Evaluation of Single vs. Dual Concentrator High Throughput VOC Systems

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Keywords

EPA Method 8260B, PY2, Appendix IX, EST Analytical, ENCON, Volatile Organic Compound, Purge and Trap, Environmental, Concentrator, Foam Sensor

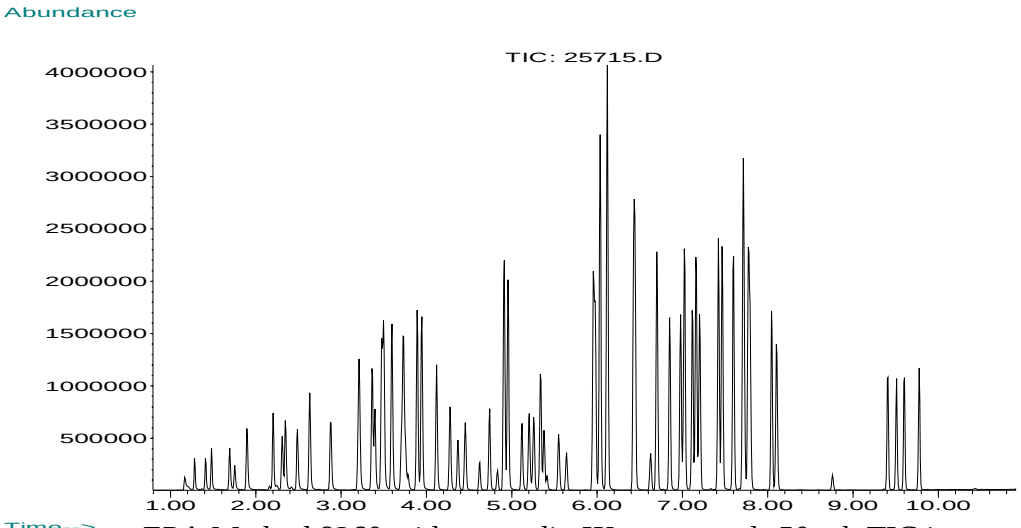
ABSTRACT

There are several demands and requirements imposed on chemists performing Volatile Organic Analysis in today's Environmental Laboratory. The first and most important is that the analysis must be performed in compliance with USEPA methodologies. Next, there is a continued trend to achieve lower levels of detection. How can the VOC chemist improve sample throughput without sacrificing data quality, meet the required level of detection and still remain compliant to the EPA method?

One limitation to improving sample throughput in Volatile Organic Analysis with a single Purge and Trap system has historically been the speed in which a syringe driven autosampler could process the sample and rinse the glassware in preparation for the next sample. As a result of this limitation the Purge and Trap Bake times were in excessive of 8 minutes to accommodate the autosampler's rinse cycle.
This paper will compare and evaluate two options to improve sample throughput up to 100% using a single fixed loop autosampler. All Quality Assurance data per US EPA methodologies using optimized methods will be presented.

INTRODUCTION

In the late 1990's, GC manufactures were able to shorten GC cycle times by improving oven heating rates and decreasing cool down time. Column manufacturers developed narrow-bore; shorter length columns which could reduce analytical run times without sacrificing resolution or sensitivity. Analyses that were once performed in 30 minutes could now been performed in under 10 minutes. (See Figure A). 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 taken advantage by chemists running Volatile applications due to the length of the Purge and Trap cycle time.



EPA Method 8260 with appendix IX compounds 50ppb TIC in under 10 minutes

To improve the sample throughput within the Volatile Organic laboratory the chemist has two options. The first option is to employ the use a second Purge and Trap concentrator to a single GC system and continue to use the traditional Purge and Trap parameters required or suggested by USEPA methodologies. The second option is to reduce the purge and trap cycle times by decreasing the Dry Purge, Desorb and Bake times. Both of these options will be evaluated and discussed.

DUAL CONCENTRATOR MODE

The first product commercially available to allow chemists to interface two Purge and Trap concentrators was the PT^2 which was introduced by EST Analytical in 1999. The PT^2 is a valve switching device which directs the sample purge gas flow from a single Water/Soil Autosampler to one of two concentrators. The device allows the customer 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 now 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 PT^2 only directs gaseous flow. Water samples had to be transferred to a 40ml vial before analysis. This configuration was a great improvement for Soil analysis; however the need to analyze water samples in a sparge tube on the front of the Purge and Trap concentrator led to the development of the Centurion water only autosampler.

CENTURION AUTOSAMPLER

The Centurion is a 100 position, fixed loop water only autosampler which 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 minutes or at the rate of the GC Cycle time, whichever is greater without the need to deviate from traditional purge and trap parameters. The rate-determining step for water sample throughput is now 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)
3. The GC cycle time. (Total time from GC start to GC ready)

See Figure B. illustrating the GC cycle time of 14 minutes as the limiting factor in sample throughput in a Dual Mode configuration.

Process Time < 0.5 min	Purge and Dry Purge Times 11 min + 2 min	Desorb, Bake and Cool Down times 4 min + 8 min + 2 min	GC Cycle Time
13.5 min		12 min	14 min

Figure B. Rate Determining steps (Dual Concentrator Mode)

EXPERIMENTAL

To demonstrate the ability of the dual concentrator option to improve VOC sample throughput, two EST Encon concentrators 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 Encons. Utilizing the Purge and Trap conditions outlined in Table 1 and the GC/MS conditions outlined in Table 2, a seven point calibration curve ranging from 1ug/L to 100ug/L consisting of 68 compounds from the 8260B list of analytes was analyzed. A batch of 52 samples including 4 "Initial Demonstration of Accuracy and Precision Check Standards" was scheduled to be run over a 12-hour period. The Encons alternated injecting samples into the GC at a rate of 1 sample every **14** minutes. 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-hour "tune" period are listed in Tables 4-6.

P&T Parameter	EST Encon
Trap	**Vocarb 3000** Type "K" **Carbopack B, Carboxen 1000**
Sample Size	5 ml
Purge Temp	Ambient
Purge Rate	40 ml/min 3 psi TPC
Purge Time	**11 minutes**
Dry Purge Time	**2 minutes**
Dry Purge Temp	**Ambient**
Dry Purge Flow	**40 ml/min**
Desorb Preheat	255^0 C
Desorb Temp	260^0 C
Desorb Time	**2 minutes**
Moisture Reduction Trap (On purge Side)	**Purge - 40^0 C** **Bake - 260^0 C**
Line Temp	130^0 C
Valve Temp	130^0 C
Bake Temp	270^0 C
Bake Time	**8 minutes**
Bake Flow	**120 ml/min** **Trap Bake flow separate from glassware flow**
Autosampler	**EST Centurion**
Sample Process Time	**30 seconds**
Hot Water Rinse Cycles	**3 cycles in 90 seconds**
# of Runs / 12 hours	**52 runs (GC Injection every 14 minutes)**

Table 1. Purge and Trap Conditions (Dual Mode)

GC/MSD Parameter	Agilent 68905973
Inlet	EPC S/SS
Mode	Split
Inlet Temp	180^0 C
Split Ratio	**50:1**
Split Flow	**38.0 ml/min**
Oven Temp Program	
Initial Temp	50 degrees C
Initial Time	1.00 minutes
Ramp Rate A	18.0 degrees C/min
Final Temp A	190 degrees C
Ramp Rate B	25^0C/min
Final Temp B	**220^0C**
Column	**DB-624 20 meter X 0.18 mm ID 1.00 µm df**
Column Flow	0.6 ml/min
Linear Velocity	33 cm/sec
Mode	Constant Flow

Table 2. GC/MS Conditions

SINGLE CONCENTRATOR MODE

The second option 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 seconds or less for 5ml volumes and 60 seconds or less for 25ml volumes the concentrator bake cycle was no longer necessary to be in excess of 8 minutes. 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, which ever is greater.
See Figure C. illustrating the total Purge and Trap cycle time as the limiting factor in sample throughput in a single concentrator configuration.

Process Time < 0.5 min	Purge and Dry Purge Times 11 min + 0.5 min	Desorb, Bake and Cool Down times 0.5 min + 4 min + 2 min	GC Cycle Time
19 minutes			14 min

Figure C. Rate Determining steps (Single Concentrator Mode)

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 200ug/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 excluding the glassware. Using the standard Encon bake flow of 120 ml/min bake cycles comprised of 8 minutes, 6 minutes, 4 minutes and 2 minutes were evaluated. The results listed in Table 7 indicate that there is little difference in the resulting "carryover" until the 2 minute bake cycle.

Compound	8 min Bake	6 min Bake	4 min Bake	2 min Bake
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 7. Amount remaining on the Concentrator after a 200 ppb soil standard (Excluding Glassware)

To further evaluate the bake out cycle, flow rates of 400 ml/min, 120 ml/min and 40 ml/min were used to bake the system after a 200ug/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 was purged in the glassware to determine the amount of analyte remaining in the entire system. The results listed in Table 8 indicate no discernible improvement in the resulting "carryover" regardless of the flow rate. The differences seen were well within the margin of error.

Compound	Determination	8 min Bake 120 ml/min	4 min Bake 400 ml/min	4 min Bake 40 ml/min	4 min Bake 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 %

Table. 8 Amount remaining on the trap (Step to Desorb) and the amount remaining in the entire system (Water Purge) determined after the analysis after a 200 ppb standard.

P&T Parameter	EST Encon
Trap	**Vocarb 3000** Type "K" Carbopack B Carboxen 1000
Sample Size	5 ml
Purge Temp	Ambient
Purge Rate	40 ml/min 3 psi TPC
Purge Time	**11 minutes**
Dry Purge Time	**0.5 minutes**
Dry Purge Temp	**Ambient**
Dry Purge Flow	**40 ml/min**
Desorb Preheat	255^0 C
Desorb Temp	260^0 C
Desorb Time	**0.5 minutes**
Moisture Reduction Trap (On purge Side)	**Purge - 40^0 C** **Bake - 260^0 C**
Line Temp and Valve Temp	130^0 C
Bake Temp	270^0 C
Bake Time	**4 minutes**
Bake Flow	**120 ml/min through trap** **40 ml/min isolated from trap flushing the glassware**
Autosampler	**EST Centurion**
Sample Process Time	**30 seconds**
Hot Water Rinse Cycles	**3 cycles in 90 seconds**
# of Runs / 12 hours	**36 runs (GC injection every 19-20 minutes)**

Table 3. Purge and Trap Conditions (Single Concentrator)

To demonstrate the ability of the single concentrator option to improve VOC sample throughput using reduced Desorb and Bake times, the Centurion autosampler was interfaced to one EST Encon concentrator which is configured to a single GC/MS. Utilizing the Conditions outlined in Tables 2 and 3 and the Encon's standard bake flow of 120ml/min, a seven point calibration curve ranging from 1ug/L to 100ug/L consisting of 68 compounds from the 8260B list of analytes was analyzed. A batch of 36 samples including 4 "Initial Demonstration of Accuracy and Precision Check Standards" was scheduled to be run over a 12-hour period. The Encon injected samples into the GC at a rate of 1 sample every 19 – 20 minutes. 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-hour "tune" period are listed in Tables 4-6.

Internal Standard Compounds	Dual Concentrator Mode		Single Concentrator Mode	
	% RSD	% Drift	% RSD	% Drift
Pentafluorobenzene			2.18	5.1
1,4- Difluorobenzene			1.73	9.8
Chlorobenzene-d5			1.83	6.5
1,4- Dichlorobenzene-d4			3.44	2.3
# of Analyses over a 12 hour period	52		36	

Table 5. Internal Standard Data

Target Compound	Minimum RF Requirement	AVG RF 0.5 min.Desorb	AVG RF 2 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

Table 6. Avg Response Factors for USEPA method 8260B System Performance Check Compounds and the 4 latest eluting compounds.

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 concentrator configuration for USEPA 8260B analysis utilizing the equipment and parameters outlined in this paper the limiting factor is still the overall Purge and Trap cycle time. 36 analytical runs are possible to be analyzed in a 12-hour "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 are still not able to be fully realized.

Using the dual Purge and Trap concentrator configuration for USEPA 8260B analysis utilizing the equipment and parameters outlined in the paper the limiting factor now truly becomes the GC cycle time. 52 analytical runs are possible to be analyzed in a 12-hour "tune" period resulting in 38000 analyses per year, a 31% increase in throughput over the single concentrator option. The difference in sample throughput comparing both options discussed results in 12,000 additional analyses per year using the dual concentrator configuration.

From the data presented, the Dual concentrator configuration gives the greatest improvement in sample throughput fully realizing the improvements made to GC cycle times and still allows for the traditional Purge and Trap parameters to be used while the single concentrator configurations require compromises in purge and trap conditions and is limited to the overall cycle time of the autosampler!