EPA Method 524.2 Volatile Organics in Drinking Water

This method is an example of EPA Method 524.2 Drinking Water analysis using the Shimadzu QP-2010 GC/MS. This Method is suitable to identify and quantitate volatile organics at low levels in aqueous matrix. The Environmental Protection Agency requires that this analysis be performed in compliance with the protocol specified in the United Stated Federal Register 40 CFR, and this method is not meant to replace this criteria.

The following is an example of the instrument setup and the performance achieved under these conditions in accordance with Method 524.2. For specific information to customize your application, contact your local Shimadzu representative or our corporate technical support staff.

Experimental

Equipment

This analysis was performed using the Shimadzu QP-2010 Mass-Spectrometer, the standard GC-2010 Gas Chromatograph with Advanced Flow Control, the Tekmar 3100 Purge and Trap and Aqua Tek 70 Water Autosampler.

Using the standard SPL-2010 split/splitless injection port on the GC-2010 as a gas flow splitter, the Method was performed with a Shimadzu 3.4mm. id. liner. These results were obtained using a 20m X 0.18mm X .5 um phase VRX column from Restek Corporation.

Standards

The Standards were prepared in accordance with the Method specifications and transferred to 40mL vials for sampling. The concentrations used for the 5ml injection volumes were .25ppb – 10ppb. The internal standards and surrogates were held constant at 5ppb. During the sampling, the water was spiked with the Internal Standards and Surrogates and transferred to the Purge and Trap. The calibration curve was run and the results processed to determine the RSD for each compound in the target analyte list.

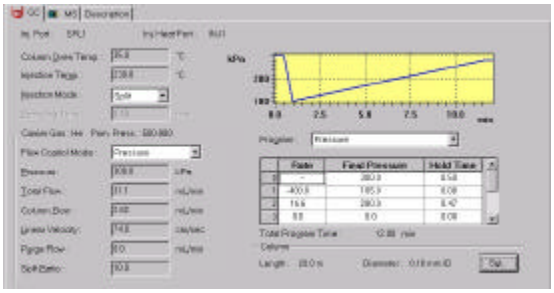
Mass-Spectrometer

The QP-2010 method file setup specified that the mass filter was to be scanned and data acquired from mass 35 to mass 260. The scan rate was set to scan the chromatographic peaks 10-15 times for the narrowest chromatographic peak.

GC

The GC-2010 was set up with a multi-rate temperature profile and the Advanced Flow Control was programmed to provide a constant flow from the column into the mass spectrometer ion source. The last peak eluted in less than 10.5 minutes.

GC Control Display



QC

After the QP-2010 was tuned using the Automatic tuning function, the qualification standard of 1µL of a 5µg/mL Bromoflourobenzene (BFB) solution was purged and the instrument passed all ion criteria requirements.

Next, the Initial Calibration Curve was acquired and processed. The day following the Initial Calibration Curve acquisition, a Continuing Calibration Standard was injected after a fortified laboratory blank and all compounds met the stability criteria. Lastly, a detection limit study was performed following 524.2 Method criteria.

Tuning

Normal spectrum testing of the system is required for every 8 hours of operation. Any time the responses for the spectrum of the acceptance testing criteria compound Bromoflourobenzene do not fall within the range of acceptable deviations shown, maintenance or adjustment is required to conform to the method criteria.

Tuning results achieved by performing this analysis and meeting the method criteria are in the table show to the right. The tune stability was tested and showed consistent tune, passing the acceptance criteria for over 30 calibration check standards. No readjustment of the hardware to correct the instrument spectral generation was required. When readjustment is required, the automatic tuning software resets the optics parameters to the required levels to reestablish the results shown above.

m/z	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
50	15.0 - 40.0% of mass 95	20.2
75	30.0 - 60.0% of mass 95	40.4
95	Base peak, 100% relative abundance	100.0
96	5.0 - 9.0% of mass 95	6.5
173	Less than 2.0 of mass 174	0.0 (0.0)1
174	50.0 - 100.0% of mass 95	81.6
175	5.0 - 9.0% of mass 174	4.5 (5.5)1
176	95.0 - 101.0% of mass 174	98.9
177	5.0 - 9.0% of mass 176	5.0 (6.2)2

1 - Value is % mass 174 2 - Value is % mass 176

Results

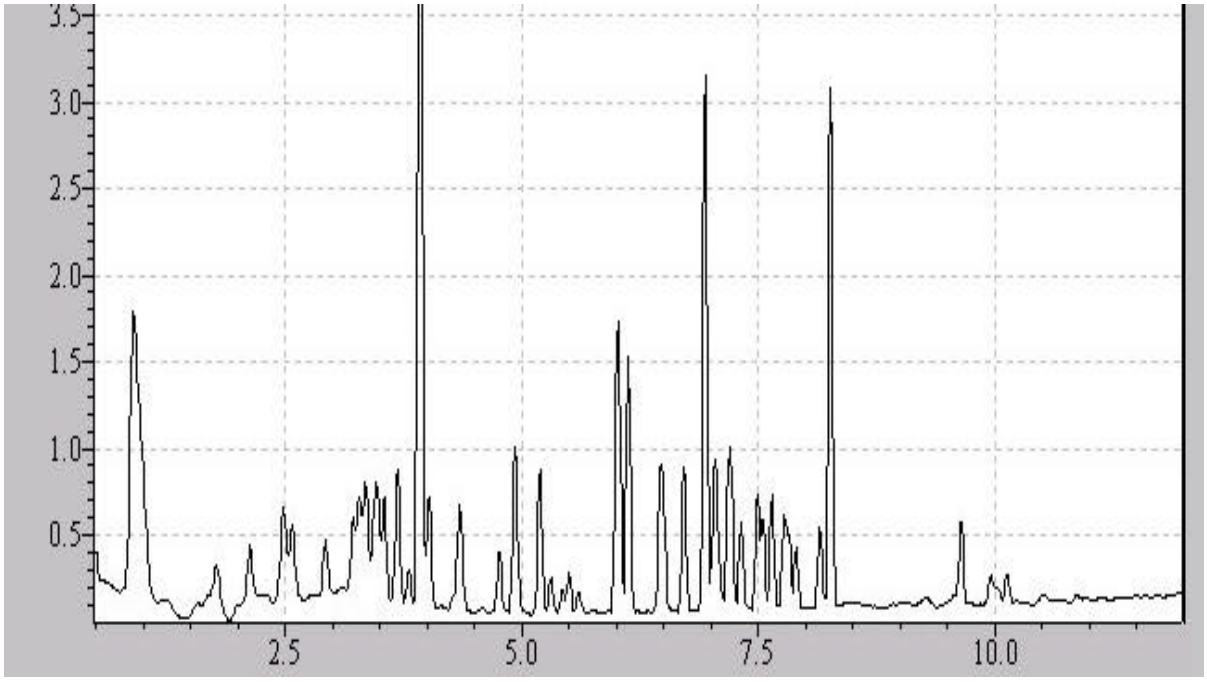


Figure 1: Chromatogram of 0.5ppb calibration standard for Method 524.2 on the QP-2010 GC/MS

Quality Control Data

		RRF	%RSD	%Dev			RRF	%RSD	%Dev
1	dichlorodifluoromethane	0.093	10.71	-16.3	32	1,2-dibromoethane	0.129	9.9	-3.774
2	chloromethane	0.164	5.34	-8.32	33	chlorobenzene	0.826	9.46	3.741
3	vinyl chloride	0.246	9.02	-6.05	34	m,p-xylene	0.477	9.26	-0.941
4	bromomethane	0.149	11.13	-4.43	35	1,1,1,2-tetrachloroethane	0.466	11.23	6
5	chloroethane	0.013	6.99	4.545	36	ethylbenzene	1.82	11.65	-5.041
6	trichloroflouromethane	0.028	6.06	-11.6	37	o-xylene	0.878	10.25	2.094
7	1,1-dichloroethane	0.662	8.81	1.17	38	styrene	0.61	11.56	-0.351
8	methylene chloride	0.22	8.72	-15.3	39	bromoform	0.057	19.2	2.174
9	trans-1,2-dichloroethene	0.332	8.16	-4.29	40	isopropylbenzene	1.14	9.72	-0.78
10	1,1-dichloroethene	0.255	11.34	4.202	41	Bromoflourobenzene-Surr	0.343	0.91	5.831
11	cis-1,2-dichloroethene	0.545	6.37	-2.8	42	bromobenzene	0.201	8.01	0
12	2,2-dichloropropane	0.576	11.82	-8.19	43	n-propylbenzene	1.05	10.29	-6.793
13	bromochloromethane	0.097	9.05	4.255	44	1,1,2,2-tetrachloroethane	0.12	9.59	-9.836
14	chloroform	0.638	8.88	-0.32	45	2-chlorotoluene	0.809	7.17	-7.143
15	carbon tetrachloride	0.585	10.29	5.682	46	1,2,3-trichloropropane	0.136	8.96	6.667
16	1,1,1-trichloroethane	0.639	9.12	0	47	1,3,5-trimethylbenzene	0.732	8.44	-4.091
17	1,1-dichloropropene	0.52	9.18	-1.06	48	4-chlorotoluene	0.594	7.24	-6.022
18	benzene	1.339	7.62	-6.3	49	tert-butylbenzene	0.664	5.32	-0.508
19	1,2-dichloroethane	0.32	8.96	0	50	1,2,4-trimethylbenzene	0.589	5.66	-0.687
20	fluorobenzene IS				51	sec-butylbenzene	0.787	8.53	-2.712
21	trichloroethene	0.371	7.4	-4.07	52	4-isopropyltoluene	0.658	9.8	-0.412
22	dibromomethane	0.097	9.38	-4	53	1,3-dichlorobenzene	0.287	7.39	-2.767
23	1,2-dichloropropane	0.298	9.84	-1.84	54	1,4-dichlorobenzene	0.271	8.11	-0.833
24	bromodichloromethane	0.341	11.13	0	55	n-butylbenzene	0.583	8.67	-12.15
25	cis-1,3-dichloropropene	0.401	10.66	-2.17	56	1,2-dichlorobenzene-d4 Surr	0.195	9.6	9.312
26	toluene	1.476	7.21	-5.71	57	1,2-dichlorobenzene	0.252	12.89	4.211
27	trans-1,3-dichloropropene	0.286	9.93	-0.8	58	1,2-dibromo-3-chloropropane	0.019	11.78	9.091
28	tetrachloroethene	0.298	8.36	-2.73	59	hexachlorobutadiene	0.129	12.09	-0.581
29	1,1,2-trichloroethane	0.114	11.27	-3.33	60	1,2,4-trichlorobenzene	0.124	6.18	2.439
30	dibromochloromethane	0.165	11.2	8.235	61	naphthalene	0.219	8.66	0.671
31	1,3-dichloropropane	0.277	10.05	2.83	62	1,2,3-trichlorobenzene	0.101	10.29	4.762

Calibration

The above table shows the results of calibration for levels of a five-point curve from .5 ppb. to 10 ppb. To achieve the results shown by the process used, first establish the chromatography and integration parameters based on repeated injection of the low standard. Then inject the high standard and adjust the multiplier/detector voltage to a level that ensures that the ion intensities for the high standard approach the instrument's electrical saturation point. This setting is then used to create the method offset voltage for comparison to the automatic tuning voltage result and thereby ensures that when the ion optics are adjusted the system is returned to operating parameters in the shortest possible time. The graphic below shows the chromatography of the gases for the next to the lowest standard.

RSD values for all compounds were shown to be well within the method requirements for all compounds.

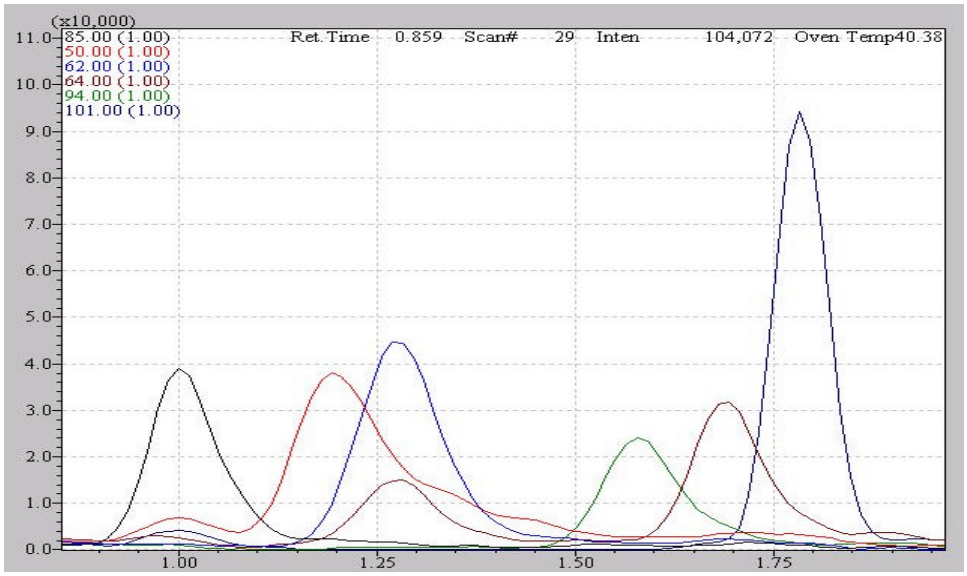


Figure 2: Shows the chromatography of the first six gas compounds at the 0.5ppb concentration level

Detection Limit Study

The table below shows the detection limit results for this analysis setup with 1ppb and 7 replicates SD times 3.143

Compound	1	2	3	4	5	6	7	8	stddev	Det limit
dichlorodifluoromethane	0.481	0.437	0.4470	0.426	0.436	0.444	0.433	0.490	0.023396	0.07014
chloromethane	0.384	0.336	0.3600	0.368	0.44	0.448	0.358	0.434	0.043346	0.129951
vinyl chloride	0.284	0.301	0.2910	0.313	0.308	0.339	0.333	0.326	0.019744	0.059194
bromomethane	0.254	0.28	0.3130	0.314	0.256	0.309	0.301	0.342	0.030573	0.091657
chloroethane	0.310	0.301	0.3060	0.281	0.313	0.350	0.363	0.353	0.029347	0.087983
trichloroflouromethane	0.248	0.2585	0.25929	0.22737	0.27854	0.27392	0.27507	0.294	0.020639	0.061874
1,1-dichloroethene	0.26812	0.24866	0.22565	0.22747	0.28116	0.26293	0.26525	0.253	0.019568	0.058666
methylene chloride	0.22493	0.2709	0.23301	0.25356	0.25999	0.25326	0.28337	0.306	0.026249	0.078695
trans-1,2-dichloroethene	0.22657	0.22308	0.22368	0.21921	0.23109	0.21913	0.2411	0.24537	0.009858	0.029555
1,1-dichloroethane	0.2043	0.198	0.23818	0.19888	0.23225	0.22186	0.24308	0.25199	0.021094	0.063241
cis-1,2-dichloroethene	0.19698	0.20727	0.19132	0.19015	0.19557	0.21785	0.23282	0.21055	0.014809	0.044397
2,2-dichloropropane	0.16699	0.19288	0.17254	0.15734	0.17428	0.17557	0.17612	0.17588	0.00997	0.029891
bromochloromethane	0.21649	0.1949	0.2301	0.20458	0.25413	0.2043	0.23788	0.23378	0.02025	0.060709
chloroform	0.24773	0.23961	0.24516	0.22871	0.23659	0.25799	0.26171	0.25798	0.011705	0.035093
carbon tetrachloride	0.18622	0.1938	0.21615	0.20435	0.22362	0.20082	0.20734	0.2171	0.012581	0.037716
1,1,1-trichloroethane	0.21617	0.21061	0.2261	0.19002	0.2236	0.22335	0.21786	0.21705	0.011471	0.03439
1,1-dichloropropene	0.22083	0.20938	0.22759	0.19515	0.22363	0.2519	0.25522	0.25314	0.022104	0.066267
benzene	0.20716	0.21919	0.23189	0.20735	0.23376	0.24066	0.24132	0.24598	0.015336	0.045976
1,2-dichloroethane	0.185	0.18596	0.2047	0.183	0.19714	0.22093	0.20858	0.21484	0.014508	0.043494
fluorobenzene IS										
trichloroethene	0.237	0.22939	0.25637	0.22829	0.24548	0.24014	0.26253	0.27305	0.016104	0.04828
dibromomethane	0.222	0.20858	0.1969	0.17613	0.204	0.191	0.18926	0.20227	0.013848	0.041516
1,2-dichloropropane	0.205	0.2012	0.23812	0.201	0.213	0.23577	0.2217	0.24982	0.018722	0.056129
bromodichloromethane	0.174	0.1897	0.203	0.18463	0.207	0.208	0.18994	0.199	0.011907	0.035697
cis-1,3-dichloropropene	0.188	0.18623	0.18371	0.17849	0.197	0.18318	0.19595	0.19228	0.006521	0.019549
toluene	0.225	0.22692	0.24413	0.18695	0.247	0.24214	0.25116	0.25835	0.022547	0.067595
trans-1,3-dichloropropene	0.17132	0.17376	0.1936	0.17132	0.196	0.20202	0.18283	0.18618	0.011894	0.035658
tetrachloroethene	0.21207	0.20027	0.20889	0.18608	0.23917	0.224	0.184	0.23518	0.020763	0.062246
1,1,2-trichloroethane	0.17687	0.18896	0.23037	0.20524	0.218	0.17615	0.20383	0.20252	0.018974	0.056884