



Watch

Guest Author
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“Column Watch” guest author Cameron George discusses recent advances in purge-and-trap systems that enable considerable reduction in analysis times. He describes a complete purge-and-trap system and a new technique that doubles sample throughput for volatile organic compound analyses.

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High-Speed Analysis of Volatile Organic Compounds in Environmental Samples Using Small-Diameter Capillary Columns and Purge-and-Trap GC–MS Systems

The analysis of volatile organic compounds (VOCs) in environmental matrices is a well-understood and developed practice that uses purge-and-trap concentration before sample introduction into capillary gas chromatography (GC) or GC–mass spectrometry (MS) systems. Most work performed for the analysis of VOCs adheres to U.S. Environmental Protection Agency (EPA) method guidelines for solid waste or sludge (1), wastewater (2), and drinking water (3). During the past two decades many advances in instrumentation have been made in efforts to improve upon the early systems developed by Bellar and Lichtenberg (4). These advances were driven by a need for improved analyte identification confidence (resolution), improved sensitivity, and reduced analysis times.

Before further discussions about these advances, I first must explain the interfacing requirements between a typical purge-and-trap system and a GC or GC–MS system. Several steps in purge-and-trap concentration directly involve the sample being analyzed. First, an inert gas purges the vapor phase over the sample for a finite period of time. This vapor is swept through heated gas lines to a solid-phase trap that sorbs and concentrates the volatile analytes, as well as some matrix compounds, from the sample. Finally, the analytes of interest are thermally desorbed from the trap to a GC or GC–MS system.

Using purge-and-trap systems with capillary GC and GC–MS systems forces a continual compromise of gas flow rates. At the

time of sample introduction during the trap thermal desorption step, the total flow of gas through the trap directly affects desorption efficiency. Purge-and-trap concentrators excel at high desorption flow rates, and capillary columns and MS detectors excel at low flow rates (≤ 1.5 mL/min). Thus, gas flow compromises must occur. In older systems that use packed GC columns, the carrier-gas flow through the column was the same flow used to desorb analytes from the trap. In these systems, the purge-and-trap concentrator and the packed column operated in an optimized state, both with high flows generally between 30 and 40 mL/min. However, this high carrier-gas flow needed to be reduced greatly before entering the MS detector. This flow rate reduction was managed using a jet separator that removed most of the carrier flow immediately before it entered the MS detector ion source. Figure 1 is an example chromatogram for this type of system. The room for improvement is evident, even for this simple mixture analyzed using older EPA methodology (2).

During the 1980s, chromatographers formed a very strong movement toward using fused-silica capillary columns. This movement occurred throughout the analytical testing industry, including laboratories analyzing VOCs in environmental samples. This change was driven primarily by the massive improvement in analyte resolution that these capillary columns provided compared with their packed column counterparts. This increased resolving power became paramount with expanding target

analyte lists. Three columns were developed specifically for the analysis of VOCs: the DB-1301 cyanopropyl phenyl methyl substituted column (J&W Scientific [now Agilent Technologies], Folsom, California), which led to the DB-624 column (5,6); the Vocol phenyl methyl substituted column (Supelco, Bellefonte, Pennsylvania) (7); and the Rtx-502.2 phenyl methyl substituted column (Restek Corp., Bellefonte, Pennsylvania). The columns used with purge-and-trap concentrators possessed moderate-to-large inner diameters — typically 0.53–0.75 mm — by today's capillary column standards. The large inner diameters allowed for a high carrier gas-trap desorption flow of 10–15 mL/min. This flow, although not optimum, still allowed the purge-and-trap system to operate reasonably well. When coupled with the increase in column efficiency, huge gains in analyti-

cal performance were realized. At this time, systems still required a jet separator or some other form of flow reduction before sample introduction into the MS detector ion source. Direct interface of the column to the MS detector was highly desirable, because jet separators introduced discriminatory effects for more-volatile analytes and had high maintenance requirements (8).

In an ideal situation, a high-desorption flow rate coupled with a small-diameter gas capillary column (0.25 mm or smaller) and direct column insertion into an MS detector would provide the best overall performance. This type of system would enable efficient trap desorption, increased column efficiency, minimal discrimination, and reduced maintenance. Developed in the late 1980s, the split-injection interface addressed all of these issues. This interface enabled a high desorption flow rate while

splitting off most of the flow at the GC inlet, which provided an optimized carrier-gas flow rate and direct column insertion into the MS detector. Abeel and colleagues (8) demonstrated an optimized system that used a split-injection interface with a 60 m × 0.25 mm, 1.4 μm *d_f* DB-VRX capillary column (J&W Scientific). They obtained excellent resolution of more than 80 analytes in less than 30 min, which was a significant improvement compared with previous work.

The split-injection configuration using 50- and 60-m columns was considered state of the art until recently. Although chromatographers desired additional advances in the analysis of VOCs, several obstacles hampered further improvements. Two obstacles were the general resistance toward the use of cryogenic ovens or inlets with liquid nitrogen and the design limitations of bench-top MS detector units. However, recent improvements in bench-top MS detector design have provided better sensitivity and the opportunity for continued advancement.

The goal of this month's "Column Watch" is to briefly discuss a GC-MS volatile compound analysis system that uses recent advances in instrumentation allowing for method optimizations to improve the speed and performance of VOC measurements. These improvements will bring significant advantages to environmental laboratories and should be considered for incorporation into official analysis methods.

System Considerations

To make significant improvements in the analysis of VOCs, analysts must ensure that each part of a system is optimized, including the purge-and-trap configuration, interface configurations, capillary column dimensions and phase type, detector configuration and operating conditions, and experimental conditions. These areas obviously are interdependent, and although users are concerned about moving to small-diameter capillary columns for fast VOC analysis, they must remember to consider all system parameters.

The idea of changing to small-diameter, short columns to decrease analysis time while maintaining resolution certainly is not new. The obstacles in sensitivity and desorption efficiency become very important, however, with VOC analyses using purge-and-trap concentration. Decreasing the column inner diameter translates into a decreased carrier-gas flow, and, with

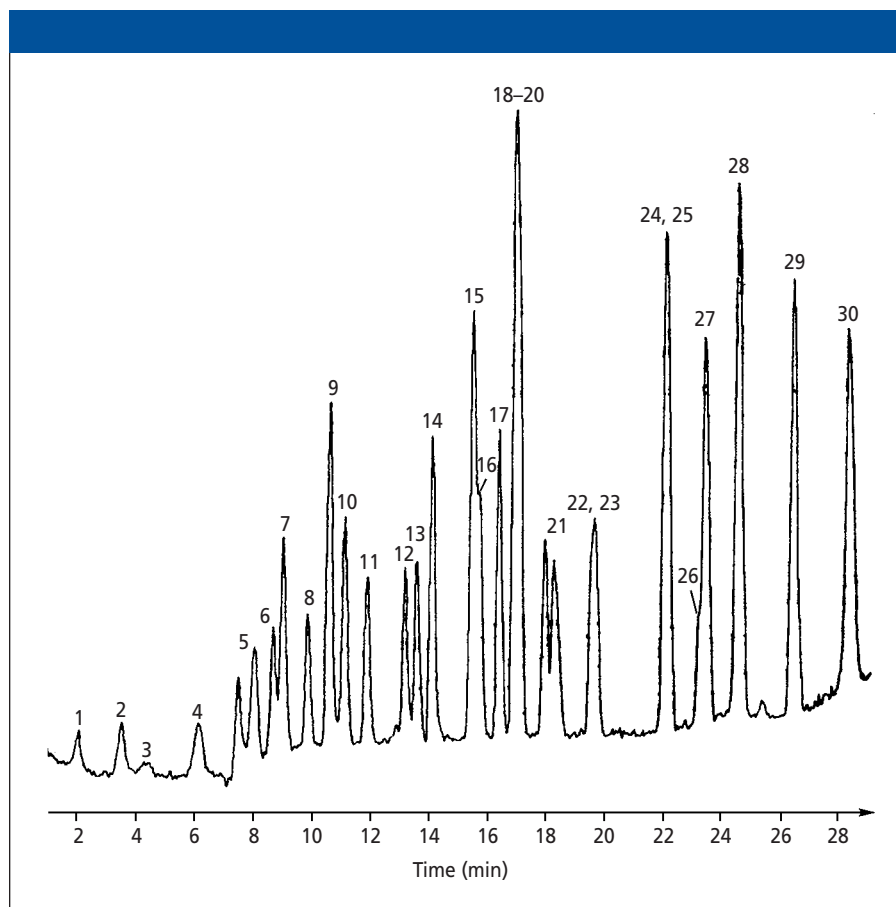


Figure 1: The analysis of 30 purgeable organic compounds using MS detection. Chromatography was achieved using a 6 ft × 0.1 in. column packed with 1% SP-1000 (Supelco) coated on 60/80 mesh Carbopack B. Oven program: 45 °C for 3 min, then 45–220 °C at 8 °C/min. Peaks: 1 = chloromethane, 2 = vinyl chloride, 3 = chloroethane, 4 = methylene chloride, 5 = trichlorofluoromethane, 6 = 1,1-dichloroethene, 7 = bromochloromethane, 8 = 1,1-dichloroethane, 9 = *trans*-1,2-dichloroethane, 10 = chloroform, 11 = 1,2-dichloroethane, 12 = 1,1,1-trichloroethane, 13 = carbon tetrachloride, 14 = bromodichloromethane, 15 = 1,2-dichloropropane, 16 = *cis*-1,3-dichloropropene, 17 = trichloroethene, 18 = 1,1,2-trichloroethane, 19 = benzene, 20 = dibromochloromethane, 21 = fluorobenzene, 22 = 1,4-difluorobenzene, 23 = bromoform, 24 = 1,1,1,2-tetrachloroethane, 25 = tetrachloroethene, 26 = pentafluorobenzene, 27 = toluene, 28 = chlorobenzene, 29 = ethylbenzene, 30 = 4-bromofluorobenzene.

constant total desorption flow rates, this change results in increased split ratios. With small-diameter columns (less than 0.2-mm i.d.), split ratios of 60:1 or greater are common. Higher split ratios introduce less sample to the column and, hence, less sample to the detector. Many older benchtop MS detector systems simply were not equipped to handle these low sample-to-detector quantities. Newer MS detector systems with optimized source configurations, improved electron multipliers, and improved mass filter designs have improved detector sensitivity so that this situation no longer exists as a hindrance to further VOC analysis development.

Capillary Column Considerations

The choice of columns becomes quite broad with these improvements in instrumentation. A move from 0.20- or 0.25-mm i.d. columns to 0.1-mm i.d. or even smaller columns is quite tempting. However, an abrupt change in column dimensions perhaps would be a bit overzealous, despite the many advances in detector technology. Extremely high split ratios, low column capacities, and excessive inlet pressures are some of the reasons that make this step impractical. A more realistic compromise is to step down from typical 60 m \times 0.20 mm (or 0.25 mm) columns to more reasonable 20 m \times 0.18 mm capillaries. In reviewing the effects of column diameter and length upon theoretical efficiency, it becomes apparent that the 20 m \times 0.18 mm configuration has less resolving power than the 60 m \times 0.20 mm column. Considering the potential analysis time improvement, however, this slight loss in resolution is deemed acceptable. The 0.18-mm column provides superior resolution per unit time.

When considering column dimensions for VOC analysis, it is important to keep the phase ratio (β) in mind. Phase ratio has a significant effect on analyte retention. It is beneficial in the process of scaling methods from large- to small-diameter columns to keep β constant. Maintaining the phase ratio will yield a column with an equivalent level of retentive character toward the analytes of interest and will provide more accurately scaled methods. For this reason, chromatographers most frequently use a 1.0- μ m film thickness with 0.18-mm i.d. columns for VOC analysis.

Another important parameter affecting VOC analysis is the choice of stationary phase. Several common GC stationary phases were examined with varying results.

Although columns with cyanopropylphenyl dimethylpolysiloxane (624 type) and diphenyl dimethylpolysiloxane (502.2 type) phases provided analytical methods that were easily scaled down for use with smaller capillaries and resulted in analysis times typically shorter than 15 min, certain critical compounds were coeluted. Some of these coelutions caused problems with quantitation. As a result, other potential stationary phases were examined.

The 60 m \times 0.2 mm, 1.1- μ m d_f HP-VOC capillary column (Agilent Technologies, Wilmington, Delaware) provided excellent selectivity when used with older MS detector systems; however, it did not possess the required characteristics for fast VOC analysis. In particular, the GC method used for the larger capillaries did not scale down appropriately for use with smaller capillaries. The temperature program ramp rates required to achieve proper scaledown were unattainable with most common GC ovens, and using improperly scaled methods resulted in a severe resolution loss.

After considerable investigation, it was determined that the VRX phase was the stationary phase that possessed the desired characteristics. The GC method used for the 60 m \times 0.25 mm DB-VRX column easily scaled down for use with smaller capillaries. The selectivity of this stationary phase was computer-designed for VOC analysis, and, as a result, the selectivity for the designated analytes in EPA Methods 524.2 and 8260 is ideal (9). The excellent selectivity of this phase for critical analyte pairs that share primary quantitation ions enabled additional optimization of the oven-temperature program and carrier-gas velocity. This phase type and dimensional configuration exhibited the best performance of the examined columns.

Analysis Conditions

Of the conditions listed in the accompanying sidebar, "High-Speed VOC Analysis Conditions," the initial oven temperature is of particular interest. Although using an initial oven temperature of 35 $^{\circ}$ C may provide slightly better resolution for the early eluted analytes, this relatively low temperature adds significantly to cooldown times, thus increasing the overall oven cycle times. Increasing the initial oven temperature to 45 $^{\circ}$ C significantly reduces cooldown times from the final oven temperature of 225 $^{\circ}$ C. In addition to shortened cooldown times, fast oven ramping rates also decrease oven cycle times. Oven

ramp rates of 36 $^{\circ}$ C/min to 190 $^{\circ}$ C and 20 $^{\circ}$ C/min to 225 $^{\circ}$ C are difficult to achieve using many older gas chromatographs, but they are readily attainable with newer oven designs.

An average carrier-gas velocity of 55 cm/s (1.5 mL/min) for helium is greater than optimum, but, again, incremental resolution losses are acceptable in light of the potential for analysis time reduction. A split ratio of 60:1 provides a total desorption flow of 91.5 mL/min. High desorption flow and temperature combine to reduce the necessary desorption time to 1 min. Shorter desorption times lead to a reduction in the water and methanol transferred to the GC-MS system, which results in less baseline disturbance and better sensitivity for early eluted analytes. The response for late-eluted analytes was unaffected by this reduction in desorption time. Additional reductions in desorption

High-Speed VOC Analysis Conditions

GC Conditions

Column: 20 m \times 0.18 mm, 1.0- μ m d_f DB-VRX
 Carrier gas: helium at 55 cm/s (1.5 mL/min)
 Interface: split injector at 150 $^{\circ}$ C; 60:1 split ratio
 Oven program: 45 $^{\circ}$ C for 3.0 min, 45-190 $^{\circ}$ C at 36 $^{\circ}$ C/min, 190-225 $^{\circ}$ C at 20 $^{\circ}$ C/min, and 225 $^{\circ}$ C for 0.5 min

MS Detector Conditions

Scan range: full scan at m/z 35-260
 Scan rate: 3.25 scans/s
 Quad temperature: 150 $^{\circ}$ C
 Source temperature: 200 $^{\circ}$ C
 Transfer line temperature: 200 $^{\circ}$ C

Purge-and-Trap Conditions

Trap: Vocarb 3000 (Supelco); 35 $^{\circ}$ C during purge
 Sample volume: 5 mL
 Purge: 11 min
 Desorb preheat: 245 $^{\circ}$ C
 Desorb: 1 min at 250 $^{\circ}$ C
 Bake: 10 min at 260 $^{\circ}$ C
 Line and valve temperature: 100 $^{\circ}$ C

Sample Concentration

- Halogenated and aromatic analytes spiked at 40 ppb
- Internal standards spiked at 20 ppb
- Polar analytes such as alcohols, ethers, and ketones spiked at 100-800 ppb

time are likely possible but were unexplored in this study.

Figure 2 shows the analysis of 114 VOCs according to EPA Method 8260B using the conditions listed in the sidebar. Taking advantage of the benefits of small-diameter columns, optimized instrumenta-

tion, and experimental conditions, VOC analysis time was reduced from 30 min (8) to 7.6 min and a comparable level of resolution and confirmation confidence was maintained. This fast VOC analysis time is achieved by optimizing the entire system and keeping all compromises in mind.

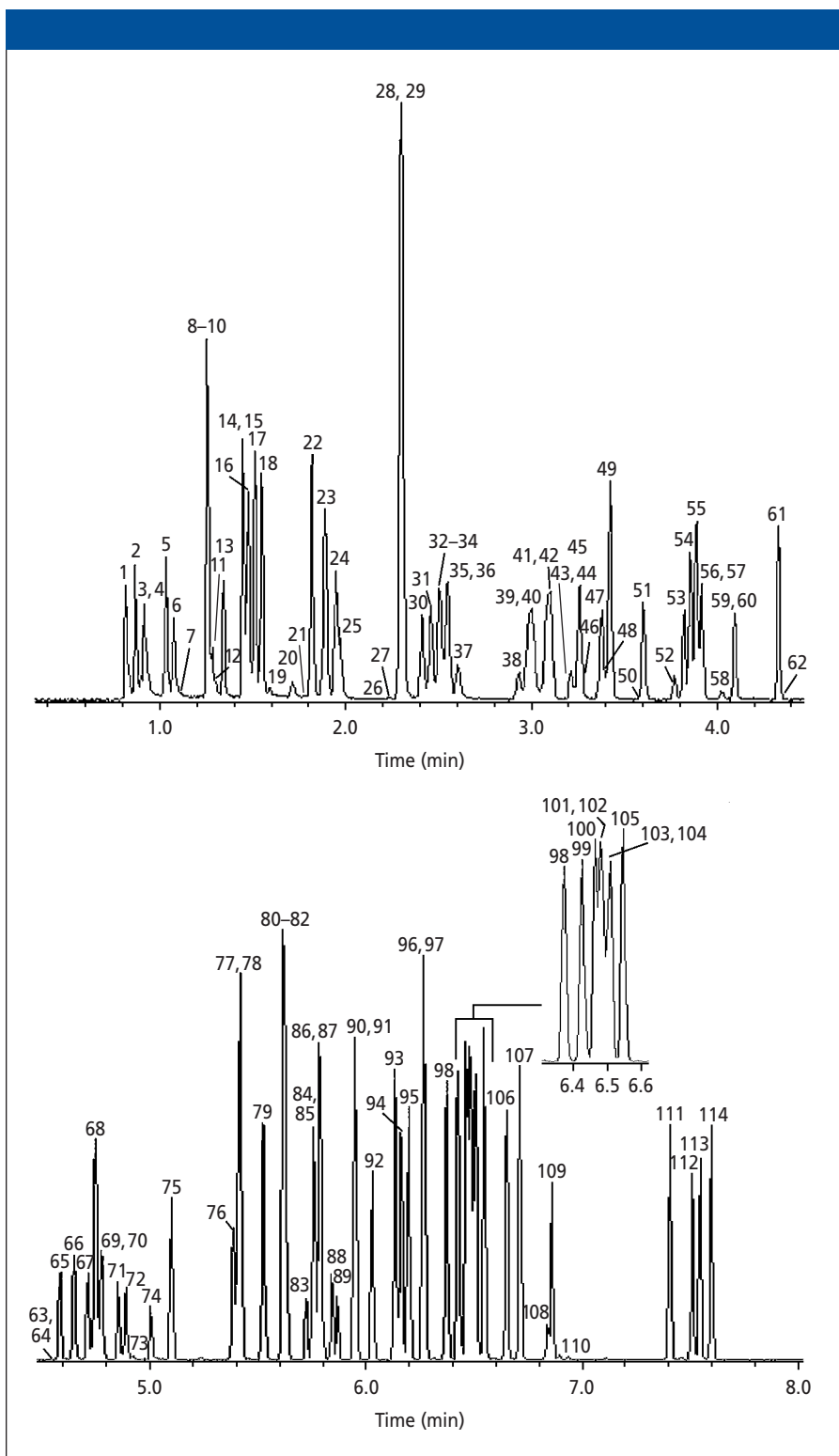


Figure 2: Chromatogram from EPA Method 8260B analysis of volatile organic compounds using fast GC-MS. Table I lists the compounds and retention times by peak number.

Improvements in Purge-and-Trap Technology

With a VOC analysis time of less than 8 min and a typical purge-and-trap cycle time of more than 20 min, the purge-and-

trap system now becomes the rate-limiting step. With this situation in mind, investing effort into achieving fast VOC analyses would appear to be a fruitless endeavor. However, new technologies from EST

Analytical (Cincinnati, Ohio) and Tekmar-Dohrmann (Cincinnati, Ohio) could make improvements in purge-and-trap throughput possible. EST Analytical's PT² and Tekmar-Dohrmann's Duet dual purge-and-

Table I: Volatile organic compounds illustrated in Figure 2

Peak Number	Compound	Retention Time (min)	Peak Number	Compound	Retention Time (min)	Peak Number	Compound	Retention Time (min)
1	Dichlorodifluoromethane	0.82	39	Pentafluorobenzene	2.98	77	1-Chlorohexane	5.42
2	Chloromethane	0.87	40	1,2-Dichloroethane	3.00	78	Chlorobenzene	5.42
3	Hydroxypropionitrile	0.92	41	1,1,1-Trichloroethane	3.08	79	Ethylbenzene	5.52
4	Vinyl chloride	0.92	42	1-Chlorobutane	3.11	80	Bromoform	5.62
5	Bromomethane	1.03	43	Crotonaldehyde	3.21	81	<i>m</i> -Xylene	5.62
6	Chloroethane	1.07	44	2-Chloroethanol	3.21	82	<i>p</i> -Xylene	5.62
7	Ethanol	1.09	45	1,1-Dichloropropene	3.26	83	<i>trans</i> -Dichlorobutene	5.72
8	Acetonitrile	1.26	46	1-Butanol	3.29	84	1,3-Dichloro-2-propanol	5.74
9	Acrolein	1.26	47	Carbon tetrachloride	3.38	85	Styrene	5.76
10	Trichlorofluoromethane	1.26	48	Chloroacetonitrile	3.40	86	1,1,2,2-Tetrachloroethane	5.78
11	Isopropyl alcohol	1.28	49	Benzene	3.42	87	<i>o</i> -Xylene	5.78
12	Acetone	1.30	50	<i>tert</i> -Amylmethyl ether	3.57	88	1,2,3-Trichloropropane	5.84
13	Ethyl ether	1.34	51	Fluorobenzene (internal standard)	3.61	89	<i>cis</i> -Dichlorobutene	5.87
14	1,1-Dichloroethene	1.45	52	2-Pentanone	3.77	90	4-Bromofluorobenzene (internal standard)	5.95
15	<i>tert</i> -Butyl alcohol	1.47	53	Dibromomethane	3.82	91	Isopropylbenzene	5.95
16	Acrylonitrile	1.48	54	1,2-Dichloropropane	3.85	92	Bromobenzene	6.03
17	Methylene chloride	1.51	55	Trichloroethene	3.89	93	Propylbenzene	6.14
18	Allyl chloride	1.55	56	Bromodichloromethane	3.92	94	2-Chlorotoluene	6.16
19	Allyl alcohol	1.62	57	2-Nitropropane	3.93	95	4-Chlorotoluene	6.20
20	1-Propanol	1.71	58	1,4-Dioxane	4.02	96	1,3,5-Trimethylbenzene	6.27
21	Propargyl alcohol	1.78	59	Epichlorohydrin	4.10	97	Pentachloroethane	6.27
22	<i>trans</i> -1,2-Dichloroethene	1.82	60	Methyl methacrylate	4.10	98	<i>tert</i> -Butylbenzene	6.37
23	Methyl- <i>tert</i> -butyl ether	1.89	61	<i>cis</i> -1,3-Dichloropropene	4.33	99	1,2,4-Trimethylbenzene	6.42
24	1,1-Dichloroethane	1.95	62	Propiolactone	4.35	100	<i>sec</i> -Butylbenzene	6.46
25	Propionitrile	1.97	63	Bromoacetone	4.56	101	1,3-Dichlorobenzene	6.48
26	2-Butanone	2.18	64	Pyridine	4.56	102	Benzylchloride	6.49
27	Diisopropyl ether	2.23	65	<i>trans</i> -1,3-Dichloropropene	4.58	103	1,4-Dichlorobenzene- <i>d</i> ₄ (internal standard)	6.50
28	<i>cis</i> -1,2-Dichloroethene	2.30	66	1,1,2-Trichloroethane	4.65	104	1,4-Dichlorobenzene	6.51
29	Methacrylonitrile	2.32	67	Toluene- <i>d</i> ₈ (internal standard)	4.72	105	Isopropyltoluene	6.55
30	Bromochloromethane	2.41	68	Toluene	4.75	106	1,2-Dichlorobenzene	6.65
31	Chloroform	2.46	69	1,3-Dichloropropane	4.78	107	Butylbenzene	6.71
32	2,2-Dichloropropane	2.51	70	Paraldehyde	4.78	108	1,2-Dibromo-3-chloro propane	6.84
33	Ethyl acetate	2.51	71	Ethyl methacrylate	4.85	109	Hexachloroethane	6.37
34	Ethyl- <i>tert</i> -butyl ether	2.51	72	Dibromochloromethane	4.89	110	Nitrobenzene	6.94
35	Methyl acrylate	2.55	73	3-Chloropropionitrile	4.96	111	1,2,4-Trichlorobenzene	7.41
36	Dibromofluoromethane (internal standard)	2.56	74	1,2-Dibromoethane	5.00	112	Naphthalene	7.51
37	Isobutanol	2.60	75	Tetrachloroethene	5.10	113	Hexachlorobutadiene	7.55
38	Dichloroethane- <i>d</i> ₄ (internal standard)	2.94	76	1,1,1,2-Tetrachloroethane	5.39	114	1,2,3-Trichlorobenzene	7.60

trap system interfaces allow users to interface two purge-and-trap concentrators with a single GC-MS system using single-computer control (see Figure 3). These purge-and-trap systems alternate sample injections into the GC-MS system. With two concentrators working in synchronization, users can double sample throughput on a single analytical system.

To achieve the full benefit of a dual purge-and-trap system, the total chromatographic cycle time must be reduced to approximately 13 min. This time will allow both concentrators to be fully optimized and to sacrifice none of their integrity for speed; however, sample throughput would be approximately doubled.

Using a DB-VRX capillary column configured as in the sidebar, analysts can achieve a 7.6-min analysis time with a cooldown time of approximately 5.5 min. This total cycle time of slightly more than 13 min is ideal for dual purge-and-trap applications. A properly optimized dual purge-and-trap system can achieve a sample throughput of 4–5 samples/h. This advancement will allow laboratories to meet sample demand, expedite turnaround

times, and satisfy sample hold-time requirements with minimal added capital expense.

Conclusion

The improved sensitivity of modern bench-top mass spectrometers has provided the opportunity for development toward the use of capillary columns with smaller inner diameters for the analysis of volatile organic compounds. A combination of improved detector design with optimized capillary column phases and dimensions gives laboratories the opportunity to pursue advancements in VOC analysis. Using dual purge-and-trap concentrators interfaced with a single GC-MS system will allow environmental testing laboratories to increase sample throughput greatly and improve overall productivity and efficiency.

Acknowledgments

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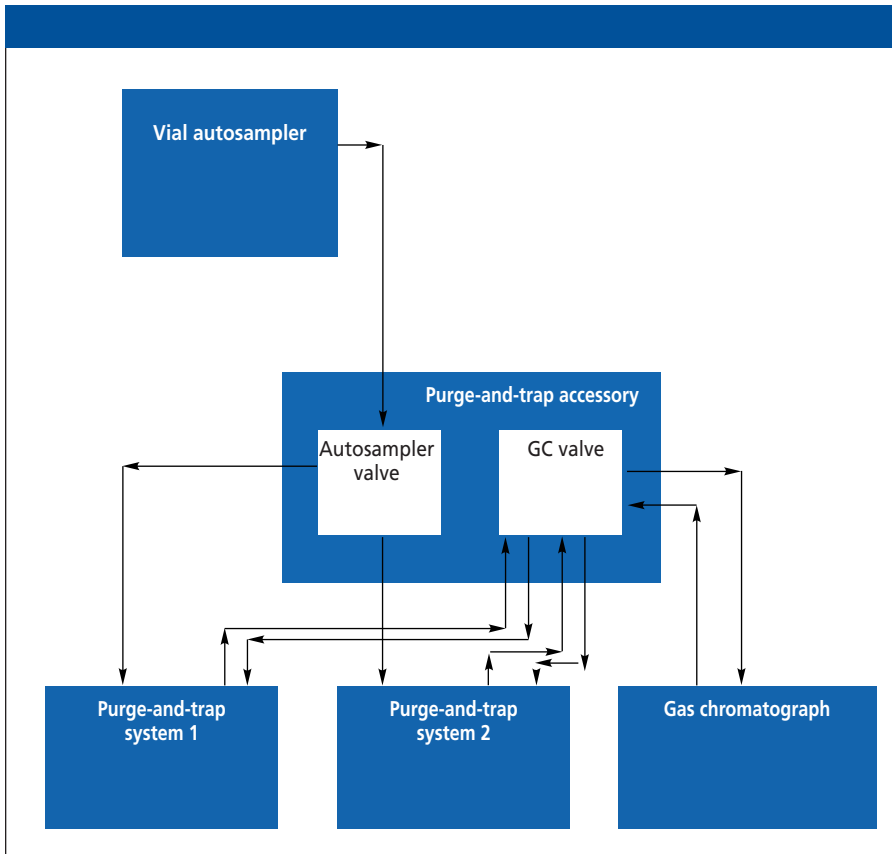


Figure 3: Block diagram of a dual purge-and-trap GC system. (Courtesy of EST Analytical.)

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