EST analytical

Maximizing Sample Throughput In Purge And Trap Analysis

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INTRODUCTION

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 EPA methodologies. Next, there is the continued demand to improve productivity. The key to productivity is to analyze as many samples as possible which meet the required quality assurance criteria in the 12 hours after a successful BFB tune check. The need to re-run samples due to moisture interference and carry-over certainly limits productivity. However, the most limiting factor of all is the length of the purge and trap cycle time. This paper will present the optimum purge and trap system conditions used to overcome these productivity limitations. Analytical results including calibration, accuracy and precision data will be presented for both water and soil matrices.

DISCUSSION

PURGE AND TRAP CYCLE TIME

As previously mentioned the most limiting factor to improving sample throughput is the length of the purge and trap cycle time. The typical purge and desorb parameters recommended or required by EPA methodologies are 12 to 15 minutes. In addition, a bake-out cycle is commonly used to clean the system before the next sample is analyzed, thus making the complete purge-and-trap cycle time nearly 25 minutes. Injections can only be made in 25 minute intervals which equal 28 injections per 12 hours. It is now common for GC cycle times to be as fast as 15 minutes when performing VOC analysis. How can the analyst take advantage of fast GC conditions to boost production without changing the required conditions governed by the EPA and without sacrificing data quality? The answer is to employ the use of a second purge and trap concentrator to the same GC/MSD system and continue to use the traditional conditions required by EPA methods.

The **EST Centurion WS Autosampler** incorporates a mode referred to as the **Dual Concentrator Option** which easily connects two concentrators to the same GC and the same autosampler. This configuration allows the concentrator to alternate injections to the GC. As the first concentrator begins desorbing a sample, the Centurion WS sends the next sample to the second concentrator to begin purging. The rate-determining step for maximum sample throughput is now one of three factors.

1. The total timed needed for the auto-sampler 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 pre-heat to purge-ready).
3. The total GC cycle time (total time from GC start to GC-ready).

In addition to the unique dual mode capabilities, the Centurion WS dramatically reduces the sample process and rinse time due to the absence of a syringe mechanism. The Centurion WS uses only pressure and gas flow to transfer samples and rinse water by using a pre-measured sample loop.

Table 1 illustrates the GC cycle time of 15 minutes as the limiting factor in sample throughput in the dual concentrator configuration.

Table 1. Rate-Determining Steps

PROCESS TIME <0.5 min	PURGE AND DRY PURGE TIMES 11 min + 1 min	DESORB, BAKE AND COOL DOWN TIMES 1 min + 8 min + 2 min	GC CYCLE TIME
12.5 min		11 min	**15 min**

MOISTURE INTERFERENCE

As part of the purging process, water vapor is carried along with the purge gas. It is well known that moisture can cause interferences in the GC/MS chromatogram causing elevated detection levels and poor vacuum readings which lead to inconsistent analytical results. This interference can cause sample re-runs and greatly reduce the lab's productivity. The management of this moisture prior to GC introduction is crucial to maximizing sample throughput.

The **EST Encon Evolution Purge and Trap Concentrator** utilizes a unique **Moisture Reduction Trap (MoRT)** to decrease the amount of moisture introduced to the GC. Unlike other concentrators the Evolution positions the moisture management device before the analytical trap to remove the water from the purge gas as illustrated in **Figure 1**. Through the use of an 8-port valve, the Evolution's MoRT is excluded from the desorb pathway during the transfer of analytes to the GC as illustrated in **Figure 2**.

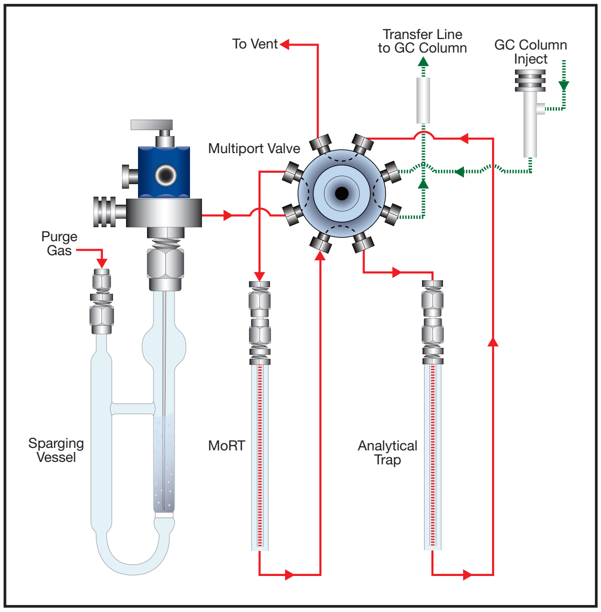

Figure 1. Purge Pathway

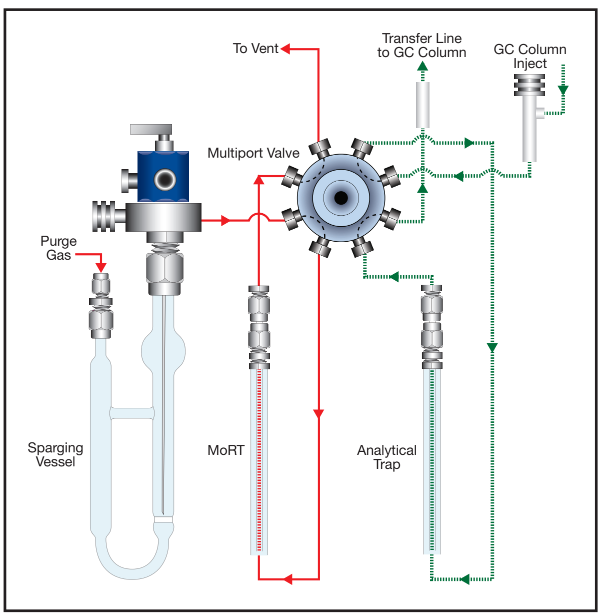

Figure 2. Desorb Pathway

By positioning the water management device before the trap, "dead volume" and "cold spots" are eliminated from the desorb pathway to deliver superb peak symmetry and sensitivity over the entire chromatogram as shown in **Figure 3**.

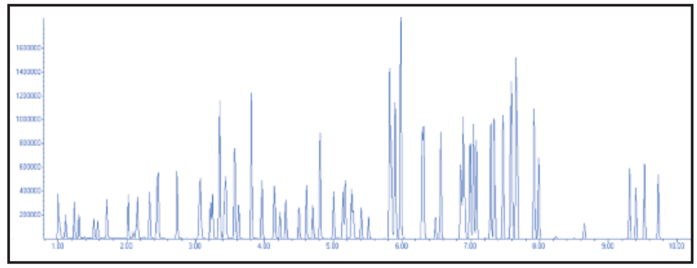

Figure 3. Total Ion Chromatogram of the 10 ppb VOC standard

CARRY-OVER REDUCTION

As detection limits are pushed lower, carryover from check standards and contaminated samples has caused more frequent re-runs of samples. In the past, efforts have been made to reduce carryover with inert sample pathways and programmable flow rates during the bake cycle. Little has been done to deal with the primary cause of the carryover… the sparge vessel itself. The Encon Evolution employs a patented mode which heats the sparge vessel during the rinsing process as shown in **Figure 4**. This takes place during the normal Evolution bake cycle therefore no additional time is added to the overall cycle time. The result is the lowest level of carry-over of any concentrator available today. The bake-out of the glassware delivers superior analytical results and reduces, if not eliminates completely, the number of blanks needed after high standards and contaminated samples.

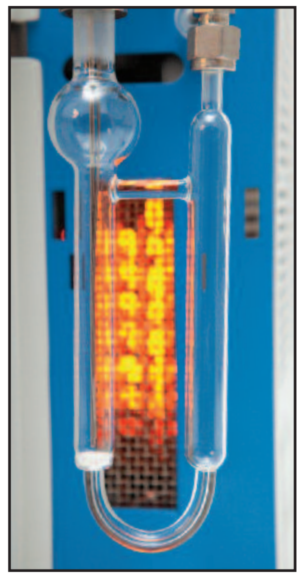

Figure 4. Sparge Tube Carry-Over Reduction System

EXPERIMENTAL RESULTS

A single EST Centurion WS autosampler and two EST Encon Evolution purge and trap concentrators were interfaced to a single GC/MSD to demonstrate the ability of the Dual Mode option to provide quality data with maximum sample throughput. The system conditions used to obtain the results are listed in **Tables 2** and **3**. The linear range of the system was first established by analyzing a nine-point calibration curve (1ppb-200ppb) for both water and soil samples in accordance to the procedure in EPA method 8260B. The concentration of the internal standards was constant at 50ppb in all analyses. The percent relative standard deviation (%RSD) of the initial calibration (ICAL), the mean percent recovery of ten 1ppb measurements and the percent relative standard deviation of ten 1ppb measurements for each concentrator and matrix are shown in **Table 4**.

Table 2. Purge and Trap Conditions

PURGE & TRAP CONCENTRATOR	EST ENCON EVOLUTION
Trap Type	EV1 – Proprietary
Valve Oven	130 °C
Transfer Line	130 °C
Moisture Reduction Trap (MoRT) Temp	39 °C
Purge Time	11 minutes
Purge Flow	40 ml/min
Purge Gas	Helium
Dry Purge	Ambient 1 minute
Dry Purge Flow	40 ml/min
Desorption Pressure	12 psi
Desorb	260 °C for 2 minutes
Bake Temperature	265 °C for 8 minutes
Bake Flow	120 ml/min
Sparge Heater Carry-Over Reduction System	Purge – Ambient Bake – 110 °C
PURGE & TRAP AUTOSAMPLER	**EST CENTURION W/S**
Water Sample Size	5 ml
Soil Sample Size	5 grams/10 ml H20
Internal Standard Volume	5 ul
Minimizer Carry-Over Reduction Time	2 minutes

Table 3. GC/MSD Conditions

GC/MS	AGILENT 7890/5975*
Inlet	EPC S/SS
Inlet Head-Pressure	17.3 psi
Inlet Temperature	200 °C
Mode	Split
Split Ratio	40:1
Total Flow	38.8 ml/min
Column	RTX-624**
	20 m X 0.18mm I.D.
	1.0 µm Film Thickness
Oven Temp. Program	45 °C for 1 minute
	45 °C - 220 °C at 18 °C/min
	220 °C for 0.5 minute
Column Flow Rate	0.8 ml/min
Mode	Constant Flow

**Agilent Technologies (Wilmington, DE)*
***Restek Corporation (Bellefonte, PA)*

Table 4. Quality Assurance Data

TARGET COMPOUND	ICAL %RSD 1ppb-200ppb Water Matrix	Accuracy at 1ppb Water Matrix (%Recovery) n=10	Precision at 1ppb Water Matrix (%RSD) n=10	ICAL %RSD 1ppb-200ppb Soil Matrix	ICAL %RSD 1ppb-200ppb Water Matrix	Accuracy at 1ppb Water Matrix (%Recovery) n=10	Precision at 1ppb Water Matrix (%RSD) n = 10	ICAL %RSD 1ppb-200ppb Soil Matrix
	CONCENTRATOR #1				CONCENTRATOR #2			
Dichlorodifluoromethane	11.8	81.0	11.7	11.8	13.1	80.6	7.1	10.9
Chloromethane	12.3	105.1	8.6	13.1	14.1	99.8	4.4	10.6
Vinyl Chloride	6.5	95.6	7.9	11.3	9.3	90.4	9.6	5.2
Bromomethane	11.6	118.4	3.9	13.4	5.8	106.4	4.8	12.9
Chloroethane	10.7	96.6	4.0	11.0	7.2	96.4	6.1	10.2
Trichlorofluoromethane	3.7	89.8	5.4	11.2	4.5	93.9	4.4	6.5
1,1-Dichloroethene	4.9	98.0	5.6	9.0	6.3	99.1	6.7	8.8
Acetone*	0.999	92.3	5.9	0.997	0.997	114.8	7.3	0.998
Carbon disulfide	4.4	103.8	5.0	11.3	5.3	109.4	5.1	10.2
Methylene Chloride	4.0	103.0	5.0	10.5	3.7	109.5	7.8	11.5
MTBE	3.9	95.4	5.4	9.3	4.4	98.5	4.2	6.3
trans-1,2-Dichloroethene	3.5	98.9	7.0	10.9	7.5	109.9	7.0	11.0
1,1-Dichloroethane	4.7	98.0	4.6	8.4	3.9	101.1	5.9	5.5
cis-1,2-Dichloroethene	3.3	100.6	3.8	8.1	5.5	103.9	8.3	5.6
2-Butanone	6.5	105.1	9.0	14.8	5.5	104.3	6.6	13.5
2,2-Dichloropropane	3.6	81.8	5.1	8.5	8.4	86.8	6.2	9.7
Bromochloromethane	5.4	105.4	6.7	9.5	4.9	107.4	6.0	7.7
Chloroform	6.3	100.0	6.2	7.8	4.1	101.0	3.6	6.3
1,1,1-Trichloroethane	3.1	102.8	8.7	8.6	4.7	103.6	7.1	10.5
2-Chloroethylvinylether	7.5	96.8	8.0	11.1	9.3	99.8	4.9	7.8
Carbon Tetrachloride	2.7	89.8	7.0	10.0	5.0	96.8	4.7	4.7
1,1-Dichloropropene	5.0	91.1	5.6	11.3	4.2	100.0	7.0	8.0
Benzene	2.6	99.5	4.2	9.3	3.6	103.6	1.9	5.8
1,2-Dichloroethane	4.4	99.0	4.1	10.3	4.6	104.3	3.0	9.3
Trichloroethene	4.4	99.0	7.3	8.3	6.2	104.5	4.4	5.2
1,2-Dichloropropane	5.8	101.8	6.9	7.5	4.6	103.1	4.9	6.5
Dibromomethane	3.7	93.0	6.4	7.7	9.7	102.9	5.3	10.2
Bromodichloromethane	6.0	98.6	6.4	7.7	3.4	98.5	4.0	7.3
cis-1,3-Dichloropropene	4.5	89.9	6.8	11.0	4.5	97.0	7.5	7.6
Toluene	4.5	96.5	4.5	9.9	4.8	100.0	7.3	10.1
trans-1,3-Dichloropropene	6.0	93.0	8.8	7.5	4.5	95.3	7.5	6.2
1,1,2-Trichloroethane	3.2	101.3	7.9	8.7	4.5	104.4	5.8	10.8
Tetrachloroethene	1.9	98.0	5.5	8.6	5.9	94.4	4.8	8.3
1,3-Dichloropropane	4.1	99.5	4.5	12.7	4.2	101.6	3.2	8.0
Dibromochloromethane	3.7	91.5	5.0	6.7	6.3	92.3	5.7	8.5
2-Hexanone	7.6	85.9	7.0	10.1	7.7	91.3	5.7	9.8
1,2-Dibromoethane	5.2	100.3	6.1	12.2	4.8	97.7	7.7	6.8
Chlorobenzene	3.1	99.8	4.1	7.6	5.2	104.9	6.5	5.0
1,1,1,2-Tetrachloroethane	6.4	91.4	5.6	11.1	4.7	96.1	6.3	6.4
Ethylbenzene	4.4	96.3	5.6	7.1	3.6	96.3	4.8	5.3
Xylene (M&P)	3.9	94.9	5.4	6.2	3.5	94.3	3.9	4.6
Styrene	6.3	92.3	4.0	5.6	5.0	95.1	6.9	5.1
Xylene (o)	4.9	95.1	4.1	6.5	4.8	93.9	3.8	6.3
Bromoform	11.5	90.5	5.4	10.9	9.1	89.1	6.9	7.8
Isopropylbenzene	5.4	91.9	5.2	8.1	4.2	91.5	4.7	7.3
Bromobenzene	3.5	101.6	5.9	5.1	5.7	102.9	5.4	6.6
1,2,3-Trichloropropane	3.6	92.5	7.4	11.5	4.6	97.8	8.0	6.9
1,1,2,2-Tetrachloroethane	3.2	101.0	6.7	11.3	4.3	98.1	5.9	13.7
n-Propylbenzene	4.9	94.5	5.0	5.8	3.9	94.4	4.7	4.3
2-Chlorotoluene	6.1	102.1	6.3	7.1	4.4	97.6	5.6	4.4
4-Chlorotoluene	3.7	98.3	7.0	5.8	5.0	102.0	4.3	3.5
1,3,5-Trimethylbenzene	5.4	89.5	5.1	5.0	4.7	90.4	4.3	6.6
tert-Butylbenzene	2.9	91.8	7.1	6.9	3.4	92.4	5.5	5.2
sec-Butylbenzene	5.6	100.3	7.0	6.1	3.2	96.4	9.5	6.8
1,2,4-Trimethylbenzene	5.5	92.1	3.3	5.4	2.6	94.6	5.8	6.1
1,3-Dichlorobenzene	3.0	100.6	6.4	5.6	3.9	103.3	5.4	6.7
1,4-Dichlorobenzene	2.6	101.8	3.7	5.4	8.4	105.5	4.7	5.7
Isopropyltoluene	7.7	90.8	5.6	6.4	3.4	88.5	5.6	7.2
1,2,-Dichlorobenzene	2.6	103.1	4.7	5.7	4.8	102.1	5.0	5.5
n-Butylbenzene	6.3	89.6	6.4	4.9	5.2	95.1	3.9	7.2
1,2-Dibromo-3-chloropropane	10.1	91.6	7.5	8.3	3.8	93.9	9.8	11.9
1,2,4-Trichlorobenzene"	5.8	100.4	5.1	5.4	3.8	96.5	4.9	9.4
Naphthalene	11.5	87.0	4.7	5.8	4.3	93.3	6.6	7.1
Hexachlorobutadiene	7.8	87.9	9.6	7.5	5.8	95.8	4.7	6.2
1,2,3-Trichlorobenzene	7.1	95.3	4.8	7.1	4.7	101.4	7.2	9.2

**Compound was linear regressed*

CONCLUSION

From the data presented the instrument configuration and operating conditions described above produce outstanding performance for EPA Method 8260B. In addition to the improved quality of the data, the configuration also maximizes sample throughput by an additional 40 injections per day over conventional configurations by enabling analysts to be able to inject sample every 15 minutes!

This translates to an improvement of an additional 34 revenue generating samples each day per instrument. The Centurion WS and Encon Evolution also offer a number of other unique user features and benefits. These include a programmable internal standard delivery mechanism and a sampling routine which only transports soil vials.

Centurion WS Autosampler

Encon Evolution