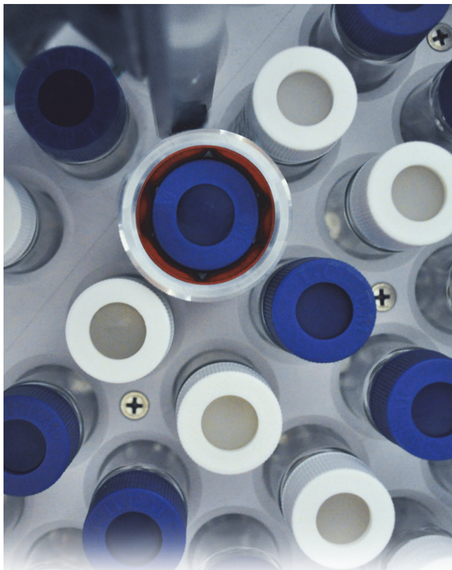

4100 Water / Soil Sample Processor Design & Performance Characteristics

Introduction

Environmental laboratories performing GC-MS analysis of VOCs in drinking water, wastewater, groundwater, soil and sediment samples require a versatile and reliable automation platform to transfer samples to purge-and-trap GC-MS systems. Sample requirements cited in U.S. EPA methods directly affect the design and performance characteristics of VOC analysis autosampler workstations.

This whitepaper presents information on a new water/soil sample processor that meets the operational needs of environmental testing laboratories and fulfills U.S. EPA hardware and quality control requirements. Design and performance characteristics of this new sample processor are presented along with representative data obtained on water and soil samples using USEPA-approved 524.3 and 8260 methods.

Instrument Design

The OI Analytical 4100 Water/Soil Sample Processor (Figure 1) automates the handling and processing of samples in 40-mL VOA vials for purge-and-trap analysis of VOCs in accordance with U.S. EPA methods. The 4100 efficiently processes up to 100 drinking water, wastewater or soil samples and operates with single or dual purge-and-trap instruments.

Figure 1. 4100 Water / Soil Sample Processor

VOA Constrictor™ Vial Gripper

The 4100 is an X-Y-Z robotic platform with digitally controlled linear drive rails for X-Y motions and pneumatically-actuated Z-axis mechanism. A pneumatically-actuated cylindrical vial gripper lifts and transports 40-mL VOA vials to and from water and soil sampling stations. The VOA Constrictor™ gripper mechanism (Figures 2 and 3) surrounds and conforms to each vial ensuring reliable vial handling. Figure 3 shows the VOA Constrictor™ gripper mechanism pressurized without a vial inside.

The unique cylindrical design handles vials with all types of labels and eliminates dropped or broken vials. A built-in sensor enables the gripper to detect and confirm the presence of a vial, or signal if a vial is missing.

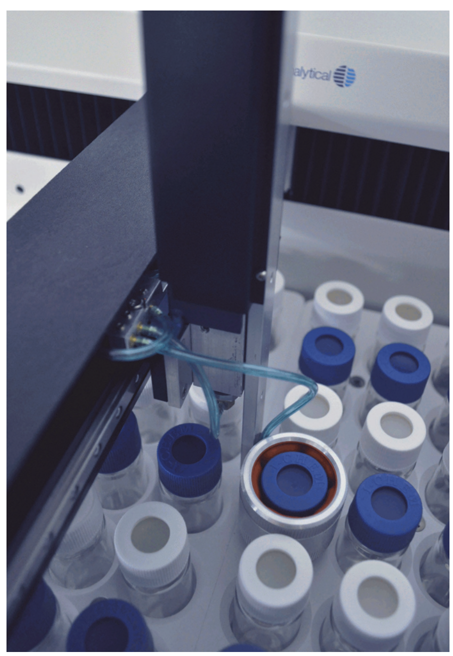

Figure 2. VOA Constrictor™ Vial Gripper

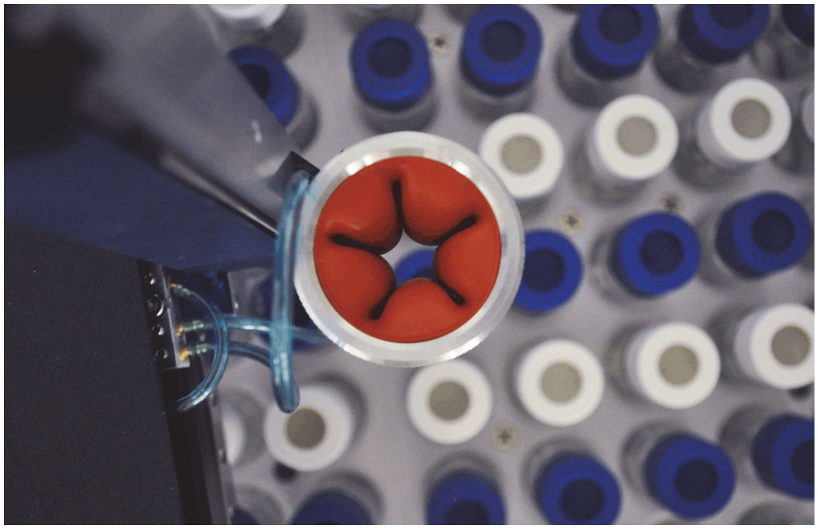

Figure 3.   VOA Constrictor™ Vial Gripper Mechanism Pressurized without Vial

Standards Addition Manifold

Integrated into the tower of the 4100 is a standards addition manifold with two 3-mL reservoirs and electronically controlled high-speed injection valves that automate the addition of internal standards, surrogate or matrix spike standards. Injection volumes of 1 µL, 2 µL, 5 µL, 10 µL, or 20 µL are user selectable through VOA View™ software. An option allows expansion of standard reservoirs and injection valves from 2 to 4 separate channels (Figure 4).

Figure 4. Standards Addition Manifold with 4 Standard Reservoirs and Injection Valves

The high-speed injection valves inject programmed volumes of standard with no excess overfill volume and waste that fixed-loop based systems require to operate. This significantly reduces standard usage and operating costs for expensive standards.

The 3-mL reservoirs are constructed of amber glass to protect standards from UV light and degradation. The cover, which fits over the standards addition manifold has a dry erase panel for noting information about the standards in use (Figure 5).

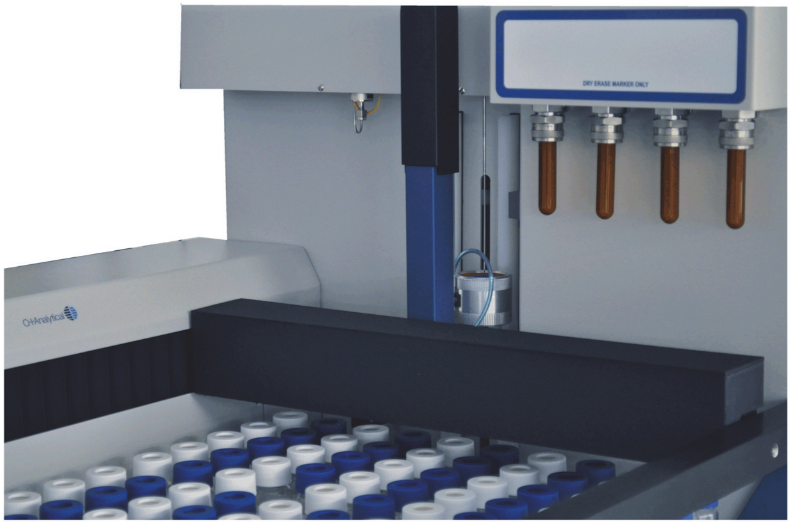

Figure 5. Standards Addition Manifold with Dry Erase Panel

Sampling Station

The sampling station has dedicated positions for vials containing water or soil samples. The VOA Constrictor™ gripper places vials into the sampling station. A lift mechanism raises the sampling station with a vial to engage the sample probe as shown in Figure 6.

Figure 6. 4100 Sampling Station with Lift Mechanism Raised

Vial Cooling Option

A vial cooling option is available to maintain a deck full of 100 sample vials at 10 °C or less prior to analysis for compliance with U.S. EPA method 524.3 requirements. Two 50-position insulated vial racks (Figure 7) fit into a cooling base fitted with quick-disconnects for easy connection to a recirculating chiller.

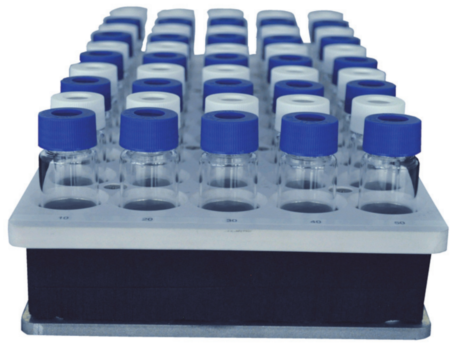

Figure 7. Insulated 50-position Vial Rack for 4100 Sample Processor

VOA View™ Software

Programming and operation of the 4100 is controlled by VOA View™ software. Operating system requirements for VOA View™ software are Microsoft Windows® 7 or Windows® 8 and 8.1 with Microsoft.NET Framework 4.0 or higher.

VOA View™ is a Windows®-based graphical user interface (GUI) that enables users to program methods, sequences, and internal standard addition (Figures 8 and 9). The VOA View™ run screen visually depicts water and soil samples, the status of vials that have been processed, and provides details of the method being run (Figure 10).

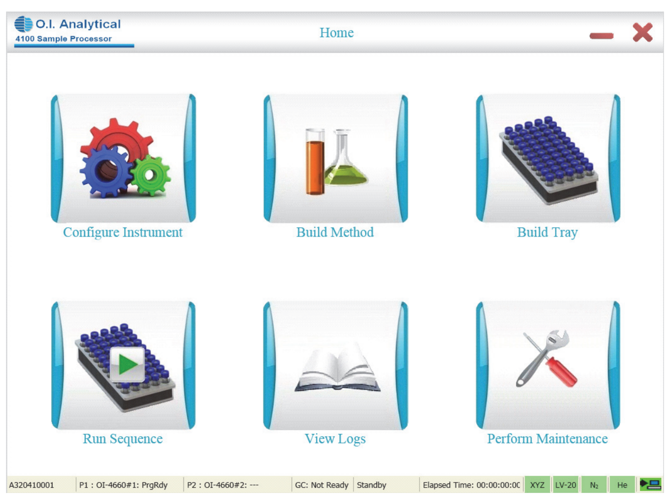

Figure 8. VOA View™ Software Windows®-based GUI

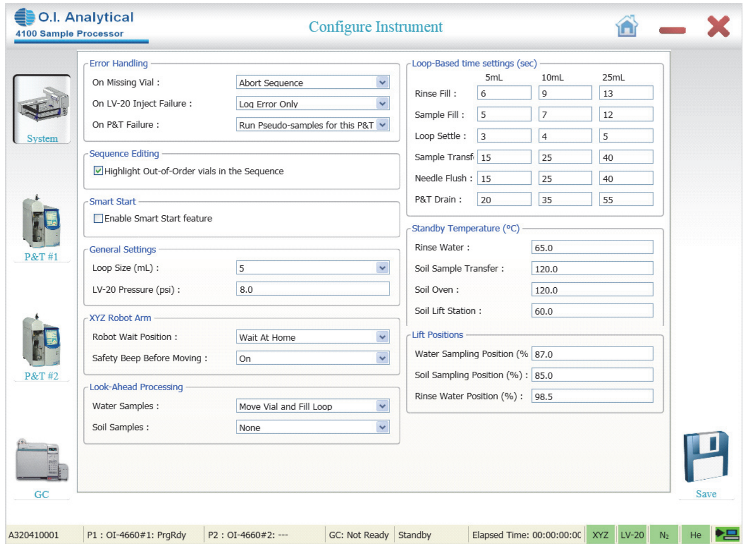

Figure 9. VOA View™ 4100 Instrument Configuration Screen

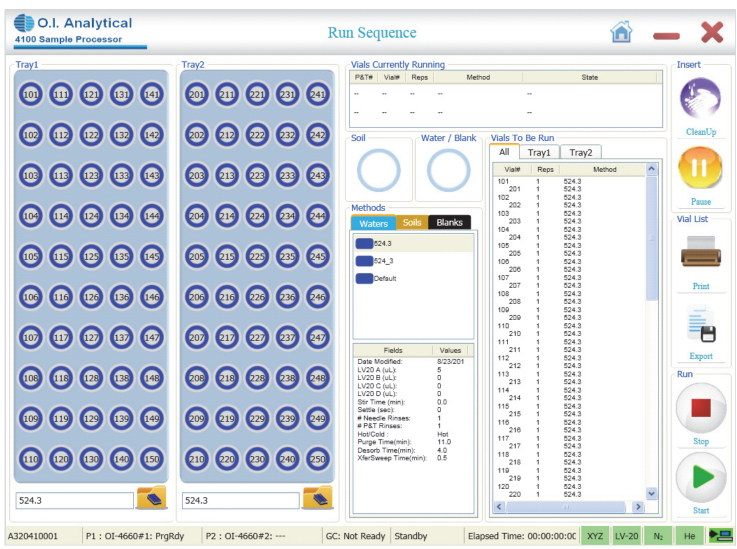

Figure 10. VOA View™ Run Screen

VOA View™ software enables a 4100 to communicate and operate concurrently with two purge-and-trap instruments to improve sample throughput and laboratory productivity. Optional kits containing the hardware required to connect a 4100 Sample Processor to a second Eclipse 4660 purge-and-trap instrument and for a benchtop stand to position two purge-and-traps alongside a 4100 are available (Figure 11).

Figure 11. 4100 Water / Soil Sample Processor Arranged for Operation with Dual Eclipse 4660 Purge-and-Trap Sample Concentrators

4100 Specifications

Specifications for the 4100 Water / Soil Sample Processor are presented in Table 1.

Table 1: 4100 Water / Soil Sample Processor Specifications

Purge-and-Trap Capability	Operates with one or two Eclipse 4660 Instruments
Sample Capacity	100 standard USEPA 40-mL VOA vials
Sample Loop	5mL standard loop, 10 or 25 mL loops optional
Automated Standard Addition	(2) 3mL reservoirs standard, expansion to (4) optional
Sampling Mode - Water	Aspiration and transfer to purge-and-trap instrument sparge vessel
Sampling Mode - Soil	In-vial needle sparging and transfer to trap of purge-and-trap instrument
Sample Transfer Pathway - Water Samples	Silcosteel® 316L stainless steel and PEEK®
Sample Transfer Pathway - Soil Samples	Silcosteel® 316L stainless steel and PEEK®
Blank Water Transfer	PFA-Teflon®
Vial Trays	(2) 50-position VOA vial trays
Vial Gripper Mechanism	Pneumatically actuated cylindrical gripper with vial sensing
Vial Cooling Option	Cooling base for two 50-position vial trays with quick-disconnect fittings for recirculating chiller
X/Y-Axis Mechanism	Digitally controlled linear drive rails
Z-Axis Mechanism	Pneumatically actuated
Operating Software	VOA View Windows®-based GUI
Operating System Requirements	Windows® 7 or Windows® 8 or 8.1 and Microsoft.NET Framework 4.0 or higher
PC to 4100 Communications	USB port for each 4100 instrument connected to PC
Water Supply	Clean, VOC-free water for rinsing sample pathway
Gas Requirements - Sample Transfer	99.999% (UHP Grade) He or N_2
Gas Requirements - Gripper / Z-axis Actuator	Nitrogen
Power Requirements	110VAC / 60HZ or 230VAC / 50HZ
Dimensions	27 in. W x 24 in. D x 21 in. H
Weight	32.1Kg (70.75 lbs)
Certifications	CE Safety and EMC EN50082-1/EN55011 Group 1 Class A

Instrument Performance

Performance tests for two different, USEPA-approved VOC analysis methods (8260 and 524.3) were conducted using the 4100 sample processor. Details of the experimental parameters are provided in Tables 2 and 3.

Table 2: Instrument Operating Conditions for USEPA Method 8260

Purge-and-Trap	Eclipse 4660 P&T Sample Concentrator
Autosampler	OI 4100 with 4 standards addition channels
Traps	#10 trap; Tenax®/Silica Gel/CMS
Purge Gas	zero-grade helium at 40 mL/min
Purge Time	11 minutes
Sample Temperature	45 °C
Desorb Time	1 minute
Bake Time	5 minutes
OI #10 Trap Temperature	ambient during purge 180 °C during desorb pre-heat 190 ° C during desorb 210 °C during bake
Water Management	120 ° during purge ambient during desorb 210 °C during bake
Transfer Line Temperature	125 °C
Six-Port Valve Temperature	125 °C
Autosampler Gas	nitrogen for 4100 system gas zero grade helium for sample purge
Gas Chromatograph	**Agilent 7890A**
Column	Restek RTX-VMS 20 meter, 0.18 mm ID, 1 µm film
Carrier Gas	zero grade helium
Inlet Temperature	250 °C
Column Flow Rate	0.6 mL/minute
Split Ratio	100:1
Oven Program	Hold at 40 °C for 1.5 minutes 16 °C/minute to 180 °C 40 °C/minute to 220 °C Hold at 220 °C for 1.5 minutes Total GC run time 12.75 minutes

Mass Spectometer	Agilent 5975C
Mode	Scan 35-300 amu
Scans/second	5.19
Solvent Delay	1.40 minutes
Transfer Line Temperature	240 °C
Source Temperature	230 °C
Quadrupole Temperature	150 °C

Table 3: Instrument Operating Conditions for U.S. EPA Methods 524.3 (THMs) and 8260 (BTEX) Using Dual Purge-and-Traps

Purge-and-Trap	Eclipse 4660 P&T Sample Concentrator
Autosampler	OI 4100 with 4 standards addition channels
Traps	#10 trap; Tenax®/Silica Gel/CMS
Purge Gas	zero-grade helium at 45 mL/min
Purge Time	8 minutes
Sample Temperature	35 °C for 524.3 THMs; 45 °C fo r8260 BTEX
Desorb Time	1 minute
Bake Time	4 minutes
OI #10 Trap Temperature	ambient during purge 180 °C during desorb pre-heat 190 ° C during desorb 210 °C during bake
Water Management	120 ° during purge ambient during desorb 210 °C during bake
Transfer Line Temperature	125 °C
Six-Port Valve Temperature	125 °C
Autosampler Gas	nitrogen for 4100 system gas zero grade helium for sample purge
Gas Chromatograph	**Agilent 7890A**
Column	Restek RTX-VMS 20 meter, 0.18 mm ID, 1 µm film
Carrier Gas	zero grade helium

Inlet Temperature	250 °C
Column Flow Rate	0.6 mL/minute
Split Ratio	50:1 for 524.3; 150:1 for 8260 BTEX
Oven Program	Hold at 50 °C for 1minute 30 °C/minute to 220 °C Hold at 220 °C for 1 minute Total GC run time 7.67 minutes
Mass Spectometer	**Agilent 5975C**
Mode	Scan 35-300 amu
Scans/second	5.19
Solvent Delay	2 minutes
Transfer Line Temperature	240 °C
Source Temperature	230 °C
Quadrupole Temperature	150 °C

Method 8260 Results

Instrument calibration data for Method 8260 are presented in Table 4, including; the average response factors for the calibration from 5 to 150 ppb, and the relative standard deviations for the response factors. Samples were processed in both water mode (aliquot drawn from the vial and purged in the P&T) and in soils mode (water added to the vial and vial purge sent to P&T) for comparison. A peak-labeled chromatogram for the 50-ppb water standard is presented in Figure 5 for reference.

Table 4: Method 8260 Average Response Factors and Response Factor RSDs for Water and Soils Modes

Analyte	Compound	CAS Number	Waters RF	%RSD	Soils RF	%RSD
1	pentafluorobenzene (IS)	363-72-4				
2	dichlorodifluoromethane	75-71-8	0.350	3.01	0.391	3.09
3	chloromethane	74-87-3	0.490	3.41	0.551	2.25
4	vinyl chloride	75-01-4	0.540	3.59	0.593	3.09
5	bromomethane	74-83-9	0.293	6.19	0.342	4.51
6	chloroethane	75-00-3	0.348	6.34	0.394	2.47
7	richlorofluoromethane	75-69-4	0.650	4.76	0.693	3.71
8	ethyl ether	60-29-7	0.321	3.48	0.290	4.02
9	1,1-dichloroethene	75-35-4	0.381	6.49	0.409	3.49

Analyte	Compound	CAS Number	Waters RF	%RSD	Soils RF	%RSD
10	carbon disulfide	75-15-0	1.086	4.86	1.472	2.88
11	1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	0.403	5.65	0.401	3.19
12	methyl iodide	74-88-4	0.594	6.19	0.664	2.76
13	allyl chloride	107-05-1	0.261	2.87	0.265	7.00
14	methylene chloride	75-09-2	0.468	3.48	0.479	3.51
15	acetone	67.64-1	0.078	3.71	0.053	19.99
16	*trans*-1,2-dichloroethene	156-60-5	0.448	4.92	0.499	6.18
17	methyl *tert*-butyl ether	1634-04-4	1.232	3.60	1.037	4.78
18	acetonitrile	75-05-8	0.104	9.67	0.074	8.65
19	chloroprene	126-99-8	0.829	7.71	0.812	6.95
20	1,1-dichloroethane	75-34-3	0.993	1.80	0.968	2.70
21	acrylonitrile	107-13-1	0.306	6.83	0.191	5.16
22	*cis*-1,2-dichloroethene	156-59-2	0.495	2.11	0.495	3.72
23	2,2-dichloropropane	594-20-7	0.417	7.13	0.465	3.42
24	bromochloromethane	74-97-5	0.240	2.93	0.224	4.30
25	chloroform	67-66-3	0.902	3.44	0.863	2.29
26	methyl acrylate	96-33-3	0.629	1059	0.407	9.30
27	carbon tetrachloride	56-23-5	0.607	3.40	0.620	3.91
28	dibromofluoromethane (SS)	1868-53-7	0.507	2.27	0.487	2.47
29	1,1,1-trichloroethane	71-55-6	0.652	2.69	0.660	3.36
30	2-butanone	79-93-3	0.097	1.92	0.060	8.69
31	1,1-dichloropropene	563-58-6	0.640	3.86	0.666	5.71
32	1,4-difluorobenzene (IS)	540-36-3				
33	benzene	71-43-2	1.231	2.95	1.263	3.68
34	methacrylonitrile	126-98-7	0.306	7.80	0.195	10.20
35	1,2-dichloroethane-d_4 (SS)	17060-07-0	0.086	1.78	0.074	1.69
36	1,2-dichloroethane	107-06-2	0.482	2.44	0.439	3.08
37	trichloroethene	79-01-6	0.306	2.88	0.309	5.05
38	dibromomethane	74-95-3	0.205	3.03	0.180	5.73

Analyte	Compound	CAS Number	Waters RF	%RSD	Soils RF	%RSD
39	bromodichloromethane	75-27-4	0.430	3.03	0.402	5.02
40	1,2-dichloropropane	78-87-5	0.350	3.43	0.325	6.85
41	methyl methacrylate	80-62-6	0.240	10.18	0.168	13.45
42	2-chloroethyl vinyl ether	110-75-8	0.229	13.99	0.168	15.24
43	*cis*-1,3-dichloropropene	10061-01-5	0.471	6.31	0.444	8.29
44	chlorobenzene-d_5 (IS)	3114-55-4				
45	toluene-d_8(ss)	2037-26-5	1.387	1.70	1.407	1.34
46	toluene	108-88-3	0.852	3.27	0.875	3.04
47	2-nitropropane	79-46-9	0.144	7.29	0.093	12.42
48	4-methyl-2-pentanone	108-10-1	0.067	10.41	0.041	15.19
49	tetrachloroethene	127-18-4	0.289	3.59	0.297	5.12
50	*trans*-1,3-dichloropropene	10061-02-6	0.510	8.34	0.461	8.24
51	ethyl methacrylate	97-63-2	0.461	11.94	0.344	15.50
52	1,1,2-trichloroethane	79-00-5	0.297	2.70	0.246	5.30
53	chlorodibromomethane	124-48-1	0.336	7.42	0.294	9.40
54	1,3-dichloropropane	142-28-9	0.602	3.35	0.514	5.56
55	1,2-dibromoethane	106-93-4	0.326	2.91	0.269	5.53
56	2-hexanone	591-78-6	0.415	11.54	0.225	15.73
57	chlorobenzene	108-90-7	0.946	3.29	0.925	4.07
58	ethylbenzene	100-41-4	1.630	3.83	1.626	5.76
59	1,1,1,2-tetrachloroethane	630-20-6	0.316	4.36	0.304	6.10
60	*m,p*-xylenes	1330-20-7	0.580	5.93	0.584	8.54
61	*o*-xylene	95-47-6	0.541	7.83	0.546	8.93
62	styrene	100-42-5	0.944	9.92	0.895	12.65
63	bromoform	75-25-2	0.259	6.79	0.192	11.98
64	isopropylbenzene	98-82-8	1.474	8.40	1.504	9.33
65	*cis*-1,4-dichloro-2-butene	1476-11-5	0.219	5.85	0.140	9.97
66	1,4-dichlorobenzene-d_4 (IS)	3855-82-1				
67	4-bromofluorobenzene (SS)	460-00-4	0.973	2.19	0.986	1.40

Analyte	Compound	CAS Number	Waters RF	%RSD	Soils RF	%RSD
68	bromobenzene	108-86-1	0.729	3.53	0.739	4.57
69	*n*-propylbenzene	103-65-1	3.725	4.48	3.965	7.65
70	1,1,2,2-tertrachloroethane	79-34-5	1.041	3.28	0.801	6.43
71	2-chlorotoluene	95-49-8	2.355	4.56	2.495	7.52
72	1,3,5-trimethylbenzene	108-67-8	2.339	6.07	2.495	10.47
73	1,2,3-trichloropropane	96-48-4	1.330	4.90	0.980	8.61
74	*trans*-1,4-dichloro-2-butene	110-57-6	0.396	8.05	0.264	11.77
75	4-chlorotoluene	106-43-4	2.212	5.76	2.289	6.47
76	*tert*-butylbenzene	98-06-6	2.298	4.74	2.471	8.56
77	pentachloroethane	76-01-7	0.413	5.43	0.424	8.17
78	1,2,4-trimethylbenzene	95-63-6	2.358	7.34	2.464	10.59
79	*sec*-butylbenzene	135-98-8	3.142	5.30	3.411	9.34
80	*p*-isopropytoluene	99-87-6	2.465	7.94	2.649	11.12
81	1,3-dichlorobenzene	541-73-1	1.398	2.69	1.437	3.35
82	1,4-dichlorobenzene	106-46-7	1.449	2.89	1.497	3.98
83	*n*-butylbenzene	104-51-8	2.542	7.59	2.758	9.18
84	1,2-dichlorobenzene	95-50-1	1.340	3.29	1.326	3.88
85	1,2-dibromo-3-chloropropane	96-12-8	0.222	9.54	0.137	16.18
86	hexachlorobutadiene	87-68-3	0.423	6.25	0.512	6.21
87	1,2,4-trichlorobenzene	120-82-1	0.795	9.32	0.827	6.35
88	naphthalene	91-20-3	2.371	10.20	1.748	11.99
89	1,2,3-trichlorobenzene	87-61-6	0.746	10.22	0.751	6.62

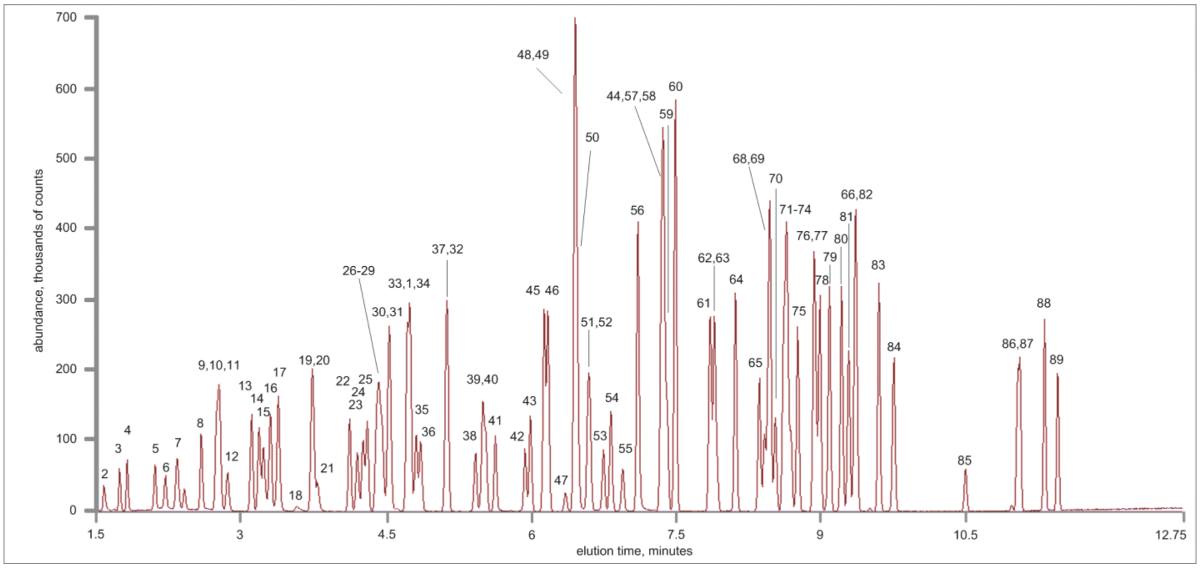

Figure 12. Method 8260 Chromatogram for a 50-ppb Water Standard

Method 524.3 THM and Method 8260 BTEX Results

The results of a seven-point calibration for Method 524.3 trihalomethanes (THMs) are presented in Table 5. The results of a seven-point calibration for Method 8260 BTEX are presented in Table 6. These calibrations were carried out on a dual purge-and-trap configuration for Method 524.3 THMs. Both purge-and-trap concentrators received samples processed in the water mode for Method 524.3. For Method 8260 BTEX both water and soil mode processing was used. To identify the separate sample paths for the Method 524.3 THM work, a specific marker compound was used to identify the P&T #2 sample path. The absence of that compound identified the opposite path. For the Method 8260 BTEX work, the same species was instead used to identify the P&T #1 sample path, to prove a lack of contamination.

Table 5: Results of a 7-Point Calibration (0.5 to 40 ppb) for Method 524.3 THMs Comparing Dual Purge-and-Traps

Compound	CAS Number	Waters RF	%RSD	Waters RF	%RSD
		Purge and Trap #2		Purge and Trap #1	
fluorobenzene (Marker)	462-06-6				
1,4-difluorobenzene (IS)	540-36-3				
methyl *tert*-butyl ether-d_3 (SS)	29366-08-3	00.986	2.07	0.966	5.09
chloroform	67-66-3	0.655	1.37	0.600	4.59
chlorobenzene-d_5 (IS)	3114-55-4				

Compound	CAS Number	Waters RF	%RSD	Waters RF	%RSD
		Purge and Trap #2		Purge and Trap #1	
bromodichloromethane	75-27-4	0.535	3.12	0.503	4.28
chlorodibromomethane	124-48-1	0.327	4.15	0.322	4.38
bromoform	75-25-2	0.206	3.66	0.483	2.33
4-bromofluorobenzene (SS)	460-00-4	0.503	1.94	0.483	2.33
1,4-dichlorobenzene-d_4 (IS)	3855-82-1				
1,2-dichlorobenzene-d_4 (SS)	2199-69-1	0.962	2.50	0.991	3.39

Table 6: Results for 7-Point Calibration (5 to 400 ppb) of Method 8260 BTEX Comparing Dual Purge-and-Traps Operating in Water and Soils Modes

Compound	CAS Number	Waters RF	%RSD	Soils RF	%RSD
		Purge and Trap #1		Purge and Trap #2	
fluorobenzene (Marker)	462-06-6				
pentafluorobenzene (IS)	363-72-4				
methyl *tert*-butyl ether	1634-04-4	1.456	2.25	1.205	3.55
dibromofluoromethane (SS)	1868-53-7	0.536	2.37	0.543	2.41
1,4-difluorobenzene (IS)	540-36-3				
benzene	71-43-2	1.518	2.24	1.447	2.78
1,2-dichoroethane-d_4 (SS)	17060-07-0	0.083	3.43	0.069	2.76
chlorobenzene-d_5 (IS)	3114-55-4				
toluene-d_8 (SS)	2037-26-5	1.367	2.69	1.410	4.41
toluene	108-88-3	0.975	2.59	0.947	3.51
ethylbenzene	100-41-4	1.771	2.65	1.715	3.08
m,p-xylenes	1330-20-7	0.662	5.37	0.645	4.38
o-xylene	95-47-6	0.615	5.57	0.617	2.80
1,4-dichlorobenzene-d_4 (IS)	3855-82-1				
4-bromofluorobenzene (SS)	460-00-4	1.107	1.20	1.062	0.96

The total cycle time for the dual purge-and-trap measurements of THMs and BTEX was 12 minutes injection-to-injection, this allows approximately 60 GC runs to be carried out in a 12-hour mass spectrometer tune time. In the case of THM and BTEX analyses this equates to a 40% time savings over the same measurements carried out with the 4100 feeding a single purge-and-trap concentrator, which had a 20 minute cycle time. All of the instrument operating conditions, except the split ratio, were the same for both these two methods. This would allow either of the two methods to be run without changing any other parameters.

Summary

Innovative technologies built into the 4100 improve sample processing reliability, analytical performance, laboratory operating costs, and productivity.

The digitally controlled linear drive rails and pneumatically-actuated VOA Constrictor™ vial gripper combine to lift and transport 40-mL VOA vials to and from the sampling station with exceptional reliability.

The electronically controlled high-speed injection valves in the Standards Addition Manifold inject user programmed volumes of standard with no excess overfill volume or waste that fixed-loop systems require to operate. This approach significantly reduces standard usage and operating costs for expensive standards.

Analytical data obtained from performance testing the OI Analytical 4100 Water / Soil Sample Processor yielded good results running U.S. EPA Methods 524.3 and 8260.

A total cycle time of 12 minutes injection-to-injection for THMs and BTEX was achieved by operating the 4100 sample processor in a dual purge-and-trap configuration. For THM and BTEX analyses this represents a 40% time savings versus measurements with a single purge-and-trap and would allow approximately 60 GC runs to be conducted in a 12-hour mass spectrometer tune time.

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