Application Note: 51899

Latest Advances in the Analysis of Volatile Organic Compounds by Single Quadrupole GC-MS

Jessie Butler, David Steiniger, Eric Phillips, Trisa Robarge, Thermo Fisher Scientific, Austin, TX, USA

Key Words

- ISQ Single Quadrupole GC-MS
- Environmental Analysis
- EPA Method 524.3
- Single Quadrupole GC-MS
- Volatile Organic Compounds

Introduction

A method was developed for the analysis of volatile organic compounds (VOCs) with the Thermo Scientific ISQ single quadrupole GC-MS using quality control requirements based on United States Environmental Protection Agency (EPA) methodologies. This requires integration of a range of instrumentation, from the sample introduction system to the gas chromatograph and mass spectrometer, to the software for data interpretation, analysis and reporting.[1] While the overall process of analyzing VOC is a mature technique, there are continuous innovations that allow laboratories to meet lower detection limits and analyze new compounds to comply with changing regulations, with higher throughput and improved quality.

Experimental Conditions

For this experiment, a standard GC/MS method for VOC analyses was developed according to published quality control and method guidelines. After establishing a baseline of performance according to these guidelines, improvements to the method were tested by combining changes to the chromatography, taking advantage of the performance capabilities of the hardware, and applying a software package developed around routine environmental GC/MS workflows. By combining these techniques, laboratories can achieve an average decrease of 50% of the analyst review time combined with an increased number of samples that can be analyzed during a 12-hour time period.

The ISQ™ GC-MS (Figure 1) was evaluated at a scanning speed of 2,650 u/sec, which represents 10 full scan mass spectra taken per second (scanning *m/z* 35 to 300 in 0.1 sec). An OI Eclipse™ 4660 Purge-and-Trap Sample Concentrator equipped with a sample heater and 4551A autosampler were used to deliver 5 mL of sample for analysis. The internal standard and surrogates were added by the Standard Addition Module (SAM) unit. The calibration curve range was 0.4 µg/L to 40 µg/L in the sample. The on column amount for each compound was .05 ng to 5 ng due to the 40 mL/min split flow during the injection.

Figure 1: ISQ GC-MS

Purge and Trap Parameters	Conditions
Sample Volume:	5 mL
Sample Purge Temperature:	40 °C
Trap:	#10 (Tenax, silica gel, cms)
Purge:	40 mL/min for 11 min
Water Management Temperature:	Purge: 110 °C, Desorb: 0 °C, Bake: 240 °C
Desorb Preheat Temperature:	180 °C
Desorb Temperature:	190 °C for 0.5 min
Bake Rinse Cycles:	twice
Bake Cycle:	210 °C for 10 min

GC-MS Parameters	Conditions
Column:	Thermo Scientific TRACE TR 524 20 m × 0.18 mm, 1.0 µm
Inlet Liner:	P and T adapter kit
Inlet Temperature:	175 °C
Split Flow:	40 mL/min
Column Flow:	25 psi at constant pressure
GC Temperature Program:	40 °C for 4 min, 18 °C/min to 100 °C, 40 °C/min to 230 °C for 5 min
Solvent Delay:	0.5 min before activating filament
MS Source Temperature:	250 °C
Full Scan:	*m/z* 35 to 300
Scan Speed:	2,650 u/sec (0.1 sec)

Table 1: Instrument parameters

Results and Discussion

Peak Shape

EPA Method 524.3 recommended, and allowable, range of values for the purge and trap parameters reduces the cycle time of the purge and trap and minimize the amount of water injected. The shorter desorb time and rapid oven temperature program on a narrow-bore 0.18 mm ID capillary column gives an analysis time of 15 minutes (Figure 2). Improvement in the carrier gas control reduced band broadening of the first 6 gases, resulting in more Gaussian peak shapes (Figure 3). A scan rate of 2,650 u/sec offered excellent precision and was compatible for use with the faster chromatographic method. This, combined with shortened data review times, leads to an increase in productivity as shown in Figure 4.

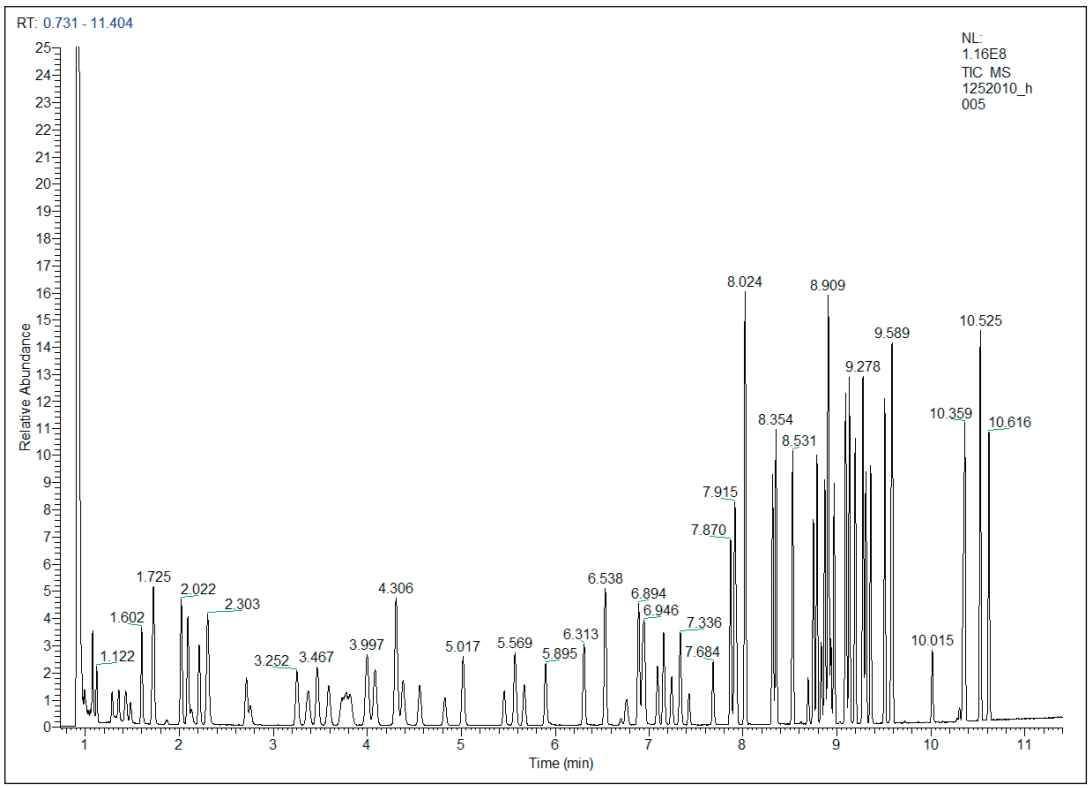

Figure 2: TIC of 20 µg/L standard

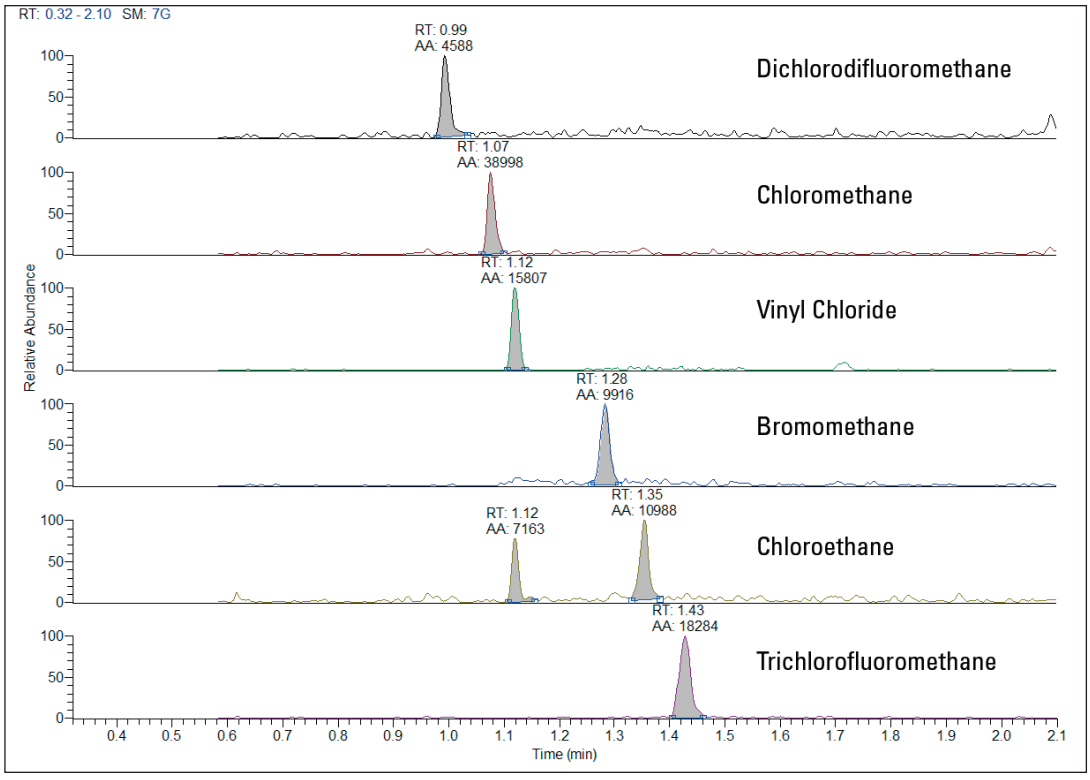

Figure 3: Extracted ion profile of first 6 gases

Calibration Curve

A calibration curve was made from 0.4 to 40 ppb. A 5 mL sample was purged onto a trap using the OI Eclipse 4660 and 4551 liquid autosampler. The internal standard (fluorobenzene) and surrogates (4-bromofluorobenzene and 1,2-dichlorobenzene-d4) were added automatically by the SAM at a final concentration of 5 µg/L. The average %RSD of all compounds was 8 %RSD and the internal standard fluorobenzene was 6 %RSD. The results are shown in Table 2.

Method Detection Limits

Method Detection Limits (MDLs) were generated by analyzing seven replicates at 0.4 µg/L in organic free water or .05 ng to the mass spectrometer. The average MDL was 0.104 µg/L. The results are shown in Table 3.

Conclusions

Improvements to the method were tested by combining changes to the chromatography, employing the capabilities of the hardware, and applying a software package developed around routine GC/MS workflows. By combining these techniques, laboratories can achieve an average decrease of 50% of the analyst review time combined with an increased number of samples that can be analyzed during a 12-hour time period while also attaining lower MDLs. All of these improvements resulted in doubling the throughput of samples analyzed in a 12-hour time period – from 24 to 48 samples. The ISQ single quadrupole GC-MS was evaluated and found to provide good sensitivity, spectral purity, and linear dynamic range for the method.

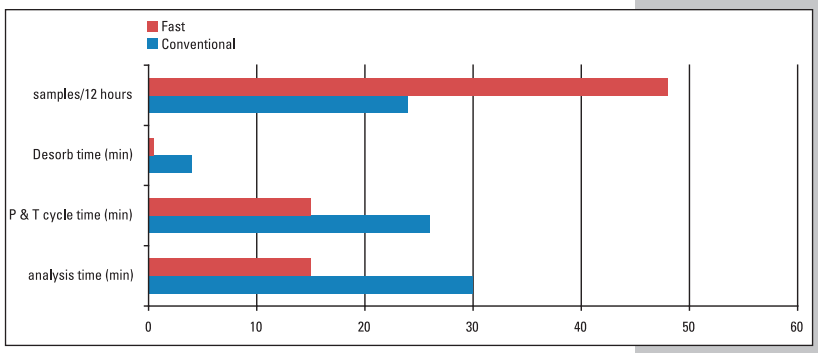

Figure 4: Reduction of analysis time

References

1. EPA Method 524.3 Measurement of Purgeable Organic Compounds in Water by Capillary Column gas Chromatography/Mass Spectrometry, U.S. Environmental Protection Agency, Cincinnati, OH, Version 1, June 2009

	% RSD		% RSD		% RSD
dichlorodifluoromethane	10	methacrylonitrile	9	styrene	8
chloromethane	8	1,2-dichloroethane	7	isopropylbenzene	10
vinylchloride	8	fluorobenzene (ISTD)	6	4-bromofluorobenzene (surr)	5
bromomethane	10	trichloroethylene	5	bromobenzene	4
chloroethane	9	dibromomethane	10	n-propylbenzene	5
trichlorofluoromethane	10	1,2-dichloropropane	6	1,1,2,2-tetrachloroethane	7
diethylether	7	bromodichloromethane	6	2-chlorotoluene	3
1,1-dichloroethylene	7	methyl methacrylate	9	1,2,3-trichloropropane	4
carbon disulfide	14	*cis*-1,3-dichloropropene	9	1,3,5-trimethylbenzene	7
allyl chloride	6	toluene	7	*trans*-1,4-dichloro-2-butene	5
methylene chloride	7	chloroacetonitrile	5	4-chlorotoluene	8
trans-1,2-dichloroethylene	10	1,1-dichloro-2-propanone	8	p-isopropyltoluene	8
methyl tert-butyl ether	6	tetrachloroethylene	10	tert-butylbenzene	11
1,1-dichloroethane	5	2-nitropropane	9	1,2,4-trimethylbenzene	7
acrylonitrile	11	4-methyl-2-pentanone	9	pentachloroethane	4
cis-1,2-dichloroethylene	7	*trans*-1,3-dichloropropene	10	sec-butylbenzene	12
2,2-dichloropropane	13	1,1,2-trichloroethane	9	1,3-dichlorobenzene	12
bromochloromethane	5	ethyl methacrylate	6	1,4-dichlorobenzene	8
chloroform	6	dibromochloromethane	11	n-butylbenzene	3
carbon tetrachloride	10	1,3-dichloropropane	9	hexachloroethane	10
tetrahydrofuran	7	1,2-dibromoethane	8	1,2-dichlorobenzene	9
methyl acrylate	9	2-hexanone	5	1,2-dichlorobenzene d4 (surr)	6
1,1,1-trichloroethane	5	chlorobenzene	8	1,2-dibromo-3-chloropropane	5
1,1-dichloropropylene	7	ethylbenzene	6	nitrobenzene	10
1-chlorobutane	9	1,1,1,2-tetrachloroethane	5	hexachlorobutadiene	8
2-butanone	9	m&p-xylene	5	1,2,4-trichlorobenzene	12
benzene	6	o-xylene	6	naphthalene	10
propionitrile	11	bromoform	4	1,2,3-trichlorobenzene	6

Table 2: Calibration curve results (0.4, 2, 4, 20 µg/L)

	Avg Conc (µg/L)	Std Dev	% RSD	MDL (µg/L)		Avg Conc (µg/L)	Std Dev	% RSD	MDL (µg/L)
dichlorodifluoromethane	0.34	0.016	5	0.051	2-nitropropane	0.41	0.035	8	0.109
chloromethane	0.43	0.028	7	0.087	4-methyl-2-pentanone	0.41	0.031	8	0.098
vinylchloride	0.4	0.02	5	0.062	*trans*-1,3-dichloropropene	0.38	0.021	5	0.065
bromomethane	0.45	0.047	11	0.148	1,1,2-trichloroethane	0.4	0.022	5	0.069
chloroethane	0.45	0.077	17	0.242	ethyl methacrylate	0.37	0.022	6	0.069
trichlorofluoromethane	0.41	0.039	9	0.121	dibromochloromethane	0.37	0.027	7	0.084
diethylether	0.45	0.031	7	0.097	1,3-dichloropropane	0.38	0.019	5	0.059
1,1-dichloroethylene	0.42	0.049	12	0.154	1,2-dibromoethane	0.38	0.019	5	0.061
carbon disulfide	0.43	0.032	7	0.099	2-hexanone	0.47	0.061	13	0.193
allyl chloride	0.42	0.041	10	0.13	chlorobenzene	0.39	0.016	4	0.052
methylene chloride	0.46	0.032	7	0.101	ethylbenzene	0.4	0.019	5	0.059
acetone*	4.79	0.399	8	1.255	1,1,1,2-tetrachloroethane	0.42	0.038	9	0.119
trans-1,2-dichloroethylene	0.41	0.046	11	0.144	m&p-xylene	0.79	0.041	5	0.13
methyl tert-butyl ether	0.42	0.019	4	0.058	o-xylene	0.4	0.009	2	0.03
1,1-dichloroethane	0.42	0.027	7	0.085	bromoform	0.37	0.047	13	0.147
acrylonitrile	0.41	0.036	9	0.115	styrene	0.39	0.017	5	0.055
cis-1,2-dichloroethylene	0.41	0.029	7	0.092	isopropylbenzene	0.39	0.018	5	0.057
2,2-dichloropropane	0.38	0.026	7	0.083	4-bromofluorobenzene (surr)	5.27	0.234	4	0.735
bromochloromethane	0.39	0.042	11	0.131	bromobenzene	0.4	0.029	7	0.092
chloroform	0.41	0.021	5	0.066	n-propylbenzene	0.39	0.02	5	0.064
carbon tetrachloride	0.42	0.03	7	0.096	1,1,2,2-tetrachloroethane	0.38	0.022	6	0.069
tetrahydrofuran	0.48	0.087	18	0.272	2-chlorotoluene	0.4	0.022	6	0.069
methyl acrylate	0.39	0.041	11	0.128	1,2,3-trichloropropane	0.41	0.017	4	0.053
1,1,1-trichloroethane	0.43	0.035	8	0.112	1,3,5-trimethylbenzene	0.39	0.018	5	0.057
1,1-dichloropropylene	0.39	0.03	8	0.093	*trans*-1,4-dichloro-2-butene	0.4	0.025	6	0.078
2-butanone	0.52	0.099	19	0.31	4-chlorotoluene	0.36	0.014	4	0.045
1-chlorobutane	0.35	0.096	28	0.302	p-isopropyltoluene	0.36	0.014	4	0.045
benzene	0.4	0.011	3	0.036	tert-butylbenzene	0.36	0.012	3	0.039
propionitrile	0.43	0.062	14	0.194	1,2,4-trimethylbenzene	0.4	0.017	4	0.053
methacrylonitrile	0.42	0.053	13	0.166	pentachloroethane	0.4	0.051	13	0.16
1,2-dichloroethane	0.4	0.024	6	0.076	sec-butylbenzene	0.39	0.017	4	0.053
fluorobenzene (ISTD)			5		1,3-dichlorobenzene	0.44	0.013	3	0.042
trichloroethylene	0.41	0.025	6	0.077	1,4-dichlorobenzene	0.52	0.019	4	0.061
dibromomethane	0.39	0.05	13	0.156	n-butylbenzene	0.39	0.017	4	0.054
1,2-dichloropropane	0.4	0.026	7	0.082	hexachloroethane	0.37	0.019	5	0.059
bromodichloromethane	0.38	0.024	6	0.075	1,2-dichlorobenzene	0.42	0.025	6	0.078
methyl methacrylate	0.38	0.032	8	0.099	1,2-dichlorobenzene d4 (surr)	5.44	0.435	8	1.369
cis-1,3-dichloropropene	0.38	0.024	6	0.077	1,2-dibromo-3-chloropropane	0.38	0.046	12	0.144
toluene	0.38	0.008	2	0.025	nitrobenzene	0.02	0.046	19	0.144
chloroacetonitrile	0.31	0.086	28	0.27	hexachlorobutadiene	0.39	0.039	10	0.122
1,1-dichloro-2-propanone	0.35	0.082	23	0.257	1,2,4-trichlorobenzene	0.42	0.023	5	0.071
tetrachloroethylene	0.39	0.079	20	0.248	naphthalene	0.38	0.012	3	0.038
* lab air contamination					1,2,3-trichlorobenzene	0.42	0.025	6	0.079

Table 3: Method detection limits (7 replicates at 0.4 µg/L)

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa-Other
+27 11 570 1840

Australia
+61 3 9757 4300

Austria
+43 1 333 50 34 0

Belgium
+32 53 73 42 41

Canada
+1 800 530 8447

China
+86 10 8419 3588

Denmark
+45 70 23 62 60

Europe-Other
+43 1 333 50 34 0

Finland/Norway/ Sweden
+46 8 556 468 00

France
+33 1 60 92 48 00

Germany
+49 6103 408 1014

India
+91 22 6742 9434

Italy
+39 02 950 591

Japan
+81 45 453 9100

Latin America
+1 561 688 8700

Middle East
+43 1 333 50 34 0

Netherlands
+31 76 579 55 55

New Zealand
+64 9 980 6700

South Africa
+27 11 570 1840

Spain
+34 914 845 965

Switzerland
+41 61 716 77 00

UK
+44 1442 233555

USA
+1 800 532 4752

www.thermoscientific.com

Legal Notices: *©2010 Thermo Fisher Scientific Inc. All rights reserved. OI Eclipse is a trademark of OI Corporation All other trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific Inc. products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.*

ISO 9001 REGISTERED COMPANY

Thermo Fisher Scientific, Austin, TX USA is ISO Certified.

AN51899_E 05/10M