HRVOC Monitors for Flares and Cooling Towers

Analytical Opportunities and Solutions

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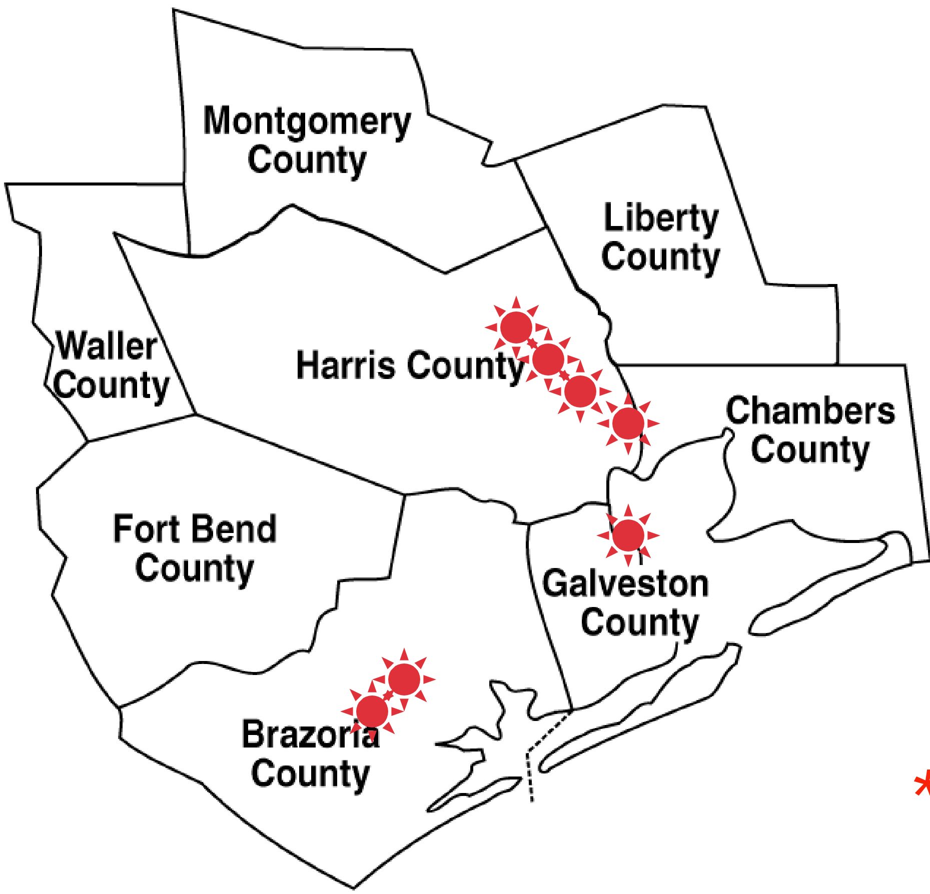
Project Overview

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)

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.*

January 2003 Rule Changes

- Reg VII - NOx point source reduction requirements changed from 90% to 80%
- Reg V - New regulations regarding highly-reactive volatile organic compounds (HRVOC) issued to replace the air quality benefit of the last 10% NOx
- Reg V - Changes to VOC rules to increase the stringency of requirements for fugitive emission sources and industrial waste water streams

Background for 2003 Rule Changes

- BCCA AG lawsuit challenging 90% NOx reduction requirements for point sources
- Per consent order - A scientific evaluation was conducted by TCEQ, which led to regulation of HRVOC to replace last 10% of NOx point source controls
- Scientific evaluation strongly supported by the Texas 2000 air quality study

Background for 2003 Rule Changes

- Texas 2000 Air Quality Study reveals the following:
  - Ethylene, propylene, and 1,3 butadiene play a big role in increases in hourly ozone concentrations
  - Industrial VOC emissions could be understated in emission inventories
  - Plumes with HRVOC and NOx are more efficient at forming ozone than plumes with just NOx emissions

Major Elements of Reg V Changes

- HRVOC Emission Reduction is the focus
- HRVOC Emission (lb./hr.) cap on a 24-hour rolling average is established for each air quality account
- HRVOC Emissions from vents, flares, and cooling towers are subject to the site cap
- Additional monitoring for fugitive emission sources in HRVOC and in VOC service

HRVOC Emission Caps

- Cap includes vents, flares, and cooling towers
- Vents - Test one time or use a CEMS
- Flares - Measure mass flow of HRVOC to the flare and calculate emissions
- Cooling Towers - Measure mass flow of HRVOC in cooling water return
- Compile emission data hourly and compare to cap
- Emissions associated with emissions events and unpermitted MSS activities are excluded from the cap

HRVOC Emission Caps

- Compliance date is April 1, 2006
- Caps are set higher than annual average emissions (RY 2000) by a factor of about 1.5, but do not take into account the variable nature of hourly emissions
- Is an improvement over original specific proposed emission rates, but will take significant review of permits and operations to determine what emission reductions may be necessary

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

Project Activities To Date

February	-	Project Team chartered
March	-	Project Team in place
April-June	-	Source database established
May-Current	-	Feasibility Studies initiated
June-Sep	-	Commercial Agreements

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:

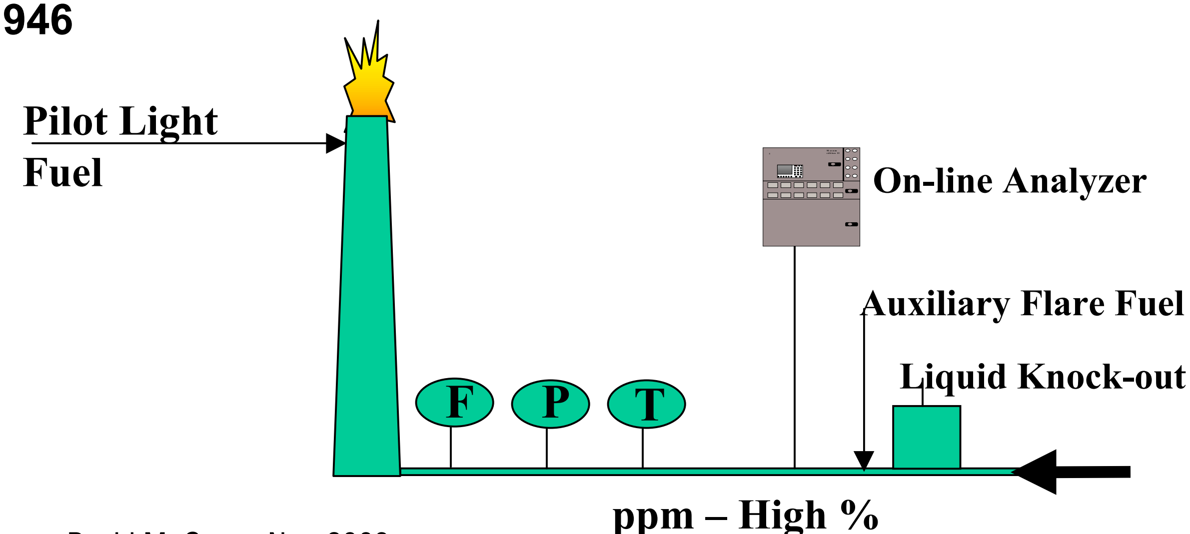
Components: HRVOC + enough composition for +/- 5% accuracy of BTU and average molecular weight determination.

Range: ppm -% (process, flow & site-cap depend. Frequency: Min. every 15 minutes; speciated Continuous for P, T, F

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

Uptime: >95%

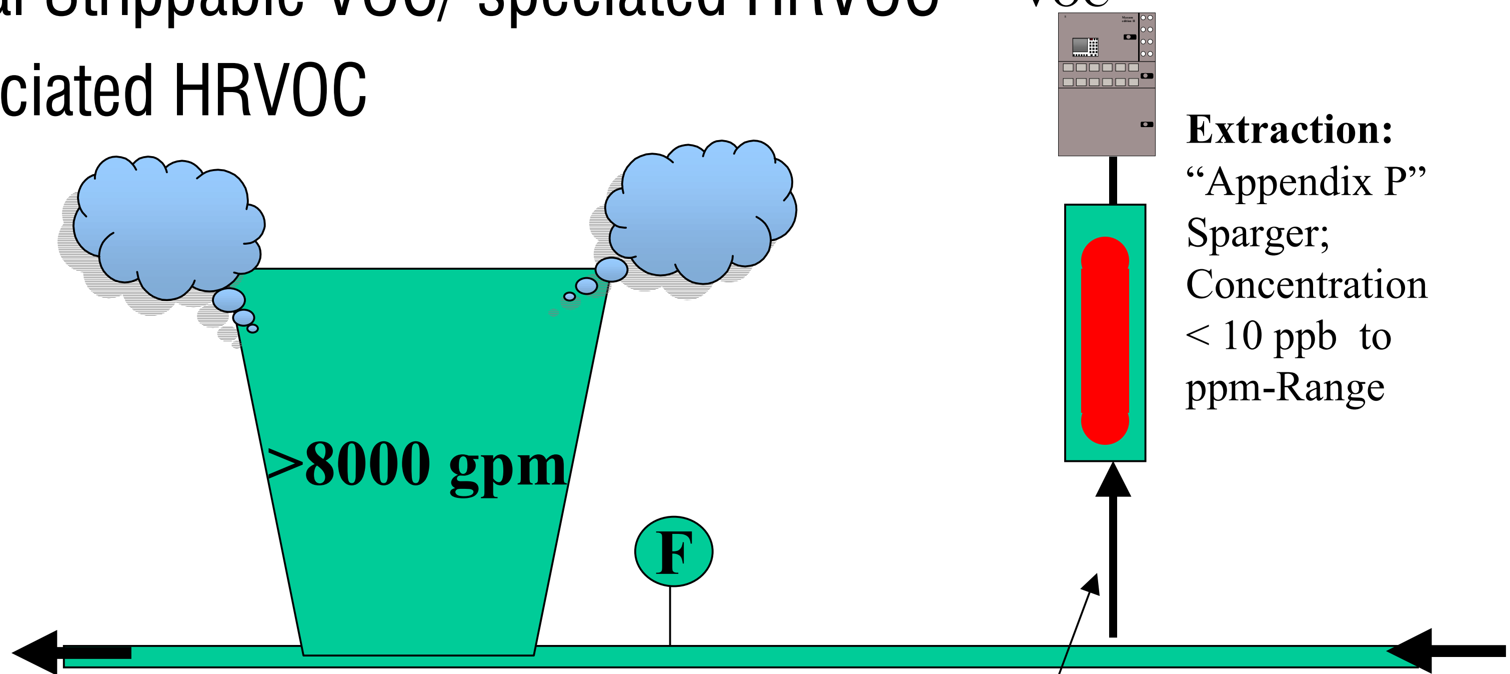
Analyzer Failure:Lab every 24 hours, according 40CFR60 Appendix A, Method18 and ASTM 1946



Cooling Tower - Analysis Requirements

Cooling Towers: **> 8000 GPM**

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



Sampling Issues

- Flare Sample--Gas
- Cooling Tower Sample--Liquid

Determining CTHES Sampling Options

Two Goals:

- Selection of the sampling system technology for continuous monitoring of the cooling tower heat exchange systems with a design capacity to circulate 8,000 gpm or greater.

- Selection of the sampling system technology for continuous monitoring of the cooling tower heat exchange systems with a design capacity to circulate less than 8,000 gpm.

Steps to Reach the Goal

- Determine environmental testing requirements
- Evaluate options for sampling system
- Evaluate best potential option
- Determine specific plant speciation requirements
- Plant sampling to determine 50 ppbwt level

Options and Issues

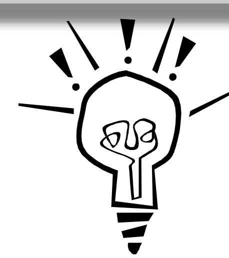
Choice of Sample System

- Air-stripper
- Membrane probe
- Thin Film Headspace (TFHS)
- Air-Sparging

Considerations

- Approval Potential TCEQ
- Capabilities to meet regulations
- Direction of Industry / TCC
- Technique
  - Calibration
  - Components detected
  - Response

Technology Evaluation



Air-Stripping

- Provides a gaseous sample that represents emissions from cooling towers
- Is the sample system mandated for grab samples ("El Paso")

Membrane/TFHS/Sparging

- Integrated with the analyzer to measure total content in the water

Evaluation Tool: Matrix

Wt.= Weighting Factor
A = Air-stripping Appendix P
B = Membrane Probe
C = Thin Film Headspace (steady state operation)
D = Sparging technology

Evaluation Area	Criteria	Wt.	A	B	C	D
TCEQ Approval	Specified Sampling for out-of-order periods	1	9	0	0	1
	Specified Sampling for monthly requirement	1	9	0	0	1
	Rep. emissions of VOCs from cooling towers	1	9	1	1	3
	Results Equiv. to Appendix P for HRVOC	1	9	9	9	9
	Results Equiv. to App. P for other VOCs	1	9	1	1	3
	Quick TCEQ Approval	2	3	1	0	1
Operation	Calibration Labor Costs	2	9	1	3	9
	Calibration Equipment Costs	1	3	1	1	3
	System Maintenance	2	1	9	3	3
	Sensitivity	1	1	9	9	3
Investment	Capital Costs	1	9	3	3	3
	Availability	1	9	9	9	3

Evaluation Tool: Matrix

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Evaluation Area	Criteria	Wt.	A	B	C	D
Adaptability	Allow choice of THC or GC/FID	1	9	9	9	9
	Coupled with GC for speciated analysis	1	3	1	1	3
	Potentially meet Regulations	1	3	1	1	3
	TOTAL		**105**	65	55	67

CTHES Sampling Conclusion

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

Commercial Sample Systems

Tech.	Model	Supplier	Reference
Air Stripper	RT 201/ RT 202	Houston Analytial Systems Co.	El Paso
Air Stripper		Horiba	El Paso
Air Stripper	In Dev.	Measurementation	El Paso
Sparger		Siemens	
Sparger	In Dev.	PAAI	
Sparger	8280	Thermo Onix (Fluid Data)	
Membrane	8280	Thermo Onix (Fluid Data)	
Membrane	204	KECO	
Membrane	Aqua-Cop	California Analytical Instruments	
Sparger	Process Analytics	ABB	

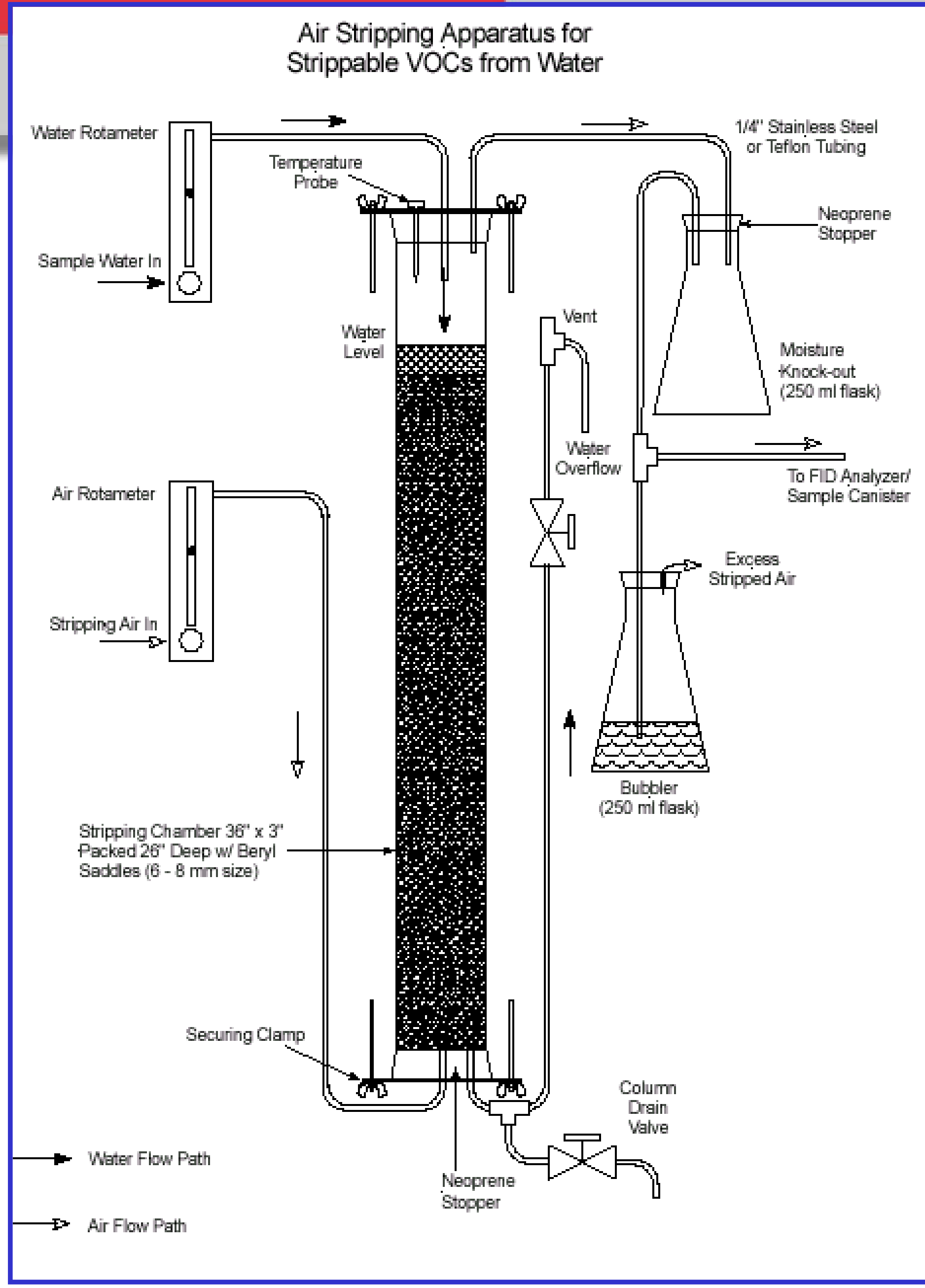
What is available?

- Limited choices of "process hardened" El Paso designs.
- Decision to work with suppliers to develop an acceptable design.

Requirement

- Appendix P has specific guidelines
  - Chamber
  - Operation
  - Sample line

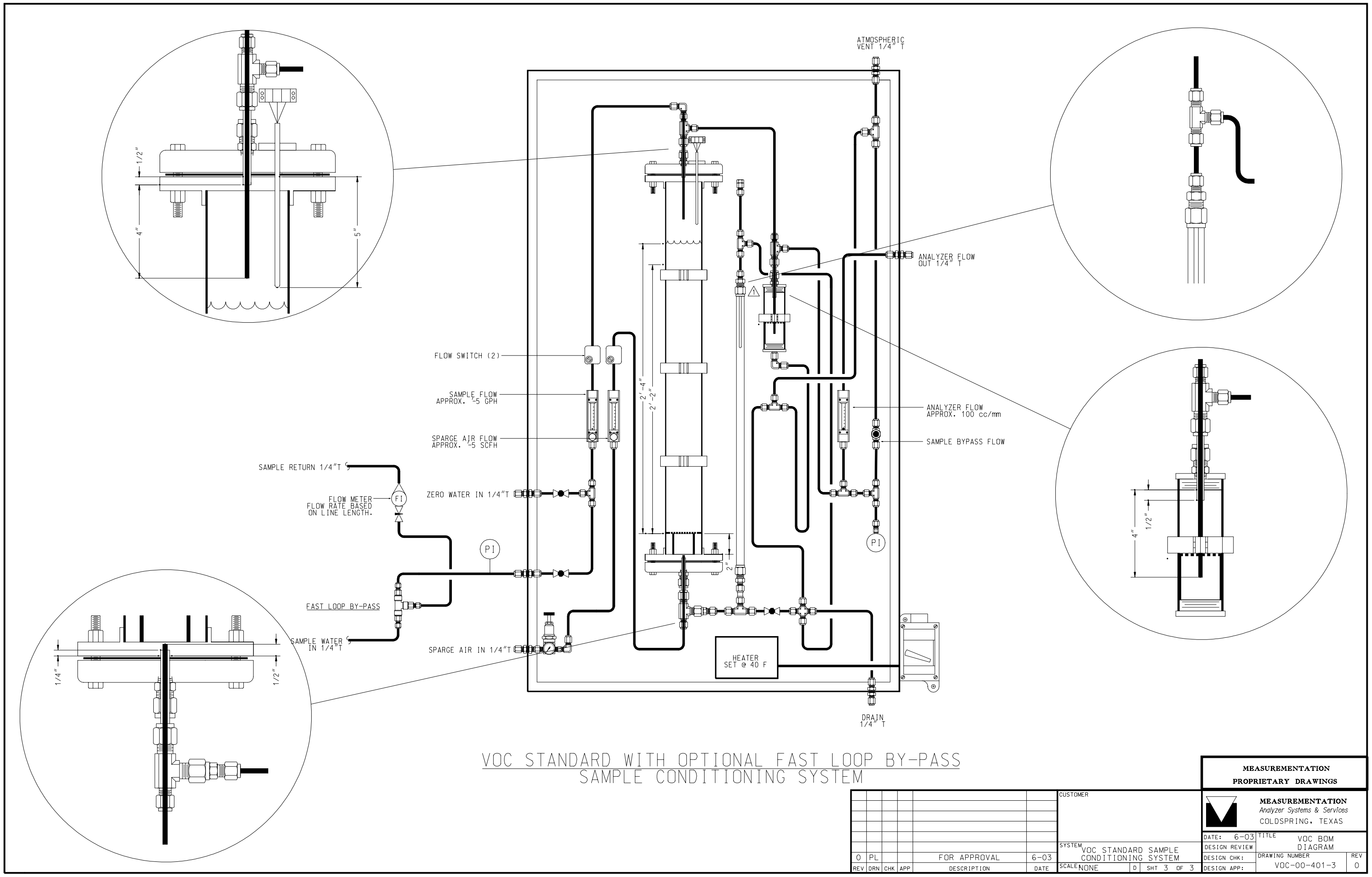
Appendix P: Modified El Paso Method



<u>Issues:</u>

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

Suggested On-line Design



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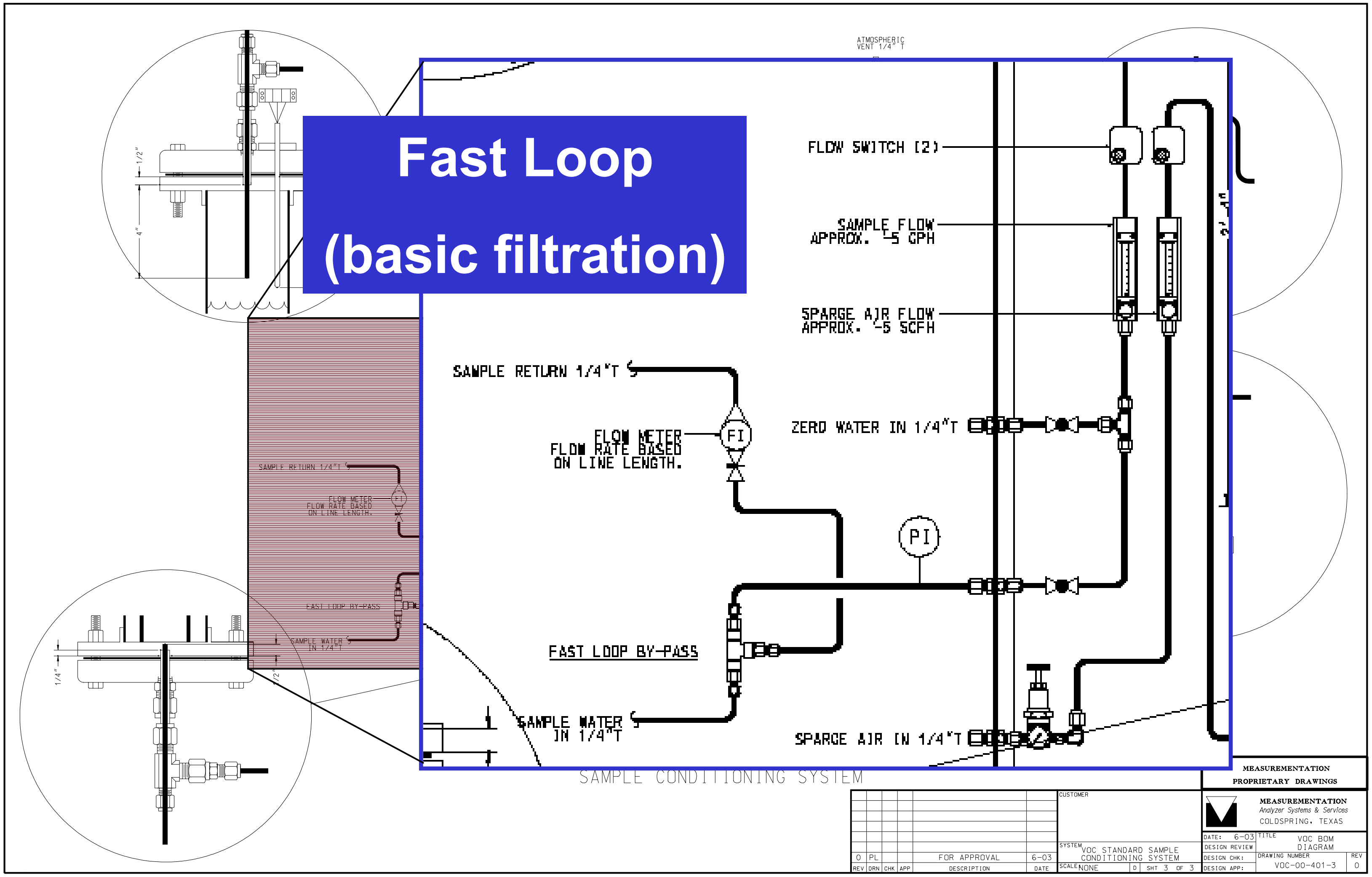

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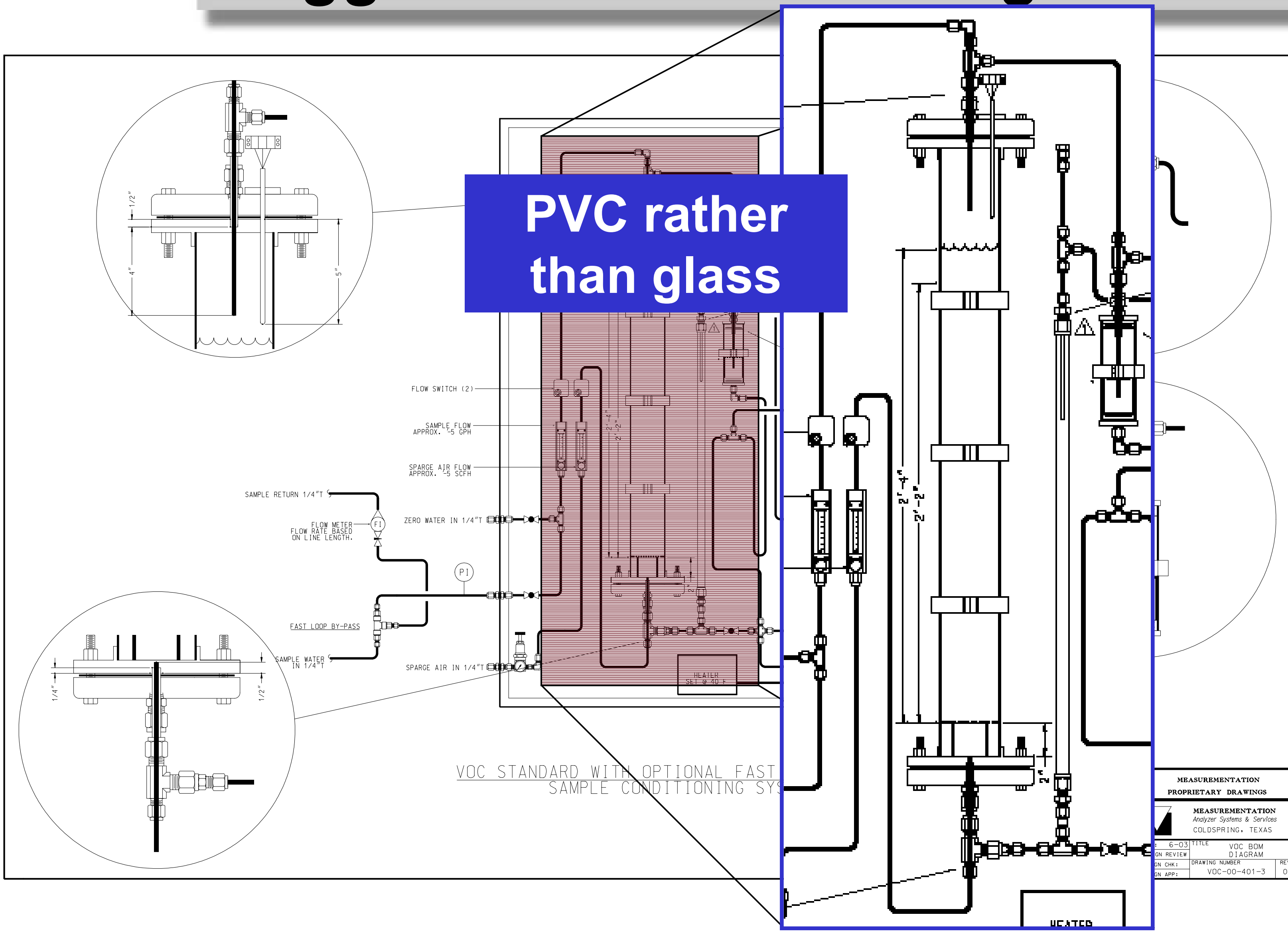

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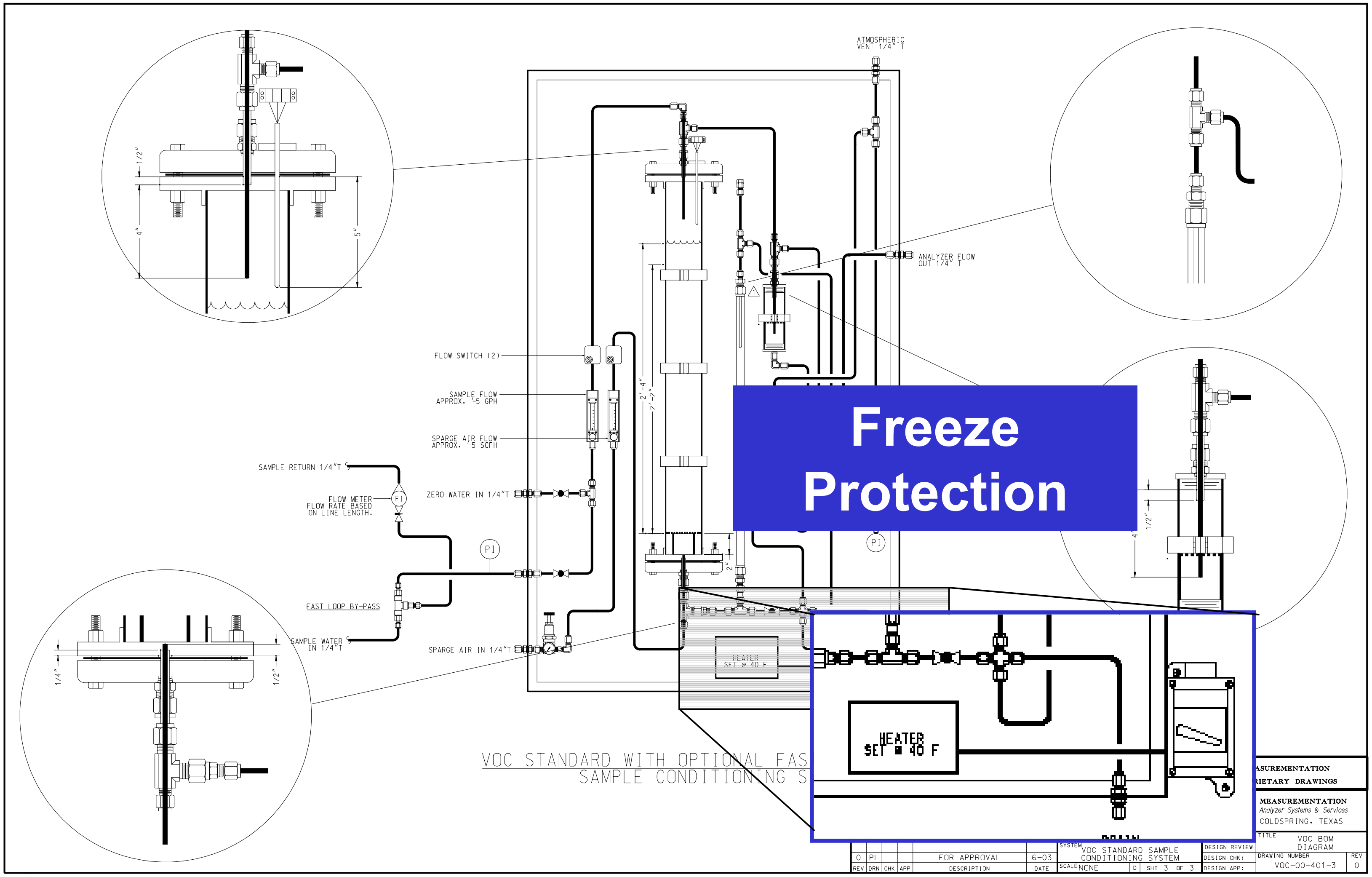

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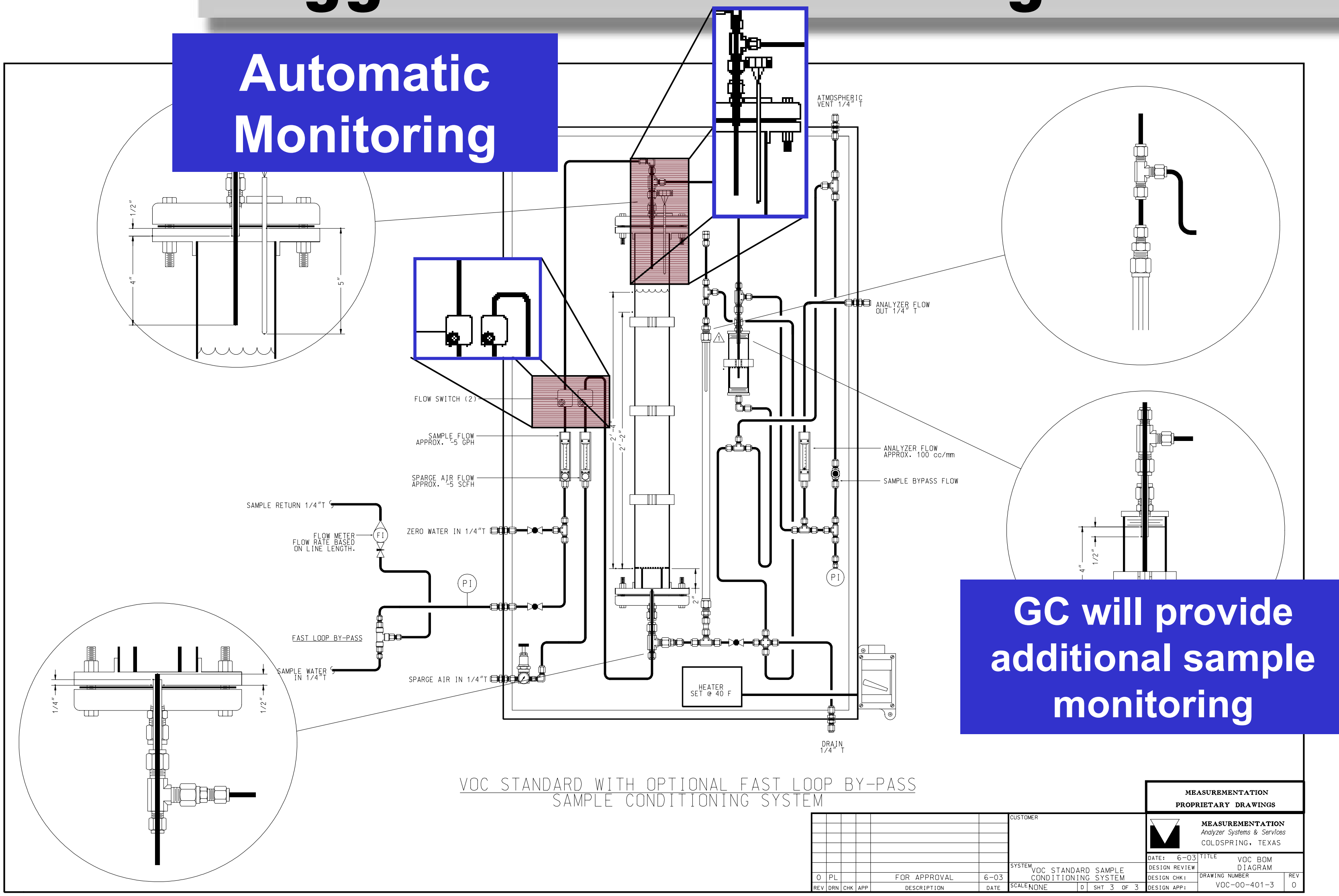


Evaluation of Sampling Technology

- Two scenarios:
  - A cleaner cooling tower
  - A dirtier (particulate loading) cooling tower: dust, algae growth, etc.

☑ Validate Improvement

☑ Validate Improved Performance for Business Impact

☑ Validate Key Input / Process Variable Limits

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.

Analytical Options

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

Analytical Options

- Mass Spectrometry
  - Too Costly (Distributed Locations/Single Stream)
  - Difficulties Resolving Isomers of Butene
- FT-NIR
  - High initial cost
  - Limited speciation capabilities
- Filter IR
  - Cannot Make Measurement (Lack of Spectral Differences)

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

- Class 1, Div II Area Classification
- Ease of Maintenance is a Key:
  - Parallel Chromatography
    - Faster Measurements
    - Simplified Measurements
    - Single Platform
  - Modularity (Applet Concept)
    - Rapid Repair

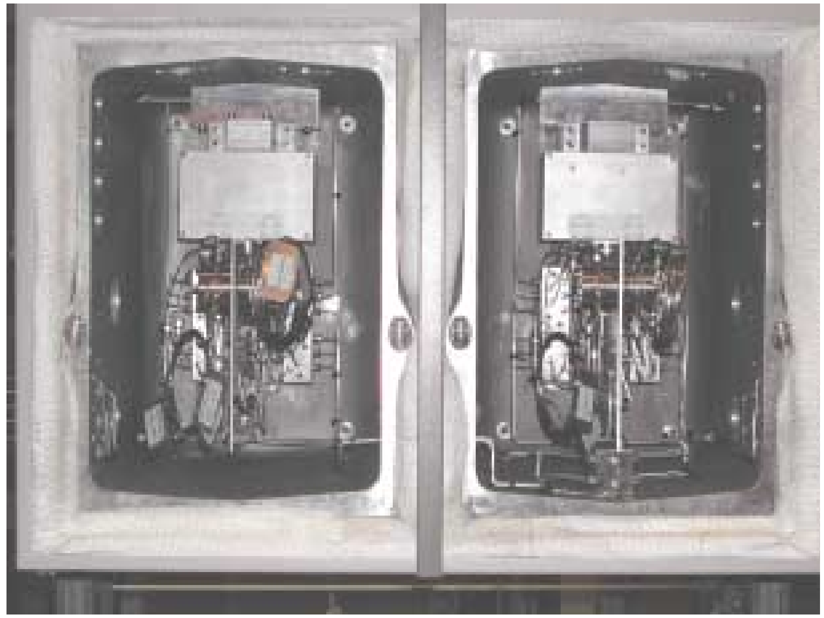
GC Requirements

- 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

Flare Application: Comprehensive Analysis



Utility Gases:
- Hydrogen carrier
- Nitrogen carrier and valve gas
- Calibration gas
- Airless Oven

Applet Concept

Package Principles in Dow

- Goal: Reliable, accurate measurements satisfying analytical requirements.
- Implications: Analyzers sheltered from weathering, corrosion, washdown and changes in ambient temperature

Packaging Justification

- Reduction of electronics failures
- Increase in analyzer precision
- Elimination of degradation
- Reduction of maintenance requirements
- Increased safety during analyzer maintenance
- Security

Impact of Packaging

- Proposal: Appropriate package can result in at least a 1% improvement in analyzer reliability.
- Impact

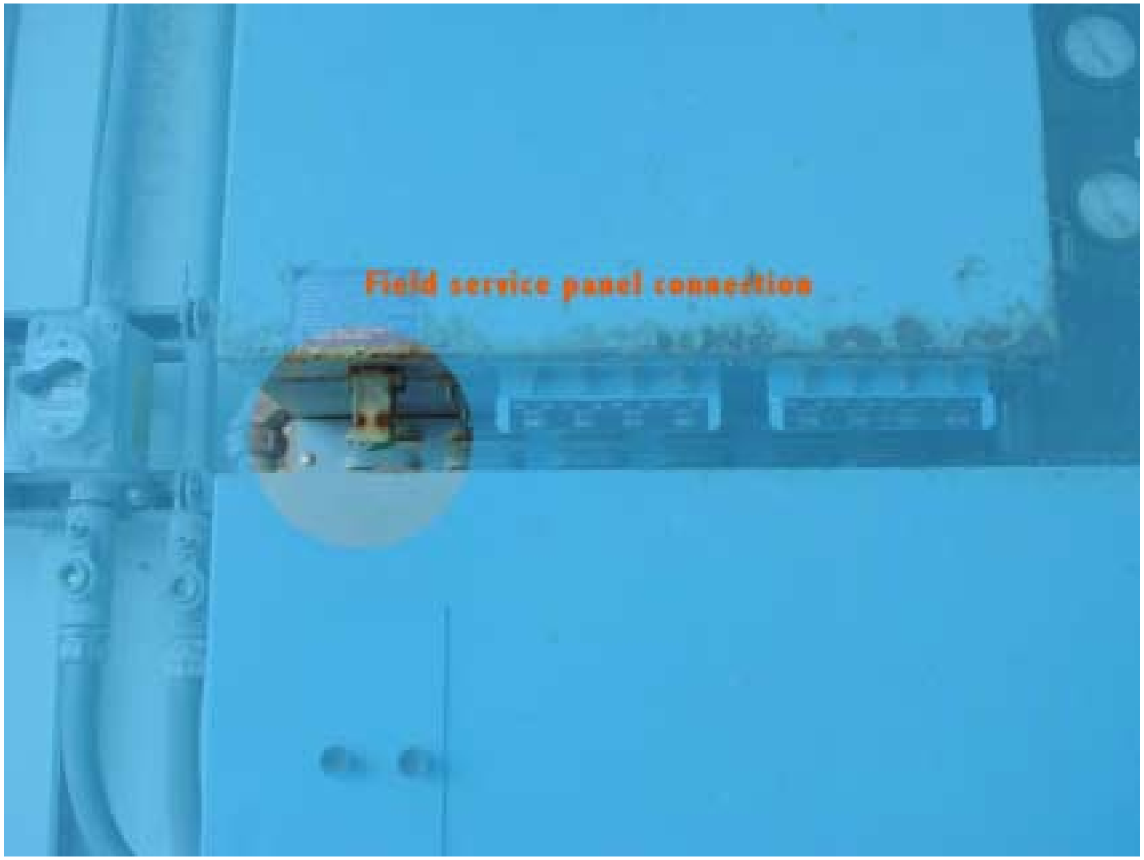
Lab Costs	$ 7,200
Labor Costs	$ 8,400
Total Potential Impact:	***$15,600***

Packaging Options that were Reviewed

- Open enclosure
  - Very limited environmental protection
  - No temperature control

Experiences with Open Shelters

- Installed in 1995



Packaging Options that were Reviewed

- Analyzer Enclosure--Air Cooled
  - Requires large volumes of instrument air (140 scfm of 100 PSIG instrument air) to overcome heat generated by GC
  - Exposure to elements when performing maintenance

Packaging Options that were Reviewed

- Analyzer Enclosure--HVAC
  - Exposure to elements when performing maintenance
  - Limited savings over expanding cabinet to proposed solution

Cost Comparison

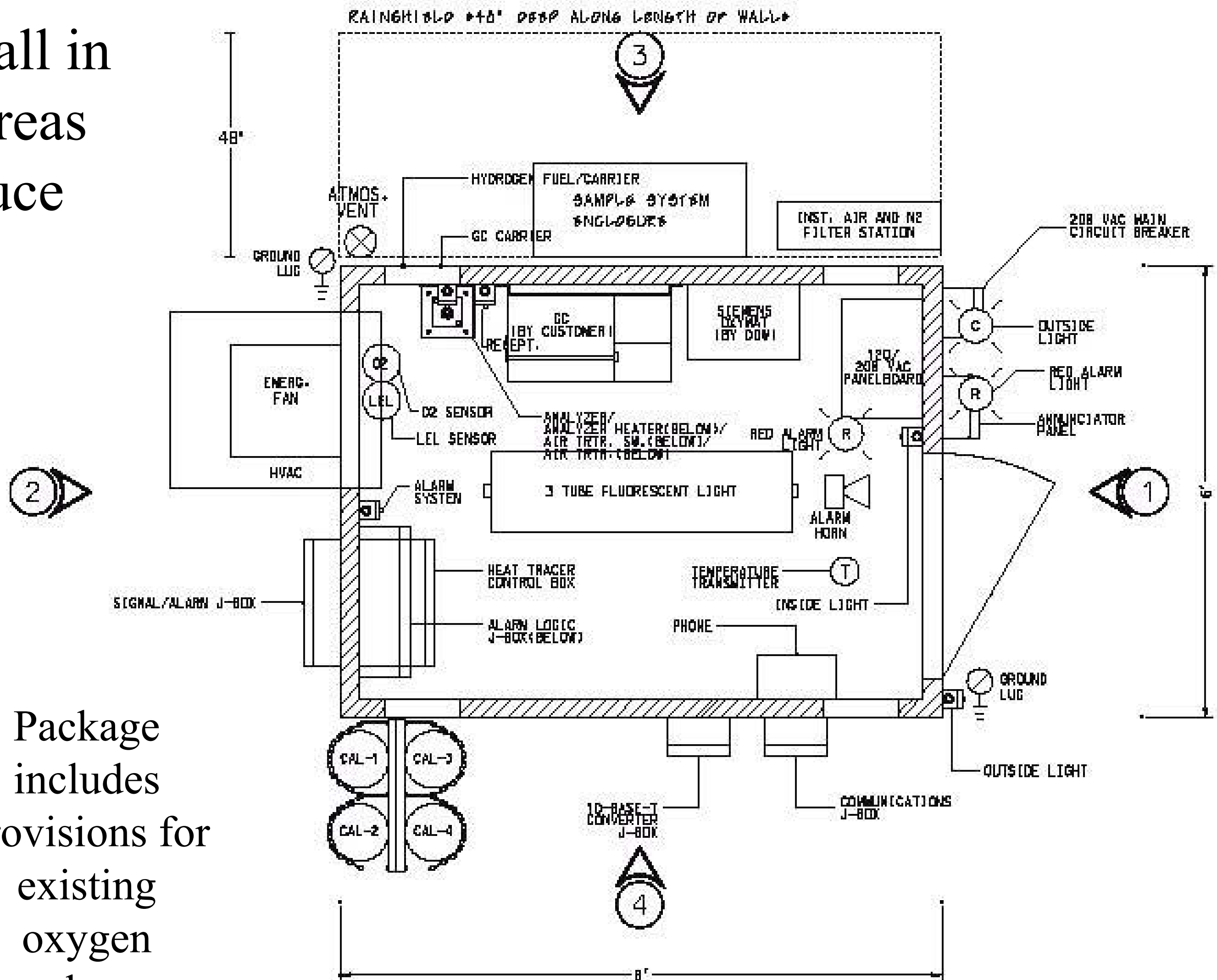
Open enclosure (8' x 5')	$30K
HVAC enclosure (8'8" x 4'4")	$40K
Analyzer Building (8' x 6')	$65K

Proposed Packaging

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

Proposed Packaging

Would aim to install in G.P. areas to reduce costs.



Package includes provisions for existing oxygen analyzers

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.

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

SIP Future Activities

- TCEQ will make technical corrections to the rules - Propose in April and adopt in September October
- TCEQ will conduct a mid-course review in April, 2004
- Implementation efforts must start 1Q 2004 to meet the various compliance dates

Acknowledgements

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

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.