
Measurements of HRVOC Emissions from Oil Refinery Processes

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Targeted Sources

■ Oil/Water Separators

- ❑ Poor emission factors
- ❑ Data suggesting high levels of VOC emissions
- ❑ Impact of seasonal variability unknown

■ Cokers

- ❑ Suspected of being a high level emission source
- ❑ Limited data on emissions

■ Tanks

- ❑ DIAL studies indicating high level emission source
- ❑ Heavy reliance on EPA TANKS program for emission factors

■ Cooling Towers

- ❑ Suspected of being a high level emission source
- ❑ Limited data to correlate process water VOC content to emission rates

■ Catalytic Crackers

- ❑ Recent data suggests emissions may be significantly overestimated
- ❑ Limited analysis of test data to characterize emissions

Relevance to TERC Strategic Research Plan

- **Section 1.2** – *various VOCs and HRVOCs are understated in existing inventories. These compounds are ozone precursors and HAPs.*
- **Section 1.3** – *improve emissions estimates for formaldehyde and HRVOCs from wastewater treatment, cokers, storage tanks, cooling towers, and cat crackers.*

Emissions are Difficult to Measure

- **Proposed sites are area and fugitive sources – not ducted**
- **Emissions have high temporal variability – sensitive to ambient conditions and process parameters**
- **No standardized methodologies or procedures for measurement**
- **Complexity of emissions require adaptation of advanced, high resolution measurement and meteorological techniques to novel applications**

Measurement Programs

■ Objective

- Identify emission points
- Demonstrate emissions quantification techniques
- Quantify emissions
- Measure temporal variability of emissions
- Develop emission factors

■ Approach

- Identify sources, locations, sampling points, logistics
- Prepare test plan and QA project plan for peer review
- Identify emission points and characterize VOC species
- Select measurement technique(s)
- Field validate measurement system
- Conduct measurements for specified time period
- Analyze data
- Prepare and submit reports

Site Evaluation

■ Site Selection

- ❑ Able to host long-term measurement program
- ❑ Process data availability

■ Source Characterization

- ❑ Design details – *Is this source typical of its category?*
- ❑ Emissions profile – *Conduct screening study to select analytical approach.*
- ❑ Ability to install test equipment – *Will installed equipment create interferences with site maintenance or operations?*

Applicable Techniques

- **Field GC**
 - Extractive (point source) measurements
 - Good VOC species resolution

- **IR Cameras**
 - Emerging technology with both active and passive systems
 - EPA demonstrations have been focused on LDAR activities

- **FTIR**
 - Capable of speciated hydrocarbon measurements
 - Open path and extractive measurements possible

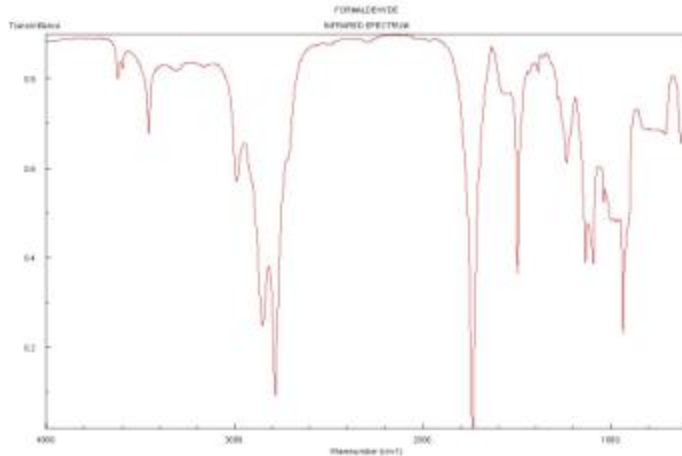
- **DOAS**
 - Capable of measurements for some compounds difficult for FTIR
 - Open path predominant use with some extractive systems available

- **TDLAS**
 - Generally single component measurements
 - Used for tomography studies

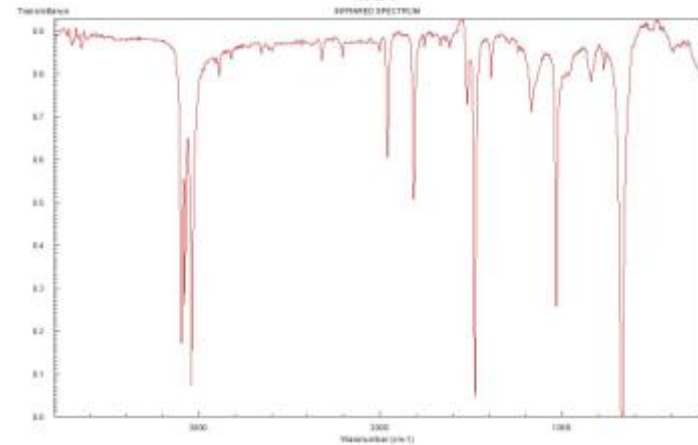
- **Advanced Optical/Ultrasonic Flow Monitors**
 - Ultrasonic anemometers provide 3-dimensional flow vectors
 - Optical methods provide path-averaged flow measurements

Selected HAP IR Absorbance Spectra

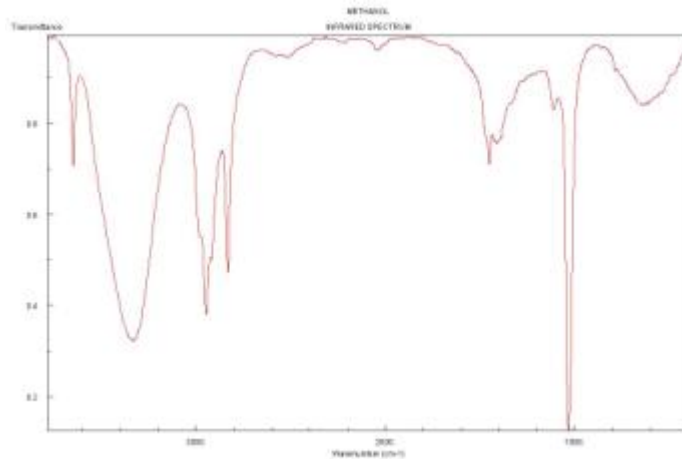
Formaldehyde IR Absorption Spectrum



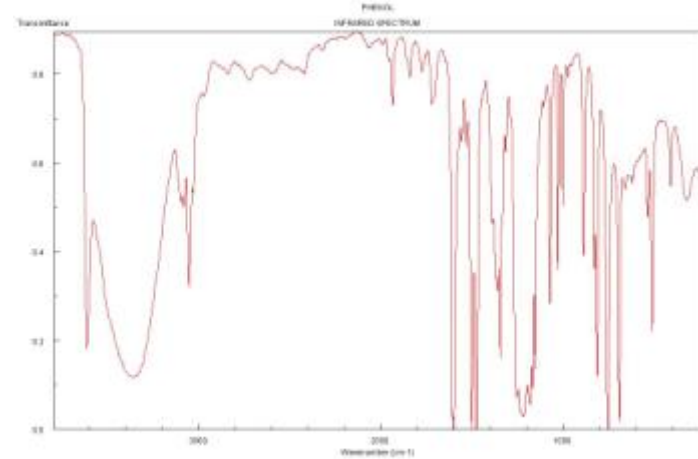
Benzene IR Absorption Spectrum



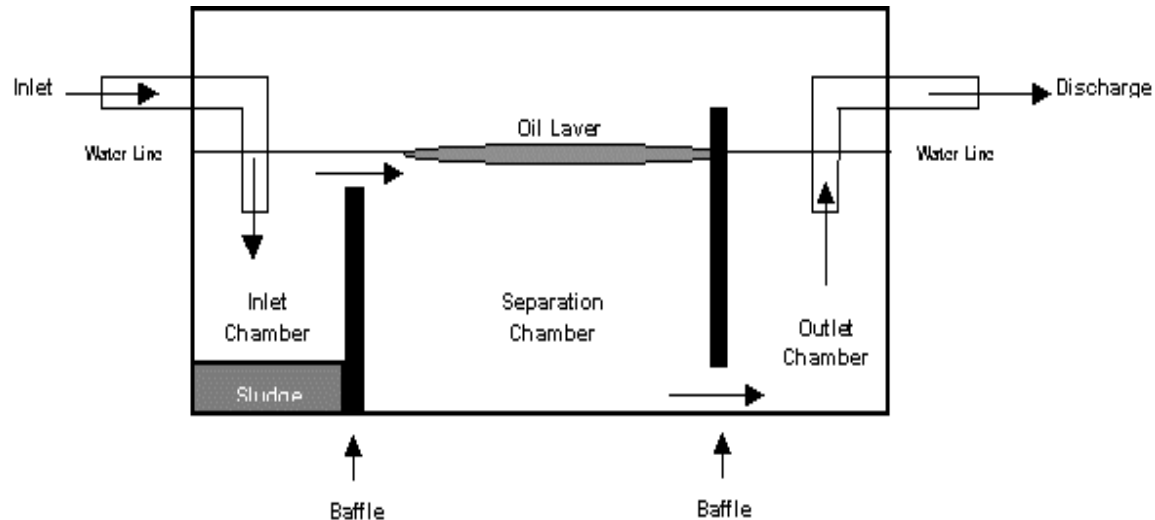
Methanol IR Absorption Spectrum



Phenol IR Absorption Spectrum



Oil/Water Separators



- AP-42 emission factors rated D: 5 – 0.2 lbs/1,000gal (uncontrolled/controlled)
- References 1959, 1960, 1973, 1973
- 2006 measurement from TCEQ w/IR camera finds emissions of up to 80,000 ppm VOC

Oil/Water Separators Budget

- **Short-term (two weeks) testing at each of three units - \$200,000**
- **Long-term (six month) testing of one unit - \$213,000**

Cokers



- No AP-42 emission factors for VOC emissions for either fluid-bed or delayed cokers
- Emissions occur during hydrodrilling and transfer of coke to holding areas
- Typically 16-hour operation with variable emissions

Cokers - Budget

- **Method demonstration and testing at one bank of cokers for two weeks of data collection**

- **\$233,000**

Storage Tanks

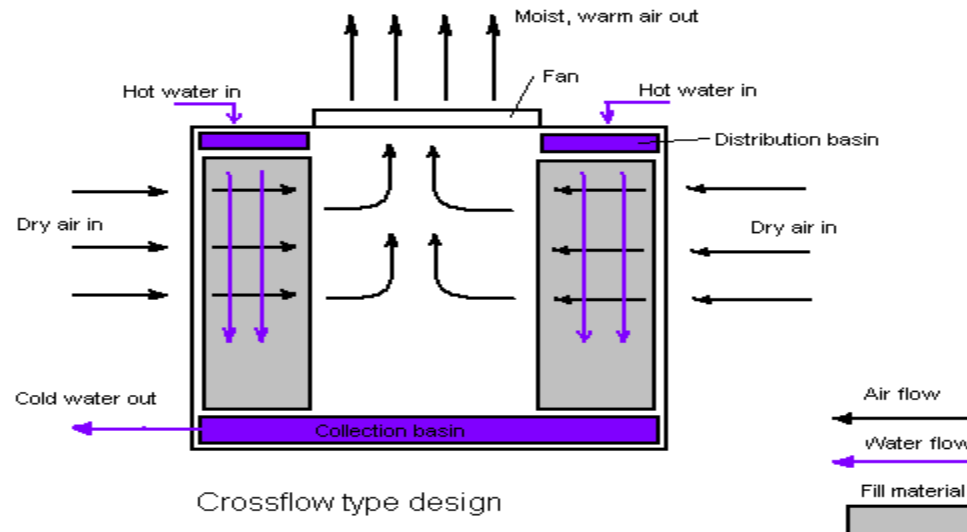


- Emissions are estimated using API-developed TANKS software. Inputs required are tank size, roof design, condition, meteorological conditions, and physical/chemical properties of liquid.
- Several different tank designs
- Flow measurements a challenge
- Current TCEQ program to measure emissions from fixed roof tanks

Storage Tanks - Budget

- **Method demonstration and testing at one tank for two weeks - \$220,000**
- **\$25,000 for each additional tank located in close proximity**
- **\$100,000 for TDLAS tomography data generation for comparison with SOF**

Cooling Towers



- DIAL measurements at Alberta refinery indicate that VOC emissions are substantial
- TCEQ guidance (1/2006) suggests measuring VOC concentrations in cooling water and using water flow rate to estimate emissions
- Because of high moisture content and low air flow rates we will use extractive FTIR and optical or ultrasonic flow measurements

Cooling Towers - Budget

- **Method demonstration and two weeks testing at one cooling tower -\$200,000**

Catalytic Crackers



- Recent API member data indicates that formaldehyde and other VOC emissions are about two orders of magnitude lower than AP-42 emission factors developed in the 1950s and 1960s.
- The original test reports need to be collected and analyzed to develop new emission factors for inclusion in AP-42 and WebFire

Catalytic Crackers Budget

- **Report Review and data analysis - \$50,000**