

INTRODUCTION

The EPA Office of Ground Water and Drinking Water set out to create a new volatile organic compound (VOC) method for drinking water which provided more flexibility than previously offered. The new method was promulgated in June 2009 as 524.3, "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry." The purpose of this paper is to discuss the significant changes and improvements of the method and to present optimized system conditions necessary to ensure results meeting data quality objectives for compliance monitoring. Analytical results including calibration, accuracy, and precision data will be presented for both reagent grade water and tap water.

DISCUSSION

SYSTEM OPERATING PARAMETERS

In recognition of the technological advancements in analytical instrumentation and techniques, method 524.3 permits modifications to be made to the purge-and-trap parameters. However, five key parameters are restricted to prescribed ranges. These ranges are listed in **Table 1**. The values for these five key parameters must never exceed the "allowable" range, and the sample size cannot be varied from the 5mL volume prescribed in the method.

Table 1. Purge-and-Trap Prescribed Ranges

PARAMETER	RECOMMENDED		ALLOWABLE	
	Minimum	Maximum	Minimum	Maximum
Sample Temperature	Ambient	40 °C	Ambient	60 °C
Purge Flow Rate	40 mL/min	80 mL/min	20 mL/min	200 mL/min
Purge Volume	360mL	520mL	240mL	680mL
Desorb Time	1 min	2min	0.5 min	4 min
Purge Volume + Dry Purge Volume	360mL	720mL	240mL	880mL

Encon Evolution



Centurion WS Autosampler



A noteworthy modification is the recommendation of utilizing a desorb time in the range of 1-2 minutes. Previous methods required a 4-minute desorb time. A shorter desorb time helps to minimize the amount of water which is transferred from the trap to the GC. However, purge-and trap systems which use water management systems during desorb will see a corresponding decrease in the efficiency of these moisture control traps with the reduced desorb time. The EST Encon Evolution utilizes a unique **Moisture Reduction Trap (MoRT)** to decrease the amount of moisture introduced to the GC. Unlike other concentrators, the moisture management device is positioned before the analytical trap to remove the water during the purge cycle

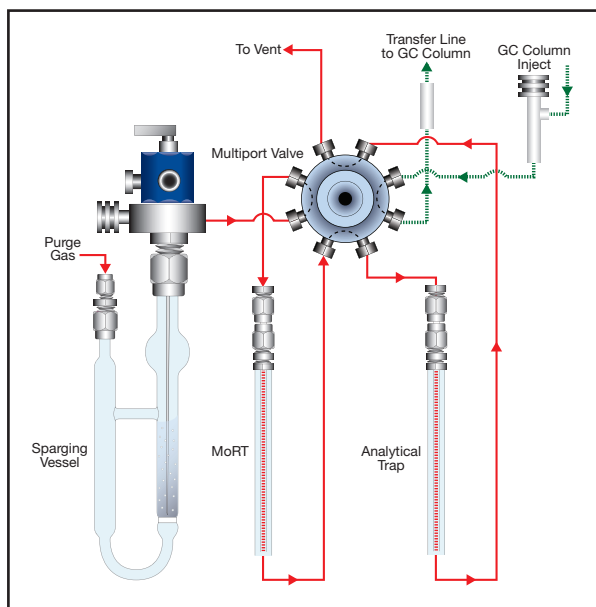


Figure 1. Purge Pathway

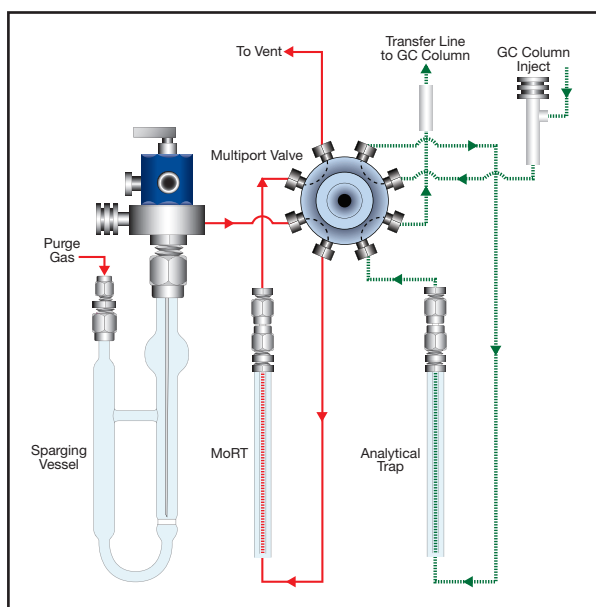


Figure 2. Desorb Pathway

as illustrated in **Figure 1**. The Evolution is able to manage the water during the entire purge cycle rather than the shortened desorb cycle. 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**.

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**.

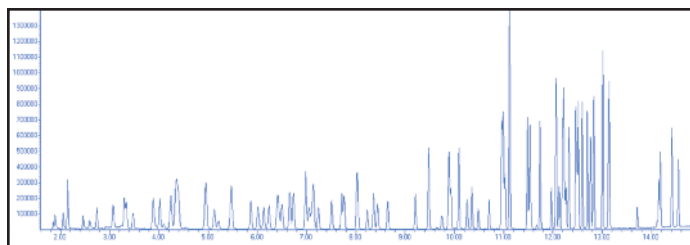


Figure 3. Total Ion Chromatogram of the 10 ppb VOC standard

QUALITY CONTROL (QC REQUIREMENTS)

Method 524.3 contains two significant differences regarding the QC requirements. The first is the system must be checked for carryover by analyzing a Laboratory Reagent Blank (LRB) immediately following the highest calibration standard. The resulting carryover must be less than 1/2 the lowest calibration standard. If this criterion is not met, then carryover is present, and the cause must be identified and eliminated. A number of features to minimize carryover have been developed which include accelerated flow rates during the bake cycle, hot water rinses, and the use of inert sample pathways.

However, very little has been done to deal with the primary cause of the carryover... the sparging vessel itself. The Encon Evolution employs a patented mode which heats the sparging vessel during the rinsing process as shown in **Figure 4**. Carryover is now virtually eliminated!

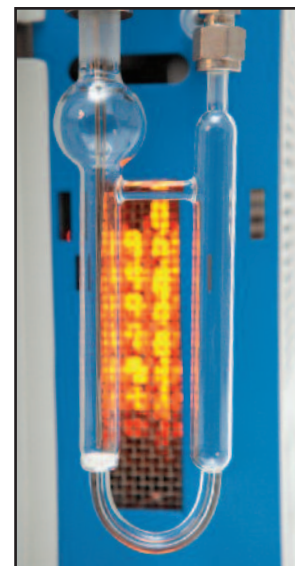


Figure 4. Sparge Tube Carry-Over Reduction System



Figure 5.
Foam Sensor

The second significant difference regarding the QC requirements is the manner in which the calibration curve is evaluated and validated. The method requires a procedural calibration, in which the calibration standards are processed through the entire method including the addition of preservatives. The new preservation technique uses ascorbic acid and maleic acid instead of hydrochloric acid. Although this new preservation scheme is not

as hazardous, it poses a new problem of mild to moderate foaming depending on the purge flow rate. Due to this foaming phenomenon, instruments with foam sensors placed in the bulb of the sparging vessel will be prone to false foaming detection, thereby stopping the sequence. The Encon Evolution eliminates this problem by positioning the foam sensing device in the neck of the sparging vessel allowing the bulb to break the effervescent bubbles as shown in **Figure 5**.

The method requires the curve to be validated by fitting the calibration points with either a linear or a quadratic regression. The concentrations of the analytes for each of the calibration points are calculated by use of the regression equations. The lowest standard must calculate to be within $\pm 50\%$ of the true value. All other calibration points must calculate to be within $\pm 30\%$ of their true value.

EXPERIMENTAL RESULTS

To determine the optimal purge-and-trap conditions an EST Centurion Autosampler and EST Encon Evolution purge-and-trap concentrator were interfaced to a GC/MS.

The system conditions which were identified to provide superior performance are listed in **Tables 2** and **3**.

Table 2. Purge and Trap Conditions

PURGE & TRAP CONCENTRATOR	EST ENCON EVOLUTION
Trap Type	EV1 - Proprietary
Valve Oven	120 °C
Transfer Line	120 °C
Moisture Reduction Trap (MoRT) Temp	39 °C
Purge Time	7 minutes
Purge Volume	385 mL
Purge Flow	55 mL/min
Purge Gas	Helium
Dry Purge	Ambient 1 minute
Dry Purge Flow	40 mL/min
Purge Volume + Dry Purge Volume	425 mL
Desorption Pressure	4 psi
Desorb	255 °C for 1 minute
Bake Temperature	265 °C for 6 minutes
Bake Flow	120 mL/min
Spurge Heater Carry- Over Reduction System	Purge – 40 °C: Bake – 110 °C
PURGE & TRAP AUTOSAMPLER	EST CENTURION
Water Sample Size	5 ml
Internal Standard Volume	5 ul

Table 3. GC/MS Conditions

GC/MS	AGILENT 7890/5975*
Inlet	EPC S/SS
Inlet Head-Pressure	6.62 psi
Inlet Temperature	200 °C
Mode	Split
Split Ratio	30:1
Total Flow	38.8 ml/min
Column	RTX-VMS** 30 m X 0.25mm I.D. 1.4 µm Film Thickness
Oven Temp. Program	45 °C for 4.5 minutes 45 °C - 100 °C at 12 °C/min 100 °C - 230 °C at 25 °C/min 230 °C for 1.32 minutes
Column Flow Rate	0.9 mL/min
Mode	Constant Flow

*Agilent Technologies (Wilmington, DE)

**Restek Corporation (Bellefonte, PA)

After establishing the optimal conditions, the linear range of the system was established by analyzing a seven-point calibration curve (0.5ppb-40ppb). The concentration of the three internal standards and surrogate compounds were constant at 5ppb in all analyses. The quadratic regression values and % recovery of seven calibration points are listed in **Table 4** (page 5). Since the surrogate analytes are added at a single concentration level to each calibration standard, average response factors were used and reported. Seven replicates each of reagent grade water and tap water were fortified at concentrations of 1 ppb and 10 ppb. These replicates were calculated against the curve. The precision and accuracy results for each compound at each level for both matrices were well below the required acceptance criteria of 20% RSD and $\pm 20\%$ average recovery, as shown in **Table 5** (page 6).

CONCLUSION

While the new method purge-and-trap parameters allow analysts more freedom in the lab to optimize their analytical results, the changes in 524.3 also create more challenges. The use of operating conditions with the EST instruments described here not only produces outstanding data performance, but also helps analysts overcome these new challenges.

Table 4. Quality Assurance Data

TARGET COMPOUND	QUADRATIC REGRESSION VALUE	0.5ppb	1ppb	2ppb	5ppb	10ppb	20ppb	40ppb
dichlorodifluoromethane	1.000	110.0	105.0	110.5	102.2	101.9	99.0	100.1
chlorodifluoromethane	1.000	114.0	91.0	100.0	105.4	98.7	101.5	100.0
chloromethane	1.000	96.0	112.0	102.0	103.2	100.2	99.5	100.1
vinyl chloride	1.000	100.0	103.0	101.5	101.2	100.5	99.7	100.0
1,3-butadiene	1.000	114.0	102.0	104.0	102.0	99.6	99.9	100.0
bromomethane	1.000	112.0	111.0	104.0	93.2	102.6	100.2	100.0
trichlorofluoromethane	1.000	102.0	105.0	104.0	106.0	97.0	100.4	100.0
diethyl ether	1.000	110.0	101.0	102.0	98.6	101.4	99.6	100.0
1,1-dichloroethene	1.000	106.0	105.0	102.5	98.6	99.6	100.2	100.0
carbon disulfide	1.000	130.0	106.0	104.0	95.2	97.0	101.5	99.9
methyl iodide	1.000	86.0	85.0	94.0	96.8	99.5	100.7	99.9
allyl chloride	1.000	118.0	95.0	96.5	93.8	100.0	100.8	99.9
methylene chloride	1.000	104.0	92.0	96.5	92.4	104.6	99.2	100.1
trans-1,2-dichloroethene	1.000	96.0	106.0	98.0	104.0	102.6	98.7	100.1
methyl acetate	1.000	100.0	111.0	103.0	99.8	104.9	98.1	100.2
methyl-t-butyl ether-d3*	5.32 % RSD	94.2	98.8	93.2	98.6	102.8	107.2	105.4
methyl-t-butyl ether (MTBE)	1.000	92.0	99.0	95.5	103.8	104.2	98.2	100.2
t-butyl alcohol (TBA)	0.998	136.0	124.0	114.0	105.0	111.1	102.9	100.4
diisopropyl ether (DIPE)	1.000	94.0	95.0	96.0	99.2	102.1	99.4	100.1
1,1-dichloroethane	1.000	94.0	106.0	93.0	100.0	100.2	100.1	100.0
t-butyl ethyl ether (ETBE)	1.000	94.0	96.0	97.5	98.2	102.9	99.2	100.1
cis-1,2-dichloroethene	1.000	106.0	103.0	98.5	97.4	104.1	98.8	100.1
bromochloromethane	1.000	120.0	105.0	107.0	99.6	103.9	98.5	100.1
chloroform	1.000	92.0	97.0	99.5	98.0	101.9	99.6	100.0
carbon tetrachloride	1.000	102.0	105.0	100.5	99.0	96.9	101.2	99.9
tetrahydrofuran	1.000	110.0	96.0	100.0	102.8	98.2	100.3	100.0
1,1,1-trichloroethane	1.000	90.0	88.0	97.0	95.4	99.2	100.9	99.9
1,1-dichloropropene	1.000	98.0	105.0	98.0	102.6	98.1	100.5	100.0
1-chlorobutane	1.000	92.0	97.0	99.0	96.0	100.3	100.4	100.0
benzene	1.000	102.0	96.0	97.0	95.4	101.6	100.0	100.0
t-amyl methyl ether (TAME)	1.000	88.0	97.0	95.5	99.2	102.8	99.2	100.1
1,2-dichloroethane	1.000	100.0	94.0	91.5	102.6	104.7	98.2	100.2
trichloroethene	1.000	90.0	108.0	105.5	104.0	101.8	98.8	100.1
t-amyl ethyl ether (TAE)	1.000	96.0	99.0	93.0	97.8	101.9	99.7	100.0
dibromomethane	0.999	112.0	98.0	96.0	100.8	107.6	97.2	100.2
1,2-dichloropropane	1.000	96.0	98.0	100.5	100.0	103.4	98.7	100.1
bromodichloromethane	1.000	94.0	104.0	95.0	98.0	100.6	100.1	100.0
cis-1,3-dichloropropene	1.000	100.0	98.0	95.5	98.8	103.8	98.9	100.1
toluene	1.000	108.0	106.0	102.5	100.6	100.0	99.9	100.0
tetrachloroethene	1.000	94.0	99.0	100.0	98.6	96.9	101.3	99.9
trans-1,3-dichloropropene	1.000	86.0	99.0	102.5	98.2	101.4	99.7	100.0
ethyl methacrylate	1.000	108.0	89.0	97.5	97.8	101.0	100.0	100.0
1,1,2-trichloroethane	1.000	86.0	104.0	99.5	106.0	101.2	99.0	100.1
dibromochloromethane	1.000	94.0	87.0	98.5	99.6	101.9	99.5	100.1
1,3-dichloropropane	1.000	86.0	103.0	102.5	102.2	102.5	98.8	100.1
1,2-dibromomethane	1.000	100.0	96.0	99.0	100.8	103.4	98.8	100.1
chlorobenzene	1.000	94.0	98.0	96.0	102.0	102.5	98.9	100.1
ethylbenzene	1.000	100.0	100.0	99.0	98.8	101.0	99.8	100.0
1,1,1,2-tetrachloroethane	1.000	106.0	99.0	100.0	98.0	98.5	100.8	99.9
xylene (m+p)	1.000	96.0	97.0	99.5	98.2	102.7	99.3	100.1
xylene (o)	1.000	102.0	97.0	104.0	99.8	101.6	99.4	100.1
styrene	1.000	88.0	96.0	97.5	98.6	102.0	99.5	100.0
bromoform	1.000	94.0	100.0	97.0	100.8	103.5	98.8	100.1
isopropylbenzene	1.000	96.0	100.0	102.0	100.4	101.9	99.2	100.1
4-bromofluorobenzene*	4.61 % RSD	95.0	95.0	102.2	100.8	103.6	96.4	107.0
bromobenzene	1.000	102.0	102.0	104.5	101.2	103.6	97.8	100.2
n-propylbenzene	1.000	96.0	98.0	104.0	103.2	103.6	98.3	100.2
1,1,2,2-tetrachloroethane	0.999	98.0	101.0	103.0	101.8	106.4	97.4	100.2
2-chlorotoluene	1.000	92.0	95.0	108.0	98.2	102.5	99.2	100.1
1,3,5-trimethylbenzene	1.000	92.0	95.0	100.0	100.4	104.4	98.4	100.2
1,2,3-trichloropropane	0.999	96.0	100.0	99.0	103.2	109.0	96.3	100.4
4-chlorotoluene	0.999	98.0	91.0	105.5	105.0	106.9	96.9	100.3
t-butylbenzene	1.000	100.0	104.0	111.5	100.4	103.8	98.3	100.2
pentachloroethane	0.999	104.0	100.0	104.0	105.2	105.9	97.2	100.2
1,2,4-trimethylbenzene	1.000	98.0	96.0	100.5	102.0	104.8	98.0	100.2
sec-butylbenzene	1.000	98.0	97.0	104.0	104.2	103.8	98.1	100.2
4-isopropyltoluene	1.000	96.0	101.0	103.0	105.0	103.7	98.1	100.2
1,3-dichlorobenzene	1.000	92.0	98.0	104.0	100.6	104.7	98.1	100.2
1,4-dichlorobenzene	1.000	90.0	94.0	105.5	104.4	106.3	97.1	100.3
n-butylbenzene	1.000	92.0	96.0	106.5	109.6	103.3	97.7	100.2
hexachloroethane	0.999	118.0	115.0	118.0	103.2	109.7	95.6	100.4
1,2-dichlorobenzene-d4*	3.27 % RSD	105.6	101.4	98.7	97.8	95.2	100.9	100.4
1,2-dichlorobenzene	0.999	90.0	94.0	105.5	104.4	106.3	97.1	100.3
1,2-dibromo-3-chloropropane	0.998	110.0	101.0	105.0	101.6	113.2	95.0	100.4
hexachlorobutadiene	0.999	104.0	98.0	102.0	104.6	106.1	97.2	100.3
1,2,4-trichlorobenzene	1.000	88.0	98.0	100.0	100.0	103.3	98.8	100.1
naphthalene	0.999	100.0	97.0	99.5	101.4	105.2	95.9	100.7
1,2,3-trichlorobenzene	1.000	98.0	91.0	102.5	101.4	102.1	99.1	100.1

*Surrogate

Table 5. Quality Assurance Data

TARGET COMPOUND	1ppb REAGENT WATER, n=7		10ppb REAGENT WATER, n=7		10ppb TAP WATER, n=7	
	%Recovery	%RSD	%Recovery	%RSD	%Recovery	%RSD
dichlorodifluoromethane	101.6	4.9	113.9	4.1	111.8	4.9
chlorodifluoromethane	107.7	8.0	98.2	3.6	107.2	3.6
chloromethane	108.0	8.1	109.7	2.0	117.0	2.2
vinyl chloride	101.1	5.0	101.2	3.6	107.2	4.3
1,3-butadiene	101.3	6.1	95.2	1.8	97.8	3.4
bromomethane	111.4	5.7	105.1	4.8	112.4	4.2
trichlorofluoromethane	101.0	2.9	95.4	1.9	98.4	3.5
diethyl ether	104.1	3.3	100.9	1.1	104.4	2.1
1,1-dichloroethene	106.1	6.6	97.8	1.5	101.8	2.0
carbon disulfide	109.0	12.6	92.2	3.3	93.6	2.3
methyl iodide	80.3	5.1	92.2	1.4	101.7	1.6
allyl chloride	101.1	5.7	96.9	4.4	102.3	2.3
methylene chloride	102.6	5.8	100.5	1.5	107.8	1.3
trans-1,2-dichloroethene	104.1	6.7	102.6	1.7	108.4	2.7
methyl acetate	105.1	5.8	103.7	1.9	102.4	3.3
methyl-t-butyl ether-d3	112.9	1.2	115.0	1.5	115.1	1.4
methyl-t-butyl ether (MtBE)	104.9	3.0	104.8	1.5	111.4	1.4
t-butyl alcohol (TBA)	116.9	12.4	112.6	3.8	105.1	5.4
diisopropyl ether (DIPE)	101.7	1.2	102.7	1.2	109.0	0.9
1,1-dichloroethane	97.9	3.1	103.2	2.1	109.9	2.2
t-butyl ethyl ether (ETBE)	103.0	1.8	102.8	1.1	107.9	1.3
cis-1,2-dichloroethene	104.9	5.1	103.3	1.9	110.3	2.5
bromochloromethane	109.7	6.5	108.1	2.9	112.8	1.4
chloroform	103.6	3.3	101.8	2.4	136.3	1.6
carbon tetrachloride	99.1	4.3	98.4	1.3	103.3	2.6
tetrahydrofuran	100.9	12.8	105.8	3.7	106.0	3.3
1,1,1-trichloroethane	100.9	4.3	97.2	1.8	103.8	2.7
1,1-dichloropropene	104.3	4.5	99.6	3.8	106.8	2.8
1-chlorobutane	99.9	2.8	97.7	1.3	103.8	2.6
benzene	100.6	3.2	101.3	1.8	107.4	1.7
t-amyl methyl ether (TAME)	102.9	3.5	103.2	1.7	106.4	1.4
1,2-dichloroethane	103.4	6.2	103.4	1.0	108.2	0.9
trichloroethene	103.6	5.2	101.8	2.3	109.7	3.0
t-amyl ethyl ether (TAEE)	99.9	1.5	101.1	2.2	107.1	1.0
dibromomethane	108.7	5.7	104.2	0.6	109.8	1.6
1,2-dichloropropane	103.6	2.8	101.5	2.0	109.4	1.9
bromodichloromethane	101.4	3.7	101.7	2.5	178.8	1.4
cis-1,3-dichloropropene	100.7	3.5	101.8	2.2	106.4	1.3
toluene	103.1	4.1	97.3	1.2	103.1	1.9
tetrachloroethene	95.9	3.5	95.6	2.9	101.2	2.9
trans-1,3-dichloropropene	99.3	3.3	98.7	2.1	101.4	0.7
ethyl methacrylate	100.6	4.7	100.1	2.0	100.2	2.5
1,1,2-trichloroethane	102.3	6.1	101.7	1.3	105.5	1.2
dibromochloromethane	94.0	2.9	100.2	1.9	210.3	1.0
1,3-dichloropropane	101.4	3.8	102.4	1.0	105.4	1.4
1,2-dibromomethane	101.6	3.4	101.6	2.1	103.0	1.8
chlorobenzene	100.1	3.8	98.6	1.8	102.8	1.4
ethylbenzene	99.0	3.3	97.5	1.6	102.7	1.7
1,1,1,2-tetrachloroethane	99.0	5.0	97.8	1.4	102.2	1.5
xylene (m+p)	95.4	3.4	97.4	1.5	102.0	2.2
xylene (o)	99.4	4.5	100.0	2.1	105.1	1.8
styrene	98.0	5.5	97.6	2.7	100.4	1.6
bromoform	100.1	5.7	98.7	2.3	164.4	0.8
isopropylbenzene	98.4	3.3	97.2	1.9	103.5	1.7
4-bromofluorobenzene	105.2	1.8	111.9	3.0	109.1	2.5
bromobenzene	103.0	3.2	102.9	1.7	106.4	1.8
n-propylbenzene	99.3	3.8	99.9	1.9	104.0	1.7
1,1,2,2-tetrachloroethane	98.7	4.9	102.7	1.4	101.3	2.6
2-chlorotoluene	97.3	6.0	100.4	1.7	103.4	1.8
1,3,5-trimethylbenzene	95.3	2.1	100.1	2.4	104.2	1.8
1,2,3-trichloropropane	96.7	9.8	101.0	3.0	100.9	1.9
4-chlorotoluene	100.1	3.3	101.0	1.7	104.8	1.5
t-butylbenzene	98.9	3.5	99.0	1.6	104.3	2.9
pentachloroethane	97.7	4.6	105.5	1.5	109.3	1.9
1,2,4-trimethylbenzene	98.3	3.5	101.5	1.3	105.8	1.3
sec-butylbenzene	97.7	4.4	99.5	1.4	103.2	1.6
4-isopropyltoluene	97.7	4.7	100.2	1.9	104.1	1.6
1,3-dichlorobenzene	99.7	3.6	101.1	1.7	104.8	2.3
1,4-dichlorobenzene	100.0	5.0	102.5	1.5	105.0	1.9
n-butylbenzene	100.6	4.2	100.8	1.2	105.5	1.7
hexachloroethane	107.6	8.6	104.6	2.0	108.5	3.5
1,2-dichlorobenzene-d4	100.0	0.0	100.0	0.0	100.0	0.0
1,2-dichlorobenzene	100.0	5.0	102.5	1.5	105.0	1.9
1,2-dibromo-3-chloropropane	100.7	4.9	100.8	3.3	100.3	1.2
hexachlorobutadiene	101.6	4.6	102.9	1.4	102.7	2.6
1,2,4-trichlorobenzene	98.4	3.1	99.7	2.2	102.7	1.3
naphthalene	100.6	2.6	99.7	1.0	99.3	1.1
1,2,3-trichlorobenzene	100.3	4.2	98.3	1.9	101.1	1.2
	101.4	4.6	101.3	2.0	108.6	2.1
INTERNAL STANDARD	%RSD					
1,4-difluorobenzene	3.0					
chlorobenzene-d5	3.0					
1,4-dichlorobenzene-d4	3.0					
SURROGATE	%RSD					
methyl-t-butyl ether-d3	2.7					
4-bromofluorobenzene	2.7					
1,2-dichlorobenzene-d4	3.0					