

A CONTINUOUS ON-LINE GENERATOR FOR TRACE VOC STANDARDS IN WATER

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ABSTRACT

Analyzers for monitoring water quality in process or waste water streams require calibration with liquid standards. Traditional techniques for preparing these standards are cumbersome and often inadequate in their functions.

These problems are rectified with the use of permeation tubes to continuously add trace VOCs to a clean water stream to generate the standards on line. Permeation tubes have been used extensively and successfully in setting up gas standards, and this paper addresses extending the method to liquid standards.

INTRODUCTION

Environmental regulations necessitate the monitoring of a variety of process water streams for trace levels of benzene and other toxic, volatile organic compounds. Typically, the analysis is done by gas chromatography of a vapor sample created by sparging an inert gas through the liquid sample. The sparging process yields a clean gas sample containing the analytes at concentrations proportional to their respective concentrations in the water sample. See Figure 1.

Calibration and validation of these on-line systems, however, has been a problem. To account for the partition process, a water standard containing a known amount of each analyte must be used for calibration. A typical system will require about one gallon of standard per point for each calibration or validation. Since the concentrations of interest are low and the components are volatile, the standards typically do not store well and must be prepared fresh for each use. The standard is then manually fed to the analyzer as shown in Figure 2.

Preparing suitable standards in the laboratory is straightforward but labor intensive. Process analyzer maintenance personnel rarely have direct access to good laboratory facilities, thus, they must either schedule sample preparation through the laboratory or "make do" with lab equipment equivalent to "buckets and shovels".

When an environmental episode is in progress, scheduling work through

another department is rarely acceptable. The result is that often the calibration of these analyzers is questionable. Manual calibration is expensive and a serious maintenance nuisance.

Given the potential consequences of relying on a malfunctioning analyzer in this application, on-line calibration is a more practical approach. As an effort in that direction, some systems provide for the introduction of a gas standard directly into the GC as illustrated in Figure 3. Unfortunately this method complicates the basic problem by providing a false sense of security. It can validate calibration of the GC, but does not test the sampling process. Thus, the user could fail to detect a major spill even though the analyzer function appears perfect.

PROBLEM DEFINITION

Since mixtures containing volatile compounds do not store well, an on-line calibration system must be an on-line standards generation system. The most generally applicable approach is to dynamically mix the trace component(s) into a flowing stream of clean water.

A typical sparger sample system requires 50 to 100 ml/min. sample flow. For benzene in chemical process waste water, a typical maximum concentration requirement is 500 ppb(w/w). For other toxic VOCs and other applications, the range requirement could be from less than 1 ppb to a few ppm.

For the benzene application, dynamically blending the required standard requires the addition and mixing of less than 100 microliters of benzene per minute into the clean water stream. This flow rate is well below the minimum for common metering pumps and flow measuring devices.

Thus, the key problem is finding a way to reliably add the required flow rate of component compound to a flow of clean water. One option for consideration is permeation tubes. Permeation tubes have been used extensively to prepare trace concentration gas standards, but they have not been used for liquid standards.

PERMEATION TUBES

A permeation tube is a device which uses the permeation of vapor through a membrane as a means of dispensing a small flow of that vapor. Figure 4 shows a classical permeation tube. Liquid component compound (analyte) is sealed inside a short length of Teflon® tubing. When the tube is held at constant temperature, component vapor flows steadily out of the device through the tubing wall. The emission rate can be measured by holding the tube at constant temperature and weighing it repeatedly to measure the rate of weight loss.

The emission rate characteristics of these devices are very stable over extended time periods. If a known flow of dilution gas is passed over the tube, a known concentration mixture results. Since the permeate flow is measured gravimetrically and all controlling variables can be made traceable to NIST, mixture concentration is also traceable to NIST.

The permeation method, however, has not been generally used for liquid standards. One reason is that the emission rates possible from the conventional tube design are generally lower than needed for liquid standards applications. Also, the classical design is not easily adapted to liquid service.

Newer tube designs which extend the emission rate range available to over one milligram/min. are now available. Figure 5 shows a diagram of a high emission design of particular interest for this application.

The permeation membrane is a long coil of thin-walled Teflon® tubing suspended in a stainless steel canister. Pure analyte liquid and vapor surround the membrane. Dilution gas passing through the tubing mixes with the component vapor permeating through the membrane tube.

This design can yield emission rates of over 150 times greater than a conventional tube. Table 1 shows emission rates obtainable for some common toxic VOCs. Additional key features of this design are (1) it provides a large analyte fill capacity, and (2) it can be refilled with analyte without disturbing the certified permeation membrane. Thus, it can provide a long, unattended service life even in continuous high emission rate service.

ADAPTING TO LIQUID SERVICE

The primary problem that had to be addressed in adapting the permeation tube method to liquid standards generation was certifying the emission rate into a liquid (water). Could the gravimetric method used in gas service be used for liquid service, or would an "indirect" technique be required?

An experimental "certification unit" was set up to try certifying a modified LFH tube using water as the diluent. Figure 6 shows a flow diagram of the test jig. Benzene was chosen as the test analyte. The tube was operated at 60°C, and weighed periodically to measure the rate of weight loss.

Two measurement strategies were tested. The first strategy was to fill the membrane core with water and take all weights with the core full. The second strategy was to make all weight measurements with the tube core dry. The total weight of the device was about 585 gm.

Initial tests using the first strategy were unsatisfactory. Variations were in the region of $\pm 30\%$. The second strategy was much more effective. Results of a 13 day run at 15 ml/min. water flow using the second strategy are shown in Table 2.

It took about 2 days for the weight loss rate to stabilize after introduction of water as diluent. This equilibration time can be attributed to back flow of water vapor entering the canister and reducing the weight loss. Thereafter, the weight loss rate remained stable and within $\pm 2\%$ of the average value.

STANDARDS GENERATOR DESIGN

Permeation based standards generators require precise measurement and control of permeation tube temperature, and diluent fluid flow. For effective use on-line, the generator should operate unattended for extended periods. Long term stability of those controls is essential. It is also essential that diluent flow over the membrane be continuous. Additional considerations include providing a "blank sample" for zero check, and delivering the standard at the same temperature and flow rate as the sample.

For gas systems diluent preheat is a minor consideration since both the flow rate over the tube and heat capacity of the gas are low. For water, however, diluent preheat is a primary consideration.

Also, there is a wide variety of simple, mass flow measurement and control devices available for low flow rates of gases. For liquids, the choices are much more limited. We tested four flow control options: (1) constant-differential-pressure control coupled with a Pelton Wheel flowmeter, (2) a peristaltic type metering pump, (3) a variable stroke syringe type pump, and (4) a variable stroke rate syringe type pump. Our tests indicated that the best control is provided by a syringe type metering pump. Both the constant-differential-pressure and peristaltic pump methods failed to provide the long term stability required for an on-line system.

The variable stroke and variable rate syringe pumps both provided excellent long term flow control. The variable stroke method was chosen for single point generation on the basis of its simplicity. For multiple concentration point applications, the variable stroke rate system would be preferred.

Figure 7 shows a flow diagram for a single component standards generator. Pure water enters the system and divides into two parts. One part enters a metering pump which supplies continuous, "carrier flow" to the permeation tube. Carrier flow is preheated and then flows through the permeation tube where it picks up the permeated analyte. This primary mixture goes to a solenoid valve where it is routed either to the final mixture, or to the drain.

The second, larger portion of the flow goes to the main dilution pump. This flow serves as the "blank" (zero) flow and makes up the balance of dilution flow required to reach the desired "span" concentration. The final mixture goes through a flowmeter which indicates the total dilution flow.

Because the heated carrier flow is diluted by a larger flow of ambient temperature diluent, additional cooling of the final mixture is not usually required. For special situations where the sample is unusually hot or cold, it may be desirable to add a heat exchanger to bring the span liquid to the same temperature as the sample.

FUTURE WORK

Current efforts are centered on developing techniques for working with a wider range of analyte compounds, and designing a variable concentration system. The ability to use the permeation technique to make reliable gas standards does not necessarily predict success in making liquid standards of that analyte. As hinted in the permeation data in Table 2, the reverse permeation of diluent water into the analyte can skew gravimetric data. With some hygroscopic compounds like methanol, the direct gravimetric method of certification will produce an incorrect result. Thus other methods must be developed.

The variable concentration system design is virtually complete and requires only field evaluation.

CONCLUSIONS

This work has demonstrated that permeation tubes can be adapted to generate trace concentration organic standards in a water background. It has also been shown that the emission rate of the tubes can be certified by weight loss using water as the diluent. Thus, the resulting standards can be made traceable through physical standards to N. I. S. T.

Design considerations for this application include the need for a special permeation tube design for liquid diluent service, and precision preheat for the carrier which flows over the tube. Syringe type metering pumps offer the best solution to precision flow control for diluent water.

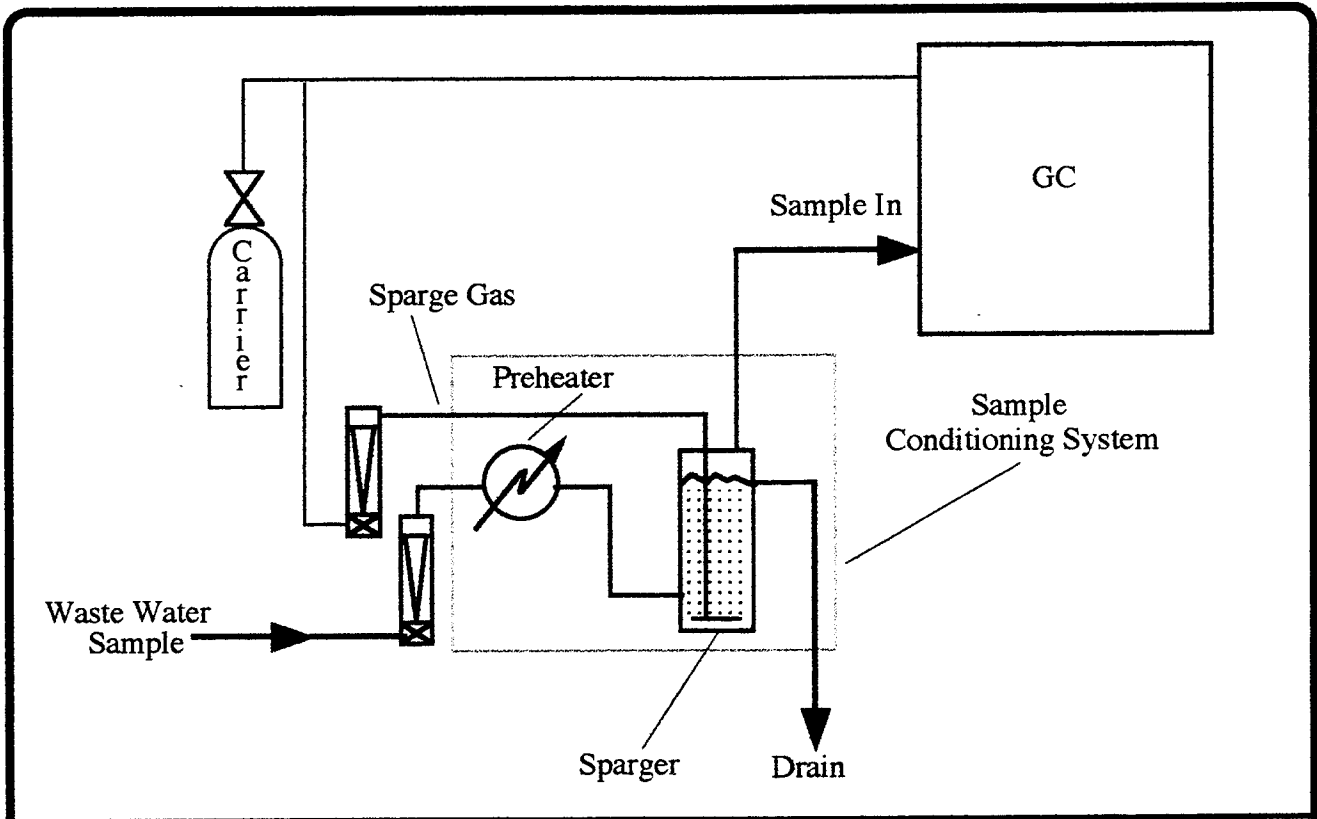


Fig. 1 Sparger Sample System

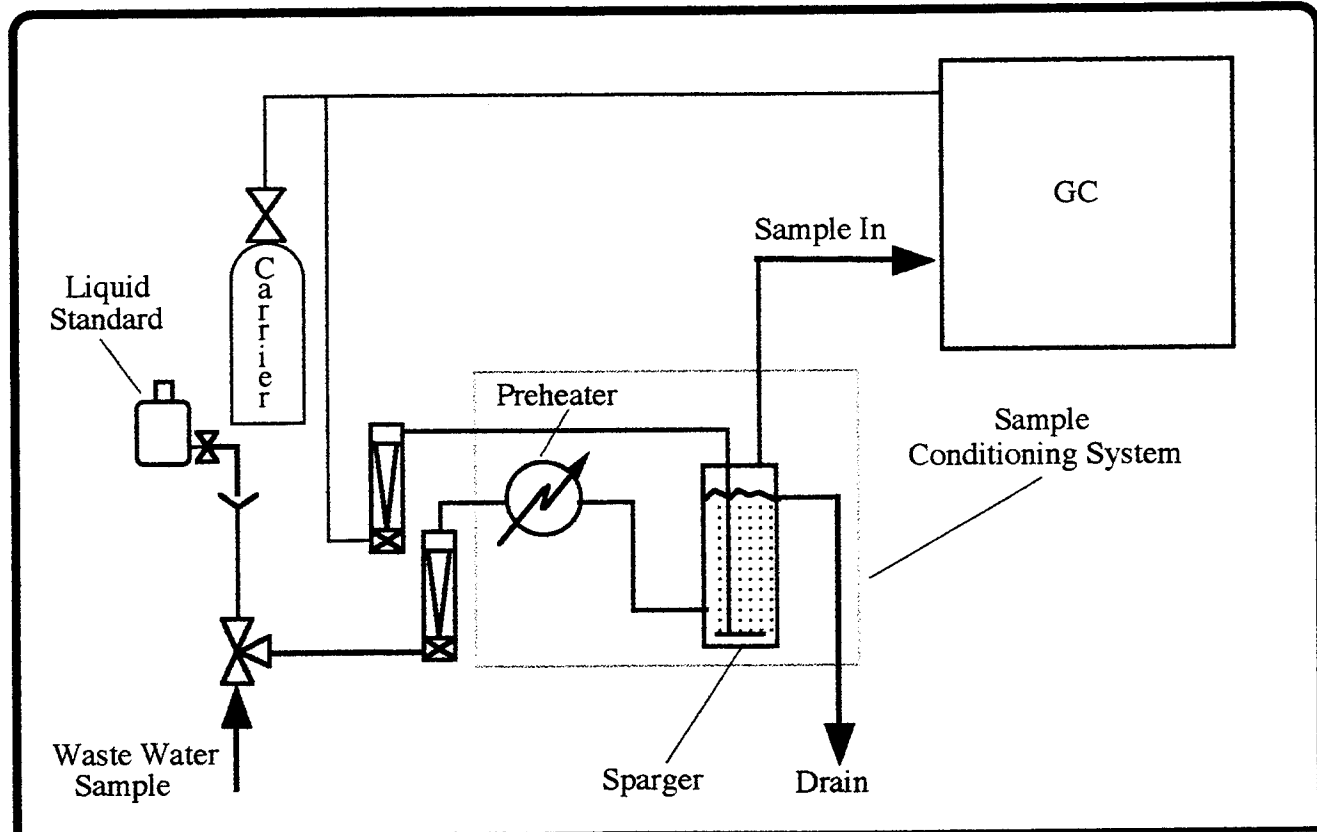


Fig. 2 Manual Calibration Method

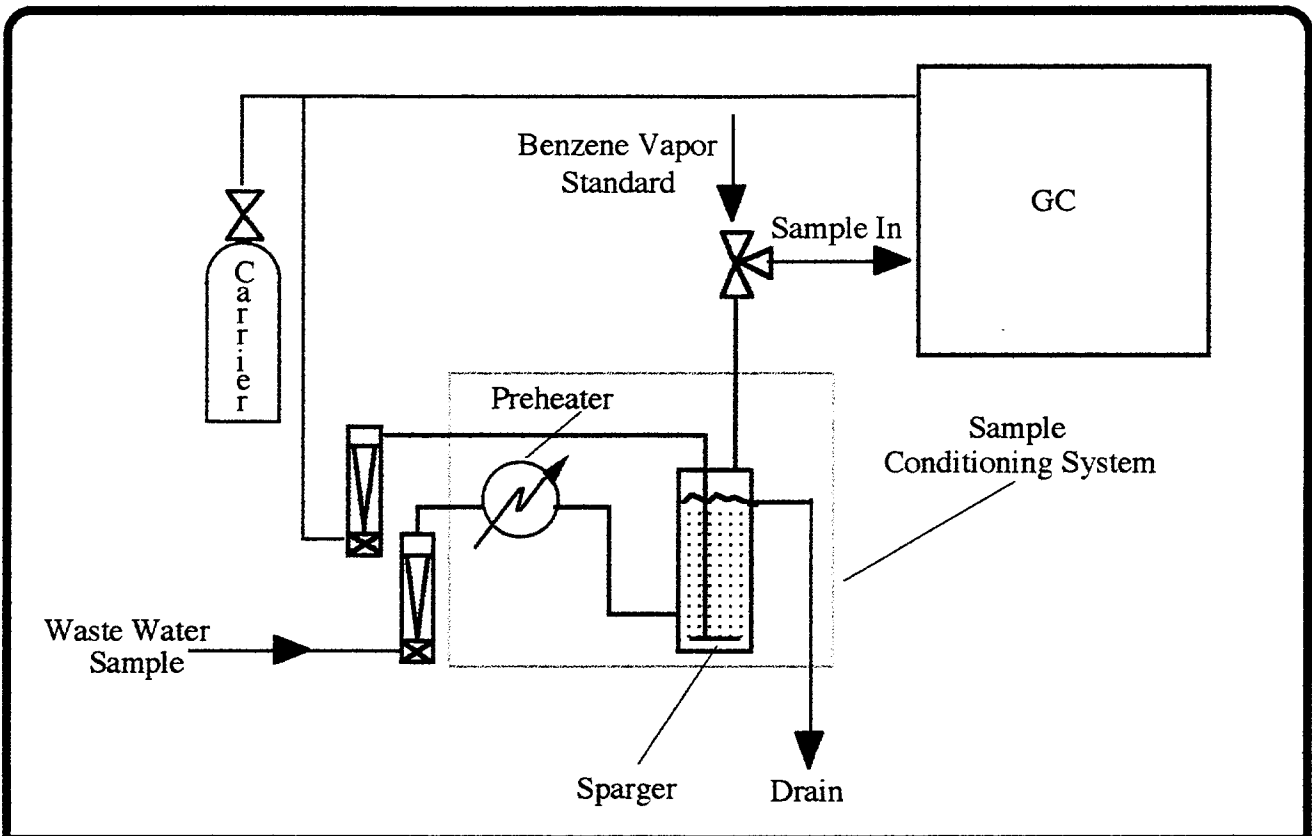
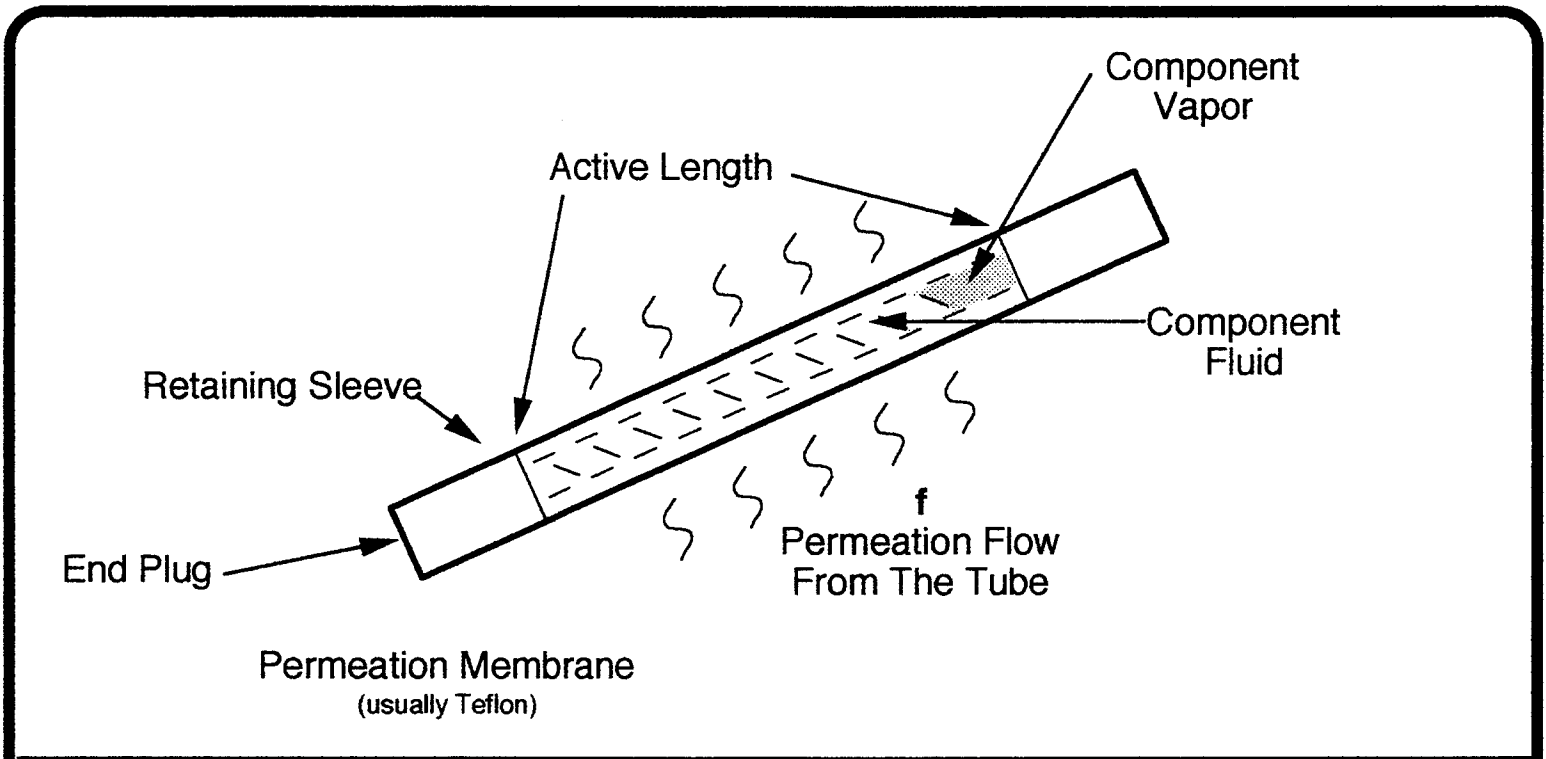


Fig. 3 Vapor Validation Method



**BASIC PERMEATION TUBE
FIGURE 4**

DILUENT IN

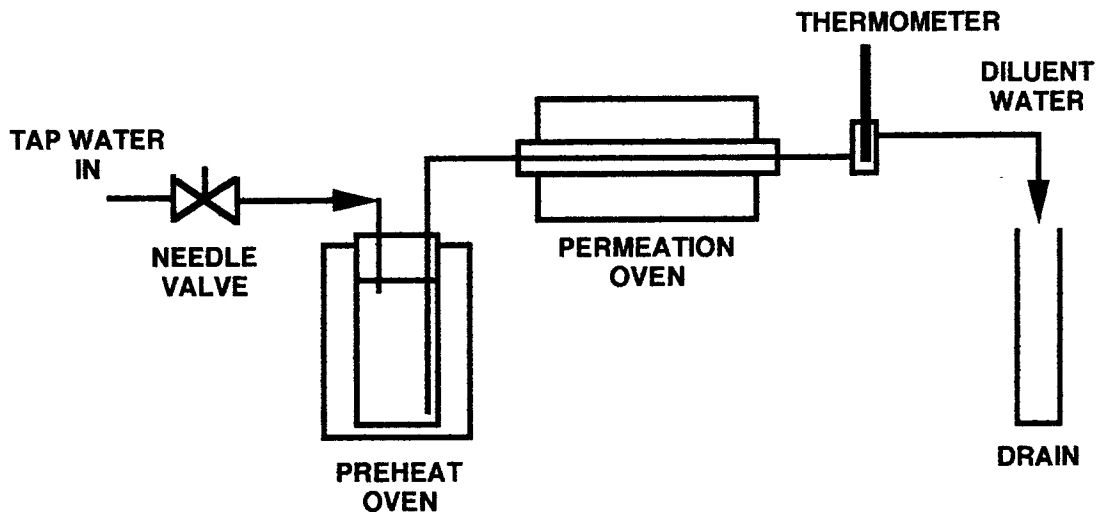
**DILUENT + ANALYTE
OUT**



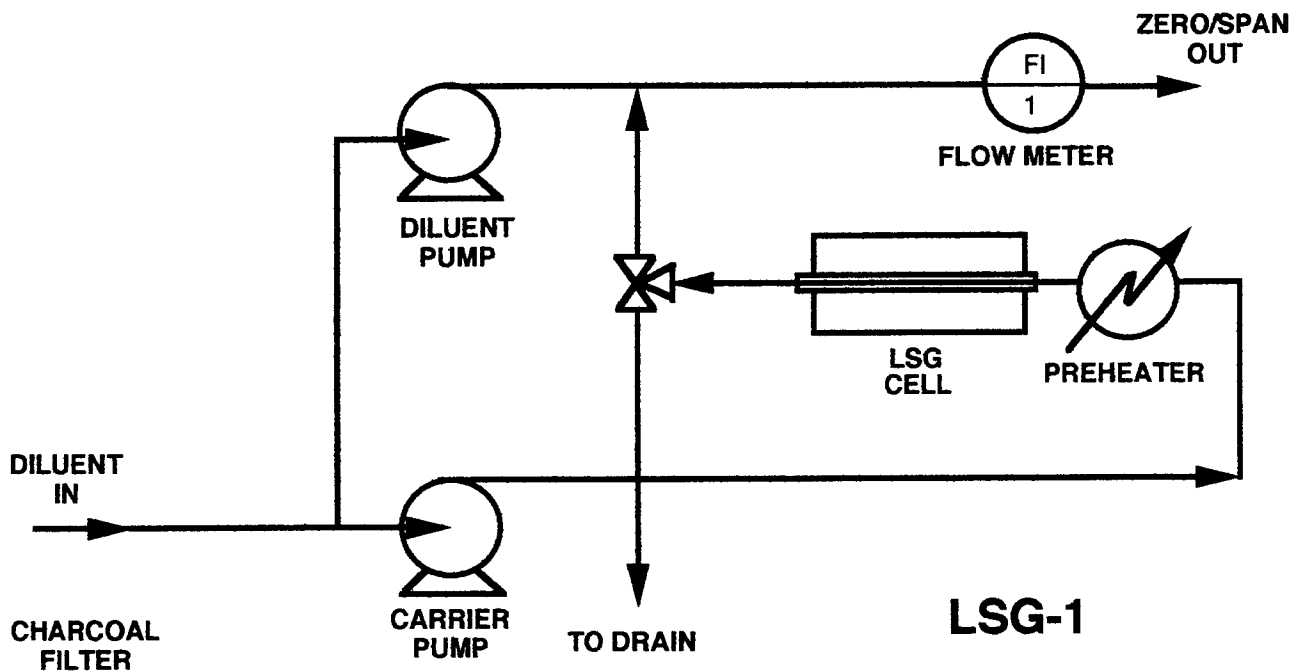
**PERMEATION
MEMBRANE
TUBE**

**ANALYTE
LIQUID**

**HIGH EMISSION PERMEATION TUBE
FIGURE 5**



**FLOW DIAGRAM OF EXPERIMENTAL SET-UP
FIGURE 6**



**FLOW DIAGRAM FOR SINGLE POINT
LIQUID STANDARDS GENERATOR
FIGURE 7**

COMPOUND	RATE μg/min.	TEMP. °C	MAX. CONC. ppm
ACRYLONITRILE	533	60	5.3
BENZENE	1,386	80	13.8
CARBON TET.	1,157	80	11.5
EDC	1,550	80	15.5
METHANOL	815	80	8.1
STYRENE	475	80	4.7

**MAXIMUM CONCENTRATIONS
TABLE 1**

NO.	WEIGHT	ELAPSED TIME	RATE/CM
0	594.093		TARE
1	593.079	2435	236.6
2	592.358	1635	250.6
3	590.407	4357	254.4
4	589.683	1618	254.2
5	589.039	1447	252.9
6	585.867	7133	252.7

**CERTIFICATION DATA
TABLE 2**