Paper # 844
Comparison of Sparging and Direct Injection Techniques for the On-Line Determination of Low Levels of VOC's in Water

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Objectives

- **To provide an alternative to grab sampling of VOC's in water which can lead to expensive fines if not found in a timely fashion**
- **To provide a faster method (< 1 hour) of analysis than the laboratory (3 hours to weeks)**
- **To provide a means for process control- rapid feedback of results**

Objectives

- To compare direct injection with dynamic headspace (DHS) sparging for monitoring VOC's and polar species in water
- To determine whether DHS with Auto GC-photoionization (PID) can be used to provide a rapid & more sensitive alternative to Lab P&T
- To provide a means for process control-rapid feedback of results

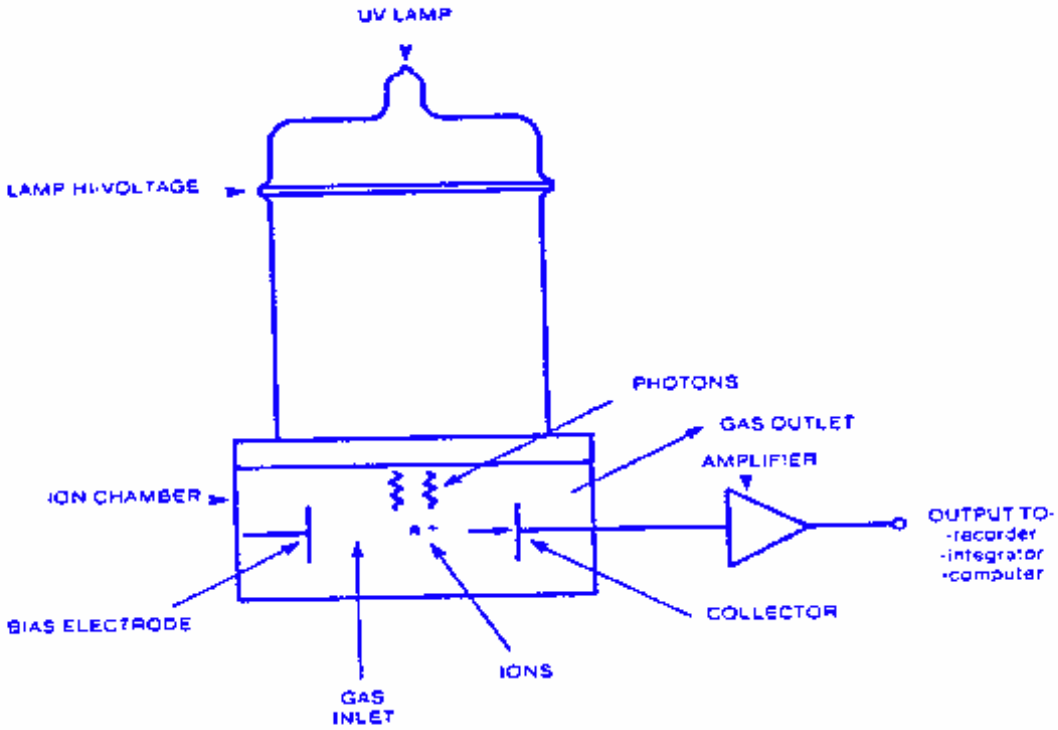
Customer Applications

- **Application #1- Measurement of ppb levels of benzene in presence of hundreds of ppm of IPA and acetone- batch process; no lab or additional presonnel wanted**
- **Application #2- Measurement of ppb levels of non polar VOC's and/also alcohols (polar) in waste stream; 2 shifts 7 days per week**

Applications Fulfillment

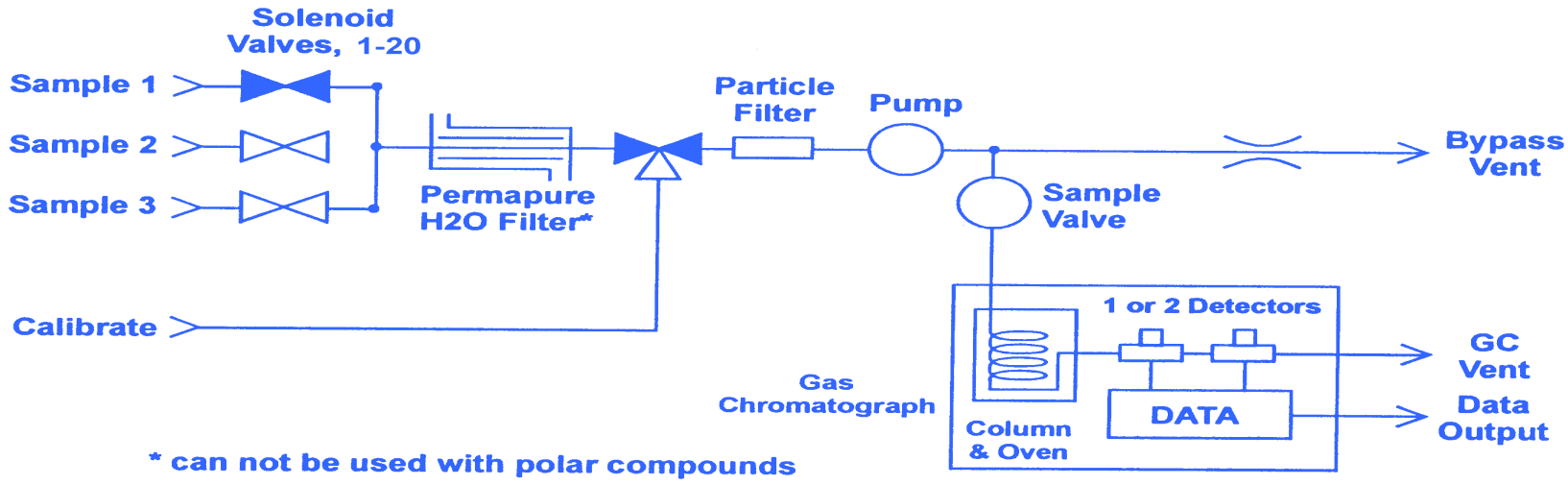
- **Application #1-GC is required & PID is detector of choice- need to do ppb levels & better selectivity than FID for aromatic hydrocarbons**
- **Application #2- GC is required & PID is detector of choice- need to monitor low < 20 ppb levels for agency compliance**

Schematic of the PID



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

Schematic of Automatic GC



Sparging System Principle

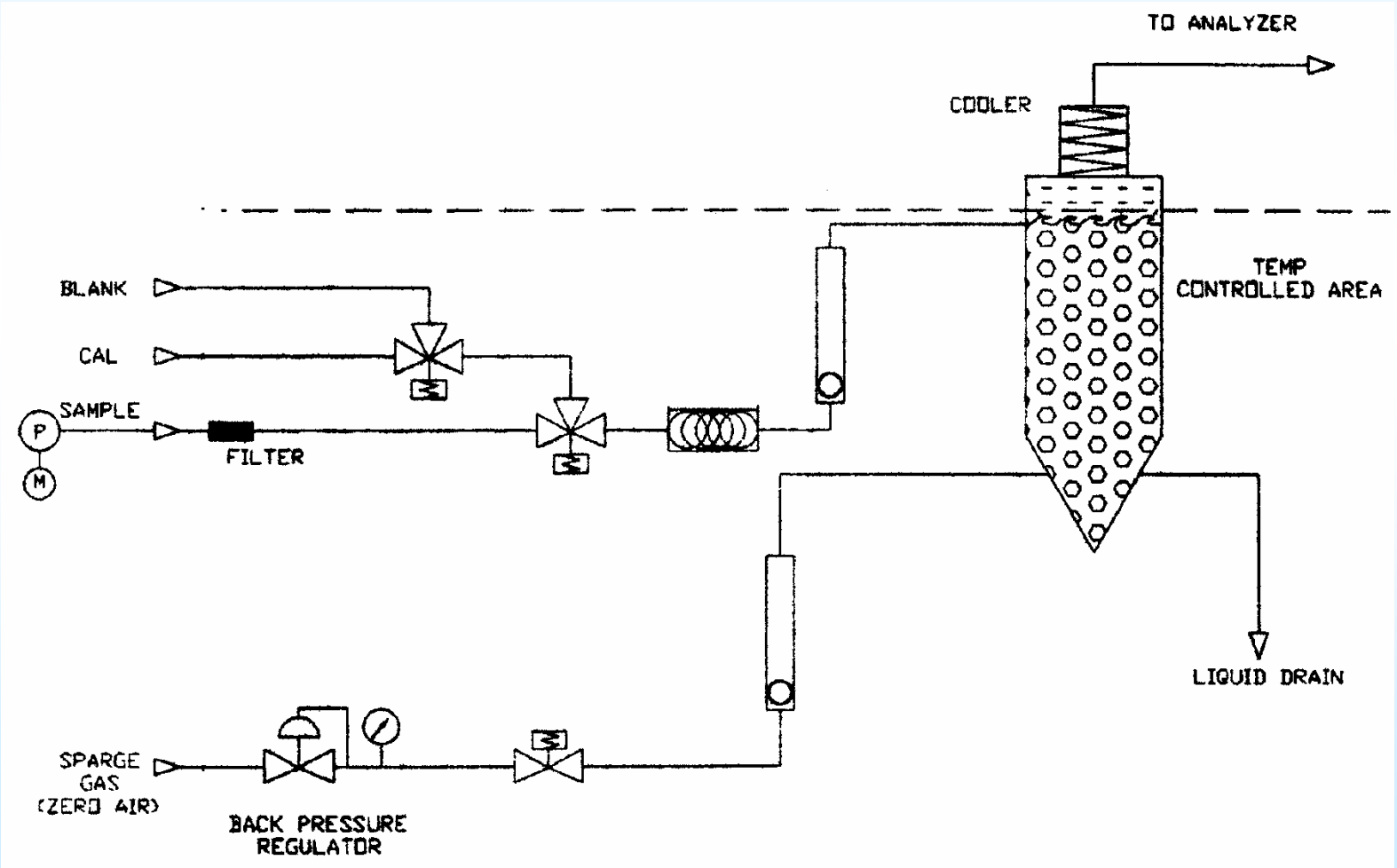
The measurement of low concentrations of organics in water can be accomplished through the application of Henry's Law which states that, at equilibrium, the solubility of a gas in a liquid is proportional to the partial pressure of a gas in contact with a liquid as given below:

$$\textbf{Benzene (aq)} = \textbf{K } P_{\textbf{Benzene}}$$

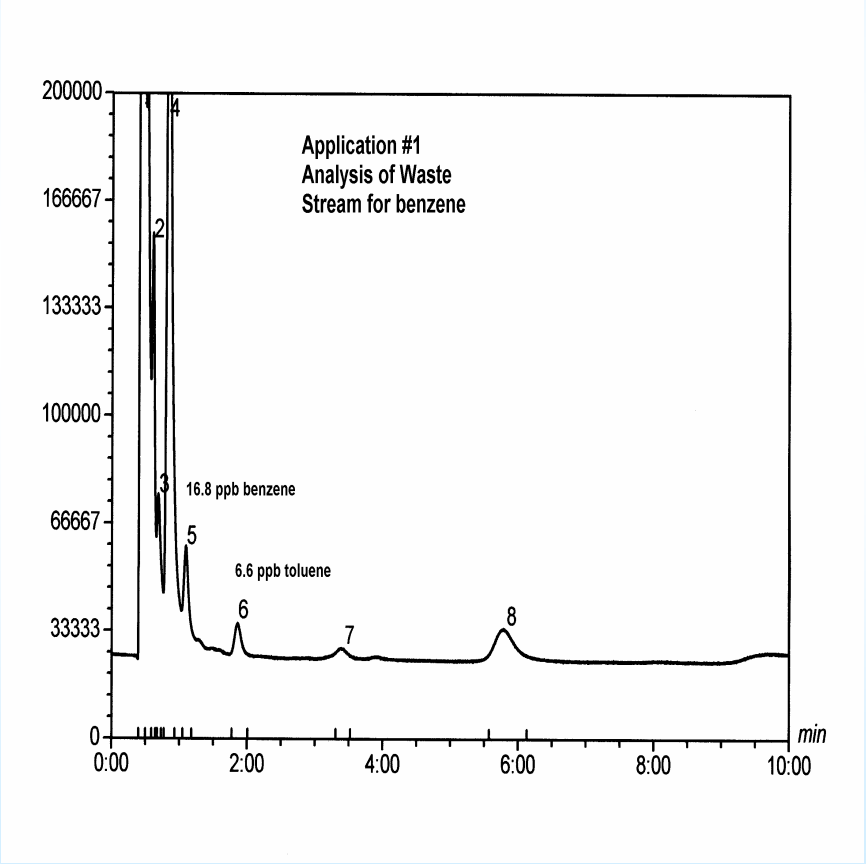
*where **Benzene (aq)** is the concentration of benzene in the liquid phase, **K** is the Henry's Law constant which governs the solubility of gases in water, and* $P_{Benzene}$ *is the partial pressure of benzene in the gas phase.*

As a result of the above equation, it can be seen that if the concentration of benzene in the gas phase and at equilibrium is measured, this is related to the concentration of benzene in the dilute aqueous solution by a proportionality constant (**K**) that can be determined by calibration.

VOC Sparger Schematic



Chromatogram for Application #1



Comparison of Prepared and Measured ppb Levels

Prepared Std. ppb benzene	Measured ppb benzene
1.0	1.39
5.0	5.3
16.5	16.4
17.0	17.1
17.5	17.6

Brief Specs for Benzene in Water Analyzer

- **Response time- 3 minutes**
- **Sample flow rate- 250-500 ml/min.**
- **Range < 1 ppb to > 1000 ppm**
- **Sample pressure- 5-50 psi**
- **Weight- 60 Kg**
- **Size- 60 cm W x 55 cm D x 120 cm H**
- **Power consumption- 400 watts**

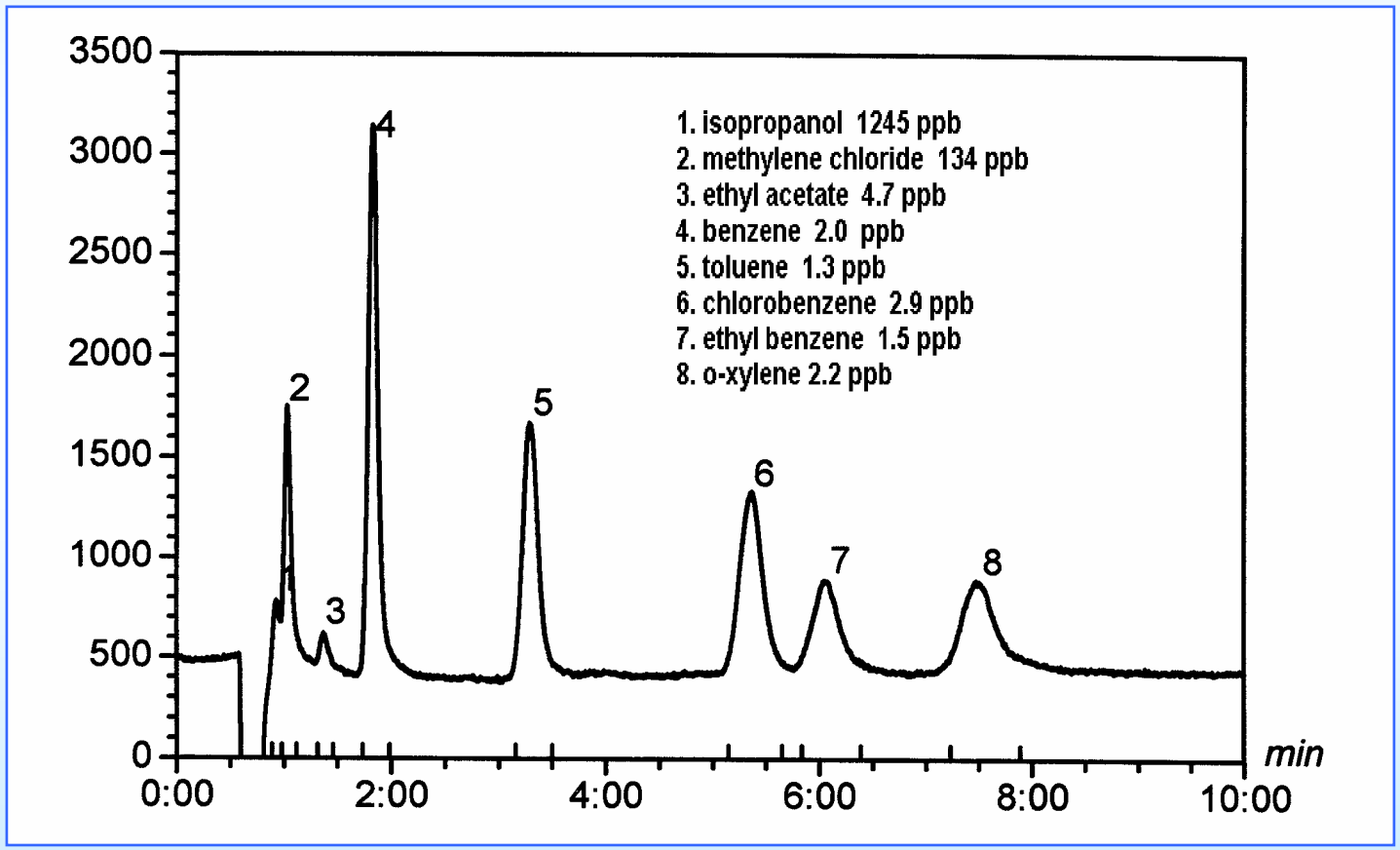
Benefits

- **Sparging system with GC-PID provided low ppb detection limits needed for permit**
- **System is specific for benzene**
- **Analysis time is fast < 3 min.**
- **System is automatic with low maintainence- no lab needed**

Application #2

- **Need capability of monitoring low ppb levels of VOC's and alcohols**
- **Need rapid analyses so that results could be used for process control**
- **Need 2 or 3 shifts and 7 days per week monitoring**

VOC's in Water at ppb Levels Application #2



Reproducibility of VOC's in Water at ppb Levels

Cpd.	RT	#1	#2	#3	#4	#5	#6	Ave.
MC	1.02	150	149	136	133	133	132	139
EA	1.23	4.3	4.5	4.8	4.4	4.4	4.9	4.6
Ben.	1.50	2.4	2.4	2.3	2.3	2.3	2.2	2.3
Tol.	3.18	1.6	1.6	1.6	1.6	1.6	1.5	1.6
0Xyl.	7.31	2	2.3	2.4	2.4	2.4	2.4	2.3

Reproducibility of VOC's Continued

Cpd.	Ave. ppb	Std. Dev.	CV %
MC	139	8.4	6.03
EA	4.6	0.24	5.34
Ben.	2.3	0.08	3.25
Tol.	1.6	0.04	2.58
o-Xyl.	2.3	0.16	6.92

Benefits

- **Exceeded agency monitoring requirements**
- **Fast analysis provided feedback for process improvement and minimization of pollutant emissions**
- **Detection limits of 0.1 ppb were lower than the lab detection limits of 5 ppb**
- **Reduced outside lab costs from $>200K to < $40K operating costs**

Comparison of Capabilities of Various Instruments

	201-FID	201-PID	301-A GC	501-A GC w QScan
Total VOC's	X	X		X
Speciated VOC's			X	X
Range	Sub ppm-%	High ppb-low %	Sub ppb-%	Sub ppb-%

Summary

- **We have shown that a PID based GC with a sparging system is capable of monitoring complex effluents from processes at low ppb levels**
- **The system can be controlled remotely and the data can be logged automatically for regulatory purposes**
- **Sparging provides the best approach for VOC's or polar species**

Costs

- Outside Laboratory
- In-House Laboratory
- Automatic GC with Sparging System