UCMR 3 Low-Level VOC Analysis by Purge and Trap Concentration and GC/MS using Selective Ion Monitoring

Application Note

Abstract

The United States Environmental Agency (USEPA) has established the Unregulated Contaminant Monitoring Program to collect data for contaminants suspected to be present in drinking water.[1] The USEPA is currently proposing Unregulated Contaminant Monitoring Rule 3 (UCMR 3) which will collect data from January 2013 through December 2015. Because of the impact on public health and safety, it is vital to have a system that can detect and analyze for these compounds at low levels. This study will validate the analysis of the Volatile Organic Compounds (VOCs) present on the UCMR 3 analyte list. USEPA Method 524.3, used to monitor the VOCs, allows for the use of Single Ion Monitoring (SIM) to reach the part-per-trillion (ppt) levels required by UCMR 3.[2]

This study uses a Teledyne Tekmar Stratum Purge and Trap Concentrator (PTC) and AQUATek 100 Autosampler coupled to a Thermo ISQ Single Quadrupole GC-MS. A calibration curve and detection limits will be determined for the VOCs on the UCMR 3 analyte list.

Introduction

The USEPA Contaminant Monitoring Program reviews the list of analytes every five years based on the Contaminant Candidate List; a list of compounds not regulated by the national primary drinking water regulations. These contaminants are known or anticipated to occur in public water systems. The compounds being monitored in UCMR 3 are 28 “List 1” chemicals for “Assessment Monitoring” and two “List 3” viruses for “Pre-screen Testing”. Assessment monitoring is required for those compounds with existing analytical methods, while the pre-screening methods are new analytical techniques for monitoring the viruses.

The thirty contaminants that will be monitored by UCMR 3 are divided into several groups and can be found in Table 1. This study focuses on the analysis of the nine VOCs, which can be analyzed using USEPA Method 524.3, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry* according to UCMR 3.

USEPA Method 524.3 allows for the use of SIM scan for low-level analysis. This ensures that contaminants present in water sources can be analyzed at the part-per-trillion level and monitored accordingly. This study will use a Stratum PTC and AQUATek 100 Autosampler with a Thermo ISQ GC-MS to establish a calibration and detection limit for the nine VOCs listed as contaminants in UCMR 3.

Unregulated Contaminant Monitoring Rule 3 Analyte List			
Volatile Organic Compounds	1,2,3-Trichloropropane	Hormones	17-β-estradiol
	1,3-Butadiene		17-α-ethynylestadiol
	Chloromethane		16-α-hydroxyestradiol
	1,1-Dichloroethane		Equilin
	n-Propylbenzene		Estrone
	Bromomethane		Testosterone
	sec-Butylbenzene		4-androstene-3,17-dione
	Chlorodifluoromethane	Perfluorinated Compounds	Perfluorooctane sulfonate
	Bromochloromethane		Perfluorooctanoic acid
Metals	Vanadium		Perfluorononanoic acid
	Molybdenum		Perfluorohaxane sulfonic acid
	Cobalt		Perfluoroheptanoic acid
	Strontium		Perfluorobutane sulfonic acid
Synthetic Organic Compounds	1,4-Dioxane	Viruses	Enteroviruses
Oxyhalide Anion	Chlorate		Noroviruses

Table 1: UCMR 3 Proposed Contaminants List (VOC Compounds in Yellow)

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 autosampler were coupled to the Thermo ISQ GC/MS system for analysis. The Thermo ISQ was configured with a Restek Rtx-624 20m x 0.18mm x 1.0µm column. The GC-MS parameters are outlined in Tables 2 and 3. The SIM ions used for quantification and conformation for the analytes in this study can be found in Table 4**.**

A Tekmar proprietary #9 trap was the analytical trap of choice. Table 5 outlines the PTC and autosampler conditions.

GC Parameters	
GC:	Thermo Trace GC Ultra
Column:	Restek Rtx®-624 20m x 0.18mm x 1.0µm
Oven Program:	45° C for 4.5 min, to 100° C at 15° C/min, for 0 min, to 240° C at 25 ° C/min for 0.33 min
Inlet:	200° C
Column Flow:	1.0 mL/min
Gas:	Helium
Pressure:	21.76 psi
Split Ratio:	25:1

MS Parameters	
MSD:	Thermo ISQ
Source:	275° C
Transfer Line Temp:	230°C
Solvent Delay:	0.5 min
SIM ions:	See Table 4
Ionization Mode:	EI+
Emission Current	25 uA

Tables 2 & 3: Thermo ISQ GC/MS Parameters

Compound	Retention Time	Q-Ion	Confirmation Ion
Chlorodifluoromethane	1.14 min	51	67
Chloromethane	1.26 min	50	52
1,3-Butadiene	1.33 min	54	53
Bromomethane	1.53 m in	94	96
1,1-Dichloroethane	3.48 min	63	65
Bromochloromethane	4.45 min	128	130
n-Propylbenzene	9.80 min	91	120
1,2,3-Trichloropropane	9.94 min	110	112,75
sec-Butylbenzene	10.30 min	105	134

Table 4: Retention Times, Quantification Ions, and Confirmation Ions for SIM scan

Stratum PTC and AQUATek 100 Parameters			
Variable	**Value**	**Variable**	**Value**
Pressurize Time	0.25 min	Purge Time	6.00
Sample Transfer Time	0.50 min	Purge Temp	20 °C
Rinse Loop Time	0.50 min	Purge Flow	60 mL/min
Sweep Needle Time	0.30 min	Dry Purge Time	2.00 min
Bake Rinse	On	Dry Purge Temp	30 °C
Bake Rinse Cycles	1	Dry Purge Flow	100 mL/min
Bake Rinse Drain Time	0.50 min	GC Start	Start of Desorb
Presweep Time	0.35 min	Desorb Preheat Temp	245 °C
Water Temp	90 °C	Desorb Drain	On
Valve Oven Temp	150 °C	Desorb Time	1.00 min
Transfer Line Temp	150 °C	Desorb Temp	250 °C
Sample Mount Temp	90 °C	Desorb Flow	300 mL/min
Purge ready Temp	35 °C	Bake Time	2.00 min
Condenser Ready Temp	40 °C	Bake Temp	280 °C
Condenser Purge Temp	20 °C	Bake Flow	400 mL/min
Standby Flow	10 mL/min	Condenser Bake Temp	200 °C
Pre-Purge Time	0.5 min		
Pre-Purge Flow	40.0 mL/min		
Sample Heater	Off		
Sample Preheat Time	1.00 min		
Sample Temp	40 °C		

Table 5: Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in Blue)

Calibration Data

A 1ppm stock solution containing the analytes of interest was prepared in methanol. From this stock solution, an eight-point calibration curve from 2.5-1000ppt was prepared in de-ionized water. Thermo Scientific EnviroLab Forms software was used to process the calibration data.

Figure 1 illustrates calibration curve results for sec-butylbenzene, one of the contaminants to be monitored according to UCMR 3. Curve data was evaluated using quadratic regression, with equal weighting. The results of these calibrations can be found in Table 6.

Internal standards and surrogates were added to each sample in 10uL aliquots to the sample providing a constant 50ppt final concentration. The internal standards and surrogates were evaluated for reproducibility; the results can be found in Table 7.

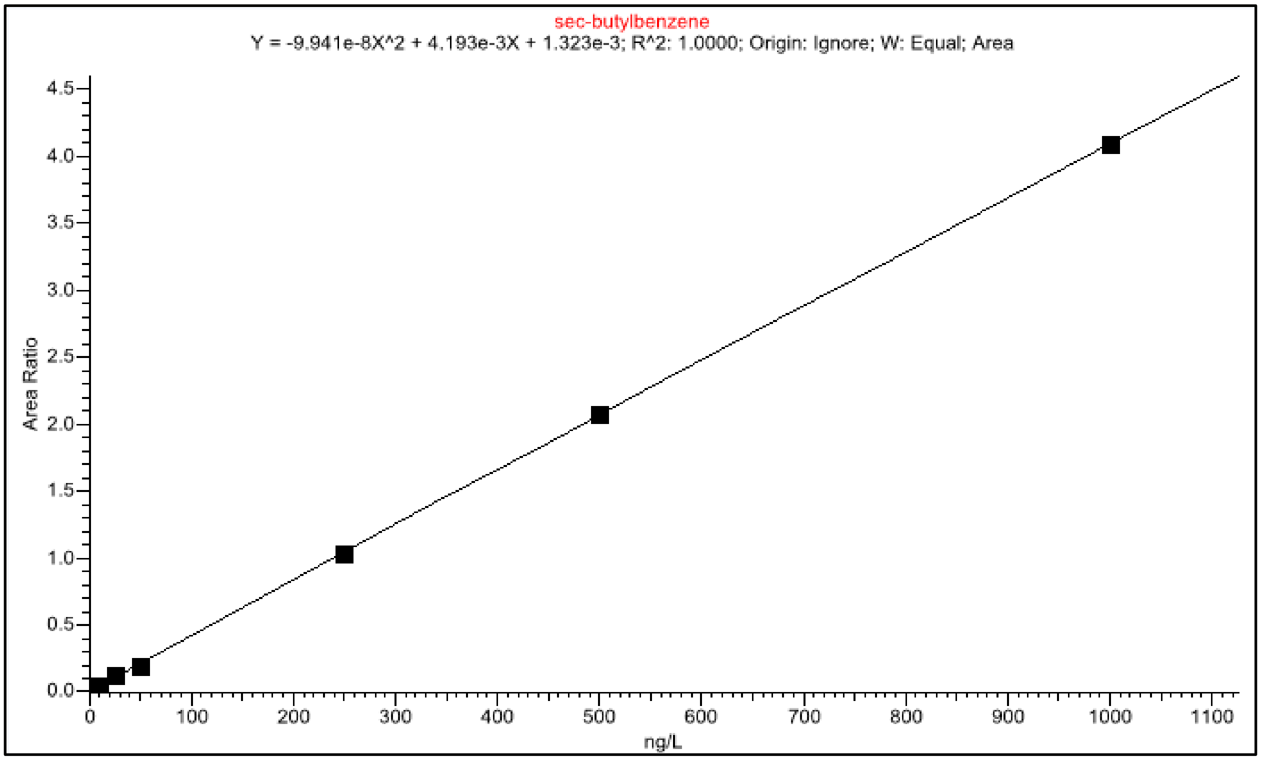

Figure 1: Calibration Curve for sec-butylbenzene.

Contaminant	Quadratic Regression Factor (r^2)
Chlorodifluoromethane	0.9998
Chloromethane	0.9996
1,3-Butadiene	1.0000
Bromomethane	0.9998
1,1-Dichloromethane	0.9998
Bromochloromethane	0.9996
n-Propylbenzene	0.9997
1,2,3-Trichloropropane	0.9994
sec-Butylbenzene	1.0000

Table 6: Calibration Curve data for UCMR 3 VOC Contaminants

Internal Standard/Surrogate	%RSD
1,4-Diflurorobenzene	4.52
Chlorobenzene-d5	4.27
4-Bromofluorobenzene	3.02
1,2-Dichlorobenzene-d4	2.77
1,4-Dichlorobenzene-d4	5.57

Table 7: Internal Standard/Surrogate Standard Data

Method Detection Limits

In order to complete this ppt analysis, SIM scanning was used. As recommended by the USEPA, the ions utilized for the analysis of each contaminant can be found in Table 3. Figures 2 and 3 are images from Thermo Scientific EnviroLab Forms software illustrating the quantification and confirming ions for 1,2,3-trichloropropane (TCP), individually and overlaid to show there are no interferences.

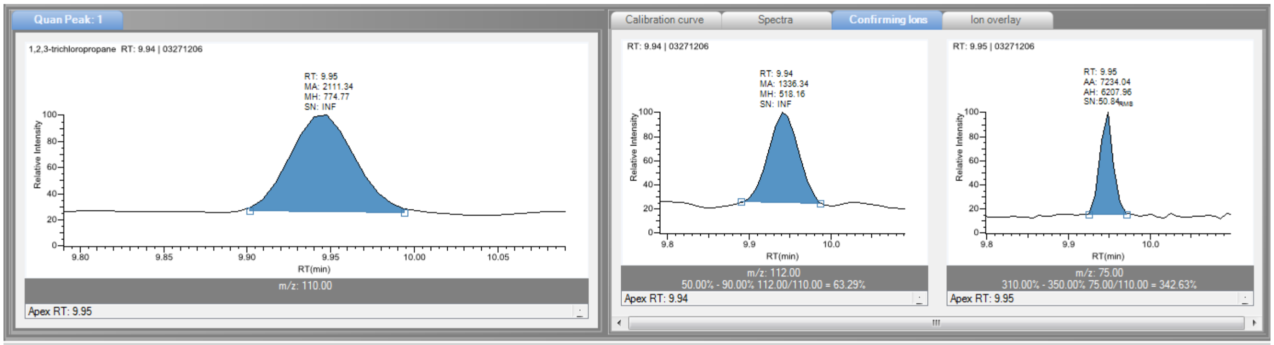

Figure 2: Quantification Ion (110m/z) and Confirming Ions (112m/z and 75 m/z) for TCP

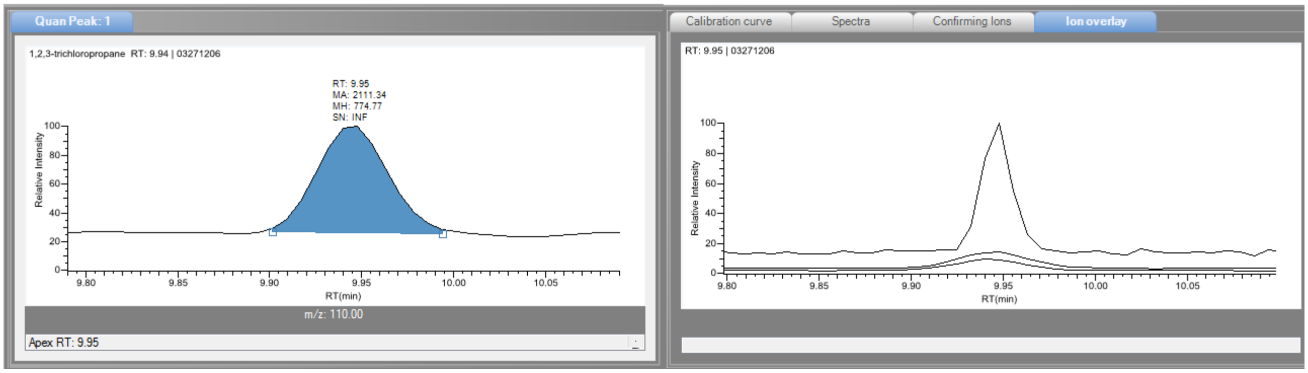

Figure 3: Ion Overlay of the Quantification Ion (110m/z) and Confirming Ions (112, 75 m/z) for TCP

Method detection limits (MDLs) were established by analyzing seven replicate samples at a concentration of 10 ppt for each contaminant. The detection limit is a statistical determination which identifies the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the concentration is greater than zero.[2]

The detection limit is determined with the following equation, where S is the standard deviation and t is the t-value for the 99% confidence level. For seven replicates, the t value is 3.143.[2]

$$\mathrm{DL} = \mathrm{S} * \mathrm{t}_{(\mathrm{n}-1,1-\alpha=0.99)}$$

Table 8 illustrates the replicate data and MDL results for the VOC contaminants in UCMR 3.

	Repetition										
Analyte	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**Average**	**Stdev**	**%RSD**	**MDL**
Chlorodifluoromethane	7.86	7.69	7.31	7.22	8.18	7.20	8.01	7.64	0.40	5.23	**1.26**
Chloromethane	9.68	10.31	9.96	10.41	10.36	9.82	10.28	10.12	0.29	2.89	**0.92**
1,3-Butadiene	7.22	7.00	8.27	8.25	6.81	7.27	6.49	7.33	0.69	9.37	**2.16**
Bromomethane	8.52	8.45	8.37	9.01	8.89	9.29	8.50	8.72	0.35	3.98	**1.09**
1,1-Dichloromethane	9.99	10.22	10.51	10.07	9.68	10.20	9.49	10.02	0.34	3.44	**1.08**
Bromochloromethane	9.37	9.34	9.85	9.72	9.72	10.86	9.32	9.74	0.54	5.53	**1.69**
n-Propylbenzene	8.31	8.61	8.30	8.86	8.57	8.32	8.01	8.43	0.28	3.27	**0.87**
1,2,3-Trichloropropane	10.33	10.36	9.90	10.42	10.13	9.74	10.44	10.19	0.28	2.70	**0.86**
sec-Butylbenzene	8.94	9.04	9.27	9.05	8.92	9.18	8.70	9.01	0.19	2.07	**0.59**

Table 8: MDL data for VOC Contaminants Listed in UCMR 3

Conclusions

The USEPA has established the Unregulated Contaminant Monitoring Program to collect data for contaminants suspected to be present in drinking water. The current proposal, UCMR 3, will collect data on 30 contaminants from January 2013 through December 2015. This study validates the capability of Teledyne Tekmar Stratum PTC and AQUATek 100 Autosampler coupled with a Thermo ISQ for low-level detection of the nine VOC contaminants listed in UCMR 3.

Using a SIM scan, as permitted in USEPA method 524.3, MDLs were established for all VOC contaminants to be monitored according to UCMR 3. With concerns for public health and safety, notification levels of harmful compounds are being pushed lower and lower, driving the demand for more sensitive instrumentation. All contaminants in this study had MDL levels under 2.5 ppt, proving purge and trap to be a superb analytical tool for this analysis.

References

1. Unregulated Contaminant Monitoring Program
   http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/
2. USEPA Method 524.3, "Measurement of Purgeable Organic Compounds by Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)," Revision 1, 2009.