

Evaluation of Single- and Dual-Concentrator High-Throughput VOC Systems

by Jeff Sheriff

There are several demands and requirements imposed on chemists performing volatile organic analysis (VOC) in today's environmental laboratory. The first and most important is that the analysis must be performed in compliance with U.S. EPA methodologies. Next, there is a continued trend to achieve lower levels of detection. This paper describes ways to improve sample throughput without sacrificing data quality, meet the required level of detection, and still remain compliant to the U.S. EPA method.

Historically, limitations to improving sample throughput in volatile organic analysis with a single purge-and-trap system have been the length of the complete purge-and-trap cycle. The purge-and-desorb parameters recommended or required by U.S. EPA methodologies take 12–15 min. In addition to these purge-and-desorb time requirements, the time needed for a syringe-driven autosampler to rinse the sample glassware in preparation for the next sample also required bake times in excess of 8 min. This 22–25 min complete purge-and-trap cycle time limited the number of VOC samples capable of being analyzed in a 12-hr tune period.

This paper compares and evaluates two options for improving sample throughput up to 100% using a single fixed-loop autosampler. All quality assurance data per U.S. EPA methodologies using optimized methods will be presented.

In the late 1990s, GC manufacturers shortened GC cycle times by improving oven heating rates and decreasing cool-down times. Column manufacturers developed narrow-bore, shorter-length columns that reduced analytical run times without sacrificing resolution or sensitivity. Analyses that were once performed in 30 min could be performed in less than 10 min (see *Figure 1*). These significant improvements to the GC cycle time were immediately realized with semi-volatile applications; however, the benefits of fast GC run times could not be realized by chemists running volatile applications due to the length of the purge-and-trap cycle time.

There are two options available to the chemist to improve sample throughput in the volatile organic laboratory. The first is to employ the use of a second purge-and-trap concentrator to a single GC system and continue to use the traditional purge-and-trap parameters required or recommended by U.S. EPA methodologies. The second option is to reduce the total purge-and-trap cycle time of a single purge-and-trap concentrator by decreasing the traditional dry purge, desorb, and bake times. Both of these options will be evaluated and discussed.

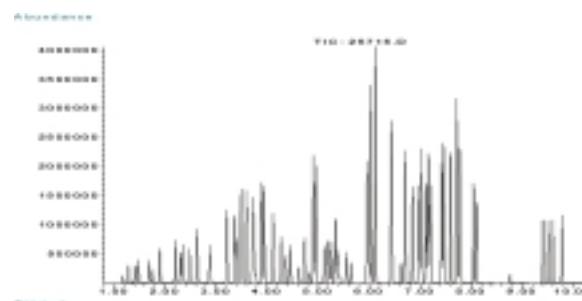


Figure 1 U.S. EPA Method 8260 with Appendix IX compounds, 50 ppb total ion chromatogram (TIC) in less than 10 min.

Dual-concentrator mode

The first commercially available product to allow chemists to interface two purge-and-trap concentrators was the PT² (EST Analytical, Cincinnati, OH), a valve-switching device that directs the sample purge gas flow from a single water/soil autosampler to one of two concentrators. It allows users to switch back and forth between the two concentrators to process the samples.

Once the first concentrator reaches desorb, a signal is sent to the second concentrator and the autosampler to begin purging the next sample. The samples are then ready to be injected as fast as the GC can run them, thus improving sample throughput up to 100%. However, the one disadvantage of the PT² is that all samples must be purged on the soil position of the autosampler since the device only directs gaseous flow. Water samples had to be transferred to a 40-mL vial before analysis. This configuration was a significant improvement for soil analysis; however, it was still necessary to analyze water samples in a sparge tube on the front of the purge-and-trap concentrator, which led to the development of the Centurion water-only autosampler (EST Analytical) (*Figure 2*).

The 100-position, fixed-loop water-only autosampler incorporates a liquid-switching valve to transfer aqueous samples to glassware on two separate purge-and-trap concentrators. The concentrators are then interfaced in series to a single GC via the PT-Link interface. For example, the transfer line of one concentrator is plumbed into the valve oven of the other concentrator whose transfer line is plumbed to the GC injection port. The concentrators alternate desorbing samples into a single GC every 13–15 min or at the rate of the GC cycle time,



Figure 2 Centurion autosampler.

whichever is greater, without the need to deviate from traditional purge-and-trap parameters. As one concentrator is desorbing the sample to the GC, the second begins to purge the subsequent sample. The rate-determining step for water sample throughput is one of three factors: 1) The total time needed for the autosampler to process, transfer, purge, and dry purge the sample (total time from purge ready to desorb ready); 2) the total desorb, bake, and cool-down time of the concentrator (total time from desorb preheat to purge ready); or 3) the GC cycle time (total time from GC start to GC ready).

Table 1 illustrates the GC cycle time of 14 min as the limiting factor in sample throughput in a dual-mode configuration using traditional purge-and-trap parameters.

Experimental

To demonstrate the ability of the dual-concentrator option to improve VOC sample throughput, two Encon concentrators (EST Analytical) (*Figure 3*) were configured via the PT-Link interface to a single GC-MS. The Centurion's two aqueous transfer lines were then interfaced to the glassware of two separate Encon concentrators. Using the purge-and-trap conditions outlined in *Table 2* and the GC-MS conditions in *Table 3*, a seven-point calibration curve ranging from 1 to 100 µg/L con-

Table 1 Rate-determining steps (dual-concentrator mode)

Process time, <0.5 min	Purge and dry times 11 min + 2 min	Desorb, bake, and cool-down times, 4 min + 8 min + 2 min	GC cycle time 14 min
	13.5 min		



Figure 3 Encon concentrator.

sisting of 68 compounds from the 8260B list of analytes was analyzed. A batch of 52 samples, including four Initial Demonstration of Accuracy and Precision Check Standards, was scheduled to be run over a 12-hr period. The Encon concentrators alternated injecting samples into the GC at a rate of one sample every 14 min. The linearity results of the calibration curve, accuracy and precision of the check standards, average response factors of the system performance check compounds, and internal standard results of the 52 samples over the 12-hr tune period are listed in Tables 4–6.

Single-concentrator mode

The second way to improve VOC sample throughput is to reduce the total purge-and-trap cycle time. As the result of the Centurion's ability to perform hot water rinse cycles of the concentrator glassware in 30 sec or less for 5-mL volumes and 60 sec or less for 25-mL volumes, it was no longer necessary that the concentrator bake cycle be in excess of 8 min, thereby allowing the purge-and-trap cycle time to be reduced. The rate-determining step in a single concentrator system now becomes either the total purge-and-trap cycle time or the total GC cycle time, whichever is greater. Table 7 illustrates the total purge-and-trap cycle time as the limiting factor in sample throughput in a single-concentrator configuration.

Experimental

To determine the minimum amount of time needed to efficiently recondition or bake the concentrator in preparation for the analysis of the next sample, a 200- $\mu\text{g}/\text{L}$ standard was purged on the soil side of an autosampler. A blank was then analyzed on the glassware of the Encon purge-and-trap concentrator to determine the amount of analyte remaining on the concentrator. Using the standard Encon bake

Table 2 Purge-and-trap conditions (dual mode)

Purge-and-trap parameter	Encon Vocarb 3000 Type K (EST)
Trap	
Sample size	5 mL
Purge temp	Ambient
Purge rate	40 mL/min, 3 psi Trap Back Pressure (TPC)
Purge time	11 min
Dry purge time	2 min
Dry purge temp	Ambient
Dry purge flow	40 mL/min
Desorb preheat	255 °C
Desorb temp	260 °C
Desorb time	4 min
Moisture reduction trap (on purge side)	Purge –40 °C, bake –260 °C
Line temp	130 °C
Valve temp	130 °C
Bake temp	270 °C
Bake time	8 min
Bake flow	120 mL/min, trap bake flow separate from glassware flow
Autosampler	Centurion
Sample process time	30 sec
Hot water rinse cycles	3 cycles in 90 sec
No. of runs/12 hr	52 runs (GC injection every 14 min)

Table 3 GC-MS conditions

GC-MSD (mass selective detector) parameter	Agilent 68905973*
Inlet	Electronic Pressure Control (EPC) Split/Splitless (S/SS)
Mode	Split
Inlet temp	180 °C
Split ratio	50:1
Split flow	38.0 mL/min
Oven temp program	
Initial temp	45 °C
Initial time	1.00 min
Ramp rate A	18.0 °C/min
Final temp A	190 °C
Ramp rate B	25 °C/min
Final temp B	220 °C
Column	DB-624, 20 m × 0.18 mm i.d., 1.00 μm df*
Column flow	0.6 mL/min
Linear velocity	33 cm/sec
Mode	Constant flow

*Agilent Technologies (Wilmington, DE).

flow of 120 mL/min, bake cycles of 8, 6, 4, and 2 min were used to evaluate the amount of time needed to effectively recondition the purge-and-trap concentrator prior to the next sample. The results listed in Table 8 indicate that there was little difference in the resulting carryover until the 2-min bake cycle.

To further evaluate the bake step, flow rates of 400, 120, and 40 mL/min were used to bake the system after a 200- $\mu\text{g}/\text{L}$ standard was analyzed. This standard was followed by manually stepping the concentrator to desorb to determine that amount of analyte remaining on the trap.

Next, a blank water sample was purged in the glassware to determine the amount of analyte remaining in the entire system. The results listed in Table 9 indicate no appreciable improvement in the resulting carryover, regardless of the flow rate.

To demonstrate the ability of the single concentrator option to improve VOC sample throughput using reduced desorb and using the bake times, the Centurion autosampler was interfaced to one Encon concentrator configured to a single GC-MS. Utilizing the conditions outlined in Table 3 and Table 10, and the Encon's standard bake flow of 120 mL/min, a seven-point calibration curve ranging from 1 to 100 $\mu\text{g}/\text{L}$ consisting of 68 compounds from the 8260B list of analytes was analyzed. A batch of 36 samples, including four Initial Demonstration of Accuracy and Precision Check Standards, was scheduled to be run over a 12-hr period. The Encon concentrator injected samples into the GC at a rate of one sample every 19–20 min. The linearity results of the calibration curve, accuracy and precision of the check standards, average response factors of the system performance check compounds, and internal standard results of the 36 samples over the 12-hr tune period are listed in Tables 4–6.

Conclusion

Both of the options discussed in this paper result in improved VOC sample throughput in the environmental laboratory without sacrificing data quality. Using the single purge-and-trap

A P P L I C A T I O N N O T E

Table 4 QA/QC data

Compound name	Dual-concentrator mode			Single-concentrator mode	
	Initial calibration (ICAL)		Accuracy	% RSD ICAL	Accuracy
	% RSD purge-and- trap 1	% RSD purge-and- trap 2			
Dichlorodifluoromethane	12.10	7.67	3.54	8.99	2.4
Chloromethane	12.07	6.34	0.96	7.66	0.7
Vinyl chloride	7.64	1.68	1.27	6.79	1.3
Bromomethane	10.20	8.53	3.43	5.53	1.4
Chloroethane	4.95	4.99	1.19	3.67	1.5
Trichlorofluoromethane	6.82	3.56	1.26	7.66	0.8
1,1-Dichloroethene	4.99	3.49	0.33	6.24	1.8
Acetone	0.993	0.994	4.98	0.995	4.3
Iodomethane	17.14	12.22	9.09	7.40	2.1
Carbon disulfide	8.15	5.23	1.86	5.99	1.0
Methylene chloride	9.08	5.32	0.46	21.59	1.3
Trans-1,2-Dichloroethene	7.16	1.91	6.17	6.66	1.8
Vinyl acetate	5.66	10.59	5.40	6.26	8.1
1,1-Dichloroethane	6.41	2.31	1.32	6.61	1.2
Cis-1,2-Dichloroethene	4.92	2.71	1.53	9.05	1.2
2-Butanone	0.997	0.998	1.82	0.997	1.7
2,2-Dichloropropane	7.91	8.07	1.42	12.14	2.5
Bromochloromethane	6.93	7.26	1.89	3.27	1.1
Chloroform	7.10	3.25	0.75	2.95	0.7
1,1,1-Trichloroethane	4.91	2.29	0.92	11.35	1.3
2-Chloroethyl vinyl ether	5.65	8.50	2.08	12.43	1.2
Carbon tetrachloride	6.24	13.29	1.68	13.39	1.5
1,1-Dichloropropene	5.25	3.27	0.92	11.56	2.5
Benzene	5.69	3.08	0.74	4.63	0.9
1,2-Dichloroethane	5.04	3.24	0.83	7.83	1.1
Trichloroethene	8.51	5.10	1.38	6.89	0.9
1,2-Dichloropropane	3.94	2.45	0.19	4.08	1.3
Dibromomethane	3.76	2.53	1.51	6.22	0.8
Bromodichloromethane	4.42	4.98	7.08	9.02	0.8
Cis-1,3-Dichloropropene	2.19	5.00	2.25	10.67	1.5
4-Methyl-2-pentanone	2.94	7.57	2.15	6.59	2.0
Toluene	5.02	3.60	1.42	6.75	1.2
Trans-1,3-Dichloropropene	4.58	7.27	1.29	10.67	1.5
1,1,2-Trichloroethane	3.24	3.97	1.62	6.31	1.8
Tetrachloroethene	4.91	4.86	1.42	6.62	0.5
1,3-Dichloropropane	2.05	3.36	0.78	9.45	2.1
Dibromochloromethane	3.83	8.37	1.41	19.91	0.9
2-Hexanone	3.06	5.63	1.11	6.25	2.0
1,2-Dibromoethane	2.46	4.10	0.88	8.30	2.2
Chlorobenzene	3.84	3.52	0.71	3.07	0.2
1,1,1,2-Tetrachloroethane	8.08	8.91	1.80	18.51	0.8
Ethylbenzene	7.14	6.12	1.24	5.98	1.0
Xylene (M&P)	6.66	6.52	0.90	9.95	0.6
Styrene	10.80	10.63	0.67	10.75	0.8
Xylene (O)	8.34	8.52	0.88	8.38	0.5
Bromoform	10.86	14.49	0.96	20.67	3.0
Isopropylbenzene	8.29	7.59	0.56	9.92	1.0
Bromobenzene	8.08	4.42	1.62	6.71	1.0
1,2,3-Trichloropropane	8.32	6.96	1.01	6.44	1.3
1,1,2,2-Tetrachloroethane	5.92	6.42	2.11	5.71	1.7
n-Propylbenzene	8.34	4.58	1.18	9.54	0.9
2-Chlorotoluene	7.61	6.83	1.08	5.36	0.9
4-Chlorotoluene	8.33	4.22	1.19	5.36	0.8
1,3,5-Trimethylbenzene	7.45	3.31	1.22	11.25	1.0
Tert-Butylbenzene	4.90	3.21	0.54	11.46	0.5
Sec-Butylbenzene	4.58	3.40	1.58	13.41	1.8
1,2,4-Trimethylbenzene	8.02	3.32	1.04	11.25	1.0
1,3-Dichlorobenzene	6.97	2.32	0.65	6.34	0.3
1,4-Dichlorobenzene	8.76	5.26	0.53	3.26	1.5
Isopropylbenzene	4.90	3.21	0.54	11.46	0.5
1,2-Dichlorobenzene	6.90	4.86	0.74	2.69	1.2
n-Butylbenzene	5.09	3.33	1.00	8.55	1.3
1,2-Dibromo-3-chloropropane	5.53	3.68	3.68	11.51	2.7
1,2,4-Trichlorobenzene	3.37	3.37	1.43	4.37	1.6
Naphthalene	8.35	5.36	0.88	10.44	2.0
Hexachlorobutadiene	5.22	2.63	0.77	3.75	2.0
1,2,3-Trichlorobenzene	3.83	4.56	1.27	5.18	1.0

Table 5 Internal standard data

Internal standard compounds	Dual-concentrator mode		Single-concentrator mode	
	% RSD	% Drift	% RSD	% Drift
Pentafluorobenzene	3.24	6.7	2.18	5.1
1,4-Difluorobenzene	2.16	8.4	1.73	9.8
Chlorobenzene-d5	2.42	7.2	1.83	6.5
1,4-Dichlorobenzene-d4	3.78	3.6	3.44	2.3
No. of analyses over a 12-hr period	52		36	

Table 6 Average response factors (RF) for U.S. EPA Method 8260B System Performance Check Compounds and the four latest-eluting compounds

Target compound	Minimum RF requirement	Avg RF, 0.5-min desorb	Avg RF, 4-min desorb
Chloromethane	0.1	1.242	0.667
1,1-Dichloroethane	0.1	1.238	1.171
Chlorobenzene	0.3	1.034	1.067
Bromoform	0.1	0.215	0.228
1,1,2,2-Tetrachlorethane	0.3	1.101	1.07
1,2,4-Trichlorobenzene	NA*	0.724	0.801
Naphthalene	NA	2.603	2.809
Hexachlorobutadiene	NA	0.340	0.376
1,2,3-Trichlorobenzene	NA	0.801	0.841

*Not applicable.

Table 10 Purge-and-trap conditions (single concentrator)

Purge-and-trap parameter	Encon
Trap	Vocarb 3000, Type K
Sample size	5 mL
Purge temp	Ambient
Purge rate	40 mL/min, 3 psi TPC
Purge time	11 min
Dry purge time	0.5 min
Dry purge temp	Ambient
Dry purge flow	40 mL/min
Desorb preheat	255 °C
Desorb temp	260 °C
Desorb time	0.5 min
Moisture reduction trap (on purge side)	Purge -40 °C, bake -260 °C
Line temp and valve temp	130 °C
Bake temp	270 °C
Bake time	4 min
Bake flow	120 mL/min through trap, 40 mL/min isolated from trap-flushing the glassware
Autosampler	Centurion
Sample process time	30 sec
Hot water rinse cycles	3 cycles in 90 sec
No. of runs/12 hr	36 runs (GC injection every 19–20 min)

Table 7 Rate-determining steps (single-concentrator mode)

Process time, <0.5 min	Purge and dry purge times, 11 min + 0.5 min	Desorb, bake, and cool-down times, 0.5 +4 min + 2 min	GC cycle time
		19 min	14 min

Table 8 Amount of analyte remaining on the concentrator after a 200-µg/L VOC standard

Compound	Bake (8 min)	Bake (6 min)	Bake (4 min)	Bake (2 min)
1,2,4-Trichlorobenzene	0.13%	0.23%	0.18%	0.19%
Naphthalene	0.11%	0.22%	0.21%	0.32%
Hexachlorobutadiene	0.03%	0.11%	0.15%	0.71%
1,2,3-Trichlorobenzene	0.10%	0.17%	0.15%	0.32%

Table 9 Amount remaining on the trap (step to desorb) and amount remaining in the entire system (water purge) determined after a 200-µg/L standard

Compound	Determination	Bake (8 min), 120 mL/min	Bake (4 min), 400 mL/min	Bake (4 min), 40 mL/min	Bake (4 min), 120 mL/min
1,2,4-Trichlorobenzene	Step to desorb	0.11%	0.11%	0.16%	0.21%
	Water purge	0.44%	0.42%	0.53%	0.44%
Naphthalene	Step to desorb	0.11%	0.22%	0.17%	0.20%
	Water purge	0.32%	0.28%	0.43%	0.33%
Hexachlorobutadiene	Step to desorb	0.11%	0.22%	0.25%	0.16%
	Water purge	0.49%	0.51%	0.58%	0.53%
1,2,3-Trichlorobenzene	Step to desorb	0.12%	0.31%	0.22%	0.25%
	Water purge	0.45%	0.41%	0.55%	0.50%

concentrator configuration for U.S. EPA 8260B analysis with the equipment and parameters outlined in this paper, the limiting factor is still the overall purge-and-trap cycle time. It is possible to analyze 36 analytical runs in a 12-hr tune period, resulting in 26,000 analyses per year. Although this is an improvement to sample throughput, the improvements made to GC cycle time's still cannot be fully realized.

Using the dual purge-and-trap concentrator configuration for U.S. EPA 8260B analysis with the equipment and parameters outlined above, the limiting factor truly becomes the GC cycle time. It is possible to analyze 52 analytical runs in a 12-hr tune period, resulting in 38,000 analyses per year, a 31% increase in throughput over the single-concentrator option. The difference in sample throughput comparing both options results in 12,000 additional analyses per year using the dual-concentrator configuration.

From the data presented, the dual-concentrator configuration provides the greatest improvement in sample throughput. It takes advantage of the improvements made to GC cycle times while still allowing the traditional, recommended purge-and-trap parameters to be used. In contrast, the single-concentrator configurations require compromises in purge-and-trap conditions and are limited to the overall cycle time of the autosampler.

Mr. Sheriff is Purge-and-Trap Product Manager, EST Analytical, 503 Commercial Dr., Fairfield, OH 45014, U.S.A.; tel.: 513-642-0100, 800-283-3510; fax: 513-642-0106; e-mail: jsheriff@estanalytical.com.