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Open-Path UV Air Monitoring Systems to Replace Passive Diffusive Tubes Using EPA Method 301

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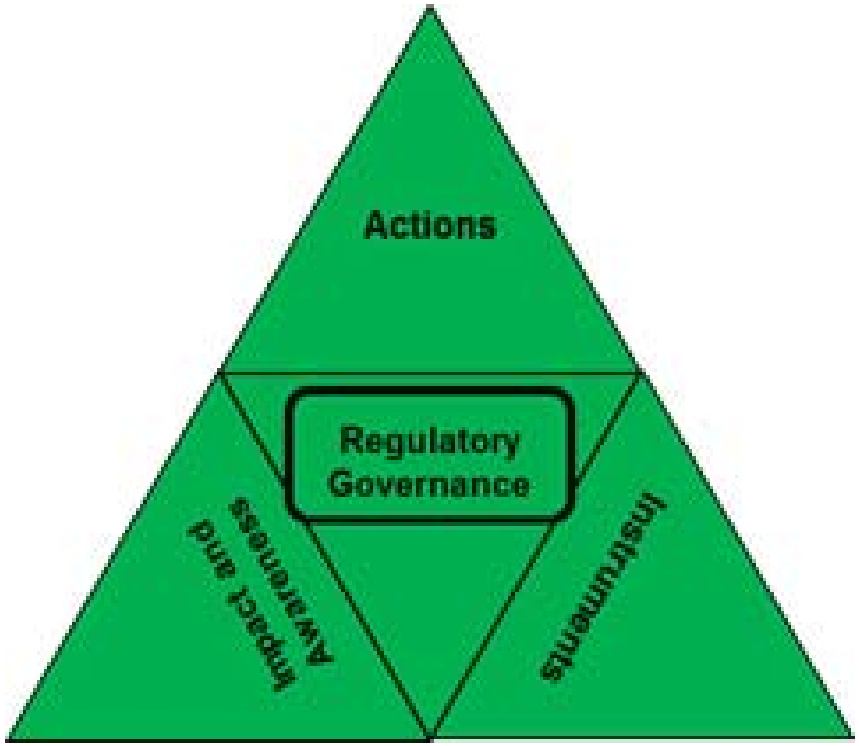
Regulatory Action

- EPA's Refinery MACT
  - Requires passive sampling for benzene
  - Goal – to determine long-term exposure
- Bay Area Air Quality Management District Regulation 12, Rule 15
  - Requires near real-time measurement of BTEX, THC, H_2S and other compounds that may increase risk
  - Goal – to determine long-term exposure, provide real-time information to the public and industry resulting in decreased emissions
- South Coast Air Quality Management District 1180 and California AB 1647
  - Similar to the above
- Colorado Oil and Gas Rule
  - Requires fence-line monitoring at oil and gas fields with potential for larger implementation



Refinery MACT - Passive Sampling

Advantages

- Low Minimum Detection Limit (MDL) and capital cost

Disadvantages

- Only requires benzene be quantified
  - Other compounds can be analyzed for but are not required.
- Meteorological impacts difficult to determine due to lack of time resolution in the method
- Release of data is well after the collection
- Long-term costs associated with collection and analysis can be high

Open Path Methodologies

Advantages

- Results available in near real-time
- Can be used to measure a large number of compounds that assist in source determination, among other things
- Can cover an entire fence line as opposed to points along the fence line

Disadvantages

- MDLs related to path length
- Interferences and potential weather impacts
- Power and other infrastructure is required

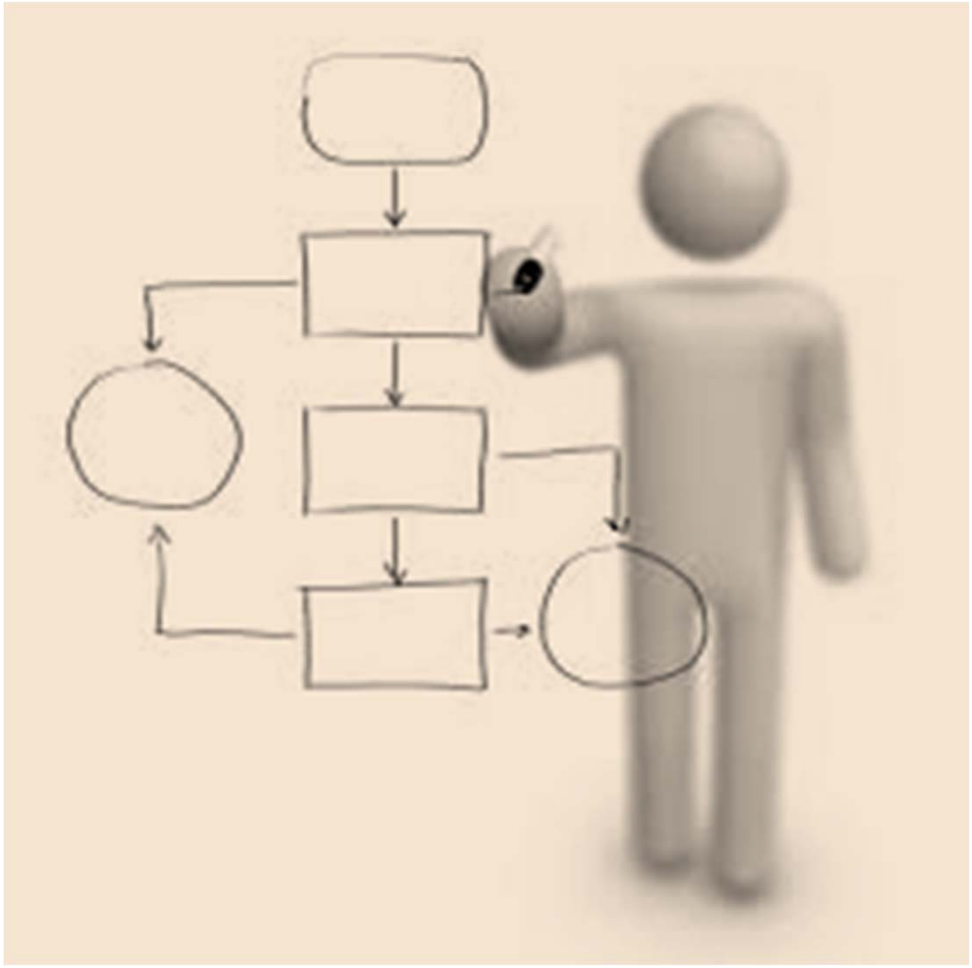
40 CFR 63.658 – Alternative Method Requirements

Provisions allow a refinery owner or operator to submit a request for an alternative test method, such as open-path instrumentation.

The use of this type of technology presents the opportunity to meet the requirements of the rule in a more simplified, cost-effective way, providing real-time information to the public and industry.

Issues associated with Method 301 designations – MDL method is not directly applicable to open-path measurements.

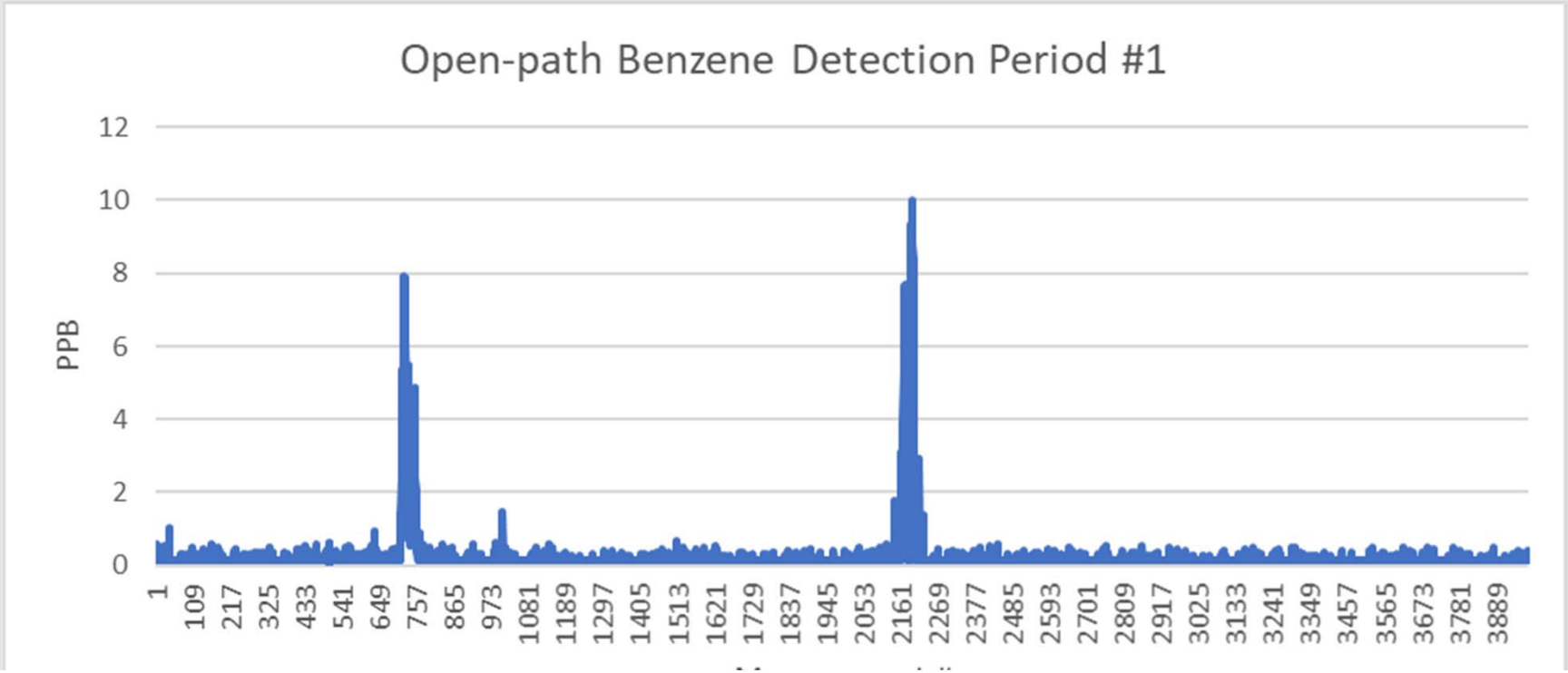
Offers advantages in terms of potentially identifying and eliminating data points not associated with refinery operations and identification of sources causing excess emissions.



Study Outline

- Open-path system set up along the fence-line of a refinery
- Passive samplers setup at 10 meter intervals along the beam-path
- Open-path set up to collect data in five-minute intervals
- Passive samplers set up to sample the air at 14 day intervals.

14 Day Output of Open-path System



What the Data Shows

During each of the 14-day time periods, detection limits were calculated using procedures outlined in the ETV guidance documentation.

- During each time period, the detection limits when no gases were present in the light beam produced results lower than the detection limits of the sorbent tubes (0.28 ppb).

- During Measurement Period #1 one set of detection limits yielded results higher than the 0.28 limit. However, subsequent analysis indicated the presence of p-Xylene in numerous single-beam spectra. This skewed the results for Benzene detection limits.

ETV – System Checks

Data Quality Check	Description	Results
Minimum Detection Limit	Collect back-to-back spectra and average results to determine MDLs.	Calculated MDL should be less than 0.9 µg/m^3.
Linearity of Gas Concentration	Insert known quantity of gases into beam and measure response.	Plot response and generate calibration curve.
Linearity of Gas Concentration as a function of signal	Insert known quantity of gases into beam and measure response as function of light signal.	Tabulate results and determine percentage difference between actual and measured concentrations.
Measurement Accuracy	Insert known quantify of gas into beam and measure concentration using various background spectra.	Tabulate results and determine percentage difference between actual and measured concentrations.
Measurement Precession	Insert a known quantity of gas into beam and collect 25 consecutive measurements.	Determine the average and standard deviation of the measurement results. Use the results to determine measurement precisions.

Data Performance Checks

- Argos evaluated system performance by integrating data quality checks into the measurement process. Indicators such as response linearity, precision, accuracy, and minimum detection limits were used to gauge instrument performance.

- All data quality checks were remotely performed using gas standards with concentrations verified using NIST traceable reference libraries.

Data Quality Requirements – Lessons Learned

- Operational and MDL claims made based on laboratory performance and field operations were quite different – Field verification and defined QA/QC is key
- QAPP following EPA guidance required to describe data quality objectives, data quality indicators, and data validation criteria
- Provide real-time data with appropriate, defensible and transparent QA/QC
- Data Completeness

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- Determine appropriate methods to calculate MDLs that meet EPA requirements (method, setting – laboratory versus field determination).
- Work with EPA to ensure regulatory requirements are met while recognizing the MDL determination issues, potential advantages of better time resolution and collection of additional information that allows for quicker response and potential to reduce emissions.
- Submit application and ensure that, should the method gain approval, appropriate and verifiable QA/QC requirements are incorporated into that approval.

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- While each fence-line application may be unique, the need for well-defined and consistent standards are required.
- ISO 17025
- Data quality is critical to gain public and industry trust of fence-line measurements.
- Data that can be verified through metadata or other independent operational parameters provides surety for both the refineries and the public.

QUESTIONS?

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