DETERMINING THE CORRECT CONCENTRATIONS OF VOC IN COOLING TOWER WATER

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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

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

4. System MDL must be no greater than 10 ppbw

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

(Above subject to 2004 TCEQ midcourse correction)

Water Monitoring Considerations

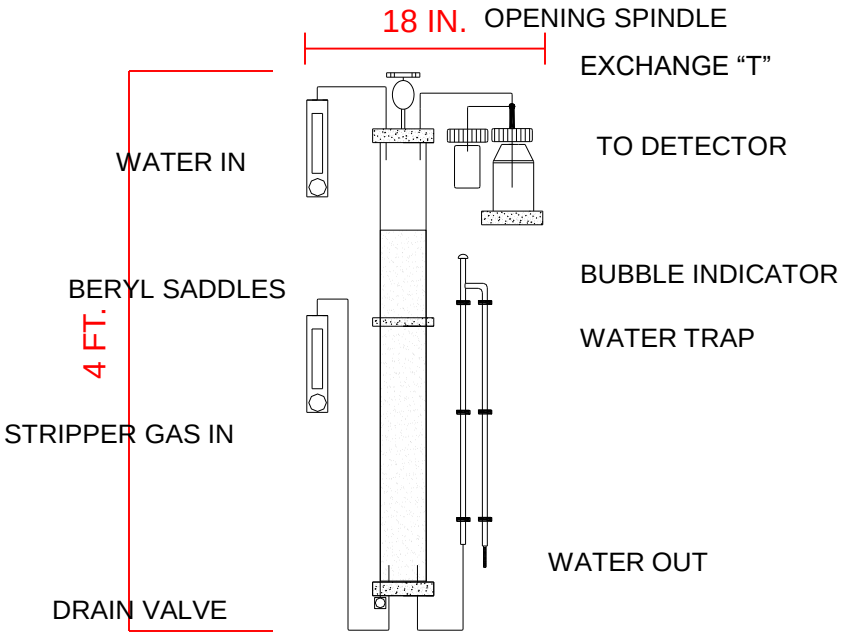


Figure 1

El Paso Stripper (Stand-Alone Unit)

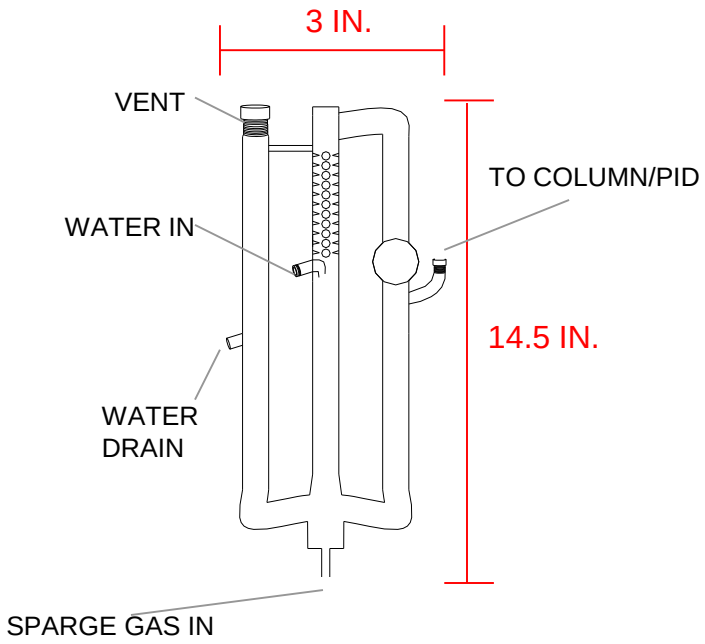


Figure 2

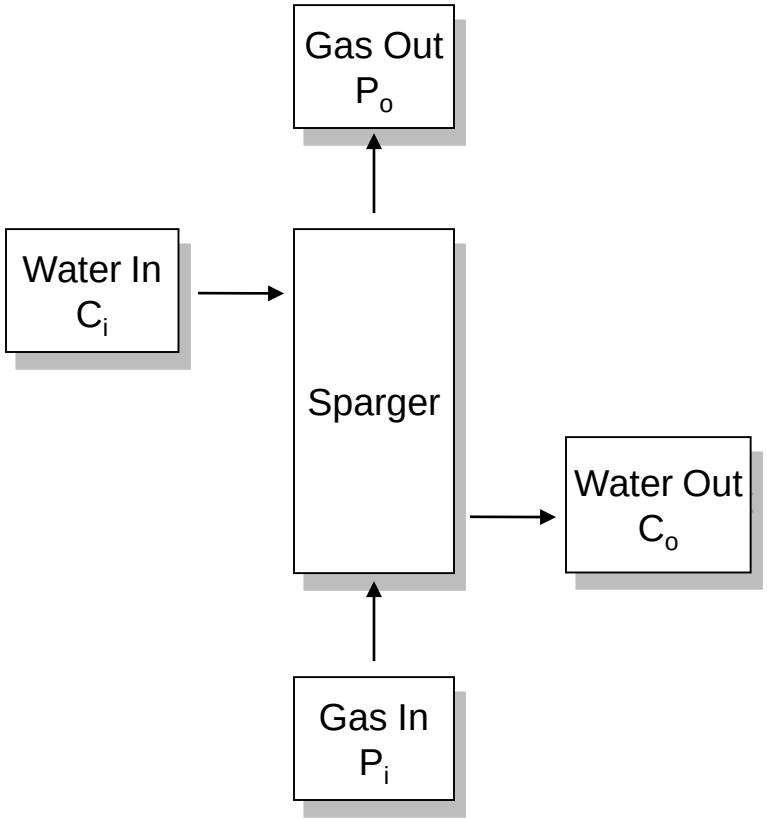
Star Sparger (Integral to the Analyzer)

TCEQ Rule	**El Paso Stripper Requirement**
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.
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.
MDL of < 10ppbw	Rules silent on procedure. Presumably USEPA/Std. Methods/accepted best practices will be required.
Calibration	Rules silent on calibration. Presumably USEPA/Std. Methods/accepted best practices will be required.

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

$P_o / C_i = S$

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

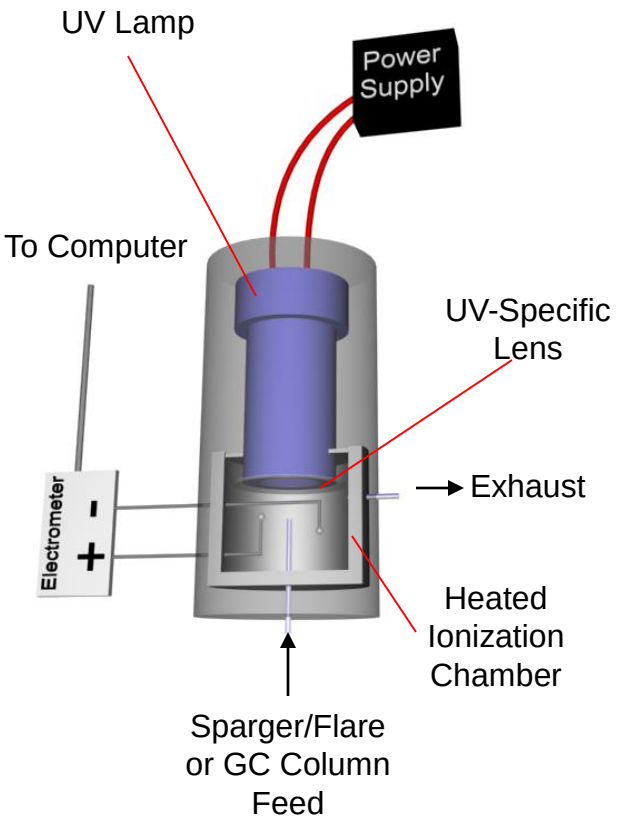
Choice of Detectors

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



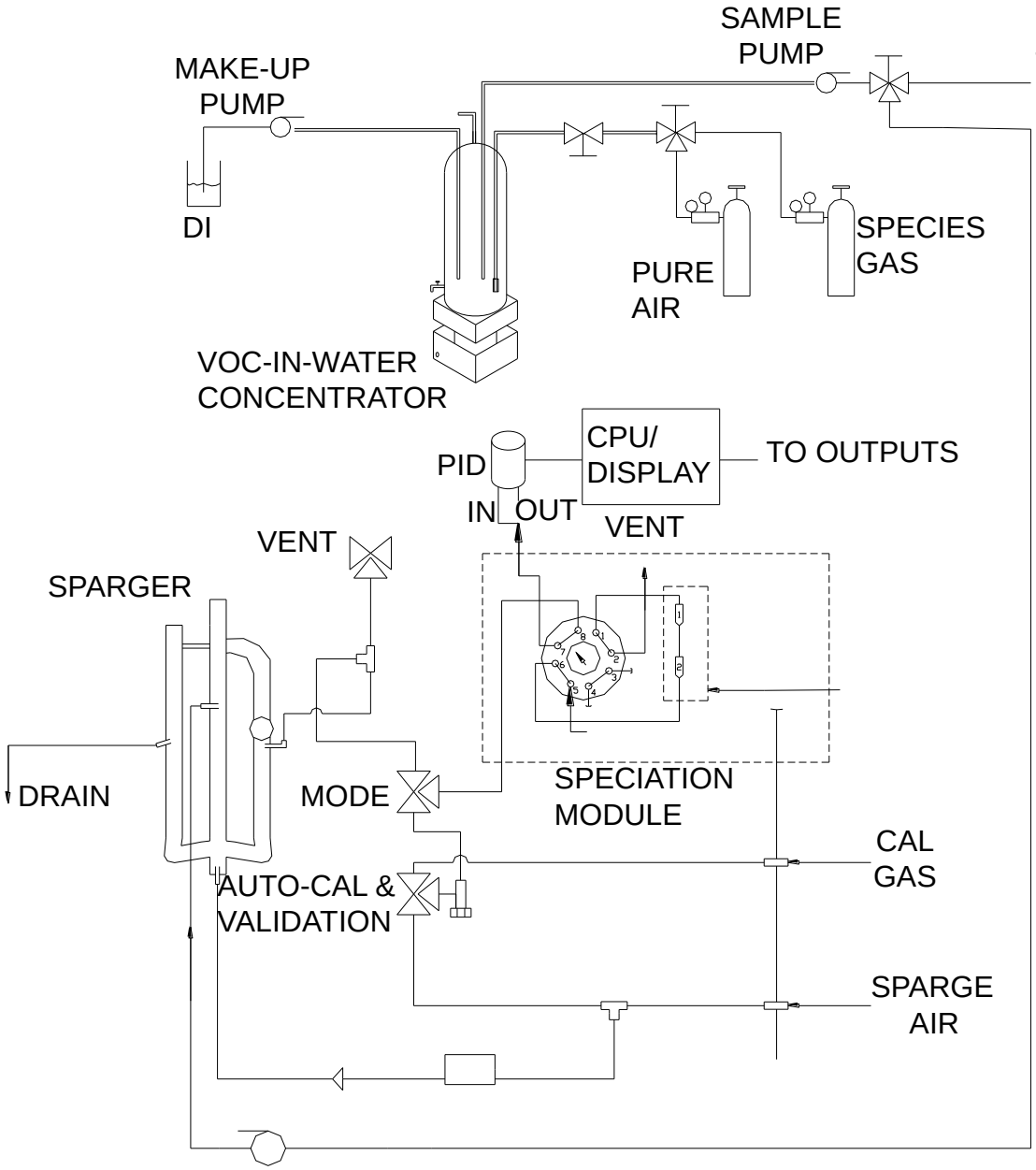
$$R + h\nu \longrightarrow R^{+} + e^{-}$$

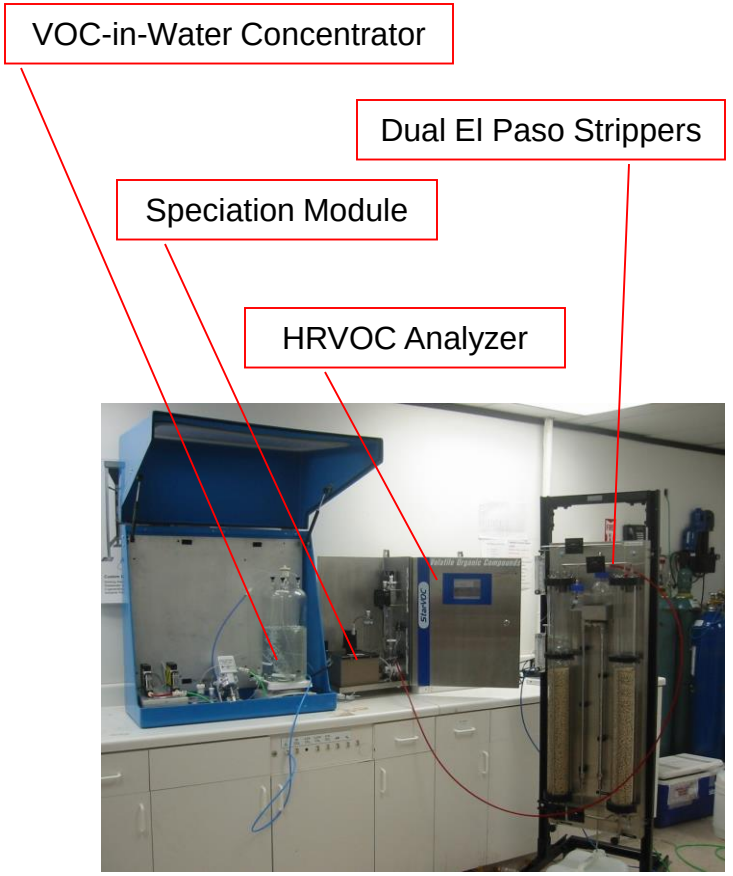
Sparger Recovery Tests

Method 301

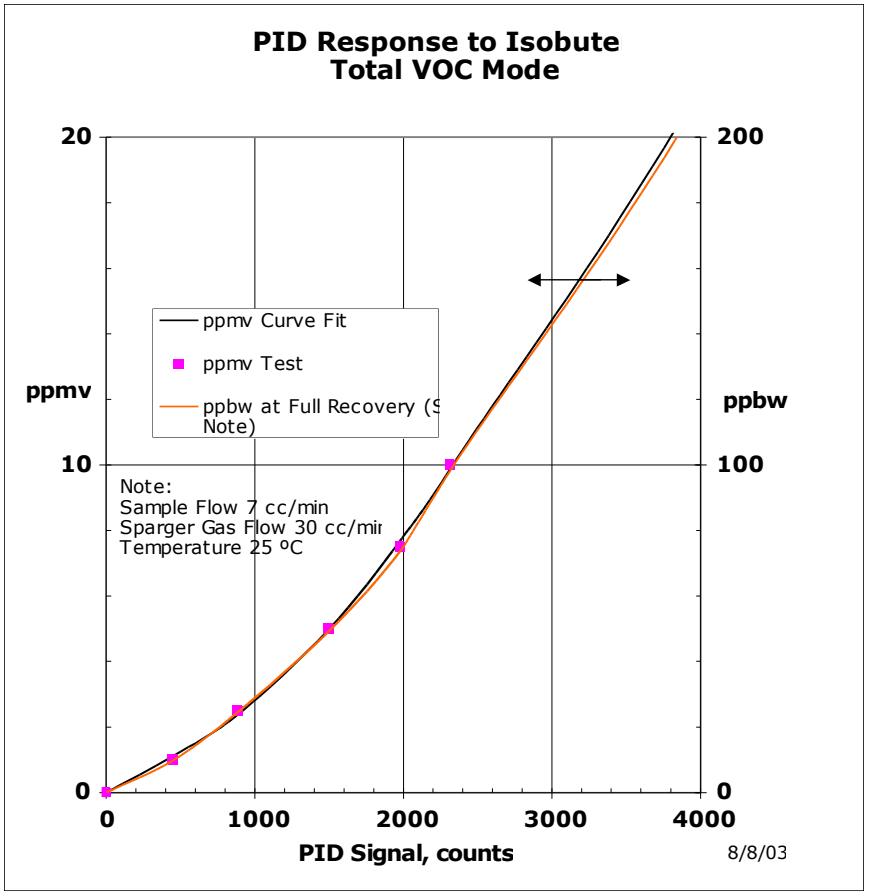
System MDL Tests

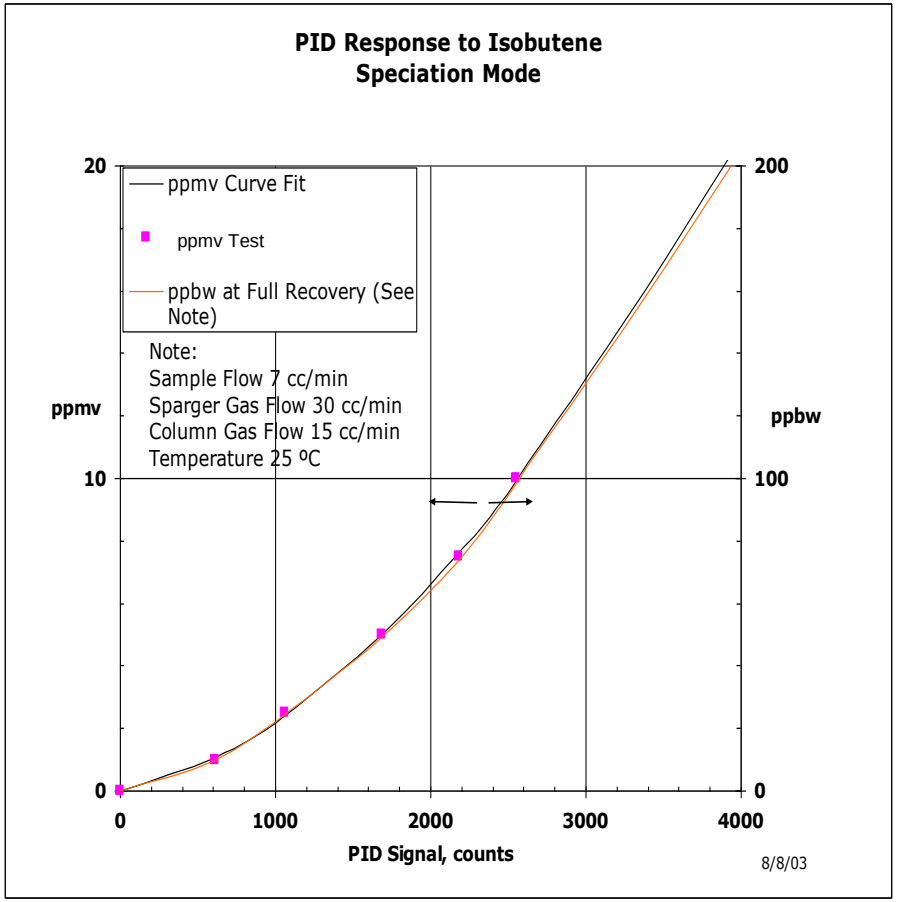
Sparger Recovery Tests
Method 301
System MDL Tests





Representative Sparger Recovery Data





Comparative Results (TCEQ Analysis)

Compound	Spike Level (ppbw)	Sparger Results (ppbw)[A]	Stripper Results (ppbw)[A]
Isobutene	26.3	26.6 +/- 0.4	25.6 +/- 0.2
Propylene	20	20.3 +/- 0.5	19.3 +/- 0.3
Accuracy (Recovery)		101.3%	96.9%
Precision (RSD)		2.0%	1.2%

A = Result is the mean and standard deviation of 10 replicate tests in which water standards were prepared individually of each compound and side by side tests conducted to compare stripper/sparger results(3).

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