TCEQ – Chapter 115 Rules

Revised 10/22/03

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

2. If use a Total HRVOC Analyzer:
   - No on-line speciation is required
   - Total HRVOC reporting satisfies rules
   - Speciation module available (if required monthly)

3. If use a GC Analyzer:
   - Report total HRVOC.
   - When 50 ppbw total VOC is exceeded for over one hour; report speciated HRVOC.

4. 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 to 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

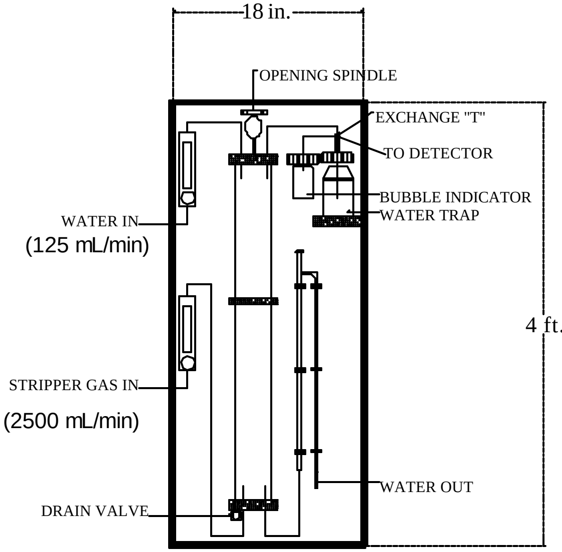
5. Record analyzer "up-time":
   - If a malfunction exceeds 8 consecutive hours, must sample & lab speciate within 24 hours of failure & daily thereafter until analyzer is repaired.

6. 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 12/31/05.

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

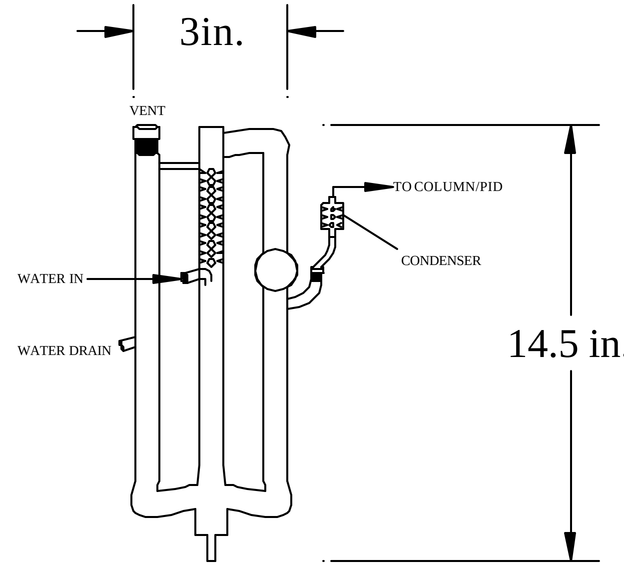
8. 12/31/05 – Monitoring systems operational, including validated, defensible reporting.

Cooling Towers



El Paso Stripper

(TCEQ Approved Standard)



Star Sparger

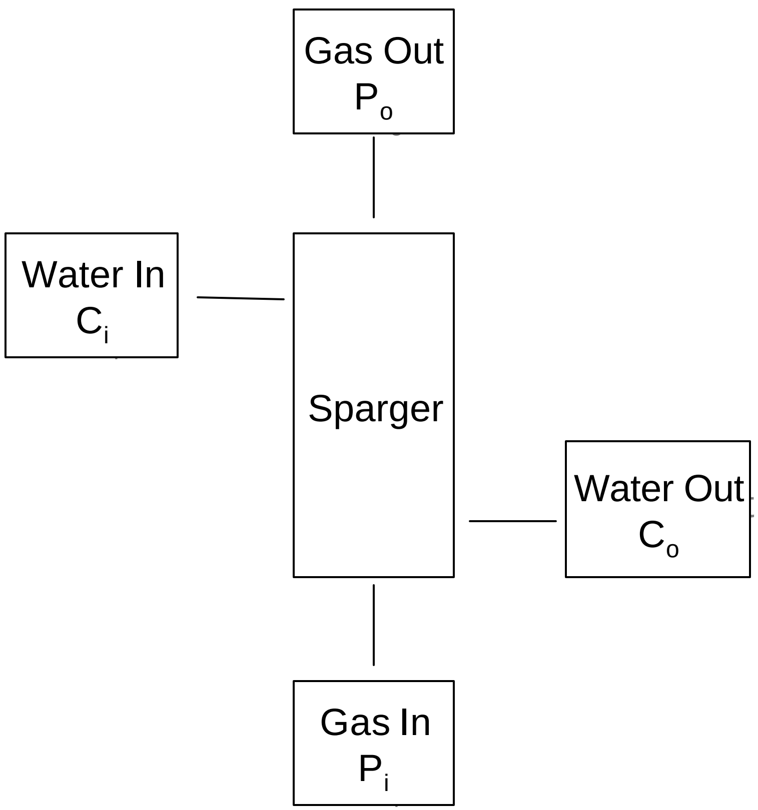
(TCEQ Approved)

<u>TCEQ Rule</u>	**<u>El 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

<u>El Paso Stripper Cleaning Procedure</u>

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

(Ci - Co) * q = (Po - Pi) * D * Q

Solubility at Equilibrium

$P_o / C_i = S$

The recoverable VOC gas concentration is determined by solving the above equations:

$P_o = C_i / D * q / Q$

Legend

Pi = VOC partial pressure in sparger input gas, ppmv

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

Ci = VOC concentration in sparger input water sample, ppbw

Co = VOC concentration in sparger output water, ppbw

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

M = Molecular Weight of gas

P_t = 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

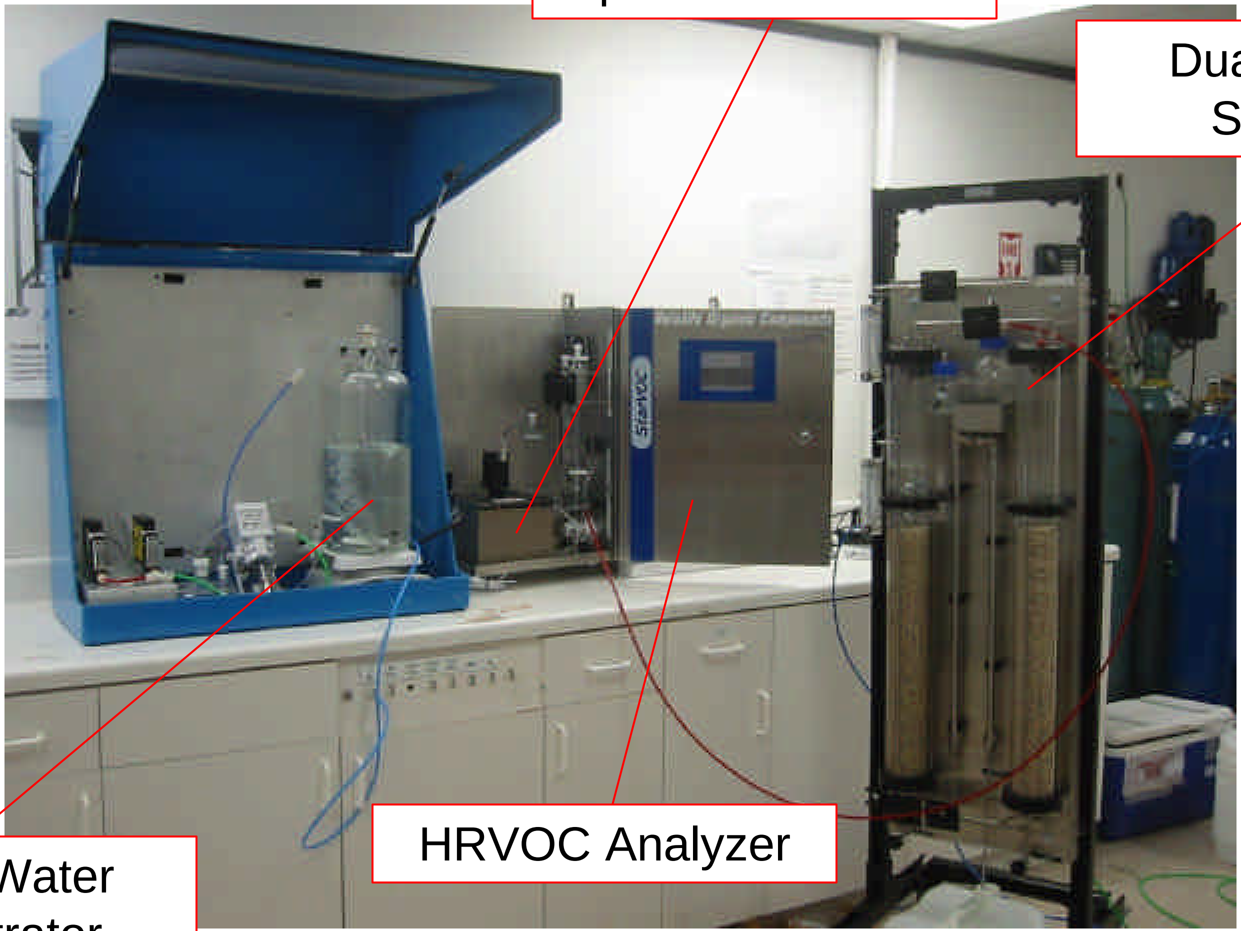
T = Temperature, ºK

S = Gas solubility, ppmv / ppbw

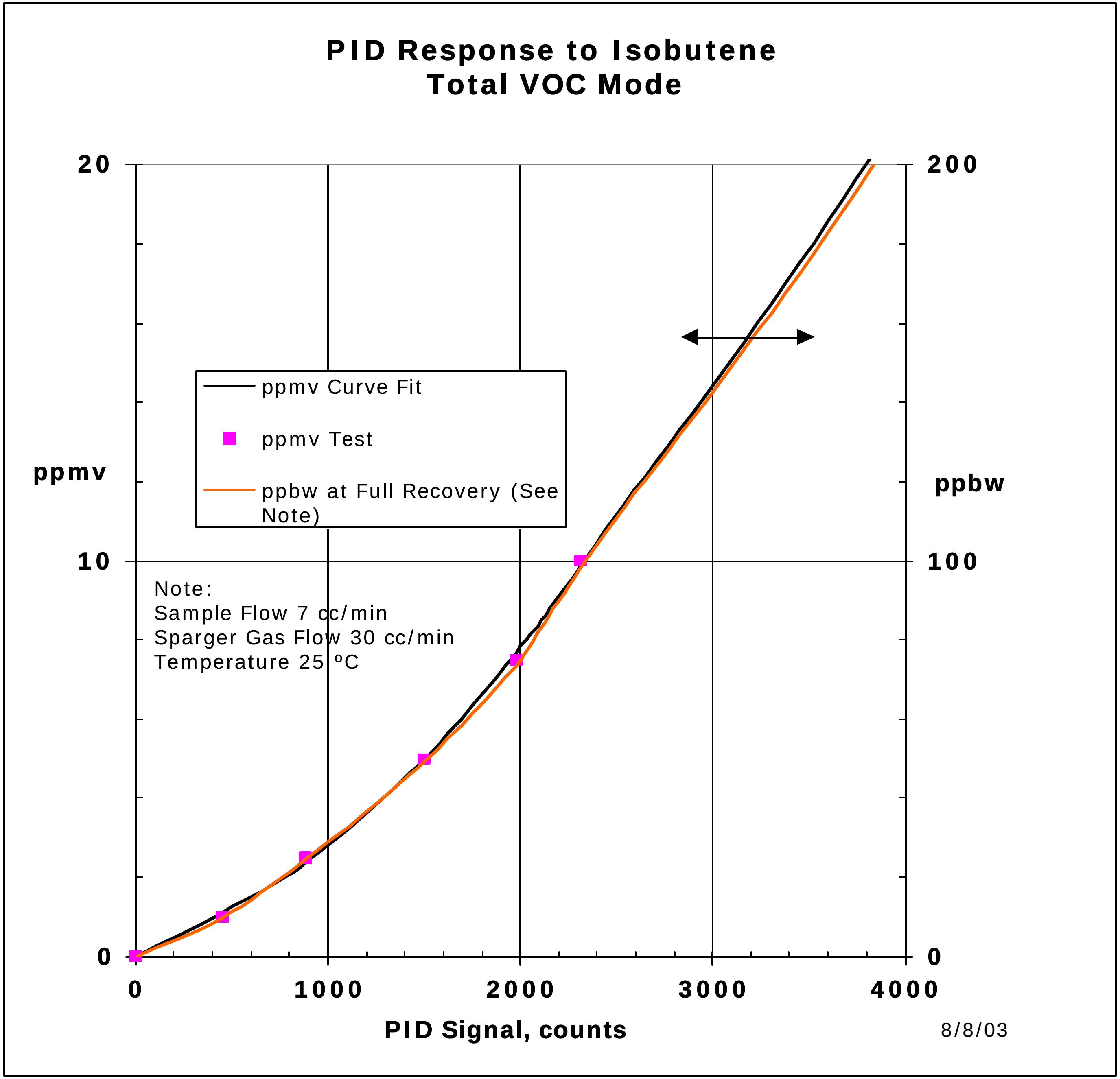
= (H-1) * 18.01 /M /1,000

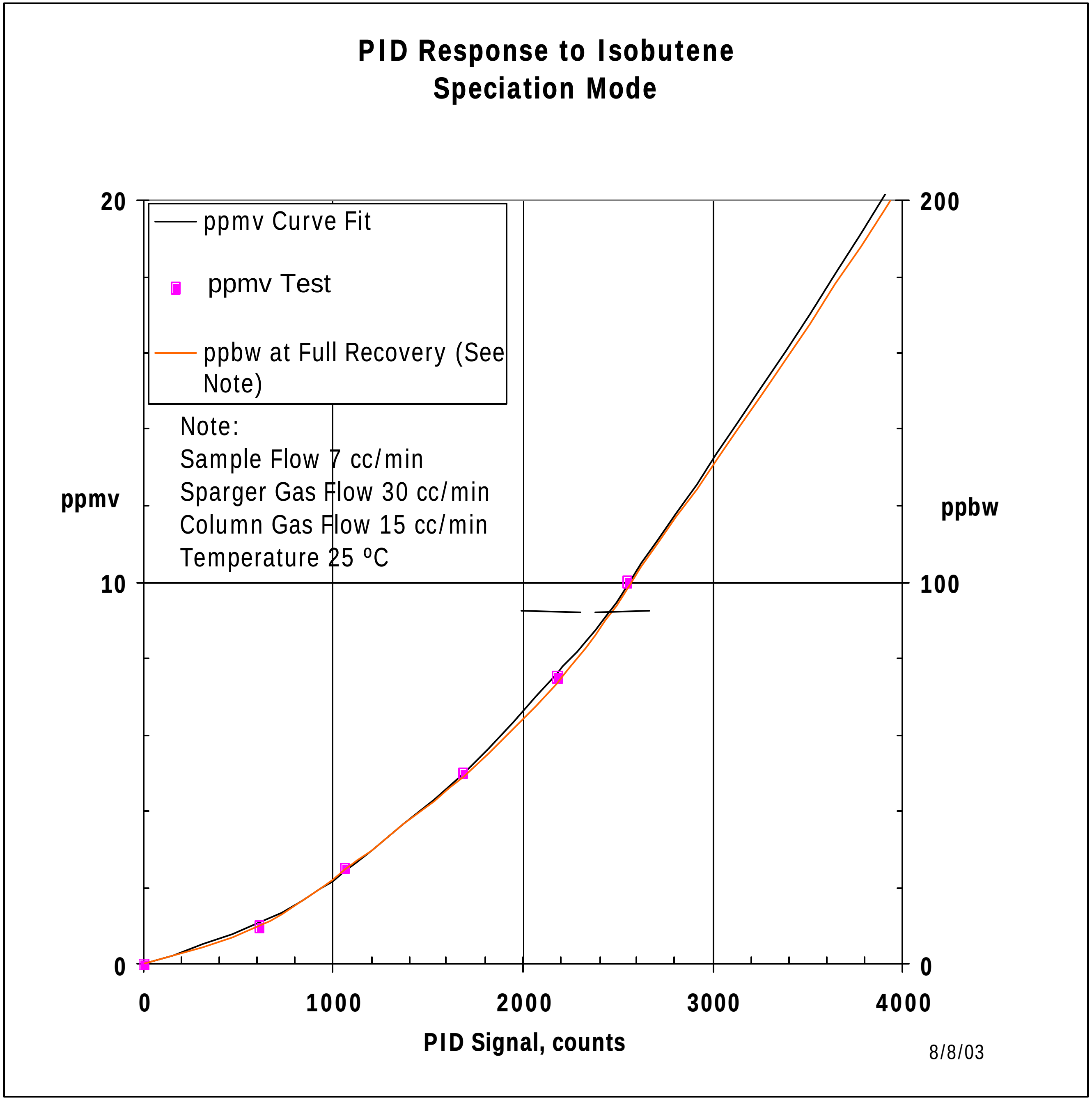
H = Henry's Law Constant for VOC gas, atm-mol/mol

Test Setup



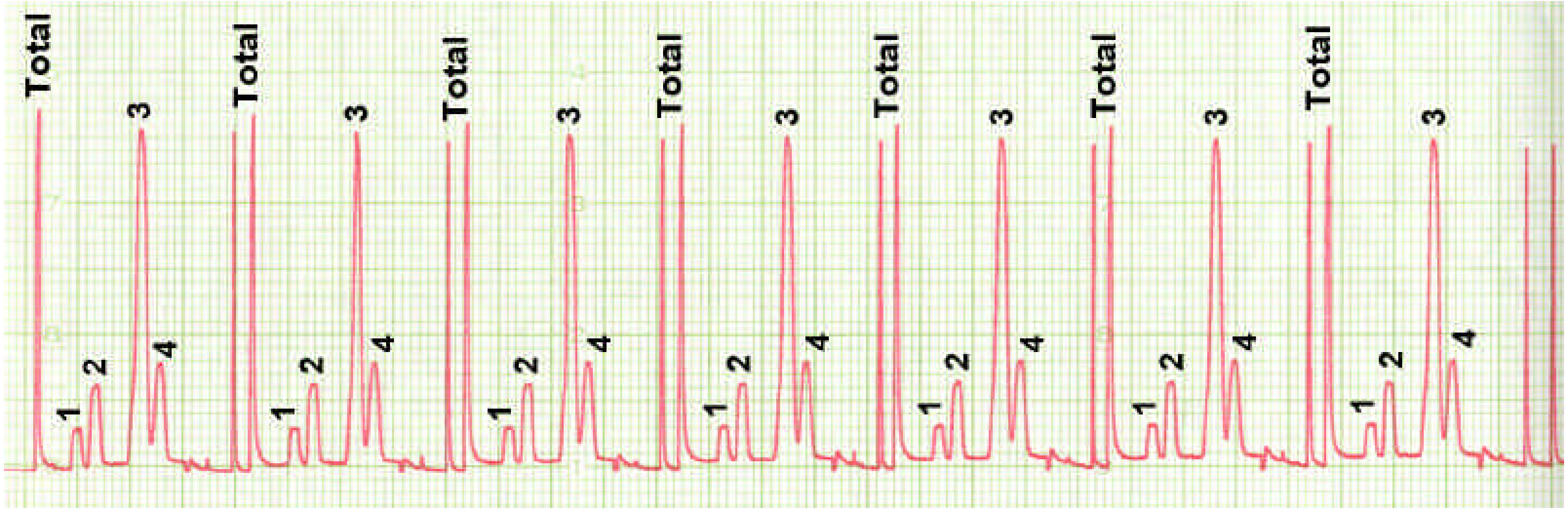
- Sparger Recovery Tests
- Method 301
- MDL Tests


PID Response to Isobutene
Total VOC Mode
ppmv
ppbw
20
10
0
200
100
0
0
1000
2000
3000
4000
PID Signal, counts
ppmv Curve Fit
ppmv Test
ppbw at Full Recovery (See Note)
Note:
Sample Flow 7 cc/min
Sparger Gas Flow 30 cc/min
Temperature 25 ºC
8/8/03


PID Response to Isobutene
Speciation Mode
ppmv Curve Fit
ppmv Test
ppbw at Full Recovery (See Note)
Note:
Sample Flow 7 cc/min
Sparger Gas Flow 30 cc/min
Column Gas Flow 15 cc/min
Temperature 25 ºC
ppmv
ppbw
20
10
0
200
100
0
0
1000
2000
3000
4000
PID Signal, counts
8/8/03

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

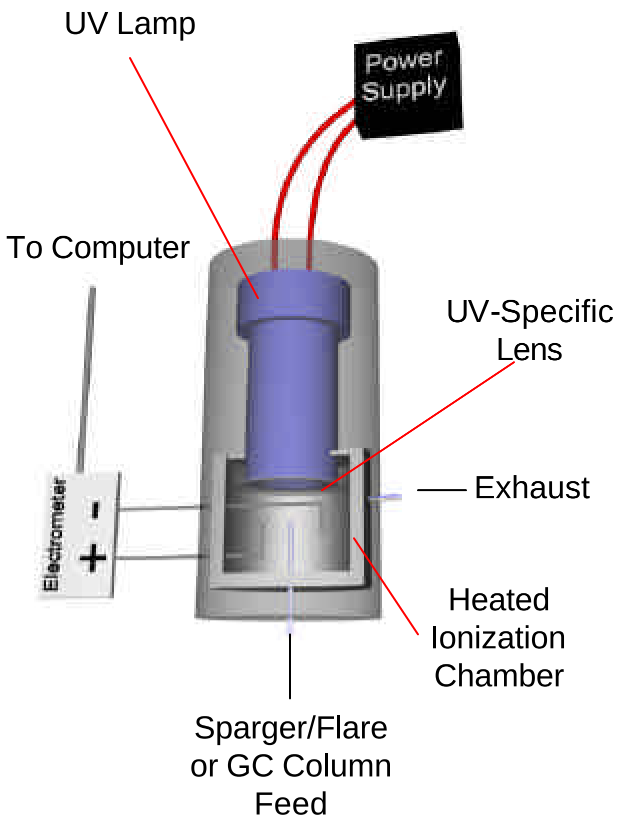
Choice of Detectors

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)

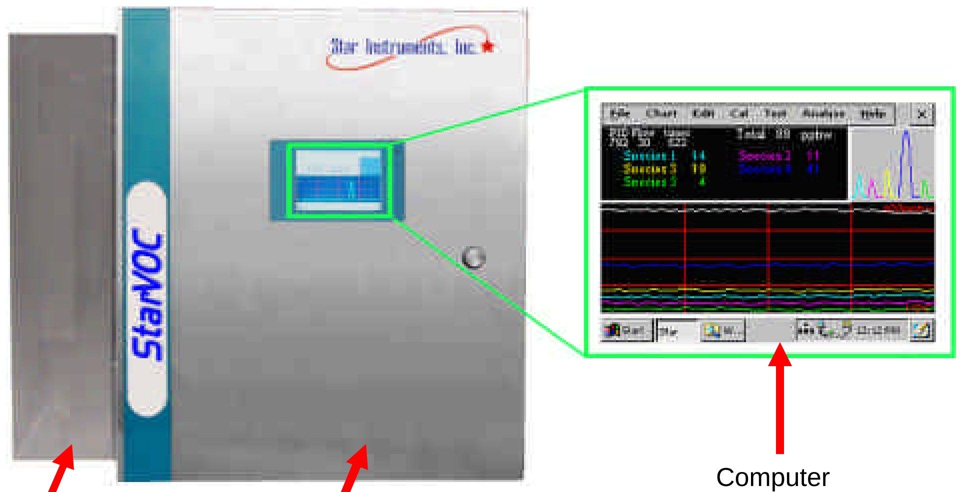
(Detector Selected)

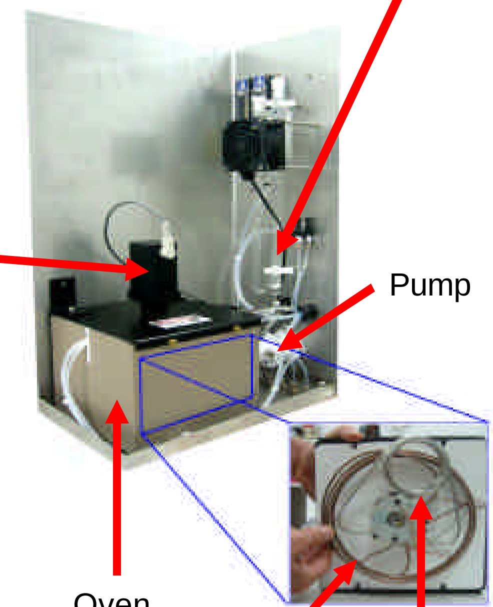
PID

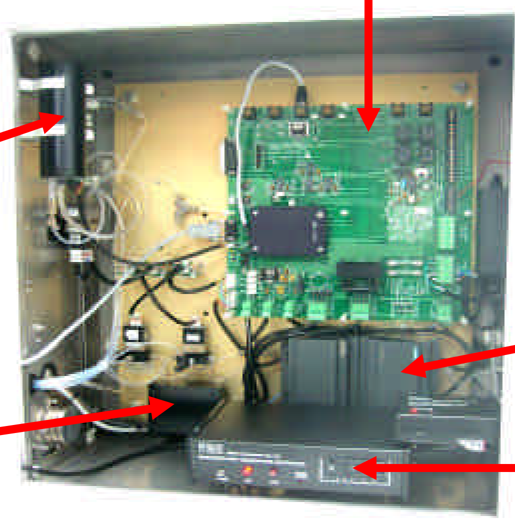


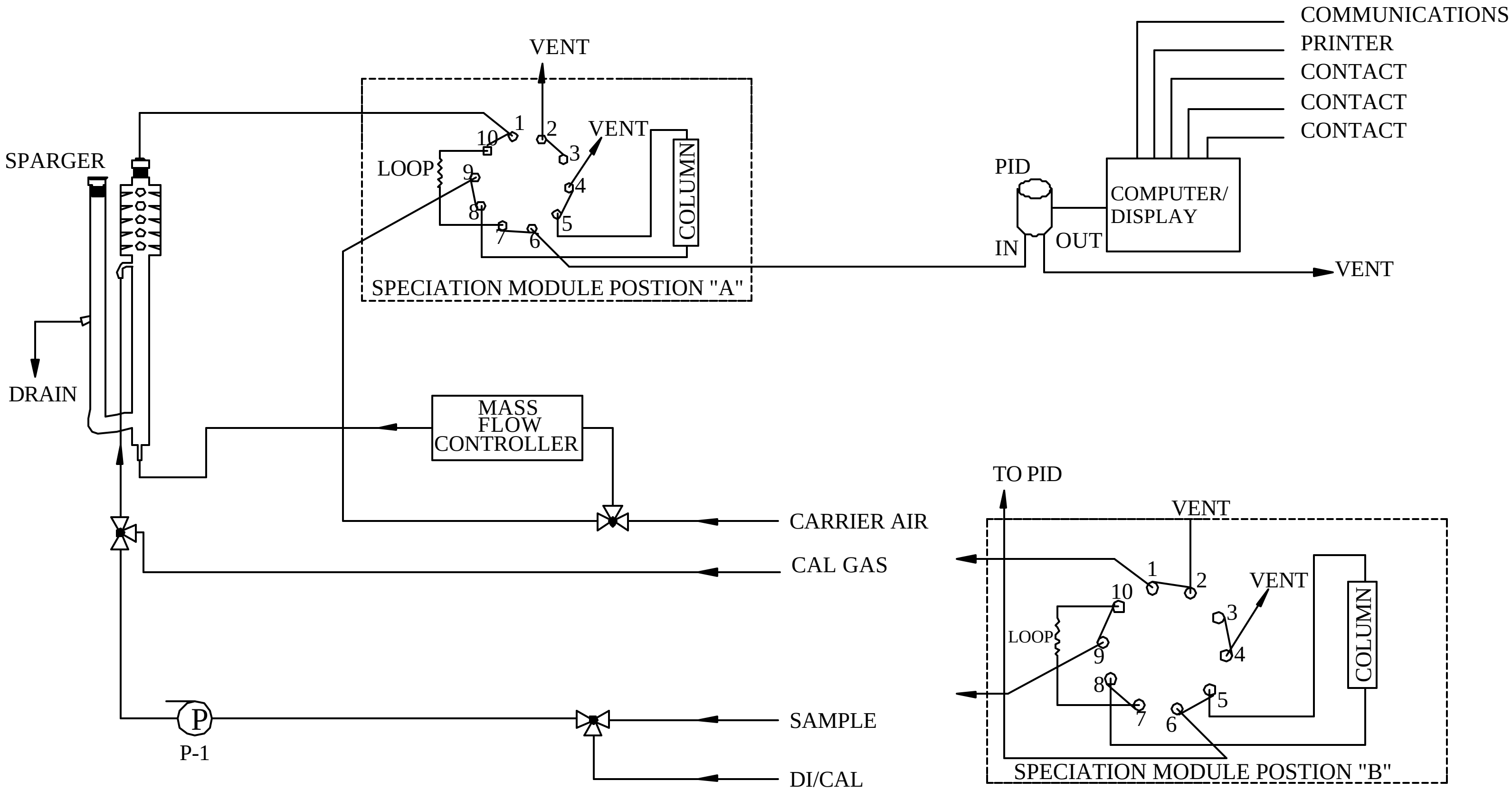
$$R + hv \longrightarrow R^{+} + e^{-}$$

HRVOC Analyzer



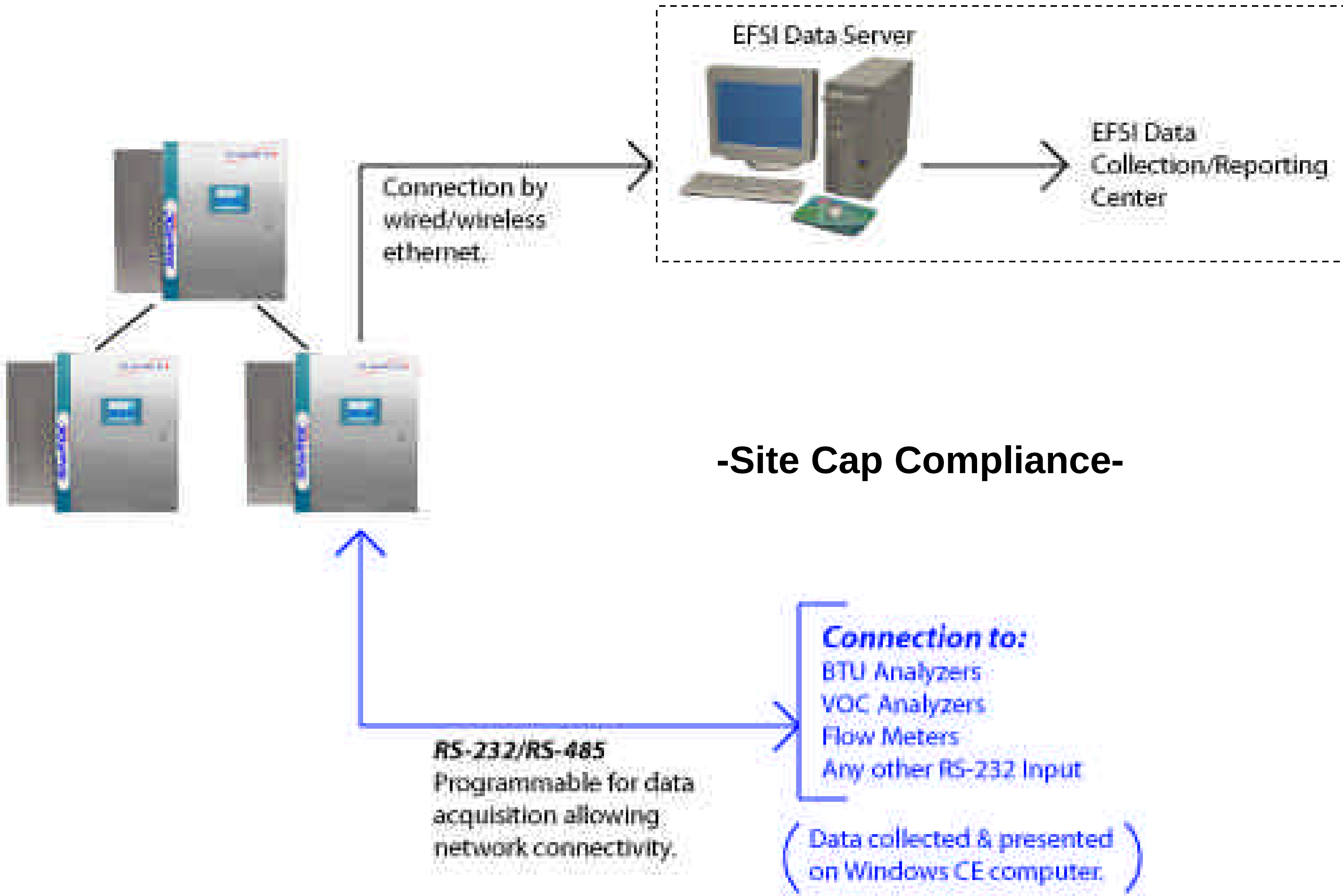





COMMUNICATIONS
PRINTER
CONTACT
CONTACT
CONTACT
VENT
VENT
SPARGER
LOOP
COLUMN
PID
COMPUTER/ DISPLAY
IN
OUT
VENT
SPECIATION MODULE POSTION "A"
DRAIN
MASS FLOW CONTROLLER
TO PID
VENT
CARRIER AIR
CAL GAS
VENT
LOOP
COLUMN
SAMPLE
P
P-1
DI/CAL
SPECIATION MODULE POSTION "B"

Data Gathering and Reporting

Defensible Data Reporting



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