

ISA Houston Analysis Subsection

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HRVOC Analyzer

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Star Instruments, Inc.

TCEQ – Chapter 115 Rules

Revised 10/22/03



Continuously monitor Total HRVOCs, at least every 15 minutes (cooling towers and flares).

If use a Total HRVOC Analyzer:

- No on-line speciation is required
- Total HRVOC reporting satisfies rules
- Speciation module available (if required monthly)

If use a GC Analyzer:

- Report total HRVOC.
- When 50 ppbw total VOC is exceeded for over one hour; report speciated HRVOC.

Flare BTU approved monitoring methods:

a. If performed by GC:

- Flare gas must be speciated for HRVOC & other constituents related to molecular weight & net heating value within 5% (eg. hydrogen, carbon monoxide, oxygen, nitrogen, carbon dioxide, methane, and ethane).

b. If performed by calorimeter:

- BTU/SCF Monitored (Temporary Flares)
- Method 301 to be performed for stationary flares

Record analyzer “up-time”:

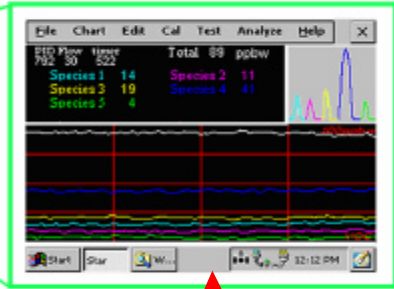
- If a malfunction exceeds 8 consecutive hours, must sample & lab speciate within 24 hours of failure & daily thereafter until analyzer is repaired.

QA Plan/Test Program – due in “sufficient” time for agency approval before equipment purchase (180 day TCEQ approval cycle including resubmissions). If submitted after 4/30/05 & Agency issues a deficiency notice in 180 days, no relief for compliance by 2/31/05.

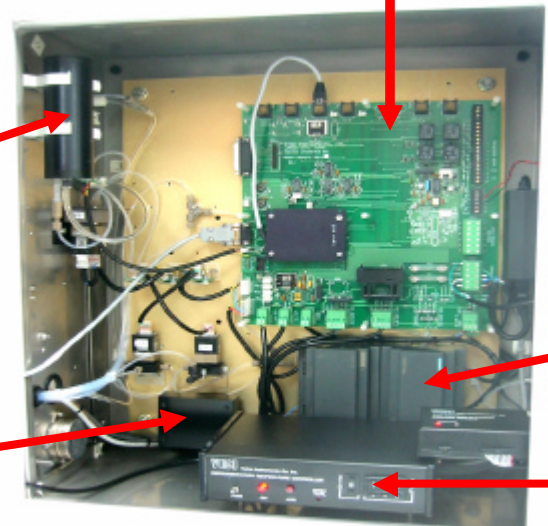
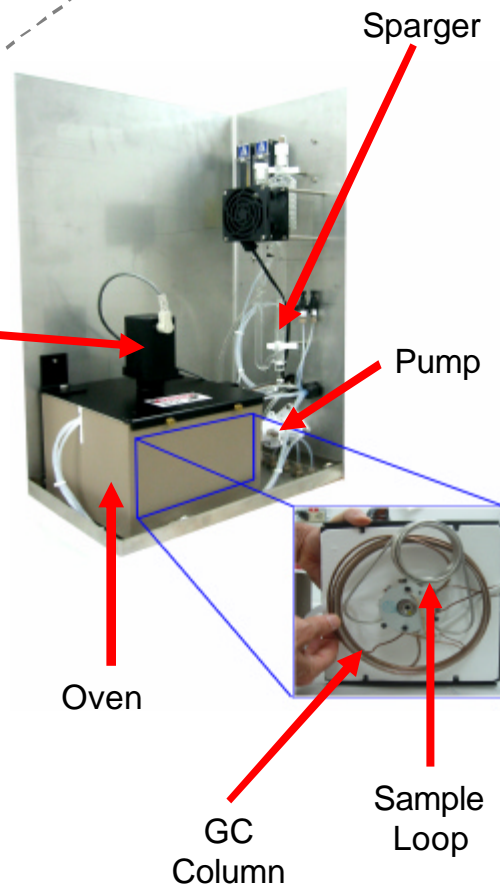
Audits – 50% of process units by 12/31/04 & remainder by 12/31/05.

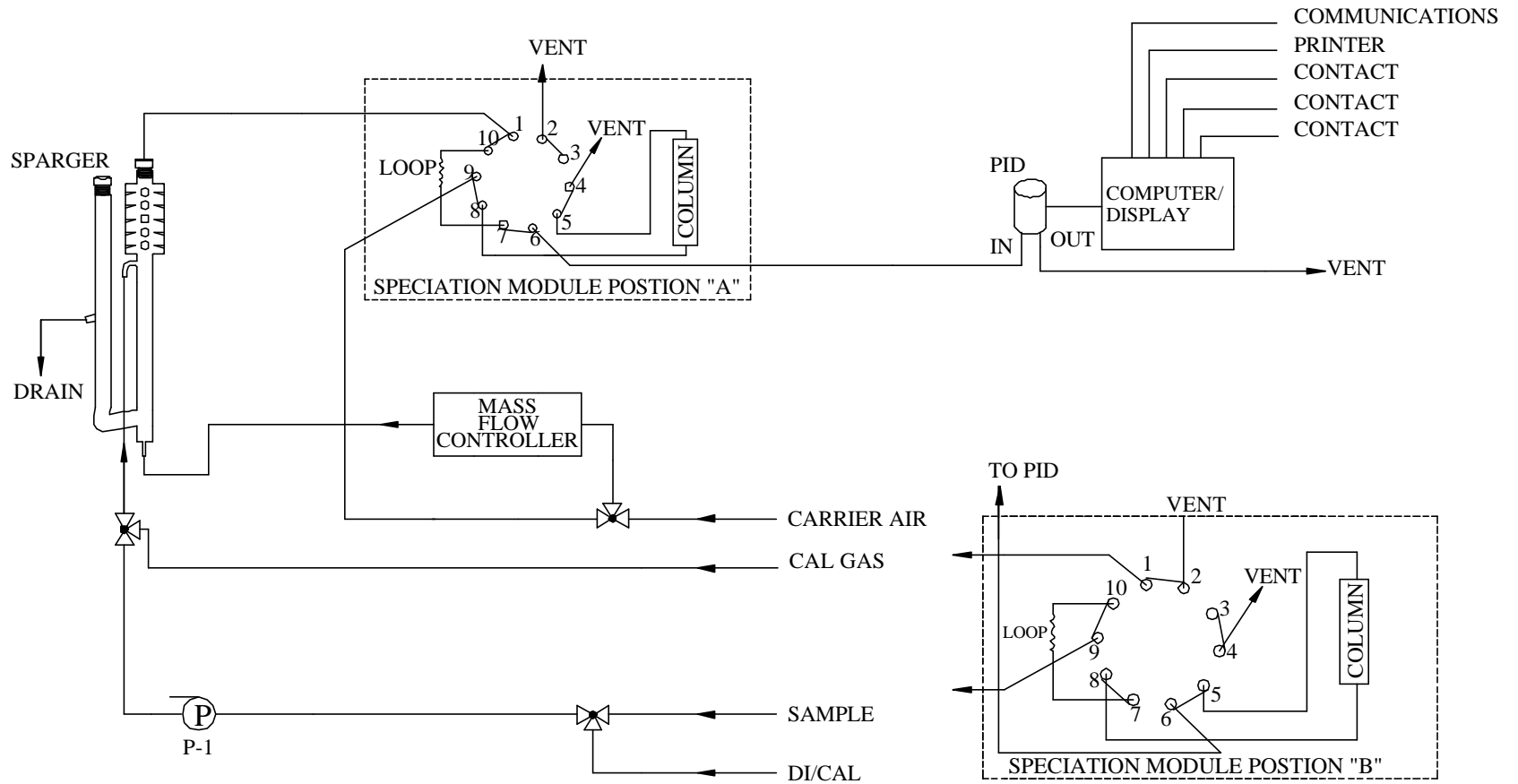
12/31/05 – Monitoring equipment must be in place and operating by this date for all units.

HRVOC Analyzer

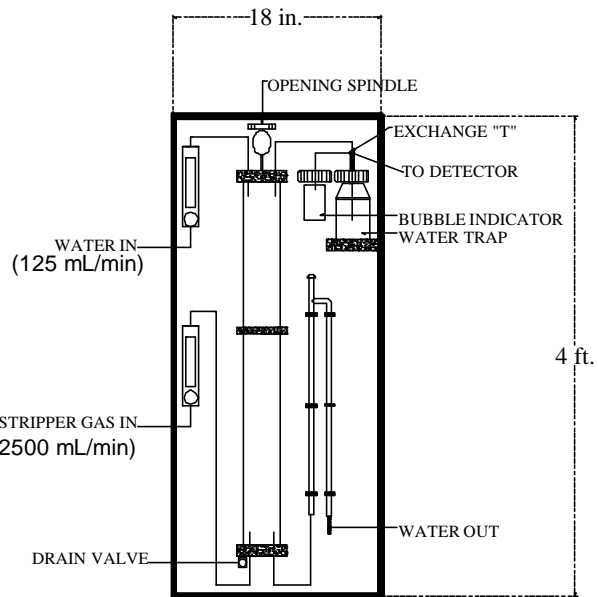


Computer

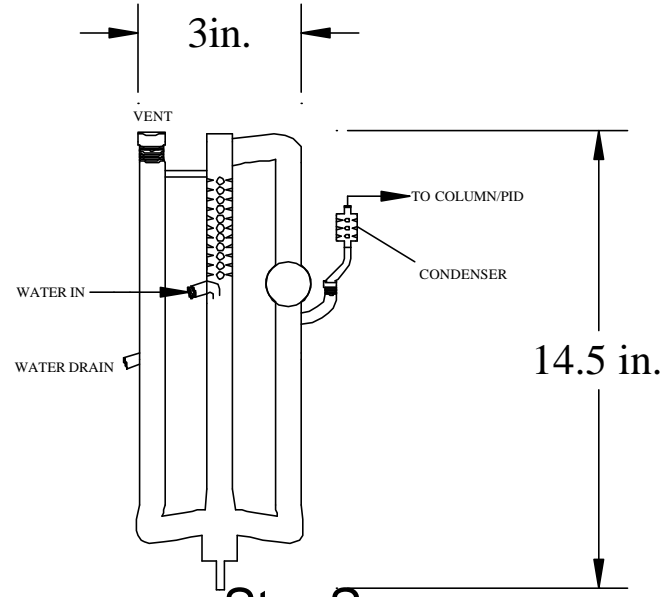




Cooling Towers



EI Paso Stripper



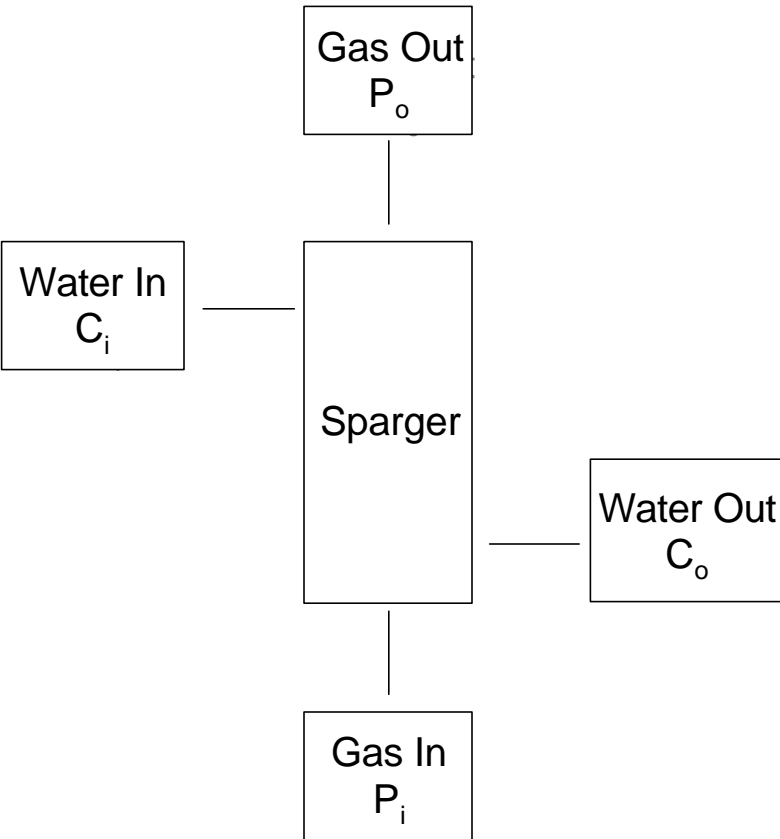
**Star Sparger
(TCEQ Approved)**

<u>TCEQ Rule</u>	<u>EI Paso Stripper Requirement</u>	<u>Analyzer Sparger Implementation</u>
Zero Air Blank Check	Monitor stripping air flowing through an empty stripper with previously calibrated detector. If background exceeds 1.0 ppmv as methane, thoroughly clean* stripper. Record results.	Auto-Validation Check Auto-Zero Utility Mass Flow Controller (Computer Controlled) Computer Logged Results
Water Blank Check	Flow de-ionized (D.I.) water through all sample lines & stripper. If background exceeds 1.0 ppmv as methane, thoroughly clean* stripper. Record results.	Auto-Validation Check Auto-Calibration with D.I./Standard Auto-Clean Utility Computer Logged Results
MDL of < 10ppbw	Rules silent on procedure. Presumably USEPA/Std. Methods/accepted best practices will be required.	Automatic Test Utility Computer Logged Results
Calibration	Rules silent on calibration. Presumably USEPA/Std. Methods/accepted best practices will be required.	Automatic "end-to-end" Calibration Utility Auto-Validation Check

****EI Paso Stripper Cleaning Procedure***

Chamber, beryl saddles, and all associated glassware to be cleaned with hot, soapy water, followed by 5 rinses of tap water, 5 rinses of distilled water, then baked off in an oven at 150 °C for 1 hour. Chamber may be air-dried if available oven too small.

Counter-Current Flow Sparger



Mass Balance

$$(C_i - C_o) * q = (P_o - P_i) * d * Q$$

Solubility at Equilibrium

$$P / C = S$$

P_i = VOC partial pressure in sparger input gas, ppmv

P_o = VOC partial pressure in sparger output gas to detector, ppmv

C_i = VOC concentration in sparger input water sample, ppbw

C_o = VOC concentration in sparger output water, ppbw

D = VOC gas density, g/l
= PT * M / (R * T)

M = Molecular Weight of gas

PT = Total pressure, atm.

Q = Sparge gas flow rate, cc/min

q = Water sample flow rate, cc/min

R = Gas Constant = 0.08206 L - atm / g-mol - °K

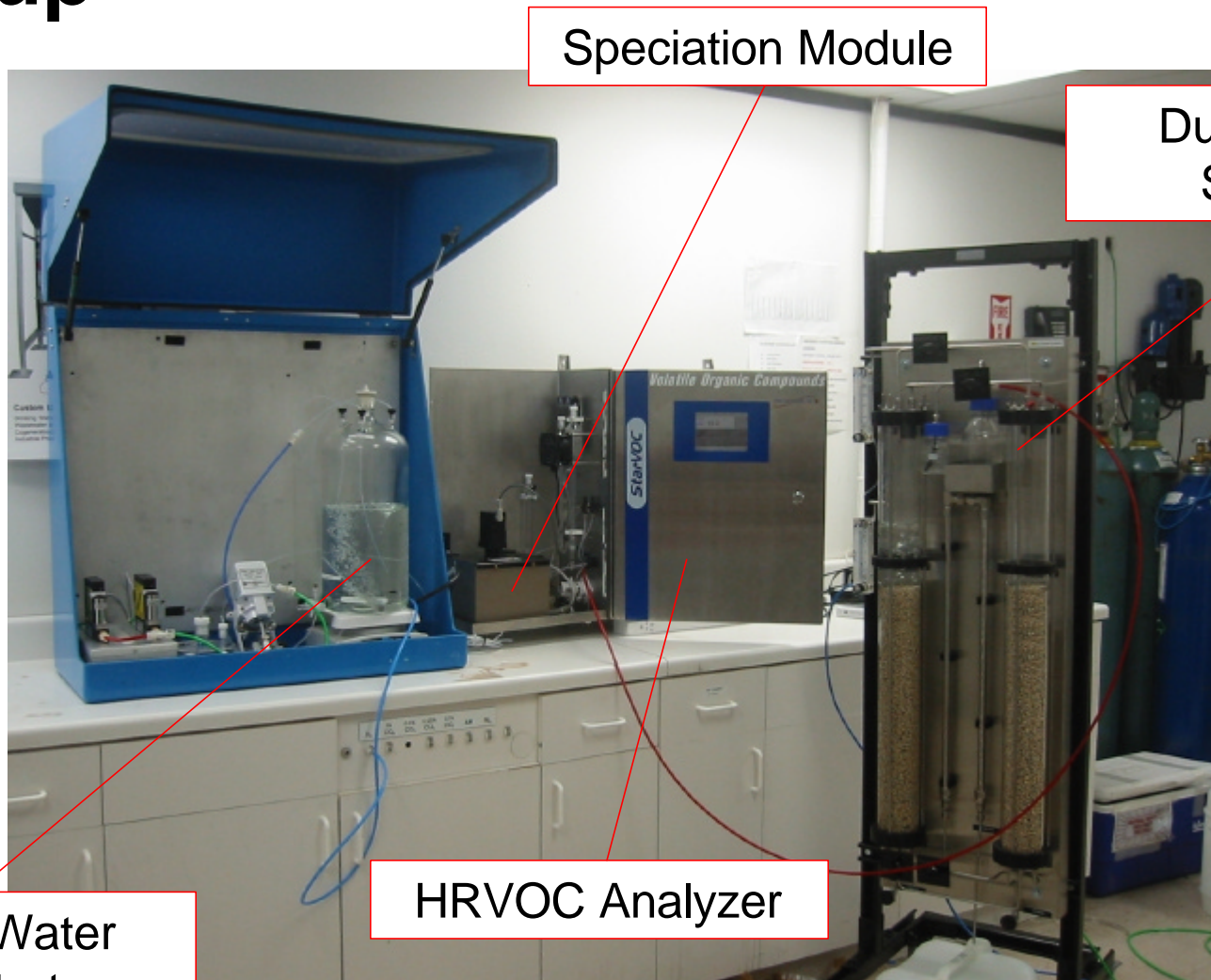
T = Temperature, °K

S = Gas solubility, ppmv / ppbw

$$= (H-1) * 18.01 / M / 1,000$$

H = Henry's Law Constant for VOC gas, atm-mol/mol

Test Setup



Speciation Module

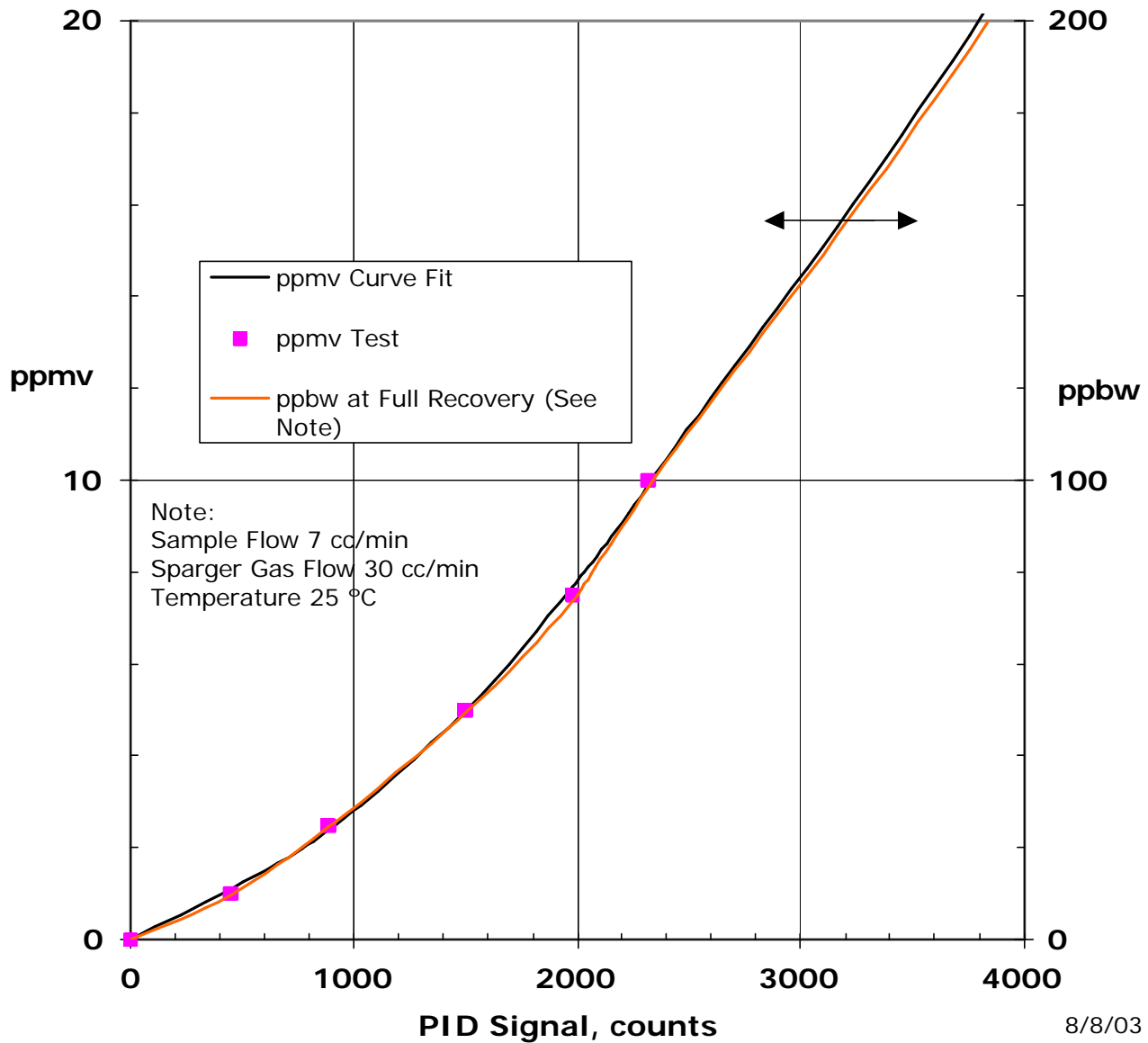
Dual EI Paso Strippers

VOC-in-Water Concentrator

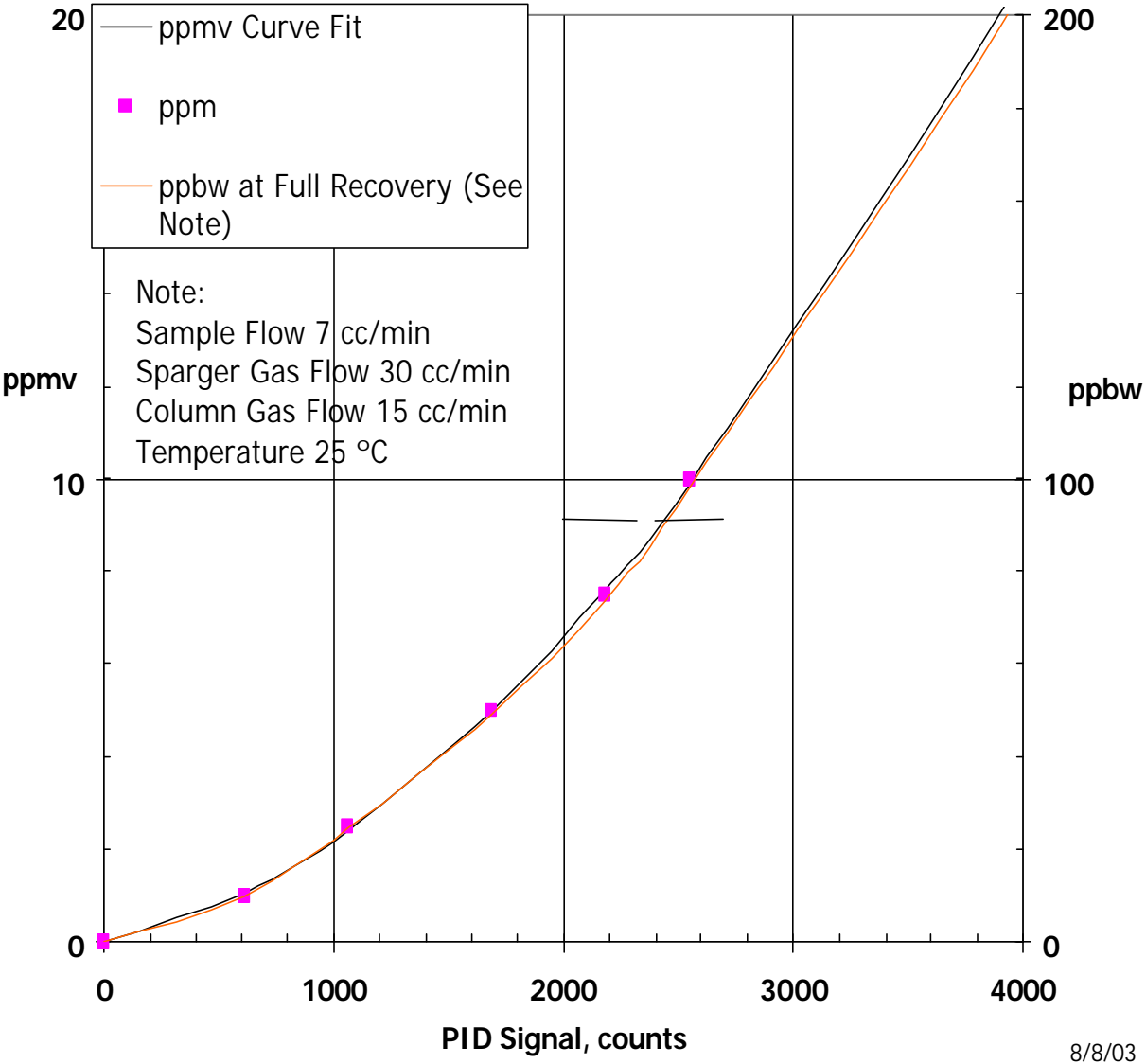
HRVOC Analyzer

- Sparger Recovery Tests
- Method 301
- MDL Tests

PID Response to Isobutene Total VOC Mode

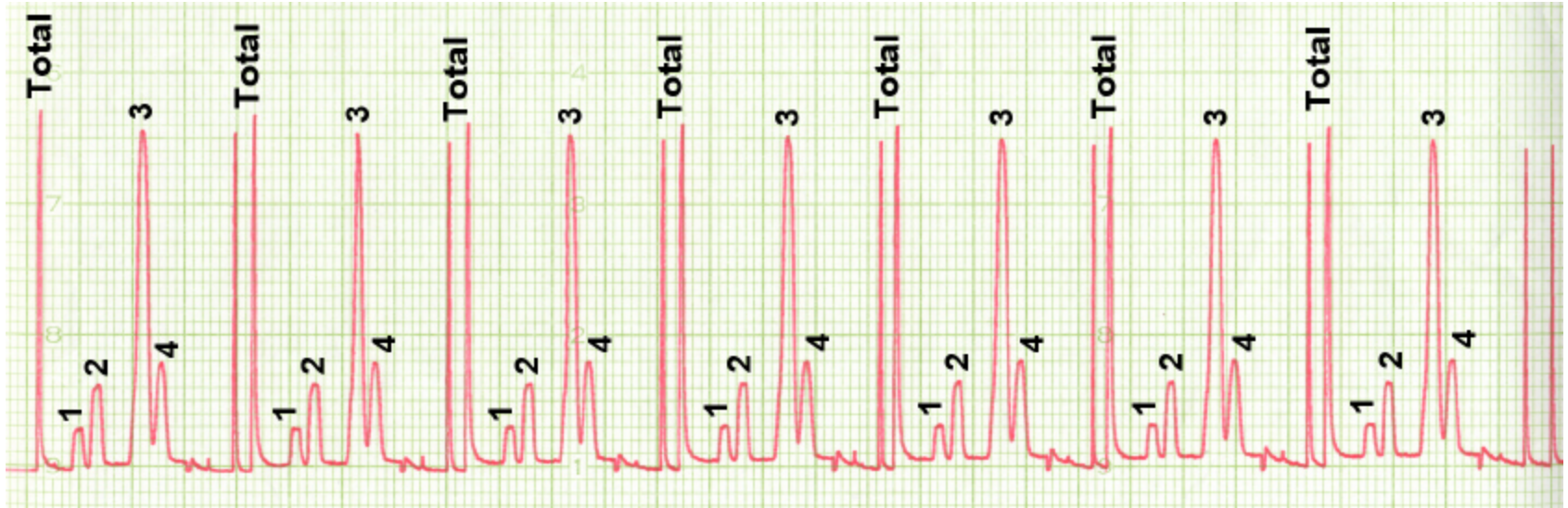


PID Response to Isobutene Speciation Mode



MDL Test Data

(Cooling Tower Water)



SPECIES	CAL STANDARD MIXTURE (ppbw)	STD.DEV	MDL (ppbw)
1 - Ethylene	2.1	.045	0.141
2 - Propylene	2.6	.049	0.153
3 - Butenes	9.2	.091	0.285
4 - 1,3 Butadiene	3.6	.085	0.267

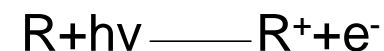
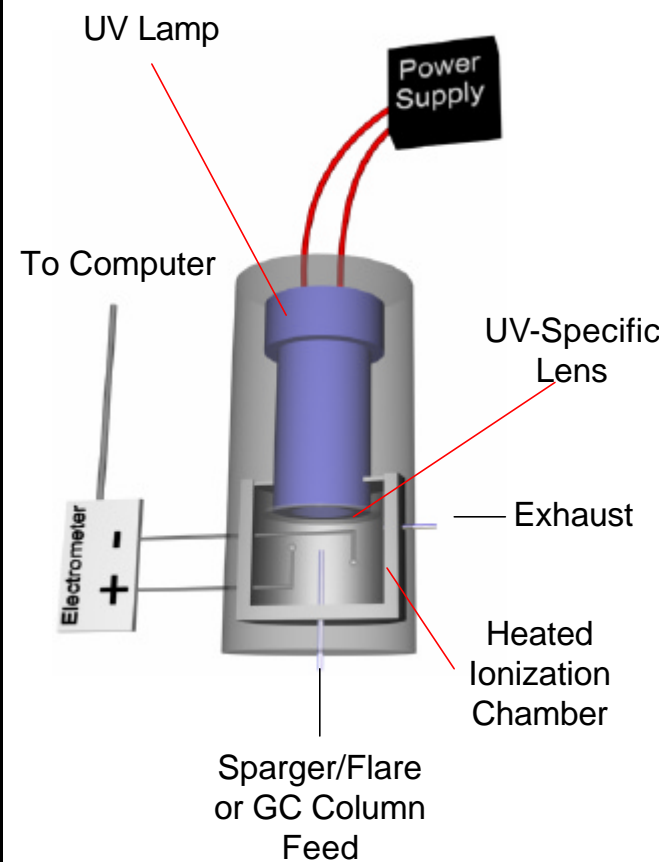
Choice of Detectors

FID & PID Basic Characteristics

	<u>Basic Characteristics</u>	<u>Interferences</u>	<u>Disadvantages</u>
FID	<p>Widely Used</p> <p>Higher MDL</p> <p>More Complex</p> <p>Fast</p> <p>Less Selective (Oxidizable C Response)</p> <p>Not Continuous (If Need Concentration)</p>	<p>Major methane interference may require dual units and subtraction technique, resulting in poor accuracy and repeatability.</p> <p>Ethane interference most difficult to avoid.</p>	<p>Hydrogen Required</p> <p>More Operator Attention</p> <p>Baseline Drift</p> <p>Questionable Sensitivity and selectivity as Continuous VOC Analyzer</p>
PID	<p>EPA Preferred (VOC)</p> <p>Lower MDL (~1ppbw in Water)</p> <p>Simpler</p> <p>Faster</p> <p>More Selective (Species Response)</p> <p>Continuous</p>	<p>Minor (Using Application Algorithms)</p>	<p>Lamp Life (<i>Remedy:</i> Improved 10,000 Hour Design Life)</p> <p>Possible Residue Buildup (<i>Remedy:</i> Auto-Cal/Auto-Clean)</p> <p>Gradual Sensitivity Decrease with age (<i>Remedy:</i> Auto-cal)</p>

(Detector Selected)

PID



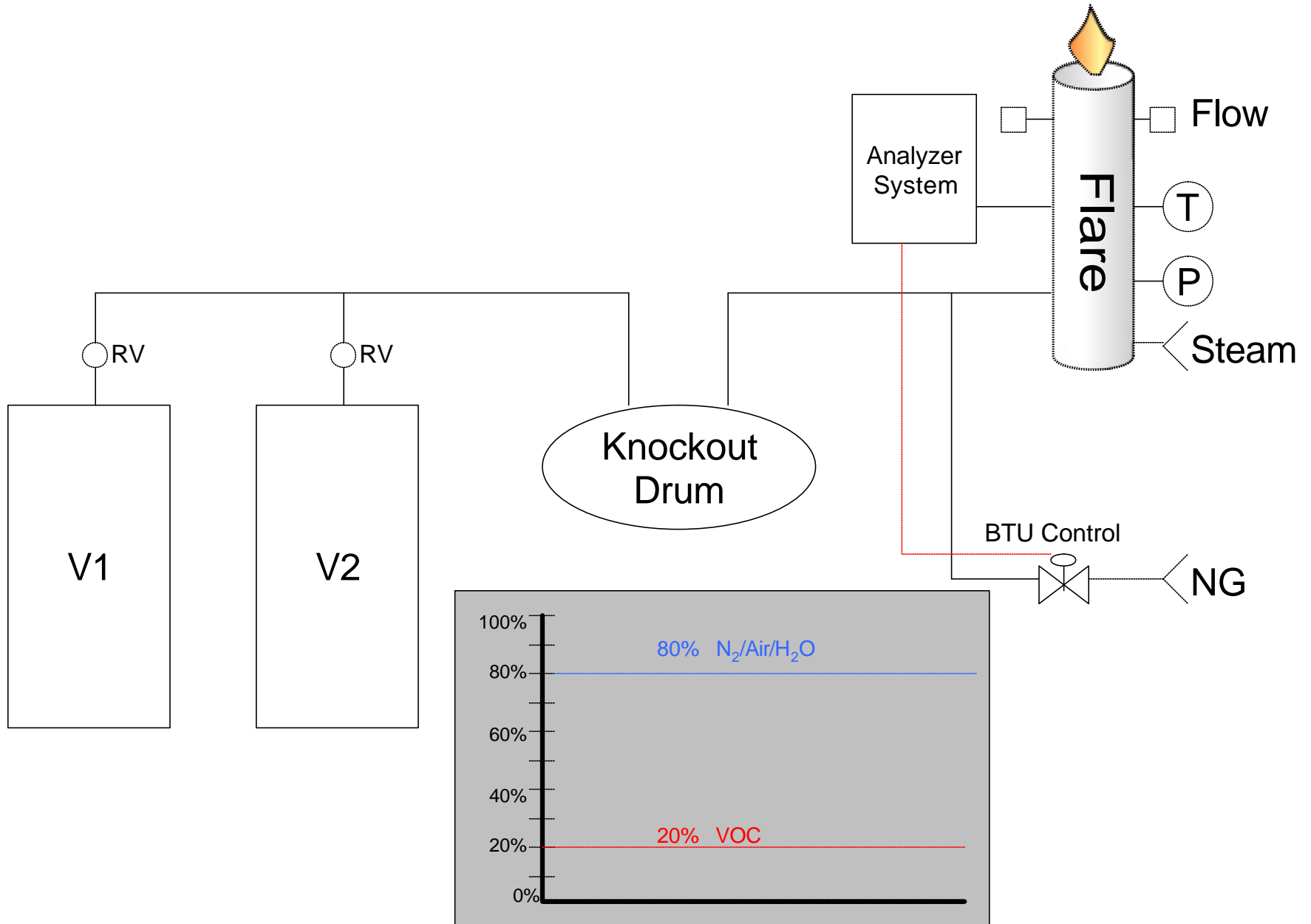
Flares

Typical Flare Gas Stream

STREAM DATA	No.	Typical Composition Include Units of Mol%, Wt%, Lv%, ppm, Etc.)		
<i>Components</i>		NORMAL	MAX.	UNITS
Hydrogen	1	Trace	Trace	wt%
Carbon Monoxide	2			wt%
Oxygen	3			wt%
Nitrogen	4	75.40		wt%
Water	5	1.00		wt%
Methane	6	12.40	80	wt%
Ethane	7		20	wt%
Ethylene	8	trace		wt%
Propylene	9	5.30		wt%
Propane	10	0.40		wt%
N-Butane	11			wt%
IsoButane	12	0.16		wt%
Butene-1	13	trace		wt%
Hexane	14	1.80		wt%
Hexene	15	Trace		wt%
C6+	16			wt%
TOTAL COMPONENTS (FLOW)		19,377	700,000	lb/hr

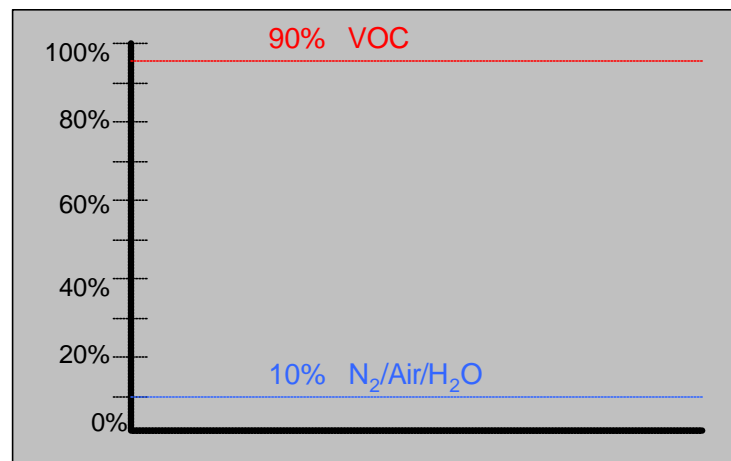
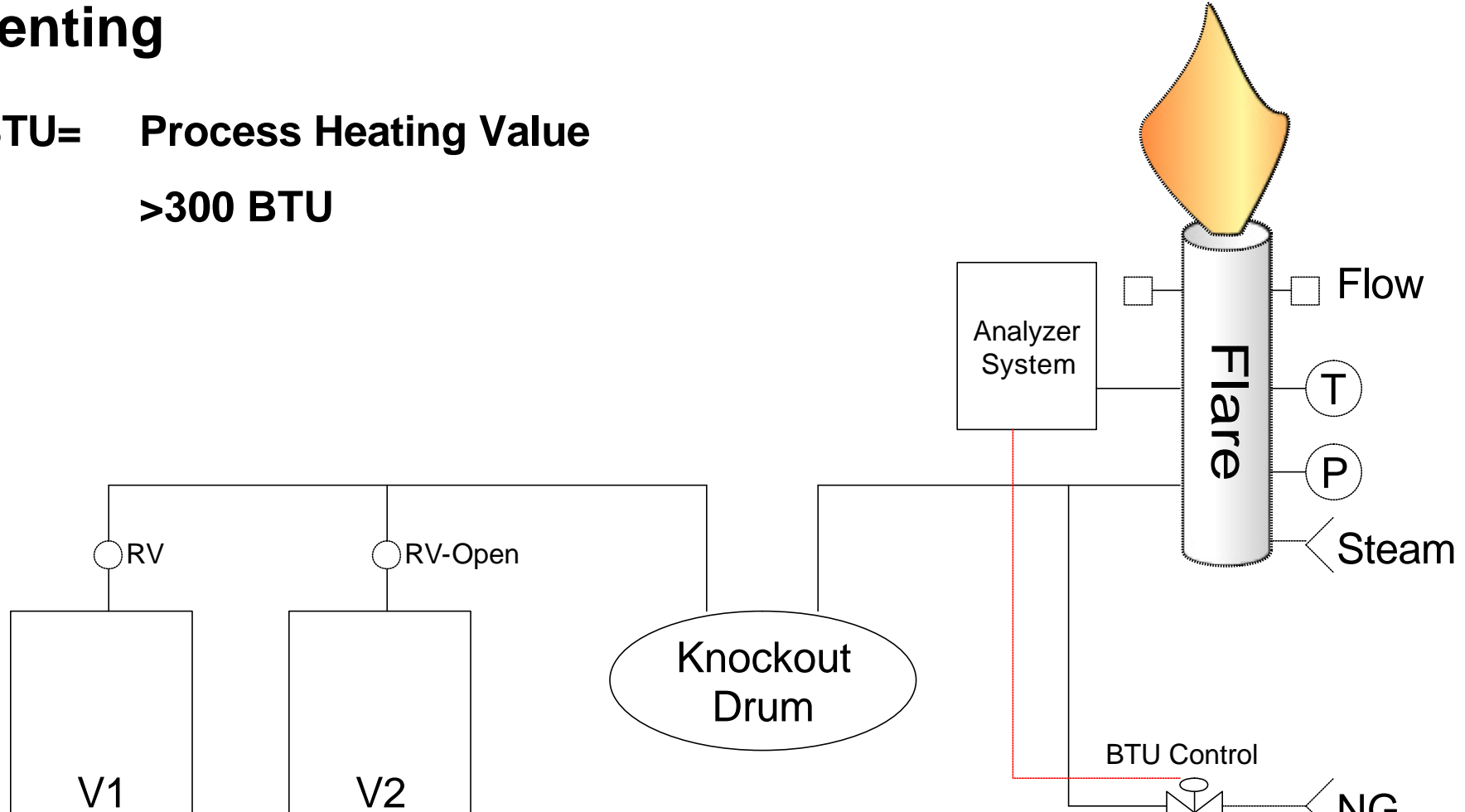
Non-Venting

BTU= >300



Venting

BTU= Process Heating Value
>300 BTU



Analyzer

Design / Operational Considerations

- Dynamic Range / Downturn
- Accuracy with Changing Matrices
- Response Time

Combustion Calorimeter



Features

- Direct measurement
- Responds to all unknown compounds
- Continuous, high-speed
- Wide dynamic range:
 - Incorporates a support gas burner (pilot light) for small baseline addition. Flame will never go out, regardless of flare gas composition.
 - Auto-switching of Wobbe second range orifice.
- Defensible reporting

Continuously burns small gas sample:

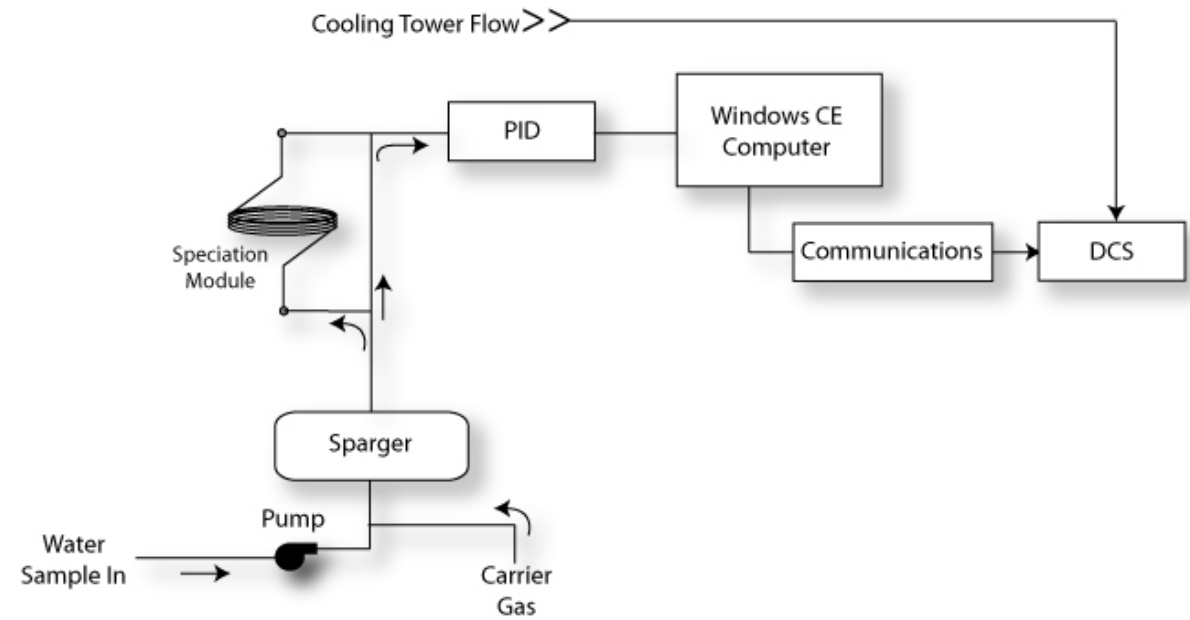
- Measures temperature rise (thermopile)
- Measures Wobbe Index*
- Measures specific gravity

$$\text{Calorific Value} = \text{Wobbe Index} \sqrt{\text{Specific Gravity}}$$

(1% Accuracy)

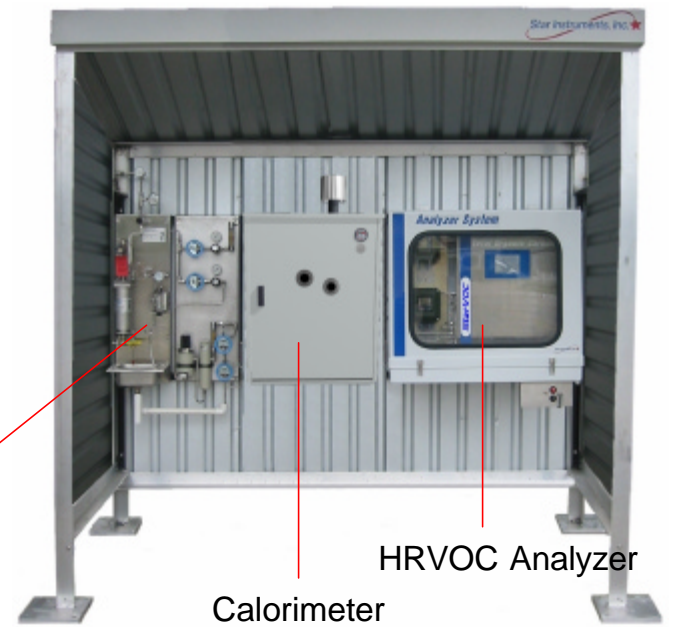
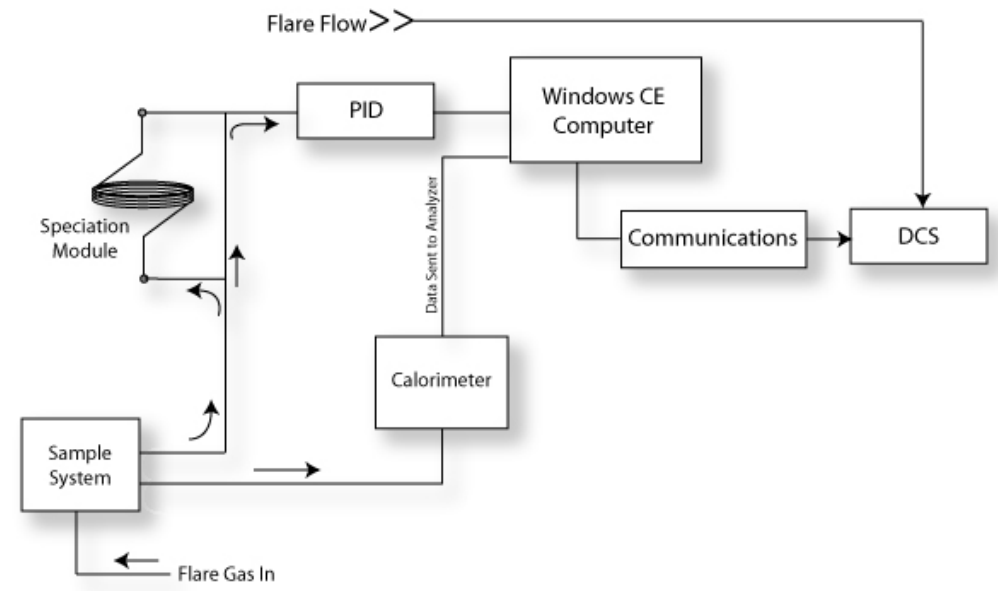
Wobbe Index: gross heating value. Determines how quickly a gas will move through an orifice to support a flame.

Cooling Tower System



HRVOC Analyzer

Flare System



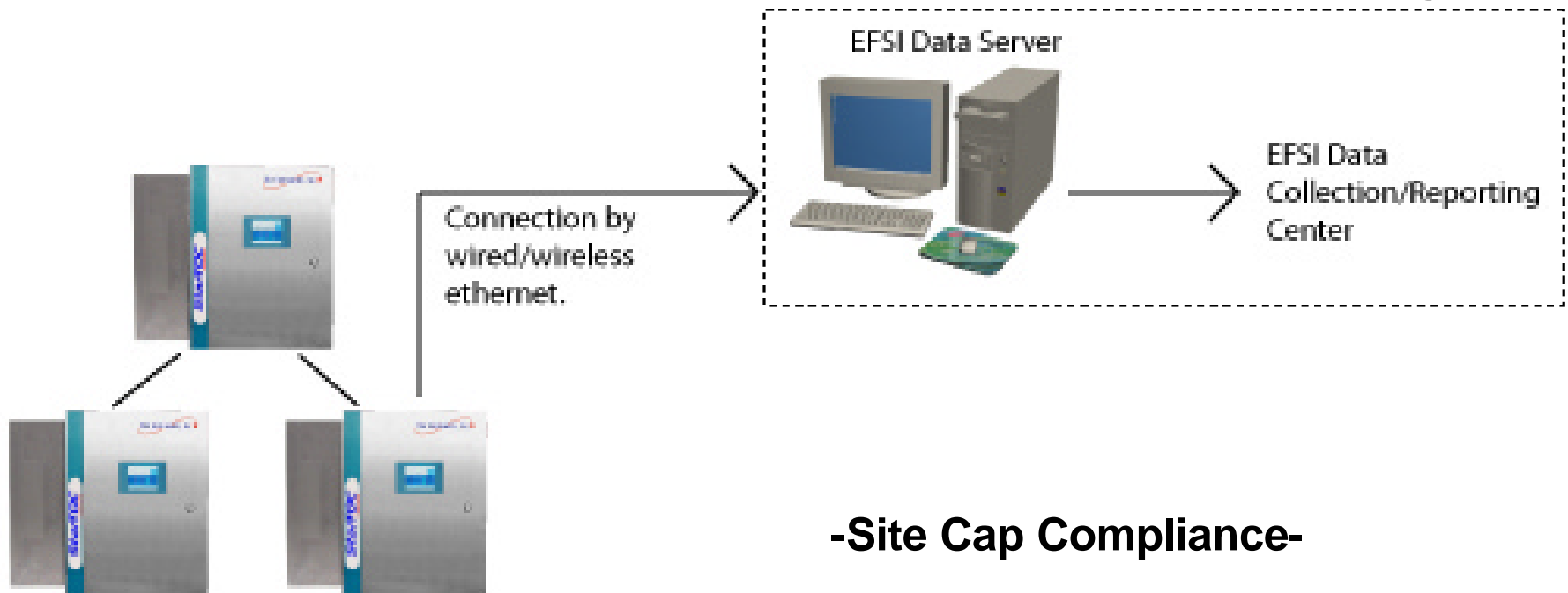
Sample System

Calorimeter

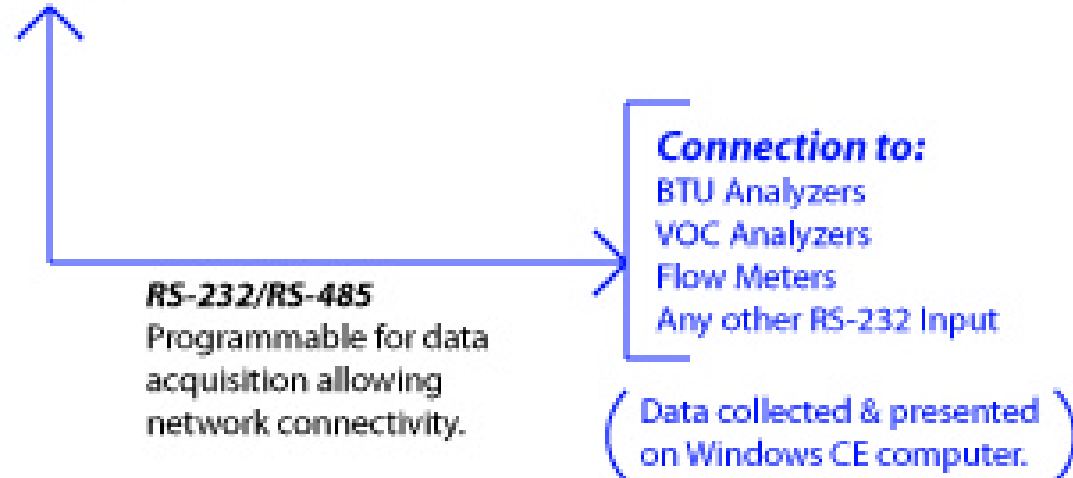
HRVOC Analyzer

Data Gathering and Reporting

Defensible Data Reporting



-Site Cap Compliance-



Conclusion

Cooling Towers

- HRVOC analyzer to monitor and report HRVOC.

Flares

- HRVOC analyzer to monitor and report HRVOC.

+

- BTU analyzer (calorimeter / Specific Gravity / Wobbe Index) to monitor and report flare BTU.

Site Cap Compliance

- Ethernet communications and data reporting.