EPA Method 524 for Determination of VOCs in Drinking Water Using Agilent 5975T LTM GC/MSD with Static Headspace

Application Note

Environmental

Authors

Xiaohua Li
Agilent Technologies (Shanghai) Co., Ltd.
412 Ying Lun Road
Waigaoqiao Free Trade Zone
Shanghai 200131 P.R.China

Abstract

Due to an increase in urgent cases of water pollution, requirements for onsite water quality monitoring with transportable instruments has grown for the analysis of organic contaminates in drinking water. Monitoring volatile organic compounds (VOCs) in drinking water is a key application for mobile water quality monitoring labs. Mobile labs usually require fast response and accurate results for target and unknown contaminates. An ultra fast method was developed based on the Agilent 5975T LTM GC/MSD and the Agilent 7694E headspace sampler. This method can separate 54 target VOCs in 9 min. The method detection limits (MDL) ranged from 0.199–0.968 µg/L in 10 mL water at SIM mode depending on the compounds separated. All of the method performance results for calibration, recovery and repeatability are described in this application note. A new deconvolution reporting library was created and applied by using Agilent's DRS software to reduce the identification time for unknown compounds.

Agilent Technologies

Introduction

VOC's in drinking water are hazardous to human health. Hundreds of VOCs have been produced for use in a variety of products, including gasoline, dry cleaning solvents, and degreasing agents. When these products are improperly stored or disposed, or when a spill occurs, VOCs can contaminate ground water and drinking water supplies. Therefore, it is critically important to monitor VOCs and give fast quantitative and qualitative results in the event of an emergency. However, for most mobile labs the biggest challenge is to provide fast monitoring results without sacrificing analysis accuracy.

US EPA Method 524.2 [1] provides a general purpose method for the identification and simultaneous measurement of volatile organic compounds in surface water, ground water, and drinking water. EPA Method 8260 [2] is a similar standard but for more comprehensive sample matrices such as waste solvents, aqueous sludges, oily wastes, soils, and sediments. The optimized equipment and conditions presented here provide data compliant with the rigorous Method 524.2 criteria. Detection limits, calibration results, precision and accuracy data are presented for the 54 common targeted VOC compounds. It is also applicable for analyzing a wide range of volatile organic compounds in source water, ground water and so forth.

This application note provides a proven method for the determination of VOCs in drinking water, based on the transportable Agilent 5975T LTM GC/MSD and the Agilent 7694E headspace sampler. This verified method can be used in an onsite or mobile lab because of the sample preparation adopted in this solution. The Agilent ChemStation is easy to operate for all users. The unique DRS software provides quantitative and qualitative reports in less than 1 minute. These features combined, provide mobile lab chemists with fast and accurate monitoring results.

Experimental

Method Parameters

The optimized instruments conditions for the Headspace (HS) and GC/MS System are listed in Tables 1 and 2.

Table 1.   HS Instruments Conditions for VOC Analysis

Static Headspace System

Instrument	Agilent 7694E headspace sampler
GC cycle time	13 min
Vial equilibration time	10 min
Injection time	1 min
Sample loop	1 ml
Shake	low
Vial temp	80 °C
Needle temp	90 °C
Transfer line	200 °C

Table 2.   GC/MS Instruments Conditions for VOCs Analysis

Transportable GC/MS System

Instrument	Agilent 5975T LTM GC/MS
Inlet liner	splitless liner (Agilent p/n 18740-80200)
Injector temp	220 °C
Carrier gas	He
Inlet pressure	18 psi (constant)
RTL	Toluene retention time locked to 4.571 min
Split flow	30 mL/min (measured)
Column	LTM DB-624 20 m × 0.18 mm, 1.0 µm
LTM program	50 °C (1min) > 120 °C (0 min) @20 °C/min > 220 °C (2.5 min) @50 °C/min
GC total run time	9 min
Small oven	220 °C
Transfer line	220 °C
Solvent delay	2.5 min
Data aquiring mode	Scan and SIM
Scan mass range	35-300 amu
Source temp	230 °C
Quad temp	150 °C

Instrument BFB Tuning

Method 524.2 requires BFB tuning and evaluation to test instrument performance. A standard solution of 4-bromofluorobenzene (BFB) was analyzed and the spectra compared to the abundance criteria listed in the method. The BFB standard was prepared by spiking 10 µL of a 50-µg/mL BFB standard into 10 ml of organic-free water and injected into the headspace. The results in Table 3 demonstrate the ability of the integrated system to pass the BFB test.

Table 3.   BFB Evaluation Results

Target mass	Rel. to mass	Lower limit%	Upper limit%	Rel. abn%	Raw abn	Result pass/fail
50	95	15	40	18	951	Pass
75	95	30	60	39.8	2100	Pass
95	95	100	100	100	5272	Pass
96	95	5	9	7.8	410	Pass
173	174	0	2	0.3	14	Pass
174	95	50	100	88.6	4671	Pass
175	174	5	9	8.2	385	Pass
176	174	95	101	98.3	4591	Pass
177	176	5	9	6	275	Pass

Preparation of Calibration and Spiking Sample

Twenty-five microliters of 2000 µg/mL EPA 502/524 VOC standard (SUPELCO) was added to less than 10 mL methanol in a 10-mL volumetric flask and methanol added to the flask to the 10-mL line. This diluted a secondary standard-stock solution at a concentration of 5 µg/mL to 0.5 µg/mL. VOC-free water was used to prepare the final water-standard solution. For all caibration levels, 10 mL of water standard solution were added to each headspace vial.

All water samples and calibration water standards were spiked with internal standards. The internal standard solution was prepared by adding 250 µL of 2000-µg/mL mix (SUPELCO) to less than 10 mL methanol in a 10-mL volumetric flask and filling the balance with methanol. This made a final concentration of 50 µg/mL. A 10-µL amount of 50 µg/mL internal standard solution was added to each sample and water standard.

Table 4.   Preparation of Calibration Sample

Calibration level	Water standard concentration in 10 mL water	Secondary standard stock solution added into 10ml water	Secondary standard stock solution concentration in methanol
1	1 µg/L	20 µL	0.5 µg/mL
2	2 µg/L	40 µL	0.5 µg/mL
3	5 µg/L	100 µL	0.5 µg/mL
4	20 µg/L	40 µL	5 µg/mL
5	50 µg/L	100 µL	5 µg/mL
6	100 µg/L	200 µL	5 µg/mL
7	200 µg/L	400 µL	5 µg/mL

Results

Fast LTM column separation

Low thermal mass (LTM) technology has been proven to deliver fast gas chromatogram separation in many applications. The rapid heating and cooling of LTM technology provides an ultra fast GC method with a narrow column Agilent DB624 20 m × 0.18 mm, 1.0 µm column. Figure 1 shows the TIC chromatogram at 20 µg/L VOC standards mix showing good separation for 54 target compounds in less than 9 minutes. Compared to other methods for the analysis of VOCs in water using purge and trap with the Agilent series 5975 MSD [3], the method described here provides shorter cycle times. LTM technology provides fast heating and cooling, reducing the cycle time per sample to 13 min depending upon environmental temperature. For a typical environmental temperature of 25 °C, the cooling down time from 220 °C to 50 °C is about 3 minutes.
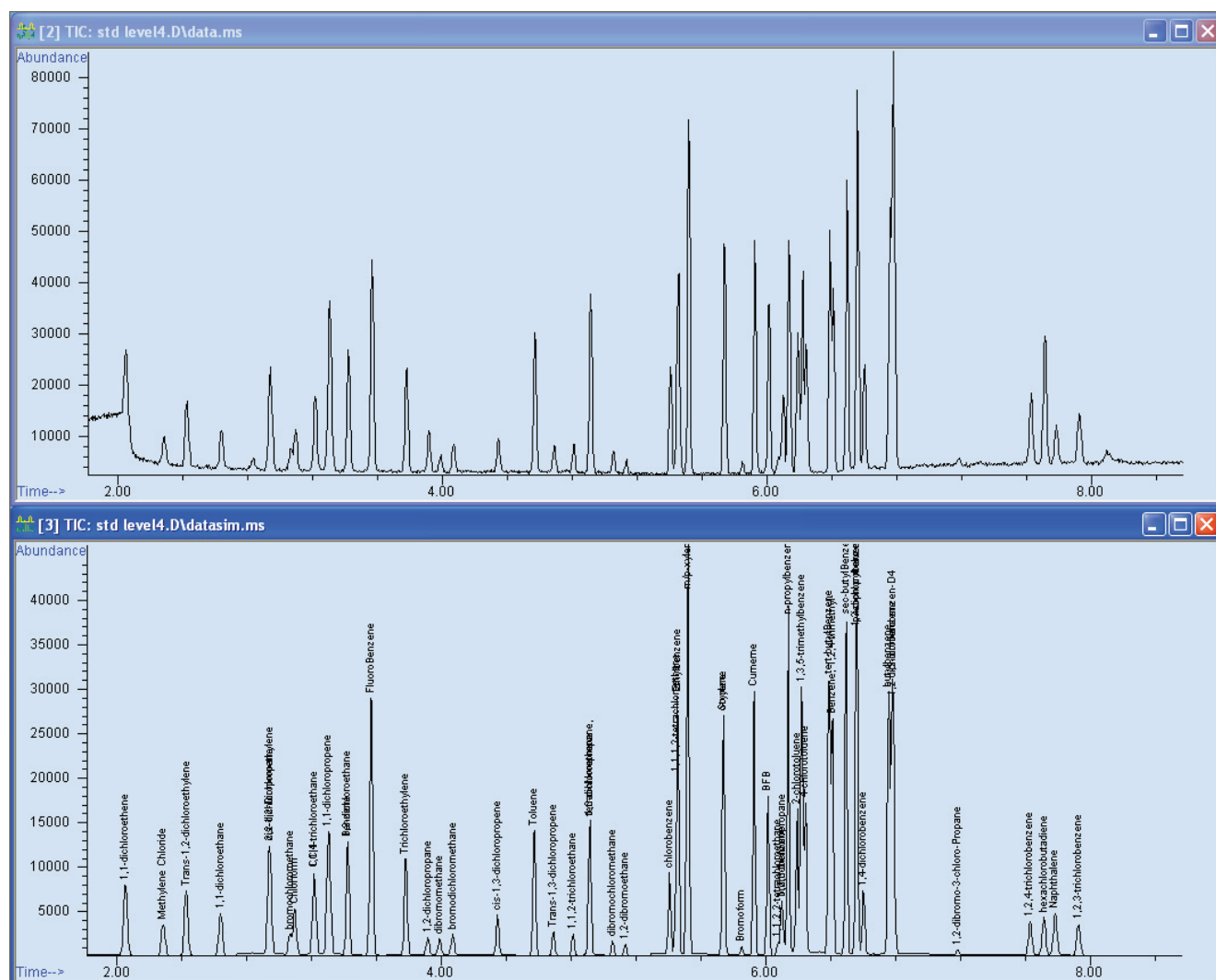

Figure 1.   Twenty micrograms per liter of VOC standards mix in 10 mL water with 50 µg/L of internal standards (Scan and SIM).

Calibration

The calibration data presented here are the results of seven level standards, specifically 1.0, 2.0, 5.0, 20.0, 50.0, 100 and 200 µg/L (a range of 200) in 10 mL of water. Each calibration standard contains 50 µg/L of internal standards. The average RF and %RSD of the RFs were calculated for each compound over the 1–200 µg/L range. As shown in Table 5, all the %RSD results are much less than 15%, which meets the EPA 524.2 criteria. An example of a calibration curve is provided here in Figure 2.
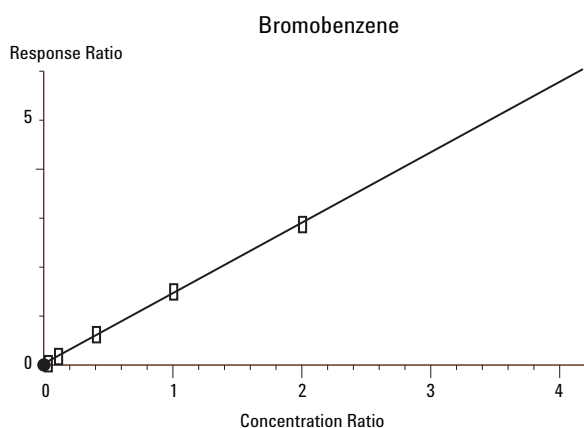
Method Detection Limit

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero (EPA 524.2). It is determined with seven repeated measurements of the target compound at a concentration near the expected detection limit. The standard deviation is calculated for the seven concentrations, and multiplied by the confidence coefficient 3.14. By employing this approach, seven headspace vials with first calibration level standard solution were prepared to determine the MDL. All the MDL results for 54 target compounds are listed in Table 5.

Figure 2.   Calibration curve for bromobenzene (1-200 µg/L).

Table 5.   Method Performance for VOCs in Water

	Compounds	RT	Ave RF	RSD% (RF) n=7	Calib range (µg/L)	MDL (µg/L)	RSD% (spike) n=5	***Rec range (%)
IS*	FluoroBenzene	3.567	------	------	------	------	------	------
T**	1,1-dichloroEthene	2.052	0.552	6.86	1-200	0.432	3.19%	93-101
T	Methylene Chloride	2.285	0.255	14.48	1-200	0.479	3.34%	90-96
T	Trans-1,2-dichloroethylene	2.424	0.476	4.77	1-200	0.253	0.54%	100-101
T	1,1-dichloroEthane	2.637	0.487	4.96	1-200	0.463	1.44%	99-102
T	cis-1,2-Dichloroethylene	2.936	0.39	3.03	1-200	0.284	2.00%	97-102
T	2,2-dichloropropane	2.941	0.475	5.07	1-200	0.968	5.68%	95-108
T	Bromochloromethane	3.065	0.164	3.81	1-200	0.291	2.39%	92-97
T	Chlorform	3.095	0.443	3.48	1-200	0.278	2.07%	105-110
T	1,1,1-trichloroethane	3.217	0.643	7.79	1-200	0.446	2.25%	102-108
T	1,1-dichloropropene	3.303	0.613	7.59	1-200	0.231	3.71%	99-108
T	CCl4	3.217	0.098	5.5	1-200	0.963	3.33%	99-106
T	1,2-dichloroethane	3.42	0.168	5.09	1-200	0.678	2.00%	92-96
T	Benzene	3.424	1.161	4.1	1-200	0.283	2.10%	99-104
T	Trichloroethylene	3.779	0.508	6.56	1-200	0.679	1.81%	101-106
T	1,2-dichloropropane	3.913	0.197	2.59	1-200	0.924	1.59%	99-103
T	Dibromomethane	3.988	0.104	4.2	1-200	0.717	2.67%	98-104
T	Bromodichloromethane	4.067	0.233	2.61	1-200	0.301	2.65%	98-103

Table 5. Method Performance for VOCs in Water (continued)

T	cis-1,3-dichloropropene	4.347	0.246	2.01	1-200	0.362	1.86%	98-102
T	Toluene	4.57	1.384	1.25	1-200	0.438	0.81%	101-103
T	Trans-1,3-ichloropropene	4.688	0.179	2.74	1-200	0.411	2.20%	98-103
T	1,1,2-trichloroethane	4.811	0.123	4.91	1-200	0.960	2.58%	99-105
T	1,3-dichloropropane	4.917	0.198	3.44	1-200	0.271	2.51%	99-105
T	Tetrachloroethene	4.912	0.601	6.9	1-200	0.320	1.85%	104-109
T	Methane, dibromochloro-	5.056	0.145	4.09	1-200	0.762	2.78%	93-99
T	1,2-dibromoethane	5.134	0.108	5.54	1-200	0.906	2.83%	100-107
T	Chlorobenzene	5.407	0.738	2.52	1-200	0.474	1.65%	101-105
T	1,1,1,2-tetrachloroethane	5.444	0.214	1.86	1-200	0.441	1.73%	100-104
T	Ethylbenzene	5.455	1.593	6.38	1-200	0.285	1.23%	101-104
T	m/p-xylene	5.52	2.321	6.53	1-200	0.414	1.04%	102-105
T	o-xylene	5.734	1.062	4.95	1-200	0.436	1.21%	102-105
T	Styrene	5.743	0.651	6.36	1-200	0.843	1.16%	100-102
T	Bromoform	5.852	0.075	6.71	1-200	0.282	1.46%	92-95
T	Cumeme	5.925	1.76	8.41	1-200	0.240	1.27%	102-105
IS	BFB	6.013	------	------	------	------	------	------
T	1,1,2,2-tetrachloroethane	6.075	0.286	7.57	1-200	0.335	4.18%	99-108
T	Benzene, bromo-	6.095	1.166	2.06	1-200	0.566	2.44%	99-105
T	1,2,3-trichloropropane	6.1	0.402	3.28	1-200	0.374	3.11%	98-106
T	Propylbenzene	6.138	7.23	8.19	1-200	0.444	3.83%	97-106
T	2-chlorotoluene	6.194	3.24	3.34	1-200	0.602	1.87%	99-104
T	1,3,5-trimethylbenzene	6.219	4.497	9.63	1-200	0.301	2.14%	97-102
T	4-chlorotoluene	6.244	3.359	7.66	1-200	0.612	1.29%	99-102
T	tert-butylBenzene	6.387	5.363	12.94	1-200	0.495	2.63%	98-104
T	1,2,4-trimethylbenzene	6.412	4.077	8.84	1-200	0.395	1.46%	97-101
T	sec-butylBenzene	6.496	7.815	13.02	1-200	0.252	3.52%	97-105
T	1,3-dichlorobenzene	6.561	2.102	5.03	1-200	0.306	1.70%	98-102
T	p-isopropyltoluene	6.561	6.029	13.13	1-200	0.199	2.72%	96-103
T	1,4-dichlorobenzene	6.601	1.98	4.46	1-200	0.945	2.06%	98-103
T	1,2-dichlorobenzene	6.791	1.606	2.93	1-200	0.874	1.93%	98-103
T	Butylbenzene	6.758	5.96	11.98	1-200	0.264	3.67%	94-102
IS	1,2-dichlorobenzen-D4	6.78	------	------	------	------	------	------
T	1,2-dibromo-3-chloropropane	7.184	0.034	7.82	1-200	0.237	2.04%	103-109
T	1,2,4-trichlorobenzene	7.633	0.414	4.17	1-200	0.348	2.26%	102-108
T	hexachlorobutadiene	7.715	0.471	7.08	1-200	0.305	2.70%	101-108
T	Naphthalene	7.788	0.576	5.12	1-200	0.213	1.95%	99-104
T	1,2,3-trichlorobenzene	7.928	0.329	4.56	1-200	0.360	1.13%	101-104

*IS means internal standard
**T means target compounds
***Recovery range

Recovery and Repeatability

Method recoveries were measured by analyzing unspiked and spiked water samples. VOC mix standards were spiked into running water at a concentration of 25 µg/L in 10 mL of water. Five parallel spiked samples were analyzed in sequence by the same method to evaluate the repeatability. The RSD (%) of the five measured results for each target compounds was calculated (Table 3). All the RSD (%) were below 6%. Recovery was calculated by the following formula:

Recovery (%) =
$$\frac{(\text{conc.of spiked sample} - \text{conc.of unspiked sample})}{(\text{conc.added } (25\mu g/L))} \times 100$$

Recovery ranges of five runs for each target compounds are listed in Table 3, illustrating that all the recovery results ranged from 90% to 110%.

DRS Report

Agilent's Deconvolution Reporting Software (DRS) is an advanced tool that identifies analytes in the presence of overlapped matrix peaks. This significantly reduces the risk of both false positives and false negatives. It can be used with fast chromatography to shorten analysis times because chromatographic resolution requirements reduces as well. A new deconvolution reporting library of 54 VOCs was created and applied in this application using Agilent DRS Software according to the steps described in the technical overview "Building Agilent GC/MSD Deconvolution Reporting Libraries for Any Application" [4]. The DRS report shown in Table 6 can be run in less than 1 min. This saves data analysis time during onsite screening and identification.

Conclusions

An ultra fast method was developed for the Agilent 5975T LTM GC/MSD and Agilent 7694E Headspace Sampler for environmental mobile labs. The cycle time required per sample is reduced by 40% compared to previous work in traditional labs. Data analysis time is also reduced with the use of DRS.

The test results of this study demonstrated that the Agilent 7694E headspace sampler and transportable Agilent 5975T LTM GC/MSD can be used for the determination of VOCs in drinking water, meeting all calibration and MDL criteria specified in EPA Method 524.2.

Table 6.   Partial DRS Report for Spiked Water Sample.

MSD Deconvolution Report   Adjacent Peak Subtraction = 1
Sample Name: spike1   Resolution = Medium
Data File: C:\msdchem\2\DATA\DB624 20m\HS\sample   Sensitivity = High
spike1.D   Shape Requirements = Medium
Date/Time: 4:45:56 PM Tuesday, August 17, 2010
The Nist library was searched for the components that were found in the AMDIS target library.

| R.T. | Cas# | Compound name | Amount (ppb) | | AMDIS | | NIST | |
			Chem station	AMDIS	Match	R.T. Diff sec.	Reverse match	Hit num.
2.0491	75354	1,1-Dichloroethene	24.11		99	0.0	92	3
2.2847	75092	Dichloromethane	24.4		96	0.6	95	1
2.4221	156605	1,2-Dichloroethene (trans)	26.21		98	0.6	94	1
2.6364	75343	1,1-Dichloroethane	25.26		95	0.2	93	1
2.8393	109875	Dimethoxymethane			85	-0.0	62	75

References

1. "Methods for the Determination of Organic Compounds in Drinking Water", Method 524.2, U.S. Environmental Protection Agency

2. "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)", Method 8260, U.S. Environmental Protection Agency

3. Philip L.Wylie, "Developing an eMethod for the Analysis of Volatile Organic Compounds in Water Using Purge and Trap/GC with Agilent's New 5975 inert Mass Spectrometer", Agilent Technologies, publication 5989-3347EN

4. Xiaofei Ping, "Building Agilent GC/MSD Deconvolution Reporting Libraries for Any Application", Agilent Technologies, publication 5989-2249EN

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem

www.agilent.com/chem

Agilent Technologies