ISA Houston Analysis Subsection

December 17, 2003

HRVOC Analyzer

Jack Small

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

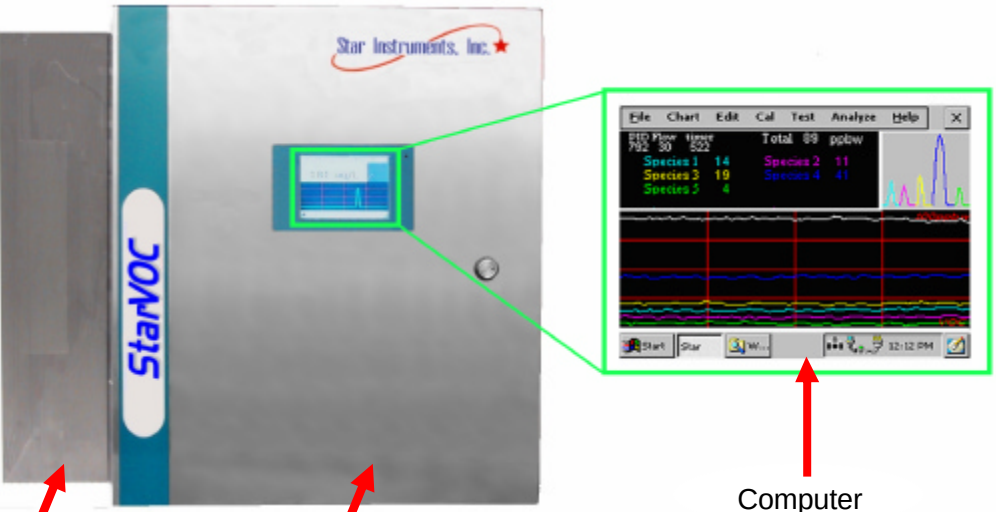
Record analyzer "up-time":

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

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

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

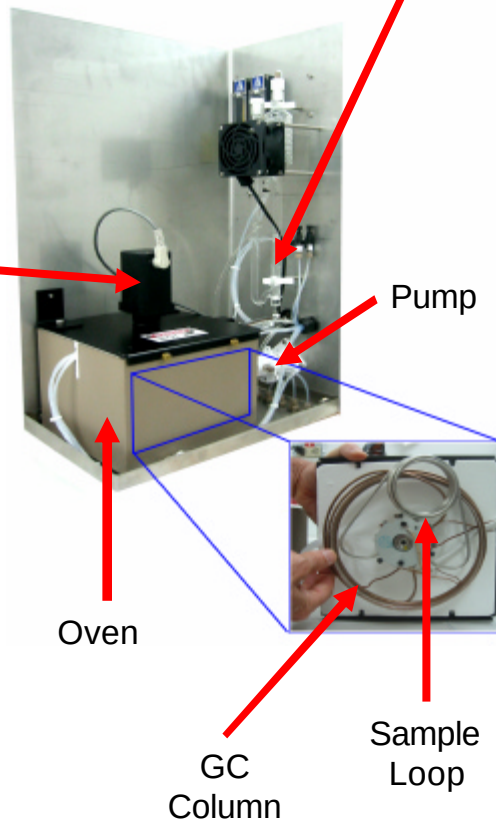
HRVOC Analyzer



peciation Module

Analysis Module

Computer



Sparger

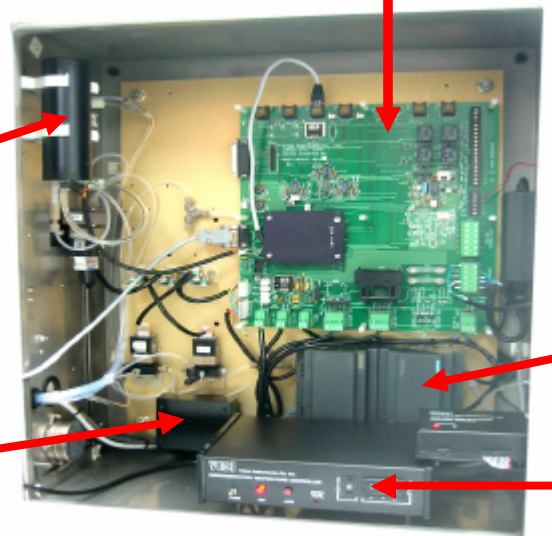
GC Valve

Pump

Oven

GC Column

Sample Loop



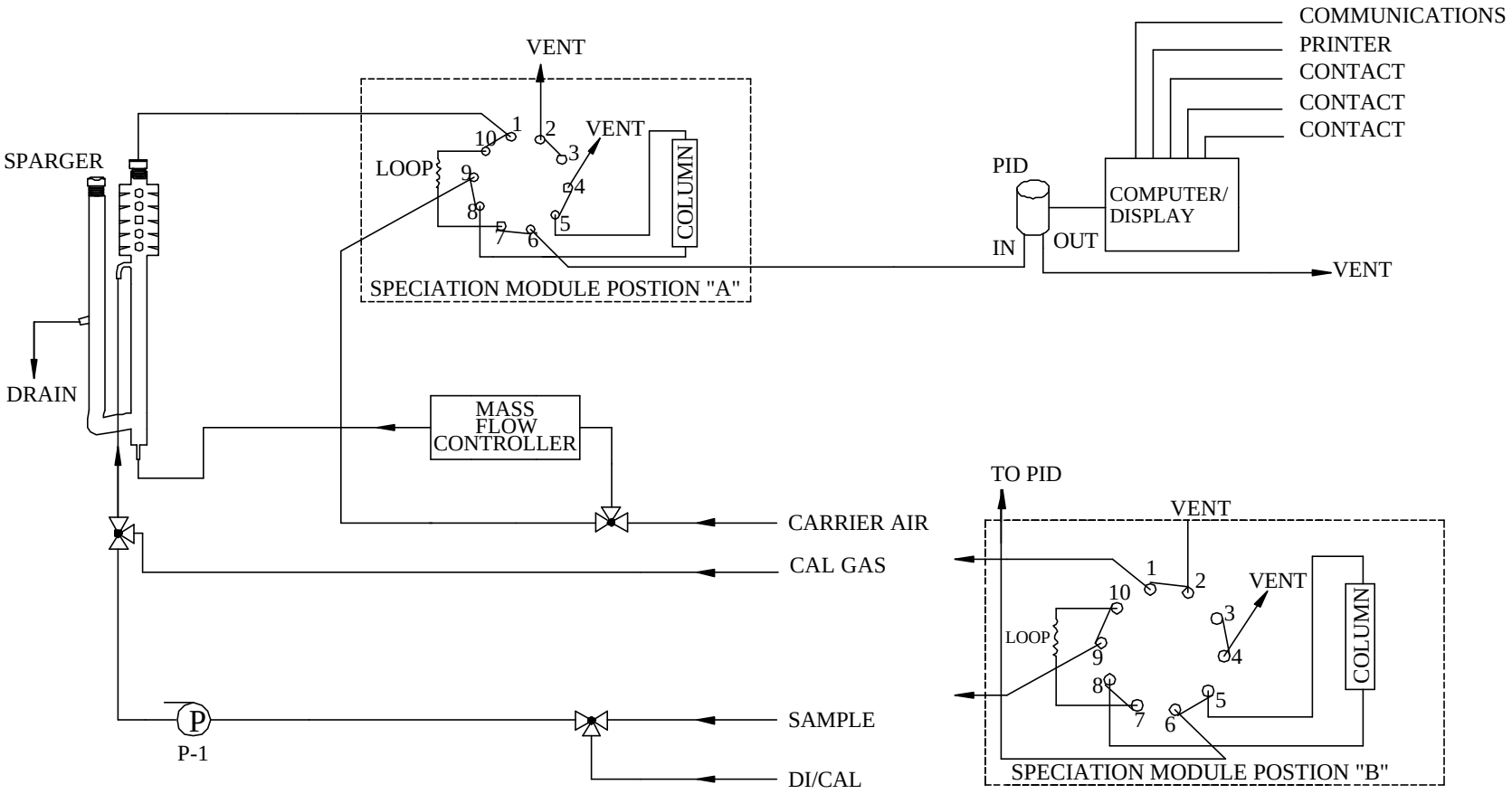
Master Interface Board

PID

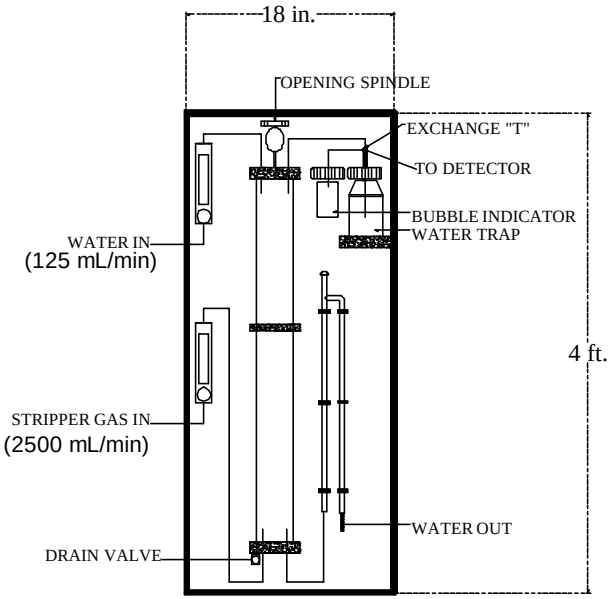
DC Power Supply

Mass Flow Controller

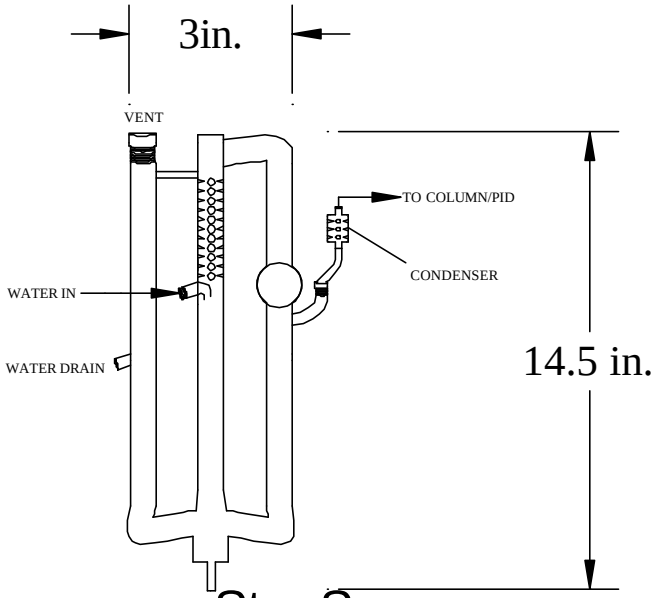
GC Oven Controller


COMMUNICATIONS
PRINTER
CONTACT
CONTACT
CONTACT
VENT
SPARGER
LOOP
COLUMN
PID
COMPUTER/
DISPLAY
IN
OUT
VENT
SPECIATION MODULE POSTION "A"
DRAIN
MASS
FLOW
CONTROLLER
CARRIER AIR
CAL GAS
SAMPLE
DI/CAL
P
P-1
TO PID
VENT
LOOP
COLUMN
SPECIATION MODULE POSTION "B"

Cooling Towers



El Paso Stripper



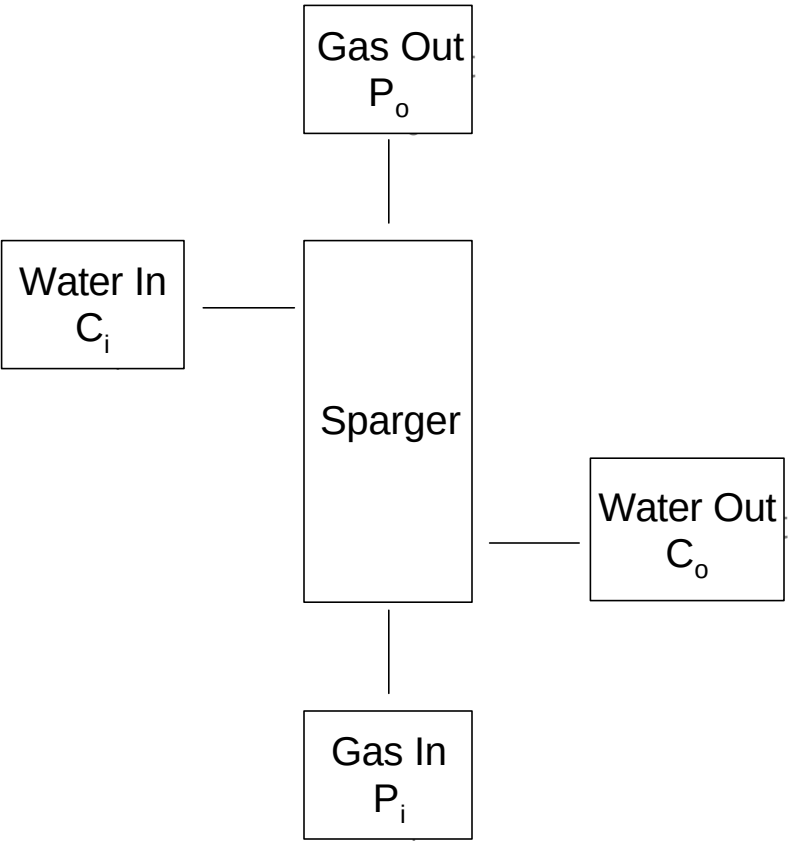
Star Sparger
(TCEQ Approved)

TCEQ Rule	**El Paso Stripper Requirement**	**Analyzer Sparger Implementation**
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

El 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 ºC 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 - ºK

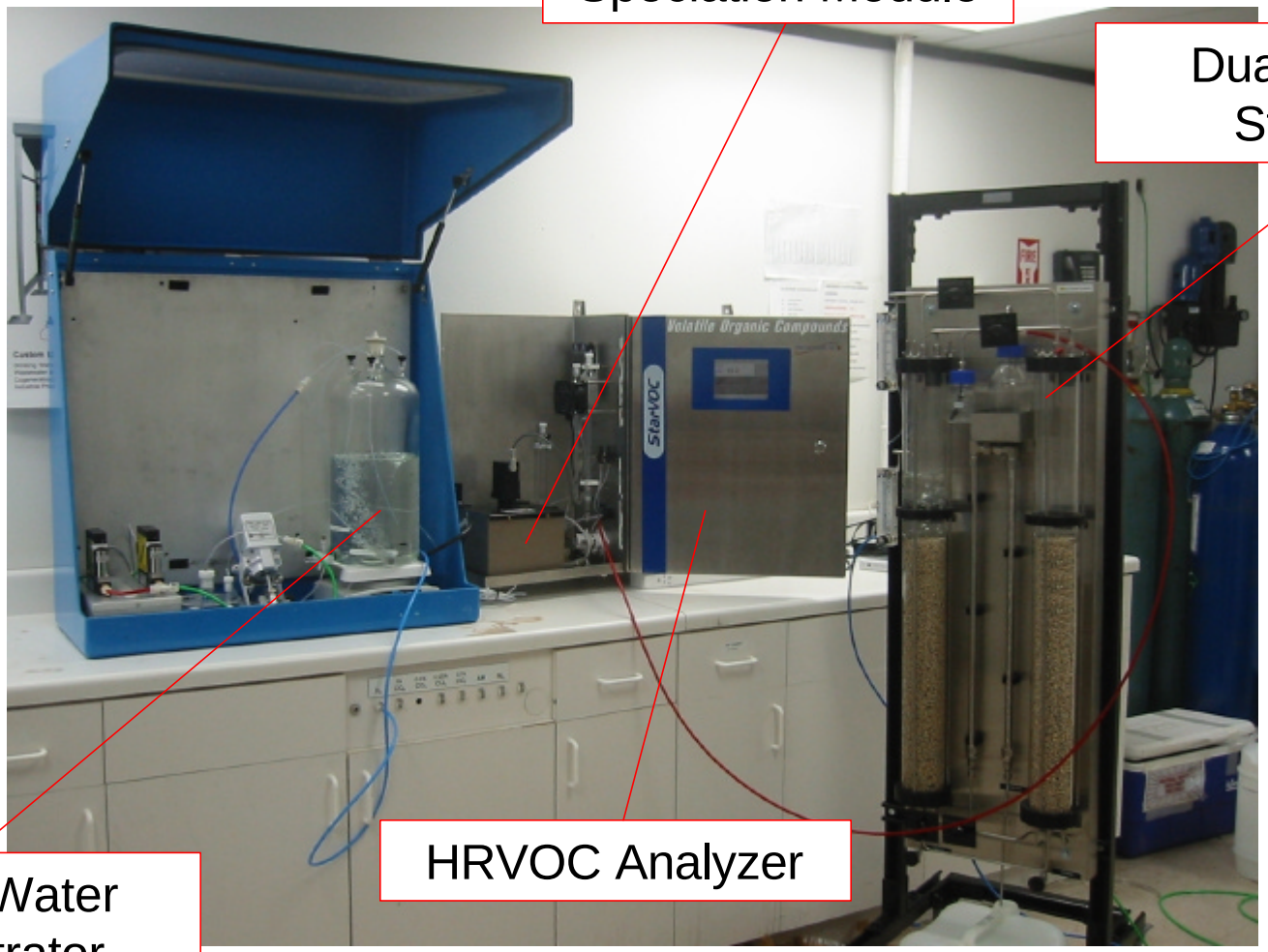
T = Temperature, ºK

S = Gas solubility, ppmv / ppbw

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

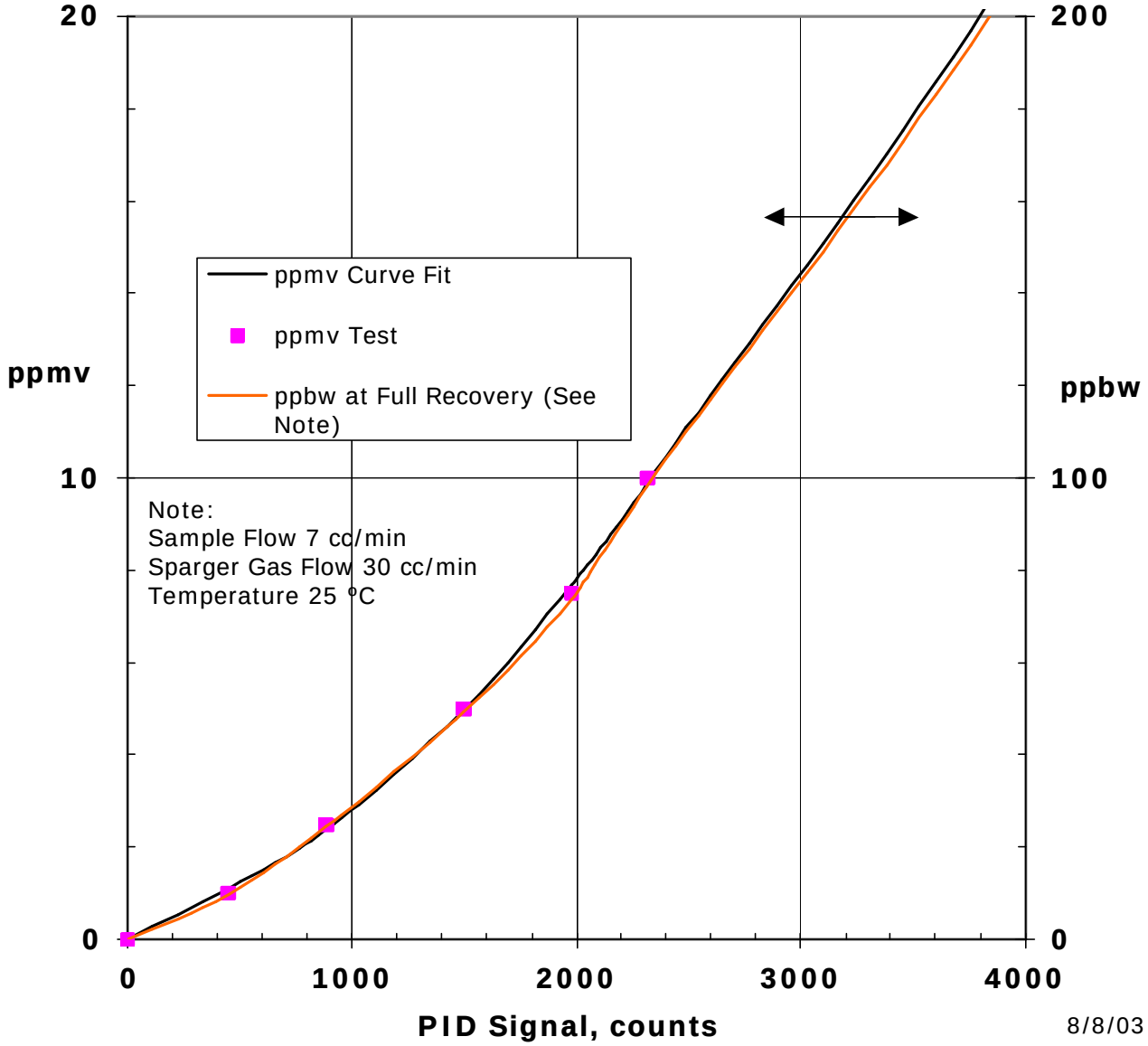
H = Henry's Law Constant for VOC gas, atm-mol/mol

Test Setup



- Sparger Recovery Tests
- Method 301
- MDL Tests

PID Response to Isobutene
Total VOC Mode



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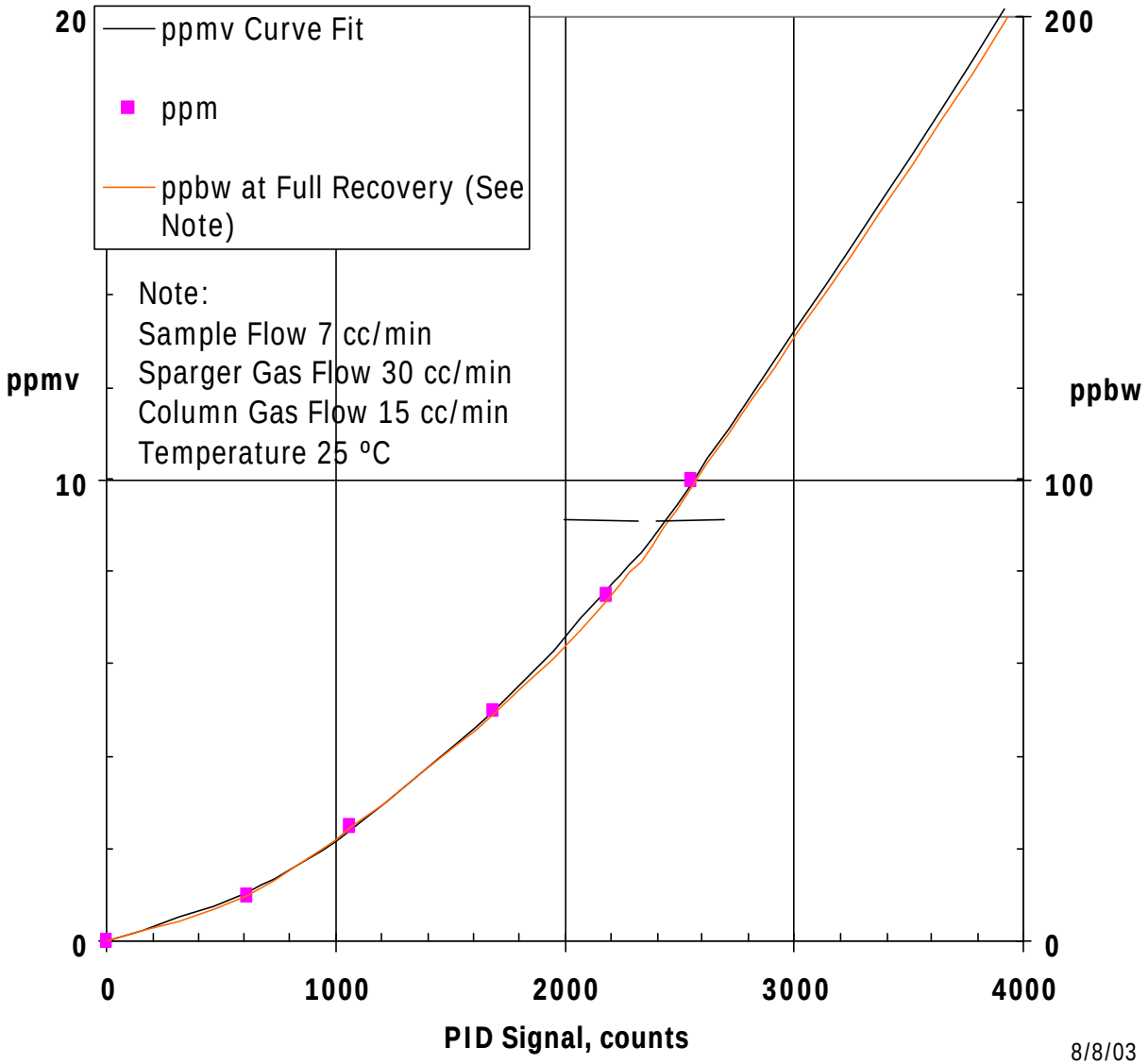
PID Response to Isobutene
Speciation Mode



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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

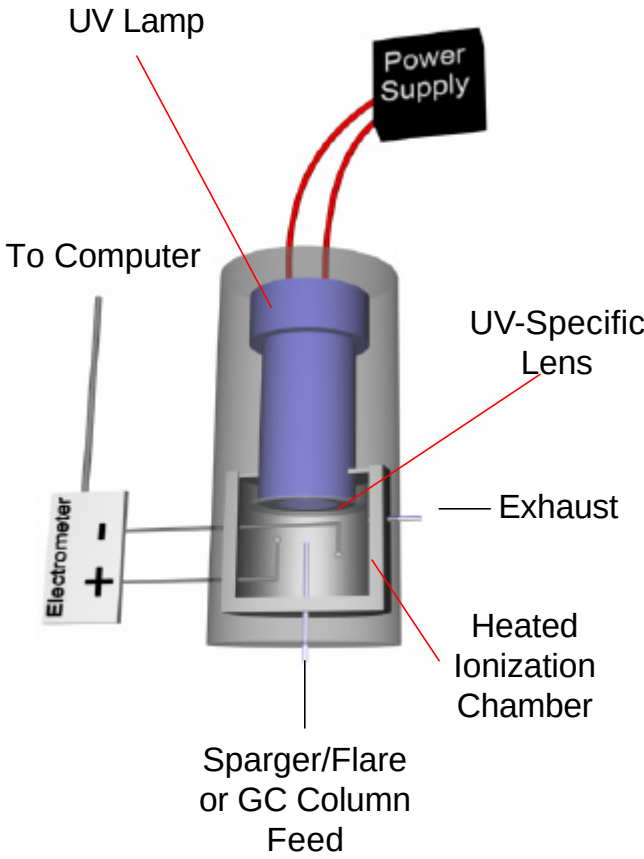
Choice of Detectors

FID & PID Basic Characteristics

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

(Detector Selected)

PID



$$R + h\nu \longrightarrow R^{+} + e^{-}$$

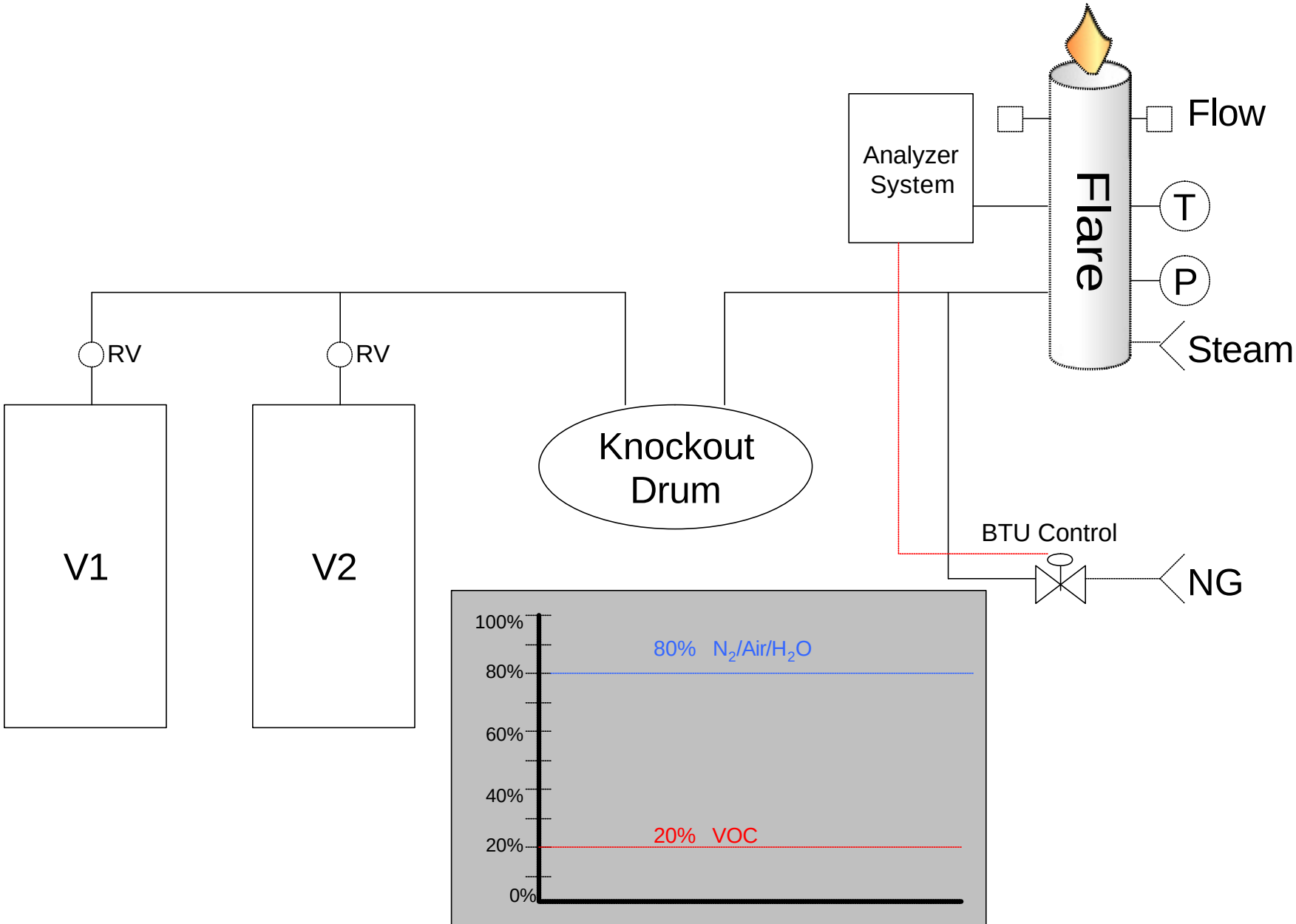
Flares

ypical Flare Gas Stream

STREAM DATA	No.	Typical Composition Include Units of Mol%, Wt%, Lv%, ppm, Etc.)		
Components		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

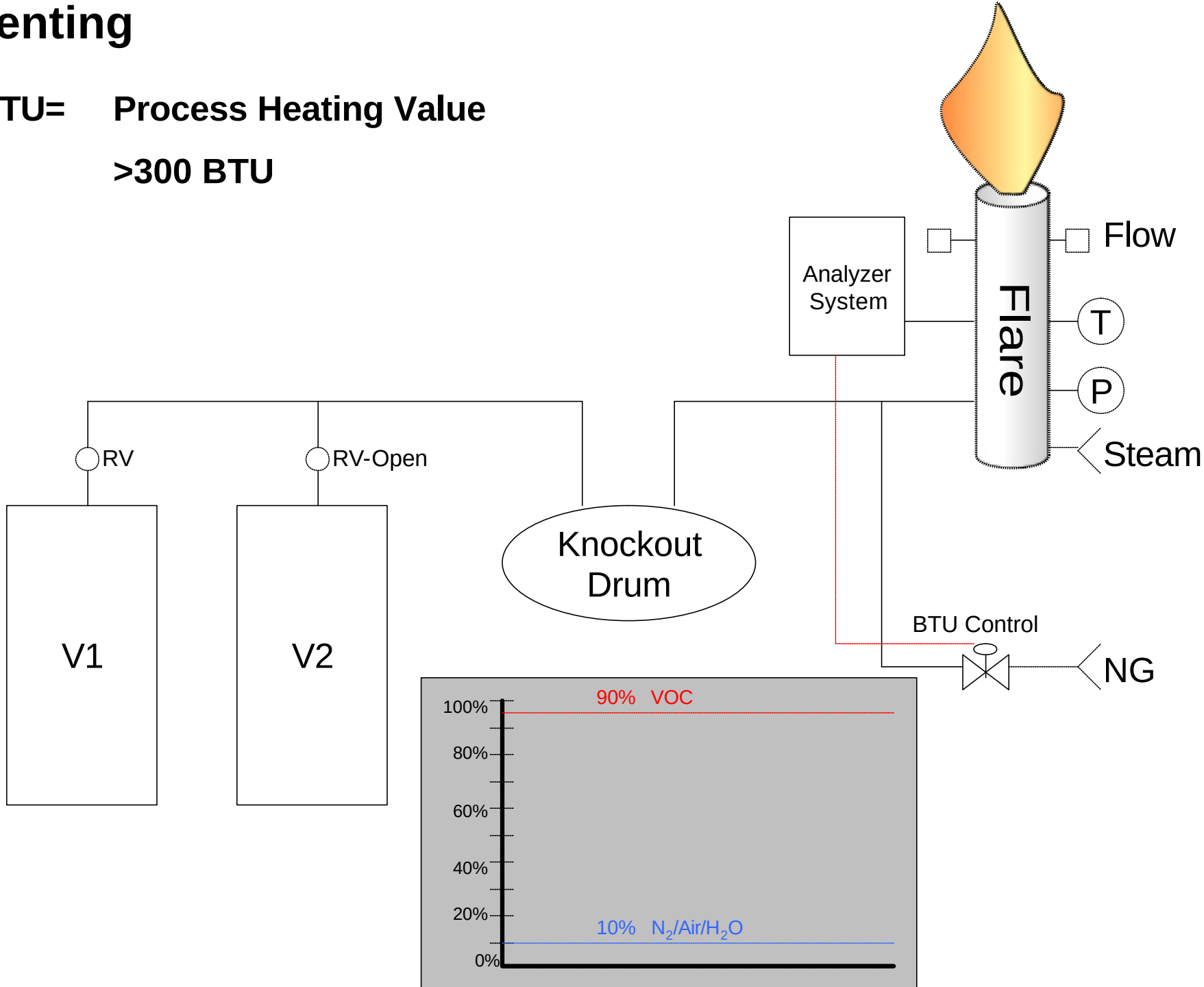
BTU= >300



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:

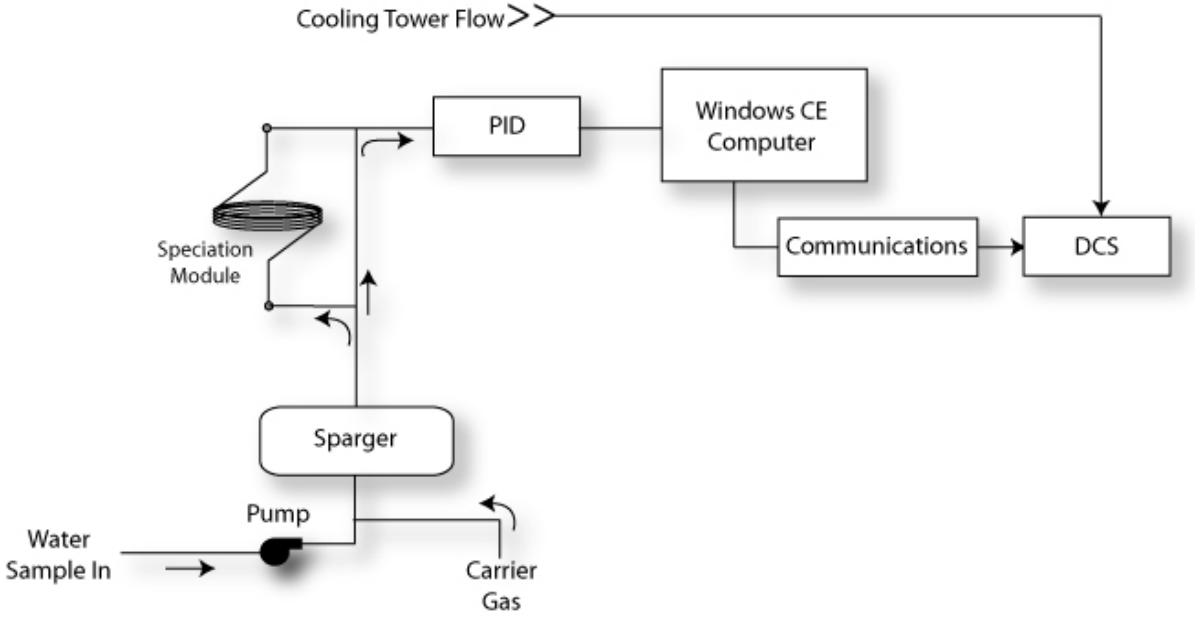
- Measures temperature rise (thermopile)
- Measures Wobbe Index*
- Measures specific gravity

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

(1% Accuracy)

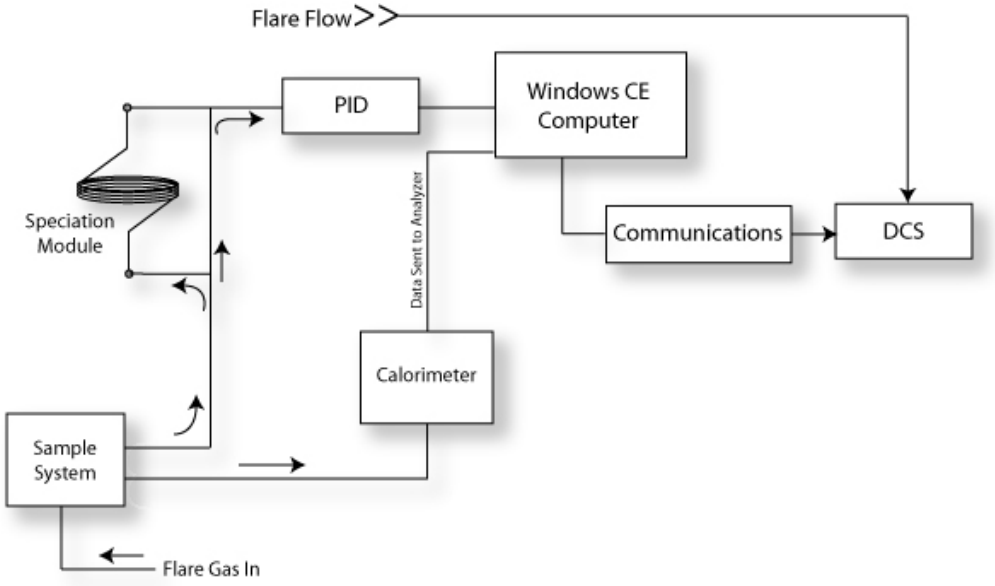
Wobbe Index: gross heating value. Determines how quickly a gas will move through an
rifice to support a flame

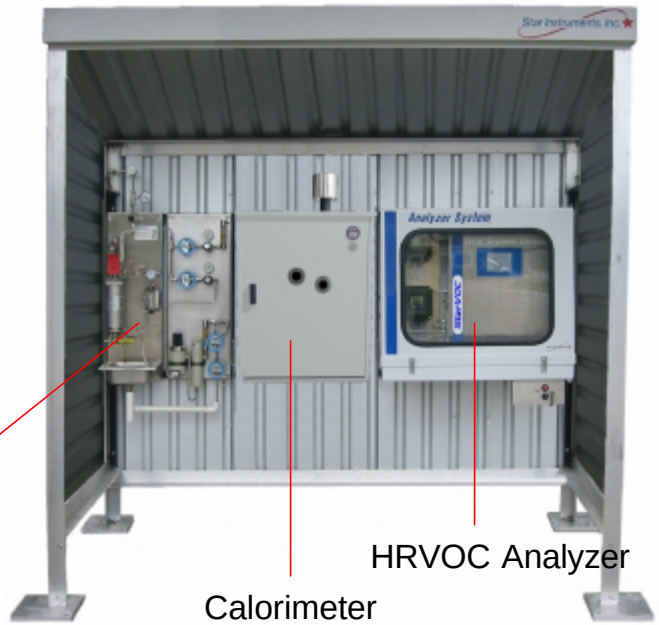
Cooling Tower System



HRVOC Analyzer

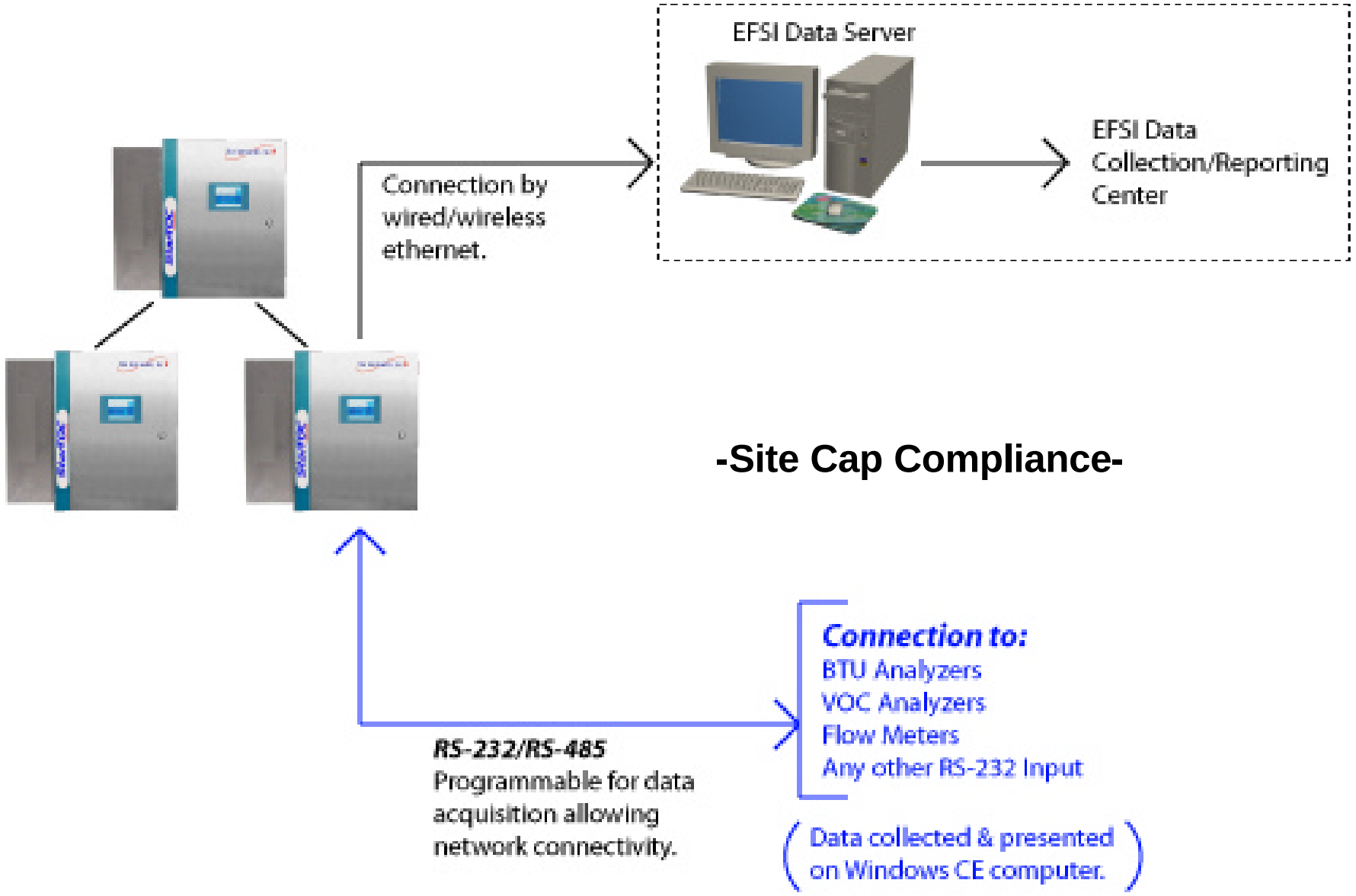
Flare System





Data Gathering and Reporting

Defensible Data Reporting



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.

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