THE DETERMINATION OF SYNTHETIC ORGANIC COMPOUNDS IN WATER BY PURGE AND SEQUENTIAL TRAPPING CAPILLARY COLUMN GAS CHROMATOGRAPHY

by

Thomas A. Bellar
and
James J. Lichtenberg
Physical and Chemical Methods Branch
Environmental Monitoring and Support Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINATI, OHIO 45268

January 1985

THE DETERMINATION OF SYNTHETIC ORGANIC COMPOUNDS IN WATER BY PURGE AND SEQUENTIAL TRAPPING CAPILLARY COLUMN GAS CHROMATOGRAPHY

Thomas A. Bellar and James J.Lichtenberg

INTRODUCTION

Based upon the limited data obtained from early purge and trap methods development reports, it was generally concluded that a single programmed temperature packed column could elute all of the compounds efficiently extracted by common purge and trap operations. As a result, several generations of purge and trap instruments were developed that were designed to operate solely with highly efficient packed column gas chromatographs. As purge and trap methods evolved with such instrumentation and as GC/MS survey data were evaluated, it became apparent that the limiting factor for a broad spectrum purge and trap analysis is not the extraction step but the inability of a single packed column to resolve and elute all of the commonly occurring synthetic organic compounds extracted from water by inert gas purging. This observation is substantiated by current Agency methodologies where a common set of extraction and trapping parameters are used for several different methods, the primary difference being the utilization of a variety of specific detectors, packed columns with unique resolving powers or complex temperature programs. Only through the use of all of these tools do packed columns provide the qualities for sensitive, accurate and precise methods for a wide variety of compounds.

Capillary columns have long been used to resolve complex mixtures of apolar compounds over an extremely wide boiling range. Moreover, with the development of chemically inert glass and fused silica columns, it is now possible to simultaneously analyze extracts containing compounds of widely varying polarities and coexisting organic acids and bases. Inert capillary columns and gas chromatographs, primarily designed for capillary columns, are now commercially available and are common to many laboratories. The unique properties of capillary systems and their acceptance by commercial laboratories suggest that their application to purge and trap methodology is practical and could significantly improve the quality of purge and trap data. Their utilization could result in a single method capable of resolving complex mixtures of reactive compounds over a wide boiling range well beyond the capabilities of a single packed column.

The experimental design of this study had three main objectives: the first, to develop and document a thorough understanding of the mechanics and limitations of purge and trap capillary column gas chromatography; secondly, to develop a simple automated analytical approach for the analysis of a number of synthetic organic compounds, and finally, to determine single laboratory method detection limits, accuracy, precision and sample stability data in order to determine if the approach can be used as a method for the analysis of diverse organic chemicals in drinking water related samples.

EXPERIMENTAL

Almost every variable encountered in purge and trap operations has a direct effect upon the accuracy and precision of the method. For this

reason, many of the basic purge and trap parameters which have been painstakenly optimized over the years for packed column operations were utilized, whenever possible. For capillary column gas chromatography, the purging and trapping functions did not require modification. However, significant modifications were required for the sample desorption injection step before acceptable capillary column performance could be obtained.

For a packed column system during desorption, an inert gas flowing at a rate between 20 and 40 mL/min backflushes the trap for approximately four minutes while the trap is flash heated to 180°C. The trapped components are released from the sorbent as the temperature is elevated and are transferred into the packed column by the inert gas. Low boiling apolar compounds leave the trap as a sharp spike while higher boiling compounds elute as broad tailing peaks. For packed columns with internal diameters larger than 2 mm and theoretical plate values of less than 1500 plates/m, compounds can be injected under isothermal conditions contained in 10-15 mL of gas without adversely affecting the performance of the column. At a flow rate of 30 mL/min low boiling materials exit the trap contained in approximately 15 mL of gas. The result is acceptable peak geometries for desorption injections of compounds even when the column is operated at temperatures at which the low boiling compounds are mobile (i.e., chromatographic separations begin at injection). Higher boiling compounds such as aromatic hydrocarbons elute from the trap over longer periods of time, e.g. 120 seconds, and, therefore, are presented to the column in a volume of gas approaching 60 mL. If the chromatographic column temperature is high enough for such compounds to be mobile at injection, the desorption profile

projects through the chromatographic column resulting in poor chromatographic peak geometries and a loss of resolution. Packed column purge and trap methods avoid this problem through temperature programming. An initial column temperature is selected so that the low boiling, ideally injected, sample components are mobile and allowed to separate as they pass through the column. At this relatively low column temperature, the higher boiling compounds are immobile and remain trapped on the first few cm of the column packing during desorption. Subsequently, as the temperature of the column is raised through temperature programming, the higher boiling components become mobile and elute from the column as well defined peaks.

In direct contrast, for proper capillary column operations the sample must be injected into a capillary column contained in a microvolume of gas. The internal diameter, linear gas flow, and film thickness of the capillary column all have a direct limit on the maximum volume of desorb gas in which the analyte can be contained before it has an adverse effect upon the performance of the capillary column. For current, commercially available glass capillaries, this volume of gas varies from about 50 to 500 μL. It is evident, therefore, that simply attaching a purge and trap unit designed for packed column operations to a capillary column will result in poor quality gas chromatograms.

This limitation has been resolved by two differing desorption/injection approaches. These approaches are commonly referred to as "cryofocusing" and "sequential trapping." Cryofocusing is a condition where the desorbed compounds are cold trapped in the analytical column or in a pre-capillary

column at a temperature between 100°C and 150°C below the normal elution temperature of those compounds. Under this condition, the low and high boiling compounds are immobile and are contained in a very short section of the capillary column. After 100 percent transfer, the cooled area is heated and the compounds are released and separated by the column. Sequential trapping is a procedure where the trap normally used for packed column operations ("A" trap) is desorbed into a second microbore trap ("B" trap). The "B" trap is in turn backflushed and desorbed into the capillary column operated at temperatures where the ideally desorbed compounds are mobile and the non-ideally desorbed compounds are cold trapped. Through temperature programming all of the desorbed compounds elute as ideal peaks.

The primary advantages of cryofocusing are:

1. The modifications to existing purge and trap packed systems are generally inexpensive and within the technical abilities of most laboratories.
2. Almost all commercially available capillary columns can be used since the volume of gas required for quantitative transfer does not affect the peak geometries of cold trapped compounds.

Some of the disadvantages or precautions one should consider for such an approach include:

1. The need to use liquid nitrogen or liquid carbon dioxide to cool the capillary column down to cryofocusing temperatures.
2. The possibility of ice crystals forming within the trapping region of the column resulting in restriction or total blockage of flow and unpredictable, non-quantitative sample transfer.

3. If the sample forms an aerosol as it is desorbed from the trap, it will not be effectively trapped in an open tubular column.

4. Ideally, the stationary phase should still be a liquid at the reconstitution temperature.

5. Variable retention data oftentimes result when cryogenic operations are performed due to the adverse effect they have upon the oven temperature and flow controllers.

The advantages of sequential trapping are:

1. Once the operational parameters are optimized the unit can be automated to perform like current packed column purge and trap instruments resulting in qualitative and quantitative data with outstanding accuracy and precision.
2. Large volumes of coolants are not required, operational expenses are lower and the unit can be set in remote locations for unattended operation.

The disadvantages are:

1. The sequential trapping operation must be carefully optimized to transfer and reconstitute all of the compounds of interest. It may not be possible to include both extremely volatile compounds and high boilers in a single analysis.
2. Microbore traps are difficult to prepare.

3. For a broad spectrum analysis sequential trapping operations are only possible using thick-film, widebore capillary columns (0.5 to 0.75 mm internal diameters).

4. New purge and trap equipment specifically designed for sequential trapping must be purchased because extensive modifications are required to update most packed column purge and trap systems.

For this study the sequential trapping system was selected to perform all of the experiments, because the equipment was commercially available and the approach appeared to be the greatest challenge.

EQUIPMENT USED

A Chemical Data Systems Model 320 (CDS-320) concentrator with the capillary option was used for the purge and trap operations. The purge and trap unit was attached to a Hewlett Packard Model 5730A gas chromatograph equipped with a CO_2 subambient column accessory and flame ionization detectors (FID). All of the retention, peak width and area data were gathered with a Hewlett Packard 3388A integrator. Three Supelco glass capillary columns were used: Grade AA SE-30-60 m long, 0.75 mm ID with a film thickness (df) of 1.0 µm and a reported coating efficiency of 115%; Grade AA, SE-30 Bonded—60m long, 0.75 mm ID with a df of 1 µm and a coating efficiency of 101%; Grade AA SE-54-30 m long, 0.50 mm ID with an unknown film thickness and unknown coating efficiency. A 50m, 0.50 mm ID Superox 4LL column from Alltech and an Analabs 50m, 0.50 mm ID SE-30 column were

also briefly evaluated. Information on the coating efficiency and film thickness was not available for the latter two columns. A Supelco direct injection capillary column inlet conversion kit was used to evaluate column performance and system activity.

SYSTEM EVALUATION

The initial evaluation of the assembled analytical system was designed to determine the performance of the capillary column gas chromatograph, the transfer line between the column and the purge and trap unit, and the sequential trapping and desorption operations. The purpose of the evaluation was to determine what types of compounds can be handled quantitatively by the entire system without regard for whether or not they can be purged from water. For this evaluation, a neutral reactives test mixture (test mixture) supplied with the Supelco SE-30 capillary column was used. The column manufacturer also supplied a chromatogram of the mixture generated by the column used for this study operated under optimum conditions. The supplied chromatogram was considered to be a "primary chromatogram" and each system component was systematically optimized whenever possible to ultimately generate a chromatogram of similar quality.

The ends of the 60m X 0.75mm glass column coated with SE-30, 1.0 μm df were straightened, deactivated and installed in the FID gas chromatograph. Prior to attaching the purge and trap unit to the gas chromatograph, proper column installation was confirmed by on-column injections of the test mixture. For the initial evaluation the widebore capillary column direct

injection conversion kit was installed in the gas chromatograph to allow direct volatilization injections of liquid and gaseous samples into the capillary column. Using helium as a carrier gas, the linear gas flow through the column was adjusted to 20 cm/second at 115°C. Helium was used as the make-up gas to increase the total flow into the FID to 40 mL/minute. Volumes between 0.25 and 1.0 µL of the neat test mixture were injected into the glass capillary column. The peak geometries and relative peak heights of the resulting chromatogram closely duplicated the primary chromatogram. The concentation of each analyte in the test mixture was such that a properly operated FID would generate nearly equal response to each analyte if the entire system is equally inert to each of the test components. The installation test recommended by the column manufacturer compares the peak heights of the reactive components to those of the non-reactive components. To compensate for peak width changes obtained during isothermal operations, a continuous curve is drawn connecting the apex of each of the non-reactive peaks (n-alkanes) in the resulting chromatogram. The percent response of each reactive analyte is calculated by dividing the theoretical height of the reactive compound by the observed peak height and multiplying by 100. This test assumes that the n-alkanes generate ideal peaks and, therefore, becomes a means of monitoring losses of reactive compounds and peak tailing effects. Percent response values for the methyl silicone column in excess of 70% are considered "good" by the column manufacturer and are representative of an inert column and proper installation. The calculated results of the initial column installation evaluations and those supplied by the column manufacturer (primary chromatogram) are shown in Table 1.

The peak geometry for each of the n-alkanes was sharp and symmetrical. The calculated response values for each of the reactive analytes (installation chromatogram) was found to be in excess of 70 percent and comparable to those obtained by the column manufacturer indicating proper chromatographic system performance. It should be noted that the primary chromatogram was generated using a splitting injector operating with a split ratio of 50:1. Through this simple test it was also shown that contrary to narrow-bore capillary column operations, volumes between 0.25 and 1.0 µL of the test mixture can be directly injected into widebore capillary columns at temperatures significantly above the boiling point of the solvent without adversely affecting the performance of the column.

The purge and trap unit was then attached to the gas chromatograph exactly according to the operators manual. The heated metal transfer line was attached directly to the 0.75 mm capillary column bypassing the capillary injector. The linear velocity through the capillary column was adjusted to 20 cm/second at 115°C using the mass flow controller supplied with the purge and trap unit. The design of the CDS-320 purge and trap unit allows liquid injections to be made into the unit at two points through heated injectors so that each of the trap/desorption functions can be monitored. Volumes of the test mixture between 0.25 and 1.0 µL were injected into the CDS-320 column injector to evaluate the performance of the heated metal transfer line and the CDS-320 column injector, both operated at 200°C. The resulting chromatogram was of poor quality. The n-alkanes tailed indicating the possibility of excessive internal volumes, cold spots, or reactive surfaces between the injector and the column. The percent

response values for the reactive compounds calculated from the chromatogram are listed in Table 1 under CDS transfer line chromatogram. The appearance of the chromatogram and the calculated data show that the injector and/or the transfer line are detrimental for isothermal capillary column analyses of compounds of similar polarities and boiling range. In an effort to resolve this problem, the transfer line was modified by threading a section of 0.32 mm ID fused silica capillary column coated with OV-1 through the transfer line. One end of the fused silica line was attached directly to the CDS-320 column injector using a zero dead volume reducing fitting and graphite ferrules and the other end was connected directly to the glass capillary using a capillary column butt-end connector. The test was again repeated and the resulting chromatogram generated sharp, symmetrical peaks for the alkanes and, with the possible exception of the alcohol, also for the reactive analytes. The calculated response values for the test mixture using the modified transfer line also appear in Table 1. The reactivity of the system to alcohol (recovery 67 percent) appears to be due to the active sites located within the injector. All of the other test compounds provided recoveries and peak geometries nearly identical to the primary and installation chromatograms. For an initial evaluation of the assembled purge and trap-capillary column system, the test solution was injected into the "A" trap through the trap injector. With the exception of the modified transfer line, the unit was operated as received using the sequential purge and trap conditions recommended in the CDS operators manual. The resulting chromatogram provided unusually wide symmetrical peaks for the n-alkanes indicating that the volume of desorb gas containing the analytes was excessive, adversely affecting the performance of the capillary column. The reactive

analytes were present but low in yield and the late eluting compounds appeared as doublets in the chromatogram. The percent response values appear in Table 1 under sequential trapping chromatogram and are, at best, estimates because of the poor quality of the chromatogram. Attempts to improve peak geometry through simple desorption parameter modifications did not improve the quality of the chromatograms. Based upon observations of these and other chromatograms, it was apparent that extensive modifications to the purge and trap system and optimization of the various parameters would be required before reliable multi-residue quantitative analyses could be performed upon water samples. Progressive experiments were then designed to determine acceptable trap internal diameters, the boiling range of neutral compounds that can be desorbed into an isothermally operated wide-bore capillary column, the sorbents and conditions best suited for capillary column purge and trap operations, the parameters required for quantitative sequential trap operations and the selection of a capillary column and the temperature program best suited for the analysis of purgeable compounds.

ANALYTE BOILING RANGE AND TRAP INTERNAL DIAMETERS

From the sequential trapping chromatogram it was evident that at least one major problem was occurring. The analytes selected for this study were contained in an excessive volume of desorb gas for proper injection into the isothermally operated capillary column. Based upon packed column experiences, it was assumed that the boiling points of the test analytes were too high, the internal volume of the trap was too large, or the trap sorbent

could not be heated fast enough to generate sharp, symmetrical desorption peaks.

To evaluate these possibilities, the following series of experiments was performed: 150 µL injections of a gaseous standard solution containing 1.0 µL of n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane/L of air (n-alkane mix) were injected into the trap injector on the CDS-320. The injected sample was swept into the "A" trap (23°C) for 11 minutes with helium flowing at 40 mL/minute. Trap "A" was then heated to 180°C and backflushed into the "B" trap for 2 minutes with helium flowing at 20 mL/minute. The "B" trap was then backflushed at 180°C into the analytical column with helium flowing at 10 mL/minute for 120 seconds. The "A" trap, common to most EPA purge and trap methods, contained only Tenax, was 23 cm long and had an internal diameter of 2.67 mm. Three different "B" traps were evaluated: the trap supplied with the unit (a 2.667 mm I.D. stainless steel tube containing 23 cm of Tenax) and two traps fabricated in the laboratory (a 1.651 mm ID copper tube containing 23 cm of Tenax, and a 1.8 mm I.D. glass lined stainless steel tube containing 23 cm of Tenax). The gas chromatographic column was maintained at 70°C for 8 minutes, then programmed at 8°/min to 100°C. Chromatographic column conditions were selected so that most of the compounds would elute under the 70°C isothermal conditions while n-decane, a compound already shown to have adversely affected isothermal peak geometries, would elute as the column is programmed. The purpose of the column program was to determine if mild temperature programming would improve the peak geometry of decane. Triplicate analyses were performed using each set of traps and the results were compared

to direct injections of the n-alkane mix into the column through the CDS 320 column injector. Retention data, peak area, peak width at half height (intergrator value) and peak height in mm (hand measurement) were recorded and averaged. Table 2 lists the resulting data.

With the exception of n-nonane, the retention data from the trapped injections are uniform and differ from direct injections by about 24 ± 2 seconds. For some unknown reason, n-nonane leaves the trap before the other analytes and differs by 12 seconds. With the equipment used the internal volumes are small, the linear gas velocities are high and all surfaces are heated; therefore, the difference in retention times between the trapped materials and direct injection are primarily due to the time it takes to heat the Tenax sufficiently to release the compounds to the backflush flow. It is interesting to note that the thermal conductivity of the trap tubing, copper vs. glass-lined stainless steel, did not influence the retention data.

Peak area comparisons between the on-column injections and the various traps in Table 2 show that, with the exception of n-pentane, nearly identical areas were obtained for each trap and these, in turn, compare favorably to direct injection areas.

Quantitative values for pentane were not obtained because under the simulated purging conditions (11 minutes at 40 mL/minute) the retention volume of pentane for trap "A" was exceeded, resulting in partial venting.

Peak height and peak width at half height comparisons show that as the internal diameter of the "B" trap decreases, the peak geometries of the peaks eluting within the isothermal area of the chromatogram more closely approximates those of direct injection. These peak data also show that decane, eluting under programmed conditions, does not exhibit peak broadening effects from desorption indicating that a minimal column temperature change (20-30°C) will sharpen the peak geometries of non-polar compounds. The visual appearance of the chromatograms indicate that for isothermal column gas chromotography the two narrow bore traps (< 2 mm ID) generate acceptable (but not ideal) chromatograms while the widebore trap (2.7 mm ID) adversely affects the performance of the capillary column to the point where closely eluting peaks may fuse.

To further determine what effects the "B" trap and chromatographic conditions may have upon the quality of capillary column chromatogram of polar compounds and higher boiling alkanes, additional test mixture injections were performed. Triplicate 1 µL aliquots were injected into the CDS-320 column injector and into the "A" trap injector. Trap "A" in each case was a standard 23 cm X 0.105" Tenax trap. The three previously described "B" traps were further evaluated. The injected materials were flushed into trap A, sequentially trapped on trap B and desorbed to the column according to the previous experiment. The desorbed compounds were separated isothermally at 115°C. The experiments were then repeated where

the sample upon desorption from the "B" trap was reconstituted on the capillary column under true cold trapping conditions. The capillary column was programmed as follows: during desorption, the column was maintained at 20°C for 2 minutes followed by a 32°/minute program (maximum rate) to 115°C. The column was then maintained at 115°C until all of the compounds eluted. All of the compounds eluted during the 115°C isothermal conditions.

The percent response values defined previously were calculated for each of the reactive analytes, the area of each peak relative to n-decane was determined and the number of theoretical plates per meter for n-tridecane was calculated. The isothermal data (non-cold trapping) appear in Table 3 and the programmed (cold trapping) data appear in Table 4.

As noted in the primary chromatogram (Table 1), where similar injections were performed, the quality of the isothermal chromatograms used to generate the data in Table 3 are, at best, poor for the hydrocarbons and totally unacceptable for the reactive compounds. Comparison of the n-decane ratio data between direct injection and the various traps indicate that the purge and trap operations are quantitative for the alkanes while there appear to be losses for the reactives. It is interesting to note that the 2.7 mm trap caused the retention time for 2,4-dimethylphenol to increase fusing it with n-undecane. As in the case of the previous experiment with normal alkanes, as the internal diameter of the trap decreases, the quality of the resulting chromatogram improves. This is further emphasized by comparing the number of theoretical plates per meter for n-tridecane.

In direct contrast, Table 4 comparisons of the number of theoretical plates obtained from the column using the various traps shows that, under cold trapping conditions, the normal alkanes elute as ideal peaks showing no adverse affects from the sequential trapping operations or the variation in traps. Comparing the area ratio data for direct injection to the various traps shows that relative to the n-decane there is quantitative transfer of the higher boiling alkanes and naphthalene. For each of the traps there was a slight tailing for the alcohol peak resulting in response determinations of 70% or less. Although peak geometries for the 2,6-dimethylphenol were acceptable, there is a slight loss (~10 percent) relative to n-decane. Other reactive compounds appear to be quantitatively transferred.

SORBENT SELECTION

Early packed column purge and trap methods development investigations evaluated a large number of potential trap sorbents. From these studies, traps packed with Tenax or combinations of Tenax, silica gel and activated carbon were selected as best suited for the analysis of purgeable priority pollutants by packed column purge and trap operations. Since these studies a number of potential sorbents with unique properties have been developed. The previously developed sorbent traps and a few potential sorbents were evaluated to determine their applicability to capillary column multi-residue purge and trap operations. The following sorbents were evaluated: Tenax GC, Silica gel, Ambersorb XE-340, Molecular seive ELZ-115, and several experimental Carbosieve-like products supplied by Supelco. For this study, stainless steel 23 cm X 2.7 mm ID "A" traps were packed with 100 percent

Tenax and 50 percent Tenax (inlet) followed by 50 percent of each of the above mentioned test materials. The "B" traps used for this study were 23 cm x 1.8 mm ID glass-lined stainless steel packed with the same sorbents as the "A" traps. The following conditions were selected: a 5 mL aqueous solution was purged at 22-25°C with helium flowing at 40 mL/minute for 11 minutes, 150 µL of gaseous injections were made directly into trap "A." During the purge cycle or injection, the "A" trap was maintained at room temperature (25-30°C). For the "A" trap to "B" trap transfer, the "A" trap was heated to 180°C and backflushed to the "B" trap with helium flowing at 20 mL/minute for 120 seconds. The "B" trap was at room temperature. For desorption to the capillary column the "B" trap was rapidly heated to 180°C while being backflushed with helium flowing at 10 mL/minute for 120 seconds. A 60m 0.75 mm ID glass capillary column coated with SE-30 1 µm df was selected as the analytical column.

The results of the investigations show that using common purge and trap conditions, sorbents other than Tenax retained too much water during the purge operations at 22-25°C for capillary column analyses. When the retained water was desorbed into the capillary column it formed a continuous liquid plug of water within the capillary column several cm long. The result was erratic detection of water soluble compounds that were flushed through the column by the water plug and variable retention times for non-polar compounds. The water plugs also extinguished the flame in the detector. Conventional forward and reverse flow trap drying operations at various trap temperatures were tried and found to be of no value. Because of the water problem associated with other than Tenax traps, Tenax "A" and

"B" traps were selected for all development work. Note: Since this evaluation the CDS 320 software was modified by the manufacturer to allow the "A" trap to be maintained at elevated temperatures during the purge cycle, it is likely that a trap temperature can be selected for other sorbents that will allow water to be vented while the target compounds are concentrated as is the case of Tenax operated at 22-25°C. It is important to add that during this lengthy sorbent evaluation numerous "water plug" analyses were performed using SE-30 bonded and non-bonded phases with no observed degradation of either capillary column.

SEQUENTIAL TRAP TRANSFER CONDITIONS

Several experiments were performed to determine the critical parameters required to quantitatively backflush a variety of compounds from the "A" trap to the "B" trap. This was accomplished by injecting 1 µL volume of the test mixture into the "A" trap injector as the purge gas was flowing at 40 mL/minute through the purging device filled with 5.0 mL of reagent water. After 11.0 minutes the "A" trap was backflushed into the "B" trap. Desorb time, flow rate and temperature were evaluated as variables. Based upon past observations of the system performance an initial evaluation was performed using a fixed flow rate of 15 mL/minute, and a fixed desorb temperature of 200°C. Desorb times were varied from 200 seconds down to 20 seconds. Table 5 lists the peak areas relative to decane obtained from a direct column injection chromatogram and those obtained from the sequential trapping operations using different transfer times. From these data it is evident that all of the compounds are not released from the trap over the same period of time. The lower boiling compounds are released first followed by the higher boiling *n*-alkanes and finally the polar compounds. Close examination of the chromatograms show that decane was almost quantitatively transferred before 20 percent of the 2,6-dimethylaniline or naphthalene was transferred. This table shows that at 15 mL/minute and 200°C it took a minimum of 100 seconds to quantitatively transfer the most retentive of the test compounds from the "A" trap to the "B" trap. Extending the transfer times up to 200 seconds did not adversely affect the quality of the data. A second set of trap conditions were then evaluated where the trap temperature was elevated to 250°C, the flow was maintained at

15 mL/minute, and the desorb times were varied as in the previous experiment. It was found that raising the trap temperature decreases the quantitative transfer time for the volatile reactive components and the n-alkanes from 100 seconds at 200°C to 80 seconds at 250°C with no evidence of thermal breakdown.

A final set of trap conditions were evaluated where the trap desorb temperature was 200°C and the transfer flow rate changed from 15 mL/minute to 10 mL/minute. As before, the desorb times were varied. Decreasing the flow rate during the trap transfer step had little effect upon the resulting data. The transfer times and recoveries were nearly identical to those obtained at the 15 mL/minute flow rate.

From this series of experiments, it is demonstrated that all of the compounds do not backflush from the sorbent trap as a sharp plug of material but elute, depending upon their boiling point and polarity. Desorb time and desorb temperature appear to be the most important variables. Similar studies involving trichlorobenzenes indicated that desorb time of 120 seconds is required for quantitative transfer. Based upon these observations and other data, backflushing the "A" trap at 180°C with a flow rate of 15 mL/min for 200 seconds was selected for subsequent studies. Higher trap temperatures were not selected because previous method development research associated Tenax trap failure with desorption temperatures in excess of 200°C and because excessive background peaks appeared in the FID blank chromatograms whenever trap temperatures exceeded 200°C.

TRAP TRANSFER TO COLUMN

A similar study was performed to determine the conditions required to quantitatively transfer compounds from the 1.8 mm ID "B" trap (loaded according to the previously described conditions) to the analytical column. Since the desorb flow rate through the "B" trap supplies the carrier gas flow to the analytical column, the flow must be adjusted to provide optimum flow conditions for the analytical column and not optimum chromatographic transfer conditions. For the column used in this evaluation, the flow was fixed at 10 mL/minute. Similarly, as previously stated, trap desorb temperatures in excess of 200°C are not desirable, therefore, only desorb times were evaluated. Trap B desorb times in excess of 20 seconds were adequate for quantitative transfer of the compounds evaluated. Extended desorb times up to 120 seconds did not appear to adversely affect the quality or the appearance of the chromatogram. For these reasons desorb times of 120 seconds were selected to insure maximum transfer of a wide variety of analytes.

COLUMN SELECTION

During the course of this study several capillary columns were briefly evaluated to determine which internal diameters and film thicknesses are best suited for sequential purge and trap analyses. For these studies, a 1.7 mm ID copper "B" trap packed with 23 cm of Tenax desorbed at 200°C for 120 seconds was used. The "B" trap desorb flow rate was adjusted to provide

a 20 to 40 cm/second linear velocity of helium through the test column. It was found that 0.2 to 0.32 mm ID fused silica columns with film thicknesses between 0.25 and 1.0 μm were of limited value because they could be used only for compounds that are reconstituted on the capillary under nearly true cold trapping conditions. Non-reconstituted compounds eluted from these columns as poorly defined broad peaks.

For glass columns with a 0.5 mm ID and film thicknesses near 1 μm, visual comparisons of chromatograms from both desorption and direct injections at isothermal temperatures showed that the desorption process adversely affected the peak geometry of the compounds eluting in the initial isothermal area of the chromatogram. Peak geometries improved after minimal programming.

By far the best chromatograms were obtained using 0.75 mm ID glass columns with film thicknesses near 1 μm. Visual comparisons of peaks eluting within the initial isothermal area of the chromatograms were nearly identical. Comparisons of the number of theoretical plates/meter for desorption chromatograms to direct injection chromatograms show that the average for pentane through octane was 1500 theoretical plates for direct injection and 1100 theoretical plates/meter thus, even for desorption chromatograms for wide bore capillary columns, the desorption process can have an adverse effect upon compounds eluting in the early isothermal area of the chromatogram. Increasing the film thickness of the column could help to minimize this problem, however, at the time these experiments were

performed film thicknessess in excess of 1 μm were not commercially available. Based upon these observations 0.75 mm ID, 1 μm df columns were selected. Furthermore, since such columns typically exhibit about 1/3 the number of theoretical plates/meter as 0.25 mm ID columns, 60 m column lengths were chosen in order to obtain the resolving power required to separate complex mixtures of synthetic organic compounds.

Selection of a liquid phase was based solely upon its commercial availability and resolution of complex mixtures of purgeable compounds of current interest to the Agency. Three phases were evaluated: methyl silicone, SE-54 and Carbowax 20M. Of these liquid phases, the methyl silicone phases were found to be superior. The SE-54 was unable to resolve many component pairs that were easily resolved by the methyl silicone phase. The Carbowax 20M chromatograms were lengthy and the early eluting components generated broad fused peaks indicating the liquid phase was unsuitable (a solid) at the temperatures required to separate the most volatile compounds tested.

A number of temperature programs were evaluated and the following was found to be best suited for resolving complex mixtures of synthetic organic chemicals of current interest to the Agency. The SE-30 column is maintained at 10°C for 4 minutes and then programmed at 4°C per minute to 210°C. The column is held at 210°C until all of the compounds elute or just before the next analysis. Helium is used as the carrier gas flowing at 20 cm/second (measured at 115°C). If only compounds eluting after methylene chloride are to be analyzed, then the initial column temperature was raised to 30-40°C.

PROCEDURE EVALUATION

Through the assessment of the previously described critical parameters and from previous purge and trap methods development programs, the conditions listed in Table 6 were selected as the most promising combination for determining a wide variety of synthetic organic chemicals in water by purge and sequential trapping capillary column gas chromatography.

In the preamble to the "National Interim Primary Drinking Water Regulations; Control of Trihalomethanes (THMs) in Drinking Water; Final Rule," it is stated that "to qualify for interim certification, laboratories will be required to demonstrate their ability to analyze the Performance Evaluation samples provided to them to within 20 percent of the "true value" for each of the THMs as well as for the total of the THMs in the samples using at least one of the approved methods." One of the initial evaluations of the proposed method was to determine if the procedure could reliably generate data within ±20 percent of the true value for an actual Performance Evaluation sample. The following experiment was designed to determine the accuracy and precision of the proposed method while minimizing the degree of operator skill required to perform the analysis. The CDS 320 controller was programmed to automatically function exactly according to the parameters described in Table 6. Primary dilutions of chloroform and dibromochloromethane at 10,000 µg/mL in methanol were obtained from the EMSL-Cincinnati Repository for Toxic and Hazardous Materials. Methanolic dilutions of bromodichloromethane and bromoform were prepared in-house according to

USEPA Method 501.1 (Ref. 1). Two multicomponent methanolic secondary dilutions were prepared from these primary standards. Dilution No. 1 contained 125 ng/µL of each trihalomethane and Dilution No. 2 contained 500 ng/µL of each trihalomethane. Three aqueous standards were prepared by spiking 1000 mL of reagent water with 20.0 µL of Dilution No. 1, 100 mL of reagent water with 20.0 µL of Dilution No. 1, and 100 mL of reagent water with 20.0 µL of Dilution No. 2. The aqueous standard solutions were analyzed starting with the low level, 2.5 µg/L, followed by the mid-range, 25 µg/L, and finally the high range, 100 µg/L, trihalomethane standards. The data system was calibrated for each trihalomethane using the three point calibration curve. The response of each THM was linear and passed through zero providing .999 or better coefficients of determination. Eight days later an EMSL-Cincinnati Quality Check trihalomethane concentrate was diluted according to instructions in reagent water and analyzed in order to verify the validity of the 8-day old calibration date. (True value data are supplied with EMSL-Cincinnati Quality Check Samples.) Each trihalomethane was found to be within 10 percent of the reported value validating the calibration curves for each THM. This system evaluation was followed by reagent water analyses (system blanks) and replicate analyses of two different trihalomethane Performance Evaluation samples (PE-1 and PE-2). The true values of PE-1 and PE-2 were unknown at the time of analysis. Each of the samples were diluted in reagent water according to instructions and analyzed in quadruplicate. A second different Quality Control Sample was analyzed between the PE-1 and PE-2 sample in order to monitor the continuing performance of the system. Tables 7 and 8 list the resulting concentrations

taken directly from the data system reports. Just prior to analyzing PE-2 Dilution No. 1, the quality control sample containing an unusually high concentration (660 µg/L) of chloroform was analyzed. It is believed that system memory (~ 0.5 percent carry-over) caused a false high chloroform value in the PE-2-1 analysis, therefore, the PE-2-1 chloroform data were deleted as an operator generated outlier. It is likely that the PE-2-2 value should be deleted also but it was not. After reporting the concentrations, the true values were obtained. Tables 7 and 8 show that the resulting data were accurate in that in no case did the average value differ from the true value by more than 10 percent. Moreover, with the exception of the PE-2-1 and PE-2-2 chloroform values, suspected to be accidently contaminated, the precision of the procedure is such that at the 99 percent confidence limit all of the THMs analyzed in the PE samples easily fall within the 20 percent acceptance criteria. This clearly demonstrated that the proposed procedure is capable of generating accurate and precise trihalomethane data utilizing operator skills with a rating of only one (Ref 2).

ACCURACY AND PRECISION STABILITY STUDY TAP WATER

Two liters of Cincinnati tap water were dechlorinated by the addition of 200 mg of sodium thiosulfate. The resulting quenched tap water was allowed to stand head-space free for 18 hours at room temperature to allow trihalomethane intermediates to decompose to provide stable THM values with time. A complex spiking mixture of organic compounds in methyl alcohol was prepared according to Table 9. The compounds were selected based upon the

current and long range needs of various Agency programs, the ability of the column to adequately resolve them for accurate measurement (retention data on Table 9) and to obtain data for representative compounds defining a wide range of purging efficiencies. Concentrations were selected so that the FID would provide similar peak height signals under the analytical conditions stated in Table 6. One liter of the quenched 18-hour-old tap water was spiked with 100 µL of the spiking solution resulting in the concentrations listed in Table 6. Twenty-four 40 mL septum seal purge and trap sample bottles were randomly filled with the resulting spiked mixture. Six of the bottles were sealed and stored at room temperature (Thio-22°C); six of the bottles were sealed and stored at 4°C (Thio-4°C). Six bottles were acidified with two drops of HCl (1+1) to give a pH of 1.8, sealed and stored at 22°C (Thio-HCl-22°C). 100 µL of $HgCl_2$ (0.5g/100 mL in reagent water) solution was added to each of six bottles and stored at 22°C (Thio-Hg-22°C). Six bottles were filled with non-spiked quenched tap water sealed and stored at 22°C (Thio-blank). On day zero (spike day) the gas chromatograph was calibrated at a single concentration using a 20.0 µL aliquot of the spiking mixture (Table 9), diluted to 100 mL in reagent water. Duplicate analyses upon a Thio-blank, Thio-22°C, Thio-HCl-22°C and a single analysis upon a Thio-Hg-22°C sample were performed. Over the next 24 days the instrument was recalibrated each analysis day and similar analyses were performed. The results appear in Tables 10 through 15.

Recovery data were corrected for the average THM values found in the Thio-blanks. The addition of HCl was selected to evaluate its performance

as a biocide and a chemical stabilization agent. $HgCl_2$ was included in the study to evaluate its performance as a biocide.

Table 10 lists the averaged results of all of the spike day data. These include two Thio-22°C; two Thio-HCl-22°C and a single Thio-Hg-22°C analysis. Most of the compounds provided accurate and precise recoveries for the spike day analyses in all the sample matrices. Noteworthy exceptions are allyl bromide, 2-chloroethyl vinyl ether, and pentachloroethane. Allyl bromide rapidly disappeared from each of the sample matrices studied. Over the 6-hour period of time represented by these data, an average recovery of only 40 percent was obtained with a 47 percent relative standard deviation. 2-chloroethylvinyl ether in the Thio-HCl-22° and Thio-Hg-22°C preserved samples also disappeared. Pentachloroethane rapidly decomposed to form tetrachloroethylene in the Thio-22°C and Thio-Hg-22°C matrices, but was stable in the Thio-HCl-22°C matrix.

Table 11 lists the method accuracy and precision for samples stored up to 24 days in the Thio-22°C matrix. Comparing the 24-day averaged recovery data to the spike day (Table 10) and 18-day recoveries (Table 15) show that most of the compounds evaluated are stable indicating little or no biological activity. It is important to note that previous studies have shown that biological activity can develop in such samples (Ref. 3). The following compounds were found to be unstable in this particular matrix: allyl chloride, allyl bromide, cis and trans-1,3,-dichloropropene,

1,1,2,2-tetrachloroethane and pentachloethane. Progressive losses of hexachloroethane and styrene indicate they too may be lost upon storage but based upon the precision of the analytical methodology not at a significant rate for this overall method. Pentachloroethane and 1,1,2,2-tetrachloroethane decomposed to form tetrachloroethylene and trichloroethylene, respectively, providing the likelihood of false positive identifications if samples are stored in this manner.

Table 12 lists the results of the quenched sample storage at 4°C. Comparing the 24-day averaged recoveries to the spike day and day 18 recoveries show that the same analytes are affected as Table 11 but generally with improved recoveries.

The addition of mercury to the matrix (Thio-Hg-22°C) appears to have a detrimental effect upon sample storage. Table 13 shows that in addition to the compounds affected by simple 22°C storage, a total loss of 2-chloroethyl vinyl ether was noted along with a significant increase in the concentration of 1,2-dichlorethane with time.

The adjustment of the sample pH with HCl was originally intended to observe its properties as a biocide. The data in Table 14 show that the addition of HCl to the sample matrix effectively halted the decomposition of tetrachloroethane to form trichloroethylene and pentachloroethane to form tetrachloroethylene. Compared to spiked day recoveries the detrimental effects of preservation with HCl are the loss of 2-chloroethyl vinyl ether and styrene.

Table 15 compares the average study recoveries and the average of duplicate analyses performed on day 17 or 18. It appears from these data that for a general analytical method the best sample storage technique would be a combination of preservation with HCl and storage at 4°C.

METHOD ACCURACY AND PRECISION AND ANALYTE STABILITY IN BIOLOGICALLY ACTIVE RIVER WATER

A prestudy evaluation of spiked Ohio River water showed that the sample of river water obtained for this phase of the evaluation demonstrated no biological activity toward any of the compounds listed in Table 9 over a one week period of time when stored at 22°C. It was not determined if one or more of the compounds present in the spiking solution inadvertently acted as a biocide or if the naturally occurring microbes were not accustomed to degrading the target compounds. In an effort to rapidly generate a biologically active sample matrix for as many compounds as possible, Ohio River water was inoculated with a mixture of commercially available bacterial cultures adapted to digest fresh water wastes containing hydrocarbons and polychlorinated biphenyls. For this experiment 2 mL of the bio-spiking solution and 1998 mL of Ohio River water was added to a 2L separatory funnel. Four hundred µL of the methanolic spiking solution described in Table 9 was injected below the surface of water (resulting in a mixture containing the compounds at two times the concentrations listed in Table 9). The separatory funnel was sealed and mixed by inverting twice. Thirty purge and trap septum seal vials were then filled to overflowing using the Teflon stopcock on the separatory funnel to control the flow and to minimize turbulence as the bottles were filled. Six bottles were sealed and immediately stored at 4°C. Six bottles were sealed and stored at 22°C. Six bottles were spiked with 100 µL of Slime-Trol RX-34 solution, sealed and stored at 22°C. Six bottles were spiked with 100 µL $HgCl_2$ solution, sealed and stored at 22°C and finally, six bottles were spiked with 5 drops

of hydrochloric acid solution (1+1), sealed and stored at 22°C. The bio-spiking solution was prepared by adding 1.0 g of Sybron PCB culture, 1.0 g of Sybron hydrocarbon culture, and 1.0 g of Polybac Hydrobac™ C1 culture to 25 mL of reagent water. The solution was allowed to stand 18 hours at 22°C with air bubbling through the mixture before use. The Slime-Trol solution was prepared by diluting 0.6 g of Slime-Trol[A] RX-34 (a commercial water soluble biocide from Betz Paperchem, Inc.) to 10.0 mL using reagent water (Ref. 4). The $HgCl_2$ solution was prepared by dissolving 0.5 g of $HgCl_2$ in 100 mL of reagent water. Ohio River water blank analyses were performed and were found to be free of any interferring compounds at levels significant to this study.

On day zero (spike day) the gas chromatograph was calibrated using spiked reagent water at concentrations identical to the levels used for the study. Spike day calibration data showed that the 2-chloroethylvinyl ether had disappeared from the spiking solution, therefore, it does not appear in the study data. Midway through this study an instrumental problem developed interrupting the planned frequency of analyses and adversely affected the precision of the data. Tables 16 through 21 list the results of the study. Individual compounds contained in the samples stored at 22°C do show statistically significant evidence of die-off due to chemical and biological activity. Storage at 4°C retards both chemical and biological losses while the addition of the three biocides appears to halt biological activity. As in the previous study, HCl addition appears to be the best preservation reagent studied since, in addition to acting as a biocide, it also retards chemical decomposition associated with pentachloroethane and tetrachloroethane. Samples preserved with Slime-Trol RX-34 demonstrate little

advantage over mercury preserved samples. After about 18 days of storage chromatograms of Slime-Trol RX-34 preserved samples provided no resolution between bromodichloromethane and 1,1,2-trichloroethylene indicating that an unknown compound was formed with time that eluted within this retention area. The appearance of this compound prevented accurate measurement of either compound. Some of the Ohio River water spiked data appears to conflict with the spiked tap water study in that the concentration of 1,2-dichloroethane did not increase with time when the sample was preserved with mercury. Also styrene disappears at a significant rate in the mercury preserved samples and at a reduced rate in the HCl preserved samples.

METHOD DETECTION LIMITS

Reagent water containing 50 mg/L of sodium thiosulfate was spiked with the methanolic mixture listed in Table 9 at the rate of 5 µL of the spiking mixture per liter of water. The concentration of each compound was selected so that each peak in the chromatogram would be at least 5 times higher than the average noise level at the most sensitive detector setting usable with the system. Actual concentrations are 0.05 times those listed in Table 9. Peak heights for the various analytes appeared in the chromatogram between 5 and 7 mm. Peaks normally occurring in reagent water analyses (system blanks) attributable to system background were well resolved from the test compounds. Four purge and trap sample bottles were filled and sealed with the dilute mixture. The gas chromatograph was calibrated with a single point calibration standard at 40 times the concentration of the method detection limit spike. Once the system was calibrated, the contents of each

sample bottle was analyzed in duplicate until seven analyses were performed. Table 22 lists the resulting data and the calculated method detection limits (Ref 5). From these data it is apparent that the method detection limit is primarily dependent upon the sensitivity of the flame ionization detector to the target compound. The method detection limit is highest for the highly halogenated compounds ~ 1 µg/L decending down to the alkyl substituted benzenes at ~ 0.1 µg/L. Although no significant peaks were noted in the blank analysis, high recoveries are attributable to an accumulation of errors associated with the failure to bracket the spike with two standards, and the additive effects of background and system memory.

SYSTEM MEMORY

Throughout this method evaluation, indications of analyte carry-over or system memory appeared whenever low level analyses followed high level samples. This problem existed even though the purging device was flushed with reagent water two or three times between analyses and after exchanging purging devices.

In an effort to document the extent of the carry-over problem, the following experiment was performed. A moderate level standard solution was prepared by diluting 20.0 µL of the spiking mixture described in Table 9 to 100.0 mL with reagent water. The purging device was flushed with reagent water followed by a reagent water analysis at the most sensitive FID setting in order to establish normal system background values. A 5-mL aliquot of the moderate level standard was analyzed followed by three reagent water

flushes of the purging device. After the moderate level standard chromatogram was completed, a 5-mL aliquot of reagent water was analyzed at the most sensitive settings. The purging device was again flushed with three reagent water flushes followed by a second reagent water analysis.

Finally the purging device was exchanged with a new one followed by a final reagent water analysis. All of these analyses were performed with the CDS-320 valve and internal plumbing oven set at 125°C. The valve and internal plumbing oven temperature was then raised to 200°C and a similar sequence of analyses were performed with the exception that the purging device was not exchanged for the final analysis. The system memory was then determined by dividing the peak area of the moderate standard into the blank corrected peak areas obtained from each of the reagent water analyses times 100. These values appear in Table 23 (system memory).

Based upon these tests it is evident that much of the system memory is due to sorption of the high boiling compounds within the CDS-320 plumbing and not the purging device as one would initially believe. Based upon these observations, system memory and not purging efficiencies and column performance appears to limit the compounds that can be accurately determined by sequential trapping capillary column gas chromatography. With the valve oven operated at 200°C it appears that compounds that exhibit less than a 2% carry-over can be successfully analyzed. Operating the valve oven at temperatures in excess of 200°C is not practical for the system evaluated as excessive background occurred due to system bleed.

CONCLUSIONS

The accuracy and precision data gathered during this study for over 40 compounds clearly demonstrate that a properly optimized automated purge and sequential trapping capillary column gas chromatograph can generate accurate and precise data for a wide variety of synthetic organic compounds contained in drinking water and related matrices. Each critical parameter was identified and optimized in the study. Once the system was optimized, the automatable features and the inherent ruggedness of the capillary FID-data system allow the system to generate dependable data with minimal operator skills. Using a flame ionization detector, the method detection limits vary between 0.1 and 1 µg/L for reagent water spikes.

The holding time data show that preservation is necessary to guarantee integrity of certain compounds. Sample storage at 4°C is far superior to storage at 22°C and the addition of HCl (pH adjustment to 2) effectively halts biological degradation and stops chemical decomposition of pentachloroethane and tetrachloroethane which form tetrachloroethylene and trichloroethylene, respectively. Other biological controls show no advantages over pH adjustment. System memory to high boiling compounds, which in turn affects accuracy and precision, appears to be the compound limiting factor for the method.

REFERENCES

1. "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method," Method 502.1, EPA 600/4-81-059, Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268. (1981).

2. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA 600/4-79-019, Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268. (1979).

3. "The Determination of Volatile Aromatic Compounds in Drinking Water and Raw Source Water," Thomas A. Bellar and James J. Lichtenberg. Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268. (1981).

4. Report on "Preservation and Sample Storage of Volatile Organics in Drinking and Raw Source Waters," USEPA Contract No. 68-03-3103. In preparation. Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268.

5. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., Budde, W.L., "Trace Analysis for Wastewaters," Environmental Science and Technology, 15, 1426 (1981).

Table 1. Initial Evaluation of the Sequential Trapping Capillary System

Percent Response Values for Test Mixture

	Compound				
	2-octanone	1-octanol	2,6-dimethyl phenol	2,6-dimethyl aniline	naphthalene
Primary chromatogram	—	71	78	79	100
Initial Installation Chromatogram	82	74	85	85	112
CDS transfer line chromatogram	75	28	29	51	84
Modified transfer line chromatogram	80	67	86	89	111
Sequential Trapping Chromatogram	38	32	16	49	33

Table 2. Effect of Various Traps Upon Chromatographic Data

	Retention Times (minutes)					
	n-C_5	n-C_6	n-C_7	n-C_8	n-C_9	n-C_{10}
Direct injection	4.03	4.52	5.58	7.88	11.35	15.18
2.7 mm stainless steel trap	4.47	4.94	5.96	8.25	11.55	15.57
1.8 mm glass trap	4.47	4.94	5.96	8.25	11.55	15.57
1.7 mm copper trap	4.46	4.93	5.98	8.25	11.54	15.44
Retention time difference[a]	.44	.42	.38	.37	.20	.39
	Peak Area Comparisons (Intregrator Units)					
Direct injection	460	437	400	365	337	310
2.7 mm stainless steel trap	376	434	387	352	333	309
1.8 mm glass trap	396	424	376	320	298	278
1.7 mm copper trap	380	446	369	308	283	265
	Peak Height Comparisons (mm)					
Direct injection	133	115	86.0	52.3	54.3	34.5
2.7 mm stainless steel trap	52.0	50.7	52.8	38.5	42.5	27.3
1.8 mm glass trap	78.2	84.3	62.0	39.8	42.1	25.8
1.7 mm copper trap	83.3	89.2	63.7	39.7	40.5	23.0
	Peak Width Comparisons (seconds)					
Direct injection	.03	.04	.045	.067	.060	.086
2.7 mm stainless steel	.069	—[b]	.070	.087	.074	.107
1.8 mm glass trap	.049	.049	.060	.077	.068	.10
1.7 mm copper trap	.044	.047	.056	.074	.067	.11

Chromatographic conditions: 70°C 8 minutes - 8°/minute to 100°C

[a]Average difference in retention time between direct injection and thermal desorption

[b]Data system malfunction

Table 3. Trap Performance Non-Cold Trapping Chromatography

	2-octanone	1-octanol	2,6-dimethyl-phenol	n-C_{11}	2,6-dimethyl aniline	naphthalene	n-C_{12}	n-C_{13}
	1.0 µL injection into column							
Percent Response	77	71	86	--	86	115	—	--
Area Ratio[a]	77	70	78	95	74	92	90	83
Theor. Plates/Meter	--	--	—	—	--	--	—	1030
	1.0 µL injection 2.7 mm ID "B" Trap							
Percent Response	53	29	ND[b]	—	22	38	—	--
Area Ratio[a]	67	57	ND[b]	147[b]	48	68	101	72
Theor. Plates/Meter	—	--	--	--	--	--	—	175
	1.0 µL injection 1.8 mm ID glass-lined "B" Trap							
Percent Response	69	44	60	—	55	55	--	—
Area Ratio[a]	66	48	56	95	60	77	80	76
Theor. Plates/Meter	--	--	—	--	--	--	—	452
	1.0 µL injection 1.7 mm ID copper "B" Trap							
Percent Recovery	73	46	65	—	60	83	—	--
Area Ratio[a]	74	64	64	116	68	90	90	87
Theor. Plates/Meter	--	--	—	--	--	--	—	492

[a]Relative to n-decane
[b]Peak for 2,6-dimethyl phenol fused with n-undecane

Table 4. Trap Performance Cold Trapping Chromatography

	2-octanone	1-octanol	2,6-dimethyl phenol	n-C_{11}	2,6-dimethyl aniline	Naphthalene	n-C_{12}	n-C_{13}
	1.0 µL injections into column							
Percent Response	86	76	95	--	97	123	—	—
Area Ratio[a]	83	77	87	101	90	110	105	107
Theor. Plates/Meter	--	--	--	--	--	—	—	1230
	1.0 µL injections 2.7 mm "B" trap							
Percent Response	no data	70	86	—	93	124	—	—
Area Ratio[a]	82	74	79	97	81	102	101	98
Theor. Plates/Meter	--	--	--	--	--	—	—	1210
	1.0 µL injections 1.8 mm glass-lined "B" Trap							
Percent Response	78	62	87	—	82	113	—	—
Area Ratio[a]	81	76	87	104	83	107	103	102
Theor. Plates/Meter	--	--	--	--	--	--	—	1220
	1.0 µL injections 1.7 mm ID Copper "B" Trap							
Percent Response	77	65	88	—	91	120	--	—
Area Ratio[a]	84	78	86	104	82	107	102	104
Theor. Plates/Meter	--	--	--	--	--	--	—	1180

[a]Relative to n-decane

Table 5. Sequential Trapping 200° C at 15 mL/minute

	Direct Injection	Desorption Time (seconds) 200	150	120	100	80	60	40	20
2-octanone	.80	.83	.81	.85	.81	.81	.80	.70	ND
1-octanol	.85	.76	.76	.77	.75	.76	.74	.46	ND
2,6-dimethylphenol	.89	.86	.84	.88	.85	.85	.62	ND	ND
n-undecane	.98	1.00	.99	1.03	1.02	1.19	1.13	.85	Trace
2,6-dimethylaniline	.91	.95	.90	.97	.87	.73	.30	ND	ND
Naphthalene	1.09	1.15	1.08	1.15	1.03	.83	.29	ND	ND
n-dodecane	.98	1.00	.98	1.07	.98	.98	.97	.70	ND
n-tridecane	1.02	1.01	.99	1.07	.98	.92	.84	.42	ND

Areas of the Resulting Peaks Relative to n-decane

Table 6. Analtyical Conditions

1. Purging conditions

Sample volume: 5.0 mL
Purge gas: Helium
Purge gas flow rate: 40 mL/minute
Sample temperature: Room Temperature (22 ± 2°C)
Trap "A": 0.105" ID stainless steel packed with 23 cm of Tenax GC 60/80 mesh sorption temperature < 29°C

2. Sequential Trapping

Backflush Trap "A" at 180°C ± 10°C
For 120 sec. flow rate
15 mL/minute
Trap "A" heating rate (outside surface) 10°/sec

Trap "B" 1.5 to 1.8 mm ID
Copper or glass lined stainless steel
packed with 23 cm of Tenax GC 60/80 mesh
operated at room temperature 22°C ± 2°C

3. Desorb "B" Trap to Column

Backflush trap "B" at 180°C ± 10°C
for 120 seconds at a flow rate between
8 and 12 mL/minute (column flow rate)
Trap "B" heating rate (outside surface)
10°/sec.

4. Column

0.75 mmID x 60 m long coated with SE-30 (Bonded)
1 μm film thickness with a reported 101 percent coating efficiency carrier gas helium flowing at 27 cm/sec measured at 115°C (10 mL/minute).

5. Program

10°C Isothermal for 4 minutes, then program at 4°/minute to 210°C.

6. Miscellaneous

With the exception of the purging device, all transfer lines and valves were maintained at 200°C. Traps were conditioned between analyses at 200°C for various periods of time to minimize carry-over.

The purging device was flushed out twice with ~ 7 mL of reagent water between each analysis.

Table 7. Analysis of Performance Evaluation Sample - PE-1

Sample Identification	Order of Analysis	Concentration (µg/L) Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform
PE-1-1	1	85.6	82.2	103	52.5
PE-1-2	2	83.0	79.9	105	55.1
PE-1-3	5	81.6	82.7	101	53.1
PE-1-4	6	81.0	78.3	101	53.1
Average		82.8	80.8	103	53.5
Std. Deviation		2.05	2.05	1.91	1.14
99 Percent Confidence Interval (µg/L)		76.7 to 88.9	74.7 to 87.0	96.8 to 108	50.1 to 56.9
True Value (µg/L)		86.8	82.1	107	54.9
20 Percent Acceptance Interval Around True Value (µg/L)		69.4 to 104	65.7 to 98.5	85.6 to 128	43.9 to 65.1
Percent Recovery		95.4	98.4	96.3	97.4

Table 8. Analysis of Performance Evaluation Sample - PE-2

Sample Identification	Order of Analysis	Concentration (µg/L) Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform
2-1	3	19.7[a]	7.91	17.8	16.0
2-2	4	17.9	8.43	18.0	16.1
2-3	7	14.7	8.30	16.7	15.9
2-4	8	15.5	8.36	17.2	15.9
Average		16.0	8.25	17.4	16.0
Std. Deviation		1.67	0.23	0.59	0.095
99 Percent Confidence Interval (µg/L)		11.0 to 21.0	7.55 to 8.95	15.7 to 19.2	15.7 to 16.3
True Value (µg/L)		15.3	9.12	17.8	16.5
20 Percent Acceptance Interval Around True Value (µg/L)		12.2 to 18.4	7.30 to 10.9	14.2 to 21.4	13.2 to 19.8
Percent Recovery		105	90.5	97.8	97.0

[a] Value deleted (see text)

Table 9. Spiking Mixture Concentrations and Retention Data

Compound	Conc. Spiking Solution (ng/μL)	Conc. Aqueous Dilution (μg/L)	Retention Time (Min.)
Pentane[b]			6.24
1,1-Dichloroethylene	99.8	10.0	6.50
Methylene chloride	375	37.5	6.69
Allyl chloride	100	10.0	6.81
t-1,2-Dichloroethylene	100	10.0	7.86
c-1,2-Dichloroethylene	99.7	10.0	9.27
Allyl bromide	99.5	10.0	9.54
Chloroform	299	29.8	9.71
1,2-Dichloroethane	100	10.0	10.78
1,1,1-Trichloroethane	175	17.5	11.19
Benzene	25	2.5	11.93
Carbon tetrachloride	303	30.3	12.18
1,2-Dichloropropane	75	7.5	13.34
Bromodichloromethane	350	35.0	13.70
1,1,2-Trichloroethylene	125	12.5	13.80
2-Chloroethylvinyl ether	125	12.5	
Heptane[b]	—	—	14.60
1,3-Dichloropropene	151[a]	15.1	15.41
1,3-Dichloropropene			16.43
1,1,2-Trichloroethane	150	15.0	16.60
Toluene	25	2.5	17.08
Dibromochloromethane	450	45.0	17.77
1,1,2,2,-Tetrachloroethylene	175	17.5	19.23
Octane[b]	—	—	19.43
Chlorobenzene	50	5.0	20.60
Ethylbenzene	25	2.5	21.55
Bromoform	498	49.8	21.81
p-Xylene	25.0	2.5	22.00
Styrene	25.0	2.5	22.73
1,1,2,2-Tetrachloroethane	250	25.0	22.95
Nonane[b]	—	—	23.99
Bromobenzene	49.9	5.0	24.33
n-Propyl benzene	25	2.5	25.70
Pentachloroethane	400	40.0	26.25
m-Dichlorobenzene	50	5.0	27.63
p-Dichlorobenzene	50	5.0	27.86
Decane[b]	—	—	28.35
o-Dichlorobenzene	50	5.0	28.81
1,2-Dibromo-3-chloropropane	250	25.0	30.20
Hexachloroethane	250	25.0	30.90
1,3,5-Trichlorobenzene	99.9	10.0	33.14

Table 9. (Continued)

Compound	Conc. Spiking Solution (ng/μL)	Conc. Aqueous Dilution (μg/L)	Retention Time (Min.)
1,2,4-Trichlorobenzene	100	10.0	34.77
Naphthalene	50	5.0	35.02
1,2,3-Trichlorobenzene	99.9	10.0	36.03
Hexachlorobutadiene-1,3	250	25.0	36.76
Dodecane[b]	—	—	40.03
1,2,4,5-Tetrachlorobenzene	151	15.1	40.33
1,2,3,4-Tetrachlorobenzene	150	15.0	41.76
1-Chloronaphthalene	150	15.0	41.84
2-Chlorobiphenyl	150	15.0	45.51

[a]Mixture of cis and trans isomers assumed to be 50/50 mixture.
[b]n-alkanes used as internal standard.

Table 10. Spike Day Accuracy and Precision Quenched Tap Water

Compound	N	Average µg/L	SD	RSD (%)	Recovery (%)
1,1-Dichloroethylene	5	9.05	0.82	9.1	91
Methylene chloride	5	35.6	1.9	5.3	95
Allyl chloride	5	8.66	0.18	2.1	87
t-1,2-Dichloroethylene	5	8.51	0.72	8.4	85
c-1,2-Dichloroethylene	5	9.26	0.40	4.4	93
Allyl bromide	5	3.99	1.9	47	40
Chloroform	5	48.6	1.4	3.0	87
1,2-Dichloroethane	5	9.60	0.18	1.9	96
1,1,1-Trichloroethane	5	15.8	0.55	3.5	90
Benzene	5	2.54	0.08	3.0	101
Carbon Tetrachloride	5	27.2	1.5	5.3	90
1,2-Dichloropropane	5	6.59	0.17	2.6	88
Bromodichloromethane	5	57.2	1.2	2.0	92
1,1,2-Trichloroethylene	5	12.2	0.75	6.1	97
2-Chloroethylvinyl ether	2[b]	12.2	—	—	97
1,3-Dichloropropene	5	6.74	0.44	6.6	45
1,3-Dichloropropene	5	6.57	0.40	6.1	44
1,1,2-Trichloroethane	5	14.0	0.95	6.8	93
Toluene	5	2.36	0.11	4.8	95
Dibromochloromethane	5	65.7	1.8	2.8	98
1,1,2,2-Tetrachloroethylene	2[c]	16.1	—	—	92
Chlorobenzene	5	4.87	0.33	6.8	97
Ethylbenzene	5	2.29	0.04	2.0	92
Bromoform	5	53.3	0.03	0.5	96
p-xylene	5	2.39	0.03	1.3	96
Styrene	5	2.27	0.08	3.4	91
1,1,2,2-Tetrachloroethane	5	24.6	0.40	1.4	98
Bromobenzene	5	4.78	0.09	2.0	96
n-propyl benzene	5	2.26	0.06	2.8	92
Pentachloroethane	2[d]	38.1	—	—	95
m-Dichlorobenzene	5	4.63	0.10	2.2	93
p-Dichlorobenzene	5	4.59	0.15	3.3	92
o-Dichlorobenzene	5	4.71	0.12	2.5	94
1,2-Dibromo-3-chloropropane	5	24.7	0.34	1.4	99
Hexachloroethane	5	22.8	0.50	2.0	91
1,3,5-Trichlorobenzene	5	9.67	0.80	8.3	97
1,2,4-Trichlorobenzene	5	9.23	0.19	2.0	92
Naphthalene	5	4.93	0.12	2.4	99
1,2,3-Trichlorobenzene	5	10.1	0.51	5.1	101

Table 10. (Continued)

Compound	N	Average µg/L	SD	RSD (%)	Recovery (%)
Hexachlorobutadiene-1,3	5	22.4	0.52	2.3	90
1,2,4,5-Tetrachlorobenzene	5	14.7	1.2	7.8	98
1,2,3,4-Tetrachlorobenzene[e]	5				
1-Chloronaphthalene[e]					
2-Chlorobiphenyl[e]					

[a]Average of 5 spike day analyses, two each non-preserved, 2 each preserved with HCl and one preserved with mercury.

[b]Average of two non-preserved samples 100% loss in HCl preserved and 60% recovery in Hg preserved.

[c]Average of two HCl preserved analyses 179% recovery for mercury preserved sample and 189% recovery for 22°C non-preserved.

[d]Average of two HCl preserved analyses - 39% recovery for non-preserved samples and 8.5% recovery for Hg preserved sample.

[e]These compounds were deleted from the study because variable retention times caused the data system errors. The error was traced to a faulty oven temperature controller.

Table 11. Spiked Quenched Cincinnati Tap Water Stored at 22°C

Compound	24 day Average Conc. (µg/L)	S.D.	RSD	Study Ave. Recover (%)
1,1-Dichloroethylene	8.32	1.20	15	83
Methylene Chloride	34.6	2.4	6.8	92
Allyl Chloride	3.82	2.7	71	38
Trans-1,2-Dichloro-ethylene	9.11	1.44	16	91
cis-1,2-Dichloro-ethylene	9.59	0.65	6.8	96
Allyl Bromide	—	—	—	—
Chloroform	51.0	2.5	4.8	91
1,2-Dichloroethane	10.1	0.7	6.7	101
1,1,1-trichloroethane	16.8	1.3	7.7	96
Benzene	2.55	0.12	4.8	102
Carbon tetrachloride	28.2	2.1	7.3	93
1,2-dichloropropane	6.94	0.47	6.8	93
Bromodichloromethane	58.2	2.4	4.0	94
1,1,2-trichloro-ethylene	19.4	3.9	20	155
2-Chloroethylvinyl ether	12.0	0.3	2.5	96
1,3-dichloropropene	1.9	2.4	123	25
1,3-dichloropropene	2.6	2.7	106	34
1,1,2-trichloroethane	14.1	0.5	3.6	94
Toluene	2.53	0.17	6.6	101
Dibromochloro-methane	65.6	2.0	3.0	97
1,1,2,2-tetrachloro-ethylene	41.8	4.7	11.2	239
Chlorobenzene	4.74	0.33	6.9	95
Ethylbenzene				
Bromoform	53.9	1.7	3.1	97
p-xylene	2.41	0.13	5.2	96
Styrene	2.16	0.14	6.3	86
1,1,2,2-tetrachloro-ethane	15.6	4.2	27	62
Bromobenzene	4.81	0.51	3.1	96
n-Propylbenzene	2.22	0.09	3.9	89
Pentachloroethane	3.36	5.9	176	8.4
m-dichlorobenzene	4.56	0.15	3.3	91
p-Dichlorobenzene	4.55	0.17	3.8	91
o-Dichlorobenzene	4.73	0.17	3.7	95
Dibromochloropropane	24.7	0.8	3.3	99
Hexachloroethane	20.9	2.4	11	83
1,3,5-trichlorobenzene	8.37	0.41	4.8	84

Table 11. (Continued)

Compound	24 day Average Conc. (µg/L)	S.D.	RSD	Study Ave. Recover (%)
1,2,4-Trichlorobenzene	8.61	0.5	5.8	86
Naphthalene	4.70	0.24	5.2	94
1,2,3-Trichlorobenzene	9.16	0.69	7.5	92
Hexachlorobutadiene,-1,3	20.1	1.5	7.6	81
1,2,4,5-Tetrachlorobenzene				
1,2,3,4-Tetrachlorobenzene				
1-Chloronaphthalene	12.8	2.4	19	
2-Chlorobiphenyl	22.7	4.6	20	76

Table 12. Spiked Quenched Cincinnati Tap Water Stored at 4°C

Compound	24 Day Study Average (µg/L)	SD	RSD %	Recovery %	Day 18 Recovery %	Spike Day Recovery %
1,1-Dichloroethylene	7.15	1.3	19	72	58	83
Methylene Chloide	32.1	2.5	7.7	86	76	91
Allyl Chloride	6.75	0.44	6.5	68	61	88
t-1,2-Dichloroethylene	7.79	1.20	15	78	93	86
c-1,2-Dichloroethylene	8.55	0.43	5.0	86	87	91
Allyl Bromide	—	—	—	—	0	50
Chloroform	44.4	1.9	4.2	80	80	86
1,2-Dichloroethane	9.21	0.26	2.8	92	94	95
1,1,1-trichloroethane	14.0	0.59	4.2	80	84	91
Benzene	2.27	0.07	3.0	91	92	100
Carbon Tetrachloride	22.7	0.98	4.3	75	78	88
1,2-dichloropropane	6.26	0.33	5.2	83	83	88
Bromodichloromethane	54.8	1.5	2.8	88	90	94
1,1,2-trichloroethylene	12.0	1.2	10	96	109	98
2-chloroethylvinyl ether	12.0	0.39	3.3	96	97	97
1,3-dichloropropene	4.33	1.3	29	58	21	96
1,3-dichloropropene	5.53	0.70	13	74	34	92
1,1,2-trichloroethane	14.2	0.70	4.7	95	97	99
Toluene	2.24	0.13	5.8	90	94	99
Dibromochloromethane	62.8	2.3	3.6	93	99	100
1,1,2,2-tetrachloro-ethylene	37.0	2.6	7.0	211	230	189
Chlorobenzene	4.27	0.35	8.2	85	79	100
Ethylbenzene	2.08	0.06	2.9	83	81	96
Bromoform	54.3	1.1	2.0	96	100	96
p-Xylene	2.16	0.05	2.4	86	88	96
Styrene	2.15	0.06	2.7	86	88	93
1,1,2,2-tetrachloro-ethane	22.8	1.1	4.6	91	92	97
Bromobenzene	4.58	0.09	2.0	92	92	95
n-Propylbenzene	1.97	0.07	3.4	79	86	91
Pentachloroethane	3.24	4.4	134	8.1	4	39
m-Dichlorobenzene	4.27	0.11	2.6	85	86	93
p-Dichlorobenzene	4.31	0.11	2.5	86	86	93
o-Dichlorobenzene	4.53	0.15	3.4	91	90	95
1,2-Dibromo-3-chloro-propane	25.3	1.3	5.0	101	111	99
Hexachloroethane	20.7	0.90	4.4	83	86	91
1,3,5-Trichlorobenzene	8.04	0.35	4.4	80	80	90
1,2,4-Trichlorobenzene	8.54	0.33	3.9	85	86	92
Naphthalene	4.86	0.18	3.7	97	103	98
1,2,3-Trichlorobenzene	9.24	0.24	4.5	92	92	97
Hexachlorobutadiene-1,3	18.9	1.1	5.6	76	76	89

Remaining compounds deleted from study because of memory effects.

Table 13. Method Accuracy and Precision
Spiked Quenched Tap Water + $HgCl_2$ Stored at 22°C

Compound	25 Day Average Conc. µg/L	SD	RSD	Spike Day Recovery %	Study Recovery %	4 Day Period	% Recovery Day 18
1,1-Dichloroethylene	9.06	1.29	14	96	91		89
Methylene Chloride	35.4	2.3	6.4	97	94		99
Allyl Chloride	3.01	3.1	104	75	30	-25	11
trans-1,2-Dichloro-ethylene	8.28	0.81	9.8	79	83		75
cis-1,2-Dichloro-ethylene	9.56	0.63	6.6	96	96		91
Allyl Bromide	—	—	—	46	—	-100	0
Chloroform	51.4	2.7	5.3	91	92		97
1,2-Dichloroethane	17.5	4.77	27	110	180	+29.9	221
1,1,1-Trichloroethane	16.9	1.34	7.9	98	97		88
Benzene	2.5	0.2	6.6	100	100		97
Carbon Tetrachloride	27.1	1.5	5.5	91	90		86
1,2-Dichloropropane	6.93	0.58	8.4	88	92		89
Bromodichloromethane	57.5	2.7	4.7	92	93		90
1,1,2-Trichloroethylene	20.0	3.2	16	133	160	+58	154
2-Chloroethylvinyl ether	1.13	2.3	201	39	9	-72	0
1,3-Dichloropropene	1.43	2.19	153	68	19	-43	0
1,3-Dichloropropene	2.23	2.25	100	73	30	-34	0
1,1,2-Trichloroethane	14.1	0.6	4.4	93	94		92
Toluene	2.48	0.16	6.3	97	99		98
Dibromochloromethane	64.2	1.1	1.7	97	95		95
1,1,2,2-Tetrachloro-ethylene	41.0	2.0	4.9	240	234	+10.4	234
Chlorobenzene	4.74	0.30	6.3	101	95		91
Ethylbenzene	2.35	0.13	5.6	95	94		92
Bromoform	51.9	1.7	3.2	96	94		93
p-Xylene	2.39	0.11	4.6	96	96		95
Styrene	2.20	0.21	9.4	95	88	+4	decay
1,1,2,2-tetrachloro-ethane	14.5	3.4	23.1	76	58	-11	58
Bromobenzene	4.79	0.20	4.1	97	96		93
n-Propylbenzene	2.19	0.15	6.9	95	85		82
Pentachloroethane	—	—	—	8.5	—	-23	0
m-Dichlorobenzene	4.53	0.25	5.6	97	91		87
p-Dichlorobenzene	4.52	0.27	5.9	93	92		87
o-Dichlorobenzene	4.70	0.26	5.2	93	94		93
1,2-Dibromo-3-chloro-propane	25.4	0.7	2.6	102	102		103
Hexachloroethane	23.4	1.5	6.5	96	94		88
1,3,5-Trichlorobenzene	8.22	0.77	9.4	96	82		77
1,2,4-Trichlorobenzene	8.67	0.73	8.4	96	87		85
Naphthalene	4.89	0.33	6.8	103	98		103
1,2,3-Trichlorobenzene	9.39	0.77	8.1	104	99		93
Hexachlorobutadiene-1,3	20.1	2.6	12.9	95	80		72

Remaining compounds deleted from study because of memory effects.

Table 14. Method Accuracy and Precision
Spiked Quenched Tap Water and HCl Stored at 22°C

Compound	25 Day Study Average Conc. (µg/L)	SD	RSD	Study Recovery (%)
1,1-Dichloroethylene	8.29	1.25	15.1	83
Methylene Chloride	34.3	2.2	6.5	92
Allyl Chloride	3.39	2.76	81	34
trans-1,2-Dichloro-ethylene	8.47	0.98	11.6	85
cis-1,2-dichloro-ethylene	9.67	0.66	6.8	97
Allyl Bromide	—	—	—	—
Chloroform	50.8	7.1	14	91
1,2-Dichloroethane	9.64	0.28	2.8	96
1,1,1-Trichloroethane	15.2	0.63	4.1	89
Benzene	2.68	0.17	6.3	107
Carbon tetrachloride	27.9	2.1	7.6	92
1,2-Dichloropropane	6.74	0.25	3.6	90
Bromodichloromethane	58.8	2.2	3.7	95
1,1,2-Trichloro-ethylene	11.7	0.6	5.2	94
2-Chloroethylvinyl ether	ND	—	—	0.0
1,3-Dichloropropene	1.63	2.42	148	22
1,3-Dichloropropene	2.04	2.33	113	15
1,1,2-Trichloroethane	14.1	0.77	5.5	94
Toluene	2.37	0.11	4.7	95
Dibromochloro-methane	66.4	2.0	3.1	99
1,1,2,2-Tetrachloro-ethylene	14.8	0.72	4.8	85
Chlorobenzene	4.76	0.25	5.3	95
Ethylbenzene	2.30	0.91	4.0	92
Bromoform	54.7	1.3	2.4	99
p-xylene	2.39	0.84	3.5	95
Styrene	1.09	0.66	60	43
1,1,2,2-Tetrachloro-ethane	25.2	0.79	3.1	101
Bromobenzene	4.76	0.14	2.9	99
n-Propylbenzene	2.14	0.10	4.5	86
Pentachloroethane	39.7	2.5	6.3	99
m-Dichlorobenzene	4.44	0.14	3.2	89
p-Dichlorobenzene	4.39	0.13	3.9	88
o-Dichlorobenzene	4.64	0.14	3.1	93
1,2-Dibromo-3-chloro-propane	25.4	1.2	4.7	102
Hexachloroethane	23.3	1.2	5.0	93
1,3,5-Trichlorobenzene	7.37	0.77	9.7	74

Table 14. (Continued)

Compound	25 Day Study Average Conc. (µg/L)	SD	RSD	Study Recovery (%)
1,2,4-Trichlorobenzene	8.38	0.64	7.7	84
Naphthalene	4.82	0.27	5.6	96
1,2,3-Trichlorobenzene	9.7	0.75	7.7	97
Hexachlorobutadiene,-1,3	19.2	1.9	9.8	77
1,2,4,5-Tetrachlorobenzene				
1,2,3,4-Tetrachlorobenzene				
1-Chloronaphthalene				
2-Chlorobiphenyl	29.9	3.9	12.9	100

Table 15. Spiked Cincinnati Tap Water

	Recovery Day 18[a]				Average Study Recovery[b]			
	22°	4°	Hg	HCl	22°	4°	Hg	HCl
1,1-Dichloroethylene	76	58	89	98	83	72	91	83
Methylene Chloride	85	76	99	112	92	86	94	92
Allyl Chloride	19	61	11	13	38	68	30	34
trans-1,2-Dichloroethylene	107	93	75	91	91	78	83	85
cis-1,2-Dichloroethylene	95	87	91	106	96	86	96	97
Allyl Bromide	0	0	0	0	—	—	—	—
Chloroform	95	80	97	118	91	80	92	91
1,2-Dichloroethane	103	94	221	100	101	92	180	96
1,1,1-Trichloroethane	94	84	88	92	96	80	97	89
Benzene	99	92	97	110	102	91	100	107
Carbon tetrachloride	90	78	86	95	93	75	90	92
1,2-Dichloropropane	90	83	89	94	93	83	92	90
Bromodichloromethane	94	90	90	98	94	88	93	95
1,1,2-Trichloroethylene	176	109	154	97	155	96	160	94
2-Chloroethylvinyl ether	94	97	0	0	96	96	9	—
1,3-Dichloropropene	0	21	0	0	25	58	19	22
1,3-Dichloropropene	3	34	0	0	34	74	30	15
1,1,2-Trichloroethane	91	97	92	95	94	95	94	94
Toluene	100	94	98	98	101	90	99	95
Dibromochloromethane	102	94	95	102	97	93	95	99
1,1,2,2-Tetrachloroethylene	255	230	234	81	239	211	234	85
Chlorobenzene	91	79	91	92	95	85	95	95
Ethylbenzene	0	81	92	93	0	83	94	92
Bromoform	99	100	93	102	97	96	94	99
p-xylene	93	88	95	94	96	86	96	95
Styrene	88	88	76	60	86	93	98	43
1,1,2,2-Tetrachloroethane	50	92	58	106	62	91	58	101
Bromobenzene	93	92	93	95	96	92	96	99
n-Propylbenzene	86	80	82	83	89	79	85	86
Pentachloroethane	0	4	0	102	8.4	8.1	-	99
m-Dichlorobenzene	89	86	87	88	91	85	91	89
p-Dichlorobenzene	89	86	87	86	91	86	92	88
o-Dichlorobenzene	95	90	93	94	95	91	94	93
1,2-Dibromo-3-chloropropane	103	111	103	110	99	101	102	102
Hexachloroethane	72	86	88	97	83	83	94	93
1,3,5-Trichlorobenzene	79	80	77	70	84	80	82	74
1,2,4-Trichlorobenzene	82	86	85	78	86	85	87	84
Naphthalene	92	103	103	101	94	97	98	96

Table 15. (Continued)

	Recovery Day 18[A]				Average Study Recovery[B]			
	22°	4°	Hg	HCl	22°	4°	Hg	HCl
1,2,3-Trichlorobenzene	87	92	93	92	92	92	99	97
Hexachlorobutadiene,-1,3	75	76	72	68	81	76	80	77
1,2,4,5-Tetrachlorobenzene								
1,2,3,4-Tetrachlorobenzene								
1-Chloronaphthalene								
2-Chlorobiphenyl								

[a]average of two analyses performed 18 days after spiking for the 22° sample 17 days after spiking

[b]average of all analyses performed from spike day to end of study
n = 11 ea 22°C, 8 ea 4°C, 11 ea Hg and 11 ea HCl

Table 16. Summary of Method Recovery Spiked Ohio River Water

	22° Spike Day (%)	Ave. Recovery Day 2 Through Day 26				
		22° (%)	4° (%)	Hg (%)	Slime-Trol (%)	HCl (%)
1,1-Dichloroethylene	90	93	92	95	84	90
Methylenechloride	91	98	104	103	97	98
Allyl Chloride	89	56	84	39	61	44
t-1,2-Dichloroethylene	92	92	91	87	90	89
c-1,2-Dichloroethylene	95	93	91	96	95	88
Allyl Bromide	48	-	15	-	-	-
Chloroform	87	91	89	85	86	84
1,2-Dichloroethane	96	98	97	94	97	95
1,1,1-Trichloroethane	88	91	97	91	96	91
Benzene	95	89	87	92	97	94
Carbon Tetrachloride	90	73	91	89	91	90
1,2-Dichloropropane	94	98	97	93	97	95
Bromodichloromethane	94	92	93	89	Fused Peaks	93
1,1,2-Trichloroethylene	90	94	88	103	Fused Peaks	85
1,3-Dichloropropene	89	46	77	30	0	31
1,3-Dichloropropene	94	46	83	28	0	29
1,1,2-Trichloroethane	100	94	97	110	88	92
Toluene	95	79	80	87	89	89
Dibromochloromethane	99	93	94	93	95	94
1,1,2,2-Tetrachloro-ethylene	107	187	112	193	210	82
Chlorobenzene	95	91	90	92	95	92
Ethylbenzene	91	89	80	87	89	87
Bromoform	102	97	99	97	100	97
p-Xylene	91	84	79	80	84	80
Styrene	94	82	77	13	95	82
1,1,2,2-Tetrachloroethane	107	96	99	78	51	95
Bromobenzene	95	85	83	87	89	87
n-Propyl Benzene	92	86	68	83	86	82
Pentachloroethane	85	38	84	7	0	96
m-Dichlorobenzene	95	92	90	87	90	86
p-Dichlorobenzene	96	92	91	87	90	86
o-Dichlorobenzene	97	98	95	90	94	92
1,2-Dibromo-3-chloropropane	114	104	98	99	100	98
Hexachloroethane	93	49	79	88	92	86
1,3,5-Trichlorobenzene	91	83	87	77	81	78
1,2,4-Trichlorobenzene	96	91	93	84	88	85
Naphthalene	107	98	85	98	100	99
1,2,3-Trichlorobenzene	98	96	95	91	92	91
Hexachlorobutadiene-1,3	83	76	79	73	75	66
1,2,4,5-Tetrachloro-benzene	93	84	86	79	78	73

Table 16. (Continued)

	22° Spike Day (%)	Ave. Recovery Day 2 Through Day 26				
		22° (%)	4° (%)	Hg (%)	Slime-Trol (%)	HCl (%)
1,2,3,4-Tetrachloro-benzene	98	93	91	84	88	83
1-Chloronaphthalene	109	105	97	96	100	96
2-Chlorobiphenyl	117	109	87	98	102	96

Table 17. Spiked Ohio River Water Stored at 22°C

	Average Concentration µg/L	S.D.	RSD	Recovery (%)
1,1-Dichloroethylene	18.6	3.2	17	93
Methylenechloride	73.3	11.	15	98
Allyl Chloride	11.1	5.4	49	56
t-1,2-Dichloroethylene	18.4	1.2	6.5	92
c-1,2-Dichloroethylene	18.7	1.3	6.8	93
Allyl Bromide	-	-	-	-
Chloroform	54.6	2.8	5.1	91
1,2-Dichloroethane	19.6	0.7	3.7	98
1,1,1-Trichloroethane	32.0	2.7	8.4	91
Benzene	4.45	0.86	19.4	89
Carbon Tetrachloride	44.5	16.8	38	73
1,2-Dichloropropane	14.7	0.4	2.9	98
Bromodichloromethane	64.7	5.8	9.0	92
1,1,2-Trichloroethylene	23.6	1.4	5.9	94
1,3-Dichloropropene	6.9	5.1	74	46
1,3-Dichloropropene	6.9	5.5	79	46
1,1,2-Trichloroethane	28.2	2.0	7.2	94
Toluene	3.93	1.29	33	79
Dibromochloromethane	83.9	7.3	8.7	93
1,1,2,2-Tetrachloroethylene	65.4	17.2	26	187
Chlorobenzene	9.04	1.2	14	91
Ethylbenzene	4.46	0.35	7.9	89
Bromoform	96.7	9.4	8.9	97
p-Xylene	4.19	0.41	9.8	84
Styrene	4.08	1.04	26	82
1,1,2,2-Tetrachloroethane	48.0	4.93	10	96
Bromobenzene	8.45	1.7	20	85
n-Propyl Benzene	4.3	0.44	10.3	86
Pentachloroethane	30.7	25	80	38
m-Dichlorobenzene	9.19	0.54	5.9	92
p-Dichlorobenzene	9.19	0.57	6.2	92
o-Dichlorobenzene	9.79	0.57	5.8	98
1,2-Dibromo-3-chloropropane	51.8	5.9	12	104
Hexachloroethane	24.3	19	77	49
1,3,5-Trichlorobenzene	18.0	1.7	9.6	90
1,2,4-Trichlorobenzene	18.2	1.6	8.7	91
Naphthalene	9.78	1.4	14	98
1,2,3-Trichlorobenzene	19.1	1.2	6.3	96
Hexachlorobutadiene-1,3	38.1	6.0	16	76
1,2,4,5-Tetrachlorobenzene	25.1	4.0	16	84
1,2,3,4-Tetrachlorobenzene	27.9	3.46	12.4	93
1-Chloronaphthalene	31.4	5.9	18.6	105
2-Chlorobiphenyl	32.6	4.6	14.1	109

Table 18. Spiked Ohio River Water Stored at 4°C[A]

	Method Ave. Concentration µg/L	S.D.	RSD (%)	Average Recovery (%)
1,1-Dichloroethylene	18.4	2.1	11	92
Methylenechloride	78.1	4.7	6.0	104
Allyl Chloride	16.7	3.4	20	84
t-1,2-Dichloroethylene	18.2	0.7	6.7	91
c-1,2-Dichloroethylene	18.2	1.3	7.2	91
Allyl Bromide	3.0	5.4	177	15
Chloroform	53.5	3.0	5.6	89
1,2-Dichloroethane	19.3	0.54	2.8	97
1,1,1-Trichloroethane	33.8	1.5	4.5	97
Benzene	4.36	0.51	12	87
Carbon Tetrachloride	54.9	3.4	6.2	91
1,2-Dichloropropane	14.5	0.3	1.9	97
Bromodichloromethane	64.8	2.6	4.0	93
1,1,2-Trichloroethylene	22.0	0.92	4.2	88
1,3-Dichloropropene	11.6	2.1	18.3	77
1,3-Dichloropropene	12.4	2.3	18.2	83
1,1,2-Trichloroethane	29.2	2.2	7.5	97
Toluene	4.02	0.86	21	80
Dibromochloromethane	84.8	4.2	4.9	94
1,1,2,2-Tetrachloro-ethylene	39.0	3.2	8.1	112
Chlorobenzene	8.98	0.72	8.0	90
Ethylbenzene	4.02	0.63	16	80
Bromoform	98.8	4.4	4.4	99
p-Xylene	3.94	0.32	8.2	79
Styrene	3.87	1.02	26	77
1,1,2,2-Tetrachloroethane	49.3	2.5	5.1	99
Bromobenzene	8.30	0.79	9.6	83
n-Propyl Benzene	3.38	1.14	34	68
Pentachloroethane	67.3	4.3	6.4	84
m-Dichlorobenzene	9.04	0.28	3.1	90
p-Dichlorobenzene	9.06	0.29	3.2	91
o-Dichlorobenzene	9.49	0.35	3.9	95
1,2-Dibromo-3-chloropropane	49.2	6.05	12	98
Hexachloroethane	39.5	9.2	23	79
1,3,5-Trichlorobenzene	17.5	0.94	5.4	87
1,2,4-Trichlorobenzene	18.5	0.78	4.2	93
Naphthalene	8.51	1.9	22	85
1,2,3-Trichlorobenzene	19.0	0.56	3.0	95
Hexachlorobutadiene-1,3	39.5	3.2	8.2	79
1,2,4,5-Tetrachloro-benzene	25.7	2.3	9.0	86

Table 18. (Continued)

	Method Ave. Concentration µg/L	S.D.	RSD (%)	Average Recovery (%)
1,2,3,4-Tetrachloro-benzene	27.3	2.2	8.2	91
1-Chloronaphthalene	29.2	3.2	11.1	97
2-Chlorobiphenyl	26.1	7.9	30	87

A No spike day analysis performed data include spike day +3 through Spike day +26
Number of analyses = 7

Table 19. Spiked Ohio River Water Preserved with Mercury (3/15 to 4/7)

	Method Ave. Concentration µg/L	S.D.	RSD (%)	Average Recovery (%)
1,1-Dichloroethylene	18.9	2.6	14	95
Methylenechloride	77.0	11.2	15	103
Allyl Chloride	7.7	4.4	57	39
t-1,2-Dichloroethylene	17.3	1.5	8.9	87
c-1,2-Dichloroethylene	19.2	2.2	12	96
Allyl Bromide				
Chloroform	50.8	4.0	7.9	85
1,2-Dichloroethane	18.8	0.9	4.9	94
1,1,1-Trichloroethane	31.7	2.4	7.5	91
Benzene	4.58	0.28	6.1	92
Carbon Tetrachloride	54.2	4.4	8.1	89
1,2-Dichloropropane	14.0	0.8	6.0	93
Bromodichloromethane	62.2	3.6	5.7	89
1,1,2-Trichloroethylene	25.6	2.3	8.9	103
1,3-Dichloropropene	4.45	4.0	89	36
1,3-Dichloropropene	4.16	4.0	96	28
1,1,2-Trichloroethane	27.5	1.8	6.7	110
Toluene	4.35	0.34	7.8	87
Dibromochloromethane	83.6	5.5	6.5	93
1,1,2,2-Tetrachloro-ethylene	67.5	3.2	4.7	193
Chlorobenzene	9.17	0.88	9.6	92
Ethylbenzene	4.33	0.31	7.1	87
Bromoform	96.9	4.2	4.3	97
p-Xylene	4.02	0.24	6.0	80
Styrene	0.66	0.52	80	13
1,1,2,2-Tetrachloroethane	38.8	7.1	18	78
Bromobenzene	8.70	0.45	5.1	87
n-Propyl Benzene	4.13	0.37	8.9	83
Pentachloroethane	5.39	6.9	128	7
m-Dichlorobenzene	8.73	0.52	5.9	87
p-Dichlorobenzene	8.65	0.50	5.8	87
o-Dichlorobenzene	8.95	0.54	6.1	90
1,2-Dibromo-3-chloropropane	49.2	4.6	9.3	99
Hexachloroethane	43.9	3.2	7.4	88
1,3,5-Trichlorobenzene	15.5	1.7	11	77
1,2,4-Trichlorobenzene	16.9	1.4	8.5	84
Naphthalene	9.80	0.60	6.1	98
1,2,3-Trichlorobenzene	18.2	1.3	6.9	91
Hexachlorobutadiene-1,3	36.3	5.2	14	73
1,2,4,5-Tetrachloro-benzene	23.6	4.2	18	79
1,2,3,4-Tetrachloro-benzene	25.2	2.9	11	84
1-Chloronaphthalene	23.7	2.4	8.5	96
2-Chlorobiphenyl	29.4	3.7	12	98

Table 20. Spiked Ohio River Water Preserved with Slime-Trol RX-34

	Method Ave. Concentration µg/L	S.D.	RSD (%)	Average Recovery (%)
1,1-Dichloroethylene	16.8	1.1	6.7	84
Methylenechloride	72.7	9.1	1.3	97
Allyl Chloride	12.2	9.0	73	61
t-1,2-Dichloroethylene	18.0	1.4	7.8	90
c-1,2-Dichloroethylene	19.1	1.1	5.7	95
Allyl Bromide	0	-	-	0
Chloroform	51.4	3.0	5.9	86
1,2-Dichloroethane	19.5	0.9	4.7	97
1,1,1-Trichloroethane	33.5	3.4	10	96
Benzene	4.85	0.27	5.5	97
Carbon Tetrachloride	55.3	3.9	7.1	91
1,2-Dichloropropane	14.5	0.7	4.5	97
Bromodichloromethane	Fused Peaks			
1,1,2-Trichloroethylene	Fused Peaks			
1,3-Dichloropropene	0	-	-	0
1,3-Dichloropropene	0	-	-	0
1,1,2-Trichloroethane	26.4	1.4	5.2	88
Toluene	4.44	0.26	5.9	89
Dibromochloromethane	85.6	4.1	4.8	95
1,1,2,2-Tetrachloroethylene	73.4	5.7	7.8	210
Chlorobenzene	9.48	0.67	7.1	95
Ethylbenzene	4.46	0.34	7.7	89
Bromoform	100	5.4	5.4	100
p-Xylene	4.18	0.22	5.3	84
Styrene	4.76	0.21	4.59	95
1,1,2,2-Tetrachloroethane	25.3	15.1	60	51
Bromobenzene	8.9	0.36	4.0	89
n-Propyl Benzene	4.3	0.36	8.5	86
Pentachloroethane	0	-	-	0
m-Dichlorobenzene	9.03	0.66	7.4	90
p-Dichlorobenzene	9.01	0.66	7.4	90
o-Dichlorobenzene	9.42	0.66	7.0	94
1,2-Dibromo-3-chloropropane	50.1	7.0	14	100
Hexachloroethane	46.2	3.9	8.4	92
1,3,5-Trichlorobenzene	16.2	1.4	8.8	81
1,2,4-Trichlorobenzene	17.5	1.2	6.7	88
Naphthalene	10.1	0.61	6.1	100
1,2,3-Trichlorobenzene	18.5	1.0	5.6	92
Hexachlorobutadiene-1,3	37.4	4.8	12.8	75
1,2,3,4-Tetrachlorobenzene	23.4	2.9	12.5	78
1,2,3,4-Tetrachlorobenzene	26.3	2.7	10.1	88
1-Chloronaphthalene	30.0	3.0	9.9	100
2-Chlorobiphenyl	30.6	4.3	14.0	102

Table 21. Spiked Ohio River Water Preserved with HCl

	Method Ave. Concentration µg/L	S.D.	RSD (%)	Average Recovery (%)
1,1-Dichloroethylene	18.1	1.5	8.4	90
Methylenechloride	73.1	8.1	11	98
Allyl Chloride	8.84	4.1	47	44
t-1,2-Dichloroethylene	17.8	1.7	9.5	89
c-1,2-Dichloroethylene	17.5	1.1	6.3	88
Allyl Bromide	0	-	-	0
Chloroform	50.2	2.8	5.6	84
1,2-Dichloroethane	19.0	1.0	5.3	95
1,1,1-Trichloroethane	31.8	3.0	9.6	91
Benzene	4.69	0.40	8.6	94
Carbon Tetrachloride	54.4	3.4	6.2	90
1,2-Dichloropropane	14.2	0.91	5.4	95
Bromodichloromethane	65.0	5.0	7.7	93
1,1,2-Trichloroethylene	21.2	1.6	7.5	85
1,3-Dichloropropene	4.7	4.0	86	31
1,3-Dichloropropene	4.40	3.9	88	29
1,1,2-Trichloroethane	27.5	1.1	4.0	92
Toluene	4.47	0.23	5.2	89
Dibromochloromethane	84.3	2.5	3.0	94
1,1,2,2-Tetrachloro-ethylene	28.5	2.7	9.4	82
Chlorobenzene	9.19	1.1	11	92
Ethylbenzene	4.37	0.34	7.8	87
Bromoform	97.3	4.0	4.1	97
p-Xylene	3.99	0.23	5.7	80
Styrene	4.11	0.55	13.4	82
1,1,2,2-Tetrachloroethane	47.5	1.2	2.5	95
Bromobenzene	8.73	0.47	5.4	87
n-Propyl Benzene	4.11	0.36	8.76	82
Pentachloroethane	78.9	3.9	5.1	96
m-Dichlorobenzene	8.64	0.65	7.5	86
p-Dichlorobenzene	8.63	0.52	6.0	86
o-Dichlorobenzene	9.17	0.51	5.6	92
1,2-Dibromo-3-chloropropane	49.0	3.8	7.7	98
Hexachloroethane	42.8	3.0	7.1	86
1,3,5-Trichlorobenzene	15.6	1.6	10	78
1,2,4-Trichlorobenzene	17.0	1.6	9.4	85
Naphthalene	9.85	0.45	4.57	99
1,2,3-Trichlorobenzene	18.1	1.34	7.39	91
Hexachlorobutadiene-1,3	32.8	3.1	9.4	66
1,2,3,4-Tetrachloro-benzene	22.0	2.7	12	73
1,2,3,4-Tetrachloro-benzene	25.0	2.7	11	83
1-Chloronaphthalene	28.9	1.9	6.4	96
2-Chlorobiphenyl	28.7	4.3	15	96

Table 22. Method Detection Limit Study

	Spike Conc. µg/L	Average Concentration µg/L	Sd	RSD %	MDL µg/L	Percent Recovery (%)
1,1-Dichloroethylene	0.5	1.01	0.40	39	1.2	248
Methylenechloride	1.88	1.50	0.62	41	1.8	80
Allyl Chloride	0.5	0.34	0.099	29	0.31	68
t-1,2-Dichloroethylene	0.5	2.02	1.53	76	4.8	404
c-1,2-Dichloroethylene	0.5	0.41	0.085	21	0.27	82
Allyl Bromide	0.5					
Chloroform	1.50	2.88	0.26	9.0	0.81	190
1,2-Dichloroethane	0.50	0.56	0.041	7.4	0.13	112
1,1,1-Trichloroethane	0.88	0.81	0.087	11	0.27	92
Benzene	0.125	0.35	0.029	8.2	0.09	280
Carbon Tetrachloride	1.52	1.43	0.41	28	1.3	94
1,2-Dichloropropane	0.375	0.34	0.013	3.8	0.04	91
omodichloromethane	1.75	1.47	0.081	5.5	0.25	84
1,1,2-Trichloroethylene	0.63	0.55	0.029	5.3	0.09	87
2-Chloroethylvinylether						
1,3-Dichloropropene	0.38	0.24	0.035	15	0.12	63
1,3-Dichloropropene						
1,1,2-Trichloroethane	0.75	0.66	0.035	5.3	0.11	88
Toluene	0.125	0.21	0.031	15	0.096	168
Dibromochloromethane	2.25	2.18	0.29	13	0.91	97
1,1,2,2-Tetrachloro-ethylene	0.88	1.72	0.37	22	1.2	195
Chlorobenzene	0.25	0.14	0.0073	5.3	0.03	56
Ethylbenzene	0.125	0.15	0.022	15	0.069	120
Bromoform	2.49	2.13	0.16	7.5	0.48	86
p-Xylene	.125	0.18	0.054	30	0.17	144
Styrene	.125	0.12	0.011	9.3	0.035	96
1,1,2,2-Tetrachloroethane	1.25	1.61	0.28	17	0.88	128
Bromobenzene	0.25	0.38	0.081	21	0.26	152
n-Propyl Benzene	0.125	0.15	0.012	9.4	0.043	120
Pentachloroethane	2.0	1.56	0.39	25	1.2	78
m-Dichlorobenzene	0.25	0.27	0.060	22	0.19	108
p-Dichlorobenzene	0.25	0.23	0.039	17	0.12	92
o-Dichlorobenzene	0.25	0.25	0.053	21	0.17	100
1,2-Dibromo-3-chloropropane	1.25	1.40	0.17	13	0.59	112
Hexachloroethane	1.25	1.38	0.11	7.7	0.34	110
1,3,5-Trichlorobenzene	0.50	0.56	0.055	9.8	0.17	112
1,2,4-Trichlorobenzene	0.50	0.52	0.031	6.0	0.097	104
Naphthalene	0.25	0.30	0.021	6.9	0.065	120
1,2,3-Trichlorobenzene	0.50					
Hexachlorobutadiene-1,3	1.25	1.29	0.071	5.5	0.11	103
1,2,3,4-Tetrachloro-benzene	0.76	1.23	0.25	20	0.78	162

Table 22. (Continued)

	Spike Conc. µg/L	Average Concentration µg/L	Sd	RSD %	MDL µg/L	Percent Recovery (%)
1,2,3,4-Tetrachloro-benzene	0.75	0.92	0.12	13	0.39	123
1-Chloronaphthalene						
2-Chlorobiphenyl	0.75	1.19	0.21	18	0.67	154

Table 23. System Memory

	Valve Oven 125°C		Valve Oven 200°C		Valve Oven 125°C
	Analysis #1 (%)	Analysis #2 (%)	Analysis #1 (%)	Analysis #2 (%)	Memory After Purging Device Exchange (%)
1,1-Dichloroethylene	0.0	0.0	0.0	0.0	0.0
Methylene Chloride	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.0	0.0	0.0	0.0	0.0
trans-1,2-Dichloroethylene	0.0	0.0	0.0	0.0	0.0
cis-1,2-Dichloroethylene	0.0	0.0	0.0	0.0	0.0
Allyl Bromide	0.0	0.0	0.0	0.0	0.0
Chloroform	0.0	0.0	0.0	0.0	0.0
1,2-Dichloroethane	0.0	0.0	0.0	0.0	0.0
1,1,1-Trichloroethane	0.0	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.0
Carbon tetrachloride	0.0	0.0	0.0	0.0	0.0
1,2-Dichloropropane	0.0	0.0	0.0	0.0	0.0
Bromodichloromethane	0.0	0.0	0.0	0.0	0.0
1,1,2-Trichloroethylene	0.0	0.0	0.0	0.0	0.0
2-Chloroethyvinyl ether	0.0	0.0	0.0	0.0	0.0
1,3-Dichloropropene	0.0	0.0	0.0	0.0	0.0
1,3-Dichloropropene	0.0	0.0	0.0	0.0	0.0
1,1,2-Trichloroethane	0.0	0.0	0.0	0.0	0.0
Toluene	1.1	0.0	0.0	0.0	0.0
Dibromochloromethane	0.0	0.0	0.0	0.0	0.0
1,1,2,2-Tetrachloroethylene	1.4	0.0	0.0	0.0	0.0
Chlorobenzene	0.0	0.0	0.0	0.0	0.0
Ethylbenzene	1.0	0.0	0.0	0.0	0.0
Bromoform	1.0	0.0	0.0	0.0	0.0
p-xylene	1.0	0.0	0.0	0.0	0.0

Table 23. System Memory (Continued)

	Valve Oven 125°C		Valve Oven 200°C		Valve Oven 125°C
	Analysis #1 (%)	Analysis #2 (%)	Analysis #1 (%)	Analysis #2 (%)	Memory After Purging Device Exchange (%)
Styrene	1.0	0.0	0.0	0.0	0.0
1,1,2,2-Tetrachloro-ethane	1.76	0.0	0.0	0.0	0.0
Bromobenzene	1.7	0.0	0.0	0.0	1.5
n-Propylbenzene	2.3	0.0	0.0	0.0	1.5
Pentachloroethane	2.3	0.0	0.0	0.0	1.4
m-Dichlorobenzene	2.5	0.0	0.0	0.0	1.4
p-Dichlorobenzene	2.6	0.0	0.0	0.0	1.4
o-Dichlorobenzene	2.9	0.0	2.2	0.0	1.4
1,2-Dibromo-3-cloro-propene	6.0	2.5	0.0	0.0	0.0
Hexachloroethane	2.9	1.2	0.0	0.0	0.0
1,3,5-Trichlorobenzene	5.3	6.2	1.0	[illegible].0	1.3
1,2,4-Trichlorobenzene	7.3	4.6	2.0	0.9	2.5
Naphthalene	8.4	4.9	2.2	0.8	3.7
1,2,3-Trichlorobenzene	9.4	5.8	1.5	0.0	4.6
Hexachlorobuta-diene,-1,3	9.9	4.3	1.3	0.0	4.1
1,2,4,5-Tetrachloro-benzene	27	12	3.0	0.6	12
1,2,3,4-Tetrachloro-benzene	48	30	8.0	2.6	16
1-Chloronaphthalene	48	30	8.0	2.6	26
2-Chlorobiphenyl	92	69	30	7.0	38