

# RACIE 2019

## Use of Open-Path UV DOAS as an Alternative Method to Meet Fence-Line Monitoring Provisions for Federal Benzene Monitoring Rule - A Case Study

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# 40 CFR 63.658

- The alternative method must be **validated**, according to Method 301 in appendix A of this part, or it must contain performance based **procedures** and indicators to ensure self-validation.
- The method detection limit must nominally be at least an order of magnitude below the action level, (*e.g.*, 0.9  $\mu\text{g}/\text{m}^3$  benzene). The **alternate test method** must describe the **procedures** used to provide field verification of the detection limit.
- For path-average concentration open-path instruments, the physical path length of the measurement shall be no more than a passive sample footprint (the spacing that would be provided by the sorbent traps when following Method 325A). For example, if Method 325A requires spacing monitors A and B at 610 meters (2000 feet) apart, then the physical path length limit for the measurement at that portion of the fence line shall be no more than 610 meters (2000 feet).
- For range resolved open-path instrument or approach, the instrument or approach must be able to resolve an average concentration over each passive sampler footprint within the path length of the instrument.
- The alternative test method approach must have wind speed, direction and stability class of the same time resolution and within the footprint of the instrument.



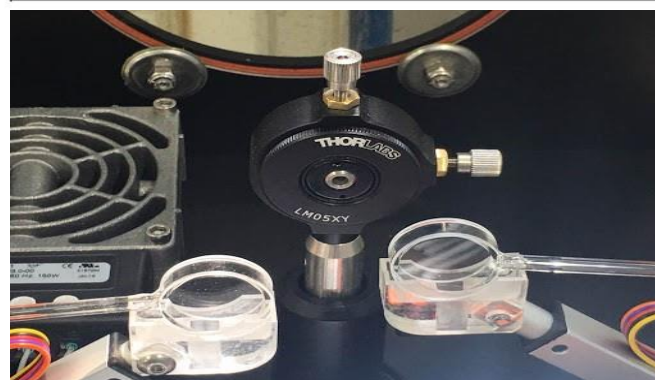
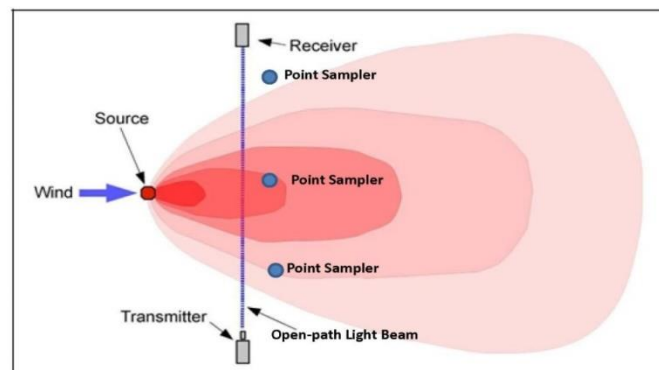
# ISO 17025

- General requirements for competence for testing and calibration laboratories
  - Covers:
    - Standard methods
    - Non-standard methods
    - Laboratory developed methods
  - Traceability to Primary Standard (NIST)
  - Execute method in a consistent manner
  - Continually improve



# Method 301 – Field Validation

- 2 Options:
  - Use a known concentration of an analyte.
  - Compare candidate method against validated method.
- Determine Bias
- Determine Precision
- Determination of Robustness/Ruggedness
- MDL Determination





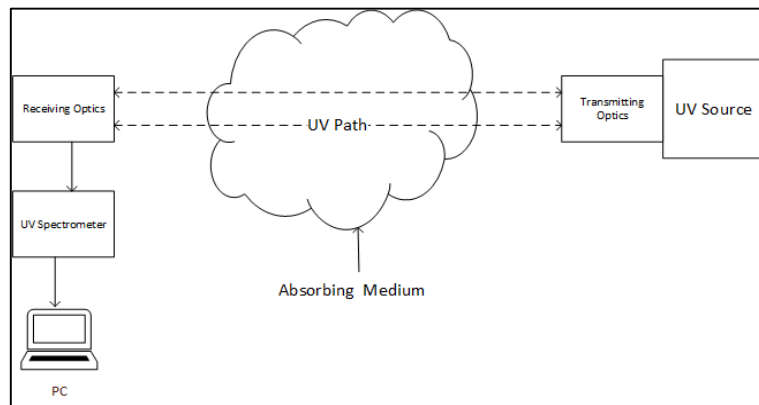
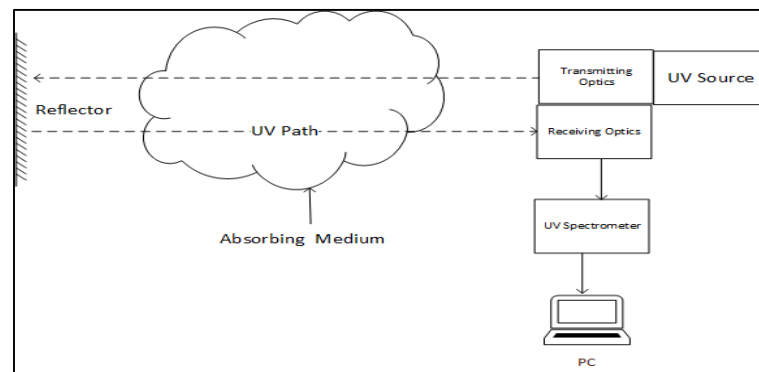
# ETV and TO-16

- TO-16 (based on IR) gives methodology for Open-path measurements.
- ETV Program – Test/QA Plan for Verification of Open-Path Monitors:
  - MDL
  - Linearity
  - Accuracy
  - Precision
  - Interferents



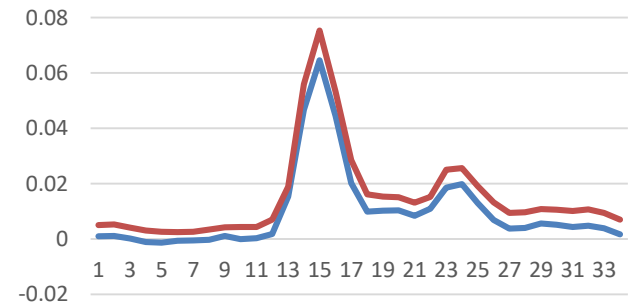
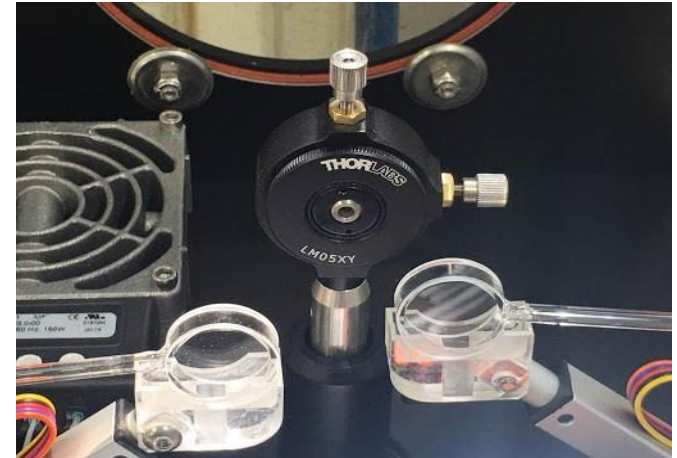
# UV Method

- The system should be capable of making spectral absorption measurements along an open-air optical path.
- The system must be able to produce and save a single beam spectrum.
- The system must be able to operate at 0.14 nm wavenumber resolution over the range 185 to 300 nm.
- The system must be capable of acquiring data by co-adding individual, single beam scans in single scan increments. At a minimum, the system must be able to co-add single beam spectrums, so that a five-minute average can be obtained.
- The system must have a mechanism where a gas cell of known concentration can be installed in the UV path, so that the whole beam passes through the cell.



# Traceability

- Create reference spectra using reference system.
- Fill sealed cells with gases for field spiking.
- Validate concentration of cell with reference system.
- Validate concentration of cell in the field.





# Verification and Validation Model

Parameter	Method Acceptable	Site-specific	Unacceptable
		Method Acceptable	
Relative Bias	$\leq 10\%$	Between 10% and 30%	$> 30\%$
Precision	Relative Standard Deviation (RSD) $\leq 20\%$		RSD $> 20\%$
MDL	N/A	N/A	N/A
Accuracy	$\leq 15\%$		$> 15\%$
Linearity	$R^2 \geq 0.9$		$R^2 < 0.9$
Robustness Temperature	$\leq 1\%$		$> 15\%$
Robustness Signal Strength	$\leq 15\%$		$> 15\%$
Robustness Sample Time	$\leq 15\%$		$> 15\%$



# Operational Model

- **Every 2 weeks**
  - A short cell with a known quantity of gas is inserted in the UV path.
- **Every 3 months**
  - The UV source is replaced and a short cell with a known quantity of gas is inserted in the UV path.
- **Every Year**
  - A full validation of the system is performed, according to the Argos Quality Assurance Project Plan Validation - *Quality Assurance Plan for Fence-line UV DOAS System (FLM-QLT-PLN-001)*.





# Results

Parameter	Value	Status
Relative Bias	2% over 5 systems	Method Acceptable
Precision	1.9% over 5 systems	Method Acceptable
MDL	0.475	> 0.09
Accuracy	5%	Method Acceptable
Linearity	0.92	Method Acceptable
Robustness Temperature	3% from 9 to 45 deg C	Method Acceptable
Robustness Signal Strength	0.74%	Method Acceptable
Robustness Sample Time	!0% from 0.5 min to 30 min	Method Acceptable



# Precision

Data Point	Benzene (ppb)	Data Point	Benzene (ppb)
1	55.54	14	58.33
2	55.57	15	58.89
3	56.16	16	59.22
4	56.52	17	58.98
5	57.37	18	58.89
6	57.59	19	59.4
7	57.28	20	59.53
8	58.36	21	59.12
9	58.07	22	59.87
10	58.00	23	60.03
11	58.62	24	60.13
12	58.76	25	60.21
13	58.24		
<b>Average (ppb)</b>	58.35		
<b>Std. Dev.</b>	1.35		
<b>% RSD</b>	2.31		

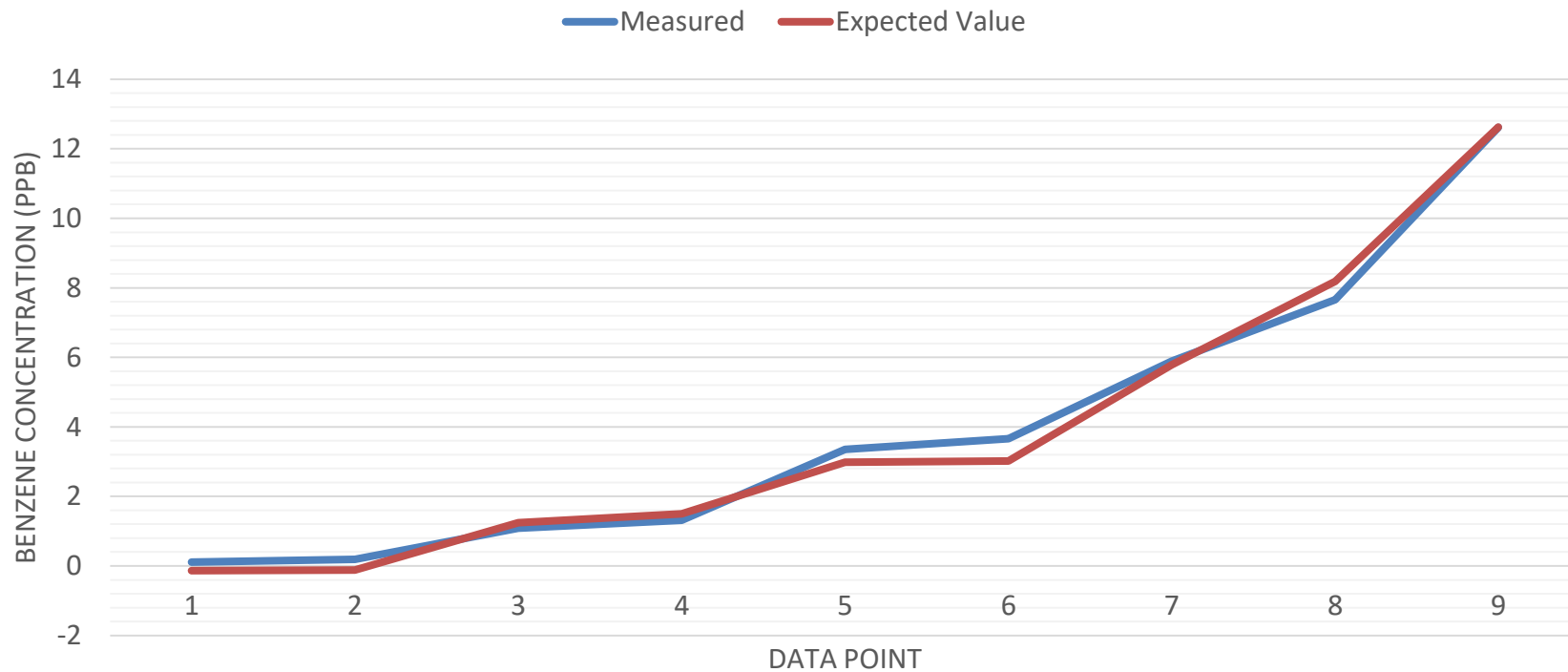
# Signal Robustness

<b>% of Max Signal</b>	<b>Measured Value (ppb)</b>
<b>79.1</b>	15.01
<b>67.1</b>	15.32
<b>45.6</b>	15.29
<b>29.5</b>	15.34
<b>14.4</b>	15.35
<b>6.9</b>	15.36
<b>3.5</b>	15.26
<b>1.3</b>	15.26





# Linearity



# Areas of Improvement

- Proficiency Testing
- More frequent MDL
- Accreditation Process
- Lower Detection Limits
- Increase trust in Data

