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Continuous automatic monitoring of volatile organic compounds in aqueous streams by a modified purge-and-trap system

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ABSTRACT

A new inexpensive modification approach enabled continuous on-line automatic analysis of volatile organic compounds (VOCs) in small (0.1–70 ml/min) sample streams while maintaining all capabilities on a purge-and-trap system. Commercially available automated VOC analyzers require large (liters-per-hour) sample streams. VOCs in laboratory experiments and small sample streams are usually monitored by grab analysis. This paper evaluates the performance of continuously and automatically monitoring VOCs in small sample streams on a modified purge-and-trap system. A 1 ml/min stream with 30 ppb (10^9) trichloroethane and 260 ppb tetrachloroethene aqueous standards was monitored unattended for 3 days with 2–3% relative standard deviations. The competitive breakthrough of VOCs through liquid chromatography carbon minicolumns was studied.

INTRODUCTION

Convenient, versatile, reliable and inexpensive on-line automatic monitoring of volatile organic compounds (VOCs) in aqueous streams is a basic need of environmental analytical chemistry since these chemicals are regulated pollutants. Commercially available on-line sampling systems include a Tekmar (Cincinnati, OH, USA) Model 6000 process stream sampler/LSC-2 purge-and-trap/gas chromatography (GC) system [1]; a Tekmar automatic process sampler/LSC2000 purge-and-trap/GC system [1]; and a Siemens (ES Industries, Voorhees, NJ, USA) P101 process chromatograph which uses dynamic headspace analysis with multidimensional GC [2–4]. These instruments are designed for large liters-per-hour aqueous sampling streams. The Tekmar 6000 automatically samples water from a flowing stream at programmable time intervals or on a sequential stream basis [1]. Because the sample flows through 1.3-cm poly(vinyl chloride) tubing in the Tekmar 6000 sample module, a sample flow of several liters-per-hour is recommended. An automatic process sampler accessory available for the Tekmar LSC2000 [1] purge-and-trap system, which interfaces to a gas chromatograph, also requires liters-per-hour sample streams.
Water sources and waste streams have also been continuously and automatical-

ly monitored using a Siemens P101 dynamic headspace analyzer [2–4]. The Siemens analyzer has sensitivity, accuracy and precision comparable to purge-and-trap systems, a fast cycle time (15 min for a few compounds) and requires a sample flow of at least 4 l/h [2–4].

In another approach, VOCs in a sample stream with a flow of 20 ml/h have been continuously monitored based on permeation of VOCs through a silicone polycarbonate membrane [5]. VOCs permeate from the sample water matrix to an inert gas stream. Detection limits in the low parts-per-billion (ppb)[a] range, and precision comparable to purge-and-trap methods, were reported.

Presently, commercially available automated VOC analyzers utilize expensive field samplers for large (liters-per-hour) sample streams. VOCs in laboratory experiments and small sample streams are usually monitored by grab analysis.

This paper evaluates the performance of continuous automatic on-line analysis of small (0.1–70 ml/min) sample streams, approximately hourly, for days at a time, on a modified purge-and-trap system. The purge-and-trap system used, a Tekmar LSC-2 orginally designed for one-at-a-time analysis of grab samples, maintained 100% of its original capabilities after these modifications. The gas chromatograph was a Varian 3300 with a 2.5-m 1% SP1000 packed column, a flame ionization detector, and a Hewlett-Packard 3292 integrator. The modified system was designed to monitor the breakthrough of trace (ppb) aqueous VOCs from a granular activated carbon (GAC) laboratory liquid chromatography (LC) column for as long as 3 weeks. A Varian 3250 liquid chromatograph with a 5-l PTFE bag reservoir pumped samples through the LC column filled with 100/230 mesh Filtrasorb 400 GAC.

EXPERIMENTAL

Original purge-and-trap/GC system

A standard LSC-2/4000 purge-and-trap system is designed for one-at-a-time analysis of grab samples. An LSC-2/4000 has a manual 3-way sample valve for opening the sparging vessel to the sample inlet or drain solenoid. Fig. 1a–c shows the sequence of events when a grab sample is analyzed on a standard LSC-2/4000 purge-and-trap system running in the fully automatic mode: during PURGE–READY a 5-ml sample is manually injected into the sparge sampler (Fig. 1a), the 3-way sample valve is turned and a start button is pushed to start each automatic cycle. During PURGE (Fig. 1b) volatiles are trapped. During DESORB (Fig. 1c) the drain solenoid opens emptying the sparge sampler, and the trap is heated to desorb volatiles to the gas chromatograph. During BAKE volatiles are vented from the hot trap. Finally, the system cools and returns to PURGE–READY, and the process can be repeated with the next sample.

Modified purge-and-trap/GC system

With the addition of a custom "T" connector, a 3-way solenoid and an electronic interface, the system maintained 100% of its original capabilities and gained the ability to continuously and automatically monitor small (0.1–70 ml/min) sample streams, on-line, unattended, for days at a time. Fig. 1d–f show that the added 3-way

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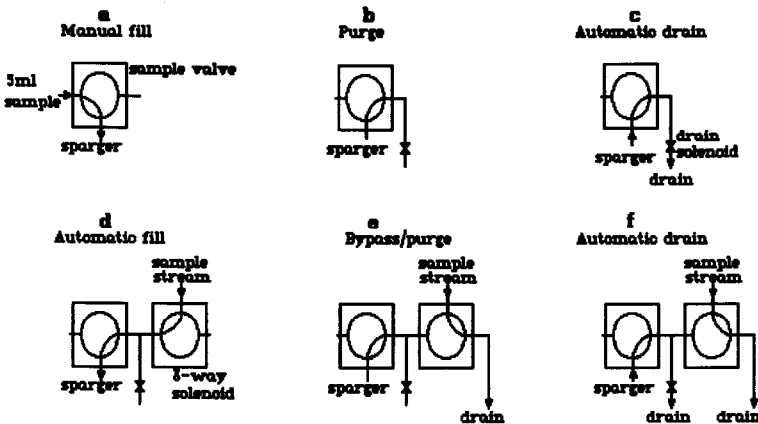[a] Throughout this article, the American billion (10^9) is meant.

Fig. 1. On the original LSC-2 purge-and-trap, a grab sample is manually injected (a), purged (b) and can be automatically drained (c). After modifications, the system maintained 100% of its original capabilities and can continuously monitor small sample streams. Sample streams can automatically fill the sparger (d) or bypass the sparger (e) and (f). The original drain solenoid automatically drains the sparger (c) and (f).

solenoid directs the sample stream to enter or bypass the sparge sampler. The original 3-way sample valve is left in the one position shown. The original drain solenoid continues to drain the sparge sampler during DESORB.

Piping interface

Fig. 2 shows the interconnection of the original sample valve and drain solenoid, and the added custom "T" connector and 3-way solenoid: A is the 1/4-28 flanged fitting on the original drain line. The "T" connector was made from 2.5 cm of
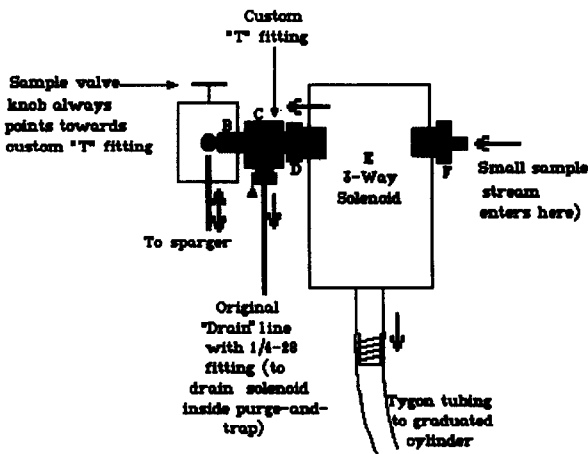

Fig. 2. Layout of the original sample valve and drain line, and added custom "T" fitting and 3-way solenoid on the modified purge-and-trap system. Arrows show all directions the sample can flow. See text for explanation.

1/4-28 threaded brass rod B (cut from a bolt), a 2-cm brass cube C, and a 1/8-in. national pipe thread (NPT) to 10-32 adapter D, after drilling and tapping C, soldering B, C, and D together, and drilling a 1.6-mm "T" path. F is also a 1/8-in. NPT to 10-32 adapter. Both 1/8-in. NPT to 10-32 adapters came with 3-way solenoid E (Allenair No. EA-5-S-120/60HZ or Tekmar part No. 14-1098-000). English 1/4-28 threads are equal to metric M6.35-1.10 threads. The 3-way solenoid has a B engraved on the influent side. The arrows in Fig. 2 show all directions the sample could flow.

Electronic interface

An electronic interface was designed to control the 3-way solenoid which allows the sample stream to enter the sparge sampler during PURGE–READY and bypass the sparge sampler at all other times. During PURGE–READY, sample enters the sparge sampler for a programmed "fill time", and then the system advances to PURGE (the automatic cycle starts, and the original drain valve drains the sparge sampler during DESORB).

Sockets 1 and 2 on the Tekmar LSC-2/4000 computer interface are an optocoupled npn transistor collector and emitter, respectively, which conduct during PURGE–READY. Sockets 4 and 5 on the LSC-2/4000 computer interface are the cathode and anode, respectively, of an optocoupled light-emitting diode which, if pulsed, advances the purge-and-trap to PURGE. The interface designed senses a transistor–transistor logic (TTL) low on sockets 1 and 2 during PURGE–READY, energizes the 3-way solenoid (to fill the sparge sampler) during PURGE–READY, and starts a timer. After the programmed time has elapsed, a TTL pulse on pins 4 and 5 advances the purge-and-trap to PURGE, the timer resets and the 3-way solenoid is off (the sample stream bypasses the sparge sampler). Note: all connections are made to the computer interface, not screw terminals on the Tekmar.

The circuit used a 7406 hex inverter and two 4020 decade counters (clocked at line frequency), a relay for the 3-way solenoid, power supply and rotary switch for selecting fill times from 4 to 2184 s. Technical details including a schematic diagram and parts list are available from the authors.

RESULTS AND DISCUSSION

Fill time

"Fill time" has been defined as the length of time that the purge-and-trap remains on PURGE–READY and sample enters the sparge sampler. Fill times of 4.27, 8.53, 17.1, 34.1, 68.3, 137, 273, 546, 1092 or 2184 s could be selected with the circuit used.

Fill volume

"Fill volume" is the volume that enters the sparge sampler. We used a 1.05-ml/ min influent and a fill time of 273 s. The actual volume that enters the sparge sampler had a relative standard deviation (R.S.D.) of *ca.* 0.6% (*i.e.*, fill volumes were 4.60, 4.66, 4.67, 4.67, 4.64, 4.60, 4.62 ml; the average and standard deviation were 4.64 ± 0.03 ml). The average fill volume did not change after months of continuous use.

Dead volume

In the above example, the influent rate was 1.05 ml/min, and the fill time was 273 s. During filling, (1.05 × 273/60) 4.78 ml passed through the influent solenoid, but only about 4.64 ml entered the sparge vessel. The difference (0.14 ml) is dead volume, which remains in the piping between analyses. Some of this dead volume is blown out between analyses during automatic draining. Blowing out of the dead volume between analyses reduces carry-over between samples. As with the original system, sample carry-over is slight, and most noticeable after switching from very high to very low concentration samples.

Sample carry-over test

The interface circuit was modified to allow the sparge sampler to alternately fill with sample and dry blanks. When compounds of approximately 10–100 ppb were analyzed, peak areas during the dry blanks usually were about 0–5% of the sample peak areas. This much carry-over seems acceptable when monitoring concentrations which do not change much between successive runs. Carry-over can be decreased by running more than one dry blanks between samples. Fig. 3 shows the chromatographic results of the analysis of two compounds in a sample stream, with automatic dry blanks between alternate analyses.

Compatibility with original system: fill/drain modes

If the electronic interface is unplugged (or the fill time is set to infinity), the 3-way solenoid is de-energized and a sample stream would bypass the purge-and-trap system. The purge-and-trap system would maintain 100% of its original capabilities, including automatic draining. If effluent (*i.e.*, from a liquid chromatograph) is monitored for days at a time, the sample stream can be temporarily bypassed and the purge-and-trap could be tested with an ordinary calibration standard. With the original or modified purge-and-trap system, the user can manually remove a sample through the original sample inlet.

The following are possible fill-and-drain modes on the original LSC-2:

(A1) manual fill with manual drain;

(A2) manual fill with automatic drain.

With the modified system, the following fill-and-drain modes are possible:

(B1) manual fill with manual drain;

(B2) manual fill with automatic drain;

(B3) automatic fill with manual drain (we do not recommend this for continuous monitoring);

(B4) automatic fill with automatic drain.

Manual fill with manual drain, before and after instrument modification (mode A1 vs. mode B1)

On the original or modified purge-and-trap system, sample can be manually injected, the sample valve can be turned to isolate the sparge sampler from the drain line/solenoid (and any added components) during purging, and sample can be manually drained after purging.

On the original purge-and-trap system, standard can be purged this way and then with automatic drain, to test for leaks in the drain line or drain solenoid.
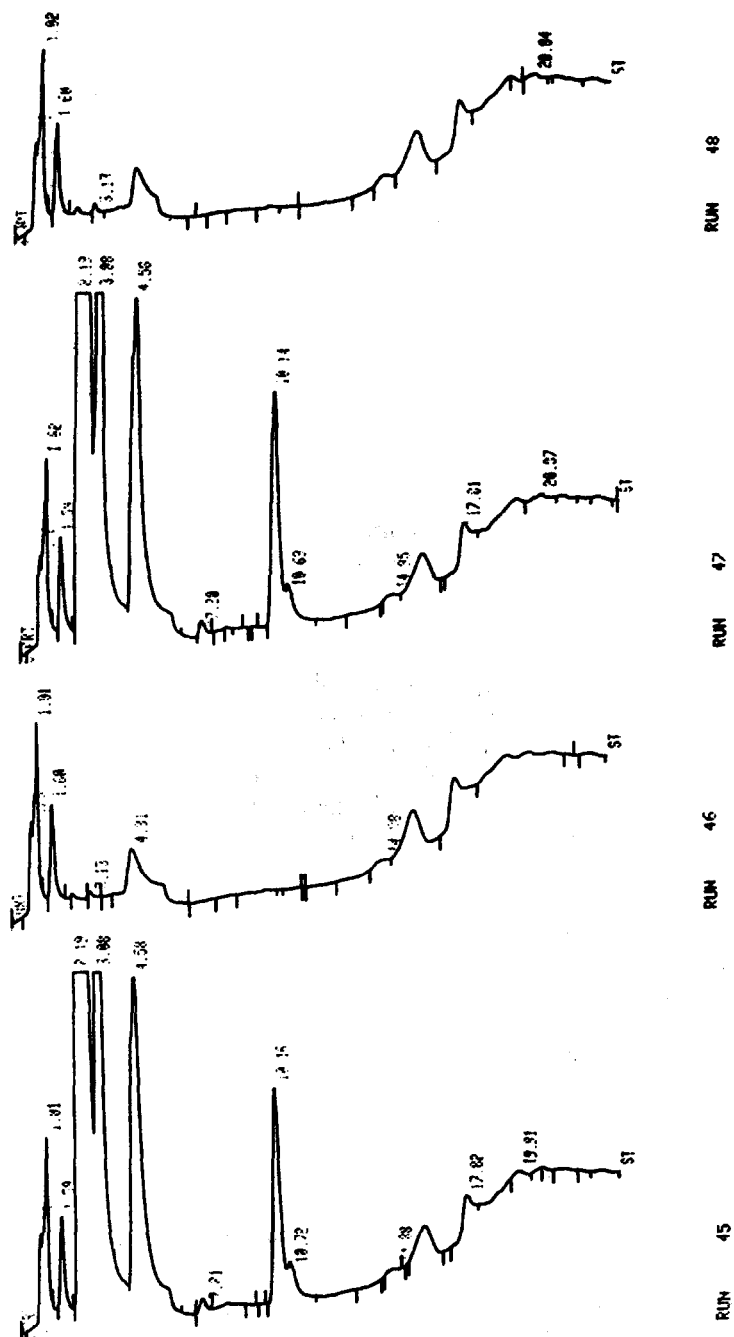
Fig. 3. Sample carry-over was tested by continuously and automatically alternating between the analysis of compounds in LC effluent (runs 45 and 47) and dry blanks (runs 46 and 48), to test the small-volume effluent monitor for sample carry-over. The LC effluent contained TCA (retention time 4.58 min), PCE retention time 10.14–10.16 min) and other VOCs. During automatic dry blanks, a small amount of sample carry-over is visible. Numbers at peaks indicate retention times in min.

On the modified purge and trap system, a standard can be purged with the sample valve isolating the custom "T"/drain line/drain solenoid/3-way solenoid. The same standard can be analyzed with automatic drain to check for analyte loss due to leaks, dead volume, etc.

Manual fill with manual drain vs. manual fill with automatic drain (mode B1 vs. mode B2)

On the modified system, fill and drain combinations B1 and B2 were compared to determine if a significant amount of VOCs are lost in the custom "T"/drain line/drain solenoid/3-way solenoid headspace area. Replicate samples of 36 ppb 1,1,1-trichloroethane (TCA) and 338 ppb tetrachloroethene (PCE) were analyzed on the modified purge-and-trap system. All samples were manually injected with a 5-ml Luer-Lok syringe. Table I shows replicate analyses of TCA and PCE with alternating manual drain and automatic drain on the modified purge-and-trap system.

(A 5-ml sample was purged 11 min, desorbed for 4 min, and the trap was baked for 12 min. A 2.5-m 1% SP1000 GC column ran isothermally at 160°C.) No significant amount of VOCs were lost using the automatic drain on the modified system, compared to manual drain with the sample valve shutting off the modified piping.

Manual fill with manual drain vs. automatic fill with automatic drain (mode B1 vs. mode B4)

A comparison was made between manually analyzing a standard with the sample valve always isolating all modifications made to the purge-and-trap (mode B1), and continuously pumping the standard at 1.05 ml/min through an LC blank column, and into the automatic small-sample-stream monitor for 69 h. A calibration curve was made by diluting a stock solution of TCA and PCE, and injecting 4.64 ml of standard into the purge-and-trap, with manual filling and manual draining and the sample valve always blocking the modified portion of the purge-and-trap (mode B1). For the TCA calibration curve, standards ranged from 5 to 100 ppb and had a

TABLE I

REPLICATE TCA AND PCE ANALYSES ON THE MODIFIED PURGE-AND-TRAP SYSTEM WITH MANUAL DRAIN (SAMPLE VALVE CLOSING OFF MODIFIED PIPING) AND AUTO-MATIC DRAIN

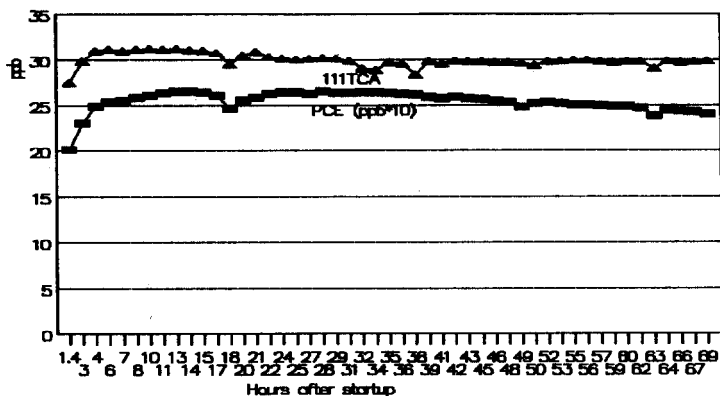|	Manual fill, manual drain	Manual fill, automatic drain	Manual fill, manual drain	Manual fill, automatic drain
Mode	B1	B2	B1	B2
Compound	TCA	TCA	PCE	PCE
Ppb	36	36	338	338
Purged (ml)	5.0	5.0	5.0	5.0
Peak area	1590	1609	13028	12929
Peak area	1605	1635	12523	13089
Peak area	1657	1612	12908	12957
Average	1617	1618	12820	12992
Recovery		100% of mode B1		101% of mode B1
R.S.D. (%)	2.2	0.9	2.1	0.7

Fig. 4. A liquid chromatograph pumped 30 ppb TCA and 300 ppb PCE at 1.05 ml/min through an empty column and into the small-volume effluent monitor. TCA was detected with 100% recovery and a R.S.D. of 2.2% over 69 h. PCE was simultaneously detected with 85% recovery and R.S.D. of 2.9%.

coefficient of correlation $r = 0.997$. For the PCE calibration curve, standards ranged from 20 to 400 ppb and had a coefficient of correlation $r = 0.987$.

A 5-l volume of 30 ppb TCA and 300 ppb PCE standard (from the same stock solution and mixed in a 5-l PTFE sampling bag) was attached to liquid chromatograph and pumped at 1.05 ml/min through an empty column into the automatic small-sample-stream monitor. The purge vessel automatically filled with 4.64 ml (± 0.03 ml) of sample, and was automatically drained during desorb (mode B4). Sample purged for 11 min, desorbed for 4 min, and the column was baked for 57 min (1.4 h elapsed between each analysis). A 1% SP1000 column was run isothermally at 160°C. Fig. 4 shows TCA and PCE concentrations entering the modified purge-and-trap system *vs.* time. Table II summarizes the results of this study, excluding the first analysis after the system started up.

There was some loss of PCE, which is less polar and much more volatile than TCA. PCE loss (14.6%) was probably due to PCE adsorbing to or escaping from the

TABLE II

REPLICATE DETERMINATIONS OF TCA AND PCE IN NATURAL WATER

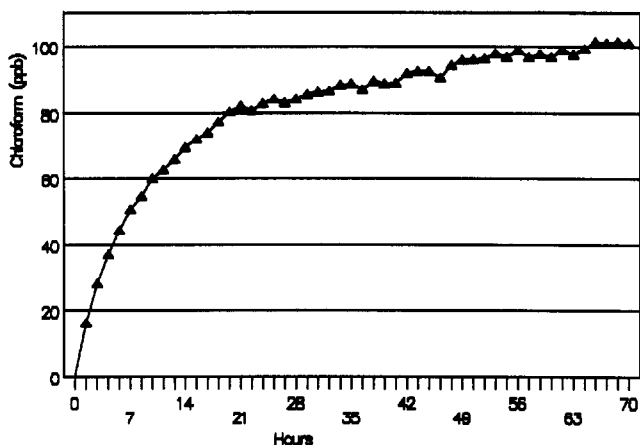|	TCA	PCE
Conc. supplying LC system (ppb)	30	300
Number of analyses	49	49
Time between analyses (h)	1.4	1.4
Time span (h)	69	69
Flow-rate (ml/min)	1.05	1.05
Minimum conc. (ppb)	28.4	239
Average conc. (ppb)	30.0	256
Maximum conc. (ppb)	31.3	265
R.S.D. of conc. (%)	2.2	2.9
Recovery (%)	100	85.4

Fig. 5. The small-scale effluent monitor continously monitored a 1.05-ml/min effluent for breakthrough of chloroform from a LC microcolumn packed with activated carbon. Chloroform concentrations were determined every 1.5 h for 70 h.

PTFE bag, tubing, etc., during the 69 h of automatic monitoring. The reproducibility of the system was excellent (R.S.D. of 2.2% for TCA and 2.9% for PCE) for 69 h of sampling time.

Application

Micro carbon columns containing 50 mg of granular activated carbon were used to study the removal of VOCs from drinking water. Contaminated-surface and well-water samples were continuously pumped through micro carbon columns for as long as two weeks, and the effluent from the carbon columns was monitored via the small sample stream monitor. Fig. 5 shows a 1.05 ml/min effluent from a micro carbon column that was analyzed on the small-sample-stream monitor for 3 days. The chloroform concentration in the influent to the micro column was approximately 100 ppb. Chloroform concentrations in effluent from the micro column ranged from 0 to *ca.* 100 ppb over *ca.* 70 hours. As activated carbon becomes saturated, contaminants breakthrough carbon columns [6–11]. In subsequent studies we monitored the competitive breakthrough of several VOCs, approximately hourly, depending on the temperature program necessary to resolve the compounds.

As mentioned before, the system could alternate between samples and blanks as quality assurance. Continuous automatic alternating analyses between two different LC systems, feeding one purge-and-trap system, was tested. A second influent solenoid and electronics were added to alternately flip-flop between activating either one of two influent solenoids during PURGE–READY. Alternating sample switching between two sample streams worked. Because the second LC system for this experiment consisted only of a 5-l sample bag, a less expensive stand-alone low-volume pump, and a GAC LC column, the flow-rate of the second small-stream system was not precise enough for further LC1/LC2 purge-and-trap GC experiments.

Reliability

Because the on-line continuous and automatic monitoring system developed uses a sparge sampler to isolate VOCs from the aqueous matrix, salts and small particles in natural water samples did not cause any downtime in our purge-and-trap or GC system. The continuous small-sample-stream monitor has run continuously for one to two weeks at a time, for eleven months, with no electronic or piping problems in this interface. Traps in the purge-and-trap were replaced every few months. The seals on the LC system for the above study were replaced twice.

Modifying a Tekmar Model 4000 or LSC-2000

Continuous monitoring of small sample streams should also be possible with a Tekmar Model 4000 (it has the same sample valve and computer interface as the LSC-2), or with a Tekmar LSC-2000 (it has a compatible computer interface and a sample valve which is a mirror image of the one on the LSC-2).

CONCLUSIONS

After low-cost modifications to a Tekmar LSC-2 purge-and-trap system which was connected to a GC analysis system, the modified system had 100% of its original capabilities, and the ability to monitor low-volume (0.1–70 ml/min) sample streams. The reproducibility of determined concentrations remained excellent after days of automatic monitoring (*i.e.*, R.S.D. values of 2.2 and 2.9%). Loss of analyte through an LC pumping system was small but consistent. With very volatile compounds, analyte loss is significant (*i.e.*, 15% loss of PCE) and should be taken into consideration when doing critical quantative work. There were no reliability problems with these modifications to the purge-and-trap system after eleven months of heavy use, with normal maintenance of the rest of the system.

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