Analysis of Volatile Organic Compounds Using US EPA Method 524.4 by CDS 7000 Series Automated Purge and Trap Concentrator

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Application Note

Environmental

Abstract

In EPA Method 524.4, nitrogen is adopted to replace helium in purging volatile organic compounds from water samples. This application note demonstrates the ability of the CDS Analytical's 7000 series purge and trap concentrator configured with a 7450 autosampler to meet and exceed the requirements of US EPA method 524.4.

Introduction

Helium, which is the coolest cryogen with boiling temperature merely at 4.2K, is commercially extracted from natural gas wells. In the past two decades, the energy sector in North America has gradually moved away from using conventional natural gas to shale oil extraction. This technology shift historically has created three major crises in helium supply, including the Helium Shortage 3.0[1] in recent years, two other shortage crises in 2005-2007 and 2012-2013 respectively[2]. To tackle with the periodical shortages and sharply arising cost of helium, US EPA has promptly altered the EPA Method 524.3, which is a VOCs testing method in drinking water, to allow using nitrogen to replace helium. This change eventually led to the birth of EPA Method 524.4 in 2013[3].

CDS Analytical invented the first micro-processor controlled Purge and Trap concentrator in 1979 and won the Industrial Research and Development 100 award in 1981. The 7450 autosampler was constructed on the 2nd generation XYZ autosampler with enhanced precision. This automation platform is specially designed for the 7000 series Purge and Trap concentrator to improve the productivity. The unique 10-port micro-loop fill valve in the autosampler enables a less than 1% volume variation in adding 2 μL of Internal Standard. This translates to a superior <3% RSDs compared to other autosamplers that are using the micro syringe injection technique. The 8-port high temperature valve in the 7000 series concentrator has the capability to provide on-line moisture management, which removes the wet trap in the desorption step to increase the efficiency. Due to the various engineering features, the results coming from this combined system exceeds the requirements of EPA Method 524.4 in Calibration, Minimum Reporting Levels (MRLs) Confirmation, Accuracy and Precision Calibration in both low and mid sample concentrations.

Experimental Setup

A CDS 7000 series concentrator, which is equipped with a proprietary Type X trap, was used as the purge and trap concentrator. A CDS 7450 autosampler was connected to the concentrator to automate the sample introduction and internal standard addition steps. The downstream analytical device is a Shimadzu QP2010 GC/MS.

Calibration standards were prepared from Restek 524.3 VOA MegaMix (Restek# 30013) and 524.3 Gas Mix (Restek # 30014) standards in deionized water with preservation reagents, which included maleic acid and ascorbic acid. The stock solution was diluted to seven concentrations ranging from 0.2 ppb to 50 ppb.

Restek 524.3 Internal Standard/Surrogate Mix (Restek# 30017) was diluted in methanol to a final concentration of 12.5 ppm as the internal standard and surrogate solution mix. In the internal standard addition, the 7450 autosampler pulled 2 µl of the internal standard and mixed with 5 ml of samples, resulting an internal standard concentration of 5 ppb. The Agilent MassHunter software was used as the data analysis tool. In the calibration data fitting, a quadratic calibration curve with 1/X weighting was adopted for all compounds.

The Calibration, MRL Confirmation and Accuracy / Precision data were calculated from seven 0.5 ppb and seven 5 ppb calibration standards with purge and trap conditions in Table 1 and GC/MS conditions in Table 2.

Table 1. Purge and trap conditions

Purge and Trap Concentrator	CDS 7000E
Trap type	Type X
Val oven temperature	130 °C
Transfer line temperature	130 °C
Trap ready temperature	45 °C
Wet trap ready temperature	30 °C
Purge time	11
Purge flow rate	40 mL/min
Dry purge temperature	35 °C
Dry purge flow rate	100 mL/min
Dry purge time	0.5
Desorb preheat temperature	245
Desorb temperature	250
Desorb time	1 min
Trap bake temperature	260 °C
Wet trap bake temperature	260 °C
Bake time	10 min
Bake flow rate	400 mL/min
Purge and Trap Autosampler	CDS 7450
Sample volume	5 mL
Internal standard volume	2 µL
Surrogate standard volume	2 µL

Results and Discussions

Figure 1 shows the chromatogram of a 20 ppb calibration standard. Figure 2 displays the gas portion of the chromatogram of a 0.2 ppb calibration standard, where the sensitivity of the system was manifested by the high signal to noise ratio and symmetric line shape. Table 3 is the RSDs data from seven system blanks by only adding internal standards and surrogates. The curve fitting coefficient (R^2), MRL, accuracy and precision data for all the compounds are shown in Table 4.

Conclusions:

The 7000 series purge and trap automated system easily meets and exceeds the EPA Method 524.4. Many of the technical advantages in the system, including the 10-port micro-loop fill valve, proprietary Type X trap, and on-line wet traps, are proven to be driving the overall performance of the system.

Table 2. GC/MS conditions

GC/MS	GCMS-QP2010
Injection mode	Split
Injection temperature	200 °C
Flow control mode	Constant linear velocity
Linear velocity	34.3 cm/sec
Column flow rate	0.9 mL/min
Split ratio	30:1
Purge flow	1.0 mL/min
Column	Restek Rtx-VMS 30m x 0.25 mm I.D. 1.40 µm (cat# 19915)
Oven temperature program	45 °C, hold for 4.5 minute 12 °C/minute to 100 °C, hold for 0.0 minute 25 °C/minute to 240 °C, hold for 1.32 minutes
Ion source temperature	185 °C
Interface temperature	225 °C
Solvent cut time	1.5 min
Scan range	1.5 min to 3.2 min: 45-260 m/z 3.2 min to 16 min: 35-260 m/z
Event time	0.3 second

Table 3. RSDs of internal standard/surrogate addition

Compound	RSD (n=7)
MTBE-d3	2.2%
Benzene, 1,4-difluoro-	1.9%
Chlorobenzene-d5	2.6%
p-Bromofluorobenzene	2.6%
1,4-Dichlorobenzene-D4	2.3%
1,2-Dichlorobenzene-d4	2.9%

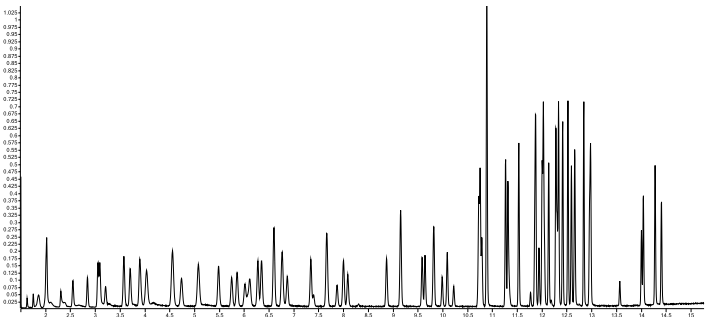

Figure 1: TIC of a calibration standard at 20 ppb

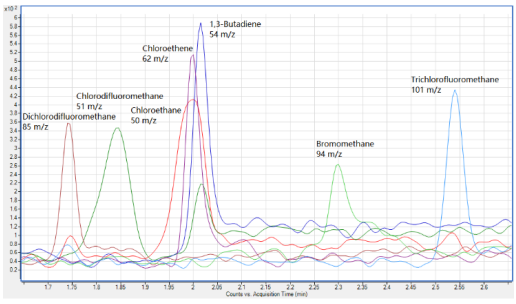

Figure 2: Quantitation Ions for the first seven gases at 0.2 ppb

Table 4. EPA Method 524.4 calibration, MRL and its confirmation, accuracy and precision data

Compound	Calibration		MRL Confirmation (0.5 ppb)		Accuracy and Precision (0.5 ppb)			Accuracy and Precision (5 ppb)		
	MDL (ppb)	CF R^2	LPIR >50%	UPIR <150%	Avg. Conc. (ppb)	Accuracy (±20%)	Precision as RSD (n=7)	Avg. Conc (ppb)	Accuracy (±20%)	Precision as RSD (n=7)
Dichlorodifluoromethane	0.08	0.997	97%	137%	0.58	117%	4.4%	5.4	109%	5.6%
Difluorochloromethane	0.10	0.997	77%	128%	0.51	103%	6.2%	5.2	104%	5.8%
1,3-butadiene	0.07	0.999	68%	102%	0.42	85%	5.1%	4.9	99%	4.0%
Chloromethane	0.09	0.998	72%	118%	0.48	95%	6.1%	5.0	100%	4.9%
Chloroethene	0.09	0.999	74%	120%	0.49	97%	6.0%	4.9	98%	5.3%
Bromomethane	0.09	0.999	72%	116%	0.47	94%	5.8%	4.9	98%	4.2%
Trichloromonofluoromethane	0.05	0.999	73%	98%	0.43	85%	3.8%	4.9	97%	4.9%
Diethyl ether	0.06	0.998	77%	106%	0.46	92%	3.9%	4.5	91%	3.0%
1,1-Dichloroethene	0.10	0.999	70%	119%	0.47	94%	6.6%	4.6	93%	3.1%
Carbon disulfide	0.10	0.999	61%	110%	0.43	85%	7.3%	4.9	97%	3.8%
Methyl iodide	0.11	0.999	73%	130%	0.51	101%	7.1%	5.0	100%	3.5%
Allyl chloride	0.08	0.999	75%	117%	0.48	96%	5.5%	4.7	94%	4.5%
Methylene chloride	0.11	1.000	73%	126%	0.50	100%	6.8%	4.9	98%	4.0%
(E)-1,2-Dichloroethylene	0.11	0.999	58%	116%	0.44	87%	8.4%	4.8	97%	4.8%
MTBE	0.05	0.992	91%	115%	0.51	103%	2.9%	4.7	94%	3.6%
MTBE-d3 (Surr)										
Methyl acetate	0.07	0.996	78%	114%	0.48	96%	4.7%	4.7	94%	2.4%
TBA	0.05	0.999	93%	120%	0.53	107%	3.2%	4.8	96%	3.7%
Diisopropyl ether	0.06	0.999	82%	112%	0.49	97%	3.9%	4.8	96%	3.4%
1,1-Dichloroethane	0.08	0.999	78%	117%	0.49	98%	5.1%	4.8	95%	4.6%
ETBE	0.08	0.999	75%	118%	0.48	96%	5.6%	4.8	95%	2.2%
(Z)-1,2-Dichloroethylene	0.07	0.999	84%	120%	0.51	102%	4.5%	4.8	96%	4.1%
Bromochloromethane	0.12	0.999	71%	133%	0.51	102%	7.6%	4.8	96%	4.1%
Trichloromethane	0.10	0.999	74%	123%	0.49	99%	6.4%	4.7	94%	4.1%
Carbon Tetrachloride	0.14	0.999	70%	140%	0.53	105%	8.4%	4.9	98%	4.7%
Tetrahydrofuran	0.11	0.996	63%	118%	0.45	90%	7.6%	4.1	82%	3.8%
1,1,1-Trichloroethane	0.09	0.999	77%	121%	0.49	99%	5.5%	4.8	95%	5.0%
1,1-Dichloropropene	0.13	0.999	72%	135%	0.52	104%	7.7%	4.9	98%	5.3%
1-Chlorobutane	0.08	0.999	78%	119%	0.49	99%	5.2%	4.8	95%	4.6%
Benzene	0.12	0.999	70%	132%	0.51	101%	7.7%	4.7	95%	3.8%
TAME	0.06	0.999	83%	113%	0.49	98%	3.9%	4.7	94%	2.2%
1,2-Dichloroethane	0.09	0.999	71%	119%	0.48	95%	6.3%	4.6	92%	3.2%
Trichloroethylene	0.07	0.998	83%	118%	0.50	100%	4.5%	4.8	95%	4.8%
1,4-Difluorobenzene (IS 1)										
TAEE	0.05	0.999	86%	112%	0.49	99%	3.3%	4.6	92%	3.3%
Dibromomethane	0.10	0.999	78%	129%	0.52	103%	6.2%	4.7	94%	3.7%
1,2-Dichloropropane	0.10	1.000	75%	128%	0.51	101%	6.6%	4.8	97%	3.9%
Bromodichloromethane	0.10	1.000	74%	126%	0.50	100%	6.6%	4.8	96%	3.7%
(Z)-1,3-dichloropropene	0.06	0.999	84%	114%	0.49	99%	3.8%	4.7	93%	3.1%
Toluene	0.07	0.999	81%	118%	0.50	100%	4.7%	4.7	95%	3.6%
Tetrachloroethylene	0.06	0.998	88%	116%	0.51	102%	3.6%	4.8	95%	5.6%
€-1,3-dichloropropene	0.03	0.999	87%	101%	0.47	94%	1.9%	4.5	90%	3.9%
1,1,2-Trichloroethane	0.09	0.999	73%	117%	0.47	95%	5.9%	4.7	94%	3.5%

Ethane, 1,2-dibromo-	0.08	0.999	76%	116%	0.48	96%	5.2%	4.7	93%	3.6%
Chlorobenzene	0.07	0.999	83%	117%	0.50	100%	4.3%	4.7	94%	3.5%
Chlorobenzene-d5 (IS 2)										
Ethylbenzene	0.06	0.998	83%	114%	0.49	99%	4.1%	4.6	93%	4.4%
1,1,1,2-Tetrachloroethane	0.10	0.998	75%	125%	0.50	100%	6.4%	4.7	93%	3.8%
m,p-Xylene	0.07	0.998	77%	115%	0.48	96%	4.9%	4.6	92%	5.1%
o-Xylene	0.06	0.998	82%	114%	0.49	98%	4.1%	4.6	92%	4.1%
Styrene	0.06	0.998	81%	113%	0.49	97%	4.2%	4.6	92%	4.4%
Tribromomethane	0.11	0.998	70%	127%	0.49	99%	7.3%	4.4	89%	3.3%
Isopropylbenzene	0.07	0.998	78%	115%	0.48	97%	4.8%	4.6	93%	5.6%
BFB (Surr)										
Bromobenzene	0.08	0.998	84%	125%	0.52	105%	4.9%	4.6	92%	4.4%
propylbenzene	0.08	0.998	77%	117%	0.48	97%	5.2%	4.6	92%	4.6%
1,1,2,2-Tetrachloroethane	0.08	0.998	73%	114%	0.47	94%	5.4%	4.4	87%	4.0%
2-Chlorotoluene	0.09	0.998	76%	123%	0.50	99%	6.0%	4.6	91%	4.2%
1,3,5-Trimethylbenzene	0.06	0.998	81%	112%	0.48	97%	4.1%	4.5	90%	4.7%
1,2,3-Trichloropropane	0.05	0.998	79%	105%	0.46	92%	3.5%	4.3	86%	3.6%
4-Chlorotoluene	0.07	0.998	78%	113%	0.48	96%	4.5%	4.6	92%	4.7%
tert-Butylbenzene	0.07	0.999	83%	118%	0.50	101%	4.4%	4.9	98%	3.5%
Pentachloroethane	0.14	0.999	68%	139%	0.52	103%	8.7%	4.9	97%	3.5%
1,2,4-Trimethylbenzene	0.07	0.999	81%	116%	0.49	99%	4.5%	4.9	98%	3.8%
sec-Butylbenzene	0.07	1.000	82%	118%	0.50	100%	4.6%	5.0	100%	4.1%
4-Isopropyltoluene	0.09	0.999	77%	121%	0.50	99%	5.5%	4.8	97%	3.4%
1,3-Dichlorobenzene	0.06	0.999	85%	118%	0.51	101%	4.1%	4.9	97%	3.4%
1,4-Dichlorobenzene	0.08	0.999	83%	121%	0.51	102%	4.7%	4.8	97%	3.5%
1,4-Dichlorobenzene-d4 (IS 3)										
n-Butylbenzene	0.05	0.999	86%	112%	0.49	99%	3.3%	4.8	96%	4.2%
Hexachloroethane	0.10	0.999	76%	126%	0.50	101%	6.3%	4.9	97%	3.7%
1,2-Dichlorobenzene-d4 (Surr)										
1,2-Dichlorobenzene	0.09	0.999	79%	124%	0.51	102%	5.5%	4.9	97%	2.7%
1,2-Dibromo-3-chloropropane	0.08	0.999	81%	122%	0.51	101%	5.1%	4.7	94%	3.2%
Hexachlorobutadiene	0.11	0.998	77%	129%	0.51	103%	6.5%	4.9	97%	4.8%
1,2,4-Trichlorobenzene	0.08	0.999	82%	120%	0.51	101%	4.8%	4.9	97%	3.2%
Naphthalene	0.07	0.999	82%	117%	0.50	99%	4.4%	4.7	95%	3.4%
1,2,3-Trichlorobenzene	0.10	0.999	77%	127%	0.51	102%	6.1%	4.9	97%	4.0%

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