On-line SFE/GC for Improved Detection of Trace Organic Pollutants in Ground Water Monitoring

Co-funded by
Department of Agriculture, Trade, and Consumer Protection
(DATCP Pesticide Research Contract 98-02)
and
University of Wisconsin Water Resource Institute
(99-SAM-3)

Final Report
November 29, 2000

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This project was supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.

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IV. Project Summary

Title: On-line SFE/GC for Improved Detection of Trace Organic Pollutants in Ground Water Monitoring

Project ID: DATCP 98-02, UWS (no number specified)

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Co-Principal Investigator: Dr. Robert J. Noll, Post-Doctoral Research Associate, Water Chemistry Program, University of Wisconsin-Madison; Current Position: Assistant Professor, Chemistry Department, Lawrence University, Appleton, Wisconsin.

Period of Contract: July 1998-Sept 1999

Background/Need: Scientists need to measure environmental pollutants with greater accuracy and with lower limits of detection.

Objectives: To improve the detection of trace organic contaminants in ground water by developing a new approach to concentrating sample analytes (on-line SFE/GC) while minimizing interferences.

Methods: Optimize the quantitative transfer of analytes from a supercritical fluid extractor (SFE) to a gas chromatograph (GC). SFE will be conducted on sorbents, such as XAD-2 or Tenax which have pre-concentrated contaminants from water matrices. An SFE/GC interface was constructed. This consisted of an independently controlled trap. A sorbent (such as Tenax) trapped analytes from the supercritical fluid extractor. Subsequent heating of the trap would desorb the analytes into a stream of chromatographic carrier gas and into the gas chromatograph (GC). A chromatographic separation could then be carried out.

Results and Discussions: The trap and SFE/GC interface was constructed. Testing of the apparatus showed that massive interferents resulted from a key valve controlling both supercritical fluid flow and chromatographic carrier gas flow. The valve also served as a sink for analytes during transfer from the trap to the GC.

Conclusions/Implications/Recommendations: This method may still be feasible with modifications. These include replacing the old valve with a Valco-type two-position, multiport valve; better and automatic temperature control of heated and cooled regions of the interface; using a commercial cryotrap at the head of the GC column; shortening transfer lines; using more inert materials for transfer lines; and improving flow control of the desorption gas and chromatographic gas.

In addition, other workers (Stone and Taylor, 2000, *Anal. Chem.,* **72:** 3085-3092) have successfully demonstrated a slightly different approach, involving the direct trapping of analytes from a supercritical fluid stream into the stationary phase of a gas chromatographic column. We recommend pursuing this method, except for where the highest level of chromatographic resolution would be required.

Finally, SFE/GC of water sampling sorbents may not be the best method for sampling water matrices for pollutants. Instead, Solid phase micro-extraction (SPME) and head space-SPME (HS-SPME) may be better methods. SPME realizes the main benefits of SFE but is less expensive. HS-SPME may more easily and effectively discriminate against ubiquitous interferents such as lipids. We recommend that future work concentrate on optimizing SPME-based methods

Related Publications: None

Key Words: PCB's, polychlorinated biphenyls, surface water, XAD, Tenax, SFE, supercritical fluid extraction, GC, gas chromatography, ECD, electron capture detection,

Funding: DATCP, UWS

V. Introduction

Human and ecosystem health effects are being attributed to increasingly lower levels of toxic contaminants like pesticides and their metabolites. To better understand and manage the fate and transport of toxic compounds, scientists need to measure contaminants with greater accuracy and at still lower levels. This project seeks to improve the detection of trace organic contaminants in ground water by developing a new approach to concentrating sample analytes while minimizing interferences.

A. History of Problem

Supercritical fluid extraction (SFE) involves exposing a sample to a supercritical fluid (a substance at pressures and temperatures above its critical point), which extracts the analyte from the matrix. A supercritical fluid can penetrate the matrix like a gas, but has the solvation capability of a liquid (Hawthorne, 1990). The most commonly used supercritical solvent is CO_2. In "off-line" SFE, the supercritical fluid/analyte extract is then directed to a sorbent trap, where the pressure is released and the CO_2 dissipated. The analyte is then washed from the trap with a minimum (5 mL) of organic solvent. SFE extraction efficiency is comparable to, and often exceeds, conventional Soxhlet extraction (Bowadt 1995). SFE is 10-50 times faster and eliminates organic solvents and their attendant safety and disposal concerns.

Our work involves modifying an existing method for determining trace quantities of chlorinated pesticides and PCB's in water (Method 1293, Wisconsin State Laboratory of Hygiene, 1996) for use with SFE. The conventional method of sampling water involves drawing either 80 or 160 liters of water per sample through XAD-2 absorbent resin, which concentrates hydrophobic compounds dissolved in the water. Subsequently, the analytes are Soxhlet extracted from the resin.

Previous studies demonstrated efficient SFE of various analytes from different sorbents. Tang, et al. (1993) extracted seven PCB congeners from C_{18} sorbent using off-line SFE (70%-99% recovery). The PCB's were spiked into reagent water at 2 ug/L each, roughly 100 times greater than typical environmental concentrations (Fachetti, 1993). In the same study, several pesticides, including hexachlorobenzene, DDE, DDT, Lindane, chlordane and endrin, also at 2 ug/L in reagent water, were extracted with recoveries between 70% and 154%. Bengtsson et al. (1994) recovered dimethoate, lindane, cyanizine, metazachlor, DDE, fenvalerate and trichloronat, spiked at sub-part per billion levels (ppb) in water, from C_{18} in yields ranging from 35%-131%. Tang and Ho (1994) extracted nitrated and chlorinated phenols from reagent water (1 ug/L) with optimized recoveries ranging between 79% and 104%. Both SDB and C_{18} sorbents were tested. Finally, using on-line SFE/GC, Slack et al. (1993) extracted explosives (e.g., trinitrotoluene) from spiked river and well waters at sub-ppb levels.

Current practice for both Soxhlet extraction and "off-line" SFE usually involves injecting 1-5 uL out of 1-5 mL total extract volume into the gas chromatograph (GC) for quantitation, using only ~0.1% of the extracted analyte. In contrast, our aim is to direct the entire amount of extracted analyte, still dissolved in the supercritical solvent, into the GC, thereby increasing method sensitivity nearly 1000-fold. Smaller sample sizes, or lower detection limits, would result. There are two main strategies for interfacing a supercritical extractor with a gas chromatograph for quantitative transfer of all analytes.

The first strategy is to route the supercritical fluid containing the analytes directly onto the GC column, analogous to a cold on-column injection. The SFE restrictor is inserted through the injection port of the gas chromatograph and into the GC column. The GC oven can be cooled, allowing cryofocussing of the analytes onto the stationary phase of the column. Although

promising, the method has several drawbacks. First, only very low flow rates, compatible with a capillary GC column, are possible (~0.1 mL fluid/min or ~50 mL gas/min). In turn, these flow rate constraints will limit SFE extraction pressures, preventing optimal extraction when higher SFE pressures are needed. Second, without additional sample handling for cleaning, this method can introduce water, modifiers and co-extracted contaminants (e.g. lipids) to the GC column, causing contamination of the column and chromatographic problems.

The second strategy involves routing the supercritical fluid containing the analytes into an external trap containing a sorbent. After deposition, the trap is heated, allowing for the thermal desorption and cryofocussing of the analytes on the GC column. It is the most general strategy and will allow the most flexibility in sample type, analyte, and SFE conditions. First, it will allow for complete transfer of analytes to the GC column, thus ensuring that the important sensitivity and detection limit advantages of on-line SFE/GC can be realized. SFE flow rate and pressure constraints should be much less severe because the flow capacity of the trap, not the GC column, will determine the flow rate. This will allow the most flexibility, because previously optimized extraction procedures can be quickly adopted without modification. The position of the trap before the GC column will also allow for more options in controlling matrix contaminants (water, modifiers, lipids). For example, trap sorbents can be chosen for their retention of particular contaminants and interferents.

B. Purpose of the Investigation

The ultimate purpose of this investigation is to improve the detection limits of trace quantities of ground water contaminants, including various non-volatile chlorinated hydrocarbons and chlorinated pesticides and their metabolites. To achieve that goal, we will develop a method to interface supercritical fluid extraction with gas chromatography.

C. Basic Scheme of Procedure and Methods

We constructed an inexpensive home-built trap based on designs in the literature. The design features a deposition/desorption trap backflushed by chromatographic carrier gas and a separate cryotrap for refocussing analytes at the head of the chromatographic column. Our plan was to demonstrate analyte transfer from the trap to the GC and then from an empty SFE cell to the GC (via the trap). Finally, if time permitted, sorbents loaded with analyte (either by directly spiking or by extracting analytes from artificial or real samples) would be extracted by SFE and the analytes transferred to the GC via the trap.

VI. Procedures and Methods

A. Trap Design

The overall design of the interface is depicted in Figure 1 and the trap is shown in Figure 2. Numbers in square brackets refer to numbered items in Figure 1. During supercritical fluid extraction, CO_2 flows from the extractor through a heated fused silica restrictor (10-50 um ID, Polymicro Technologies, Phoenix, AZ) [2], which sets the SFE flow rate. The restrictor is sheathed by a stainless steel tube [3], which can be heated to 150^{o}C. The restrictor is joined by a union [4] (Valco P/N ZU1XC, 0.15 mm bore, with reducing ferrule for fused silica restrictor, Valco P/N FS1.4-5) to a stainless steel tube [5]. Fluid flows into a two-stem, three-way valve [6] (High Pressure Equip. Co., Erie, Pa.) P/N 15-15AF2) and then into the sorbent trap [7] (25 cm, 1/8" OD stainless steel, filled with Tenax A, P/N 21059-U, Supelco, Bellefonte, PA.) or into a much smaller model trap filled with glass wool. The regular trap can be cooled during deposition of the analytes. The CO_2 exits the system through a three-way valve [8] (Whitey, P/N B-41X-S2), slightly downstream of the trap.

The analytes are deposited in the trap by the first step, or "SFE step". During the first step, chromatographic carrier gas (H_2, 99.999% purity, inlet pressure 12 psig, velocity 50 cm/s) is routed by a three-way valve [10] through the normal carrier-gas line into the injection port of the gas chromatograph. In the second step, or "desorption step", the chromatographic carrier gas is routed by the three way valve [10] to backflush and desorb the analytes from the trap into the cryotrap [14] at the head of the gas chromatograph's column.

The carrier gas flow is regulated by a micrometer valve [9] (Nupro P/N SS-SS 2) before flowing into the trap, because the carrier gas flow needed for normal operation of the GC is optimized for flow into the injector port (~100 mL/min). The carrier gas flow (with desorbed analytes) should emerge from the trap at a flow rate similar to that which actually goes through the chromatographic column (3 mL/min).

After emerging from the trap, the carrier gas and entrained analytes go through valve 6, and into a fused silica transfer line (150 um OD, 100 um ID, Polymicro Technologies) inserted completely through the GC injector port [13] and several cm into the chromatographic column [14]. The transfer line and union [11] (Valco) are enclosed by a short section of 1" OD steel tube, which was also wrapped with heating tape and glass wool. During backflushing, the trap can be heated up to 400 C.

A portion of the chromatographic column has been coiled separately to serve as a cryotrap [14] to re-focus the analytes as they are desorbed from the deposition trap. The cryotrap can be immersed in a cryogenic liquid. After a suitable waiting time (determined by separate experiments) for desorption of analytes from the trap, the cryotrap is warmed, the GC temperature program is commenced, and the cryofocussed analytes are chromatographed. Separate testing of the cryotrap with injected standards of PCB's showed 70-80% peak areas versus standard injections.

The gas chromatograph is a Hewlett-Packard 5890, with a DB-5 column (J&W, 30 m, 250 um ID, 0.25 um film thickness), and an ^{63}Ni electron capture detector. The detector was held at 330°C and makeup gas (N_2) flow rate was 26 mL/min. The temperature program was: 35°C, increase 20°C/min to 300°C, hold at 300°C for 1.75 minutes. The injector port temperature was 300°C. Conventional injections were splitless with 1.00 minute purge delay. The temperature program was performed as step 12 in the program listed below.

B. Testing of Trap

The first step in proving that the interface works is to quantitatively recover analyte spiked into the Tenax trap. A "model trap" was constructed first, to see if we could recover analyte from the trap without the additional complication of finding the exact conditions needed to elute analytes from the Tenax.

The model trap has two 1/8" to 1/4" inch Swagelok unions as endcaps. The body is a 3" stainless steel tube, 1/4" OD, swaged into the unions. The trap was plumbed into the interface system exactly as the Tenax trap would be. 1/8" OD stainless steel tubing brings the chromatographic carrier gas in from the top; analytes and carrier gas exit through the bottom of the trap. A small amount of glass wool, previously ashed at 450 °C and then washed with hexane and acetone, was placed into this trap. The trap (with the glass wool) was baked out several times at high temperature until the chromatogram baseline was flat.

The glass wool was spiked directly with 2 uL of a four congener mix of PCB's in hexane (PCB 1, 154.9 ng/mL; PCB 30, 17.60 ng/mL; PCB 155, 12.68 ng/mL; PCB 204, 9.70 ng/mL). Spiking was accomplished by removing the top of the trap and injecting the solution from above.

The top was reconnected and hydrogen carrier gas (30-40 mL/min, flow established by pre-calibration of the micrometer valve, valve 9, Figure 1) was routed to flush the trap.

The following series of steps were carried out for the recovery experiments:

1. Bring GC oven to 35°C
2. Spike sample into trap
3. Switch flow through trap; keep trap at room temperature
4. Blow H_2 through trap for 1 minute, volatilize solvent.
5. Close flow through trap
6. Cool cryotrap with liquid nitrogen (or ice water)
7. Put flow back through trap
8. Heat trap to high temperature, keep at temperature for a specified duration
9. Allow trap to cool
10. When trap has sufficiently cooled, switch flow back through GC
11. Remove liquid nitrogen from cryotrap
12. Close GC oven door, run chromatographic temperature program

VII. Results and Discussion

A. Normal Chromatographic Conditions

Figure 3 shows a chromatogram of the four congener PCB standard, using conventional injection of 2 uL of standard. The PCB congeners elute in the order 1, 30, 155, 204.

B. Recovery of PCB's from model trap

Figure 4 shows an attempt to recover the PCB congeners with the above program. In step 8, the trap was heated to 180°C and held for 14 minutes, but no PCB congeners were recovered. However, after heating the trap to 295°C and holding for 20 minutes, PCB congeners 1 and 30 were recovered, as shown in Figure 4. Our assignment of the peaks at 6.89 and 7.81 minutes is tentative because these retention times do not exactly match those under normal injection conditions (7.37 and 8.97 minutes, respectively).

The assignment seems likely for two reasons. First, trap contaminants can probably be ruled out. It seems unlikely that random trap contaminants would elute as sharp peaks, and during the previous run the trap had been baked out to 290°C. Moreover, expected trap contaminants, such as residues of machine oil and solvents, are not particularly ECD responsive. Secondly, the fused silica line had been inserted about 10 cm into the chromatographic column. This would deposit the analytes slightly downstream of where they would be deposited in a conventional (i.e., solution) injection, slightly decreasing their retention times. Retention times could be even further shortened if cryotrapping were not efficient.

After acquiring the chromatogram in Figure 4, the trap was again heated, this time to 400°C, and held for 30 minutes. The cryotrap was cooled to 0°C. Two prominent peaks are evident in the resulting chromatogram, shown in Figure 5.

The first prominent peak, at 8.82 minutes, could be PCB 155, although it is fully two minutes earlier than 10.84 minutes, the retention time under conventional injection conditions. On the one hand, it is reasonably sharp and more prominent than the surrounding peaks. PCB 155 may have been inefficiently cryotrapped at 0°C and blown significantly downstream before finally being focused in the stationary phase.

PCB 204 may be the other prominent peak, at 12.64 minutes. This corresponds to 204's retention time under standard injection conditions. Cryofocussing of this analyte, with its higher chlorine content and thus lower volatility, may have been much more efficient at 0°C.

C. System Interferents

Unfortunately, numerous additional attempts to reproduce and improve upon the results of Figures 4 and 5 were unsuccessful. Thus, the model trap was replumbed to shorten the path the analytes would travel and to prevent cold spots in the transfer line where analytes might recondense. The new plumbing scheme is depicted in Figure 6. The chromatographic column was brought up through the injector port and septum nut and connected directly into the Valco union below the two-stem, three way valve [6 in Figure 1]. This eliminated the fused silica transfer line, which was "unsiliconized" and whose inner surface may have strongly retained analytes.

Additionally, the two-stem, three way valve was turned upside down. During desorption, carrier gas would flow through the trap as previously. However, during chromatographic operation, carrier gas was brought through a bypass line parallel to the trap. The valve, trap, and transfer line were wrapped with heating tape. The temperature program followed was slightly different than before: initial temperature 35°, then 10°/min to 110°, hold for 5 min; then 20°/min to 300°, hold until no further peaks eluted. The injector port and trap were heated to 300° and the cryotrap was cooled by liquid nitrogen.

Chromatograms obtained with this new setup had large, broad peaks eluting between 19 and 28 minutes, although we do not believe that these peaks were PCB's. (Chromatograms not shown.) Peak elution temperatures do not match those from the temperature program used for conventional injection and peak broadening does not follow a systematic pattern.

The manufacturer of valve 6 (High Pressure Equipment Company, Erie, PA) confirmed that the valve's teflon packing could migrate into the wetted area of the valve, especially if the valve was heated beyond its high temperature rating (232°C). Originally, it was anticipated that the temperature would not exceed 180°C (maximum temperature for the Tenax). However, since much higher temperatures apparently were needed to recover the analyte from the model trap and the valve had been subjected to these temperatures, we decided to check whether the valve was the source of the contamination.

In Figure 7 are a series of chromatograms which show the effect of heating the valve. For these chromatograms, hydrogen carrier gas was flowed through the trap bypass (as shown in Figure 6) while the valve was heated. The continued presence of contaminants indicates that they must have originated externally to the trap—most likely from the valve. Additionally, the contaminant level increases with temperature. The contaminants appear as a series of resolved compounds, perhaps from a homologous series. The valve packing is teflon, poly(tetrafluoroethylene). Thermolysis of high molecular weight polymers usually yields a series of oligomers (viz., a homologous series). Fluorinated compounds will be very ECD responsive. We conclude that the valve is the source of the contaminants.

D. Future Directions based on SFE/GC

Although valve 6 offered superior combined resistance to both high temperatures and high pressures, its teflon packing is the source of chromatographic interferents and also a sink for analytes. We recommend replacing this valve with a two-position, six port valve, available from Valco Instruments Company, Houston, TX. Valco valves are used extensively in SFE and GC applications. They have low volume (uL) pathways, which reduce carry-over between samples. Model #C6WEY (used in our Suprex Model Prepmaster SFE) has a stainless steel body and a valve rotor made from Valcon, an inert polymer. Temperature and pressure ratings (100-125°C at pressures up to 7000 psi, up to 225°C at lower pressures) are somewhat lower than the current valve, but are still acceptable for extracting PCB's from sorbents.

Control of heated and cooled zones should be automated. First, the SFE restrictor should be heated to prevent clogging. Our Suprex Prepmaster extractor can monitor the restrictor temperature. Second, the Valco valve should be housed in its own oven (available from Valco), controlled by the auxiliary temperature card on the HP GC 5890 chromatograph. Third, a real cryotrap should be obtained (e.g., Model 971 Microcryotrap from Scientific Instrument Services, Ringoes, NJ). These cryotraps are only 1 inch long and cost about $3000 for the trap, electronic controller, and installation kit. Fourth, transfer lines, including the SFE restrictor, must be better heated, shortened and lined with stainless steel or siliconized fused silica for the most inert surfaces.

Carrier gas flow control for desorbing analytes from the trap needs drastic improvement. The micrometer valves used (Nupro, Willoughby, OH) did not indicate nominal gas flow (we counted turns from fully closed, which was very awkward). We recommend using a mechanical flow controller with an attached dial or counter for indicating nominal gas flow, such as Condyne Model FC 22SS1K (available from Valco Instruments) or Brooks Model 8744 Flow Controller.

Finally, we note a recently published paper by Stone and Taylor. (2000) Using a combination of 3 Valco valves, they routed the flow of CO_2 (and dissolved analytes) from an SFE directly into the analytical column of a GC. A 4 step program was used. In the first step, the GC column was pre-pressurized with 6.8 atm head pressure of CO_2. A high pressure of CO_2 in the column reduces the extent of expansion that occurs upon depressurization of the supercritical fluid stream. In turn, this decreases the flow rate of the depressurizing CO_2, promoting more efficient transfer of analytes into the stationary phase of the chromatographic column. In the second step, the sample is extracted by SFE. The supercritical CO_2 and analytes are directed into the analytical column and the analytes are trapped. Special metal jacketed capillary columns, which can withstand the higher pressures, are used (Restek, Bellefonte, PA). In the third step, the column is depressurized and vented of CO_2. In the fourth step, carrier gas (He) is flowed through the analytical column and the previously trapped analytes are separated as in a normal chromatographic separation.

SFE extraction was performed at 400 atm. pressure and 95°C, similar to conditions for extracting sorbents. A 2 mL extraction cell was filled with sand and spiked with non-polar or non-polar analytes at 10-50 ppb. A crimped, stainless steel restrictor set the flow rate of supercritical fluid at 0.7 or 2.2 mL/min. Recoveries of 92-101% (vs. direct chromatographic injection) were obtained. The system could also handle small amounts (2%) of water. This method could be realized straight-forwardly with our equipment (Suprex Prepmaster SFE and HP-5890 GC) and the purchase of siliconized transfer lines and a Valco Valve and oven.

E. Future Directions Based on Solid Phase Micro-Extraction

Although interfacing the SFE and GC still appears feasible, the author (RJN) believes that SFE/GC of sorbents is not the best method to sample water for trace organic pollutants. Rather, solid phase micro-extraction (SPME) is superior. SFE/GC should be reserved for solid matrices like sediments and tissues.

SPME (Arthur and Pawliszyn, 1990) involves immersing a fused silica fiber (1 cm) coated with a gas chromatographic stationary phase 7 um thick) into the liquid sample. Analytes then partition into the coating. Parameters such as sampling time, sample pH, salinity, temperature and stirring or agitation affect the results. After sampling, the fiber is withdrawn and inserted into the injection port of gas chromatograph. There, the analytes are desorbed during a short interval (5 minutes) and then chromatographed. In a variant known as head space-solid phase

micro-extraction (HS-SPME), the fiber is not immersed in the liquid sample, but samples analytes in the head space above the sample.

Both methods appear highly feasible for sampling a wide variety of pollutants from water matrices. Several Supelco Application Notes (SAN) and other reports from the literature are summarized in Table 1. Limits of detection (LOD) appear compatible with environmental concentrations of contaminants. Interferents can often be excluded by using HS-SPME.

Finally, we note that SPME realizes the main benefits of SFE: elimination of waste organic solvents, decreased extraction times, and extraction efficiencies and detection limits comparable to traditional extraction methods. In addition, SPME is less expensive than SFE ($400 vs. $10,000 for least expensive commercial SFE unit), and HS-SPME may more easily and effectively discriminate against ubiquitous interferents such as lipids. We recommend that future work concentrate on optimizing SPME-based methods.

VIII. Conclusions and Recommendations

1. The external trapping method attempted in this study was unsuccessful. A critical valve was both the source of overwhelming interferents and a sink for analytes transferring to the GC.

2. Our method may be feasible with modifications. These include replacing the valve with a Valco valve; automatic temperature control of heated and cooled regions; using a commercial cryotrap at the head of the GC column; shortening transfer lines; using inert materials for transfer lines; and improving flow control of the desorption gas and chromatographic gas.

3. Other researchers have successfully demonstrated the direct trapping of analytes in the chromatographic column. We recommend following this approach in future work.

4. SPME and HS-SPME are the best methods for extracting analytes from water matrices. SPME realizes the main benefits of SFE and is less expensive. HS-SPME may more easily and discriminate against interferents. We recommend that future work concentrate on optimizing SPME-based methods.

5. SFE/GC should be reserved for solid matrices like sediments and tissues.

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Figure 1. SFE/GC interface design

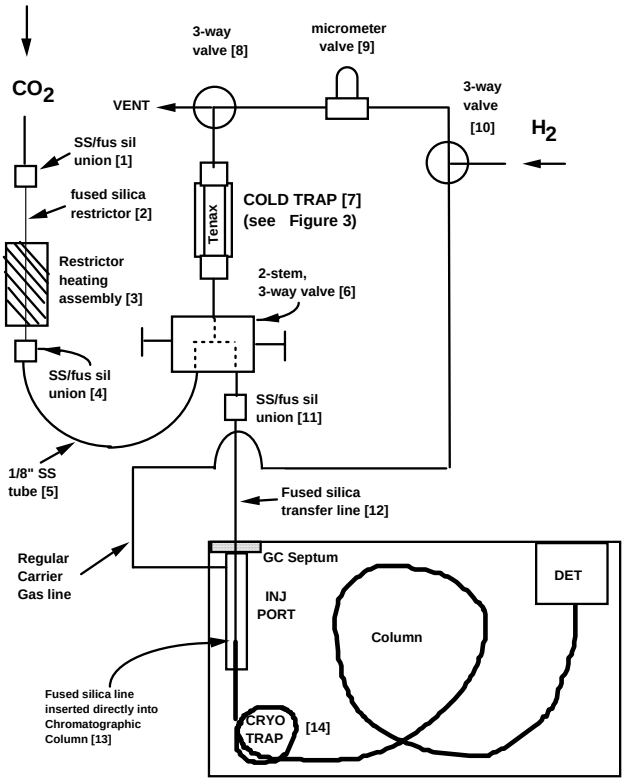

Figure 2. Analyte trap

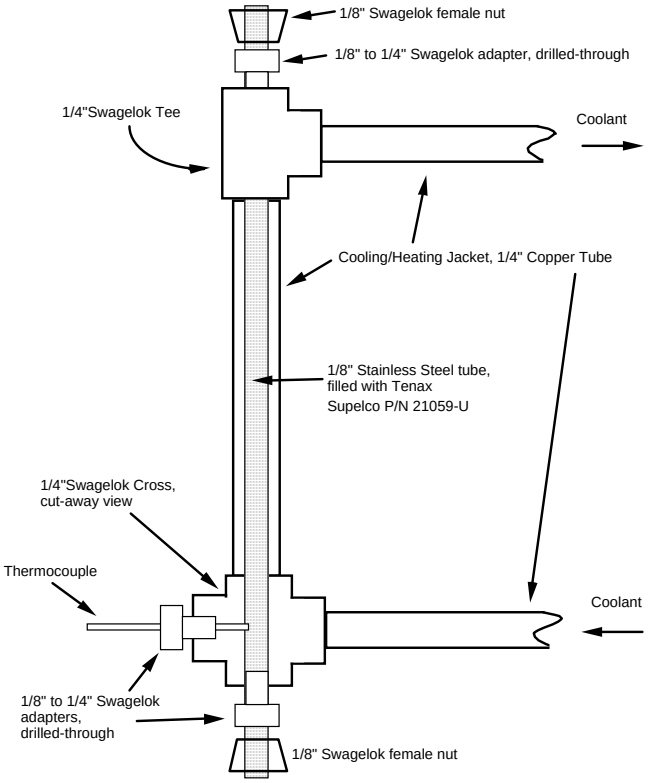

Figure 3. Chromatogram of PCB congener standard 1, 30, 155, 204, under normal injection conditions.

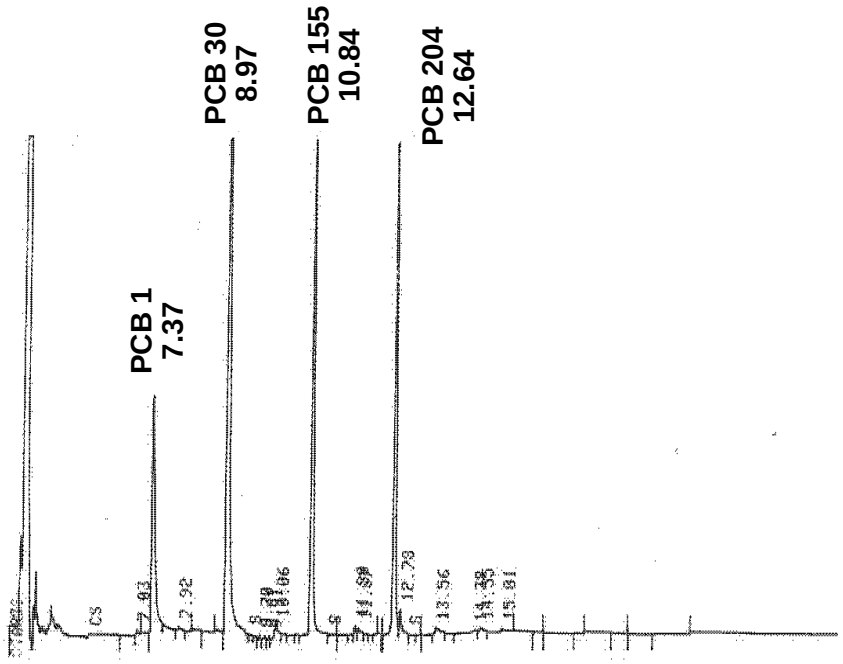

Figure 4. Chromatogram showing possible recovery of PCB's 1 and 30 from model trap.

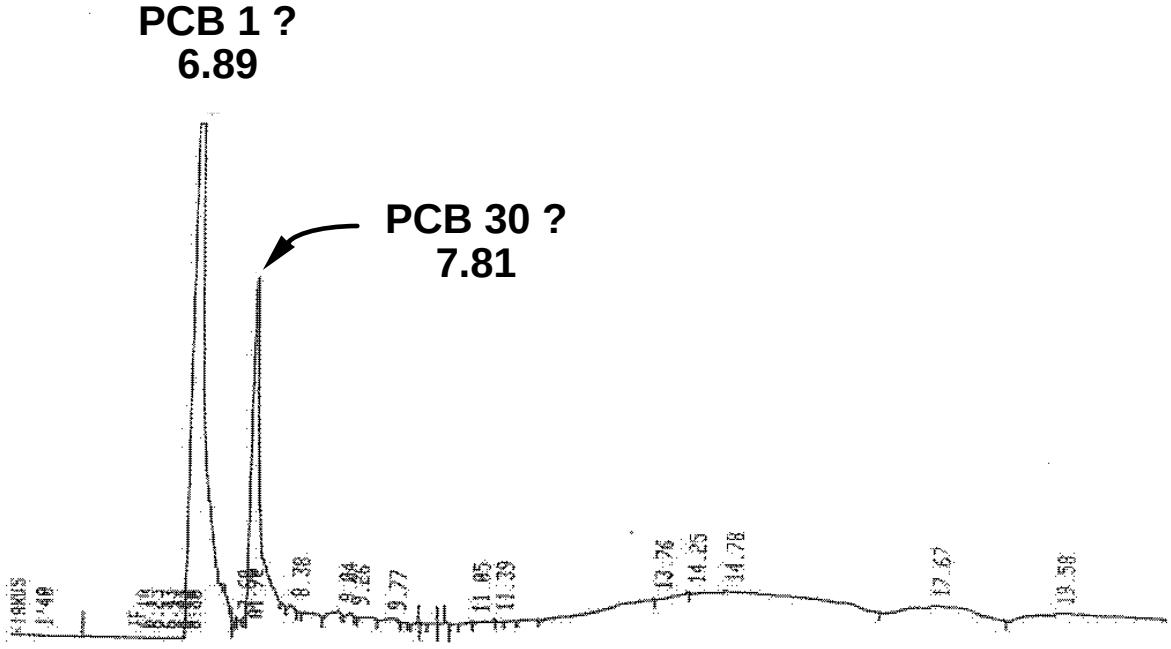

Figure 5. Chromatogram showing possible recovery of PCB's 155 and 204 from model trap.

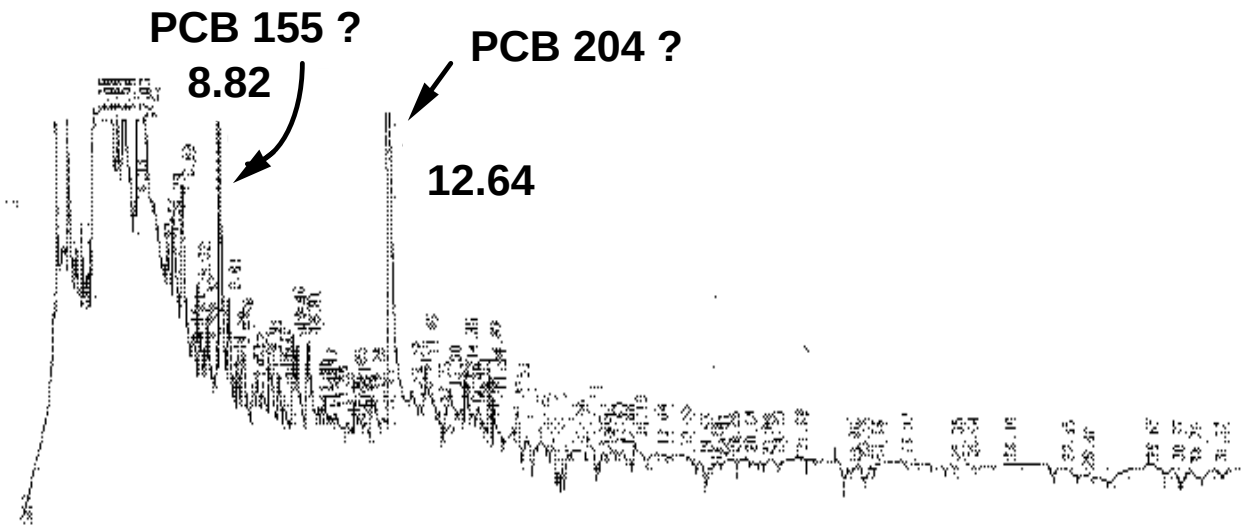

Figure 6. Modified setup for model trap

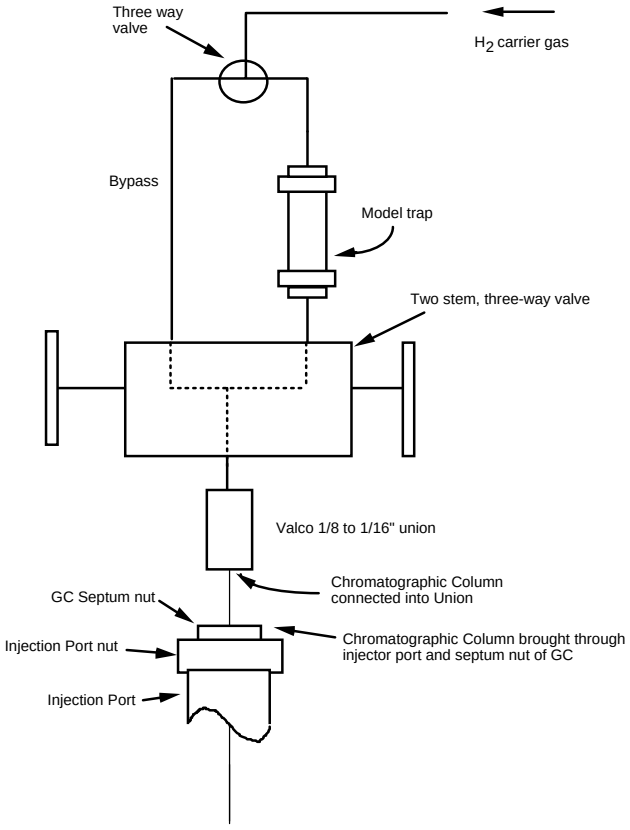

Figure 7. Carrier gas blank as function of temperature of valve 6.

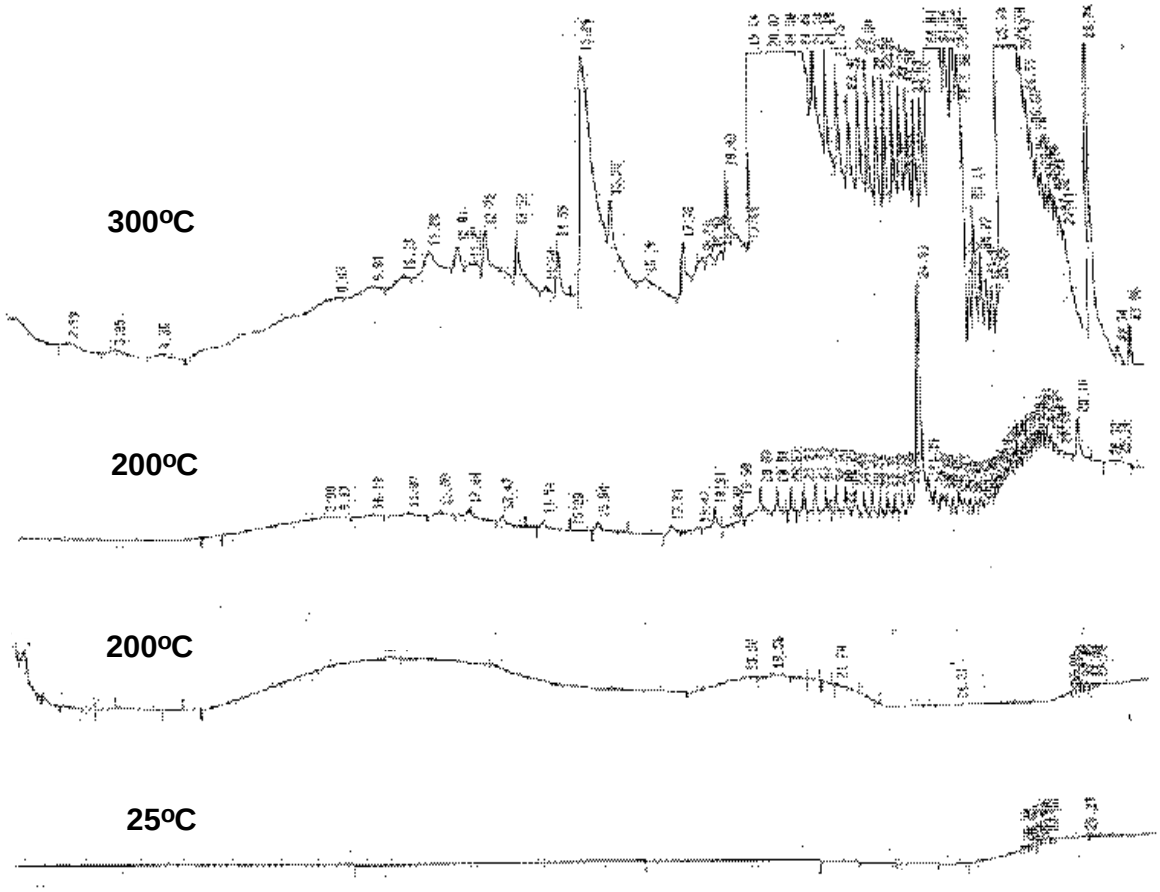

Figure 8. Position A, Deposition of Analytes for Valco Valve based design

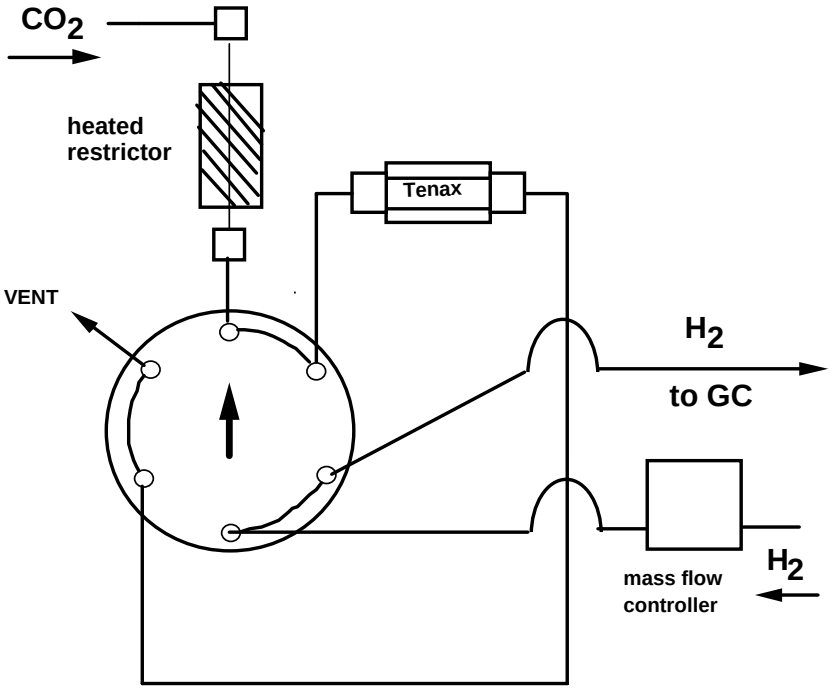

Figure 9. Position B, Desorption of Analytes for Valco Valve based design

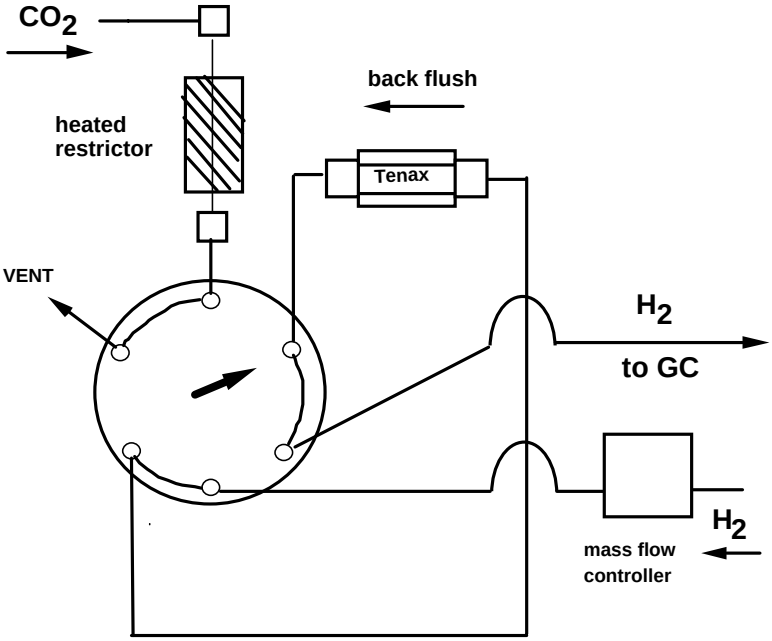

Table 1—Selected Literature Reports of Extractions from Aqueous Matrices by SPME

Analyte	% RSD[a]	LOD[b] (ppb)	Reference[c]
chlorinated pesticides	5-30	0.03[d]	SAN[e] 58
volatile organic compounds	3-23	0.7[d]	SAN[e] 56
US EPA Method 624, 524.2 analytes		1.3[d]	SAN[e] 11
Semivolatiles, PAH's	3-27	0.2[d]	SAN[e] 6
chlorinated 1,3-butadienes		0.050	Fattore 1996
PAH's			Liu 1997
PAH's	10-20		Potter 1994
PCB's		0.001	Koch 1997
PCB's		< 0.001	Llompart 1998
BTEX, chlorinated and brominated benzenes, PCB's, chlorinated pesticides			Popp 1999
chlorinated organics in mother's milk		1	Rohrig 2000

[a] Relative Standard Deviation, in percent
[b] Limit of Detection, in parts per billion (ppb)
[c] Only the first author of references are given.
[d] LOD estimated by RJN from chromatogram in reference.
[e] SAN = Supelco (Bellefonte, PA) Application Note

X. Appendix—Parts list for Figure 1.

Note: **Tubing** from SFE is 1/16'' OD stainless steel; tubing between #4, 6, 8, and 9, and between 6 and 11 is 1/8" OD SS; from valve #10 to regular carrier gas input port on GC is 1/8" OD copper tubing.

1. 1/16" SS to fused silica union—Valco P/N ZU1XC, 0.15 mm bore, with reducing ferrule for fused silica restrictor, Valco P/N FS1.4-5

2. Fused silica restrictor—20 cm x 30 um ID x 350 um OD—Polymicro P/N

3. Restrictor heating assembly—Stainless tube wrapped with heating tape (120 V, Fisher P/N 11-463-50A, controlled by PID temp controller—Cole-Parmer P/N P-89601-02) and wrapped with insulating tape.

4. Fused silica to 1/8'' union—Valco P/N ZRU21C (1/8'' to 1/16'' reducing union, 0.25 mm bore) fused silica adapter reducing ferrule in 1/16'' side, Valco P/N FS1.4-5

5. Connecting tube to Valve 6—1/8'' OD stainless steel tube

6. Double-stemmed 3-way valve—High Pressure Equip. Co. (Erie, Pa.) P/N 15-15AF2

7. Cold trap (see parts list for Figure 3)

8. 3-way brass valve—Whitey/Swagelok P/N B-41X-S2, 1/8'' Swagelok fittings

9. Micrometer (metering) Valve—Nupro/Swagelok P/N SS-SS 2, with upstream in-line filter (2 um filter—Swagelok P/N SS-2F-K4-2, Nupro filter housing, Swagelok P/N SS-2F-T7-2).

10. 3-way brass valve—As #8.

11. 1/8'' union to fused silica union—Valco P/N ZRU21C, 1/8'' to 1/16'' reducing union, 0.25 mm bore, with reducing ferrule (Valco P/N FS1.2-5) for fused silica transfer line in 1/16'' side

12. Fused Silica transfer line—10 cm x 15 um ID x 150 um OD—Polymicro P/N

13. Fused silica inserted into column

14. Cryotrap—several windings of GC column, cooled in ice water or liquid nitrogen while cold trap [7] is desorbing.