HRVOC Monitors for Flares and Cooling Towers

Analytical Opportunities and Solutions

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Ozone Issues in HGA

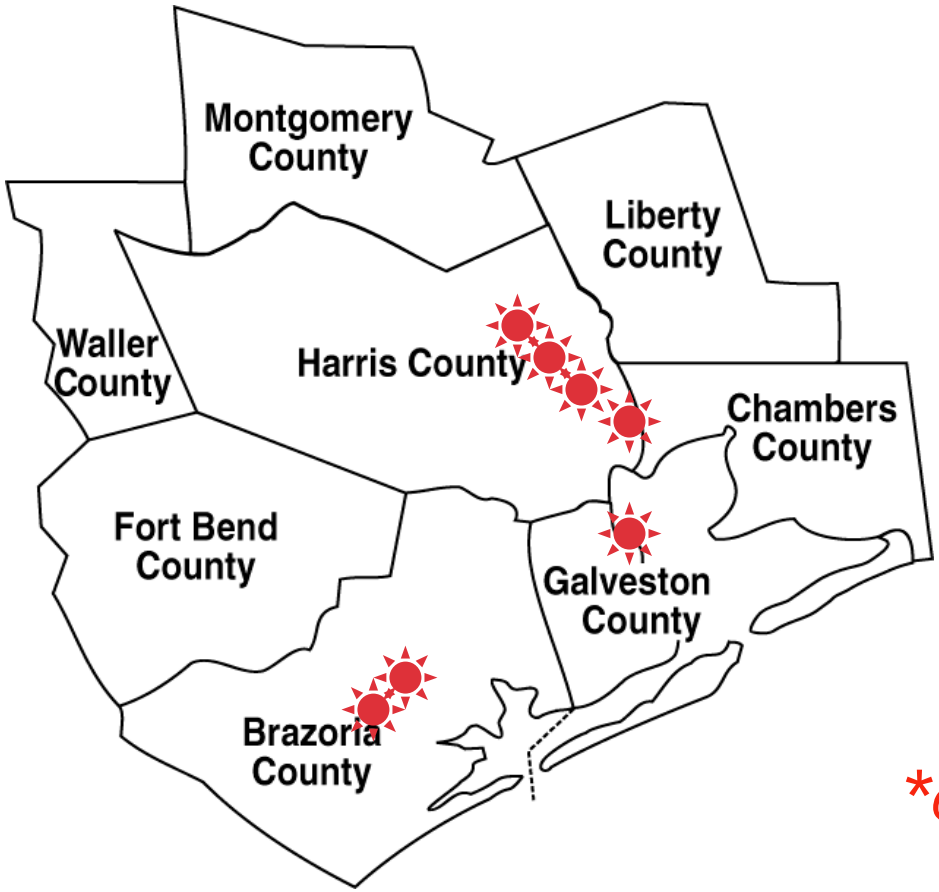
- Ozone Reduction
  - SIP (Texas – State Implementation Plan)
- Monitor and/or reduce
  - NOx
  - HRVOC (highly reactive volatile organic carbon)

Definition of Highly-Reactive VOC

- Ethylene and Propylene for 7 counties that border Harris County.
- Harris County - ethylene, propylene, 1,3 butadiene, and butenes (all isomers)

Project Overview

Dow Sites in HGA



Freeport A/B/OC

Oyster Creek Cogen*

Laporte

Texas City

Deer Park

Jacintoport

Sheldon

**Operated by Dow*

Dow HGA HRVOC Sources*

- Flares: 44
- Cooling Towers: 26
- Vents: 80

**Preliminary count. Some sources may meet exemptions.*

Dow's HRVOC Project Approach

- Centralized project team addressing compliance for all assets in HGA
- Leverages experience gained from NOx compliance effort
- Ensures more consistent approach in attaining compliance for all Dow sites in HGA

HRVOC Project Team

- 40 people on a full time or part time basis
  - Regulatory subject matter experts (SMEs)
  - Technical SMEs
    - Instrument
    - Analytical (2 Six Sigma Projects)
    - Equipment (flares and cooling towers)
    - Process
  - Project Management

Process Analytical Opportunities

Flare Vent - HR-VOC

HRVOC:

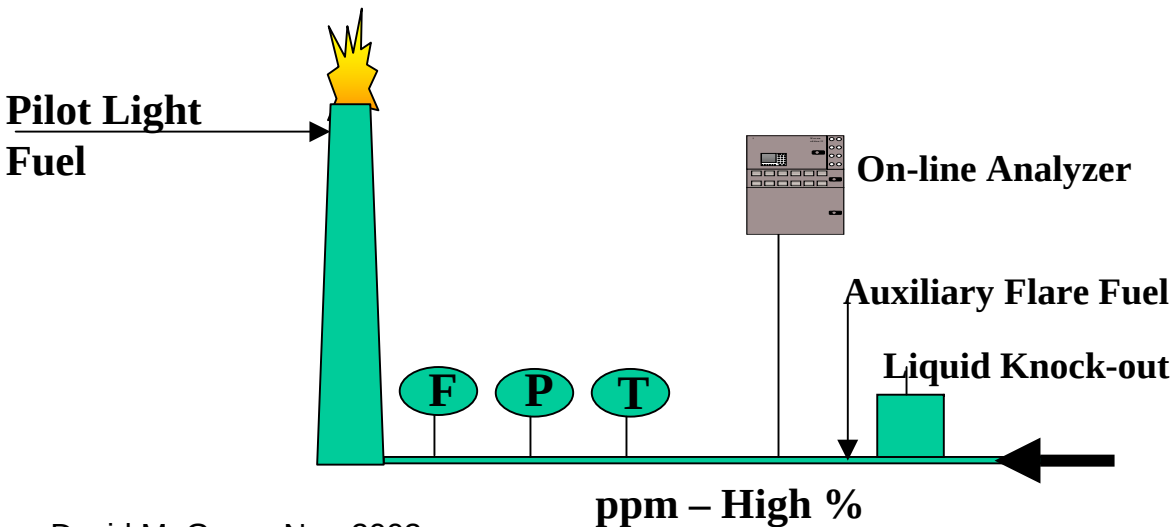
Components: HRVOC + enough composition for +/- 5% accuracy of BTU and average molecular weight determination.

Range: ppm -% (process, flow & site-cap depend. Frequency: Min. every 15 minutes

Calibration checks: 40CFR60, Appendix B, (Performance specification 9, Section 10) except: Mid-Point calibration weekly only; Multi-point calibration quarterly (Every component; linearity check)

Uptime: >95%

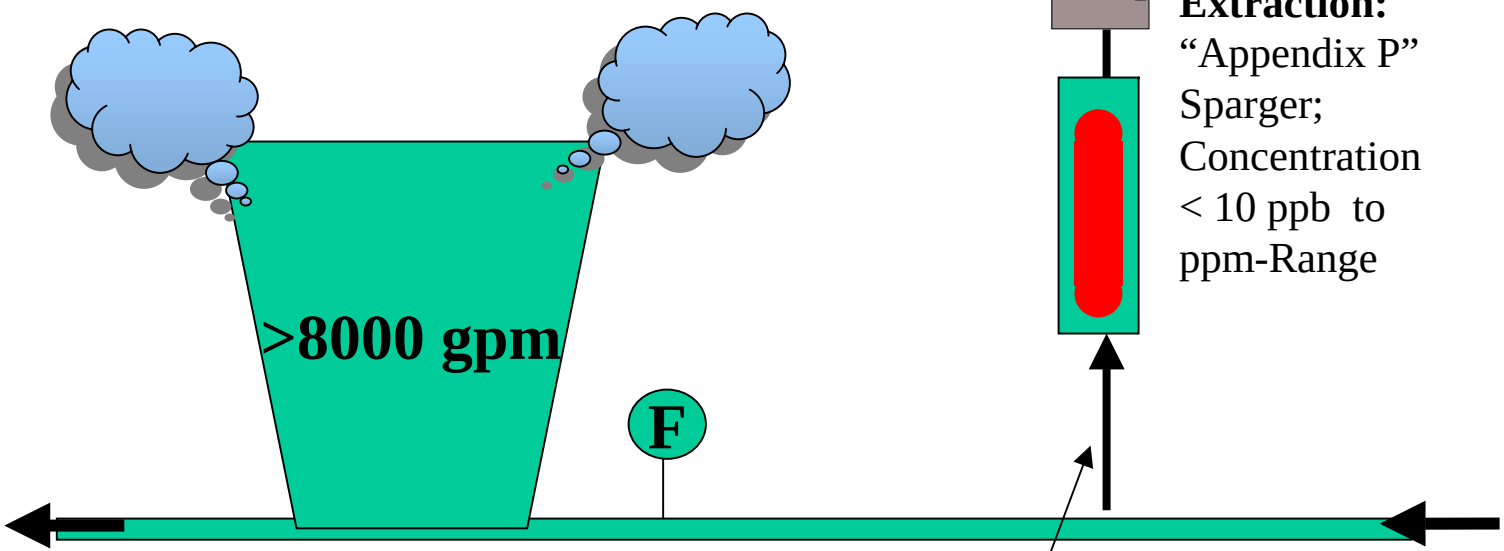
Analyzer Failure:Lab samples per regs according to 40CFR60 Appendix A, Method18 and ASTM 1946



Cooling Tower - Analysis Requirements

Cooling Towers: > 8000 GPM

- Either:
  - Total Strippable VOC/ speciated HRVOC
  - Speciated HRVOC



On-line:
Total strippable VOC

Extraction:
"Appendix P" Sparger;
Concentration < 10 ppb to ppm-Range

Extraction:
Maximum distance 200 feet (~2 min lag)

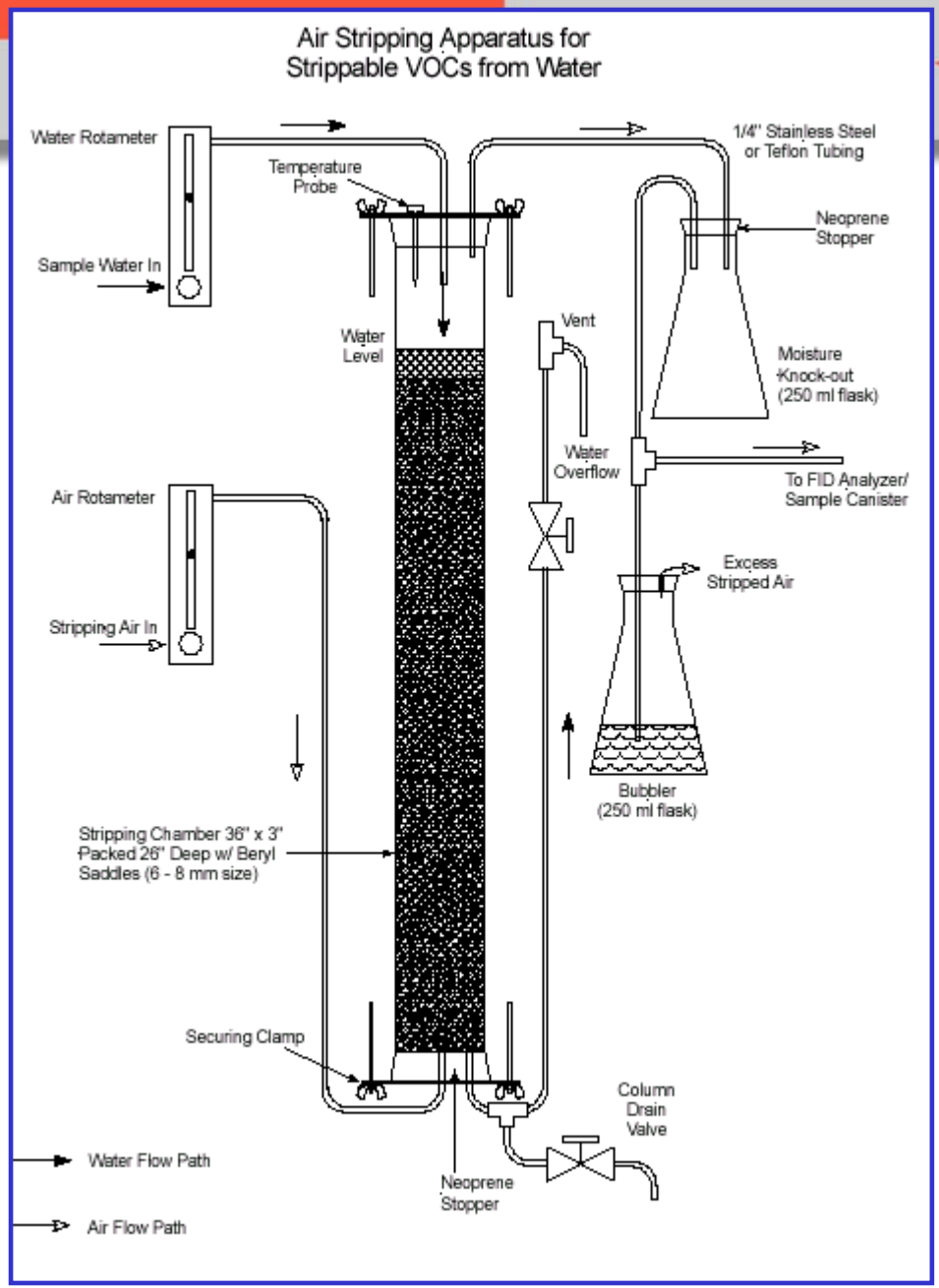
CTHES Sampling Conclusion

Utilize the Appendix P “El Paso” Air-stripping design as the standard configuration.

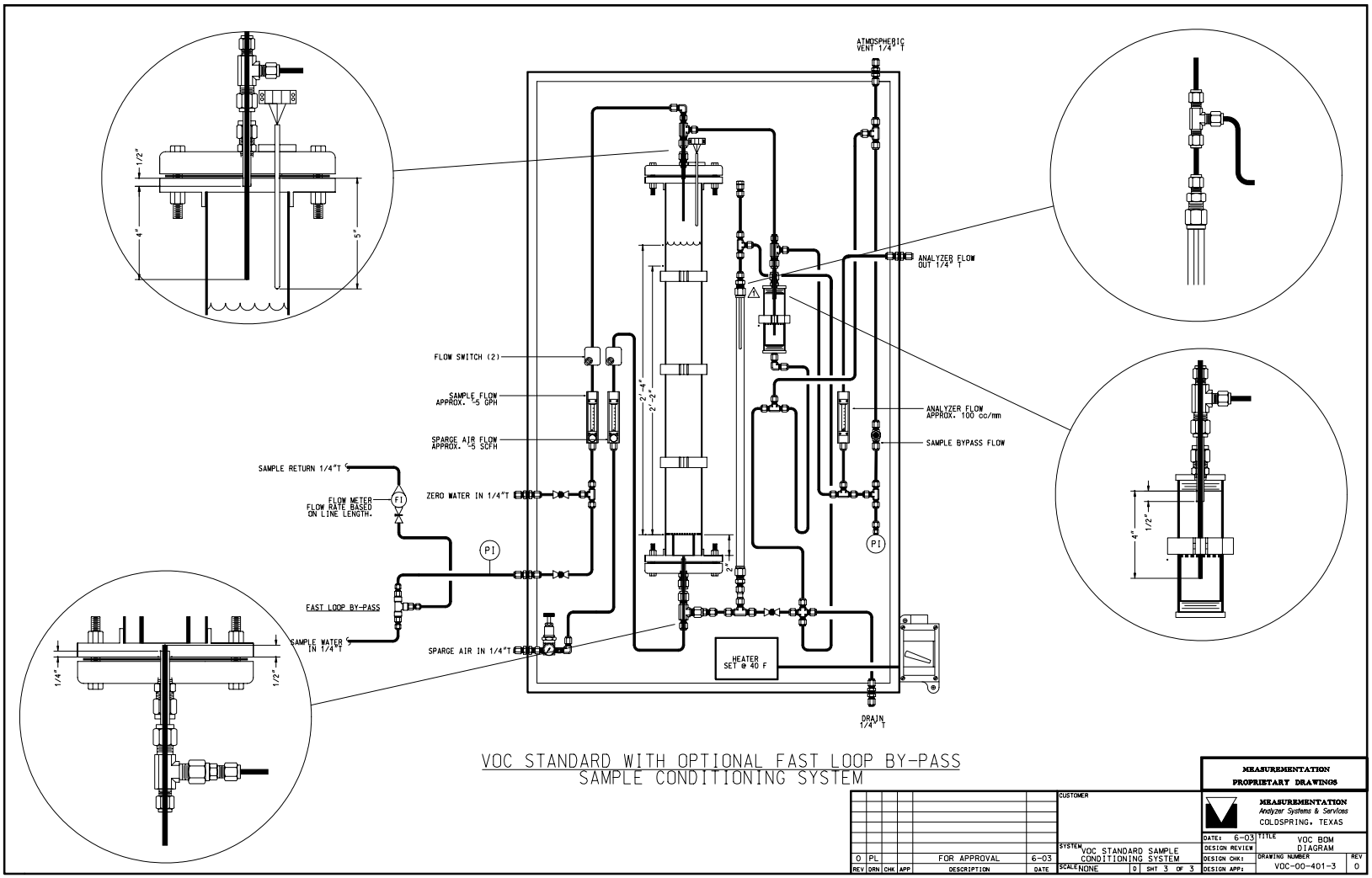
Appendix P: Modified El Paso Method

Issues:

- Glassware in process environment
- Stoppers
- 50’ line lengths
- No fast loop
- No lab sample point
- No filtration
- No monitoring



Suggested On-line Design



VOC STANDARD WITH OPTIONAL FAST LOOP BY-PASS
SAMPLE CONDITIONING SYSTEM

REV	DRN	CHK	APP	DESCRIPTION	DATE
0	PL			FOR APPROVAL	6-03

CUSTOMER

SYSTEM: VOC STANDARD SAMPLE CONDITIONING SYSTEM

SCALE: NONE | 0 | SHT 3 OF 3

MEASUREMENTATION
PROPRIETARY DRAWINGS

MEASUREMENTATION
Analyzer Systems & Services
COLDSPRING, TEXAS

DATE: 6-03 | TITLE: VOC BOM DIAGRAM

DESIGN REVIEW

DESIGN CHK: | DRAWING NUMBER: VOC-00-401-3 | REV: 0

DESIGN APP:

Additional El Paso Changes…

- What we have learned so far…
  - Clear cylinder can promote algae growth
  - Flow control via needle valves is difficult
  - Enough sample pressure to flow through fast loop.

Additonal El Paso Changes - #2

- Design today similar to proposed
- Improvements implemented after field use of initial systems
  - Condensation issues after stripper to GC
  - Flow control upgrade
  - Lab sample configurations to eliminate upset to online system

Analytical Options

- Mass Spectrometry
- FT-NIR
- Filter IR
- GC/BTU Analyzer Combination
- GC

Analytical Options

- GC/BTU Analyzer Combination
  - Viable Option for Flare Analysis
  - Simplifies GC Method (HRVOCs Only)
  - Must add Specific Gravity for Average MW
  - More Costly (Analyzer & Shelter)
- GC
  - Meets Requirements
  - Lowest Cost

GC Requirements

- Flares:
  - Measuring % Levels of H_2, O_2, N_2, CO, CO_2, C1-C4 Hydrocarbons, C5+
  - Thermal Conductivity Detection
  - Determining Concentration of HRVOCs
  - Calculating BTU Valve, Average Molecular Weight

GC Requirements

- Cooling Towers:
  - Measuring ppm Levels of Total VOCs
    - Equivalent to ppb Levels in Liquid Phase
    - Total Hydrocarbons minus Methane & Ethane
  - **Measuring ppm Levels of HRVOCs**
    - Ethylene, Propylene, Isomers of Butene, 1,3-Butadiene
  - Flame Ionization Detection

Proposed Packaging

- Prototype has been used in a “complex” GC application
- Good service environment
- Very limited future space.

Project Schedule

Feasibility Studies - April - September ’03

QA/Test Plan Development & Approval - October ’03 - February ’04

Design & Construction - October ’03 - January ’05

Equipment Order/Delivery - April ’04 - April ’05

Commissioning/Startup - May ’04 - July ’05

Dates updated based on October, 2003 amended regulation deadline or 31-Dec-2005.

Project Schedule Update

- Time lines extended
- Equipment order/delivery
  - All ordered
  - 1 remaining to be delivered (late Sept)
- Commissioning
  - Freeport complete — 33 of 35
  - TCO — 8 of 9 complete
  - CLO — Begin in Sept on 3

Key Points

- Dow has a large number of HRVOC sources
- Compliance solutions are complex
- Compliance timeline mandates a very aggressive project execution schedule
- Gaining clarity on technology approach quickly is essential to meeting compliance dates

NOx CEMS

- Total 38
- Freeport
  - 30 completed
  - 6 remaining
- CLO
  - 2 completed

HRVOC – To Date

- Total
  - Flares 23
  - Cooling Towers 24
  - Total 47
- Freeport
  - Flares 20
  - Cooling Towers 15
- TCO (Texas City)
  - Flares 2
  - Cooling Towers 7
- CLO (Clear Lake)
  - Flares 1
  - Cooling Towers 2

Implementation

- Operational commissioning complete
- Systems on process & auto validating
- Systems fine tuned based on learning experiences
- Preparing for “certification” or initial demonstration of compliance

Support Resources In Place

- Commissioning team
  - 4 full time techs for HRVOC
  - Covering Freeport, TCO, CLO
  - 2 techs for NOx (not full time at present)
- Long term support team (centralized)
  - Freeport
    - 5 full time techs
  - TCO/CLO
    - 1 full time tech (backup from Freeport)

Certification Tasks

- Certification per CFR Performance Spec 9 and Appendix P
- Multi point checks – linearity
- 7 day calibration drift
- Flow meter & temperature calibrations
- El Paso stripper checks
- Stripper air check

Data History

- Both HRVOC and NOx are networked to central data system at site
- NOx in place Mar 2005
- HRVOC currently in progress

Commissioning Work

- Early 2004 to Mar 2005
  - 17 systems in Freeport
- Mar 2005 to date
  - Freeport – 16 systems in 14 buildings
  - TCO – 8 systems in 8 buildings
  - CLO – 3 systems powered up last 2 weeks
- Spread over entire Freeport site (OCD, Plant A & B) (multiple plants & businesses)
- Spread over three different sites

2005 Plans

- Complete certifications
- Monitor systems running on process performing auto validations
- Work with plants on new analyzer implementation into operations
- Develop PM program

Acknowledgements

- Courtland Sears, Tim Logan-Sample System & Methods
- Mack Keeter, Robert Nielsen-Analyzer Engineering
- Russell Wozniak, Linda Swaim, Kevin Batt-Regulatory Issues
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Questions ??

Abstract/Summary

Early in 2003, the Texas Commission on Environmental Quality (TCEQ) issued new regulations for monitoring highly reactive volatile organic compounds in order to comply with Federal clean air regulations specifically relating to the control of air pollution from volatile organic compounds. From this guideline, 30 TAC Chapter 115 (Reg. V), flare streams and cooling tower systems have monitoring requirements in order to quantify the potential volume of HRVOC's being released into the atmosphere. These requirements have presented numerous technical challenges to the companies in the Gulf Coast area. This presentation summarizes some of the key elements of the rule along with The Dow Chemical Company's efforts to address and comply with the analytical portion of the rule.