A RAPID RESPONSE SAW-GC CHEMICAL MONITOR FOR LOW-LEVEL VAPOR DETECTION

JOHN A. ELTON and JAMES F. HOULE
EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

INTRODUCTION

Chemical vapor monitors (CVMs) are generally not sufficiently sensitive, selective, or reliable enough to detect a multiplicity of vapors in less than 2 min. There is, therefore, a need for a CVM which can simultaneously detect a variety of vapors in the presence of interferents. In addition, the detection of a specific vapor must be conclusive so that false alarms are minimized. Detection in less than 2 min requires either highly selective multiple detection methods if several vapors are present or separation so that each vapor can be detected and identified. The sensitivity for each vapor must also be sufficient to allow detection at desired or required levels.

SAW sensors have been used to detect vapors at low concentrations [1]. However, the SAW detection limits reported to date for agents such as GD and HD are much higher than the limits other devices are capable of reaching. Detection limits of approximately 100 ppb (0.6 mg/m^3) for GD and 5 ppm (32 mg/m^3) for HD have been reported. It will be shown in this paper that much lower levels may be obtained for GD and HD when the system described herein is used. In addition, results on the detection of methyl benzoate and phenyl acetone using the same system as used for CW detection will be provided.

BACKGROUND

The CVM unit contains major modifications which allow significantly improved response times. Ambient vapors are collected on a thermally desorbed type concentrator by pumping air through a glass tube packed with concentrator material (Figure 1; concentration). At the end of a fixed 20 sec interval, the concentrator is heated and the collected vapors desorbed onto the GC column. Desorption occurs in about 6 sec and provides chromatographic peaks that are compatible with the SAW detector (Figure 1; injection). An additional 4 to 8 sec is typically needed, however, in order to obtain complete injection of the vapor plug onto the GC column.

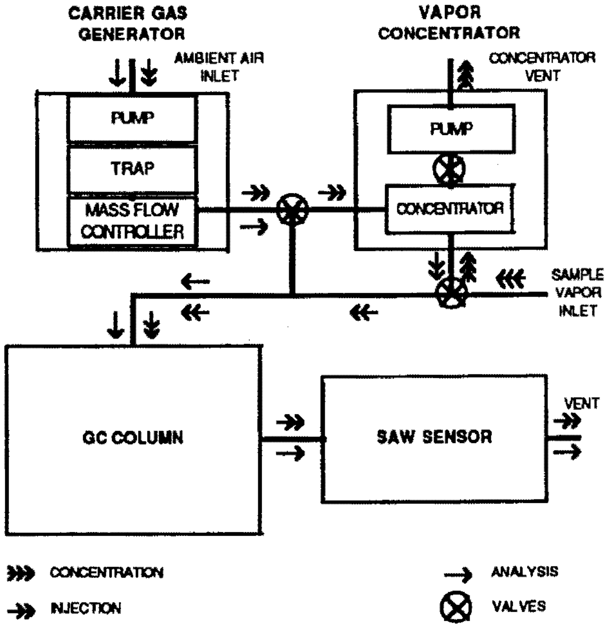

Fig. 1. Kodak's Chemical Vapor Monitor Showing Concentration, Injection, and Analysis Stages of Operation.

The GC column greatly enhances the selectivity of the system by separating the vapors (Figure 1; analysis). Each vapor plug which elutes from the GC column at a different time is immediately injected onto a SAW sensor. A second, uncoated SAW sensor located nearby is used as a reference. When combined with a frequency mixer, this configuration provides a frequency difference (Δf) that is easily measured and relates to concentration.

The CVM has several other subsystems. The sequencing of valves, concentrator, pumps, and the acquisition of SAW sensor data is controlled by a Macintosh™ computer. A second subsystem provides clean air/carrier gas to the GC column with a small pump that draws ambient air through molecular sieve and charcoal scrubbers. A solid-state mass flow controller is used to guarantee a stable carrier gas flow under varying conditions of pump and scrubber aging. A typical output of the CVM is given in Fig. 2 and shows the concentration, injection, and analysis characteristics of the device.

EXPERIMENTAL

Each SAW sensor was first tested as an individual sensor with each vapor of interest at one or more concentrations. The sensor was then incorporated into the CVM and system testing performed.

Vapor Generation and Verification

Vapors were generated using a Microsensor Systems, Inc. VG-7000 Automatic Vapor Generation System. All vapors supplied to the CVM were monitored using a Hewlett Packard 5890 Gas Chromatograph containing an FID detector. For the SAW sensor testing, periodic checks of the vapor concentration were made every 11 minutes. For the CVM tests, vapor concentration was determined by sampling the final portion of vapor which impinged upon the CVM concentrator. This procedure was performed in order to ensure verifiable vapor concentrations.

SAW Sensor Preparation

Selective coatings of ethyl cellulose (ECL) and fluoropolyol (FPOL) on SAW sensors were prepared using proprietary thin film coating techniques. All coatings were observed under a microscope to

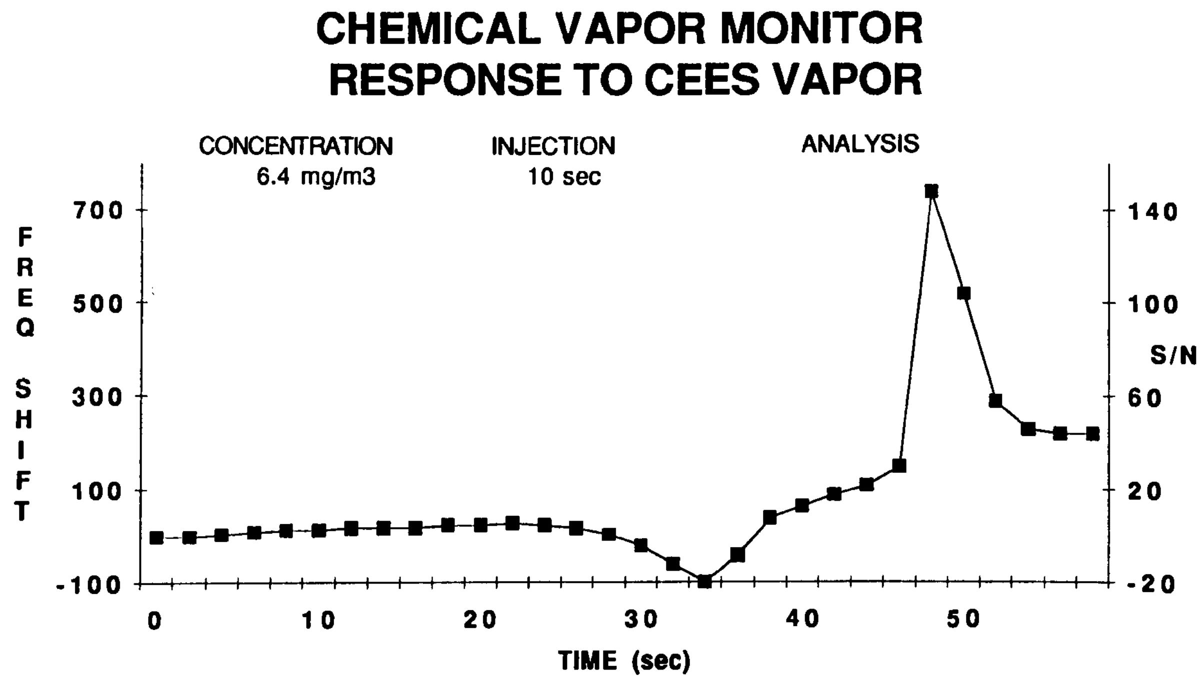

Fig. 2. Typical CVM Output

determine uniformity of the coating. Only uniform and well adhered coatings were used in this study. The thickness of a coating was determined by recording the frequency shifts of the device both before and after coating.

SAW Sensor Testing

Individual SAW sensors were tested using various concentrations of the vapors of interest. The SAW sensors were exposed to the vapors for a minimum of 20 minutes. A signal to noise ratio of at least 3:1 was chosen as a criterion for acceptable data.

CVM Testing

The general operation of the CVM was described above. Standard operation is a 20 second concentration period, a 12 second injection period, and an 88 second analysis time. Deviations from this standard will be indicated in the results section when appropriate.

RESULTS

Results were obtained using two types of SAW sensors. The first tests used a modified version of an established type of sensor (Type I). This was followed by extensive testing of a new type of SAW sensor (Type II). Both SAW sensor test results and CVM test results are reported below.

SAW Sensor Testing

Table 1 provides the frequency shifts observed from selected experiments when the ECL-I, FPOL-I, ECL-II, and FPOL-II sensors were tested with various concentrations of CEES, DMMP, methyl benzoate, and phenyl acetone.

Chemical Vapor Monitor Testing

During CVM testing the vapor flow was connected to the concentrator input of the system; flow rates through the concentrator were monitored. The results of selected tests using the first type of SAW sensor are shown in Table 2.

TABLE 1
SAW Sensor Results

Sensor	Vapor	Concentration (mg/m^3)	SAW Response* (Hz)
ECL-I	CEES**	2100	2400
FPOL-I	DMMP**	91	4,710
ECL-II	CEES	17.8	58
	DMMP	20.6	362
	MB**	2.4	75
	PA**	1.7	88
FPOL-II	CEES	516	248
	DMMP	2.3 ± 1.1	773
	MB	19.2	222
	PA	6.48	265 ± 60

*80 Hz noise level (Type I);
5 Hz (Type II)
**CEES - chloroethyl ethylsulfide; DMMP - dimethyl methylphosphonate; MB - methyl benzoate; PA - phenyl acetone

TABLE 2
Chemical Vapor Monitor Results

Sensor	Vapor	Concentration (mg/m^3)	CVM Response* (Hz)
ECL-I**	CEES	6.1	570
FPOL-I***	DMMP	17.6	1600
ECL-II	CEES	5.27	82
FPOL-II	DMMP	23.2	495
	MB	27.2	213
	PA	11.0	150

*Response obtained in less than two minutes; 2 Hz noise level unless otherwise specified
**5 Hz noise level; 10 second injection period
***10 Hz noise level; 14 second injection period

DISCUSSION

These results indicate that detection limits for GD and HD using the new type of SAW sensor should be considerably less than previously reported [1-2]. Table 3 gives extrapolated detection limits and response times for both the SAW sensor experiments and the CVM experiments. The extrapolated detection limits are determined from the values reported herein using a 3:1 signal to noise ratio.

TABLE 3
Extrapolated Detection Limits

Type	Vapor	Extrapolated Detection Limit (mg/m^3)	Response Time (min)
SAW Sensor			
Type I	CEES	210	20
	DMMP	4.6	40
Type II	CEES	4.6	20
	DMMP	0.05	40
	MB	0.48	20
	PA	0.29	20
CVM			
Type I	CEES	0.16	1
	DMMP	0.33	1
Type II	CEES	0.38	2
	DMMP	0.28	2
	MB	0.77	2
	PA	0.44	2

It should be noted that optimization of coating thickness was performed much more extensively with the Type I sensor. Significant improvements in the Type II sensor are expected in the future as further optimization of coating thickness and subsystem parameters are performed. The much lower noise level of the Type II sensor is the principal advantage of using this technology since both sensors should provide approximately the same response when the same thicknesses and types of coatings are utilized.

The results also reveal that the greatly increased sensitivity of the Type II SAW sensor is not carried over to the detection of DMMP using the complete CVM unit. FPOL coated sensors do not equilibrate as quickly with DMMP as with the other vapors. The peaks observed during all DMMP testing were much broader than for all other cases. Significant tailing of peaks was observed. Different GC columns and higher temperature operation of the SAW sensors may help to narrow the peak width and improve the detection limit for DMMP.

The results also show the response of the two sensors to methyl benzoate and phenyl acetone. It is believed that this is the first time that detection of such vapors with SAW detectors has been reported. The extrapolated detection limits indicate that relatively low levels of these vapors can be detected with SAW sensors. No effort has yet been made to develop special selective coatings for these two vapors.

CONCLUSION

Our studies have shown that SAW technology can be used to detect DMMP and CEES at concentrations below 1 mg/m^3 in less than two minutes. We have also reported for the first time the behavior of methyl benzoate and phenyl acetone to SAW sensors typically used for chemical agent detection. Concentrations below 1 mg/m^3 are also indicated for these two vapors. Because of the preliminary nature of some of the data presented herein, we anticipate even lower detection levels in the future as operational parameters and selective coatings are optimized.

ACKNOWLEDGEMENTS

The authors would like to thank Arthur Snow of the Naval Research Laboratory for providing us the fluoropolyol used in these experiments.

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PASSIVE CRYOGENIC WHOLE AIR FIELD SAMPLER

Steven J. Fernandez
Bill G. Motes
Joseph P. Dugan, Jr.
Susan K. Bird
Gary J. McManus

Westinghouse Idaho Nuclear Company
P.O. Box 4000, Mail Stop 2202
Idaho Falls, Idaho 83403

The portable, passive cryogenic sampler has been designed by the Idaho National Engineering Laboratory (INEL) for the collection of whole air samples without the loss or concentration of any atmospheric constituents. The principle of operation is the collection by bulk gas flow and condensation of a whole air sample into a previously evacuated cylinder held at liquid nitrogen temperature using a reservoir. The ability of the sampler to collect a highly compressed gas sample without concentration of condensable gases permits a large number of gas constituents to be analyzed from a single sample, even when analytes vary widely in their boiling points.

Design criteria for the portable, passive whole air sampler are listed in Table 1. The sampler, constructed in-house of readily commercially available components, is shown in Figure 1.

The sampler evaluation was performed in three phases. The first phase determined sample flowrate, sample size, resultant sample pressure, and sample collection lifetime as a function of the liquid nitrogen additions. The second phase analyzed simulated whole air samples for bulk composition, noble gases, selected chlorofluorocarbons, and tritium before and after collection in the cryogenic air sampler. In the third phase actual field samples were collected and analyzed for bulk composition and chlorofluorocarbon content. These samples were then concentrated, separated, and analyzed for noble gases. Also included in the third phase was the analysis of altered whole air samples, blindly and randomly introduced into the sample analysis scheme as a means of detecting sample tampering.

Results of the evaluation of the design criteria for the sampler are listed in Table 2. A partial listing of past customers and their application of the sampler is found in Table 3. The need of a low cost passive cryogenic sampler that can collect many whole air samples at remote locations with minimal logistical support will become widespread in the future.

We have found the sampler to meet or exceed all of the characteristics intended for it. The sampler is capable of the collection of samples without concentration or loss of any sample constituents regardless of boiling point.

The required sample volume of 100 L at STP has been successfully achieved, and samples as large as 131.2 L have been collected. Most samples are between 70 and 90 L. The volume of sample collected is dependent upon the sample duration and flowrate. By selection of the proper combination of sample duration and flowrate, samples of accurately known size from a few to 100 liters may be collected unattended within 30 minutes or over a period of time of 2 hours.

Laboratory tests on known standards demonstrate that no concentration or loss of atmospheric constituents occurs.

No electrical power is required for operation of the sampler, which would enable it to operate in hazardous environments such as where potentially explosive mixtures of hydrogen and oxygen are found.

The sampling lifetime can extend to 4 hours with refilling of the liquid nitrogen reservoir.

TABLE 1
Design Criteria for Whole Air Sampler

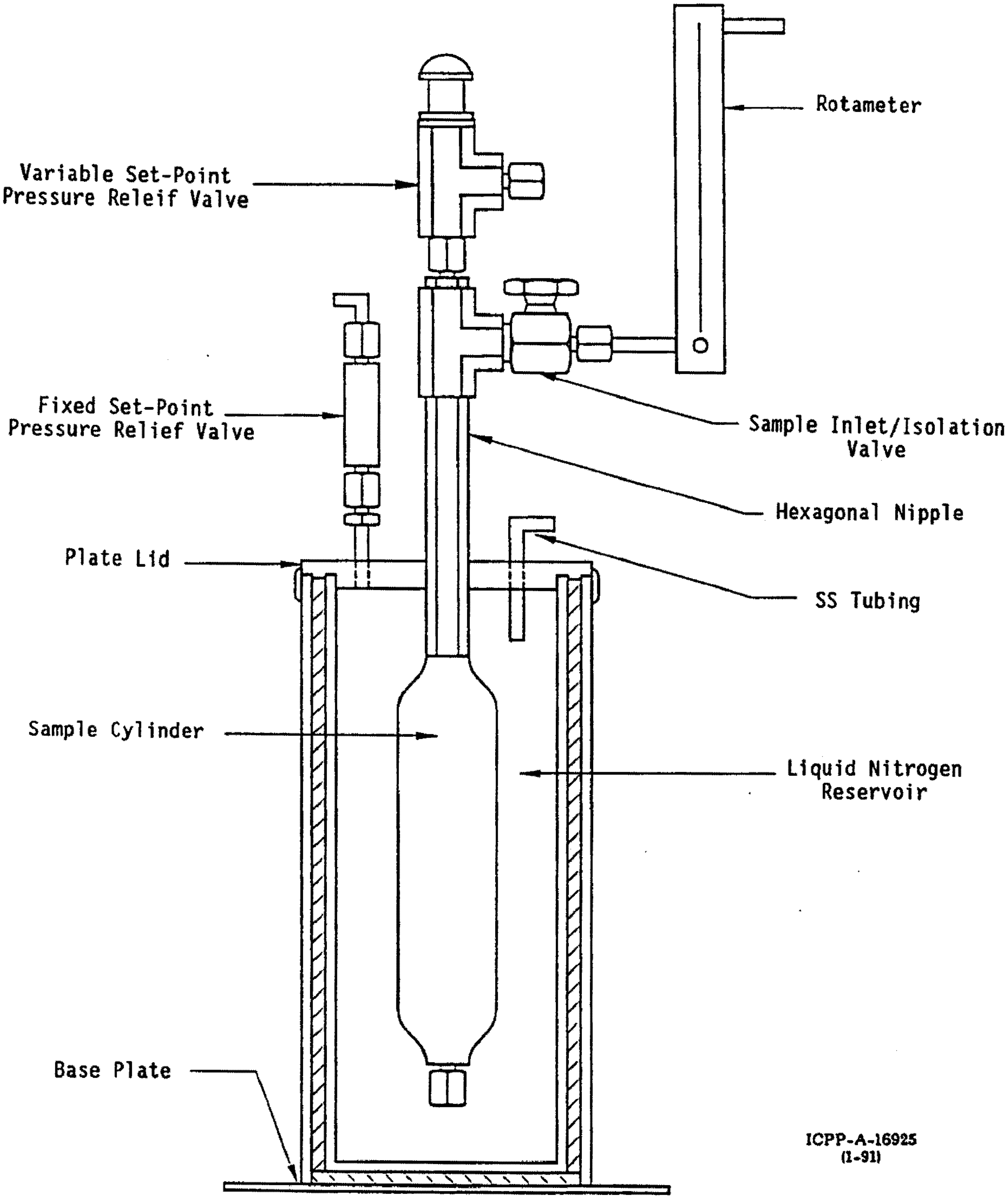
1) Sample Volume of 100 Liters
2) No Concentration or Loss of Constituents
3) Sampling Lifetime Greater Than 2 Hours
4) Small (50cm x 15cm) & Lightweight (20kg)
5) No Electrical Power
6) Operator Safety
7) Ease of Operation

TABLE 2
Development of Cryogenic Whole Air Sampler

Parameter	Results
Sample Flowrate	Controllable, 1 cc to 3 L/Min
Sample Volume	Nominally 100 Liters, 130 L Maximum
Sample Pressure	Nominal 2000 psi, 3650 psi Maximum
Sampling Lifetime	30 Min to 10 Hours
Sample Concentration	Noble Gas Ratios, Unaltered
Sample Loss Tests	Chlorofluorocarbons, 100% Recovery Tritium, 100% Recovery

TABLE 3
Past Applications of the Passive Cryogenic Whole Air Sampler

Customer	Facility	Application	Analytes
DOE- Office of Materials	ICPP	Hydrogen-Rich Off-Gas Study	Permanent Gases
US Air Force	Proposed for White Sands, KA-III Series	Fuel/Air Explosives	Combustion Products, Oxygen
DOE- Office Waste Mgt	ICPP	Environmental Sampling	^{85}Kr,N_2,O_2 Ar,CO_2
US Air Force	TREAT Pulse Reactor INEL	Environmental Sampling	Kr, Xe, Freon-11 Methyl-chloroform
DOE- Defense Programs	Advanced Test Reactor INEL	Off-Gas Studies	^{41}Ar,Kr,Xe $CFCl_3$,CH_3CCl_3 Freon-113
DOE-Office Arms Control	INEL Research	Evaluation of Arms Control Verification	^{3}H,Kr,Xe,He, N_2,O_2,Ar,H_2, Freon-12, CO_2,Freon-113
US Air Force	ICPP	Fission Products in Ar Carrier Gas	Fission Product Gases



ICPP-A-16925
(1-91)

FIGURE 1

PASSIVE CRYOGENIC WHOLE AIR FIELD SAMPLER

Effectiveness of Porous Glass Elements for Suction Lysimeters to Monitor Soil Water for Organic Contaminants

by
Stanley M. Finger, Hamid Hojaji,
Morad Boroomand, and Pedro B. Macedo
Vitreous State Laboratory
Catholic University of America
Washington, DC 20064

ABSTRACT

The objective of this effort is the development of a porous glass suction lysimeter which can be used to sample organic contaminants associated with unsaturated soil matrices. Current ceramic suction lysimeters are ineffective in sampling hydrophobic compounds since their surface chemistry is hydrophilic, effectively repelling organic species.

Methods for preparing porous glass elements with controlled porosity have been developed. Elements with air entry values (as measured by the bubbling pressure method) corresponding to effective pore sizes as small as 2 microns with high saturated hydraulic conductivities have been achieved.

The performance of porous glass elements in sampling organic contaminants in aqueous media is being evaluated. Aliphatic (1-octanol) and aromatic (ethylbenzene) compounds dissolved in water were used as the tests solutions. Tests are also being performed with inorganic constituents in the test water to determine the ability of the test elements to sample inorganics. Initial results indicate that the porous glass elements are able to effectively sample organic and inorganic constituents in the test solutions. These data indicate that analyte concentrations in the water sampled through the porous glass elements are within about 10% of the test solution concentrations.

BACKGROUND

The U. S. Environmental Protection Agency (EPA) requires vadose zone monitoring at active land treatment and disposal facilities for hazardous wastes. The state of California has extended this requirement to practically all active and closed storage, treatment, and disposal facilities for hazardous waste, solid waste, and underground storage tanks. Routine analysis of samples collected with suction lysimeters is considered an important element in the vadose zone monitoring requirement. Most of the suction lysimeters in use now were developed for the agricultural industry to monitor leachate from crops. These data are used to program the application of fertilizers and soil amendments. Another device, the tensiometer, is used in conjunction with the suction lysimeter to monitor soil moisture; this information is used to program irrigation. This same equipment is now being used to monitor the land treatment of certain hazardous wastes, e.g. refinery separator sludge and wood preservative waste. Many of the components of interest in these wastes are organics and heavy metals.

The suction lysimeter's porous element, through which soil water is drawn under vacuum, has been purposely designed to be hydrophilic to facilitate the transport of the aqueous phase. Porous elements currently in use are most frequently ceramic. However, TFE-fluorocarbon, nylon mesh and alundum have also been used. The porous element is typically treated with acid and water to remove contamination and enhance hydrophilicity. Unfortunately, the resulting hydrophilic nature of the porous element presents an effective barrier to sampling of non-polar components. Organics, whether dissolved in the aqueous phase or existing as a separate phase are significantly under-sampled by existing suction lysimeters. One recent field study of soil-pore water sampling systems showed no correlation between organics found by sampling compared with analysis of soil cores (1). Additional studies have shown that xylene (2), DDT (3), and fecal coliform (4) are not effectively sampled by ceramic suction lysimeters. In addition, a number of inorganic parameters, heavy metals in particular, are also attenuated by ceramic suction lysimeters. Simultaneously, a number of inorganic constituents are leached from ceramic suction lysimeters into soil water samples. While TFE-fluorocarbon porous elements are less prone to significant adsorption or desorption of inorganics, they also under-sample organic components. Additionally, the large pore sizes of TFE media restrict their range of operation to wetter soils than can be sampled by ceramic suction lysimeters.

Ideally, a suction lysimeter should provide a sample which accurately represents the soil liquid phases at the sampling location. This would include all components, organic as well as inorganic, dissolved in the soil water and any non-aqueous, i.e. organic, phases. While sampling all components representatively, the lysimeter should also be inert so it does not leach any chemical species into the sample. To achieve this ideal goal, the porous element must be very stable over a wide range of aqueous and organic conditions and be neither hydrophilic nor hydrophobic. Such a perfect porous element is probably unachievable. However, elements made of porous glass could form the basis for approaching this goal. Porous glass elements can be formulated which are inert to organic and aqueous media over wide ranges of pH and dissolved components. Also, the surface structure can be controlled to moderate its hydrophilicity/hydrophobicity. This control can be achieved by modifying the composition of the glass, modifying the thermal processing of the glass, and, if necessary, by chemically treating the glass to incorporate desired chemical species on the surface. This paper describes the results of laboratory studies aimed at the development of porous glass elements for use in suction lysimeters to provide more accurate sampling of organic as well as inorganic species.

EXPERIMENTS WITH HIGH SILICA POROUS GLASS ELEMENTS

Preparation of the Elements

A series of porous glass discs were prepared from powdered high silica borosilicate glass by sintering. The solid state sintering mechanism for different glass systems is well-known and, to a large degree, applies to porous glasses. Densification and the resultant reduction in porous volume occurs in two separate regimes when high silica porous glasses, as used in this research, are sintered. The onset of the first stage starts above 750°C, at which point the micro-pores start to disappear. The driving force for this process is a reduction in the surface energy. Above 950°C, the second stage of sintering begins. In this stage, neck formation occurs between the individual grains of glass, affecting the macro-pores. It is important to control the overlap of the two stages, with more emphasis on the second stage since this stage controls the macro-porosity of the system.

A systematic study was conducted to evaluate the degree of densification when sintering powdered porous glass. The objective was to gain control over the pore structure of the elements for the porous glass suction lysimeter.

The porous elements were prepared by firing at different peak temperatures. The glass was held at the peak temperature for various times ranging from 30 to 90 minutes. Heating and cooling rates were maintained constant for all the samples. Densities of the resulting glass discs were measured and normalized against the density of the solid glass having the same composition (the density of solid high silica glass with 4-5% boron oxide is approximately 2.25 g/mL). The densification and fractional porosity as a function of firing temperature (60 minute firing time) are shown in Figure 1. As can be seen in this graph, porous glass powder sintered at 1200°C for 60 minutes achieves an 85% densification. A series of scanning electron micrographs, showing the structure of porous glass elements prepared at temperatures of 1100 and 1150°C for 60 minutes and 1200°C for 90 minutes are shown in Figures 2a-c. These micrographs visually show that the pore size and fractional volume decrease with increasing firing temperature and firing time.

Pore Size and Hydraulic Conductivity Measurements

Bubbling pressure, or air entry value, measurements were performed on the porous glass elements prepared. At first, a lucite disc holder was used. This worked well at low pressures but leaked at higher pressures. A second holder, made of stainless steel was prepared which worked well over the full range of pressures studied. Figure 3 shows both the lucite and stainless steel holders.

The pore size corresponding to the air entry value was calculated by the following equation:

$$d = 30\ Y/P \qquad (1)$$

where d is the pore size in microns, P is the bubbling pressure (the pressure at which air first comes through the porous disc) in mm Hg, and Y is the surface tension of water in dynes/cm at the temperature of the experiment. At room temperature, Y is 73.05 dynes/cm. It should be noted that the pore size measured by this procedure is an effective pore size; the actual pore sizes vary as can be seen in the scanning electron micrographs (Figure 2).

Air entry value measurements were performed on a number of porous discs prepared over a range of sintering temperatures and times. The results are plotted in Figures 4 and 5. In Figure 4, the effective pore size is plotted as a function of firing time at three different firing temperatures (1050, 1150, and 1200°C). Figure 5 shows the effect of firing temperature on effective pore size when the firing time is held constant at 60 minutes. These graphs clearly show that the pore size can be varied down to 2 microns (firing at 1200°C for 60 minutes).

The flow rate through a series of the porous glass elements was also studied. These data were used to calculate the hydraulic conductivity and determine the relationship between effective pore size and hydraulic conductivity. The same holder used to measure the air entry value was used to measure the flow rate. For these experiments, the flow was induced by maintaining a vacuum on the porous glass disc. The experiments were performed using a vacuum of 63.5 cm (25 in.) of Hg. The fluid used for these experiments was deionized water, which was drawn from a burette able to measure volume to 0.1 mL. The flow through each disc was measured for at least two runs and the results averaged.

Figure 6 shows the measured flow rate as a function of sintering temperature (60 minute firing time). It also plots the pore size against the same abscissa. This graph shows that as the sintering temperature increases, the flow rate decreases along with the pore size, as would be expected.

The hydraulic conductivity was calculated using the following equation:

$$K = (Q/t) * (L/A) * h \qquad (2)$$

where Q is the volume of water flowing through the element in time, t, L and A are the thickness and cross-sectional area of the element, respectively, and h is the pressure differential across the element. Figure 7 plots the hydraulic conductivity against pore size. The data indicate a linear relationship between hydraulic conductivity and effective pore size.

The hydraulic conductivity of the porous glass elements appear larger than that of ceramic suction lysimeter elements of the same pore size. For example, the saturated hydraulic conductivity of a Soilmoisture Corporation ceramic suction lysimeter with an air entry value of 1 bar (pore size 2.1 microns) is 3.36E-7 cm/s. Figure 7 shows the saturated hydraulic conductivity of a 2 micron porous glass element to be about 1E-5 cm/s, almost two orders of magnitude greater than the ceramic element.

A series of nominal 2 micron pore size elements were prepared. The measured pore size and hydraulic conductivities of the elements are reported in Table 1. The average pore size was 2.1 microns with a standard deviation of 0.8 micron. The average hydraulic conductivity was 1.8E-6 cm/s with a standard deviation of 0.6E-6 cm/s. The pore size and hydraulic conductivity of the elements range by a factor of about 2. The hydraulic conductivities of these elements are almost an order of magnitude higher than that of a comparable Soilmoisture Corporation ceramic suction lysimeter, although not as high as the porous glass element reported in Figure 7.

Sampling Efficiency

Experiments were performed to determine the permeability of the porous glass discs to inorganics dissolved in water. Inorganic test solutions contained sodium chloride, barium chloride, lead chloride, and potassium chromate. The results of these tests are shown in Table 2. For all tests, a 61.0 cm (24 in.) Hg vacuum was maintained across the elements. The concentration of the inorganics was measured by Direct Coupled Plasma (DCP) Spectroscopy. The table shows good correlation between the concentrations in the sample solution as compared to the test solution. The average ratio of sample to test concentrations was 0.88 with a standard deviation of 0.16.

Problems Observed

Several problems were observed with the borosilicate porous glasses used in the first set of experiments. One problem was that when the porous glass powder used to make the elements was exposed to air for extended periods (hours), the resulting elements were very fragile (they tended to crack easily). It was hypothesized that this could be due to the formation of internal cracks caused by drying or by formation of silica gel within the pores. This problem was resolved by keeping the porous glass powder in water until it was used to form the elements.

A second, more serious, problem was clogging of the elements over time. It was hypothesized that components of the glass were leaching into and precipitating in the interstices of the elements. To alleviate this problem, the porous glass was modified by the addition of zirconia to produce a more durable glass matrix. The results with this zirconia glass are reported in the following sections.

EXPERIMENTS WITH ZIRCONIA GLASS POROUS ELEMENTS

Preparation of the Zirconia Glass Elements

The composition of the porous glass powder used to make the test elements was modified by the addition of 4-5% zirconia. This modification was made to produce a more durable glass which would be more consistent and less likely to clog. The glass was prepared by sintering the powder at 1150°C for 60 minutes.

Pore Size and Hydraulic Conductivity

Table 3 provides the pore size and hydraulic conductivity measured on several elements of the zirconia glass. The consistency, in terms of pore size and hydraulic conductivity, among elements was much better than the earlier test elements. However, the pore size was approximately 3 microns. Revised heat treatments should be able to lower the effective pore size to the 2 micron range.

Sampling Efficiency

Experiments were conducted to determine the permeability of the porous glass discs to organics dissolved in water. Organics used in the test solutions were ethylbenzene and 1-octanol. For all tests, a 61.0 cm (24 in.) Hg vacuum was maintained across the elements. The concentration of the organics was measured with a Total Organic Carbon (TOC) analyzer.

The test organic solutions were prepared by carefully placing a layer of the organic chemical on top of a large beaker of water. The liquids were allowed to equilibrate over several days. The water in the bottom of the beaker was periodically sampled (without disturbing the interface between the two phases) and its TOC content measured. When the TOC content of the water became constant, it was carefully removed from the beaker so that no droplets of organics were entrained.

The evaporation of the organic component from the test solutions under vacuum was studied. Figure 8 shows the significant decrease in the TOC of the test 1-octanol solution as a function of time when the solution was kept under a 61.0 cm Hg vacuum. The data is linear when plotted against the square root of time, indicating that the rate of evaporation is controlled by the diffusion of organic to the surface of the liquid. A similar experiment conducted with ethylbenzene showed no decrease in TOC as a function of time. The difference in the rate of evaporation of the two compounds is due to the (a) their volatilities, and (b) their polarity. Since ethylbenzene is less volatile than 1-octanol, it evaporates at a slower rate. Also, since ethylbenzene is more polar than 1-octanol, it forms stronger hydrogen bonds with water molecules, also retarding its rate of evaporation.

This observation is very important in the development of a suction lysimeter for sampling organics in soil water. Organic components which tend to volatilize easily from aqueous solution could be lost due to evaporation. This problem can be corrected either through capture of the evaporated organics on an adsorbent, such as carbon. Alternatively, the TOC could be corrected mathematically using calibration data such as Figure 8. Capture and subsequent analysis of volatilized organics would obviously be a more desirable approach.

The performance of the zirconia porous glass elements in sampling organic solutions is summarized in Tables 4 and 5. The ability of the zirconia porous glass elements to sample the ethylbenzene solution was excellent. The difference between the TOC in test and sample solutions was always less than 3 ppm, a error of about 4%.

The tests conducted with the 1-octanol solution, Table 5, showed the effects of octanol evaporation. However, when the TOC measurements are corrected for the octanol evaporation using Figure 8, the results are quite good. For the 1 hour suction period used in these experiments, the correction factor is 1.36. This correction factor was used to generate the column of corrected TOC's in Table 5. The average value of the corrected TOC's is 305.0 ppm compared to 298.9 ppm TOC in the test solution. This represents only a 2% error.

Thus, these data, while limited, demonstrate an excellent ability to sample organic compounds in soil water.

CONCLUSIONS

This paper documents the significant progress being made toward the development of a porous glass suction lysimeter capable of sampling organic and inorganic constituents in soil water. The ability to make porous glass elements with pore sizes as small as 2 microns with high hydraulic conductivity has been demonstrated. Also, initial experiments indicate that the elements can accurately sample organics and inorganics in water. Work is continuing to optimize the preparation, including the composition and thermal treatment, of the porous glass elements and to develop a comprehensive set of data on the ability of the optimized porous glass elements to accurately sample soil water.

Future work will evaluate optimized porous glass elements with simulated and real soils, leading to the development of a suction lysimeter using porous glass elements.

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Table 1
Pore Size and Hydraulic Conductivity of Porous Glass Elements

Element	Pore Size, microns	Hydraulic Conductivity cm/s
1	2.3	1.9×10^{-6}
2	2.1	1.6
3	3.5	2.8
4	3.5	2.6
5	2.3	1.2
6	1.6	1.2
7	1.1	1.2
8	2.3	1.2
9	1.9	1.6
10	1.3	2.5
11	3.5	2.6
12	1.2	2.6
13	1.6	1.2
14	1.6	1.4
Mean	2.1	1.8×10^{-6}
Std. Dev.	0.8	0.6×10^{-6}.

TABLE 2

TESTS WITH INORGANICS IN AQUEOUS MEDIA

Inorganic	pH	Test Concentration (ppm)	Sampled Conc. (ppm)	Ratio
NaCl	7.0	196	206	1.05
	7.0	196	198	1.01
$BaCl_2$	1.8	69.4	67.5	0.97
	1.8	69.4	66.1	0.95
$PbCl_2$	4.4	102	66.4	0.65
	4.4	102	63.6	0.62
$K_2Cr_2O_7$	6.2	94.7	81.9	0.86
	6.2	94.7	91.1	0.96
			MEAN	0.88
			STD. DEV.	0.16

TABLE 3

PORE SIZE AND HYDRAULIC CONDUCTIVITY OF ZIRCONIA POROUS GLASS ELEMENTS

Pore Size, microns	Hydraulic Conductivity, (cm/s)
3.0	7.4 E-06
3.0	7.6 E-06
2.8	7.4 E-06
3.0	5.4 E-06
3.0	5.3 E-06

TABLE 4

SAMPLING OF AQUEOUS ETHYLBENZENE SOLUTIONS

Porous Glass Element	Total Organic Carbon, ppm	
	Test Solution	Solution Sampled
1	72.95	74.83
2	72.95	72.02
3	72.95	75.92
4	72.95	78.48
5	79.07	76.83
6	79.07	76.11
7	79.07	78.68
8	79.07	78.94

Table 5

Sampling of 1-Octanol Solutions

Porous Glass Element	Total Organic Carbon, ppm		
	Test Solution	Solution Sampled	Sample Corrected for Evaporation
1	298.85	214.2	291.3
2	298.85	211.6	282.8
3	298.85	209.6	285.1
4	298.85	247.0	335.9
5	298.85	220.8	300.3
6	298.85	230.4	313.3
7	298.85	236.2	321.2

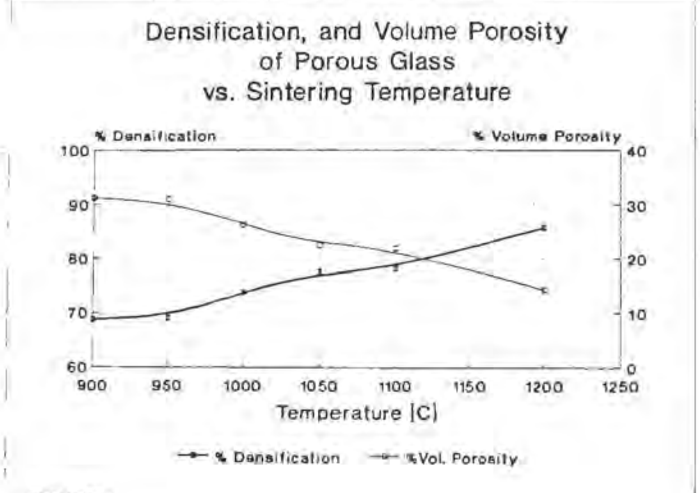
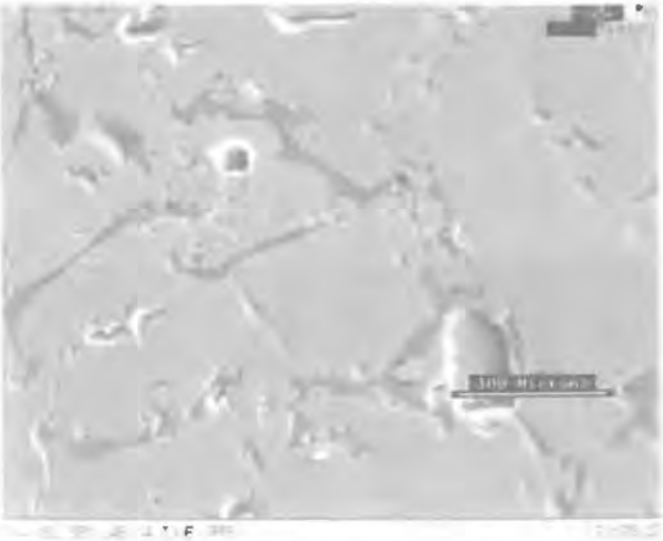

Densification, and Volume Porosity
of Porous Glass
vs. Sintering Temperature
% Densification
% Volume Porosity
100
90
80
70
60
40
30
20
10
0
900
950
1000
1050
1100
1150
1200
1250
Temperature [C]
% Densification
%Vol. Porosity

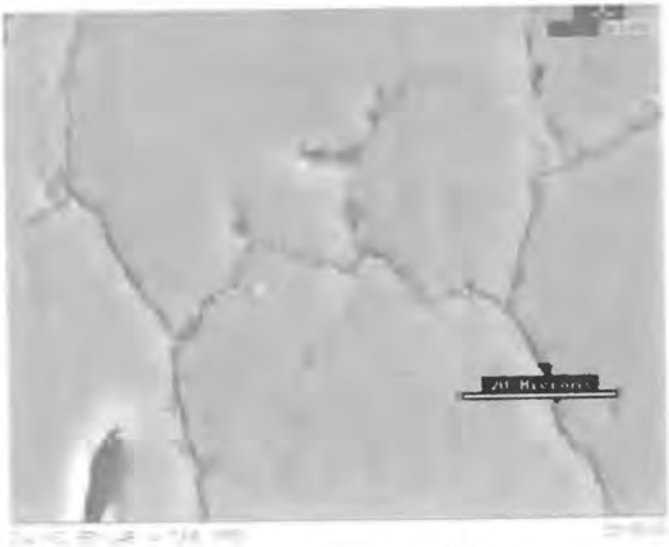
FIGURE 1

FIGURE 2A
Scanning Electron Micrographs of Porous Glass Lysimeter Elements



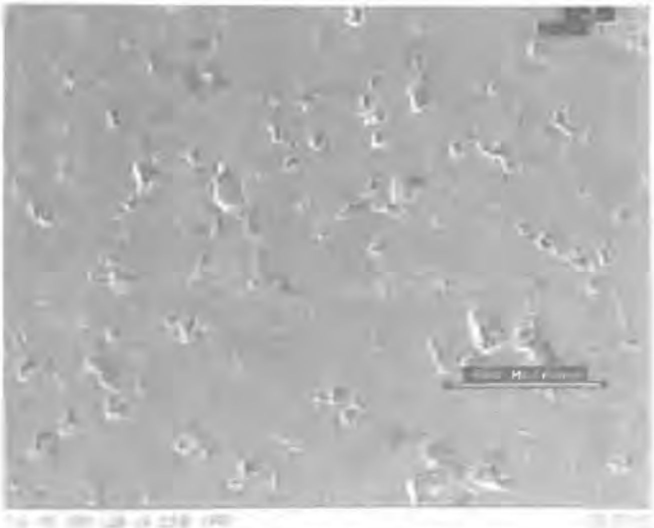
Firing Temperature: 1100° C
Firing Time: 60 minutes

Firing Temperature: 1150° C
Firing Time: 60 minutes



Firing Temperature: 1200° C
Firing Time: 60 minutes

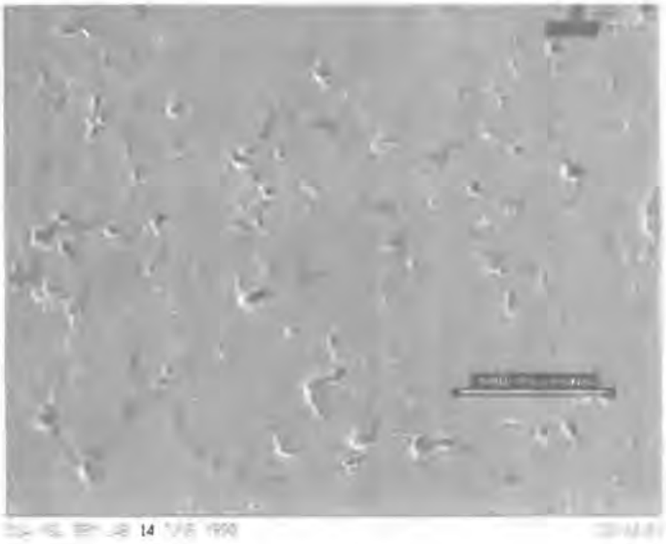
FIGURE 2B
Scanning Electron Micrographs of Porous Glass Lysimeter Elements



Firing Temperature: 1150° C
Firing Time: 60 minutes

Firing Temperature: 1100° C
Firing Time: 60 minutes

FIGURE 2C
Scanning Electron Micrographs of Porous Glass Lysimeter Elements



Firing Temperature: 1200° C
Firing Time: 60 minutes

FIGURE 3

Lucite and Stainless Steel Holders for Porous Glass Elements

(Scale: heavy grid lines are one inch apart)

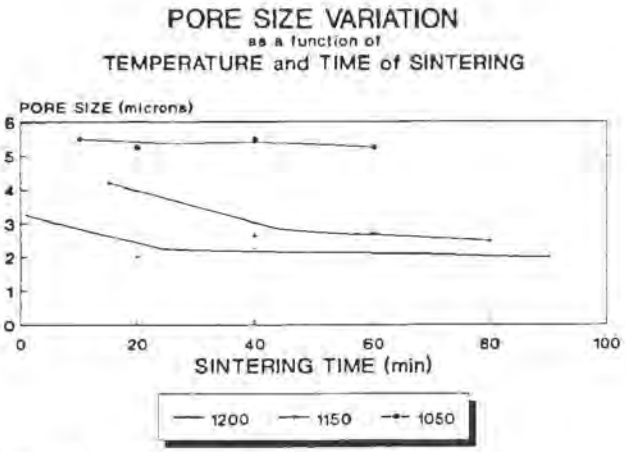


FIGURE 4. Pore size was measured by the technique.

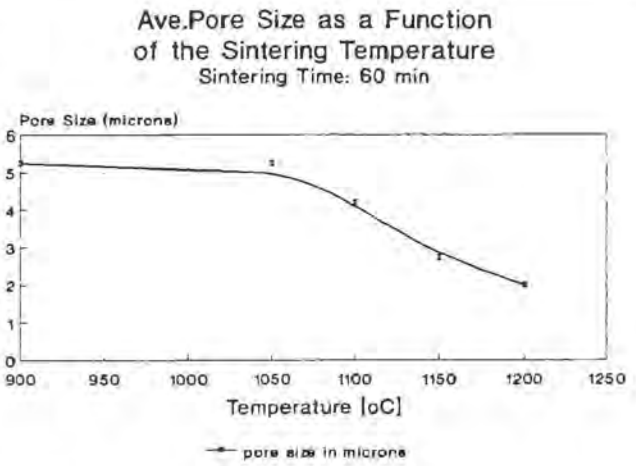


Figure 5

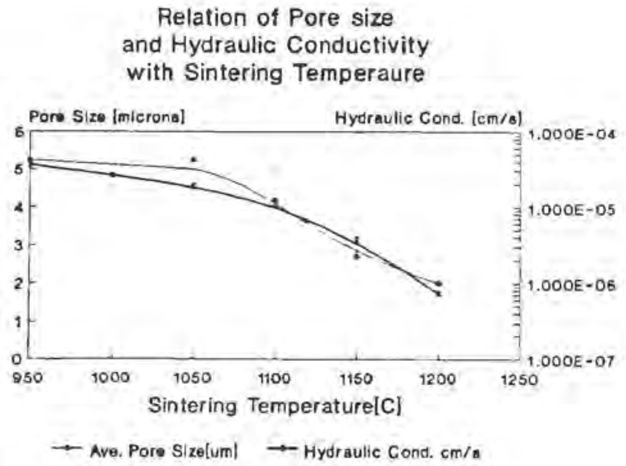


FIGURE 6

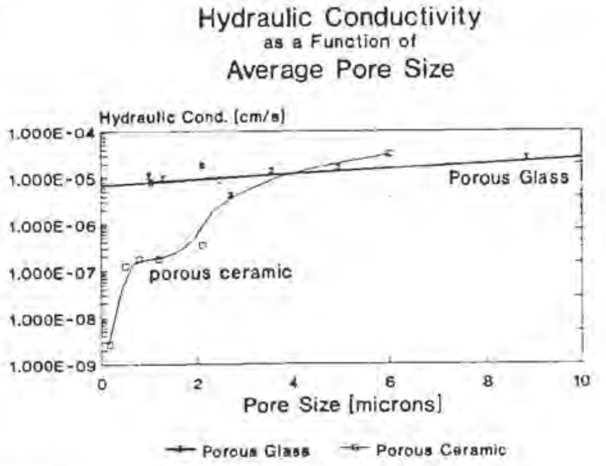


FIGURE 7

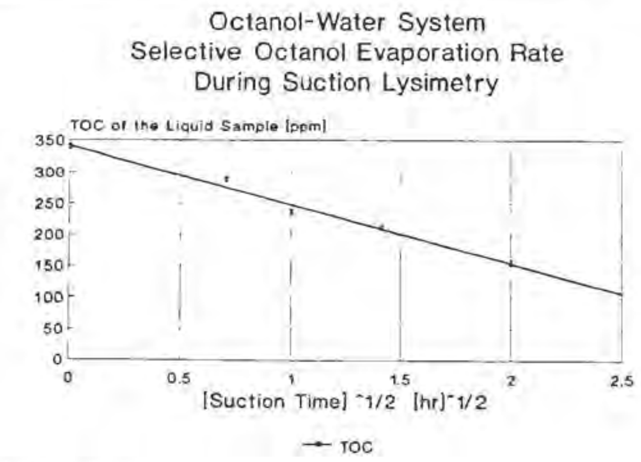

Octanol-Water System
Selective Octanol Evaporation Rate
During Suction Lysimetry
TOC of the Liquid Sample [ppm]
350
300
250
200
150
100
50
0
0
0.5
1
1.5
2
2.5
[Suction Time] ^1/2 [hr]^1/2
TOC

FIGURE 8

Second International Symposium

FIELD SCREENING METHODS FOR HAZARDOUS WASTES AND TOXIC CHEMICALS

February 12–14, 1991

Symposium Proceedings

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