An Overview of Viable Fenceline Monitoring Techniques Pertaining to the Refinery Rule

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Fenceline Monitoring Options

- Referring to the EPA–HQ–OAR–2010–0682 rule guidelines, the viable fenceline air monitoring options are:

  - Multiple single-point time integrated samplers: *Passive Diffusive (PD)* Sorbent Tubes
  - Multiple single-point (near) real-time active sampling: *Auto-GC*
  - Integrated path (near) real-time monitoring of benzene directly: *UV-DOAS*
  - Integrated path (near) real-time monitoring of surrogate compounds: *OP-FTIR*
14-day benzene samples are collected and analyzed in accordance with EPA Methods 325A and 325B.

Sample placement per Section 8.2 of Method 325A.

Meteorological data is to either be: 1) collected on site; or 2) NWS data can be used, if collected within 25 miles.

For each 14-day sampling period, a “Δc” is determined by the difference between highest and lowest sample results.

An annual average Δc is determined using the average of the 26 most recent 14-day Δc values.

The new annual average Δc must be determined within 45 days of the end of each 14-day sampling period.

The annual average Δc is compared to an action level of 9 μg/m³ (≈ 3 ppb).

If the annual average Δc is greater than 9 μg/m³, then a root cause analysis must be conducted and corrective action taken.

For many facilities, the action level is not anticipated to be exceeded, but in some cases (whether proven or anticipated), root cause analysis may warrant the use of…
Continuous, Real-Time Monitoring (CRM) Technologies

- **UV-DOAS**
  - This technology is the EPA Refinery Rule recommended CRM monitoring approach for benzene because of its low detection limits, measurement time resolution and relatively lower costs.
  - The spectrum and amount of UV light absorbed identifies (via spectral absorption “fingerprint”) and directly quantifies (via a physical property known as the Beer-Lambert Law) various molecules in its lightpath.
  - Continuous, real-time sub-ppbv level analysis of BTEX, NO\(_x\), SO\(_2\), simultaneously.

- **OP-FTIR**
  - Same description as UV-DOAS, except substitute IR light for UV light.
  - Continuous, real-time ppbv level analysis of multiple pollutants (VOCs, HRVOCs, inorganics, acids), simultaneously (often 20-40 compounds in an analysis method).

- **Auto-GC**
  - Its detector measures the quantity (by peak area) of various components, pushed by a carrier gas, that exit a chemical separation column; the sample peak retention time (peak appearance time) identifies the compound.
  - Continuous, near real-time sub-ppbv to ppbv level analysis of BTEX and select VOC’s.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>UV-DOAS</th>
<th>OP-FTIR</th>
<th>Auto-GC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling integration time</td>
<td>1-3 min.</td>
<td>1-5 min.</td>
<td>15-30 min.</td>
</tr>
<tr>
<td>Pollutants simultaneously monitored</td>
<td>BTEX, SO$_2$, NO$_x$</td>
<td>~many VOC’s</td>
<td>BTEX, select VOC’s</td>
</tr>
<tr>
<td>Benzene detection limits*</td>
<td>&lt;&lt;&lt; 1 ppbv (typically, ~200 pptv)</td>
<td>&lt; 25 ppbv (recently, &lt; 10 ppbv)</td>
<td>&lt; 5 ppbv (with PID detector)</td>
</tr>
<tr>
<td>Calibration frequency</td>
<td>None required</td>
<td>None required</td>
<td>Daily/Weekly/Monthly (depends on accuracy requirements)</td>
</tr>
<tr>
<td>(Audits/validations should be done regularly)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td># Systems per 1 km fenceline path</td>
<td>1 open-path</td>
<td>~2 open-path</td>
<td>≥3 single-point</td>
</tr>
<tr>
<td>Approx. cost per system**</td>
<td>~$75K ($7.5K per mo.)</td>
<td>~$120K ($12K per mo.)</td>
<td>~$70K</td>
</tr>
<tr>
<td>Data up-time</td>
<td>&gt;90%</td>
<td>&gt;90%</td>
<td>~100%</td>
</tr>
<tr>
<td>Data maintenance/validations</td>
<td>Infrequent</td>
<td>Frequent</td>
<td>Somewhat frequent</td>
</tr>
</tbody>
</table>

*EPA is requiring DLs < 300 pptv
**Assuming permanent installation. Does not include met tower, infrastructure, etc. costs upon installation
Monthly rental cost typically ~10% of monitoring system list price
A Full and Interior Petrochemical Plant Pollution Perimeter Monitoring Network
Conclusions

- Most refineries can/should implement PD tubes when average benzene is low/zero
  - Cheapest option
  - Lack of temporal resolution doesn’t matter
  - Remote (non-urban) facilities without excessive fugitives are certainly likely cases here

- CRM system (such as open-path UV-DOAS) deployment along fencelines on a temporary month-by-month basis is a possibility for root cause analysis
  - When difficult to differentiate fugitive benzene sources out of target refinery from background (adjacent plants)
  - When finding fugitive emissions directly from refinery tanks, or other sources

- CRM systems (such as OP-FTIR) very useful in profiling fugitive emission activity via surrogate compounds
  - Can also be deployed on a temporary basis