

Keywords

Volatile Organic Compounds (VOCs)
Purge-and-Trap (P&T)
USEPA Method 502.2
USEPA Method 8021B
Eclipse Purge-and-trap Sample Concentrator
Photoionization Detector (PID)
Electrolytic Conductivity Detector (ELCD)
pHDetect
Tandem PID/ELCD
Appendix B to Part 136 in the Federal Register

USEPA Methods 502.2 and 8021B using the Eclipse Purge-and-Trap (P&T) Sample Concentrator and PID/ELCD Tandem Detectors

Introduction

In 1986 the United States Environmental Protection Agency (USEPA) introduced Method 502.2 ⁽¹⁾ to monitor the levels of 60 aromatic and halogenated volatile organic compounds (VOCs) in drinking water. Some of the volatile contaminants on this list are halogen-containing VOCs, and others contain aromatic properties. The unique characteristics of these components make them excellent candidates to be extracted by purge-and-trap (P&T) technique and analyzed by a photoionization detector (PID) interfaced with an electrolytic conductivity detector (ELCD).

This application note describes instrumentation and analytical conditions that can be used to detect and quantify all 60 VOCs in Method 502.2 as well as Method 8021B ⁽²⁾ using P&T with PID/ELCD tandem selective detectors. Data presented includes all instrument operating parameters, representative chromatograms and analyte retention times for the PID and ELCD detectors, calibration results, accuracy and precision studies, a method detection limit (MDL) study, and analysis of a representative US drinking water.

Instrumentation

Instrumentation used for this study included an OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator equipped with a patented⁽³⁾ Infra-Sparge™ sample heater (Figure 1), a 4551A Vial autosampler, and an Agilent 6890 GC equipped with OI PID/ELCD tandem detectors.



Figure 1. Eclipse Purge-and-Trap Sample Concentrator with 4551A Vial Autosampler, Standard Addition Module (SAM), and *pHDetect* Module

Chromatography

Initially, a 105-meter mega-bore capillary column was used for USEPA methods 502.2 and 8021B, and required a run time of more than 55 minutes to separate all compounds with baseline resolution. Now, the same results can be achieved using a shorter column with a typical run time of approximately 32 minutes. The column and operating conditions used to analyze the compounds on the USEPA Method 502.2 list are described in Table 1. A description of the standards used for this method is shown in Table 2.

Table 1. Equipment Configuration and Instrument Operating Conditions

Purge-and-Trap	Eclipse 4660 Sample Concentrator
Autosampler	OI Analytical 4551A Vial Autosampler
Trap	OI Analytical #10 Trap (Tenax®/silica/cms)
Purge Time	11 minutes
Sample Temperature During Purge	40 °C
Desorb Preheat	On, 180 °C
Desorb Time	1 minute
Desorb Temperature	190 °C
Bake Time	10 minutes
Bake Temperature	240 °C
Water Management	110 °C at Purge/0 °C at Desorb/240 °C at Bake
Gas Chromatograph	Agilent 6890
Column (Restek)	Rtx-VGC, 75 m x 0.45-mm ID x 2.55- μ m film thickness
Carrier gas	He
Inlet Temperature	220 °C
Column Flow	11.0 mL/minute
Split Ratio	9:1
Gas Saver	ON
Saver Time	2.0 minutes
Oven Program	35 °C for 4 minutes 21 °C/minute to 175 °C (0 minutes) 35 °C/minute to 205 °C (7 minutes) Total GC Time = 31.95 minutes
Detectors	OI PID/ELCD Tandem Detectors
Detector Temperature	220 °C
PID Makeup Gas	He, 25 mL/minute
PID Sweep Gas	H ₂ , 100 mL/minute
PID Lamp Intensity	10 eV, setting 5
Reactor Temperature	1,000 °C
ELCD Mode	Halogen

Table 2. Sample Description

Target Compound List	USEPA Method 502.2 (all 60 compounds)
Sample Size	5-mL
Internal Standard	Fluorobenzene and 1-Chloro-2-fluorobenzene
Calibration Standards	6-point curve ranging from 0.5 to 100 ppb
MDL Study	Eleven, 5-mL aliquots with concentration of 1.0 ppb
Precision and Accuracy Standard	Ten, 5-mL aliquots with concentration of 10 ppb

The individual compounds are identified by their retention times (RT) on one or both detectors. Confirmation information is gained by comparing simultaneous response on the tandem detectors. Retention times for all the compounds on the PID and ELCD tandem detectors are shown in Table 3. Representative chromatograms of a 25-ppb standard using the PID and ELCD tandem detectors are shown in Figure 2.

Table 3. Retention Times (RT) (min.) for 60 VOCs in USEPA Method 502.2 Mix by PID and ELCD following separation on a Rtx-VGC column.

Analyte		Photoionization Detector (PID)		Electrolytic Conductivity Detector (ELCD)	
		Detected	RT (min.)	Detected	RT (min.)
1	Dichlorodifluoromethane	—	—	Yes	2.524
2	Chloromethane	—	—	Yes	2.840
3	Vinyl chloride	Yes	2.998	Yes	3.008
4	Bromomethane	—	—	Yes	3.604
5	Chloroethane	—	—	Yes	3.851
6	Trichlorofluoromethane	—	—	Yes	4.149
7	1,1-Dichloroethene	Yes	5.143	Yes	5.153
8	Methylene chloride	—	—	Yes	6.387
9	trans-1,2-Dichloroethene	Yes	6.746	Yes	6.756
10	1,1-Dichloroethane	—	—	Yes	8.176
11	cis-1,2-Dichloroethene	Yes	9.501	Yes	9.513
12	2,2-Dichloropropane	—	—	Yes	9.791
13	Bromochloromethane	—	—	Yes	10.003
14	Chloroform	—	—	Yes	10.255
15	Carbon tetrachloride	—	—	Yes	10.589
16	1,1,1-Trichloroethane	—	—	Yes	10.766
17	1,1-Dichloropropene	Yes	11.109	Yes	11.119
18	Benzene	Yes	11.780	—	—
19	1,2-Dichloroethane	—	—	Yes	12.352
20	Fluorobenzene (IS)	Yes	13.009	Yes	13.006
21	Trichloroethene	Yes	13.525	Yes	13.538
22	Dibromomethane	—	—	Yes	14.782
23	1,2-Dichloropropane	—	—	Yes	15.118
24	Bromodichloromethane	—	—	Yes	15.391
25	cis-1,3-Dichloropropene	Yes	17.543	—	17.557
26	Toluene	Yes	18.428	Yes	—
27	Tetrachloroethene	Yes	19.903	Yes	19.915
28	trans-1,3-Dichloropropene	Yes	20.073	Yes	20.084
29	1,1,2-Trichloroethane	—	—	Yes	20.523
30	Dibromochloromethane	—	—	Yes	20.959
31	1,3-Dichloropropane	—	—	Yes	21.195
32	1,2-Dibromoethane	—	—	Yes	21.453
33	Chlorobenzene	Yes	22.585	Yes	22.597
34	Ethylbenzene	Yes	22.698	—	—
35	1,1,1,2-Tetrachloroethane	—	—	Yes	22.741
36	m-and p-Xylene	Yes	22.975	—	—
37	1-Chloro-2-fluorobenzene (IS)	Yes	23.348	Yes	23.360
38	o-Xylene	Yes	23.696	—	—
39	Styrene	Yes	23.782	—	—
40	Bromoform	—	—	Yes	23.797

Table 3. Retention Times (RT) (min.) for 60 VOCs in USEPA Method 502.2 Mix by PID and ELCD following separation on a Rtx-VGC column.

Analyte		Photoionization Detector (PID)		Electrolytic Conductivity Detector (ELCD)	
		Detected	RT (min.)	Detected	RT (min.)
41	Isopropylbenzene	Yes	24.211	—	—
42	Bromobenzene	Yes	24.717	Yes	24.735
43	<i>n</i> -Propylbenzene	Yes	24.798	—	—
44	1,1,2,2-Tetrachloroethane	—	—	Yes	24.903
45	2-Chlorotoluene	Yes	24.980	Yes	24.990
46	1,2,3-Trichloropropane	—	—	Yes	25.051
47	1,3,5-Trimethylbenzene	Yes	25.061	—	—
48	4-Chlorotoluene	Yes	25.203	Yes	25.213
49	<i>tert</i> -Butylbenzene	Yes	25.489	—	—
50	1,2,4-Trimethylbenzene	Yes	25.061	—	—
51	<i>sec</i> -Butylbenzene	Yes	25.729	—	—
52	<i>p</i> -Isopropyltoluene	Yes	25.923	—	—
53	1,3-Dichlorobenzene	Yes	26.006	Yes	26.020
54	1,4-Dichlorobenzene	Yes	26.129	Yes	26.138
55	<i>n</i> -Butylbenzene	Yes	26.485	—	—
56	1,2-Dichlorobenzene	Yes	26.702	Yes	26.713
57	1,2-Dibromo-3-chloropropane	—	—	Yes	27.844
58	1,2,4-Trichlorobenzene	Yes	28.803	Yes	28.806
59	Hexachlorobutadiene	Yes	28.872	Yes	28.886
60	Naphthalene	Yes	29.438	—	—
61	1,2,3-Trichlorobenzene	Yes	29.775	Yes	29.786

Peak

- | | |
|--|--|
| 1 Dichlorodifluoromethane | 27 Tetrachloroethene |
| 2 Chloromethane | 28 <i>trans</i> -1, 2-Dichloropropene |
| 3 Vinyl chloride | 29 1, 1, 2-Trichloroethane |
| 4 Bromomethane | 30 Dibromochloromethane |
| 5 Chloroethane | 31 1, 3-Dichloropropane |
| 6 Trichlorofluoromethane | 32 1, 2-Dibromomethane |
| 7 1, 1-Dichloroethene | 33 Chlorobenzene |
| 8 Methylene chloride | 35 1, 1, 1, 2-Tetrachloroethane |
| 9 <i>trans</i> -1, 2-Dichloroethene | 37 1-Chloro-2-fluorobenzene (IS) |
| 10 1, 1-Dichloroethane | 40 Bromoform |
| 11 <i>cis</i> -1, 2-Dichloroethene | 42 Bromobenzene |
| 12 2, 2-Dichloropropane | 44 1, 1, 2, 2-Tetrachloroethane |
| 13 Bromochloromethane | 45 2-Chlorotoluene |
| 14 Chloroform | 46 1, 2, 3-Trichloropropane |
| 15 Carbon tetrachloride | 48 4-Chlorotoluene |
| 16 1, 1, 1-Trichloroethane | 53 1, 3-Dichlorobenzene |
| 17 1, 1-Dichloropropene | 54 1, 4-Dichlorobenzene |
| 19 1, 2-Dichloroethane | 56 1, 2-Dichlorobenzene |
| 20 (IS) | 57 1, 2-Dibromo-3-chloropropane |
| 21 Trichloroethene | 58 1, 2, 4-Trichlorobenzene |
| 22 Dibromomethane | 59 Hexachlorobutadiene |
| 23 1, 2-Dichloropropane | 61 1, 2, 3-Trichlorobenzene |
| 24 Bromodichloromethane | |
| 25 <i>cis</i> -1, 2-Dichloropropene | |

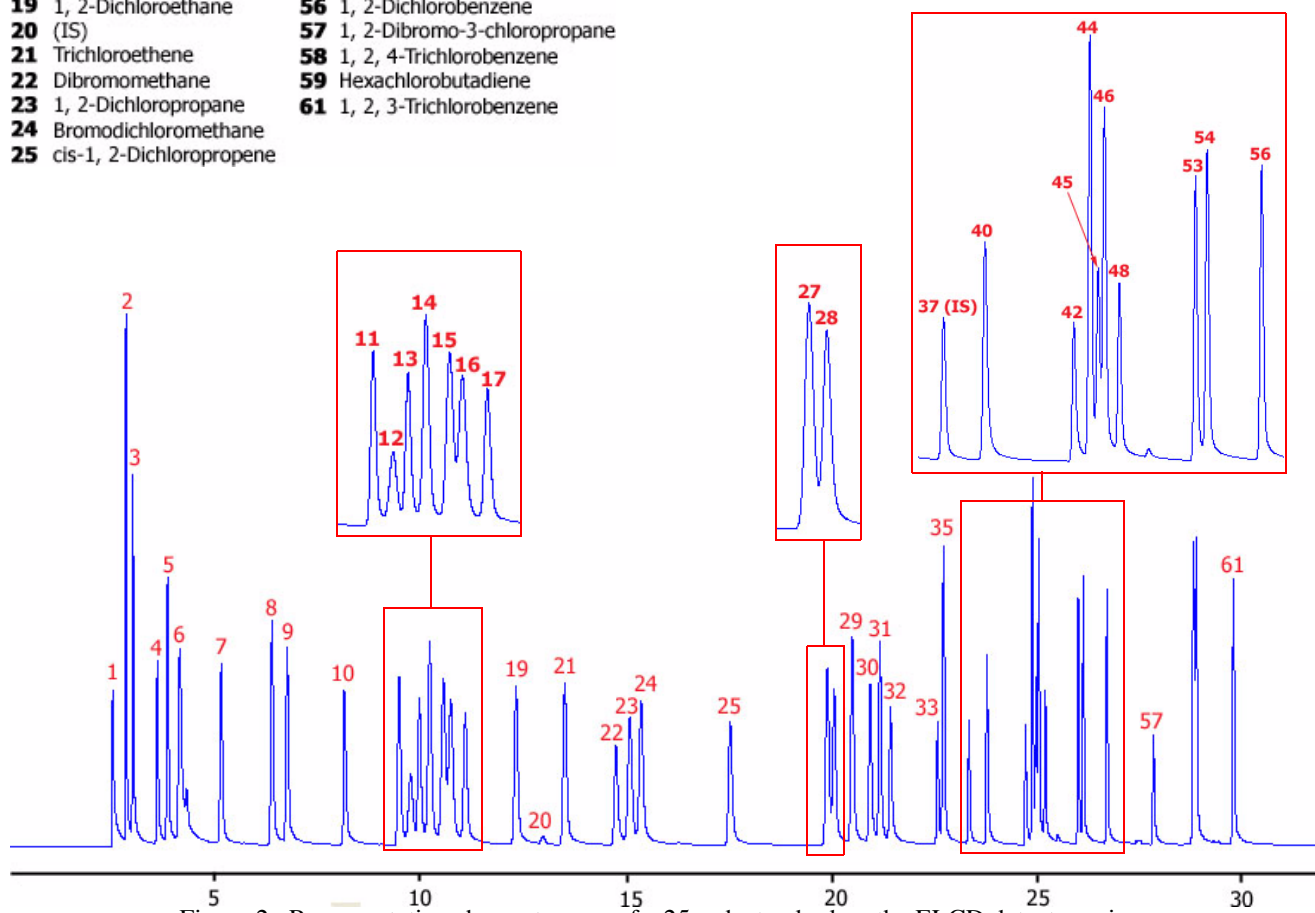


Figure 2. Representative chromatogram of a 25-ppb standard on the ELCD detector using a 75-meter Rtx-VGC column.

Peak

3 Vinyl Chloride	41 Isopropyl benzene
7 1, 1-Dichloroethene	42 Bromobenzene
9 <i>trans</i> -1, 2-Dichloroethene	43 <i>n</i> -Propylbenzene
11 <i>cis</i> -1, 2-Dichloroethene	45 2-Chlorotoluene
17 1, 1-Dichloropropene	47 1, 3, 5-Trimethylbenzene
18 Benzene	48 4-Chlorotoluene
20 Fluorobenzene	49 <i>tert</i> -Butylbenzene
21 Trichloroethene	50 1, 2, 4-Trimethylbenzene
25 <i>cis</i> -1, 3-Dichloropropene	51 <i>sec</i> -Butylbenzene
26 Toluene	52 <i>p</i> -Isobutyltoluene
27 Tetrachloroethene	53 1, 3-Dichlorobenzene
28 <i>trans</i> -1, 2-Dichloropropene	54 1, 4-Dichlorobenzene
33 Chlorobenzene	55 <i>n</i> -Butylbenzene
34 Ethylbenzene	56 1, 2-Dichlorobenzene
36 <i>m</i> & <i>p</i> -Xylene	58 1, 2, 4-Trichlorobenzene
37 1-Chloro-2-Fluorobenzene	
38 <i>o</i> -Xylene	
39 Styrene	

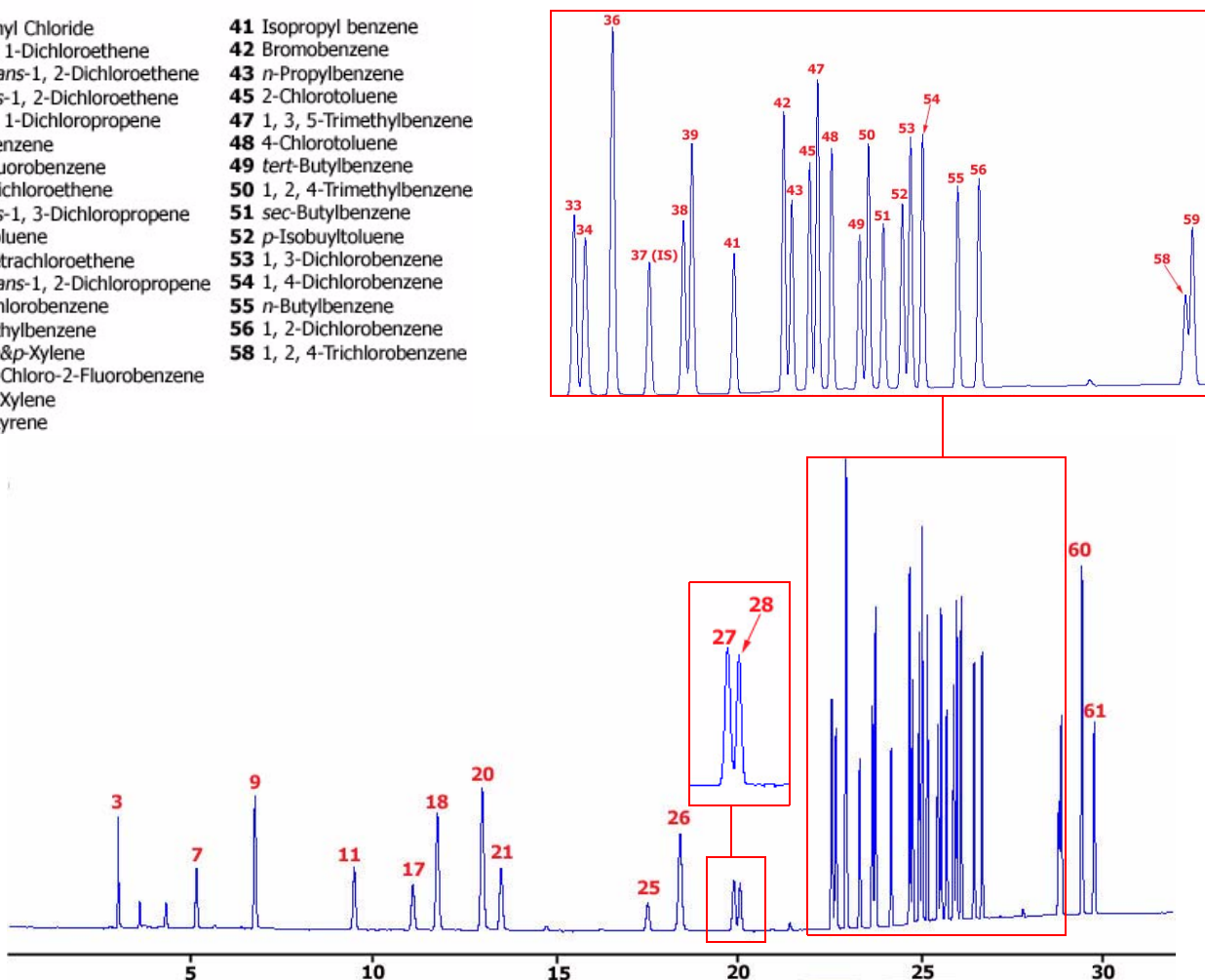


Figure 3. Representative chromatogram of a 25-ppb standard on the PID detector using a 75-meter Rtx-VGC column.

Results and Discussion

The VOCs in USEPA Method 502.2 are classified as aromatic, halogenated, or aromatic with one or more halogen atoms. The PID detects unsaturated VOCs and ELCD detects halogenated VOCs. Together the PID and ELCD detect compounds that contain both unsaturation and halogens. Out of 60 analytes, 16 are selectively detected by the PID, 25 are detected by the ELCD, and 19 can be identified by both the detectors.

Calibration Curve and Method Detection Limit (MDL) Study

To demonstrate the linearity of the method, a 6-point calibration curve ranging from 0.5 to 100 ppb was run following the method requirements outlined in USEPA Method 502.2. All compounds met the quality control criteria specified in Method 502.2 with a correlation coefficient (R^2) value of 0.998 or greater for the linear regression. The calibration range can be adjusted as necessary for individual regulations.

Method detection limits were determined for all analytes on their respective detectors using the student's *t* test and the standard deviation from eleven replicate analyses as described in Appendix B to Part 136 in the Federal Register⁽⁴⁾. All MDLs were found to be well below the target concentrations cited in the regulation when using the instrument conditions described in this study.

Accuracy and Precision Study

The same analytical conditions were applied to determine the accuracy and precision of the method by analyzing 10 aliquots of a standard fortified with all compounds at 10 ppb. Fluorobenzene and 1-Chloro-2-fluorobenzene were used as internal standards at 25 ppb. The average recovery of the analytes measured by PID and ELCD were 99.9% and 98.7% respectively. The compounds detected by PID had a relative standard deviation (RSD) of 3.0% or better with an average RSD of 1.8%. Similarly, the compounds detected by ELCD had a RSD of 5.9% or better with an average RSD of 3.0%. Results from the Calibration Curve, MDL, Accuracy, and precision studies are shown in Table 4.

Table 4. Calibration Curve, Method Detection Limits (MDL), Accuracy, and Precision studies for VOCs for USEPA Method 502.2 Mix.

Analyte		Calibration R ²		MDL (ppb)		Accuracy as %Recovery		Precision as %RSD	
		PID	ELCD	PID	ELCD	PID	ELCD	PID	ELCD
1	Dichlorodifluoromethane		0.999	—	0.06	—	99.5	—	4.5
2	Chloromethane		0.998	—	0.10	—	98.3	—	3.0
3	Vinyl chloride	0.999	0.998	0.09	0.16	98.7	96.5	2.5	2.4
4	Bromomethane		0.999	—	0.20	—	96.1	—	5.4
5	Chloroethane		0.999	—	0.15	—	95.1	—	3.0
6	Trichlorofluoromethane		0.999	—	0.24	—	94.6	—	4.9
7	1,1-Dichloroethene	0.999	0.999	0.22	0.26	99.6	95.9	2.6	4.6
8	Methylene chloride		0.999	—	0.08	—	99.7	—	2.0
9	<i>trans</i> -1,2-Dichloroethene	0.999	0.999	0.05	0.18	99.4	99.6	2.7	4.2
10	1,1-Dichloroethane		0.998	—	0.17	—	98.9	—	2.2
11	<i>cis</i> -1,2-Dichloroethene	0.999	0.998	0.08	0.06	99.3	98.8	1.3	1.7
12	2,2-Dichloropropane		0.999	—	0.13	—	101.7	—	4.7
13	Bromochloromethane		0.999	—	0.06	—	98.6	—	1.4
14	Chloroform		0.998	—	0.06	—	98.5	—	1.9
15	Carbon tetrachloride		0.999	—	0.07	—	99.6	—	2.5
16	1,1,1-Trichloroethane		0.998	—	0.09	—	99.9	—	2.4
17	1,1-Dichloropropene	0.999	0.999	0.18	0.16	101.6	97.5	2.7	5.9
18	Benzene	0.999	—	0.04	—	99.0	—	1.6	—
19	1,2-Dichloroethane		0.999	—	0.08	—	98.4	—	1.9
21	Trichloroethene	0.999	0.998	0.10	0.23	99.7	100.8	3.0	3.5
22	Dibromomethane		0.999	—	0.04	—	100.7	—	2.9
23	1,2-Dichloropropane		0.998	—	0.06	—	99.9	—	2.0
24	Bromodichloromethane		0.998	—	0.14	—	99.4	—	4.5
25	<i>cis</i> -1,3-Dichloropropene	0.994	0.998	0.15	0.10	99.8	99.4	1.0	3.0
26	Toluene	0.999	—	0.08	—	99.3	—	1.8	—
27	Tetrachloroethene	0.999	0.998	0.17	0.07	99.5	100.6	3.2	3.8
28	<i>trans</i> -1,3-Dichloropropene	0.999	0.998	0.16	0.10	99.6	100.5	0.8	1.0
29	1,1,2-Trichloroethane		0.998	—	0.13	—	99.2	—	1.5
30	Dibromochloromethane		0.998	—	0.14	—	99.1	—	1.3
31	1,3-Dichloropropane		0.999	—	0.14	—	99.4	—	1.2
32	1,2-Dibromoethane		0.999	—	0.13	—	97.3	—	4.0
33	Chlorobenzene	0.999	0.999	0.09	0.03	99.7	99.6	1.2	1.9
34	Ethylbenzene	0.999	—	0.06	—	99.5	—	1.8	—
35	1,1,1,2-Tetrachloroethane		0.998	—	0.16	—	99.0	—	2.6
36	<i>m</i> - and <i>p</i> -Xylene	0.999	—	0.14	—	99.7	—	1.9	—
38	<i>o</i> -Xylene	0.999	—	0.05	—	99.2	—	1.5	—

Table 4. Calibration Curve, Method Detection Limits (MDL), Accuracy, and Precision studies for VOCs for USEPA Method 502.2 Mix.

Analyte		Calibration R ²		MDL (ppb)		Accuracy as %Recovery		Precision as %RSD	
		PID	ELCD	PID	ELCD	PID	ELCD	PID	ELCD
39	Styrene	0.999	—	0.06	—	99.5	—	1.3	—
40	Bromoform		0.999	—	0.09	—	99.6	—	3.0
41	Isopropylbenzene	0.999	—	0.19	—	99.7	—	2.1	—
42	Bromobenzene	0.999	0.999	0.44	0.12	99.9	98.6	0.9	3.2
43	<i>n</i> -Propylbenzene	0.999	—	0.44	—	100.2	—	2.0	—
44	1,1,2,2-Tetrachloroethane		0.999	—	0.10	—	98.8	—	1.8
45	2-Chlorotoluene	0.999	0.999	0.43	0.07	100.8	100.1	2.3	2.1
46	1,2,3-Trichloropropane		0.999	—	0.12	—	97.1	—	3.8
47	1,3,5-Trimethylbenzene	0.999	—	0.24	—	100.2	—	1.9	—
48	4-Chlorotoluene	0.999	0.999	0.81	0.28	100.8	101.0	1.6	2.2
49	<i>tert</i> -Butylbenzene	0.999	—	1.08	—	100.3	—	3.3	—
50	1,2,4-Trimethylbenzene	0.999	—	0.36	—	100.1	—	1.7	—
51	<i>sec</i> -Butylbenzene	0.999	—	0.45	—	100.4	—	2.4	—
52	<i>p</i> -Isopropyltoluene	0.999	—	0.55	—	100.3	—	2.2	—
53	1,3-Dichlorobenzene	0.999	0.998	0.20	0.10	100.2	101.7	1.5	4.9
54	1,4-Dichlorobenzene	0.999	0.998	0.26	0.20	100.2	98.6	1.3	4.3
55	<i>n</i> -Butylbenzene	0.999	—	0.60	—	100.5	—	2.7	—
56	1,2-Dichlorobenzene	0.999	0.998	0.16	0.19	99.9	97.9	1.0	3.9
57	1,2-Dibromo-3-chloropropane	—	0.999	—	0.19	—	95.1	—	3.7
58	1,2,4-Trichlorobenzene	0.999	0.998	0.28	0.06	100.5	101.1	1.7	2.9
59	Hexachlorobutadiene	0.999	0.998	0.16	0.09	100.6	99.6	0.6	2.0
60	Naphthalene	0.999	—	0.14	—	99.5	—	1.0	—
61	1,2,3-Trichlorobenzene	0.999	0.998	0.17	0.07	100	98.7	0.5	1.9

pHDetect

The USEPA requires that water samples be preserved with acid to pH less than 2 for USEPA methods 502.2 or 8021B. Replicate samples must be collected in the field solely for measuring the pH. Without the pHDetect option, the analyst opens the extra vial, measures the pH manually, and records the measurement in a log; this procedure is both time-consuming and labor-intensive. Alternatively, the analyst must manually check the pH level of every vial after the VOC analysis is complete. The pHDetect option eliminates the need for collecting additional samples and the labor and materials associated with manual pH measurement. The pHDetect option electronically records all calibrations and sample pH measurements in the Eclipse database with a date and time stamp; the measurements can then be viewed, printed, or exported using the Eclipse Reporter software.

Analysis of Tap Water Sample

A tap water sample was analyzed using conditions defined in Table 1. The PID and ELCD chromatograms from this analysis are shown in Figure 3. Peaks are labeled with the compound name and concentration found.

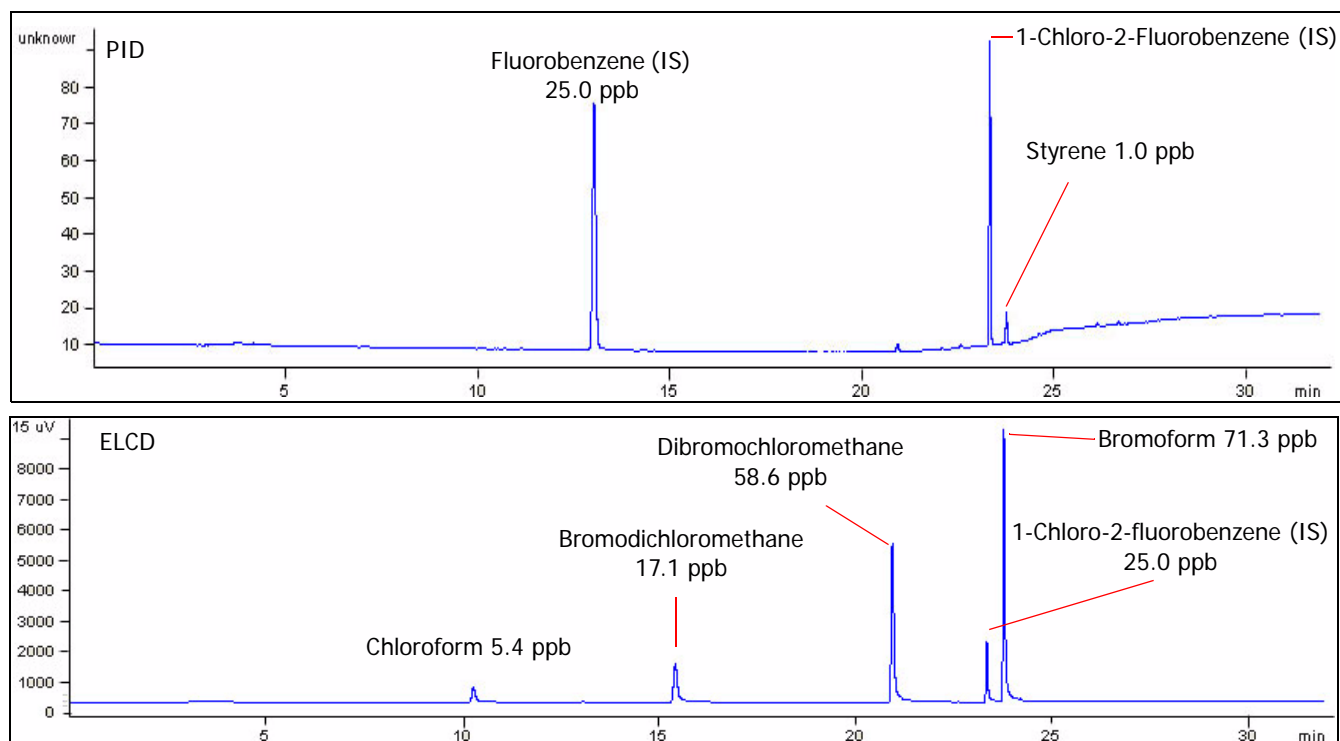


Figure 4. PID and ELCD chromatograms of a tap water sample analyzed using the OI Analytical Eclipse P&T. Peaks are labeled with the compound name and concentration found.

Conclusion

All the 60 analytes of USEPA Method 502.2 or 8021B can be easily extracted by using P&T analyzed by using PID/ELCD tandem detectors. All method requirements were easily met in single 32-minute run using Restek 75-m VGC column reducing analysis time from previous 56-minute run.

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Publication 31630508



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