analysis, which is the method used for EPA Method TO-16 in preference to other analytical algorithms, such as partial least squares, iterative least squares, and principal component analysis (USEPA 1999b).

NIST IR Available Spectra

Acetone
Acetonitrile
Acrylonitrile
Benzene
Bromomethane
1,3-Butadiene
Butane
1-Butanol
Carbon Tetrachloride
Carbon Tetrafluoride

Chloroform
Dichlorofluoromethane
1,2-Dichloroethane
1,1-Dichloroethene
Dichloromethane
1,2-Dimethylbenzene
1,3-Dimethylbenzene
1,4-Dimethylbenzene
Ethanol
Ethene

Ethyl Acetate
Ethylbenzene
Ethyl t-Butyl Ether
Ethylene Oxide
Hexafluoroethane
Methanol
Methyl t-Butyl Ether
Methyl Ethyl Ketone
Pentafluoroethane
2-Propanol

Propylene Oxide
Sulfur Dioxide
Sulfur Hexafluoride
Tetrachloroethene
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Vinyl Acetate

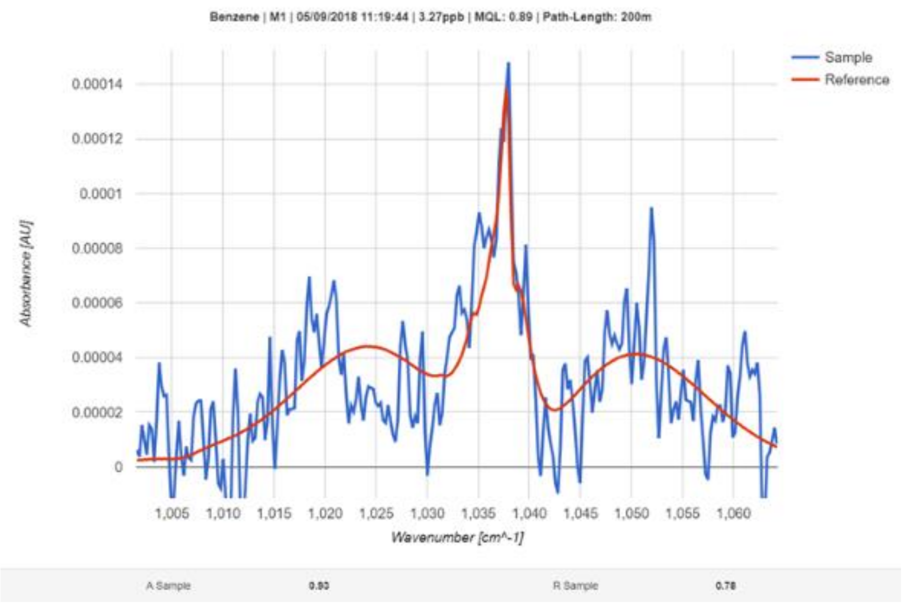


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Table 1: Detection Limits from the Different Quarterly Reports Showing No Significant Advantage for Measuring BTEX Using UV DOAS over OP FTIR

			Valero OP FTIR		Valero UV DOAS		Marathon				Torance	Chevron el segundo			P66 UCLA LP DOAS			P66
Compound	**1hr threshol**	**Published MDL in**	**avrage [ppb]**	**min [ppb]**			244	603		web		199	574	web				
1,3-Butadiene	303	0.3	0.32	0.19			8.00	3.00	5.50	3.10	7.00	5.00	2.00					11
Acetaldehyde	265	0.5	0.4	0.2			10.0	4.0	7.0	2.0	11.7	3.0	1.0					33
Acrolein	**1.1**	**0.3**	**0.6**	**0.4**			**31.0**	**12.0**	**21.5**	**16.5**	**15.6**	**4.0**	**2.0**	**0.6**				**30**
Ammonia	4662	0.1	0.1	0.1			6.0	3.0	4.5	0.7	2.4	1.0	0.4					4
Carbonyl Sulfide	273	0.1	0.0	0.0			2.0	1.0	1.5	1.6	3.3	2.0	1.0					3
Formaldehyde	45.5	2.0	0.3	0.1			2.0	1.0	1.5	6.6	2.5	2.0	1.0					30
Hydrogen Cyanide	312	3.0	3.0	0.9			3.0	1.0	2.0	22.7	35.6	34.0	12.0					50
Hydrogen Fluoride	298	1.0	0.2	0.1			NO	NO	NO	NO	6.0							
Nitrogen Dioxide	100	10.0	1.1	0.8			12.0	5.0	8.5	6.3	64.6	8.0	3.0					3
Styrene	5000	1.0	0.4	0.3			16.0	7.0	11.5	4.0	no	6.0	2.0					33
Total_Alkanes	----	1.0	0.6	0.5			12.0	5.0	8.5	6.3	54.3	10.0	3.0					32
Benzene	**8**	**1.0**	**1.7**	**1.1**	**2.3**	**1.3**	**1.0**	**0.2**	**0.6**	**0.6**	**1.0**	**1.0**	**0.2**	**0.7**	**1.2**	**1.8**		**2**
Ethylbenzene	----	10.0	0.9	0.7	13.4	8.7	4.0	2.0	3.0	0.6	6.5	1.0	0.3		2.1	3.0	1.5	20
m-Xylene	5142	1.0	1.0	0.4	2.1	1.7	2.0	1.0	1.5	0.5	1.6	2.0	0..8		1.8	2.4	2.6	2.9
o-Xylene	5142	1.0	2.1	0.6	8.9	2.0	NO	NO	no	7.8	4.5				NO	NO	2.1	9.4
p-Xylene	5142	1.0	1.0	0.4	1.3	0.5	2.0	1.0	1.5	0.7	0.6				0.6	0.9		2
Sulfur Dioxide	75	2.0	2.5	1.0	0.5	0.3	6.0	2.0	4.0	1.4	0.5	2.0	0.3		NO	NO	0.8	2
Toluene	9964	2.0	2.6	0.7	3.2	1.7	2.0	1.0	1.5	1.7	1.6	2.0	0.7		2.1	3.0	2.6	3

Chevron & Marathon “ Detection limits are approximate, as estimated by the manufacturer based on the theoretical capabilities of the instruments and supported by manufacturers’ lab tests and real-world”

Both UV DOAS and OP FTIR can get a detection limit below the Benzene notification threshold.

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Benzene Detection Limits – Atmosfir measurements UV DOAS *vs.* OP FTIR

COMPOUND	**Benzene** DL (ppb)		
PERIOD	**Q2 2020**	**Q1 2021**	**Q1 2022**
1-Hour REL [ppb]	8.6	**8.6**	**8**
FTIR DL in QAPP	1	1	1
DOAS Lab DL in QAPP	**0.2**	**0.2**	**0.2**
181 m FTIR	0.76	1.09	1.11
UVDOAS	*5.71*	*3.99*	*2.95*
326 m FTIR	0.72	1.05	1.40
UVDOAS	*4.98*	*3.93*	1.47
682 m FTIR	0.75	1.37	0.81
UVDOAS	1.21	1.19	1.05
338 m FTIR	1.51	1.90	1.32
UVDOAS	1.26	0.93	1.47
190 m FTIR	0.6	0.94	1.14
UVDOAS	1.74	1.15	1.05
593 m FTIR	0.42	0.63	0.84
UVDOAS	1.79	0.94	0.81

In field installation of a good OP FTIR together with UV DOAS no advantage was found for measuring BTEX using UV DOAS

For over 75% of the cases OP FTIR presented better measurement sensitivities DL for benzene than UVDOAS.

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Aromatics UV Spectral Signatures

UV spectroscopy applications for aromatic and double-bonds VOC is based on absorption signatures between 250 – 280 nm.

Stutz et al. 2016*:
The initial motivation for using open path UV DOAS for aromatic VOC was to monitor benzene alone when US EPA adopted a rule on "Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards" to enforce a 2-week averaged benzene concentration action level of ~3 ppb.

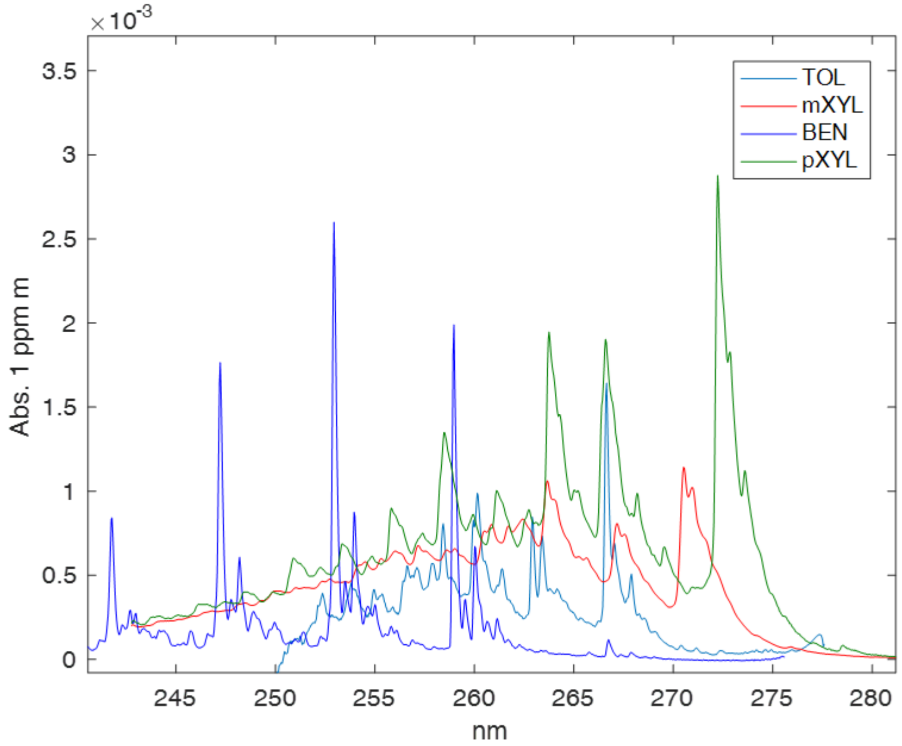

Figure 1 - Benzene Toluene, m-Xylene, and p-Xylene UV signatures. Max Plank high-resolution references

*A novel dual-LED based long-path DOAS instrument for the measurement of aromatic hydrocarbons – Jochen Stutz, Stephen C. Hurlock, Santo F. Colosimo, Catalina Tsai, Ross Cheung, James Festa, Olga Pikelnaya, Sergio Alvarez, James H. Flynn, Matthew H. Erickson, Eduardo P. Olaguer. Atmospheric Environment 147 (2016)

UV DOAS for BTEX

The spectral resolution of Commercial OP UV DOAS systems is 0.5 nm (UCLA – LED based UV DOAS has 0.35 nm resolution)

→ Degrade the fine absorbance bands of the signature, shown in 0.2 nm resolution of MP references

→ Degrade selectivity and ability to resolve significant atmospheric interferences

Benzene Toluene, and m & p-Xylenes maintain unique narrow absorbance bands after deresolution.

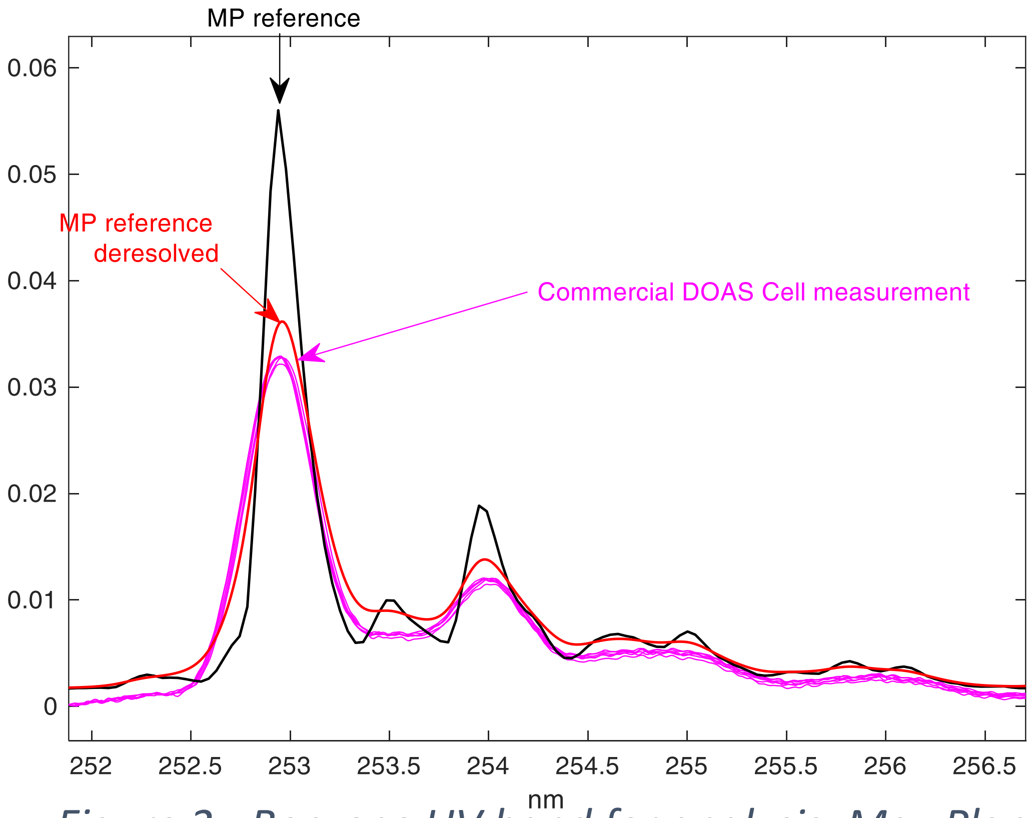

Figure 2 - Benzene UV band for analysis. Max Plank high-resolution reference (black) vs. commercial UVDOAS cell measurement of Benzene -Opsis

*MP reference was scaled to the cylinder concentration*cell path*

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UV DOAS – Not Suitable for OP Ethylbenzene (ETB) and O-Xylene

Ethylbenzene and O-Xylene which are less responsive to UV radiation and have a wider and smoother signature Deresolution by the UV DOAS optics further Degrades unique signature and selectivity.

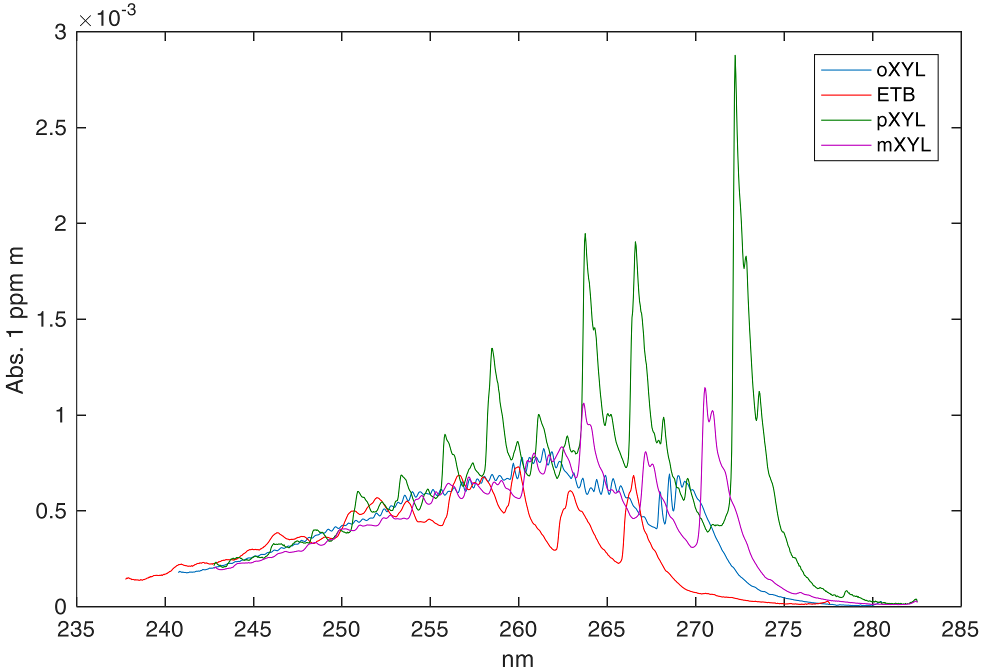

Figure 3 ETB and o-Xylene UV signatures vs. m-Xylene and p-Xylene UV signatures. Max Plank high-resolution references.

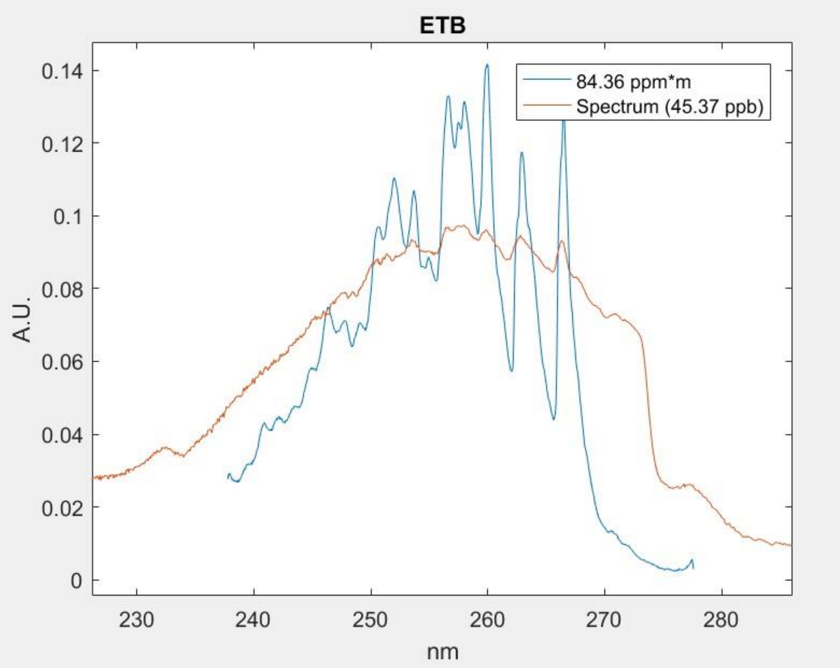

Figure 4 - Ethylbenzene cell measurement (Spectrum UVDOAS, red) vs. Max Plank reference (blue)

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UV DOAS limitations in Open Path Technology

- All commercial open-path UV-DOAS systems use Xe-arc lamps (broad band, but at 250-280 nm the emission of the lamp is only 1.5% of its power) → Stray light in the spectrometer due to suppression of light outside the 250-280 nm range (grating and filters used are not optimal).

  This can severely damage the performance of the spectrometer. No quantitative information is available, but Stutz et al. claim as much as 10%.

- UV intensity is further reduced by oxygen and ozone absorption and Rayleigh scattering
- Strong and often saturated absorptions of O_2, $O_2 \cdot O_2$, and $O_2 \cdot N_2$ (collisional complexes) overlap absorbance of target compound absorbance bands → an accurate description of these structures is crucial for a successful DOAS analysis (Stuts at al. 2016)
- Moreover, the content of O_2, $O_2 \cdot O_2$, and $O_2 \cdot N_2$ complexes is not constant and varies with temperature, pressure, and chemical reactions in the open path.
- The longer the open path the more severe the impact of the atmospheric interference (bistatic architecture is preferable in that sense)

Benzene MDL by LED based UV DOAS, Optimal Conditions, and Rigorous Subtraction of O_2 Complexes Was Found to be 1.2ppb for 270m

- Stutz et al. mention that they report detection limits determined from realistic atmospheric measurements as opposed to those reported for commercial instruments based on a calculation using anticipated noise levels or zero-span drift tests.
- **1.2 ppb Benzene detection for 270 m under optimal conditions**

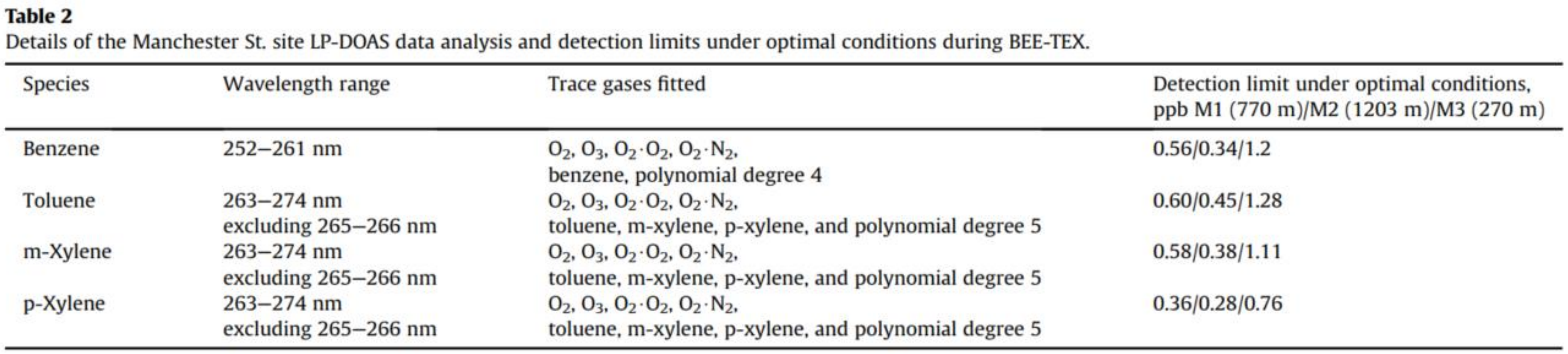
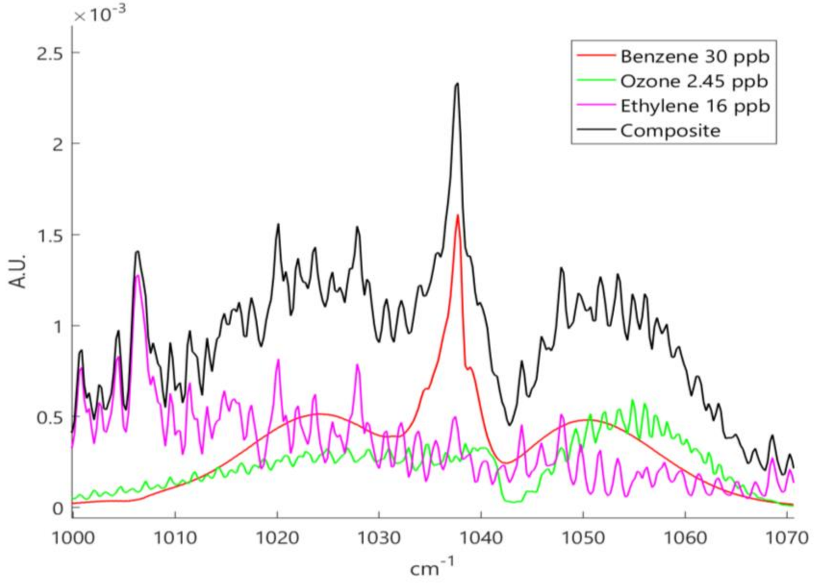


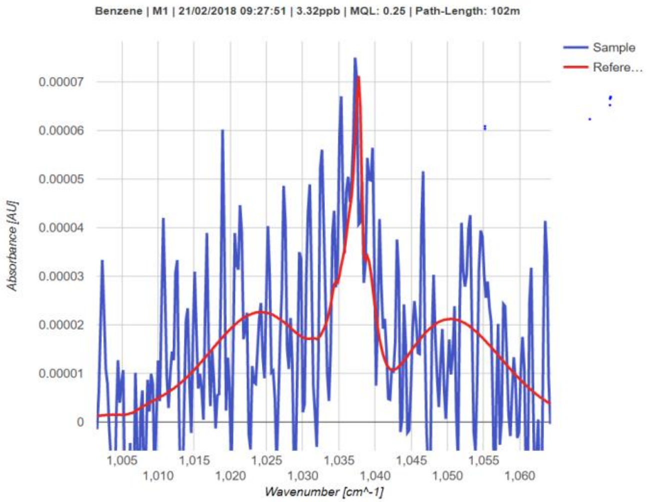
Table 2
Details of the Manchester St. site LP-DOAS data analysis and detection limits under optimal conditions during BEE-TEX.

Species	Wavelength range	Trace gases fitted	Detection limit under optimal conditions, ppb M1 (770 m)/M2 (1203 m)/M3 (270 m)
Benzene	252–261 nm	O_2, O_3, $O_2 \cdot O_2$, $O_2 \cdot N_2$, benzene, polynomial degree 4	0.56/0.34/1.2
Toluene	263–274 nm excluding 265–266 nm	O_2, O_3, $O_2 \cdot O_2$, $O_2 \cdot N_2$, toluene, m-xylene, p-xylene, and polynomial degree 5	0.60/0.45/1.28
m-Xylene	263–274 nm excluding 265–266 nm	O_2, O_3, $O_2 \cdot O_2$, $O_2 \cdot N_2$, toluene, m-xylene, p-xylene, and polynomial degree 5	0.58/0.38/1.11
p-Xylene	263–274 nm excluding 265–266 nm	O_2, O_3, $O_2 \cdot O_2$, $O_2 \cdot N_2$, toluene, m-xylene, p-xylene, and polynomial degree 5	0.36/0.28/0.76

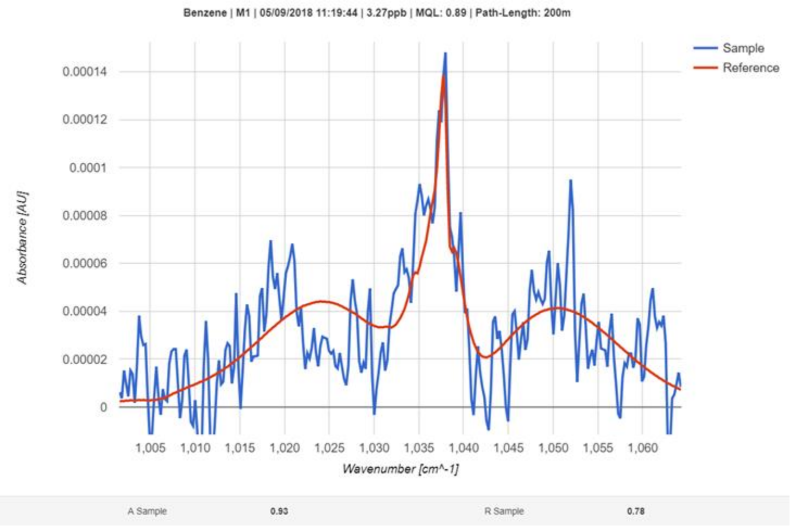
IR Spectral Window for Benzene Analysis

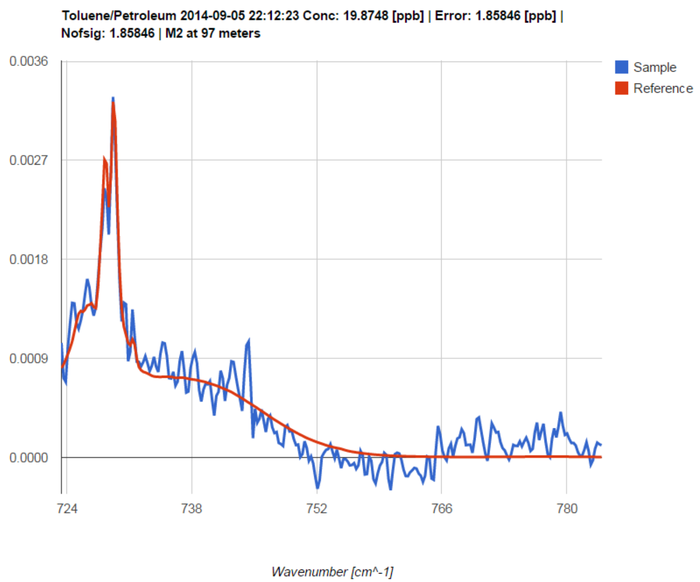


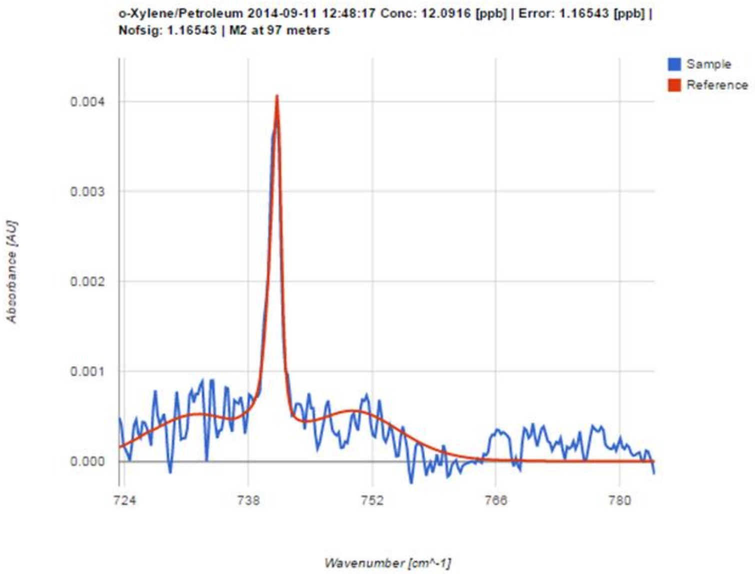
Spectral Validation of Benzene 3.3 ppb DL 0.75 measured in one of California’s Refineries

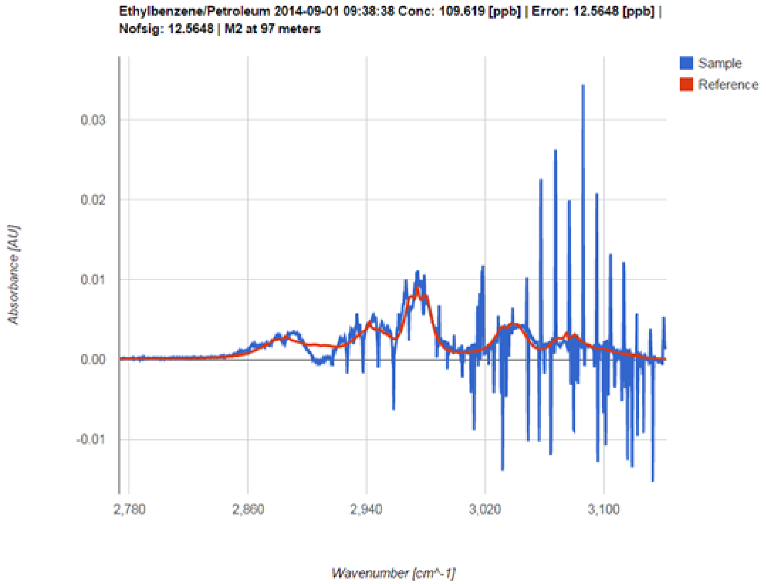


OP FTIR Field BTEX measurements – Atmosfir System Detections









SC AQMD Rule 1180 Draft Staff Report Specifically States that both FTIR and UV DOAS Can Monitor BTEX

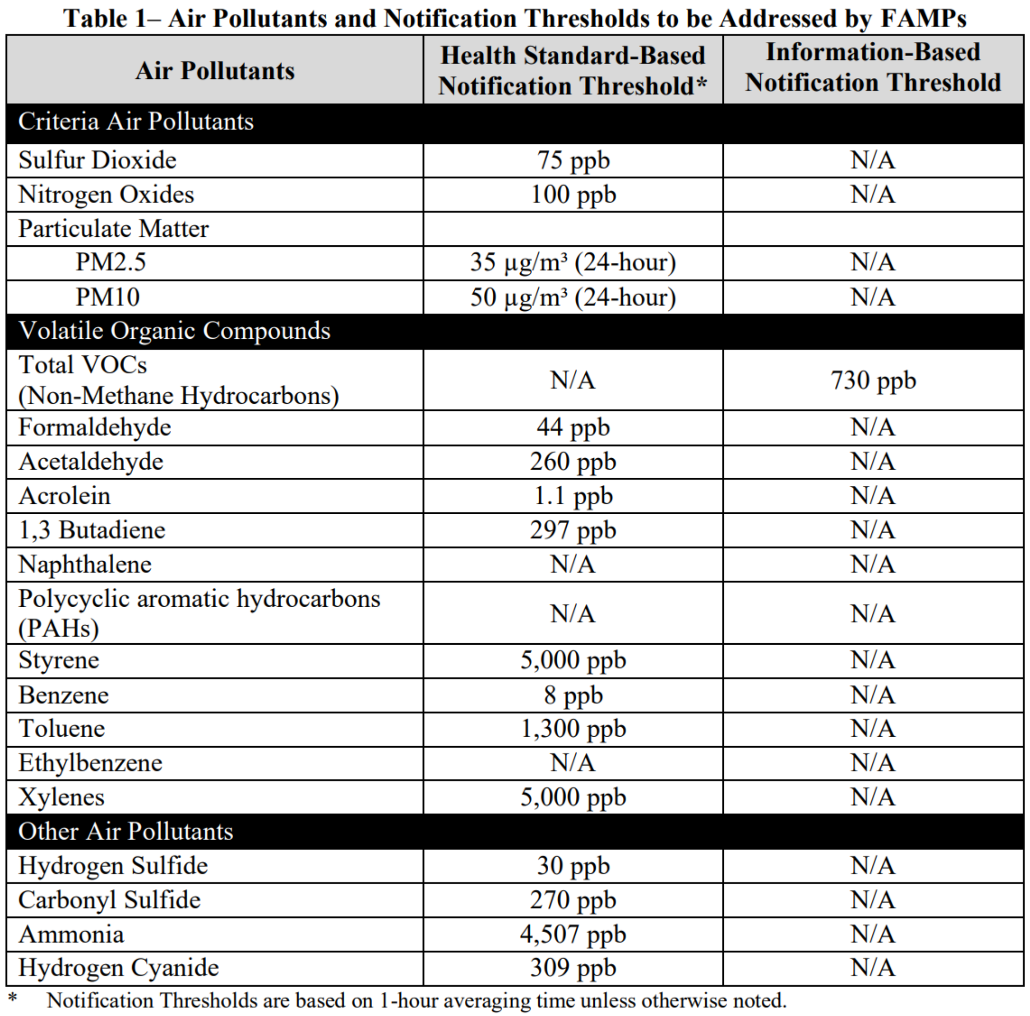
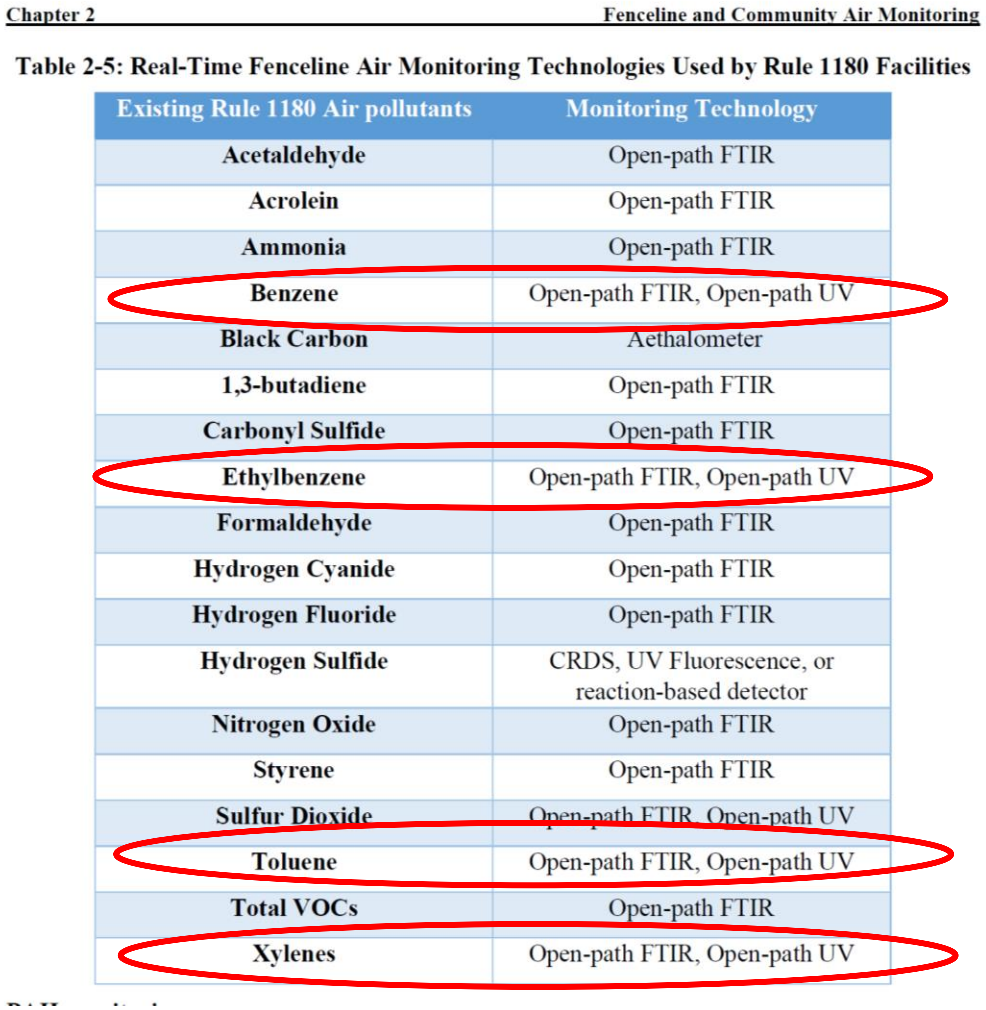


Table 1– Air Pollutants and Notification Thresholds to be Addressed by FAMPs

Air Pollutants	Health Standard-Based Notification Threshold*	Information-Based Notification Threshold
Criteria Air Pollutants		
Sulfur Dioxide	75 ppb	N/A
Nitrogen Oxides	100 ppb	N/A
Particulate Matter		
PM2.5	35 µg/m³ (24-hour)	N/A
PM10	50 µg/m³ (24-hour)	N/A
Volatile Organic Compounds		
Total VOCs (Non-Methane Hydrocarbons)	N/A	730 ppb
Formaldehyde	44 ppb	N/A
Acetaldehyde	260 ppb	N/A
Acrolein	1.1 ppb	N/A
1,3 Butadiene	297 ppb	N/A
Naphthalene	N/A	N/A
Polycyclic aromatic hydrocarbons (PAHs)	N/A	N/A
Styrene	5,000 ppb	N/A
Benzene	8 ppb	N/A
Toluene	1,300 ppb	N/A
Ethylbenzene	N/A	N/A
Xylenes	5,000 ppb	N/A
Other Air Pollutants		
Hydrogen Sulfide	30 ppb	N/A
Carbonyl Sulfide	270 ppb	N/A
Ammonia	4,507 ppb	N/A
Hydrogen Cyanide	309 ppb	N/A

* Notification Thresholds are based on 1-hour averaging time unless otherwise noted.



Chapter 2 Fenceline and Community Air Monitoring

Table 2-5: Real-Time Fenceline Air Monitoring Technologies Used by Rule 1180 Facilities

Existing Rule 1180 Air pollutants	Monitoring Technology
Acetaldehyde	Open-path FTIR
Acrolein	Open-path FTIR
Ammonia	Open-path FTIR
Benzene	Open-path FTIR, Open-path UV
Black Carbon	Aethalometer
1,3-butadiene	Open-path FTIR
Carbonyl Sulfide	Open-path FTIR
Ethylbenzene	Open-path FTIR, Open-path UV
Formaldehyde	Open-path FTIR
Hydrogen Cyanide	Open-path FTIR
Hydrogen Fluoride	Open-path FTIR
Hydrogen Sulfide	CRDS, UV Fluorescence, or reaction-based detector
Nitrogen Oxide	Open-path FTIR
Styrene	Open-path FTIR
Sulfur Dioxide	Open-path FTIR, Open-path UV
Toluene	Open-path FTIR, Open-path UV
Total VOCs	Open-path FTIR
Xylenes	Open-path FTIR, Open-path UV

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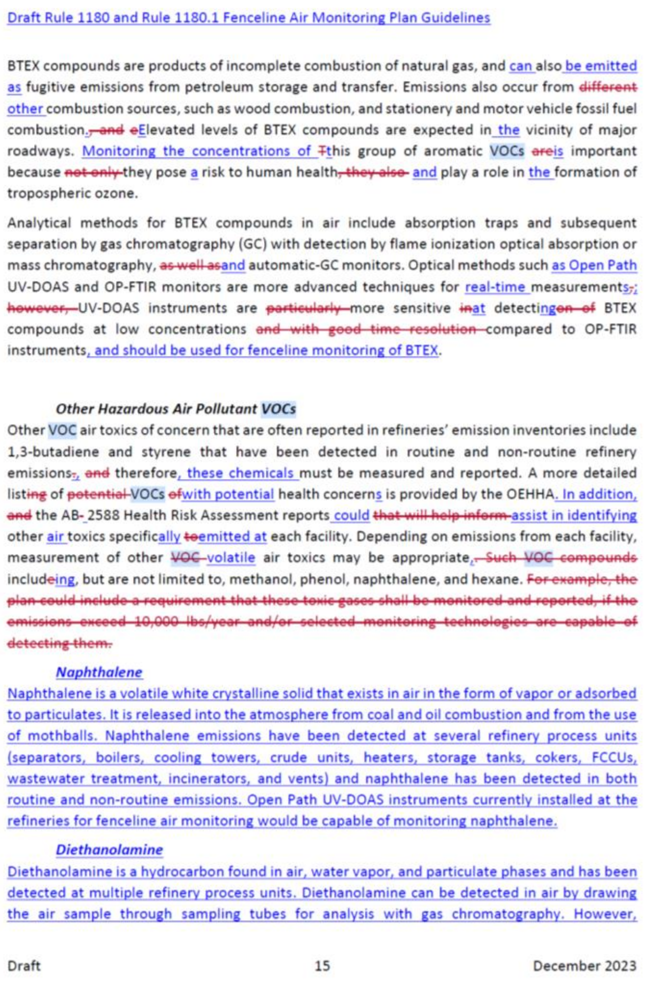
2. Naphthalene is Better Measured with OP FTIR.

The guideline calling for the use of UV DOAS for Naphthalene is not technology-neutral and should be changed.



Draft Rule 1180 and Rule 1180.1 Fenceline Air Monitoring Plan Guidelines

BTEX compounds are products of incomplete combustion of natural gas, and can also be emitted as fugitive emissions from petroleum storage and transfer. Emissions also occur from ~~different~~ other combustion sources, such as wood combustion, and stationery and motor vehicle fossil fuel combustion.~~, and~~ ~~e~~Elevated levels of BTEX compounds are expected in the vicinity of major roadways. Monitoring the concentrations of ~~T~~this group of aromatic VOCs ~~are~~is important because ~~not only~~ they pose a risk to human health~~, they also~~ and play a role in the formation of tropospheric ozone.

Analytical methods for BTEX compounds in air include absorption traps and subsequent separation by gas chromatography (GC) with detection by flame ionization optical absorption or mass chromatography, ~~as well as~~and automatic-GC monitors. Optical methods such as Open Path UV-DOAS and OP-FTIR monitors are more advanced techniques for real-time measurements~~,~~; ~~however,~~ UV-DOAS instruments are ~~particularly~~ more sensitive ~~in~~at detecting~~on of~~ BTEX compounds at low concentrations ~~and with good time resolution~~ compared to OP-FTIR instruments, and should be used for fenceline monitoring of BTEX.

Other Hazardous Air Pollutant VOCs

Other VOC air toxics of concern that are often reported in refineries' emission inventories include 1,3-butadiene and styrene that have been detected in routine and non-routine refinery emissions~~.~~, ~~and~~ therefore, these chemicals must be measured and reported. A more detailed list~~ing~~ of ~~potential~~ VOCs ~~of~~with potential health concerns is provided by the OEHHA. In addition, ~~and~~ the AB- 2588 Health Risk Assessment reports could ~~that will help inform~~ assist in identifying other air toxics specifically ~~to~~emitted at each facility. Depending on emissions from each facility, measurement of other ~~VOC~~ volatile air toxics may be appropriate,~~. Such VOC compounds~~ includ~~e~~ing, but are not limited to, methanol, phenol, naphthalene, and hexane. ~~For example, the plan could include a requirement that these toxic gases shall be monitored and reported, if the emissions exceed 10,000 lbs/year and/or selected monitoring technologies are capable of detecting them.~~

Naphthalene

Naphthalene is a volatile white crystalline solid that exists in air in the form of vapor or adsorbed to particulates. It is released into the atmosphere from coal and oil combustion and from the use of mothballs. Naphthalene emissions have been detected at several refinery process units (separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and naphthalene has been detected in both routine and non-routine emissions. Open Path UV-DOAS instruments currently installed at the refineries for fenceline air monitoring would be capable of monitoring naphthalene.

Diethanolamine

Diethanolamine is a hydrocarbon found in air, water vapor, and particulate phases and has been detected at multiple refinery process units. Diethanolamine can be detected in air by drawing the air sample through sampling tubes for analysis with gas chromatography. However,

Draft 15 December 2023

Naphthalene

Naphthalene is a volatile white crystalline solid that exists in air in the form of vapor or adsorbed to particulates. It is released into the atmosphere from coal and oil combustion and from the use of mothballs. Naphthalene emissions have been detected at several refinery process units (separators, boilers, cooling towers, crude units, heaters, storage tanks, cokers, FCCUs, wastewater treatment, incinerators, and vents) and naphthalene has been detected in both routine and non-routine emissions. Open Path **UV-DOAS** instruments currently installed at the refineries for fenceline air monitoring would be capable of monitoring naphthalene.

Suggestion:
delete the word
UV DOAS

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UV DOAS – Naphthalene

There is almost no experience with UV DOAS for Naphthalene OP-quantitative monitoring. The band will be smoother than the high-resolution MP reference, in a similar manner to ETB.

DOAS detection of naphthalene was reported in 2007* as feasible but preliminary without calibration of the DOAS measurements for quantification of naphthalene, **no assessment of the linear range of naphthalene absorptions, and the sensitivity to atmospheric interferences**.

**https://search.emsl.pnnl.gov/?project_id_search=10894*
Project Title: High-resolution Gas-phase UV- and IR-absorption Cross-sections of Naphthalene to Calibrate the First DOAS Detection of Naphthalene in Mexico City

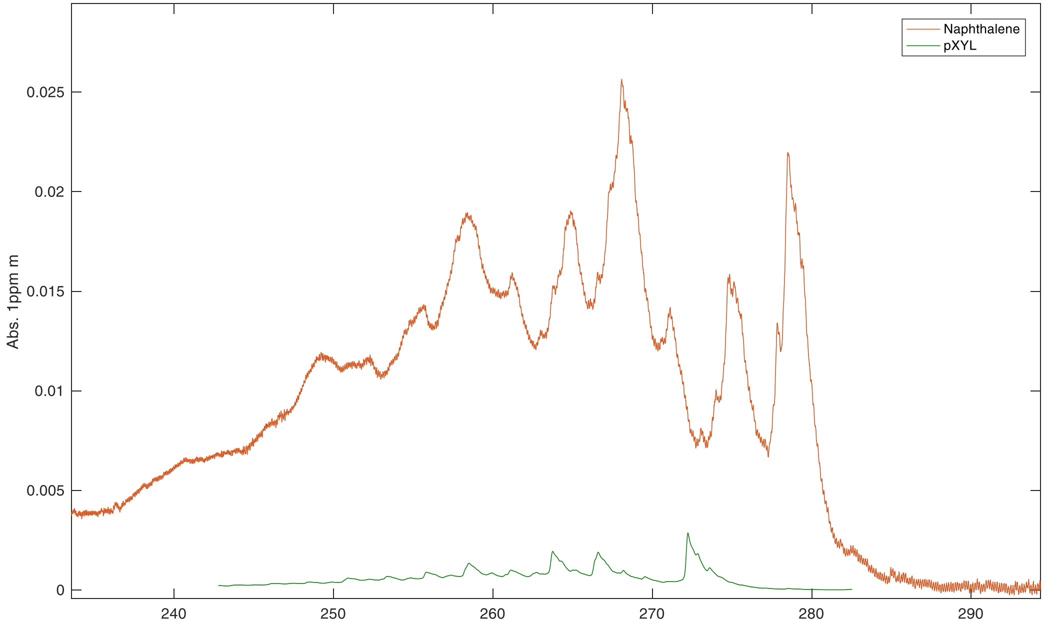
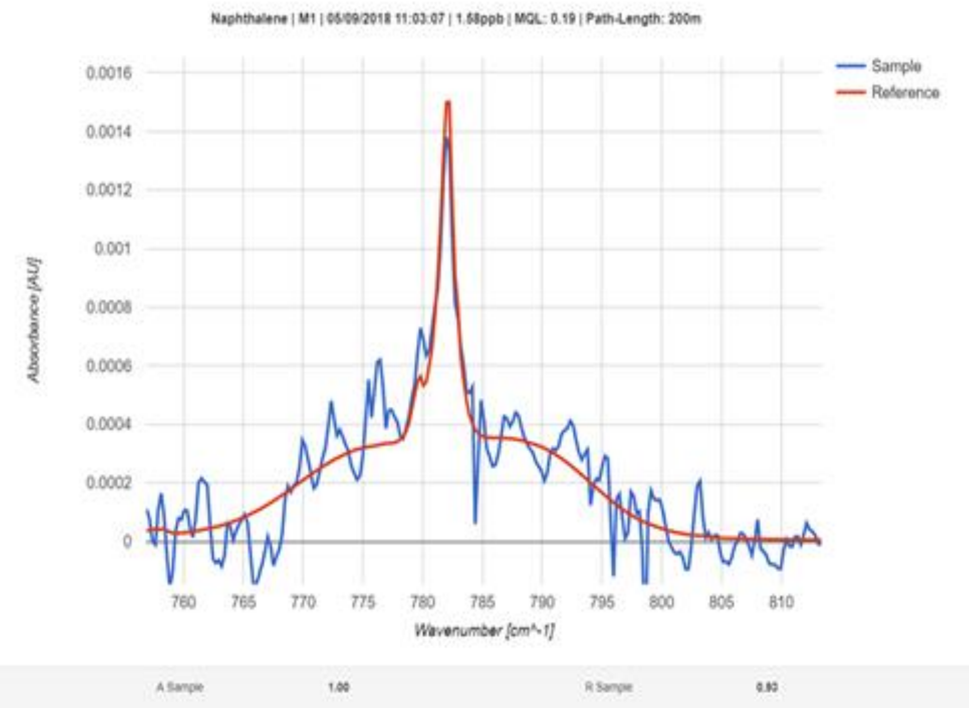


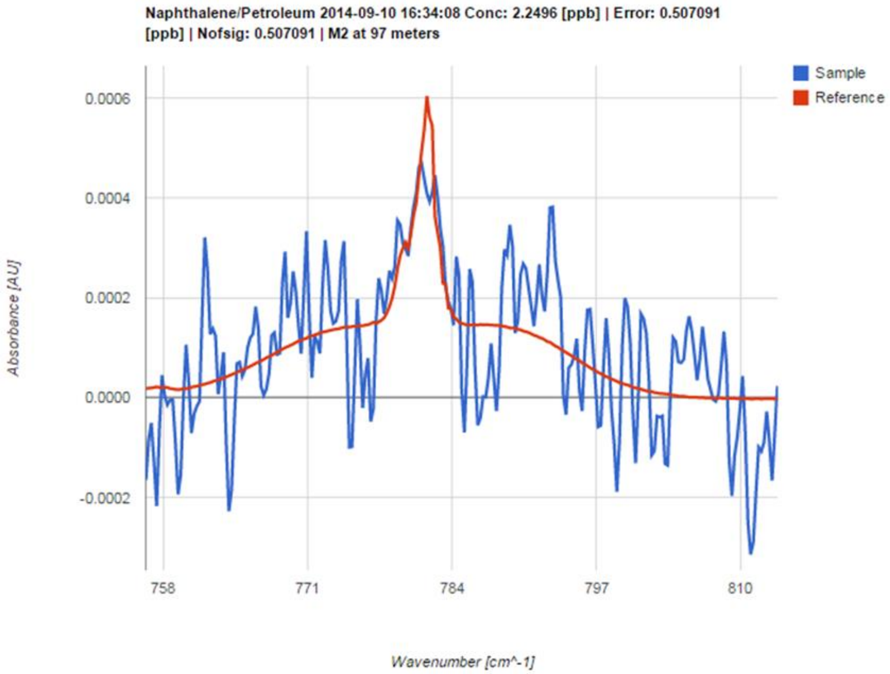
*Figure 5 Naphthalene Max Plank **high-resolution** reference*

OP FTIR Field Naphthalene Measurements Spectral Validation

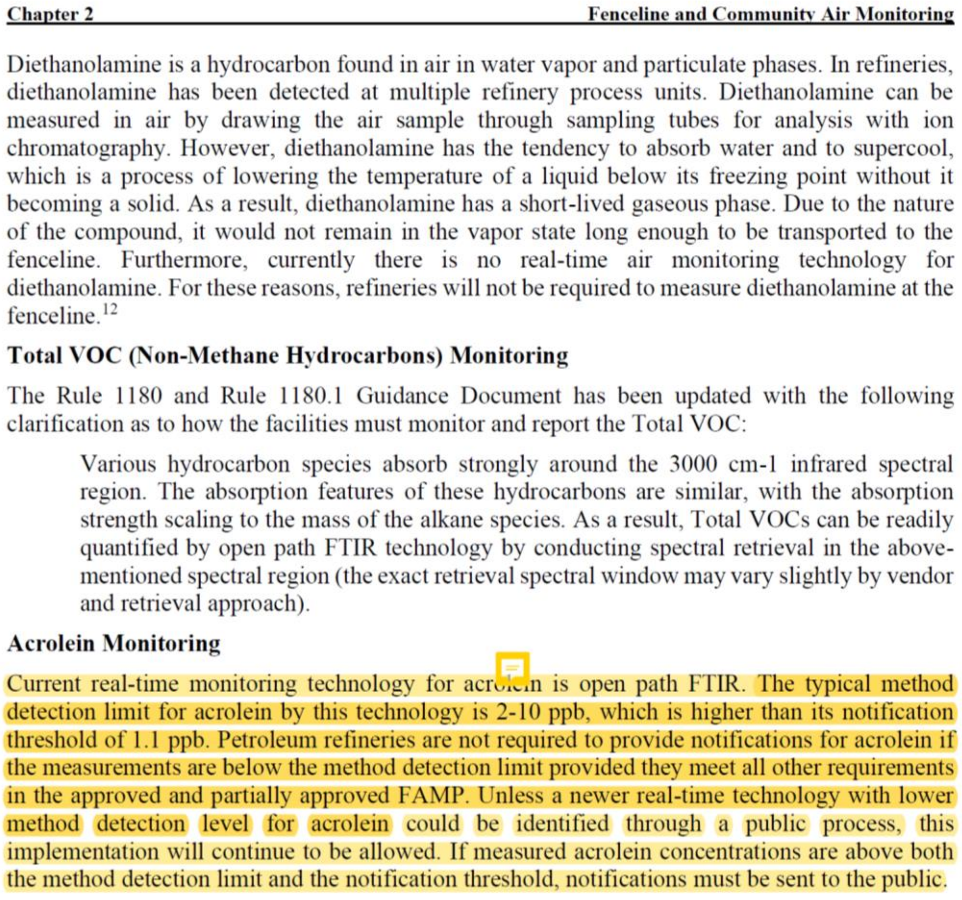
Naphthalene 1.5 ppb MDL 0.2



Naphthalene 2.5 ppb MDL 0.5 ppb



3. From the Staff Report: The Reliefs in Notification Thresholds for Acrolein Do Not Protect the Public and Should be Changed.



Chapter 2 **Fenceline and Community Air Monitoring**

Diethanolamine is a hydrocarbon found in air in water vapor and particulate phases. In refineries, diethanolamine has been detected at multiple refinery process units. Diethanolamine can be measured in air by drawing the air sample through sampling tubes for analysis with ion chromatography. However, diethanolamine has the tendency to absorb water and to supercool, which is a process of lowering the temperature of a liquid below its freezing point without it becoming a solid. As a result, diethanolamine has a short-lived gaseous phase. Due to the nature of the compound, it would not remain in the vapor state long enough to be transported to the fenceline. Furthermore, currently there is no real-time air monitoring technology for diethanolamine. For these reasons, refineries will not be required to measure diethanolamine at the fenceline.[12]

Total VOC (Non-Methane Hydrocarbons) Monitoring

The Rule 1180 and Rule 1180.1 Guidance Document has been updated with the following clarification as to how the facilities must monitor and report the Total VOC:

> Various hydrocarbon species absorb strongly around the 3000 cm-1 infrared spectral region. The absorption features of these hydrocarbons are similar, with the absorption strength scaling to the mass of the alkane species. As a result, Total VOCs can be readily quantified by open path FTIR technology by conducting spectral retrieval in the above-mentioned spectral region (the exact retrieval spectral window may vary slightly by vendor and retrieval approach).

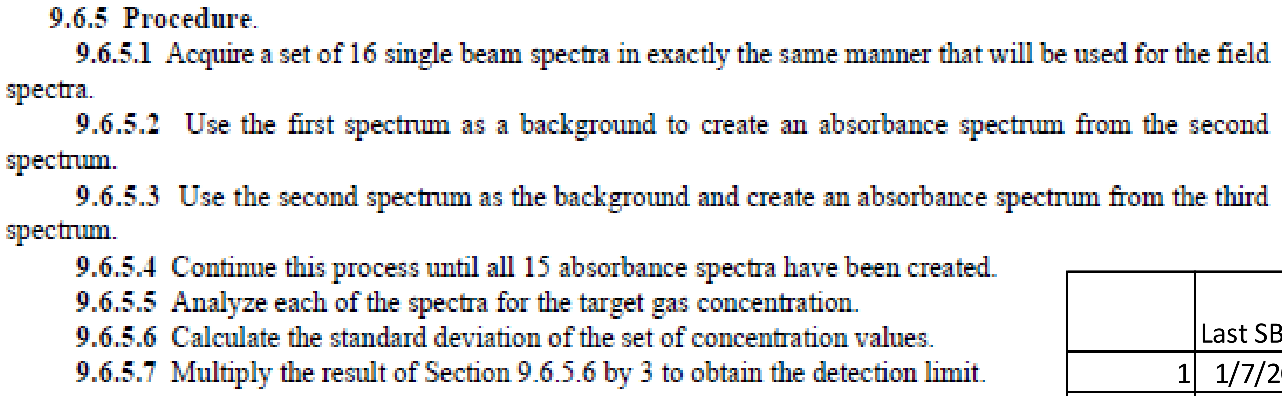
Acrolein Monitoring

Current real-time monitoring technology for acrolein is open path FTIR. The typical method detection limit for acrolein by this technology is 2-10 ppb, which is higher than its notification threshold of 1.1 ppb. Petroleum refineries are not required to provide notifications for acrolein if the measurements are below the method detection limit provided they meet all other requirements in the approved and partially approved FAMP. Unless a newer real-time technology with lower method detection level for acrolein could be identified through a public process, this implementation will continue to be allowed. If measured acrolein concentrations are above both the method detection limit and the notification threshold, notifications must be sent to the public.

“**Acrolein Monitoring**
Current real-time monitoring technology for acrolein is open path FTIR. The typical method detection limit for acrolein by this technology is 2-10 ppb, which is higher than its notification threshold of 1.1 ppb. **Petroleum refineries are not required to provide notifications for acrolein if the measurements are below the method detection limit provided they meet all other requirements in the approved and partially approved FAMP**. Unless a newer real-time technology with lower method detection level for acrolein could be identified through a public process, this implementation will continue to be allowed. If measured acrolein concentrations are above both the method detection limit and the notification threshold, notifications must be sent to the public.”

1. Acrolein can and should be monitored below the Rule 1180/1180.1 Threshold.
2. The report should specify one notification threshold for all the refineries and not give an advantage for poor quality instrumentation.
3. If SC AQMD does not think that 1.1 ppb is doable and 2 ppb is typical, SC AQMD should change the threshold to 2 ppb or at least the level of notification for all refineries.

Acrolein MDL based on US EPA TO-16 Procedure Prove MDL<1.1 ppb is Achievable



9.6.5 Procedure.

9.6.5.1 Acquire a set of 16 single beam spectra in exactly the same manner that will be used for the field spectra.

9.6.5.2 Use the first spectrum as a background to create an absorbance spectrum from the second spectrum.

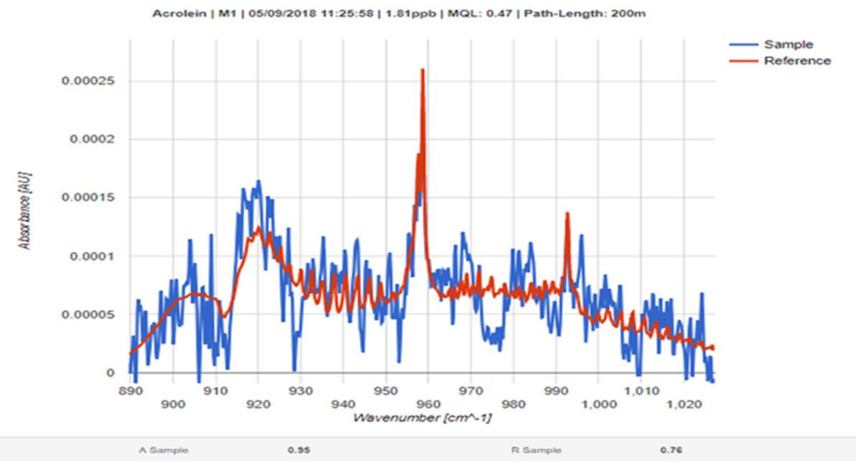
9.6.5.3 Use the second spectrum as the background and create an absorbance spectrum from the third spectrum.

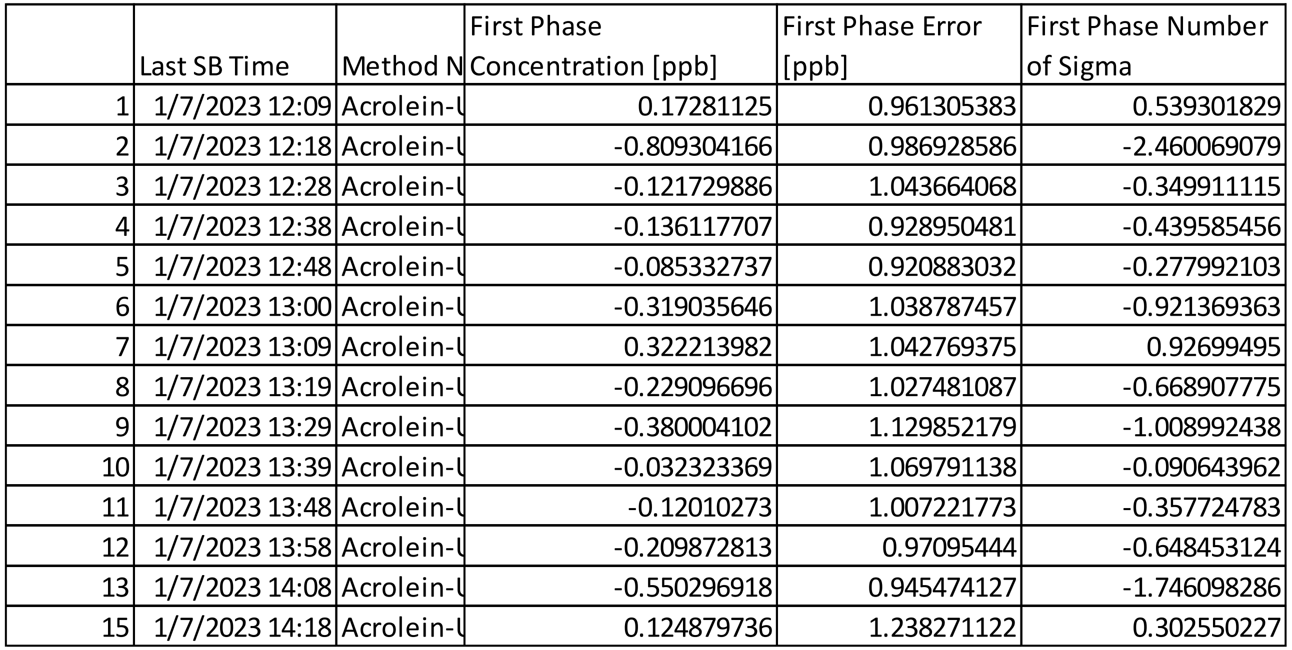
9.6.5.4 Continue this process until all 15 absorbance spectra have been created.

9.6.5.5 Analyze each of the spectra for the target gas concentration.

9.6.5.6 Calculate the standard deviation of the set of concentration values.

9.6.5.7 Multiply the result of Section 9.6.5.6 by 3 to obtain the detection limit.





	Last SB Time	Method N	First Phase Concentration [ppb]	First Phase Error [ppb]	First Phase Number of Sigma
1	1/7/2023 12:09	Acrolein-	0.17281125	0.961305383	0.539301829
2	1/7/2023 12:18	Acrolein-	-0.809304166	0.986928586	-2.460069079
3	1/7/2023 12:28	Acrolein-	-0.121729886	1.043664068	-0.349911115
4	1/7/2023 12:38	Acrolein-	-0.136117707	0.928950481	-0.439585456
5	1/7/2023 12:48	Acrolein-	-0.085332737	0.920883032	-0.277992103
6	1/7/2023 13:00	Acrolein-	-0.319035646	1.038787457	-0.921369363
7	1/7/2023 13:09	Acrolein-	0.322213982	1.042769375	0.92699495
8	1/7/2023 13:19	Acrolein-	-0.229096696	1.027481087	-0.668907775
9	1/7/2023 13:29	Acrolein-	-0.380004102	1.129852179	-1.008992438
10	1/7/2023 13:39	Acrolein-	-0.032323369	1.069791138	-0.090643962
11	1/7/2023 13:48	Acrolein-	-0.12010273	1.007221773	-0.357724783
12	1/7/2023 13:58	Acrolein-	-0.209872813	0.97095444	-0.648453124
13	1/7/2023 14:08	Acrolein-	-0.550296918	0.945474127	-1.746098286
15	1/7/2023 14:18	Acrolein-	0.124879736	1.238271122	0.302550227

STDV	0.280760109
MDL=3*STDV	0.842280327

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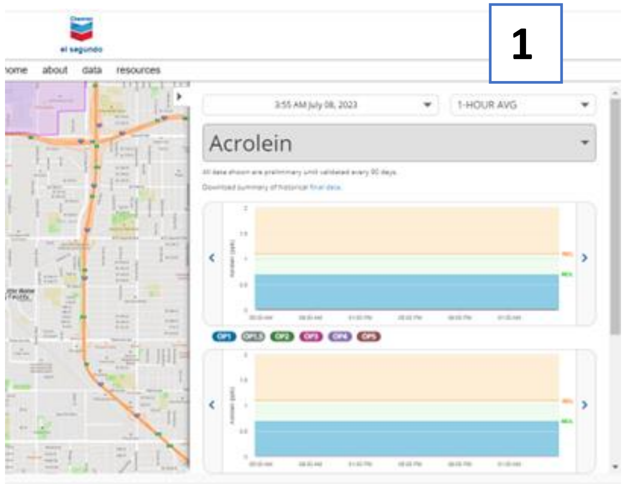
Based on the 3 Years Reported Public Data, an MDL for Acrolein <1.1ppb Can be Achieved

1. Looking at Chevron El Segundo’s website acrolein MDL <0.7ppb
2. In Marathon (Tesoro) quarterly report, monthly statistics, max concentrations of 1.8 ppb are reported.
3. In Valero quarterly report, DL for acrolein is between 0.2-0.8ppb.
4. Most of the facilities and manufacturers report acrolein in 0.3-3 ppb DL
5. In Torrance’s quarterly report, acrolein was measured 0.07% of the time with DL of 2.7ppb .

1



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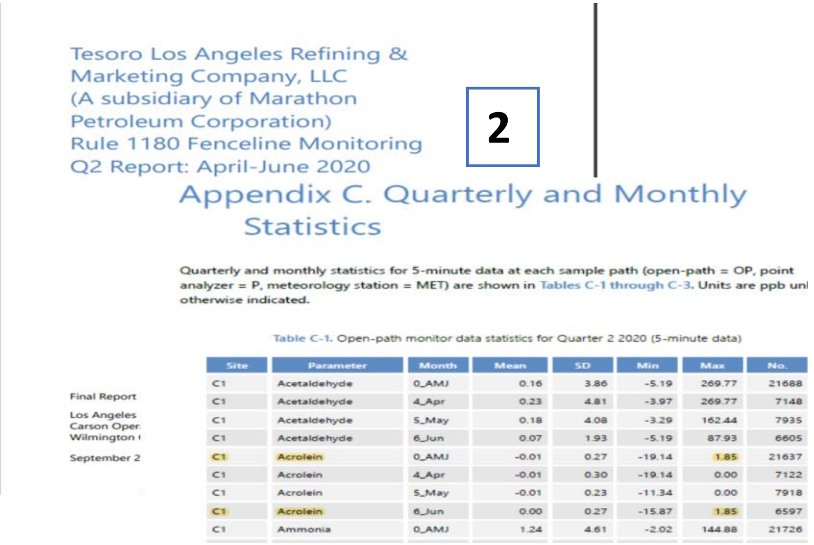


Tesoro Los Angeles Refining &
Marketing Company, LLC
(A subsidiary of Marathon
Petroleum Corporation)
Rule 1180 Fenceline Monitoring
Q2 Report: April-June 2020

Final Report

Los Angeles
Carson Oper
Wilmington (

September 2

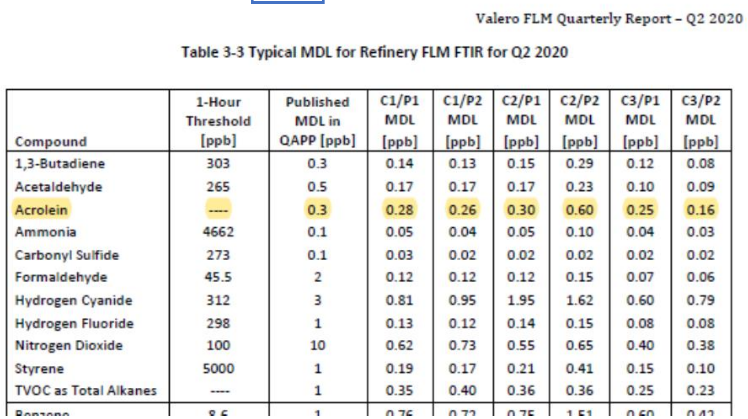
Appendix C. Quarterly and Monthly Statistics

Quarterly and monthly statistics for 5-minute data at each sample path (open-path = OP, point analyzer = P, meteorology station = MET) are shown in Tables C-1 through C-3. Units are ppb unl otherwise indicated.

Table C-1. Open-path monitor data statistics for Quarter 2 2020 (5-minute data)

Site	Parameter	Month	Mean	SD	Min	Max	No.
C1	Acetaldehyde	0_AMJ	0.16	3.86	-5.19	269.77	21688
C1	Acetaldehyde	4_Apr	0.23	4.81	-3.97	269.77	7148
C1	Acetaldehyde	5_May	0.18	4.08	-3.29	162.44	7935
C1	Acetaldehyde	6_Jun	0.07	1.93	-5.19	87.93	6605
C1	Acrolein	0_AMJ	-0.01	0.27	-19.14	1.85	21637
C1	Acrolein	4_Apr	-0.01	0.30	-19.14	0.00	7122
C1	Acrolein	5_May	-0.01	0.23	-11.34	0.00	7918
C1	Acrolein	6_Jun	0.00	0.27	-15.87	1.85	6597
C1	Ammonia	0_AMJ	1.24	4.61	-2.02	144.88	21726

3



Valero FLM Quarterly Report – Q2 2020

Table 3-3 Typical MDL for Refinery FLM FTIR for Q2 2020

Compound	1-Hour Threshold [ppb]	Published MDL in QAPP [ppb]	C1/P1 MDL [ppb]	C1/P2 MDL [ppb]	C2/P1 MDL [ppb]	C2/P2 MDL [ppb]	C3/P1 MDL [ppb]	C3/P2 MDL [ppb]
1,3-Butadiene	303	0.3	0.14	0.13	0.15	0.29	0.12	0.08
Acetaldehyde	265	0.5	0.17	0.17	0.17	0.23	0.10	0.09
Acrolein	----	0.3	0.28	0.26	0.30	0.60	0.25	0.16
Ammonia	4662	0.1	0.05	0.04	0.05	0.10	0.04	0.03
Carbonyl Sulfide	273	0.1	0.03	0.02	0.02	0.02	0.02	0.02
Formaldehyde	45.5	2	0.12	0.12	0.12	0.15	0.07	0.06
Hydrogen Cyanide	312	3	0.81	0.95	1.95	1.62	0.60	0.79
Hydrogen Fluoride	298	1	0.13	0.12	0.14	0.15	0.08	0.08
Nitrogen Dioxide	100	10	0.62	0.73	0.55	0.65	0.40	0.38
Styrene	5000	1	0.19	0.17	0.21	0.41	0.15	0.10
TVOC as Total Alkanes	----	1	0.35	0.40	0.36	0.36	0.25	0.23

5

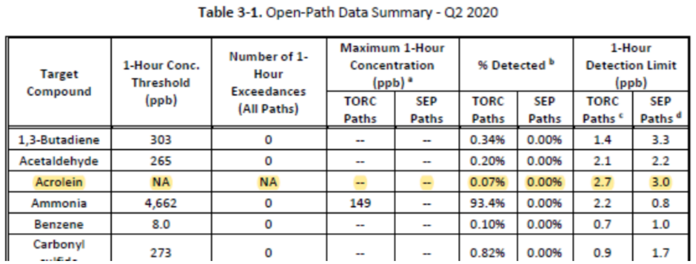


Table 3-1. Open-Path Data Summary - Q2 2020

Target Compound	1-Hour Conc. Threshold (ppb)	Number of 1-Hour Exceedances (All Paths)	Maximum 1-Hour Concentration (ppb) [a]		% Detected [b]		1-Hour Detection Limit (ppb)	
			TORC Paths	SEP Paths	TORC Paths	SEP Paths	TORC Paths [c]	SEP Paths [d]
1,3-Butadiene	303	0	--	--	0.34%	0.00%	1.4	3.3
Acetaldehyde	265	0	--	--	0.20%	0.00%	2.1	2.2
Acrolein	NA	NA	--	--	0.07%	0.00%	2.7	3.0
Ammonia	4,662	0	149	--	93.4%	0.00%	2.2	0.8
Benzene	8.0	0	--	--	0.10%	0.00%	0.7	1.0
Carbonyl	273	0	--	--	0.82%	0.00%	0.9	1.7

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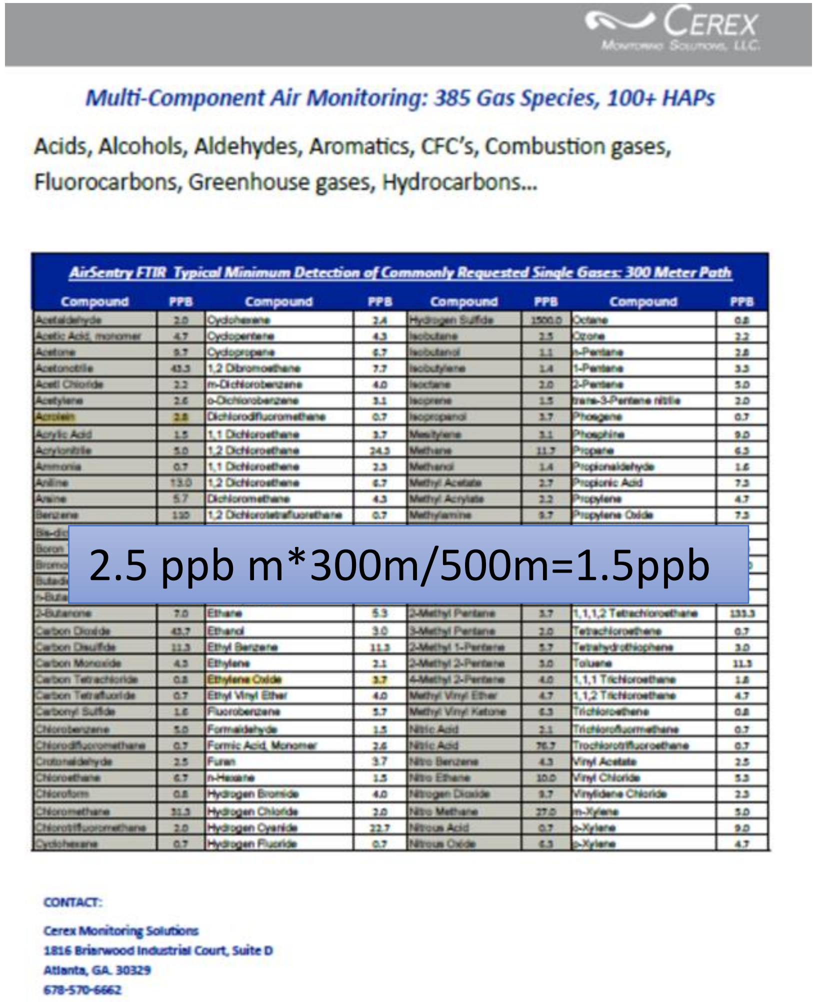
Acrolein DL in SC AQMD Refineries



CEREX
Monitoring Solutions, LLC

Multi-Component Air Monitoring: 385 Gas Species, 100+ HAPs

Acids, Alcohols, Aldehydes, Aromatics, CFC's, Combustion gases, Fluorocarbons, Greenhouse gases, Hydrocarbons...

AirSentry FTIR Typical Minimum Detection of Commonly Requested Single Gases: 300 Meter Path

Compound	PPB	Compound	PPB	Compound	PPB	Compound	PPB
Acetaldehyde	2.0	Cyclohexene	2.4	Hydrogen Sulfide	1500.0	Octane	0.8
Acetic Acid, monomer	4.7	Cyclopentene	4.3	Isobutane	2.5	Ozone	2.2
Acetone	9.7	Cyclopropane	6.7	Isobutanol	1.1	n-Pentane	2.8
Acetonitrile	43.3	1,2 Dibromoethane	7.7	Isobutylene	1.4	1-Pentene	3.3
Acetl Chloride	2.2	m-Dichlorobenzene	4.0	Isoctane	2.0	2-Pentene	5.0
Acetylene	2.6	o-Dichlorobenzene	3.1	Isoprene	1.5	trans-3-Pentene nitile	2.0
Acrolein	2.8	Dichlorodifluoromethane	0.7	Isopropanol	3.7	Phosgene	0.7
Acrylic Acid	1.5	1,1 Dichloroethane	3.7	Mesitylene	3.1	Phosphine	9.0
Acrylonitrile	5.0	1,2 Dichloroethane	24.3	Methane	11.7	Propane	6.3
Ammonia	0.7	1,1 Dichloroethene	2.3	Methanol	1.4	Propionaldehyde	1.6
Aniline	13.0	1,2 Dichloroethene	6.7	Methyl Acetate	2.7	Propionic Acid	7.3
Arsine	5.7	Dichloromethane	4.3	Methyl Acrylate	2.2	Propylene	4.7
Benzene	13.0	1,2 Dichlorotetrafluorethane	0.7	Methylamine	9.7	Propylene Oxide	7.3
Bis-dic							
Boron							
Bromo							
Butadi							
n-Buta							
2-Butanone	7.0	Ethane	5.3	2-Methyl Pentane	3.7	1,1,1,2 Tetrachloroethane	133.3
Carbon Dioxide	43.7	Ethanol	3.0	3-Methyl Pentane	2.0	Tetrachloroethene	0.7
Carbon Disulfide	11.3	Ethyl Benzene	11.3	2-Methyl 1-Pentene	5.7	Tetrahydrothiophene	3.0
Carbon Monoxide	4.3	Ethylene	2.1	2-Methyl 2-Pentene	3.0	Toluene	11.3
Carbon Tetrachloride	0.8	Ethylene Oxide	3.7	4-Methyl 2-Pentene	4.0	1,1,1 Trichloroethane	1.8
Carbon Tetrafluoride	0.7	Ethyl Vinyl Ether	4.0	Methyl Vinyl Ether	4.7	1,1,2 Trichloroethane	4.7
Carbonyl Sulfide	1.6	Fluorobenzene	5.7	Methyl Vinyl Ketone	6.3	Trichloroethene	0.8
Chlorobenzene	5.0	Formaldehyde	1.5	Nitric Acid	2.1	Trichlorofluormethane	0.7
Chlorodifluoromethane	0.7	Formic Acid, Monomer	2.6	Nitric Acid	76.7	Trochlorotrifluoroethane	0.7
Crotonaldehyde	2.5	Furan	3.7	Nitro Benzene	4.3	Vinyl Acetate	2.5
Chloroethane	6.7	n-Hexane	1.5	Nitro Ethane	10.0	Vinyl Chloride	5.3
Chloroform	0.8	Hydrogen Bromide	4.0	Nitrogen Dioxide	9.7	Vinylidene Chloride	2.3
Chloromethane	31.3	Hydrogen Chloride	2.0	Nitro Methane	27.0	m-Xylene	5.0
Chlorotrifluoromethane	2.0	Hydrogen Cyanide	22.7	Nitrous Acid	0.7	o-Xylene	9.0
Cyclohexane	0.7	Hydrogen Fluoride	0.7	Nitrous Oxide	6.3	p-Xylene	4.7

2.5 ppb m*300m/500m=1.5ppb

CONTACT:

Cerex Monitoring Solutions
1816 Briarwood Industrial Court, Suite D
Atlanta, GA. 30329
678-570-6662

	Max DL [ppb]	Min DL [ppb]	Website/ Quarterly Report	
Chevron El Segundo	4	2	0.7*	*public website
Tesoro/ Marathon	31	12	1.4**/16.53*	** Quarterly Report statistic
66 Carson	27	7	30	Measured periodically
66 Wilmington	29	5	30	Measured periodically
Torrance	3	2.7		Measured
Valero	0.3	0.7		Measured

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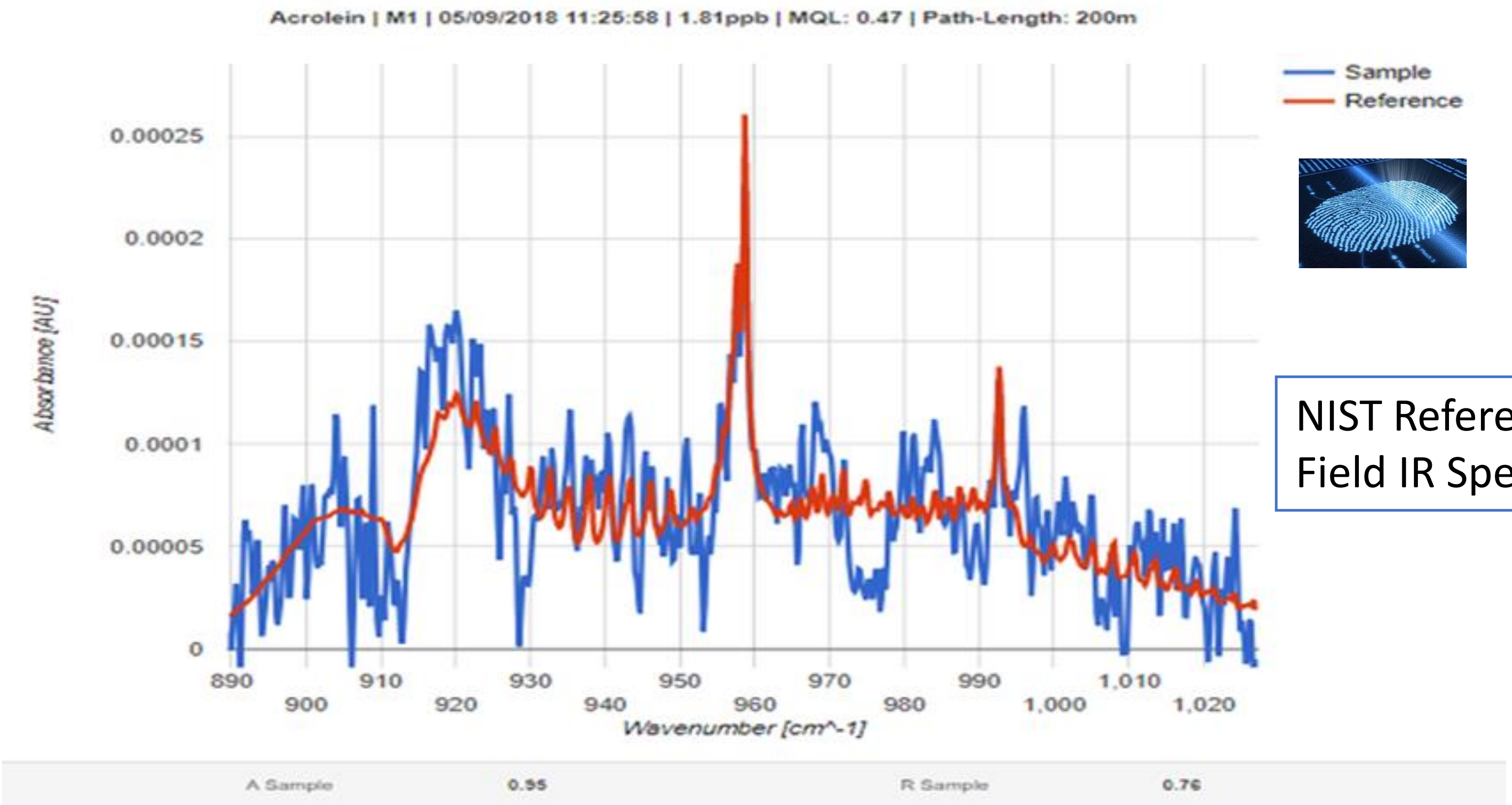
Spectral Validation of Field data Present Visible Proof of Acrolein at 1.81ppb with MQL of 0.47ppb



A Sample 0.95

R Sample 0.76

NIST Reference IR Spectrum 🟥
Field IR Spectrum 🟦

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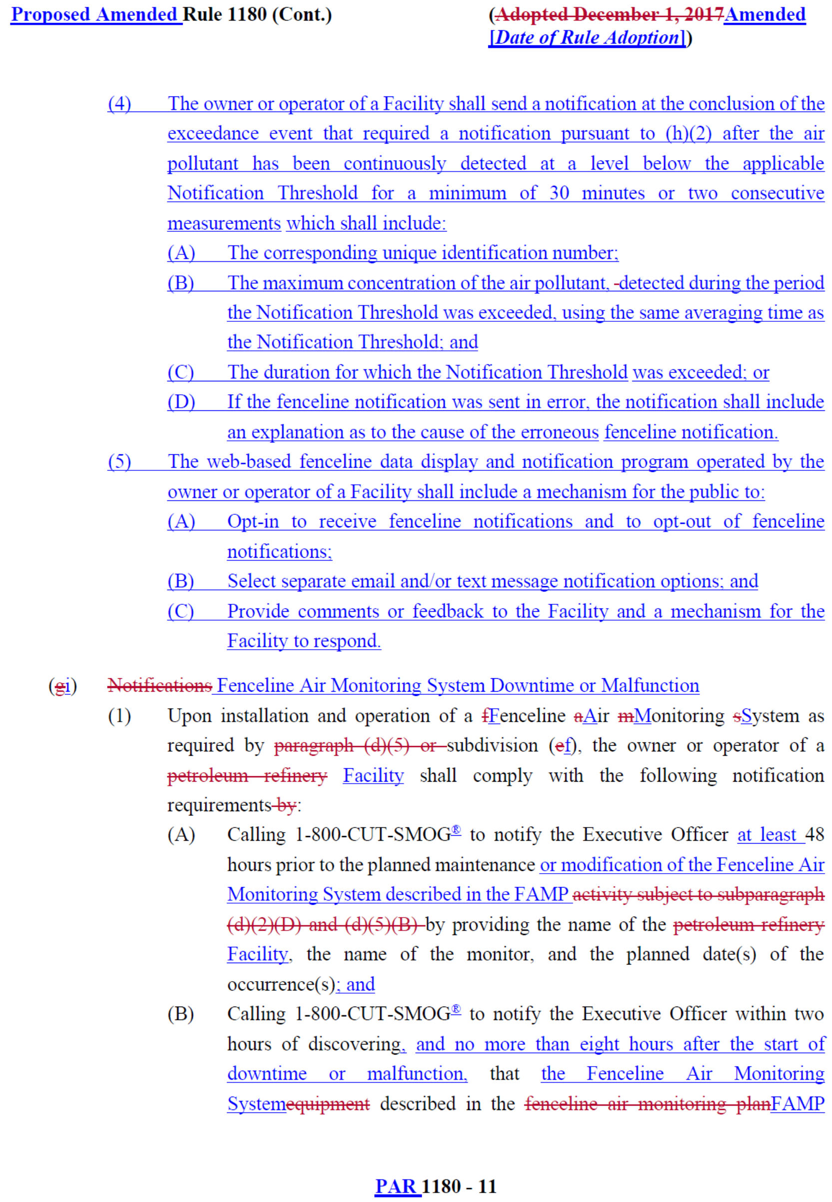
4. The Automatic Relief for Adequate Acrolein MDL in the Staff Report is in Contrast with Rule Language



Proposed Amended Rule 1180 (Cont.) (~~Adopted December 1, 2017~~Amended *[Date of Rule Adoption]*)

(4) The owner or operator of a Facility shall send a notification at the conclusion of the exceedance event that required a notification pursuant to (h)(2) after the air pollutant has been continuously detected at a level below the applicable Notification Threshold for a minimum of 30 minutes or two consecutive measurements which shall include:
  - (A) The corresponding unique identification number;
  - (B) The maximum concentration of the air pollutant, ~~-~~detected during the period the Notification Threshold was exceeded, using the same averaging time as the Notification Threshold; and
  - (C) The duration for which the Notification Threshold was exceeded; or
  - (D) If the fenceline notification was sent in error, the notification shall include an explanation as to the cause of the erroneous fenceline notification.

(5) The web-based fenceline data display and notification program operated by the owner or operator of a Facility shall include a mechanism for the public to:
  - (A) Opt-in to receive fenceline notifications and to opt-out of fenceline notifications;
  - (B) Select separate email and/or text message notification options; and
  - (C) Provide comments or feedback to the Facility and a mechanism for the Facility to respond.

(~~g~~i) ~~Notifications~~ Fenceline Air Monitoring System Downtime or Malfunction

(1) Upon installation and operation of a ~~f~~Fenceline ~~a~~Air ~~m~~Monitoring ~~s~~System as required by ~~paragraph (d)(5) or~~ subdivision (~~e~~f), the owner or operator of a ~~petroleum refinery~~ Facility shall comply with the following notification requirements ~~by~~:
  - (A) Calling 1-800-CUT-SMOG® to notify the Executive Officer at least 48 hours prior to the planned maintenance or modification of the Fenceline Air Monitoring System described in the FAMP ~~activity subject to subparagraph (d)(2)(D) and (d)(5)(B)~~ by providing the name of the ~~petroleum refinery~~ Facility, the name of the monitor, and the planned date(s) of the occurrence(s); and
  - (B) Calling 1-800-CUT-SMOG® to notify the Executive Officer within two hours of discovering, and no more than eight hours after the start of downtime or malfunction, that the Fenceline Air Monitoring System~~equipment~~ described in the ~~fenceline air monitoring plan~~FAMP

PAR 1180 - 11

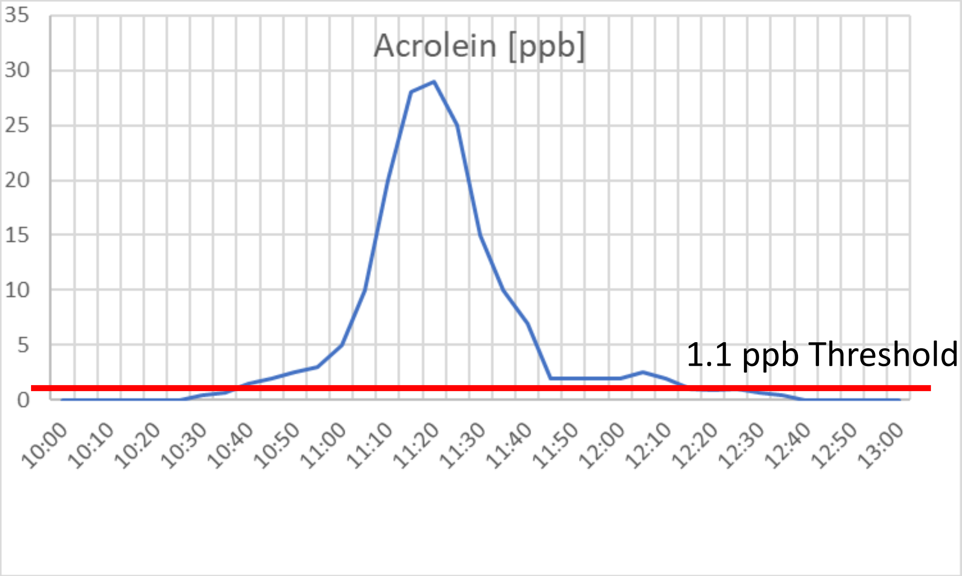
(4) The owner or operator of a Facility shall send a notification at the conclusion of the exceedance event that required a notification pursuant to (h)(2) **after the air pollutant has been continuously detected at a level below the applicable Notification Threshold** for a minimum of 30 minutes or two consecutive measurements which shall include:

This will never happen because the staff reports allow operating Fenceline system with a detection limit above the threshold for Acrolein therefore continuously detecting Acrolein at a level below the Threshold could not happen

Example Demonstrating the Current Status When Each Refinery is Allowed to Use a Different MDL for Acrolein

Time	Acrolein [ppb]
10:00	0
10:05	0
10:10	0
10:15	0
10:20	0
10:25	0
10:30	0.5
10:35	0.7
10:40	1.5
10:45	2
10:50	2.5
10:55	3
11:00	5
11:05	10
11:10	20
11:15	28
11:20	29
11:25	25
11:30	15
11:35	10
11:40	7
11:45	2
11:50	2
11:55	2
12:00	2
12:05	2.5
12:10	2
12:15	1
12:20	0.9
12:25	1
12:30	0.7
12:35	0.5
12:40	0
12:45	0
12:50	0
12:55	0
13:00	0

	Refinery A	Refinery B	Refinery C
MDL	0.5	10	30
Time of alert	10:40	11:10	Never
Back to normal	12:20	Never	Never
Event Duration	2:30	0:25	0:00
Protect the public	Yes	No	No



Refinery A is the only one that alerts the public when the OEAHH threshold for acrolein is exceeded.

Refinery B alerts the public only when the concentration passes 10ppb - nine times the threshold

.

Refinery C didn’t alert the public at all even when the acrolein concentration was 29ppb - more than 26 times the OEAHH threshold.

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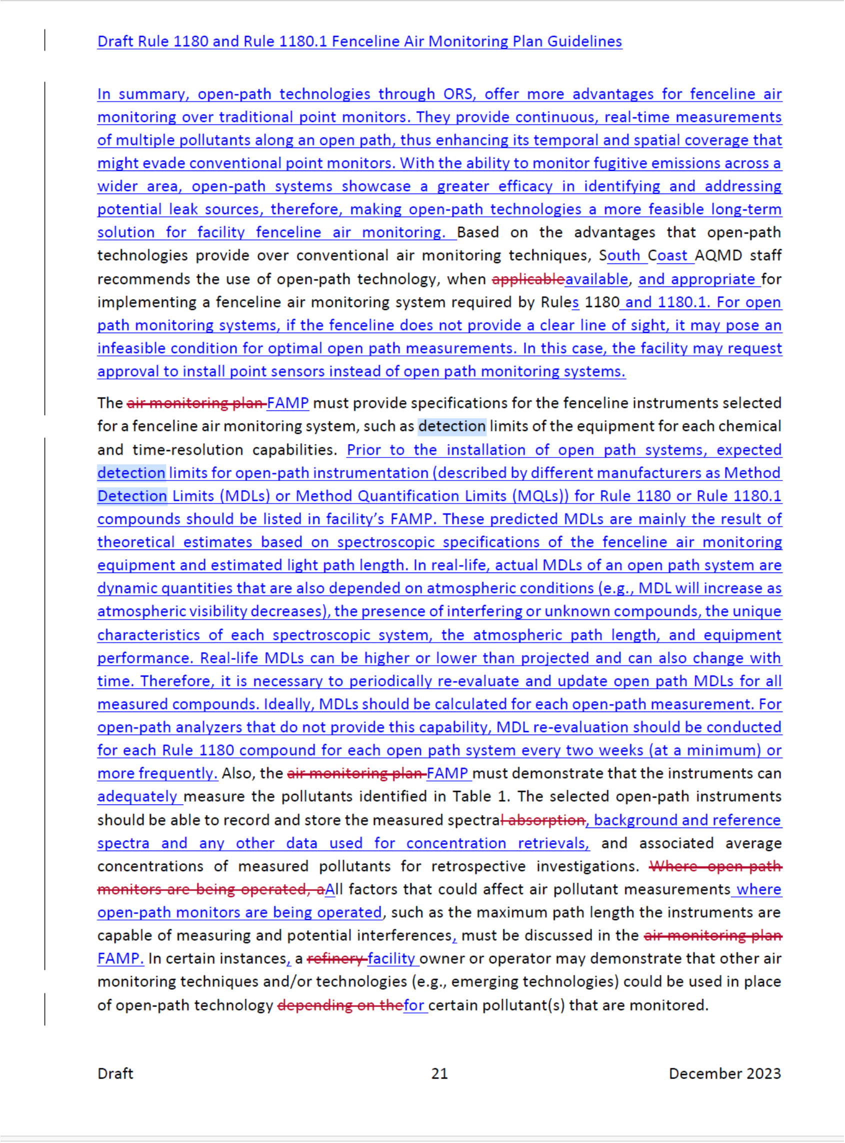
5. The Guideline is Not Specific on How to Measure the Detection Limit (MDL).



In summary, open-path technologies through ORS, offer more advantages for fenceline air monitoring over traditional point monitors. They provide continuous, real-time measurements of multiple pollutants along an open path, thus enhancing its temporal and spatial coverage that might evade conventional point monitors. With the ability to monitor fugitive emissions across a wider area, open-path systems showcase a greater efficacy in identifying and addressing potential leak sources, therefore, making open-path technologies a more feasible long-term solution for facility fenceline air monitoring. Based on the advantages that open-path technologies provide over conventional air monitoring techniques, South Coast AQMD staff recommends the use of open-path technology, when ~~applicable~~available, and appropriate for implementing a fenceline air monitoring system required by Rules 1180 and 1180.1. For open path monitoring systems, if the fenceline does not provide a clear line of sight, it may pose an infeasible condition for optimal open path measurements. In this case, the facility may request approval to install point sensors instead of open path monitoring systems.

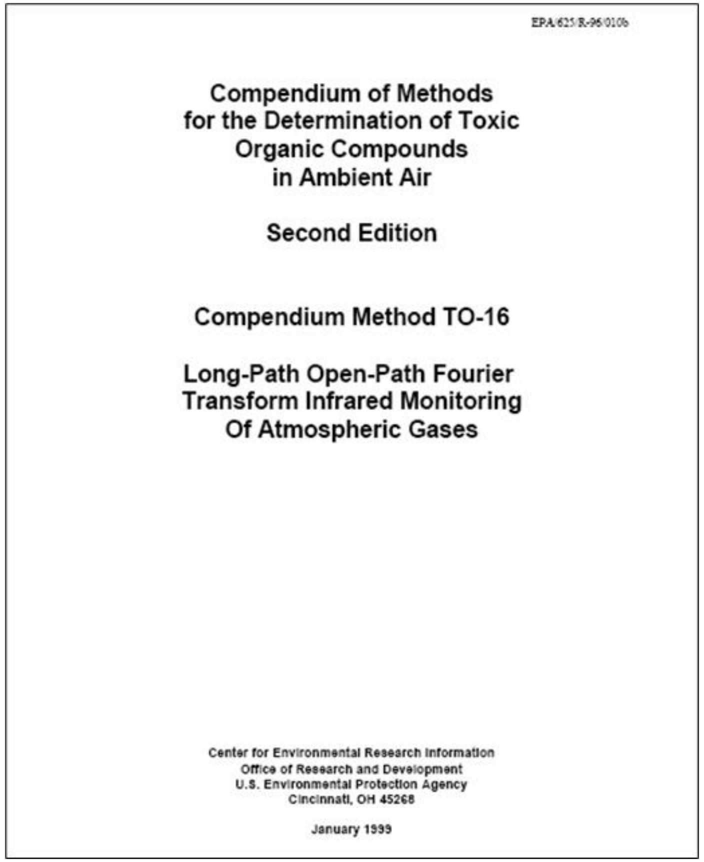
The ~~air monitoring plan~~ FAMP must provide specifications for the fenceline instruments selected for a fenceline air monitoring system, such as detection limits of the equipment for each chemical and time-resolution capabilities. Prior to the installation of open path systems, expected detection limits for open-path instrumentation (described by different manufacturers as Method Detection Limits (MDLs) or Method Quantification Limits (MQLs)) for Rule 1180 or Rule 1180.1 compounds should be listed in facility's FAMP. These predicted MDLs are mainly the result of theoretical estimates based on spectroscopic specifications of the fenceline air monitoring equipment and estimated light path length. In real-life, actual MDLs of an open path system are dynamic quantities that are also depended on atmospheric conditions (e.g., MDL will increase as atmospheric visibility decreases), the presence of interfering or unknown compounds, the unique characteristics of each spectroscopic system, the atmospheric path length, and equipment performance. Real-life MDLs can be higher or lower than projected and can also change with time. Therefore, it is necessary to periodically re-evaluate and update open path MDLs for all measured compounds. Ideally, MDLs should be calculated for each open-path measurement. For open-path analyzers that do not provide this capability, MDL re-evaluation should be conducted for each Rule 1180 compound for each open path system every two weeks (at a minimum) or more frequently. Also, the ~~air monitoring plan~~ FAMP must demonstrate that the instruments can adequately measure the pollutants identified in Table 1. The selected open-path instruments should be able to record and store the measured spectra~~l absorption~~, background and reference spectra and any other data used for concentration retrievals, and associated average concentrations of measured pollutants for retrospective investigations. ~~Where open path monitors are being operated, a~~All factors that could affect air pollutant measurements where open-path monitors are being operated, such as the maximum path length the instruments are capable of measuring and potential interferences, must be discussed in the ~~air monitoring plan~~ FAMP. In certain instances, a ~~refinery~~ facility owner or operator may demonstrate that other air monitoring techniques and/or technologies (e.g., emerging technologies) could be used in place of open-path technology ~~depending on the~~for certain pollutant(s) that are monitored.

"Ideally, MDLs should be calculated for each open-path measurement. For open-path analyzers that do not provide this capability, MDL re-evaluation should be conducted for each Rule 1180 compound for each open path system every two weeks (at a minimum) or more frequently. "

Open Path Analyzers do not provide MDL. Real-time MDL can and should be calculated for all refineries using the same procedure that should be part of the guideline. Calculating MDL once every 2 weeks does not represent the measurements and it is time and labor-consuming.

What is the Detection Limit Based on US EPA TO-16 Using Open Path FTIR

Atmosfir calculates the MDL based on US EPA TO-16, sections 5.13 and 9.6:



EPA/625/R-96/010b

Compendium of Methods
for the Determination of Toxic
Organic Compounds
in Ambient Air

Second Edition

Compendium Method TO-16

Long-Path Open-Path Fourier
Transform Infrared Monitoring
Of Atmospheric Gases

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

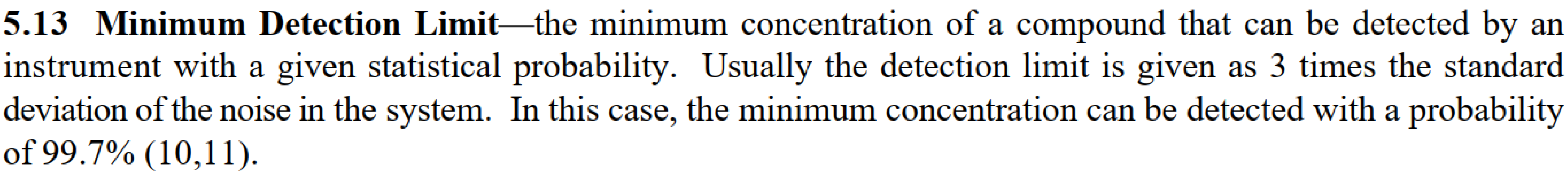
"**5.13 Minimum Detection Limit**—the minimum concentration of a compound that can be detected by an instrument with a given statistical probability. Usually, **the detection limit is given as 3 times the standard deviation of the noise in the system.** In this case, the minimum concentration can be detected with a probability of 99.7% (10,11)."

"9.6 The Determination of the Detection Limit

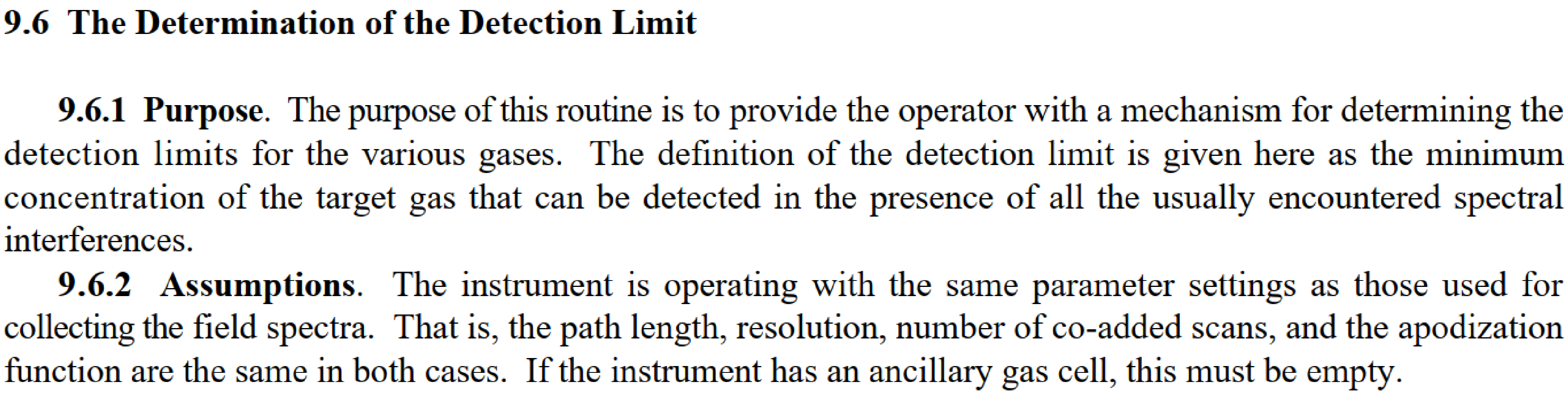
9.6.1 Purpose. The purpose of this routine is to provide the operator with a mechanism for determining the detection limits for the various gases. The definition of the detection limit is given here as **the minimum concentration of the target gas that can be detected in the presence of all the usually encountered spectral interferences.**

9.6.2 Assumptions. **The instrument is operating with the same parameter settings as those used for collecting the field spectra**. That is, the path length, resolution, number of co-added scans, and the apodization function are the same in both cases. If the instrument has an ancillary gas cell, this must be empty.

The D-fenceline^{TM} System Real Time Monitoring of Detection Level Works According to TO-16



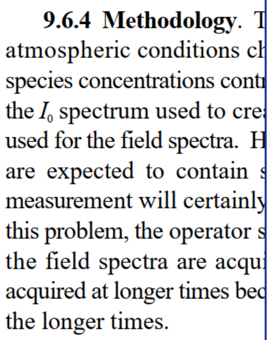
5.13 Minimum Detection Limit—the minimum concentration of a compound that can be detected by an instrument with a given statistical probability. Usually the detection limit is given as 3 times the standard deviation of the noise in the system. In this case, the minimum concentration can be detected with a probability of 99.7% (10,11).



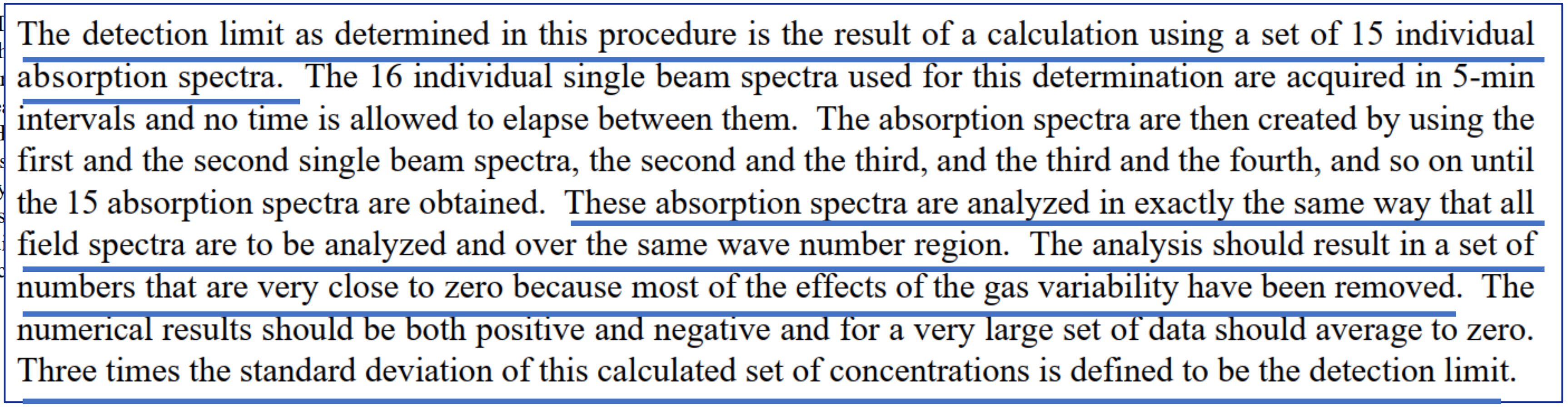
9.6 The Determination of the Detection Limit

9.6.1 Purpose. The purpose of this routine is to provide the operator with a mechanism for determining the detection limits for the various gases. The definition of the detection limit is given here as the minimum concentration of the target gas that can be detected in the presence of all the usually encountered spectral interferences.

9.6.2 Assumptions. The instrument is operating with the same parameter settings as those used for collecting the field spectra. That is, the path length, resolution, number of co-added scans, and the apodization function are the same in both cases. If the instrument has an ancillary gas cell, this must be empty.



9.6.4 Methodology. T
atmospheric conditions ch
species concentrations cont
the I_0 spectrum used to cre
used for the field spectra. H
are expected to contain s
measurement will certainly
this problem, the operator s
the field spectra are acqu
acquired at longer times bec
the longer times.



The detection limit as determined in this procedure is the result of a calculation using a set of 15 individual absorption spectra. The 16 individual single beam spectra used for this determination are acquired in 5-min intervals and no time is allowed to elapse between them. The absorption spectra are then created by using the first and the second single beam spectra, the second and the third, and the third and the fourth, and so on until the 15 absorption spectra are obtained. These absorption spectra are analyzed in exactly the same way that all field spectra are to be analyzed and over the same wave number region. The analysis should result in a set of numbers that are very close to zero because most of the effects of the gas variability have been removed. The numerical results should be both positive and negative and for a very large set of data should average to zero. Three times the standard deviation of this calculated set of concentrations is defined to be the detection limit.

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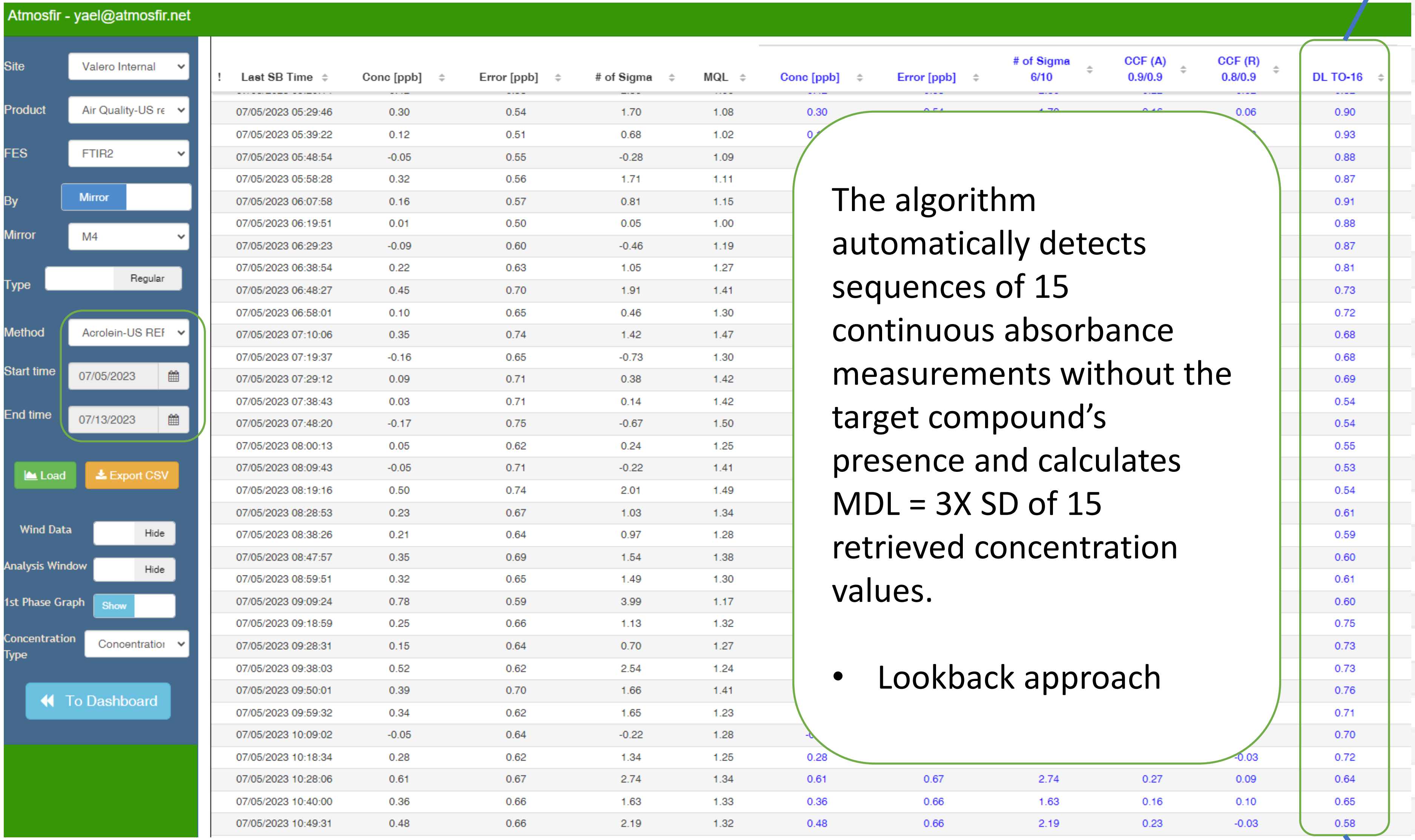
System Real Time Monitoring of Detection Level According to TO-16



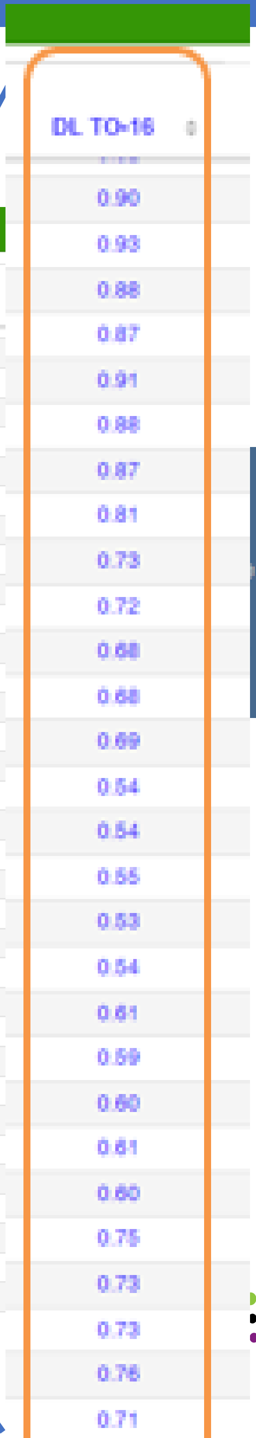
Atmosfir - yael@atmosfir.net

Site: Valero Internal
Product: Air Quality-US re
FES: FTIR2
By: Mirror
Mirror: M4
Type: Regular
Method: Acrolein-US REF
Start time: 07/05/2023
End time: 07/13/2023

!	Last SB Time	Conc [ppb]	Error [ppb]	# of Sigma	MQL	Conc [ppb]	Error [ppb]	# of Sigma 6/10	CCF (A) 0.9/0.9	CCF (R) 0.8/0.9	DL TO-16
	07/05/2023 05:29:46	0.30	0.54	1.70	1.08	0.30				0.06	0.90
	07/05/2023 05:39:22	0.12	0.51	0.68	1.02						0.93
	07/05/2023 05:48:54	-0.05	0.55	-0.28	1.09						0.88
	07/05/2023 05:58:28	0.32	0.56	1.71	1.11						0.87
	07/05/2023 06:07:58	0.16	0.57	0.81	1.15						0.91
	07/05/2023 06:19:51	0.01	0.50	0.05	1.00						0.88
	07/05/2023 06:29:23	-0.09	0.60	-0.46	1.19						0.87
	07/05/2023 06:38:54	0.22	0.63	1.05	1.27						0.81
	07/05/2023 06:48:27	0.45	0.70	1.91	1.41						0.73
	07/05/2023 06:58:01	0.10	0.65	0.46	1.30						0.72
	07/05/2023 07:10:06	0.35	0.74	1.42	1.47						0.68
	07/05/2023 07:19:37	-0.16	0.65	-0.73	1.30						0.68
	07/05/2023 07:29:12	0.09	0.71	0.38	1.42						0.69
	07/05/2023 07:38:43	0.03	0.71	0.14	1.42						0.54
	07/05/2023 07:48:20	-0.17	0.75	-0.67	1.50						0.54
	07/05/2023 08:00:13	0.05	0.62	0.24	1.25						0.55
	07/05/2023 08:09:43	-0.05	0.71	-0.22	1.41						0.53
	07/05/2023 08:19:16	0.50	0.74	2.01	1.49						0.54
	07/05/2023 08:28:53	0.23	0.67	1.03	1.34						0.61
	07/05/2023 08:38:26	0.21	0.64	0.97	1.28						0.59
	07/05/2023 08:47:57	0.35	0.69	1.54	1.38						0.60
	07/05/2023 08:59:51	0.32	0.65	1.49	1.30						0.61
	07/05/2023 09:09:24	0.78	0.59	3.99	1.17						0.60
	07/05/2023 09:18:59	0.25	0.66	1.13	1.32						0.75
	07/05/2023 09:28:31	0.15	0.64	0.70	1.27						0.73
	07/05/2023 09:38:03	0.52	0.62	2.54	1.24						0.73
	07/05/2023 09:50:01	0.39	0.70	1.66	1.41						0.76
	07/05/2023 09:59:32	0.34	0.62	1.65	1.23						0.71
	07/05/2023 10:09:02	-0.05	0.64	-0.22	1.28						0.70
	07/05/2023 10:18:34	0.28	0.62	1.34	1.25	0.28				-0.03	0.72
	07/05/2023 10:28:06	0.61	0.67	2.74	1.34	0.61	0.67	2.74	0.27	0.09	0.64
	07/05/2023 10:40:00	0.36	0.66	1.63	1.33	0.36	0.66	1.63	0.16	0.10	0.65
	07/05/2023 10:49:31	0.48	0.66	2.19	1.32	0.48	0.66	2.19	0.23	-0.03	0.58

The algorithm automatically detects sequences of 15 continuous absorbance measurements without the target compound's presence and calculates MDL = 3X SD of 15 retrieved concentration values.

- Lookback approach



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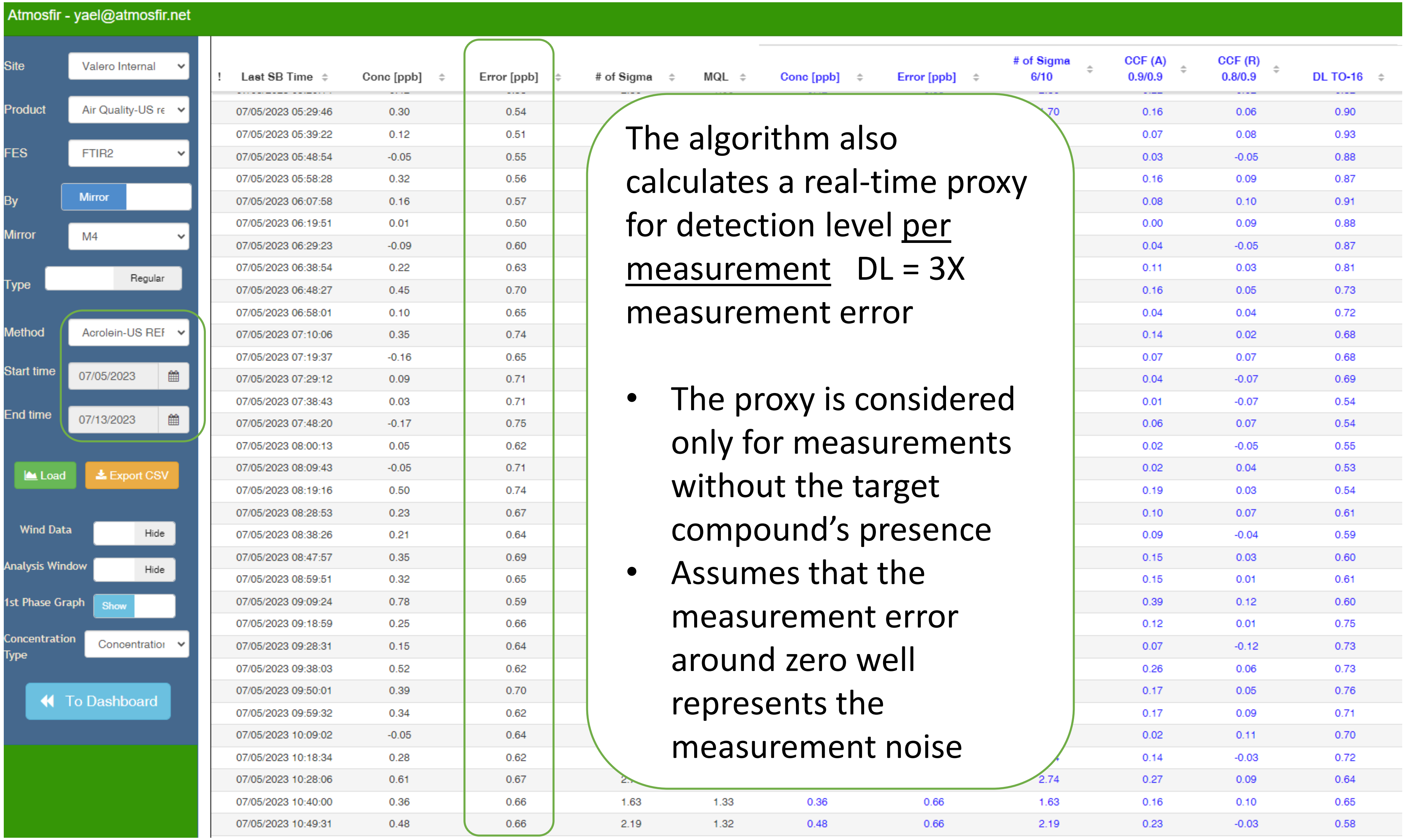
System Real Time Monitoring of Detection Level According to TO-16



Atmosfir - yael@atmosfir.net

Site: Valero Internal
Product: Air Quality-US re
FES: FTIR2
By: Mirror
Mirror: M4
Type: Regular
Method: Acrolein-US REF
Start time: 07/05/2023
End time: 07/13/2023

Wind Data: Hide
Analysis Window: Hide
1st Phase Graph: Show
Concentration Type: Concentratio

!	Last SB Time	Conc [ppb]	Error [ppb]	# of Sigma	MQL	Conc [ppb]	Error [ppb]	# of Sigma 6/10	CCF (A) 0.9/0.9	CCF (R) 0.8/0.9	DL TO-16
	07/05/2023 05:29:46	0.30	0.54						0.16	0.06	0.90
	07/05/2023 05:39:22	0.12	0.51						0.07	0.08	0.93
	07/05/2023 05:48:54	-0.05	0.55						0.03	-0.05	0.88
	07/05/2023 05:58:28	0.32	0.56						0.16	0.09	0.87
	07/05/2023 06:07:58	0.16	0.57						0.08	0.10	0.91
	07/05/2023 06:19:51	0.01	0.50						0.00	0.09	0.88
	07/05/2023 06:29:23	-0.09	0.60						0.04	-0.05	0.87
	07/05/2023 06:38:54	0.22	0.63						0.11	0.03	0.81
	07/05/2023 06:48:27	0.45	0.70						0.16	0.05	0.73
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	07/05/2023 07:10:06	0.35	0.74						0.14	0.02	0.68
	07/05/2023 07:19:37	-0.16	0.65						0.07	0.07	0.68
	07/05/2023 07:29:12	0.09	0.71						0.04	-0.07	0.69
	07/05/2023 07:38:43	0.03	0.71						0.01	-0.07	0.54
	07/05/2023 07:48:20	-0.17	0.75						0.06	0.07	0.54
	07/05/2023 08:00:13	0.05	0.62						0.02	-0.05	0.55
	07/05/2023 08:09:43	-0.05	0.71						0.02	0.04	0.53
	07/05/2023 08:19:16	0.50	0.74						0.19	0.03	0.54
	07/05/2023 08:28:53	0.23	0.67						0.10	0.07	0.61
	07/05/2023 08:38:26	0.21	0.64						0.09	-0.04	0.59
	07/05/2023 08:47:57	0.35	0.69						0.15	0.03	0.60
	07/05/2023 08:59:51	0.32	0.65						0.15	0.01	0.61
	07/05/2023 09:09:24	0.78	0.59						0.39	0.12	0.60
	07/05/2023 09:18:59	0.25	0.66						0.12	0.01	0.75
	07/05/2023 09:28:31	0.15	0.64						0.07	-0.12	0.73
	07/05/2023 09:38:03	0.52	0.62						0.26	0.06	0.73
	07/05/2023 09:50:01	0.39	0.70						0.17	0.05	0.76
	07/05/2023 09:59:32	0.34	0.62						0.17	0.09	0.71
	07/05/2023 10:09:02	-0.05	0.64						0.02	0.11	0.70
	07/05/2023 10:18:34	0.28	0.62						0.14	-0.03	0.72
	07/05/2023 10:28:06	0.61	0.67					2.74	0.27	0.09	0.64
	07/05/2023 10:40:00	0.36	0.66	1.63	1.33	0.36	0.66	1.63	0.16	0.10	0.65
	07/05/2023 10:49:31	0.48	0.66	2.19	1.32	0.48	0.66	2.19	0.23	-0.03	0.58

The algorithm also calculates a real-time proxy for detection level <u>per measurement</u>   DL = 3X measurement error

- The proxy is considered only for measurements without the target compound's presence
- Assumes that the measurement error around zero well represents the measurement noise

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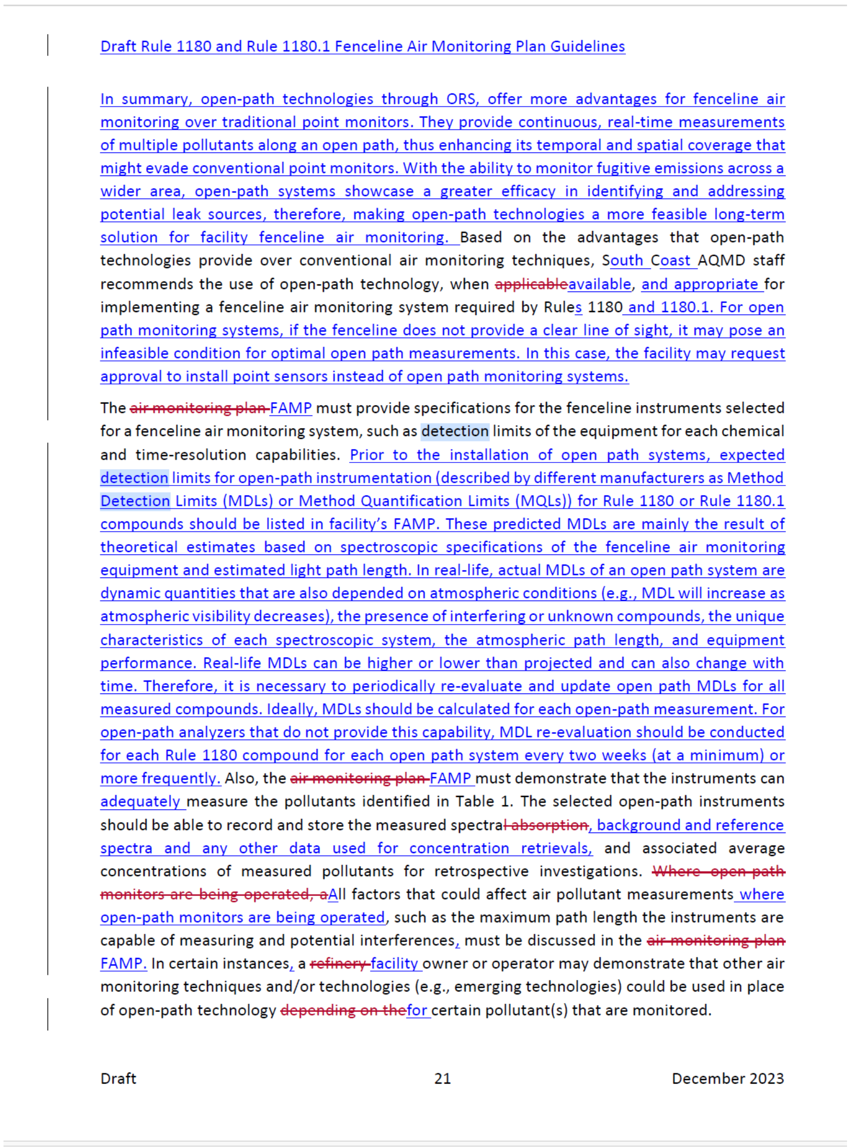
5. The Guideline is Not Specific on What the MDL Should Be Considering Rule 1180 Threshold



Draft Rule 1180 and Rule 1180.1 Fenceline Air Monitoring Plan Guidelines

In summary, open-path technologies through ORS, offer more advantages for fenceline air monitoring over traditional point monitors. They provide continuous, real-time measurements of multiple pollutants along an open path, thus enhancing its temporal and spatial coverage that might evade conventional point monitors. With the ability to monitor fugitive emissions across a wider area, open-path systems showcase a greater efficacy in identifying and addressing potential leak sources, therefore, making open-path technologies a more feasible long-term solution for facility fenceline air monitoring. Based on the advantages that open-path technologies provide over conventional air monitoring techniques, South Coast AQMD staff recommends the use of open-path technology, when ~~applicable~~available, and appropriate for implementing a fenceline air monitoring system required by Rules 1180 and 1180.1. For open path monitoring systems, if the fenceline does not provide a clear line of sight, it may pose an infeasible condition for optimal open path measurements. In this case, the facility may request approval to install point sensors instead of open path monitoring systems.

The ~~air monitoring plan~~ FAMP must provide specifications for the fenceline instruments selected for a fenceline air monitoring system, such as detection limits of the equipment for each chemical and time-resolution capabilities. Prior to the installation of open path systems, expected detection limits for open-path instrumentation (described by different manufacturers as Method Detection Limits (MDLs) or Method Quantification Limits (MQLs)) for Rule 1180 or Rule 1180.1 compounds should be listed in facility's FAMP. These predicted MDLs are mainly the result of theoretical estimates based on spectroscopic specifications of the fenceline air monitoring equipment and estimated light path length. In real-life, actual MDLs of an open path system are dynamic quantities that are also depended on atmospheric conditions (e.g., MDL will increase as atmospheric visibility decreases), the presence of interfering or unknown compounds, the unique characteristics of each spectroscopic system, the atmospheric path length, and equipment performance. Real-life MDLs can be higher or lower than projected and can also change with time. Therefore, it is necessary to periodically re-evaluate and update open path MDLs for all measured compounds. Ideally, MDLs should be calculated for each open-path measurement. For open-path analyzers that do not provide this capability, MDL re-evaluation should be conducted for each Rule 1180 compound for each open path system every two weeks (at a minimum) or more frequently. Also, the ~~air monitoring plan~~ FAMP must demonstrate that the instruments can adequately measure the pollutants identified in Table 1. The selected open-path instruments should be able to record and store the measured spectra~~l absorption~~, background and reference spectra and any other data used for concentration retrievals, and associated average concentrations of measured pollutants for retrospective investigations. ~~Where open path monitors are being operated, a~~All factors that could affect air pollutant measurements where open-path monitors are being operated, such as the maximum path length the instruments are capable of measuring and potential interferences, must be discussed in the ~~air monitoring plan~~ FAMP. In certain instances, a ~~refinery~~ facility owner or operator may demonstrate that other air monitoring techniques and/or technologies (e.g., emerging technologies) could be used in place of open-path technology ~~depending on the~~for certain pollutant(s) that are monitored.

Draft 21 December 2023

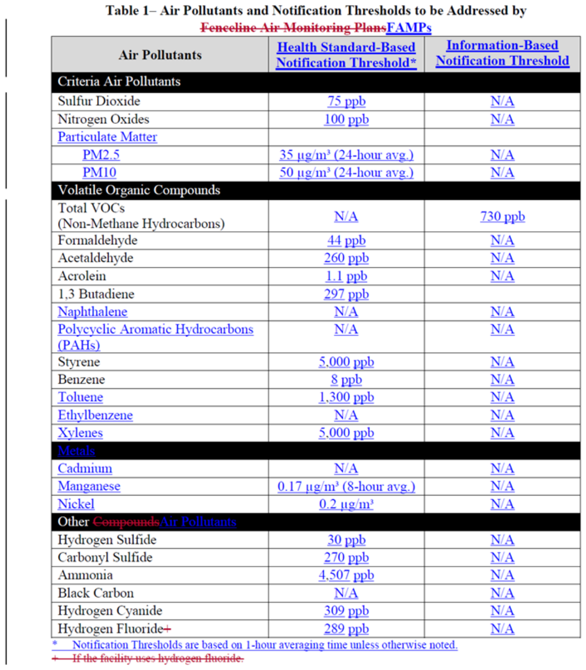


Table 1– Air Pollutants and Notification Thresholds to be Addressed by ~~Fenceline Air Monitoring Plans~~FAMPs

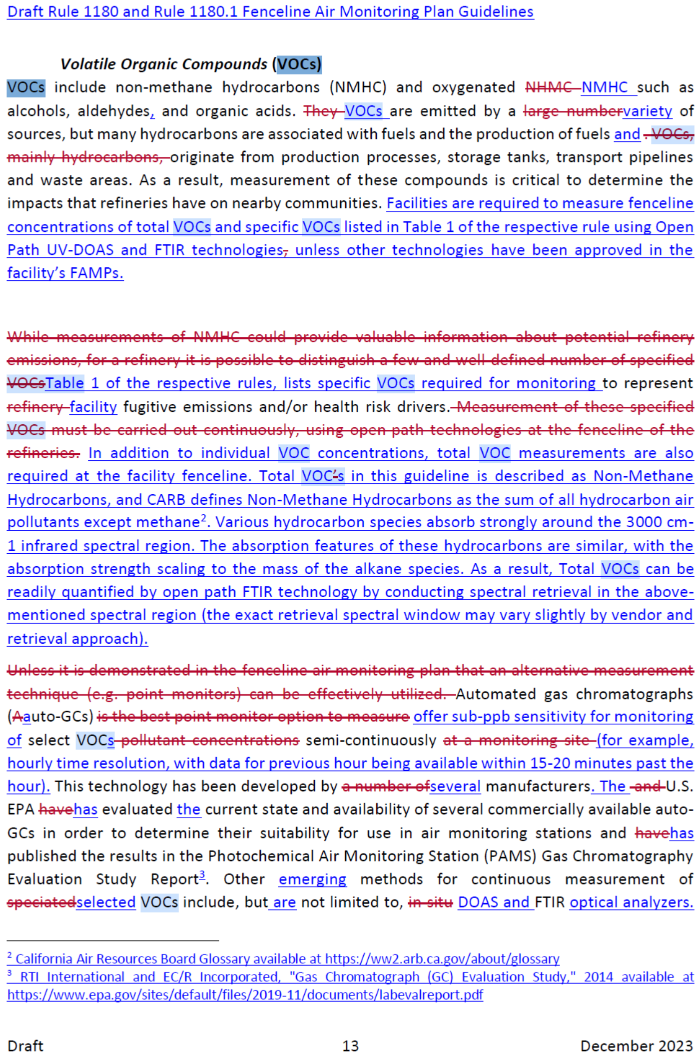
Air Pollutants	**Health Standard-Based Notification Threshold***	**Information-Based Notification Threshold**
Criteria Air Pollutants		
Sulfur Dioxide	75 ppb	N/A
Nitrogen Oxides	100 ppb	N/A
Particulate Matter		
PM2.5	35 $\mu g/m^3$ (24-hour avg.)	N/A
PM10	50 $\mu g/m^3$ (24-hour avg.)	N/A
Volatile Organic Compounds		
Total VOCs (Non-Methane Hydrocarbons)	N/A	730 ppb
Formaldehyde	44 ppb	N/A
Acetaldehyde	260 ppb	N/A
Acrolein	1.1 ppb	N/A
1,3 Butadiene	297 ppb	
Naphthalene	N/A	N/A
Polycyclic Aromatic Hydrocarbons (PAHs)	N/A	N/A
Styrene	5,000 ppb	N/A
Benzene	8 ppb	N/A
Toluene	1,300 ppb	N/A
Ethylbenzene	N/A	N/A
Xylenes	5,000 ppb	N/A
Metals		
Cadmium	N/A	N/A
Manganese	0.17 $\mu g/m^3$ (8-hour avg.)	N/A
Nickel	0.2 $\mu g/m^3$	N/A
Other ~~Compounds~~Air Pollutants		
Hydrogen Sulfide	30 ppb	N/A
Carbonyl Sulfide	270 ppb	N/A
Ammonia	4,507 ppb	N/A
Black Carbon	N/A	N/A
Hydrogen Cyanide	309 ppb	N/A
Hydrogen Fluoride~~+~~	289 ppb	N/A

* Notification Thresholds are based on 1-hour averaging time unless otherwise noted.

~~+ If the facility uses hydrogen fluoride.~~

Usually, MDL is required to be at least 30% of the Thresholds. If it is not possible it should be at least below the Threshold. Allowing MDL above the Threshold is against the rule's purpose.

7. TVOCs According to the Guidelines Plan



Draft Rule 1180 and Rule 1180.1 Fenceline Air Monitoring Plan Guidelines

Volatile Organic Compounds (VOCs)

VOCs include non-methane hydrocarbons (NMHC) and oxygenated ~~NHMC~~ NMHC such as alcohols, aldehydes, and organic acids. ~~They~~ VOCs are emitted by a ~~large number~~variety of sources, but many hydrocarbons are associated with fuels and the production of fuels and ~~. VOCs, mainly hydrocarbons,~~ originate from production processes, storage tanks, transport pipelines and waste areas. As a result, measurement of these compounds is critical to determine the impacts that refineries have on nearby communities. Facilities are required to measure fenceline concentrations of total VOCs and specific VOCs listed in Table 1 of the respective rule using Open Path UV-DOAS and FTIR technologies~~,~~ unless other technologies have been approved in the facility's FAMPs.

~~While measurements of NMHC could provide valuable information about potential refinery emissions, for a refinery it is possible to distinguish a few and well defined number of specified VOCs~~Table 1 of the respective rules, lists specific VOCs required for monitoring to represent ~~refinery~~ facility fugitive emissions and/or health risk drivers. ~~Measurement of these specified VOCs must be carried out continuously, using open path technologies at the fenceline of the refineries.~~ In addition to individual VOC concentrations, total VOC measurements are also required at the facility fenceline. Total VOC~~'~~s in this guideline is described as Non-Methane Hydrocarbons, and CARB defines Non-Methane Hydrocarbons as the sum of all hydrocarbon air pollutants except methane[2]. Various hydrocarbon species absorb strongly around the 3000 cm-1 infrared spectral region. The absorption features of these hydrocarbons are similar, with the absorption strength scaling to the mass of the alkane species. As a result, Total VOCs can be readily quantified by open path FTIR technology by conducting spectral retrieval in the above-mentioned spectral region (the exact retrieval spectral window may vary slightly by vendor and retrieval approach).

~~Unless it is demonstrated in the fenceline air monitoring plan that an alternative measurement technique (e.g. point monitors) can be effectively utilized.~~ Automated gas chromatographs (~~A~~auto-GCs) ~~is the best point monitor option to measure~~ offer sub-ppb sensitivity for monitoring of select VOCs ~~pollutant concentrations~~ semi-continuously ~~at a monitoring site~~ (for example, hourly time resolution, with data for previous hour being available within 15-20 minutes past the hour). This technology has been developed by ~~a number of~~several manufacturers. The ~~and~~ U.S. EPA ~~have~~has evaluated the current state and availability of several commercially available auto-GCs in order to determine their suitability for use in air monitoring stations and ~~have~~has published the results in the Photochemical Air Monitoring Station (PAMS) Gas Chromatography Evaluation Study Report[3]. Other emerging methods for continuous measurement of ~~speciated~~selected VOCs include, but are not limited to, ~~in-situ~~ DOAS and FTIR optical analyzers.

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[2] California Air Resources Board Glossary available at https://ww2.arb.ca.gov/about/glossary

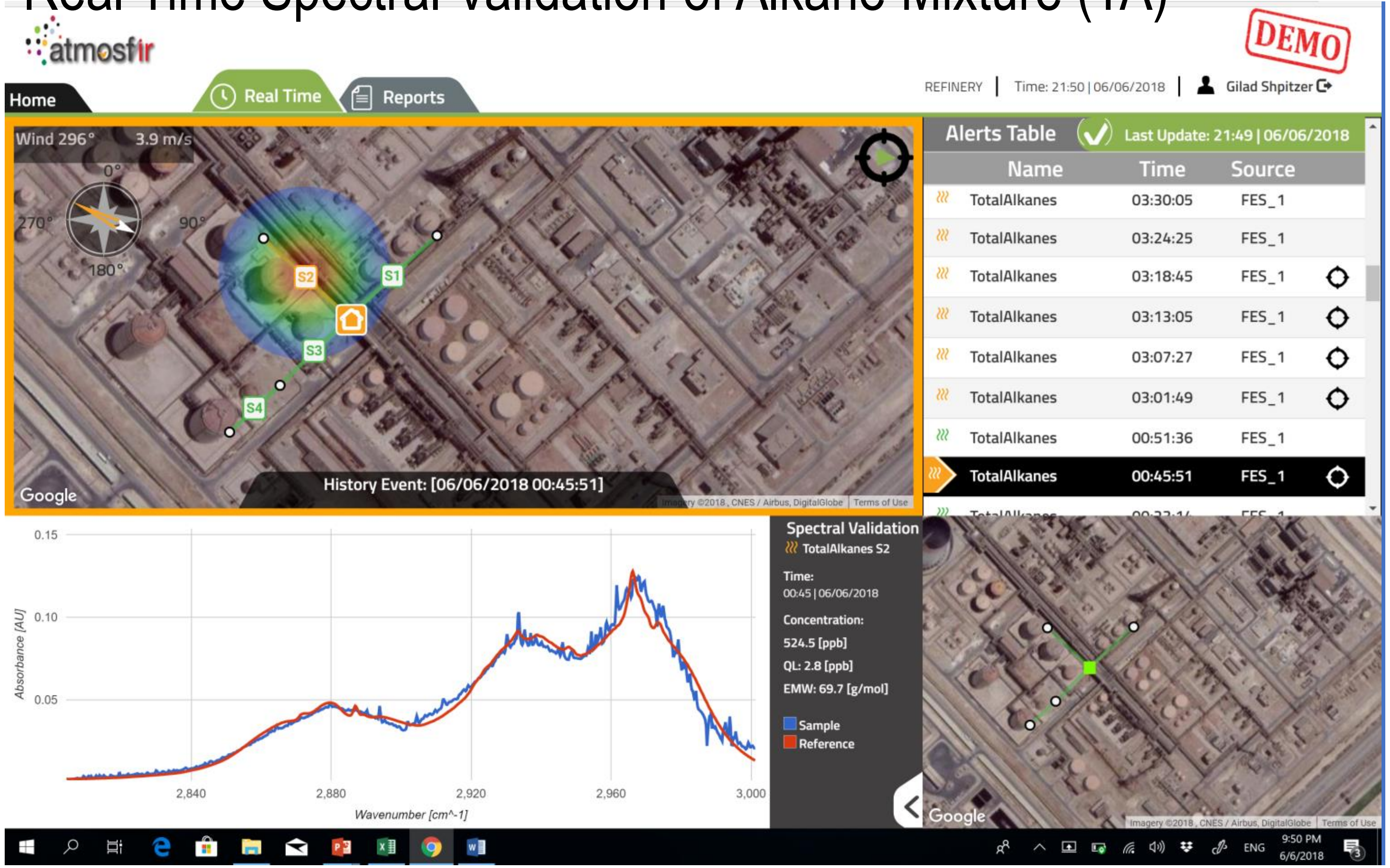
[3] RTI International and EC/R Incorporated, "Gas Chromatograph (GC) Evaluation Study," 2014 available at https://www.epa.gov/sites/default/files/2019-11/documents/labevalreport.pdf

"Various hydrocarbon species absorb strongly around the 3000 cm-1 infrared spectral region. The absorption features of these hydrocarbons are similar, with the absorption strength scaling to the mass of the alkane species. As a result, Total VOCs can be readily quantified by open path FTIR technology by conducting spectral retrieval in the above-mentioned spectral region (the exact retrieval spectral window may vary slightly by vendor and retrieval approach). "

The Guidelines should provide specific procedures for measuring TVOC/TA Otherwise, there is no uniformity between facilities.
The official EPA Procedure for measuring TA should be adopted.
When Reporting TVOC or Total Alkane Average Molecular Weight should be reported with the concentration in ppb.

SC AQMD Rule 1180 – Total VOCs

Real Time Spectral Validation of Alkane Mixture (TA)



REFINERY | Time: 21:50 | 06/06/2018 | Gilad Shpitzer

Alerts Table Last Update: 21:49 | 06/06/2018

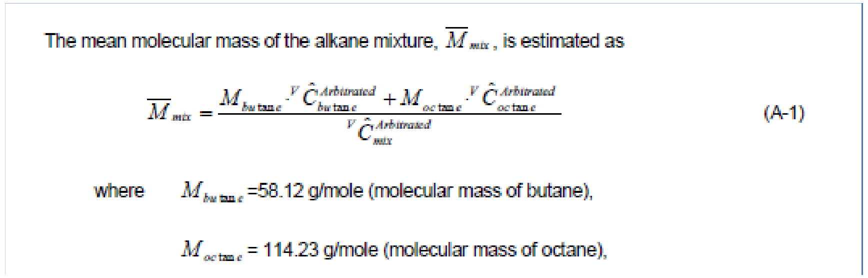
Name	Time	Source
TotalAlkanes	03:30:05	FES_1
TotalAlkanes	03:24:25	FES_1
TotalAlkanes	03:18:45	FES_1
TotalAlkanes	03:13:05	FES_1
TotalAlkanes	03:07:27	FES_1
TotalAlkanes	03:01:49	FES_1
TotalAlkanes	00:51:36	FES_1
TotalAlkanes	00:45:51	FES_1

Spectral Validation
TotalAlkanes S2
Time:
00:45 | 06/06/2018
Concentration:
524.5 [ppb]
QL: 2.8 [ppb]
EMW: 69.7 [g/mol]

🟦 Sample
🟥 Reference

US EPA has a procedure for measuring Total Alkanes or Alkanes Mixture using OP FTIR

Reporting Total VOCs as “Total Alkane” must be accompanied with molecular weight



The mean molecular mass of the alkane mixture, $\overline{M}_{mix}$, is estimated as

$$\overline{M}_{mix} = \frac{M_{butane} \cdot {}^{V}\hat{C}^{Arbitrated}_{butane} + M_{octane} \cdot {}^{V}\hat{C}^{Arbitrated}_{octane}}{{}^{V}\hat{C}^{Arbitrated}_{mix}} \qquad \text{(A-1)}$$

where M_{butane} =58.12 g/mole (molecular mass of butane),

M_{octane} = 114.23 g/mole (molecular mass of octane),

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Conclusion and Recommendations

- ☐ The Proposed Rule 1180/1180.1 and the supportive documents should be technology-neutral and should avoid privileging or penalizing one set of technologies over another. The current rule guidelines language gives an unjustified advantage to UV DOAS technology over officially proven OP FTIR technology.

- ☐ No significant superiority of LP-UV DOAS over OP-FTIR was demonstrated in field measurements that justify the new requirement to constrain OP-Fence line technology of BTEX and Naphthalene to UVDOAS.

- ☐ UV DOAS has a limitation in quantifying Naphthalene, O-Xylene, and Ethylbenzene.

- ☐ Acrolein can and should be measured below the OEAHH threshold. If SC AQMD does not think it possible despite 3 years of reporting acrolein with MDL below 1.1 ppb by the different refineries, new notification level must be determined for all the refineries.

- ☐ The Guidelines should determine the desired MDL for each compound considering the threshold (if applicable usually at least 30% of the threshold but not higher than the threshold itself).

- ☐ The Guideline should give one procedure for Detection Limit calculation based on an official method that all refineries must follow.

- ☐ The Guidelines Should be specific in the procedure for calculating Total Alkanes TA.

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Thank You.
Questions?

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