Improved Performance and Productivity of Purge-and-Trap Analyses

Application Note 17430302

Keywords
AMPS
Cyclone Water Management
Dual Purge-and-Trap System
GC/MS
PT Express
Purge and Trap
Standards Addition Module
Trihalomethane
VOC
Volatiles

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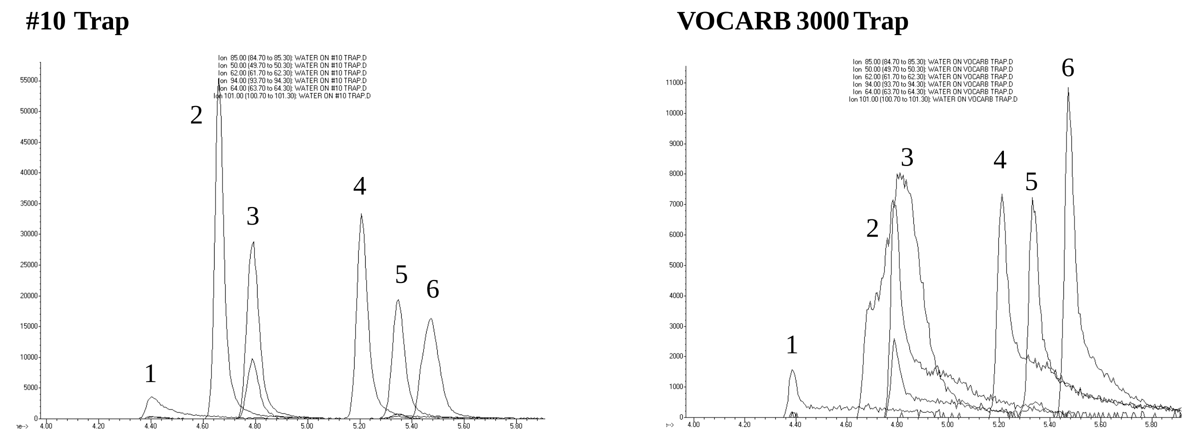
Introduction

Although purge-and-trap analysis is considered to be a mature technique, advances in the methodology and refinement of the instrumentation are still being developed. One major challenge that is always faced is the broad range of chemistries represented by the current USEPA volatiles list. Method performance criteria must be met for all target compounds simultaneously, despite a wide variability in boiling points, polarities, solubilities in water, purge efficiencies, and affinities for trap adsorbents. In addition, the increasing workloads in commercial laboratories demand that analytical cycle times be shortened to maximize throughput while still maintaining high standards for complete method performance. In this application note a selection of factors that can be used to improve overall cycle time and method performance are discussed, including proper trap selection, GC column selection, considerations for dual purge-and-trap configurations, and an autosampler for on-line analysis of VOCs in water.

Trap Selection and Performance

For VOC applications that call for a purge and trap with a mass spectrometer (MS), two common traps are most often used. They are the three-layer trap (OI Analytical #10 trap) originally specified in many USEPA methods, which contains Tenax®, silica gel, and carbon molecular sieve, and the VOCARB® 3000 trap, with layers of Carbopack B, Carboxen® 1000, and Carboxen 1001. Multiple layers of adsorbent materials allow a broad range of volatile analytes to be trapped and analyzed in a single run. The order of the sorbent layers has been carefully selected to optimize both the trapping and subsequent desorbtion of the VOCs from the trap. For best performance, the trap should be matched to the specific purge-and-trap and GC/MS configurations being used.

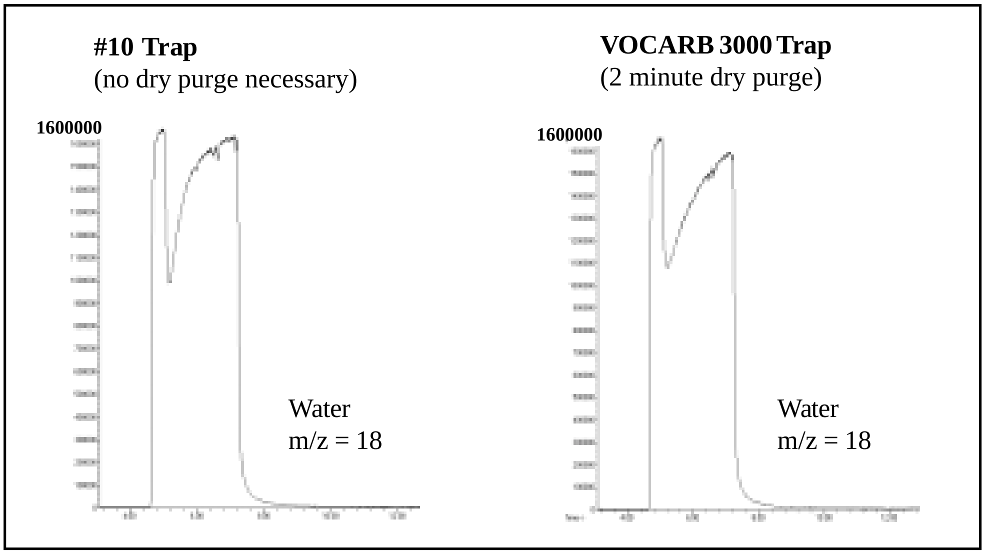
The OI Analytical #10 trap contains silica gel, which can retain water during the purge cycle. While water retention might be considered a problem for some purge-and-trap instruments, the #10 trap can be used to actually improve chromatographic peak shape when used with the OI Analytical Model 4560 Sample Concentrator. The water trapped in the silica gel bed (about 8–10 µL) is almost instantly converted to steam when the trap is rapidly heated during the desorb cycle. The steam provides a “pressure pulse” that helps to maintain the analytes in a narrow band as they are transferred to the GC column. The pressure pulse preserves sharp chromatographic peak shape, improves sensitivity, and reduces tailing. This is particularly important and useful in maintaining optimum peak heights and peak shapes of the first six peaks (“the gases”) of the method (see Figure 1). To take advantage of this trap’s benefits, it is imperative that the purge and trap used have a very effective water management system (not bypassed) to remove most of this excess water before the the sample enters the GC or GC/MS system. Failure to do this results in poor overall chromatographic performance for the earlier eluting peaks and a reduction of the MS vacuum during elution of the water. The patented Cyclone Water Management™ System in the Model 4560 effectively removes the excess water from the carrier gas before it reaches the GC. The comparative performance of these two traps is illustrated in Figures 1, 2, 3, and 4. (The conditions for Figures 1, 2, and 3 are as follows: 5 mL 20-ppb 502.2 mix, split 20:1, Rtx-VMS column, 60 m x 0.25 mm I.D. x 1.4 µm film, 60°C for 2 min, 12°C/min to 180°C, 45°C/min to 225°C, hold for 6 min.)



Purge	30°C for 11 min	Purge	30°C for 11 min
Dry Purge	not used	Dry Purge	2 min
Desorb	180°C for 4 min	Desorb	240°C for 4 min
Bake	200°C for 10 min	Bake	250°C for 10 min
Sample	5 mL, 20-ppb 502.2 stnd held at 45°C during purge	Sample	5 mL, 20-ppb 502.2 stnd held at 45°C during purge

1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane

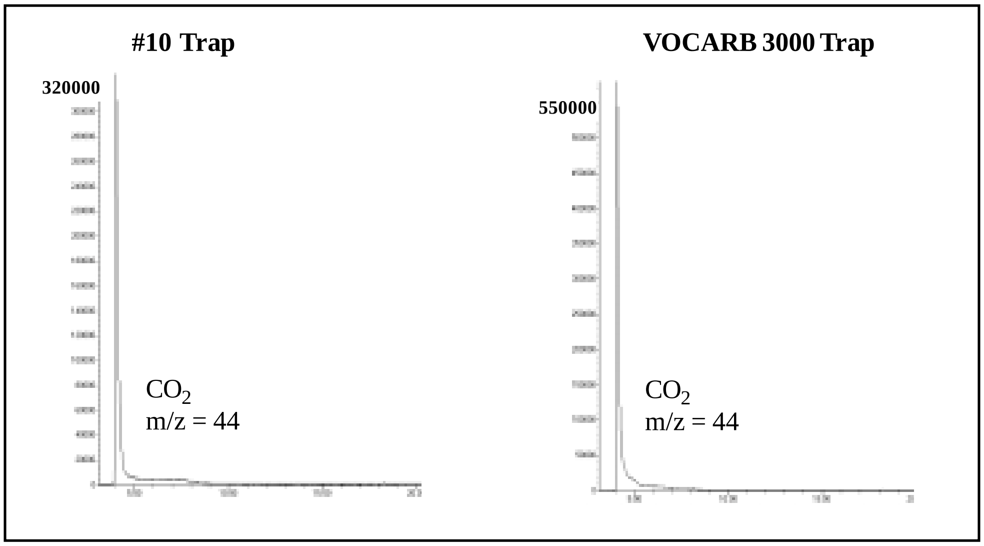
Figure 1. First Six Gases on an OI Analytical #10 Trap and on a VOCARB 3000 Trap. The Steam-Driven Pressure Pulse of the #10 Trap Improves Chromatographic Peak Shape for These Six Early Eluting Compounds When Run on the Model 4560. Both Traps were Preconditioned and Operated According to the Manufacturer’s Instructions.



#10 Trap
(no dry purge necessary)

VOCARB 3000 Trap
(2 minute dry purge)

Figure 2. Water Profile on an OI Analytical #10 Trap and on a VOCARB 3000 Trap. The Model 4560 Patented Cyclone Water Management System Effectively Removes Most of the Water Retained on the #10 Trap, Making the Volume of Water to the GC Column Comparable to that Retained on the Hydrophobic VOCARB 3000 Trap, about 0.25 µL.



#10 Trap

VOCARB 3000 Trap

Figure 3. CO_2 Profile on an OI Analytical #10 Trap and on a VOCARB 3000 Trap. Significantly less CO_2 is Generated by the #10 Trap and Transferred to the GC than with the Carbon-Based Adsorbents in the VOCARB 3000. This Reduction in CO_2 Further Improves Chromatographic Performance of the Early Eluting Compounds.

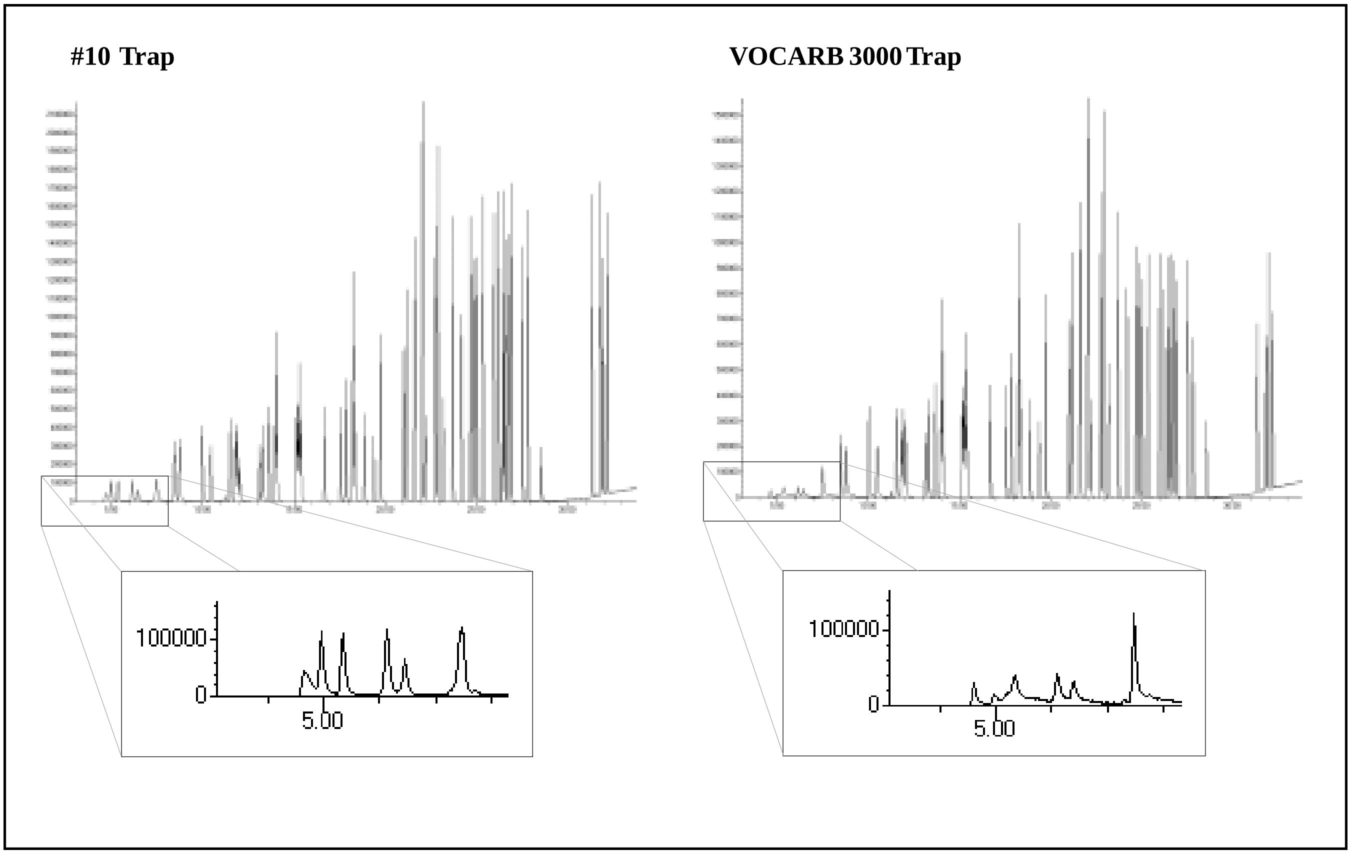


Figure 4. Full Chromatogram Using the OI Analytical #10 Trap and the VOCARB 3000 Trap. While the two Chromatograms are Nearly Identical, there is a Dramatic Improvement in Sensitivity and Peak Shape for the Early Eluting Gases when Using the #10 Trap. (5 mL 20-ppb 502.2 standard, split 9:1, DB-VRX column, 60 m x 0.25 mm I.D. x 1.4 µm film, 35°C for 4 min, 6°C/min to 175°C, 10°C/min to 220°C, hold for 2 min.) (For peak identification and detailed method results for USEPA Method 524.2, refer to OI Analtyical Application Note #1327.)

GC Column Selection and Performance

A major factor influencing lab productivity is cycle time. Up until recently, the cycle time was limited primarily by the time required by the GC program to efficiently separate all of the compounds in the latest USEPA lists (up to 84 analytes or more plus internal and surrogate standards). When a tandem PID/ELCD is used (as in USEPA Method 502.2), the 105-meter column can take up to an hour or more to separate all the peaks for unambiguous identification (see Figure 5). Using a mass spectrometer, co-elution of peaks is less of an issue as compounds are identified and quantified on the basis of selected ions. For many years a 60-meter column has been the standard used with the MS detector, reducing GC analysis time to about 33–35 minutes (see Figure 6). More recently, the latest trend is toward shorter and narrower columns. With the new columns, the total GC analysis time can be reduced to 15 minutes or less, making the purge-and-trap cycle time the rate-limiting step. Many column manufacturers recommend using high split ratios (20:1 or higher) to increase desorb flow and improve peak shape. Although this would be expected to lead to higher MDLs, the opposite is actually observed. Faster transfer of the analytes to the GC column results in sharper, more intense peaks and equivalent or even lower MDLs. In addition, the new MS design provides better sensitivity to further compensate for the additional loss to the split vent. Several different GC columns were evaluated for overall performance in terms of cycle time, sensitivity, and chromatographic peak shape. Figures 7 and 8 illustrate some of the advantages and disadvantages of each.

Figure 7a shows a chromatogram acquired using the manufacturer's recommended conditions but with the same low split ratio used for Figure 6 (9:1). Analysis time is reduced to less than 18 minutes, but peaks are tailing and chromatographic resolution in the first half of the chromatogram suffers. Little improvement is seen when switching to a "Pulsed Split" injection (Figure 7b), but using the 20:1 split ratio recommended by the manufacturer significantly improves chromatographic performance (Figure 7c). The faster desorption flow rate of about 24 mL/min, compared to 13 mL/min, is responsible for the improved peak shape. Note that overall sensitivity is improved, in spite of the increased split flow as a result of the significant improvement of overall peak shape. Further improvement in chromatographic performance of the early eluters can be achieved by reducing the initial oven temperature from 60°C to 35°C, as seen in Figure 7d. Baseline separation is seen for all six gases, and the GC run time is still less than the typical 23-minute purge-and-trap cycle.

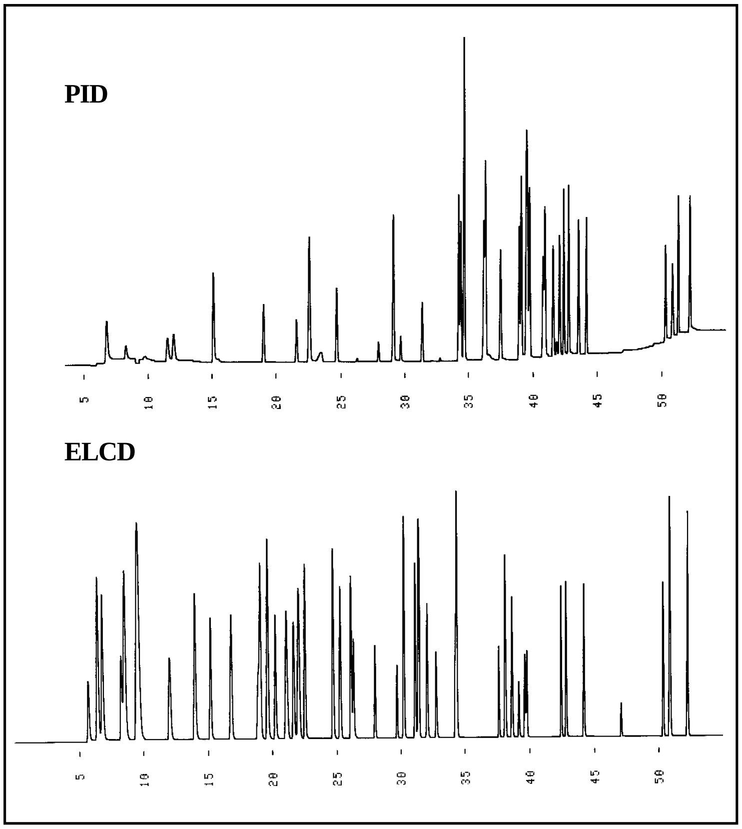


Figure 5. Rtx-502.2 Column, 105 m x 0.53 mm I.D. X 3.0 µm Film Using the Manufacturer's Recommended GC Program and an OI Analytical PID/ELCD Tandem Detector (5 mL of a 20-ppb 502.2 Standard). This Column Requires the Longest GC Run Time for Complete Peak Separation, but it Makes Use of OI Analytical's Economical and Unique Tandem PID/ELCD.

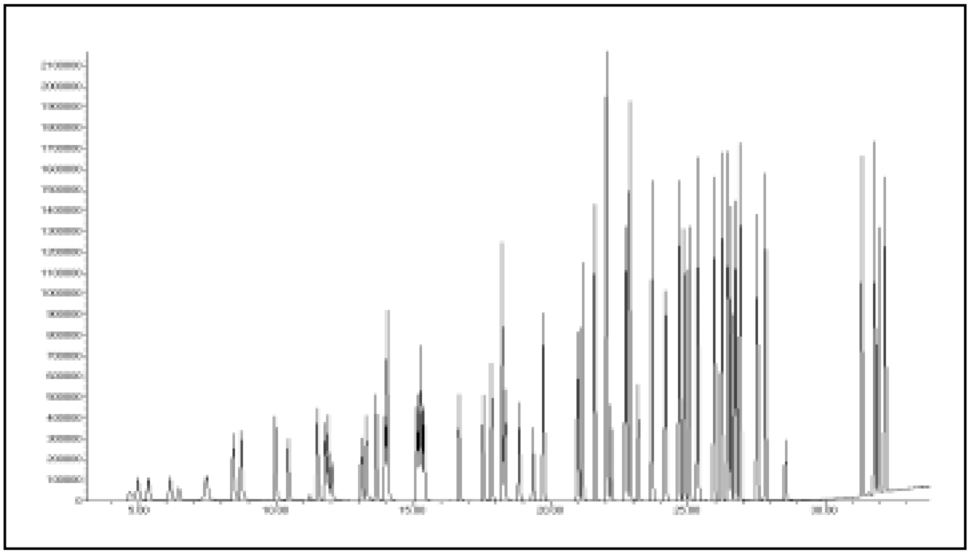


Figure 6. DB-VRX Column, 60 m x 0.25 mm I.D. x 1.4 µm film, Using the Manufacturer's Recommended GC Program (5 mL of a 20-ppb 502.2 Standard). This Column has set the Benchmark for Many Years with an Analysis Time of About 33 Minutes and Made the GC Run the Rate-Limiting Step in VOC Analyses.

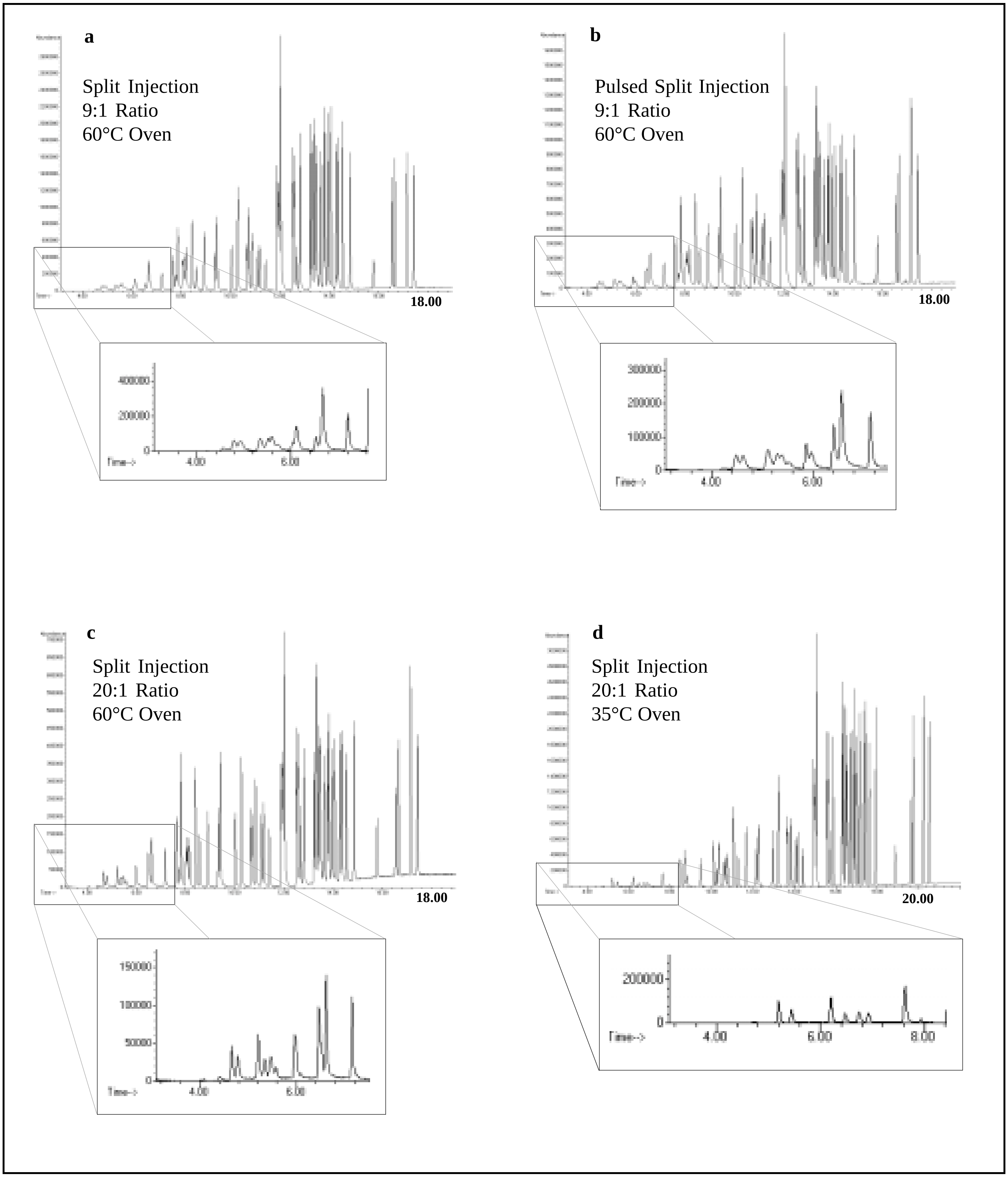


Figure 7. Rtx-VMS Column, 60 m x 0.25 mm I.D. x 1.4 µm film, Shown Using Several Different GC Programs (5 mL of a 20-ppb 502.2 Standard). This Column is Nearly Identical to the Column Used for Figure 6, and the Reduced Analysis Time is due to a Faster GC Oven Program. This Column is now a Best Seller and has Reduced GC Analysis Time to Between 18 and 21 Minutes.

The fastest cycle time was acheived with the short 20-meter DB-VRX column. Using this column and the manufacturer's recommended conditions reduced the GC run time to under 15 minutes and still maintained peak shape, resolution, and sensitivity (see Figure 8). With this column, the cycle time on the purge and trap becomes the rate limiting step.

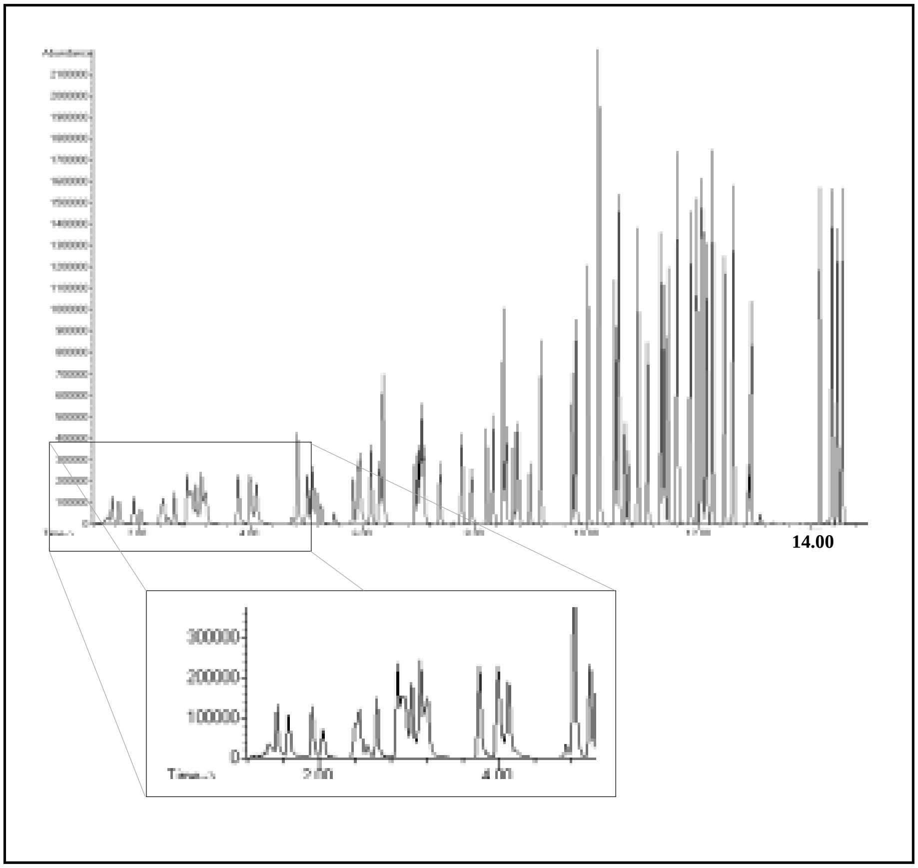


Figure 8. DB-VRX Column, 20 m x 0.18 mm I.D. x 1 µm film, Using the Manufacturer's Recommended GC Program (5 mL of a 20-ppb 524.2 standard). This Column has Reduced the GC Analysis Time to as Little as 15 Minutes, Making the Purge-and-Trap Cycle Time the Rate-Limiting Step.

Dual Purge-and-Trap Configurations

Today's production labs invest heavily in method development in order to reduce overall sample analysis cycle time and to increase instrument capacity. With shorter GC runs becoming routine, the time required for chromatographic separation is no longer the rate-limiting step in VOC analyses. The OI Analytical Model 4560 has one of the shortest purge-and-trap cycle times available today at 23 minutes or less including trap cool-down if the USEPA specificed 11 minute purge, 4 minute desorb, and 10 minute back times are maintained. The Model 4560 cycle time can be reduced significantly by heating the sample to reduce the purge time, using a #10 trap to eliminate the 2–4 minute dry purge, and using rapid trap heating to reduce the desorb step to 2 minutes. But even at 23 minutes, this is a full 8 minutes longer than the shortest GC run shown above. The shorter GC run leaves the GC/MS sitting idle for as much as 8 minutes or more waiting for the purge and trap (and autosampler) to complete a cycle.

To make full use of their capital investment and to prevent idle downtime on the MS, some labs are turning to the use of dual purge-and-trap configurations such as with the OI Analytical PT Express™ shown in Figure 9. Two purge-and-trap units with their associated autosamplers are “daisy-chained,” allowing them to alternately deliver samples to one GC/MS for analysis. While one purge and trap is completing its cycle, desorbing to the GC column and rinsing the sample path, the other purge and trap is already purging a second sample that will be ready for desorption to the GC column as soon as the first 15-minute sample run is completed. Interactions between the two purge and traps and the GC are coordinated by an electronic communications box that syncronizes all the purge and trap’s timing and prevents two samples from being desorbed simultaneously.

Figure 9. OI Analytical Dual Purge-and-Trap System Using the PT Express and SAM

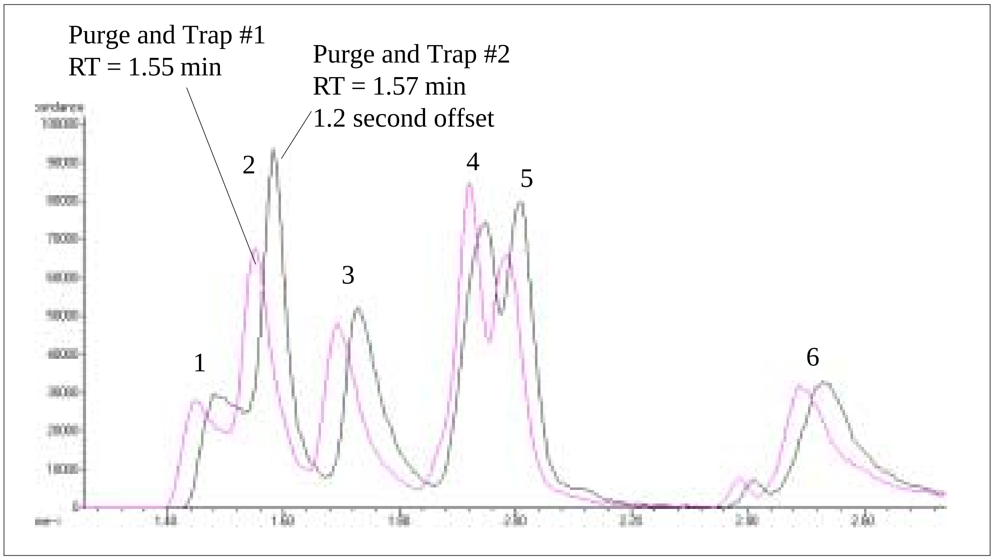
Several considerations must be taken into account when using dual configurations, including whether to use completely separate calibrations and QC samples for the two different purge-and-trap systems or whether to intersperse the calibration and QC samples by alternating back and forth between the two purge and traps. Using completely separate QC samples for each instrument is the more rigorous choice and minimizes problems if the operation of one of the instruments is interrupted during a sequence. However, this option leads to running nearly twice as many QC samples and has the effect of losing some of the time advantage that was gained by joining the two purge and traps in the first place. Alternating the calibration and QC samples between the two purge and traps is certainly more expedient, but the instruments and autosamplers must be very closely matched in terms of sample loop size, purge conditions, and trap performance for method criteria to be maintained. It is also important to use different surrogate standards in the two purge-and-trap units to quickly and easily identify which unit a particular sample was run on during data review and troubleshooting. Examples of some data run on the dual purge-and-trap system using the PT Express are shown in Table 1 and Figures 10 and 11.

Table 1 is a report of the relative standard deviations (%RSDs) for 12 replicate analyses on each of two matched purge-and-trap units over an 18-hour period. Twenty-four 5-mL aliquots of a 20-ppb BTEX standard were run alternately on the two matched purge-and-trap units, with 1 µL of the internal standard (IS), fluorobenzene, added automatically using a Standards Addition Module (SAM). The peaks in each TIC were auto-integrated using MS ChemStation software. The %RSDs were calculated for the individual matched purge-and-trap units and for the complete PT Express (dual purge-and-trap) sequence. All %RSDs were significantly below the 15% to 30% criteria suggested in most USEPA VOC methods, and the overall dual purge and trap %RSDs were all well below 10%. The highest deviation, 7.9%, was for the IS that was added using a pair of matched 1-µL loops.

Calibration curves were generated for BTEX on the two matched purge-and-trap units from 0.5 to 100 ppb. Duplicate 5-mL aliquots of five calibration standards were run alternately on the dual purge-and-trap system. Separate calibration curves were plotted for each purge and trap to demonstrate how closely the two systems were matched. Figure 11 illustrates the excellent agreement between the two curves for each compound, with similar slopes and correlation coefficients (R^2). The difference in average area counts between the two purge and traps at each concentration was less than 1%.

Table 1. Relative Standard Deviations (%RSDs) for 12 Replicate Analyses on Two Matched Purge-and-Trap Units Over an 18-hour Period

	Purge and Trap #1 Run Alone	**Purge and Trap #2 Run Alone**	**PT Express Combined Run**
Benzene	5.8	4.1	5.1
IS	6.7	7.5	7.0
Toluene	6.9	5.3	6.2
Ethylbenzene	7.2	4.8	6.1
m/*p*-Xylene	4.7	3.4	4.1
o-Xylene	5.1	3.9	4.7
SS	6.0	9.4	n/a



Purge and Trap #1
RT = 1.55 min

Purge and Trap #2
RT = 1.57 min
1.2 second offset

Figure 10. Early Eluting Peaks, Such as These Six Gases, will have a Slight Retention Time (RT) Offset of About 1 to 1.5 Seconds due to the Longer Transfer Line for the Second Purge and Trap. This RT Offset can be Used as a QC Tool to Help Identify Which Purge and Trap a Given Sample was Run on. The RT Offset is Not Observed for the Later Eluting Compounds.

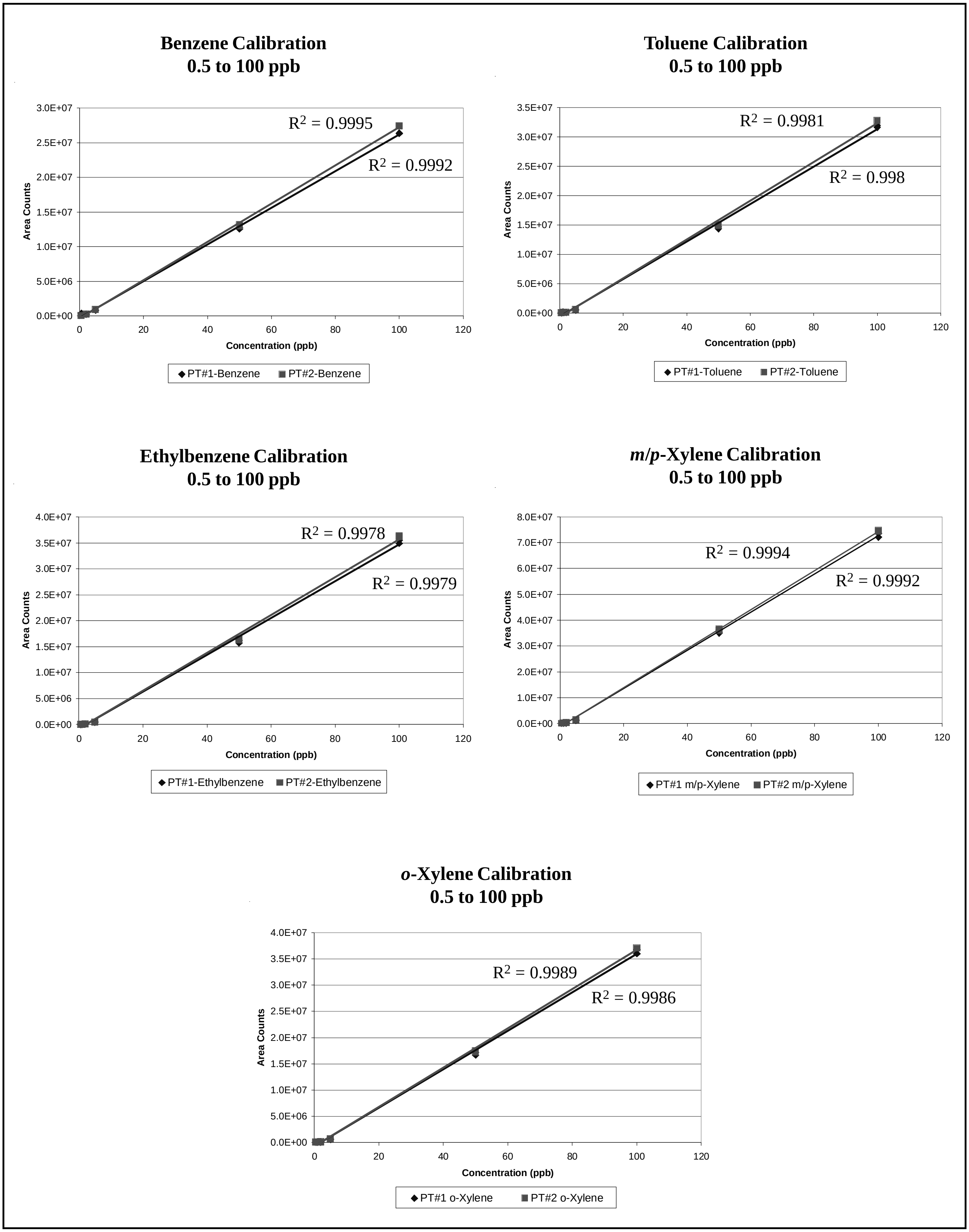


Figure 11. Calibration Curves for all Five BTEX Peaks on Two Matched Purge-and-Trap Units of a PT Express. Note the Excellent Agreement Between the Two Curves for Each Compound and the Nearly Identical Correlation Coefficients, Demonstrating How Well the Two Units are Matched.

Automated Multipoint Process Sampler for Water

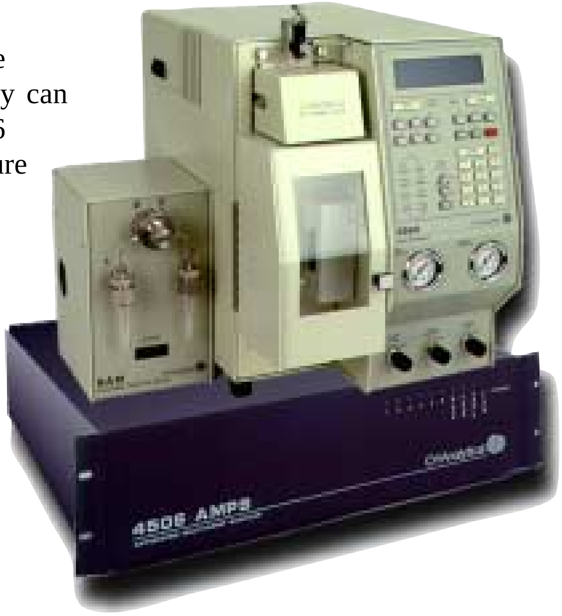


Figure 12. OI Analytical Model 4506 Automated Multipoint Process Sampler with the Model 4560 Purge-and-Trap Sample Concentrator and SAM

By automating the time-consuming and labor-intensive sample collection process in conjunction with the analysis, a laboratory can further streamline their process. The OI Analytical Model 4506 Automated Multipoint Process Sampler (AMPS) shown in Figure 12 permits computerized, sequential sampling of up to six process or drinking water streams. The system completely eliminates manual sampling, saving time and money, and reduces errors caused by improper sample handling. Since both the sampling and the analysis of the water streams are now automated, the operator is capable of maintaining continuous, 24-hour monitoring of multiple streams. Time-based or continuous sequential sampling, system rinses between sampling, analysis of water blanks, and alarm indicators are all easily programmable via the WinAMPS™ software package. Automated 24-hour monitoring of both source water and finished water streams for toxic or dangerous compounds is now possible with this system. In addition to the pharmaceutical and semiconductor industries, one of the principal application for the AMPS is the continuous monitoring of treated municipal water for trihalomethanes (THMs) following regulatory guidelines. Figures 13, 14, and 15 illustrate this common application.

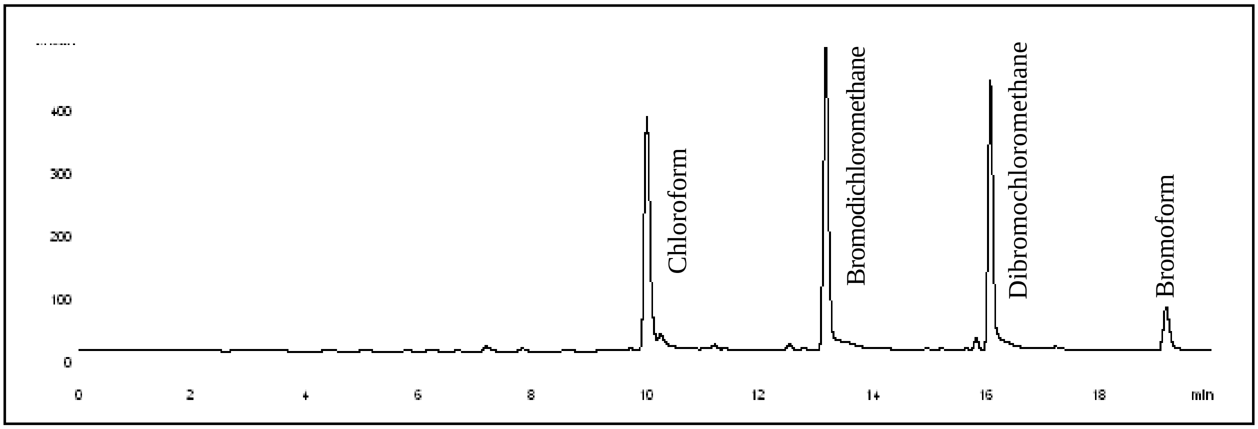


Figure 13. A Representative Chromatogram of THMs Collected During Continuous Monitoring of Local Tap Water Using the AMPS. The Analysis was Performed on an OI Analytical Halogen Specific Detector (XSD™), which Responds Only to the Halogenated Compounds Present in the Sample. The Only Peaks that are Observed in this Analysis are Low ppb Levels of the THMs.

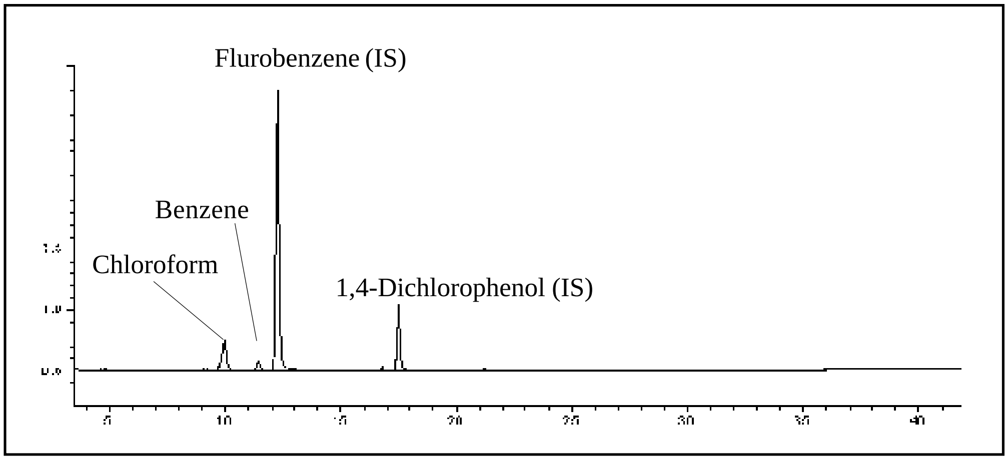
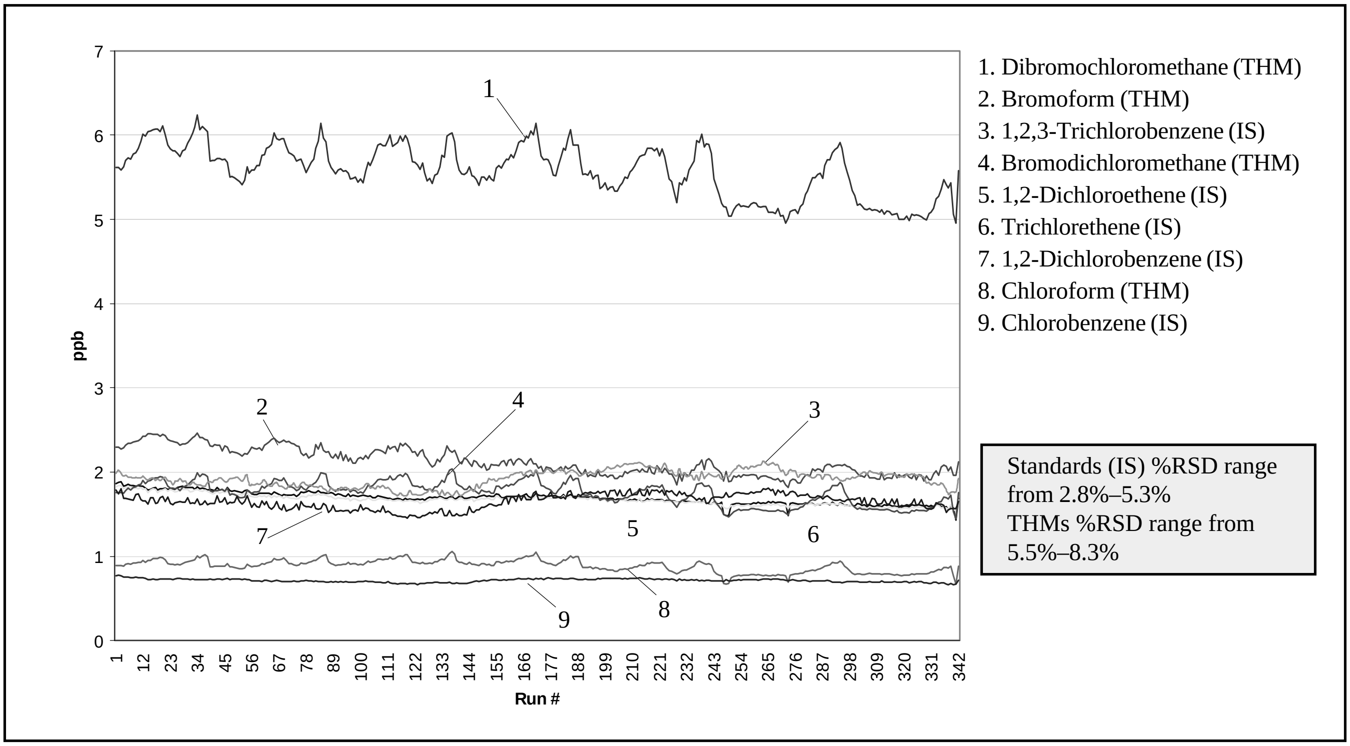


Figure 14. Chromatogram of River Source Water for a Water Utility Run on the AMPS and the Model 4560. This Fully Automated System was Configured to Monitor for 21 Key Compounds at Single-Digit ppb Levels as well as for Increases in Total VOC Concentrations.



Standards (IS) %RSD range from 2.8%–5.3%
THMs %RSD range from 5.5%–8.3%

Figure 15. Results for Both the THMs and the Internal Standards (IS) when using the Optional Standards Addition Module (SAM). The SAM was Programmed to Add the IS During each Analysis. The Stability of the Standard Response over Seven Days Verifies that the Changes Observed in the THM Concentration are Actual Minor Changes in their Concentration in the Tap Water and not Caused by any Purge and Trap/GC Related Drift.

Conclusions

Increasing workloads and cost of labor in production laboratories demand that analytical cycle times be shortened to maximize sample throughput and that the analytical process be automated as much as possible. High standards for complete method performance must be maintained or much of the advantage will be lost. When used with the OI Analytical Model 4560, the three-layer #10 trap produces superior chromatographic peak shape and sensitivity compared to the more hydrophobic VOCARB 3000 trap. Advances in capillary column technology have reduced GC run times to as little as 15 minutes or less, making the purge and trap's 23-minute cycle time the rate-limiting step and driving some labs to the introduction of dual purge-and-trap systems. The new OI Analytical PT Express can relieve the purge-and-trap bottleneck and maximize utilization of the GC/MS, but it may involve additional QC steps to monitor the system. Automation of the labor-intensive sample collection step completes the streamlining process and makes the entire application fast, routine, dependable, and durable. Rapid, automated 24-hour monitoring for toxics compounds in drinking water is now possible.

Cyclone Water Management is protected under U.S. Patent #5,250,093.

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