Application Note #281753

A Complete Solution for the Analysis of Volatile Organic Compounds (VOCs) in Water

The Scion SQ single quadrupole mass spectrometer, in combination with the Tekmar Atomx™ automated purge-and-trap sample concentrator, demonstrates excellent performance for routine analysis of volatile organic chemicals (VOCs) in drinking water. The Scion SQ's high sensitivity, scan speed, and easy to use software are distinct advantages enabling laboratories to easily meet and/or exceed EPA Method 524.3 requirements.

Introduction

Demand for lower detection limits of volatile organic compounds in drinking water requires the use of a mixed mode GC/MS analysis, i.e. simultaneous full scan and selected ion monitoring (SIM) for low-level quantitation. USEPA Method 524.3 requires a full scan analysis in addition to SIM for specified target analytes.

The Scion SQ has a unique feature known as Compound Based Scanning (CBS) for easy automated setup and optimization of complex mixed mode methods. CBS makes use of libraries that store all the essential information about a compound, such as retention time, time window, qualifier and quantifier ions. Compounds are loaded directly into a method, scan times are optimized, and data acquisition and processing tables are synchronized. Managing large numbers of SIMs in mixed mode is easy.

Experimental

The Scion SQ was set up with a Tekmar Atomx™ purge-and-trap sample concentrator to achieve a highly automated and robust solution for VOC analysis.

The purge-and trap and GC parameters are listed in Tables 1a-c. The purge-and-trap conditions for drinking water come factory installed on the Atomx. A split ratio of 1:100 was used on the gas chromatographic inlet along with a BR-624 ms column (20 m x 0.25 mm x 1.0 um).

Table 1a

Variable	Value	Variable	Value
Valve Oven Temp.	150°C	Sample Preheat Time	1.00 min.
Transfer Line Temp.	150°C	Preheat Temp.	40°C
Sample Mount Temp.	60°C	Purge Time	11.00 min.
Condenser Ready Temp.	40°C	Purge Flow	40 mL/min
Condenser Purge Temp.	20°C	Dry Purge Time	0.00 min.
Pre-purge Flow	40 mL/min.	Desorb Preheat Temp	245°C
GC Start	Start of Desorb	Desorb Time	1.00 min.
Bake Time	7.00 min.	Desorb Temp	250°C
Bake Temp.	260°C	Desrob Flow	100 mL/min.
Bake Flow	300 mL/min.	Condenser Bake Temp.	200°C

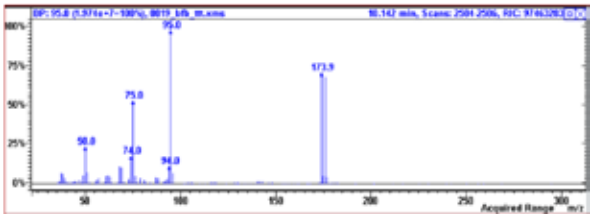
Tekmar Atomx conditions.

Table 1b

Oven	Rate	Hold	Total
Temperature, °C	°C/min	(min)	(min)
35.0	0.00	2.00	2.00
170.0	10.00	0.00	15.50
240.0	50.00	1.00	17.90

GC oven program.

Figure 1



m/z	Acceptance Criteria	Value	PASS/FAIL
50	15-40% of mass 95	23.0	PASS
75	30-80% of mass 95	52.4	PASS
95	Base peak	100.0	PASS
96	5-9% of mass 95	6.1	PASS
173	< 2% of mass 174	0.5	PASS
174	> 50% of mass 95	70.0	PASS
175	5-9% of mass 174	6.1	PASS
176	> 95% but < 101% of mass 174	97.3	PASS
177	5-9% of mass 95	6.1	PASS

Bromofluorobenzene (BFB) Tuning Criteria after Tune-to-Target.

Calibration standards were prepared at 0.1, 0.5, 1, 2, 5, 10, 20, and 40 ppb with the method preservative. Standards at lower concentrations were required for SIM, typically in the range of 5-100 ppt. A 5 mL sample size was used for the analysis as required by the method.

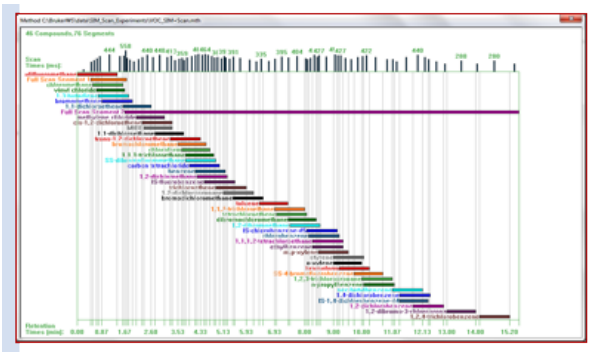
Results

The Scion SQ was tuned to meet method requirements for spectral resolution for Bromofluorobenzene (BFB-Fig. 1) using target ion ratio tuning that is built directly into the software.

Using CBS, a mixed-mode method was created by loading the compounds from a library containing all of the associated SIM ions. A Compound Graph was created, based upon the retention time and retention time window. CBS optimizes the placement of the SIM ions throughout the run for maximum sensitivity and optimal dwell times. As can be seen from Figure 2 below, the full scan segment is also shown in the Compound Graph.

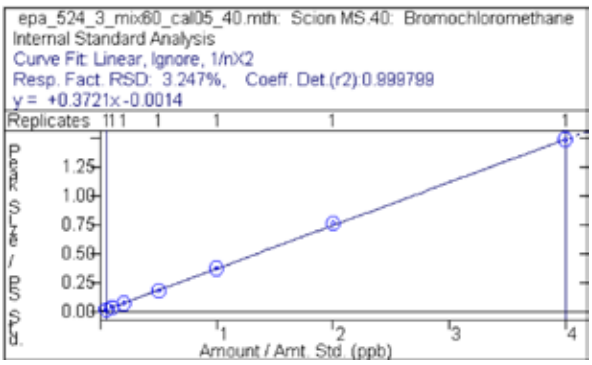
A calibration range from 0.1 to 40 ppb was used for routine quantitative analysis for all target analytes. Average calibration percent RSD and correlation coefficient for Method 524.3 analytes were 7.35% and 0.9991 respectively. Example curve for Bromochloromethane shown in Figure 3. Table 2 has calibration statistics for select compounds in the method.

Figure 2



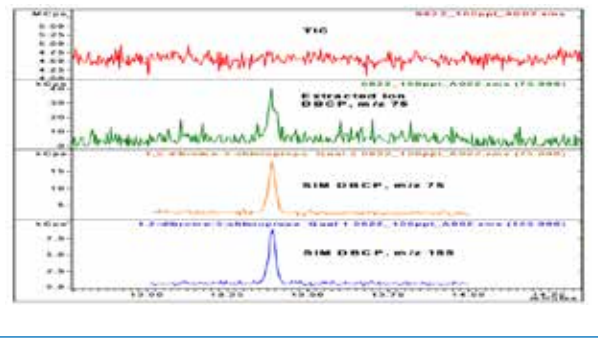
Compound Graph for mixed-mode analysis. Total scan time is represented by a bar graph on the top of the chart.

Figure 3



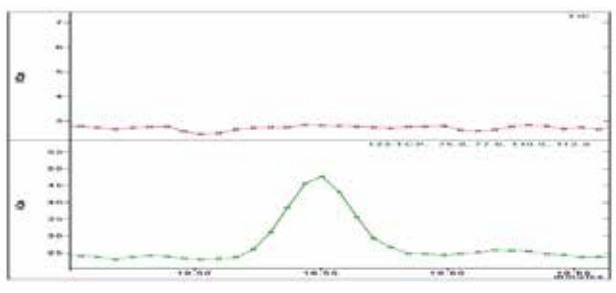
Bromochloromethane calibration curve 0.5-40 ppb full Scan.

Figure 4



SIM analysis during full scan acquisition for DBCP. SIM provides excellent sensitivity for ions m/z 75 and m/z 155 at 100 ppt.

Figure 5



TIC (full scan) for top trace, SIM ions m/z 75, 77, and 110 in bottom trace for 1,2,3-Trichloropropane at 5 ppt.

Table 2

Compound Name	Corr. Coeff.	Avg. RRF	%RSD
Dichlorodifluoromethane	0.9869	0.0733	13.56
Chloromethane	0.9972	0.2829	8.05
Vinyl chloride	0.9986	0.2507	4.81
Bromomethane	0.9968	0.3446	22.04
Chloroethane	0.9982	0.2173	5.38
Trichlorofluoromethane	0.9979	0.2719	6.66
1,1-Dichloroethene	0.9991	0.6014	3.38
Methylene chloride	0.9995	0.3270	1.86
cis-1,2-dichloroethene	0.9996	0.7666	3.49
1,1-Dichloroethane	0.9996	0.6523	2.68
2,2-Dichloropropane	0.9986	0.3364	3.63
trans-1,2-dichloroethene	0.9996	0.9507	2.15
Bromochloromethane	0.9998	0.3645	3.25
Chloroform	0.9999	1.0559	4.64
1,1,1-Trichloroethane	0.9996	0.4772	8.20
Carbon Tetrachloride	0.9994	0.6219	16.29
1,1-Dichloropropene	0.9991	0.5530	5.69
Benzene	0.9995	1.2990	1.68
1,2-Dichloroethane	0.9997	0.7074	2.52
Trichloroethene	0.9996	0.9517	4.30
1,2-Dichloropropane	0.9998	0.5672	2.80
Dibromomethane	0.9999	0.1636	8.64
Bromodichloromethane	0.9993	0.6403	15.27
trans-1,3-dichloropropene	0.9995	0.4606	13.60
Toluene	0.9997	1.3013	2.40
cis-1,3-dichloropropene	0.9993	0.4375	15.05
1,1,2-trichloroethane	0.9999	0.3189	2.74
Tetrachloroethene	0.9997	0.6481	4.38
1,3-dichloropropane	0.9999	0.6297	2.13
Dibromochloromethane	0.9968	0.2336	21.61

Compound Name	Corr. Coeff.	Avg. RRF	%RSD
1,2-Dibromoethane (EDB)	0.9999	0.6577	9.37
Chlorobenzene	0.9999	1.1600	2.51
1,1,1,2-Tetrachloroethane	0.9995	0.6940	10.42
Ethylbenzene	0.9999	2.6085	4.04
m,p-Xylene	0.9998	4.6190	5.29
o-Xylene	0.9999	2.3739	5.24
Styrene	0.9998	1.0651	11.14
Bromoform	0.9945	0.1715	22.75
Isopropylbenzene	0.9998	1.7781	6.58
Bromobenzene	0.9999	1.3909	3.64
1,1,2,2-Tetrachloroethane	0.9997	1.0195	14.87
1,2,3-Trichloropropane	0.9998	1.0271	7.95
trans14Dichloro2butene	0.9995	0.8606	10.12
n-Propylbenzene	0.9998	2.3916	8.03
2-Chlorotoluene	1.0000	1.6695	6.19
4-Chlorotoluene	1.0000	2.0170	6.16
1,3,5-Trimethylbenzene	0.9999	1.4536	9.45
tert-Butylbenzene	0.9997	1.2789	6.37
1,2,4-Trimethylbenzene	0.9998	1.3999	8.65
sec-Butylbenzene	0.9998	1.7028	9.23
1,3-Dichlorobenzene	1.0000	0.6896	4.52
p-Isopropyltoluene	0.9999	3.1700	5.76
1,4-Dichlorobenzene	0.9999	1.8504	3.67
1,2-Dichlorobenzene	1.0000	1.8145	2.97
n-Butylbenzene	0.9998	3.6870	8.03
1,2-Dibromo-3-chloropropane (DBCP)	0.9951	0.5154	17.88
1,2,4-Trichlorobenzene	0.9998	1.6642	3.14
Hexachlorobutadiene	0.9997	0.4132	6.25
Naphthalene	0.9996	3.0391	6.65
1,2,3-Trichlorobenzene	1.0000	1.6357	3.14

Calibration statistics for select VOCs by EPA 524.3 on Scion SQ.

Method detection limits (MDLs) in Tables 3a and 3b were obtained by perfroming seven replicate injections and using the following equation from Section 9.2.6 of EPA Method 524.3:

DL = S x t(n-1,1-α= 0.99)

Where t(n-1,1-α= 0.99) = Student's t value for the 99% confidence level with n-1 degrees of freedom (for seven replicate determinations, the Student's t value is 3.143 at a 99% confidence level), n = number of replicates, and S = standard deviation of replicate analyses.

Table 3a

Parameter	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	mean	sd	Calculated MDL	Target concentration
Dichlorodifluoromethane	0.202	0.203	0.186	0.209	0.201	0.199	0.189	0.198	0.00812	0.026	0.2
Chloromethane	0.175	0.211	0.200	0.202	0.180	0.203	0.182	0.193	0.01395	0.044	0.2
Vinyl chloride	0.201	0.216	0.193	0.206	0.207	0.195	0.180	0.200	0.01166	0.037	0.2
Bromomethane	0.210	0.211	0.253	0.239	0.216	0.215	0.219	0.223	0.01632	0.051	0.2
Chloroethane	0.092	0.073	0.094	0.101	0.090	0.058	0.111	0.088	0.01769	0.056	0.1
Trichlorofluoromethane	0.082	0.119	0.131	0.081	0.110	0.124	0.121	0.110	0.02026	0.064	0.1
1,1-Dichloroethene	0.088	0.078	0.079	0.055	0.073	0.078	0.078	0.073	0.00875	0.028	0.1
Methylene chloride	0.091	0.089	0.096	0.078	0.100	0.096	0.098	0.093	0.00748	0.024	0.1
cis-1,2-dichloroethene	0.074	0.100	0.086	0.090	0.104	0.105	0.103	0.095	0.01166	0.037	0.1
1,1-Dichloroethane	0.091	0.088	0.107	0.094	0.081	0.087	0.102	0.091	0.01008	0.032	0.1
2,2-Dichloropropane	0.089	0.107	0.134	0.081	0.146	0.117	0.099	0.108	0.02748	0.086	0.1
trans-1,2-dichloroethene	0.094	0.155	0.120	0.111	0.125	0.105	0.106	0.117	0.01977	0.062	0.1
Bromochloromethane	0.094	0.091	0.080	0.089	0.091	0.087	0.083	0.085	0.00858	0.027	0.1
Chloroform	0.077	0.110	0.099	0.109	0.103	0.109	0.086	0.099	0.01285	0.040	0.1
1,1,1-Trichloroethane	0.084	0.109	0.109	0.103	0.095	0.112	0.080	0.096	0.01791	0.056	0.1
Carbon Tetrachloride	0.071	0.118	0.100	0.115	0.107	0.110	0.111	0.105	0.01588	0.050	0.1
1,1-Dichloropropene	0.077	0.097	0.082	0.104	0.121	0.106	0.109	0.099	0.01546	0.049	0.1
Benzene	0.078	0.107	0.110	0.086	0.095	0.090	0.094	0.094	0.01127	0.035	0.1
1,2-Dichloroethane	0.103	0.088	0.096	0.102	0.096	0.102	0.096	0.098	0.00524	0.016	0.1
Trichloroethene	0.077	0.107	0.081	0.087	0.087	0.109	0.085	0.090	0.01253	0.039	0.1
1,2-Dichloropropane	0.087	0.091	0.088	0.081	0.114	0.105	0.112	0.094	0.01726	0.054	0.1
Dibromomethane	0.093	0.096	0.081	0.102	0.112	0.104	0.110	0.100	0.01072	0.034	0.1
Bromodichloromethane	0.071	0.113	0.103	0.088	0.105	0.105	0.091	0.097	0.01421	0.045	0.1
trans-1,3-dichloropropene	0.076	0.080	0.079	0.066	0.073	0.089	0.080	0.078	0.00709	0.022	0.1
Toluene	0.087	0.094	0.093	0.095	0.102	0.098	0.091	0.091	0.01136	0.036	0.1
cis-1,3-dichloropropene	0.090	0.096	0.104	0.082	0.094	0.101	0.100	0.095	0.0075	0.024	0.1
1,1,2-trichloroethane	0.084	0.079	0.093	0.097	0.086	0.123	0.108	0.093	0.01892	0.059	0.1
Tetrachloroethene	0.088	0.112	0.098	0.093	0.127	0.127	0.119	0.106	0.02146	0.067	0.1
1,3-dichloropropane	0.082	0.078	0.097	0.110	0.097	0.087	0.093	0.092	0.01077	0.034	0.1
Dibromochloromethane	0.111	0.104	0.107	0.110	0.125	0.109	0.105	0.110	0.00703	0.022	0.1

Table 3a

Parameter	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	mean	sd	Calculated MDL	Target concentration
1,2-Dibromoethane (EDB)	0.103	0.106	0.121	0.100	0.092	0.092	0.110	0.103	0.01026	0.032	0.1
Chlorobenzene	0.090	0.109	0.117	0.113	0.106	0.112	0.099	0.107	0.00929	0.029	0.1
1,1,1,2-Tetrachloroethane	0.094	0.117	0.124	0.125	0.120	0.113	0.104	0.114	0.01131	0.036	0.1
Ethylbenzene	0.066	0.094	0.106	0.097	0.099	0.097	0.086	0.092	0.01298	0.041	0.1
m,p-Xylene	0.070	0.110	0.102	0.105	0.118	0.109	0.100	0.102	0.01531	0.048	0.1
o-Xylene	0.100	0.113	0.125	0.121	0.103	0.104	0.108	0.111	0.0095	0.030	0.1
Styrene	0.083	0.090	0.093	0.083	0.101	0.101	0.069	0.089	0.01137	0.036	0.1
Bromoform	0.091	0.099	0.091	0.086	0.080	0.074	0.093	0.088	0.00844	0.027	0.1
Isopropylbenzene	0.067	0.113	0.114	0.098	0.104	0.112	0.098	0.101	0.01642	0.052	0.1
Bromobenzene	0.113	0.109	0.099	0.099	0.117	0.124	0.115	0.111	0.00928	0.029	0.1
1,1,2,2-Tetrachloroethane	0.117	0.106	0.108	0.099	0.120	0.102	0.084	0.105	0.01201	0.038	0.1
1,2,3-Trichloropropane	0.085	0.081	0.068	0.075	0.081	0.076	0.055	0.074	0.01016	0.032	0.1
trans14Dichloro2butene	0.093	0.101	0.094	0.096	0.111	0.106	0.081	0.097	0.00978	0.031	0.1
n-Propylbenzene	0.087	0.114	0.107	0.103	0.112	0.124	0.106	0.108	0.01139	0.036	0.1
2-Chlorotoluene	0.066	0.089	0.090	0.067	0.075	0.093	0.076	0.079	0.01121	0.035	0.1
4-Chlorotoluene	0.073	0.104	0.084	0.081	0.081	0.102	0.093	0.088	0.01166	0.037	0.1
1,3,5-Trimethylbenzene	0.088	0.095	0.104	0.099	0.090	0.120	0.104	0.100	0.01082	0.034	0.1
tert-Butylbenzene	0.083	0.114	0.109	0.116	0.116	0.128	0.111	0.111	0.01376	0.043	0.1
1,2,4-Trimethylbenzene	0.082	0.099	0.096	0.096	0.108	0.100	0.086	0.095	0.00877	0.028	0.1
sec-Butylbenzene	0.062	0.130	0.104	0.110	0.111	0.115	0.093	0.104	0.02147	0.067	0.1
1,3-Dichlorobenzene	0.084	0.122	0.111	0.104	0.098	0.105	0.084	0.101	0.01386	0.044	0.1
p-Isopropyltoluene	0.080	0.143	0.128	0.121	0.108	0.136	0.125	0.120	0.02089	0.066	0.1
1,4-Dichlorobenzene	0.093	0.107	0.085	0.097	0.097	0.094	0.090	0.095	0.00685	0.022	0.1
1,2-Dichlorobenzene	0.091	0.109	0.124	0.113	0.123	0.115	0.093	0.110	0.01323	0.042	0.1
n-Butylbenzene	0.081	0.107	0.119	0.090	0.129	0.124	0.104	0.108	0.01774	0.056	0.1
1,2-Dibromo-3-chloropropane (DBCP)	0.151	0.132	0.107	0.177	0.113	0.118	0.170	0.138	0.02809	0.088	0.1
1,2,4-Trichlorobenzene	0.069	0.072	0.118	0.105	0.105	0.099	0.106	0.096	0.01853	0.058	0.1
Hexachlorobutadiene	0.078	0.108	0.077	0.095	0.095	0.127	0.144	0.103	0.02487	0.078	0.1
Naphthalene	0.083	0.092	0.108	0.098	0.117	0.097	0.096	0.099	0.01098	0.035	0.1
1,2,3-Trichlorobenzene	0.085	0.082	0.099	0.083	0.072	0.099	0.090	0.087	0.00972	0.031	0.1

1,2-Dibromoethane (EDB), 1,2-Dibromo-3-chloropropane (DBCP), and 1,2,3-trichloropropane were quantitated in SIM mode. Figure 4 shows a DBCP analysis for a 100 ppt standard. Extraction of select ions from the TIC result in more noise and higher detection limits when compared to the SIM trace.

1,2,3-Trichloropropane was easily detected at 5 ppt in SIM during mixed-mode acquisition (Figure 5). 1,2,3-Trichloropropane (TCP) requires very low detection limits because it is suspected to be a human carcinogen and is used widely as a chemical intermediate in polymer production and extraction solvents.

Reporting of the samples and quality control is the final step that must be completed by the lab. Scion offers EnviroPro™, a Microsoft Access database that will generate all of the required reports for EPA Method 524, as well as several other methods. Example reports are tune criteria, method detection limit calculations, initial calibration reports, and continuing calibration checks. There are several graphic options available for printing chromatograms and target compounds, as well as unknown peaks (non-target analytes).

Conclusions

The Tekmar Atomx purge-and-trap sample concentrator with the Scion SQ is a total solution for EPA VOC methods. Method set-up for full scan and scan/SIM experiments is easy with unique CBS software. Performance of the system is excellent and exceeds the requirements of EPA method 524.3.

Acknowledgements

Special thanks to Teledyne Tekmar for providing the Atomx™ automated purge-and-trap sample concentrator.

Figure 6

The EnviroPro™ software package for environmental methods in Microsoft Access 2010.

References:

[1] http://www.epa.gov/ogwdw000/methods/pdfs/methods/met524-3.pdf

Authors:

Ed George

Scion Instruments

Fremont, CA · USA
Phone +1 (510) 683-4300
Fax +1 (510) 490-6586
sales@scioninst.com

www.ScionInstruments.com