

Shimadzu Guide to US EPA Method 624 for Analysis of Volatile Organic Compounds in Wastewater

■ Introduction

Environmental contamination has been at the forefront of government policy and regulation since the US EPA was established in 1970. Over the years the US EPA has developed, published, and updated multiple methods for analysis of environmental pollutants, and single-quadrupole gas chromatography-mass spectrometry (GCMS) has long been the technique of choice for determination of volatile organic contaminants (VOCs). As efforts to provide dependable analytical methods have progressed, the GCMS instrumentation has evolved, with improvements in sensitivity, reliability, and user experience, but there haven't been any significant advancements in the overall methodology since the mid-1980s.

The US EPA is currently in the process of developing a revision to US EPA Method 624¹, which was first promulgated in 1984 and specified the use of packed columns as part of the protocol to collect data on the VOC pollutants. This application note describes a GCMS purge-and-trap (P&T) method validation study conducted to evaluate operating conditions for the existing US EPA Method 624 VOC list, using updated technology and advanced GCMS instrumentation. GCMS instrument operating conditions are provided which bring the method in line with capabilities provided by contemporary laboratory equipment. This application note provides calibration results across three different ranges, complete MDL and Precision and Accuracy studies at multiple concentrations, and analysis of an independent laboratory VOC reference standard and real-world samples.

■ Experimental

This study was conducted using the Shimadzu GCMS-QP2010 SE shown in Figure 1, configured with a capillary column designed specifically for analysis of VOCs by US EPA Method 624. The GC was operated in the unique Constant Linear Velocity mode to provide optimum chromatographic resolution, symmetric peak shape, and enhanced sensitivity for all compounds. A special, narrow ID inlet liner was used to minimize band broadening and retain ideal peak shape during transfer from the P&T, while still allowing high-split injections. Data were acquired in the full scan mode; quantitation and confirmation for most compounds were conducted using the quantitation and reference ions suggested in US EPA Method 624. Changes to quantitation and reference ions for a few selected compounds were made to improve overall sensitivity of the method.

The EST Evolution P&T and Centurion Water/Soil Autosampler were used for the extraction, concentration, and sample introduction steps. The Evolution was configured with the optional sample heater to ensure that all samples were purged at precisely the same temperature for accuracy and precision of the data. The Centurion Water/Soil Autosampler was operated in the Water mode for this study; the optional syringe was used for automated dilution of the real-world samples.

Each day before starting a sample sequence, the instrument was conditioned by cycling the P&T and VOCARB 3000 trap through two Bake cycles. Simultaneously, the oven, injection port, ion source, and MS interface temperatures were all raised to 220 °C for a minimum of one hour. The instrument bake-out procedure was run on all days, whether samples were analyzed or not. Complete instrument configuration and operating conditions are shown in Table 1.



Figure 1: Shimadzu GCMS-QP2010 SE

Table 1: GCMS and P&T Operating Conditions

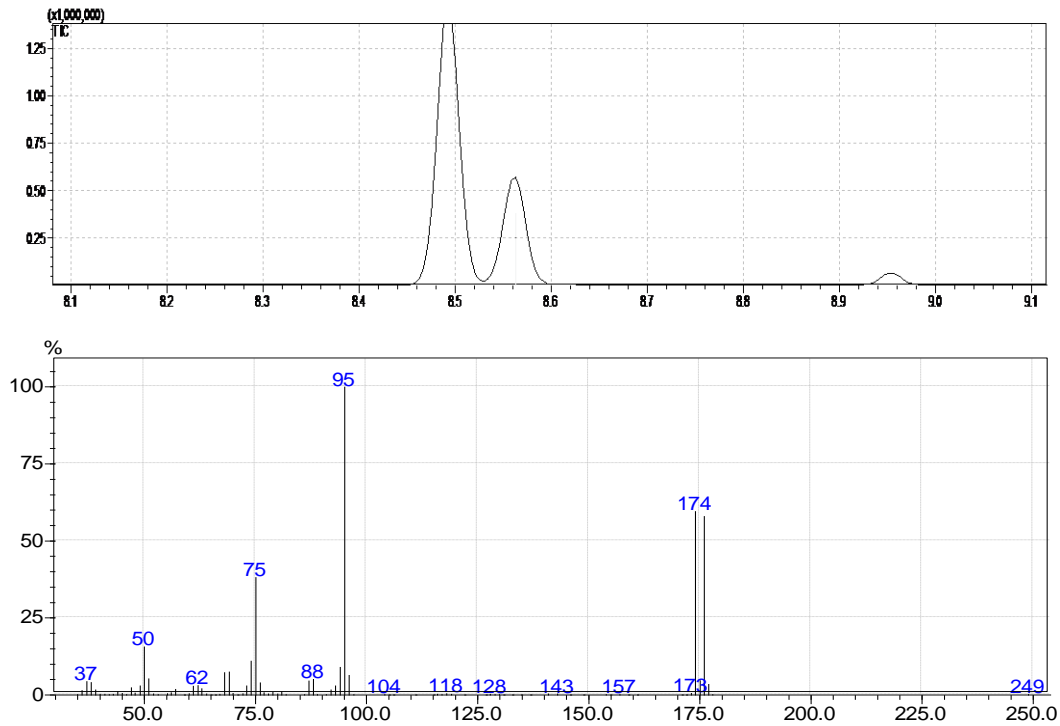
| Gas Chromatograph | | GC-2010 Plus | | | | | |
|---|--|---|----------|--------|-----------------------------------|-----------|------------|
| Column | SH-RXI-6245il MS, 30 m x 0.25 mm x 1.4 µm (Shimadzu PN 221-75962-30) | | | | | | |
| Oven Program | 45 °C, hold 0.1 minute 15 °C/minute to 220 °C, hold 3.5 minutes | | | | | | |
| Injector | Split mode, split ratio 40:1 200 °C Low volume liner, 0.75 mm ID, straight (Shimadzu PN 220-90784-10) | | | | | | |
| Carrier Gas | Helium Constant Linear Velocity mode, 36.2 cm/second | | | | | | |
| Interface Temperature | 180 °C | | | | | | |
| Mass Spectrometer | | GCMS-QP2010 SE | | | | | |
| Ion Source Temperature | 185 °C | | | | | | |
| MS Operating Mode | Full scan mode, m/z 35-260 Event time = 0.25 second/scan Solvent cut time = 0.7 minute Detector voltage set relative to tune + 0.1 kV Threshold = 100 NOTE: The scan rate was adjusted to provide a minimum of 10-12 spectra across all GC peaks for optimum quantitation | | | | | | |
| Purge-and-Trap Concentrator | | EST Encon Evolution with Centurion Autosampler | | | | | |
| Sample Volume | 5 mL | | | | | | |
| Sample Temperature at Purge | 40 °C | | | | | | |
| Trap | VOCARB 3000 | | | | | | |
| Purge Flow Rate | Helium, 40 mL/minute for 11 minutes | | | | | | |
| Dry Purge | Helium, 40 mL/minute for 3 minutes | | | | | | |
| Desorb | 250 °C for 0.5 minute | | | | | | |
| Bake | 260 °C for 10 minutes | | | | | | |
| Analysis Times | | | | | | | |
| GC Run Time | 16.2 minutes | | | | | | |
| System Cycle Time | 26 minutes | | | | | | |
| Peak # | Compound Name | Quant Ion | Ref. Ion | Peak # | Compound Name | Quant Ion | Ref. Ion |
| 1 | Chloromethane | 50 | 52 | 20 | Bromodichloromethane | 83* | 85, 47* |
| 2 | Vinyl chloride | 62 | 64 | 21 | 2-Chloroethylvinyl ether | 106 | - |
| 3 | Bromomethane | 94 | 96 | 22 | <i>cis</i> -1,3-Dichloropropene | 75 | 77 |
| 4 | Chloroethane | 64 | 66 | 23 | Toluene | 92 | 91 |
| 5 | Trichlorofluoromethane | 101 | 103 | 24 | <i>trans</i> -1,3-Dichloropropene | 75 | 77 |
| 6 | 1,1-Dichloroethene | 96 | 98* | 25 | 2-Bromo-1-chloropropane (IS) | 77 | 79 |
| 7 | Methylene chloride | 49* | 84* | 26 | 1,1,2-Trichloroethane | 97 | 83 |
| 8 | <i>trans</i> -1,2-Dichloroethene | 96 | 61 | 27 | Tetrachloroethene | 164 | 129 |
| 9 | 1,1-Dichloroethane | 63 | 65 | 28 | Dibromochloromethane | 127 | 208* |
| 10 | Bromochloromethane (IS) | 128 | 130 | 29 | Chlorobenzene | 112 | 114 |
| 11 | Chloroform | 83 | 85 | 30 | Ethylbenzene | 106 | - |
| 12 | Pentafluorobenzene (Surr) | 168 | - | 31 | Bromoform | 173 | 171 |
| 13 | 1,1,1-Trichloroethane | 97 | 119* | 32 | 1,4-Dichlorobutane (IS) | 55 | 90 |
| 14 | Carbon tetrachloride | 117 | 121 | 33 | 4-Bromofluorobenzene (Surr) | 95 | 176, 174 |
| 15 | Benzene | 78 | - | 34 | 1,1,2,2-Tetrachloroethane | 83* | 166*, 168* |
| 16 | 1,2-Dichloroethane | 62* | 98* | 35 | 1,3-Dichlorobenzene | 146 | 148 |
| 17 | Fluorobenzene (Surr) | 96 | 70 | 36 | 1,4-Dichlorobenzene | 146 | 148 |
| 18 | Trichloroethene | 130 | 95 | 37 | 1,2-Dichlorobenzene | 146 | 148 |
| 19 | 1,2-Dichloropropane | 63* | 65* | | | | |
| NOTE: Quant or Reference ions indicated with an asterisk (*) have been changed from the ions suggested in US EPA Method 624 to improve sensitivity. | | | | | | | |

■ **Results and Discussion**

BFB Tune Results

At the beginning of the project the GCMS-QP2010 SE was tunedⁱⁱ to meet the US EPA Method 624 requirements. Each day prior to running any samples, and at intervals of no longer than 12-hours during long sequences, an aliquot of the 4-bromofluorobenzene (BFB) was purged and analyzed using the method conditions shown in Table 1. The BFB spectra were evaluated using the US EPA Method 624 criteria. Since BFB was one of the Surrogate Standards added to all samples, the BFB spectrum was available for evaluation for every run. A representative example of a BFB chromatogram and spectrum are shown in Figure 2.

Table 2 lists the BFB results as compared to the method criteria from three selected analyses of BFB during one of the extended sequences. The BFB spectra met all method criteria for all samples evaluated throughout the project. The tune remained stable for over 2½ months, and the GCMS-QP2010 SE instrument did not require re-tuning at any time during the analysis period.



| Mass (m/z) | Relative Abundance Criteria | Result | Status |
|------------|-----------------------------|--------|--------|
| 50 | 15 to 40% of 95 | 16.3 | Pass |
| 75 | 30 to 60% of 95 | 43.0 | Pass |
| 95 | Base Peak, 100% | 100 | Pass |
| 96 | 5 to 9% of 95 | 5.5 | Pass |
| 173 | < 2% of 174 | 1.4 | Pass |
| 174 | > 50% of 95 | 63.4 | Pass |
| 175 | 5 to 9% of 174 | 7.1 | Pass |
| 176 | > 95% but < 101% of 174 | 97.2 | Pass |
| 177 | 5 to 9% of 176 | 6.3 | Pass |

Figure 2: Typical Results from BFB Tune Evaluation Using US EPA Method 624 Criteria

Table 2: Evaluation of BFB Spectra from 3 Different Runs across a Long Sequence, Compared to US EPA Method 624 Criteria

| m/z | Spectrum Check Criteria | Result | | Result | | Result | |
|-----|------------------------------------|--------|--------|---------|--------|---------|--------|
| | | Run #1 | Status | Run #10 | Status | Run #30 | Status |
| 50 | 15 to 40% of mass 95 | 16.0 | Pass | 15.6 | Pass | 15.4 | Pass |
| 75 | 30 to 60% of mass 95 | 41.2 | Pass | 41.5 | Pass | 43.5 | Pass |
| 95 | Base Peak, 100% Relative Abundance | 100.0 | Pass | 100.0 | Pass | 100.0 | Pass |
| 96 | 5 to 9% of mass 95 | 6.5 | Pass | 6.9 | Pass | 7.0 | Pass |
| 173 | < 2% of mass 174 | 1.0 | Pass | 1.6 | Pass | 1.5 | Pass |
| 174 | > 50% of mass 95 | 60.8 | Pass | 59.3 | Pass | 61.6 | Pass |
| 175 | 5 to 9% of mass 174 | 7.5 | Pass | 7.4 | Pass | 7.4 | Pass |
| 176 | > 95% but < 101% of mass 174 | 97.2 | Pass | 100.6 | Pass | 97.0 | Pass |
| 177 | 5 to 9% of mass 176 | 6.6 | Pass | 5.6 | Pass | 6.4 | Pass |

Initial Calibration and Continuing Calibration Verification

A series of nine initial calibration standards across the range of 0.5 to 200 µg/L (parts-per-billion, ppb) was prepared. The three internal standards (IS) were held constant at 30 µg/L, and the three surrogate standards (Surr) were held constant at 10 µg/L in all samples analyzed. A total ion chromatogram (TIC) from the 10 µg/L standard is shown in Figure 3, along with an expanded view of the chromatography of the early-eluting light gases.

The calibration curve was evaluated two ways: using correlation coefficient (R²) from a linear regression, and using the percent relative standard deviation (% RSD) of the calculated response factors (RF) for each data point in the curve. The calibration curve was

evaluated across three different concentration ranges (0.5 to 40 µg/L, 0.5 to 100 µg/L, and 0.5 to 200 µg/L) to accommodate any type of VOC project, and passed the US EPA Method 624 criteria (RF % RSD < 35%) for all compounds in all ranges.

Continuing calibration verification (CCV) standards (10 µg/L) were analyzed periodically throughout the project, as specified in US EPA Method 624. The CCV concentrations were calculated based on one of the calibration curves, and recoveries were typical for most US EPA VOC methods (80 to 120%). Complete statistical results for the initial calibration curve and three representative CCVs analyzed during the project are shown in Table 3.

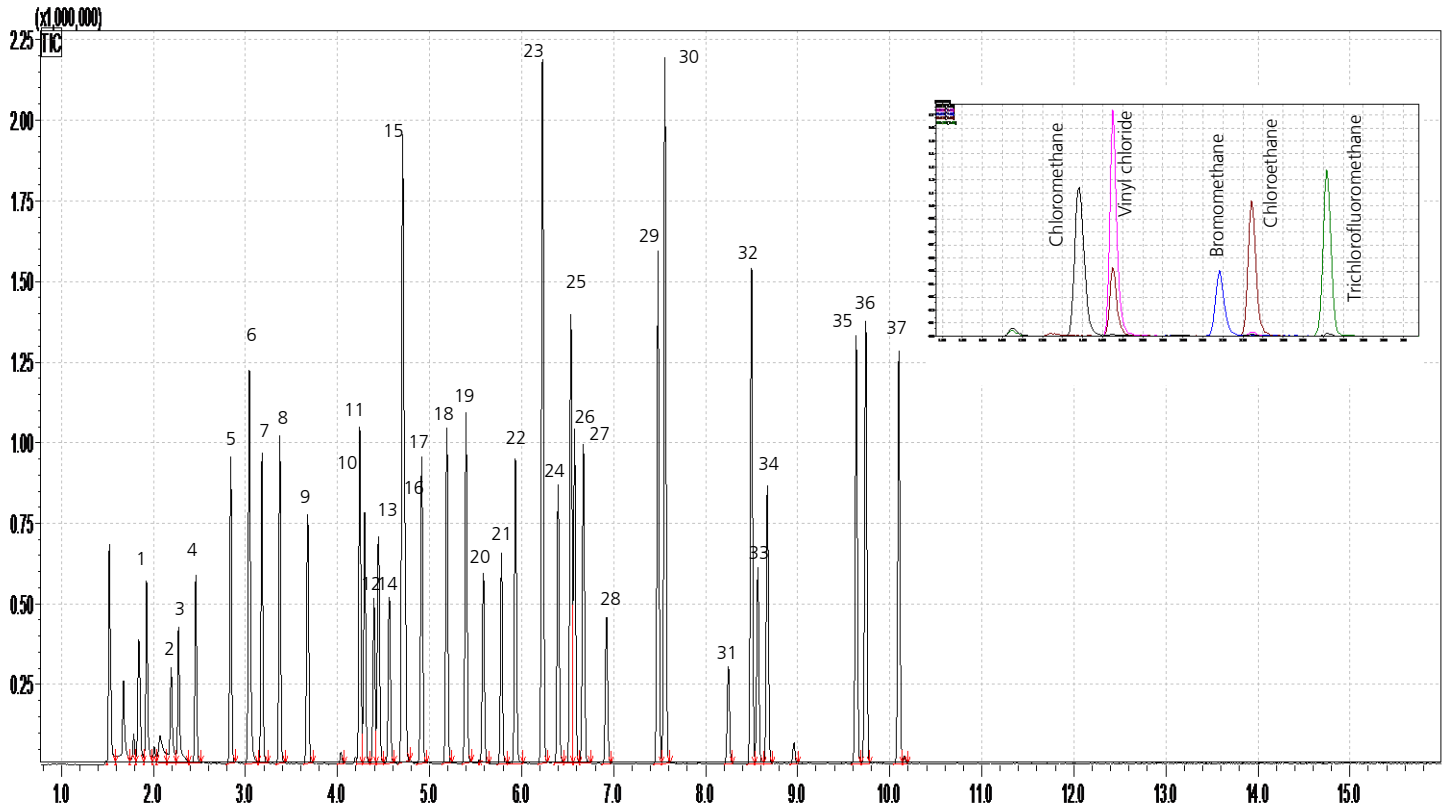


Figure 3: Total Ion Chromatogram from the 10 µg/L Calibration Standard and EICP of the Five Light Gases. Peak numbers correspond to compound names shown in Tables 3, 4, 5, and 6.

Table 3: Statistical Results from the Initial Calibration and Three Representative CCVs

| Peak # | Compound Name | 7-Point Calibration | | | 8-Point Calibration | | | 9-Point Calibration | | | CCV #1 | CCV #2 | CCV #3 |
|--------|-----------------------------------|---------------------|--------|----------|---------------------|--------|----------|---------------------|--------|----------|--------------------------|--------|--------|
| | | 0.5 to 40 µg/L | | | 0.5 to 100 µg/L | | | 0.5 to 200 µg/L | | | Calculated Concentration | | |
| | | R ² | Avg RF | RF % RSD | R ² | Avg RF | RF % RSD | R ² | Avg RF | RF % RSD | µg/L | µg/L | µg/L |
| 1 | Chloromethane | 0.9998 | 3.01 | 10.2 | 0.9990 | 3.03 | 9.6 | 0.9995 | 3.03 | 9.0 | 8.0 | 8.1 | 8.2 |
| 2 | Vinyl chloride | 0.9998 | 3.22 | 8.9 | 0.9995 | 3.23 | 8.3 | 0.9998 | 3.23 | 7.7 | 8.4 | 8.4 | 8.5 |
| 3 | Bromomethane | 0.9996 | 1.24 | 10.9 | 0.9994 | 1.25 | 10.2 | 0.9998 | 1.25 | 9.6 | 8.3 | 8.1 | 8.3 |
| 4 | Chloroethane | 1.0000 | 2.18 | 9.7 | 0.9998 | 2.18 | 9.0 | 0.9999 | 2.16 | 8.6 | 8.7 | 8.7 | 8.6 |
| 5 | Trichlorofluoromethane | 1.0000 | 2.65 | 8.9 | 0.9999 | 2.63 | 8.4 | 0.9998 | 2.64 | 7.9 | 8.7 | 8.8 | 8.7 |
| 6 | 1,1-Dichloroethene | 0.9999 | 2.09 | 6.9 | 0.9999 | 2.10 | 6.5 | 1.0000 | 2.11 | 6.1 | 9.1 | 9.1 | 9.2 |
| 7 | Methylene chloride | 1.0000 | 3.38 | 6.5 | 1.0000 | 3.37 | 6.1 | 1.0000 | 3.36 | 5.8 | 9.2 | 9.2 | 9.1 |
| 8 | <i>trans</i> -1,2-Dichloroethene | 1.0000 | 2.34 | 7.7 | 0.9998 | 2.34 | 7.2 | 0.9999 | 2.35 | 6.8 | 9.0 | 9.0 | 9.0 |
| 9 | 1,1-Dichloroethane | 1.0000 | 4.40 | 4.6 | 0.9999 | 4.41 | 4.3 | 1.0000 | 4.43 | 4.2 | 9.3 | 9.3 | 9.4 |
| 11 | Chloroform | 1.0000 | 3.47 | 5.1 | 1.0000 | 3.46 | 4.7 | 1.0000 | 3.45 | 4.5 | 9.3 | 9.3 | 9.3 |
| 12 | Pentafluorobenzene (Surr) | NA | 3.83 | 2.3 | NA | 3.82 | 2.2 | NA | 3.85 | 3.2 | 9.7 | 9.6 | 9.7 |
| 13 | 1,1,1-Trichloroethane | 0.9999 | 2.55 | 3.2 | 1.0000 | 2.56 | 3.2 | 0.9999 | 2.56 | 3.0 | 9.4 | 9.4 | 9.3 |
| 14 | Carbon tetrachloride | 0.9999 | 1.77 | 7.5 | 0.9999 | 1.80 | 8.1 | 0.9991 | 1.80 | 7.6 | 9.2 | 9.2 | 9.3 |
| 15 | Benzene | 1.0000 | 10.27 | 4.4 | 1.0000 | 10.28 | 4.1 | 0.9993 | 10.20 | 4.5 | 9.3 | 9.3 | 9.3 |
| 16 | 1,2-Dichloroethane | 1.0000 | 2.86 | 7.3 | 1.0000 | 2.85 | 7.0 | 1.0000 | 2.83 | 6.8 | 9.2 | 9.3 | 9.2 |
| 17 | Fluorobenzene (Surr) | NA | 10.47 | 1.4 | NA | 10.47 | 1.3 | NA | 10.54 | 2.4 | 9.8 | 9.8 | 9.8 |
| 18 | Trichloroethene | 0.9999 | 2.23 | 3.2 | 1.0000 | 2.23 | 2.9 | 1.0000 | 2.24 | 2.8 | 10.4 | 10.4 | 10.4 |
| 19 | 1,2-Dichloropropane | 1.0000 | 0.73 | 4.1 | 0.9999 | 0.73 | 3.8 | 0.9997 | 0.74 | 3.9 | 9.5 | 9.4 | 9.5 |
| 20 | Bromodichloromethane | 0.9999 | 0.69 | 2.7 | 0.9999 | 0.69 | 3.0 | 0.9997 | 0.70 | 4.2 | 9.4 | 9.3 | 9.4 |
| 21 | 2-Chloroethylvinyl ether | 0.9996 | 0.13 | 11.2 | 0.9994 | 0.13 | 11.2 | 0.9999 | 0.13 | 10.9 | 9.7 | 9.6 | 9.8 |
| 22 | <i>cis</i> -1,3-Dichloropropene | 0.9995 | 0.88 | 6.1 | 0.9996 | 0.90 | 7.7 | 0.9999 | 0.92 | 8.7 | 9.0 | 8.9 | 9.2 |
| 23 | Toluene | 0.9998 | 1.76 | 7.8 | 1.0000 | 1.76 | 7.2 | 0.9996 | 1.76 | 6.9 | 9.7 | 9.7 | 9.7 |
| 24 | <i>trans</i> -1,3-Dichloropropene | 0.9991 | 0.76 | 8.5 | 0.9995 | 0.78 | 10.1 | 0.9998 | 0.80 | 11.1 | 8.8 | 8.6 | 9.0 |
| 26 | 1,1,2-Trichloroethane | 0.9999 | 0.64 | 7.1 | 1.0000 | 0.64 | 6.9 | 0.9999 | 0.63 | 6.4 | 9.3 | 9.4 | 9.3 |
| 27 | Tetrachloroethene | 0.9999 | 0.45 | 6.2 | 0.9999 | 0.44 | 6.4 | 0.9976 | 0.43 | 8.8 | 9.3 | 9.5 | 9.2 |
| 28 | Dibromochloromethane | 0.9998 | 0.35 | 5.8 | 0.9999 | 0.35 | 6.0 | 0.9997 | 0.36 | 6.7 | 9.4 | 9.3 | 9.5 |
| 29 | Chlorobenzene | 0.9999 | 1.38 | 2.4 | 1.0000 | 1.38 | 2.3 | 0.9996 | 1.38 | 2.5 | 9.7 | 9.7 | 9.7 |
| 30 | Ethylbenzene | 0.9999 | 0.80 | 8.4 | 0.9999 | 0.81 | 8.0 | 0.9978 | 0.80 | 8.0 | 10.3 | 10.4 | 10.4 |
| 31 | Bromoform | 0.9993 | 0.22 | 8.4 | 0.9996 | 0.23 | 9.4 | 0.9997 | 0.23 | 10.4 | 9.7 | 9.5 | 9.9 |
| 33 | 4-Bromofluorobenzene (Surr) | NA | 0.81 | 1.7 | NA | 0.81 | 2.3 | NA | 0.81 | 2.2 | 10.2 | 10.2 | 10.2 |
| 34 | 1,1,2,2-Tetrachloroethane | 1.0000 | 0.81 | 3.1 | 1.0000 | 0.80 | 3.4 | 1.0000 | 0.80 | 3.6 | 8.3 | 8.3 | 8.2 |
| 35 | 1,3-Dichlorobenzene | 0.9998 | 0.94 | 3.4 | 0.9997 | 0.94 | 3.2 | 0.9979 | 0.93 | 5.2 | 10.0 | 10.1 | 9.9 |
| 36 | 1,4-Dichlorobenzene | 1.0000 | 0.93 | 4.2 | 1.0000 | 0.94 | 4.0 | 0.9975 | 0.92 | 5.4 | 10.2 | 10.3 | 10.2 |
| 37 | 1,2-Dichlorobenzene | 1.0000 | 0.88 | 4.3 | 0.9998 | 0.88 | 3.9 | 0.9979 | 0.87 | 5.4 | 10.3 | 10.4 | 10.3 |

Method Detection Limit Study

A Method Detection Limit (MDL) study was conducted by analyzing 8 replicate aliquots each of the 0.5 and 1.0 µg/L standards. The MDLs were calculated using the procedure outlined in the Federal Registerⁱⁱⁱ, and all MDLs easily met the

criteria, and exceeded the MDLs cited in the US EPA Method 624 by approximately a factor of 10 or more. Table 4 lists the details of the MDL study results.

Table 4: Method Detection Limit (MDL) Study Results

| Peak # | Compound Name | 0.5 µg/L n = 8 | | 1.0 µg/L n = 8 | |
|--------|-----------------------------|-------------------|------|-------------------|------|
| | | % RSD | MDL | % RSD | MDL |
| 1 | Chloromethane | 8.6 | 0.14 | 4.3 | 0.12 |
| 2 | Vinyl chloride | 5.5 | 0.08 | 3.7 | 0.11 |
| 3 | Bromomethane | 11.5 | 0.21 | 15.0 | 0.51 |
| 4 | Chloroethane | 4.8 | 0.08 | 5.1 | 0.15 |
| 5 | Trichlorofluoromethane | 8.2 | 0.14 | 1.9 | 0.06 |
| 6 | 1,1-Dichloroethene | 5.4 | 0.08 | 7.4 | 0.22 |
| 7 | Methylene chloride | 6.2 | 0.10 | 8.8 | 0.29 |
| 8 | trans-1,2-Dichloroethene | 8.0 | 0.12 | 9.5 | 0.30 |
| 9 | 1,1-Dichloroethane | 4.8 | 0.07 | 5.2 | 0.15 |
| 11 | Chloroform | 4.6 | 0.07 | 5.7 | 0.18 |
| 12 | Pentafluorobenzene (Surr) | 1.1 | 0.34 | 1.8 | 0.51 |
| 13 | 1,1,1-Trichloroethane | 8.1 | 0.11 | 5.8 | 0.16 |
| 14 | Carbon tetrachloride | 4.6 | 0.06 | 9.1 | 0.25 |
| 15 | Benzene | 2.8 | 0.04 | 5.1 | 0.15 |
| 16 | 1,2-Dichloroethane | 3.8 | 0.06 | 6.9 | 0.22 |
| 17 | Fluorobenzene (Surr) | 1.4 | 0.40 | 1.2 | 0.37 |
| 18 | Trichloroethene | 3.3 | 0.05 | 8.6 | 0.26 |
| 19 | 1,2-Dichloropropane | 3.1 | 0.05 | 3.6 | 0.11 |
| 20 | Bromodichloromethane | 7.1 | 0.10 | 7.3 | 0.22 |
| 21 | 2-Chloroethylvinyl ether | 12.4 | 0.17 | 5.3 | 0.14 |
| 22 | cis-1,3_Dichloropropene | 4.8 | 0.07 | 9.7 | 0.27 |
| 23 | Toluene | 5.7 | 0.08 | 4.7 | 0.13 |
| 24 | trans-1,3-Dichloropropene | 7.6 | 0.10 | 9.2 | 0.27 |
| 26 | 1,1,2-Trichloroethane | 3.6 | 0.06 | 3.0 | 0.09 |
| 27 | Tetrachloroethene | 4.6 | 0.07 | 8.0 | 0.24 |
| 28 | Dibromochloromethane | 5.4 | 0.08 | 5.4 | 0.17 |
| 29 | Chlorobenzene | 4.7 | 0.07 | 5.2 | 0.16 |
| 30 | Ethylbenzene | 3.6 | 0.04 | 8.2 | 0.21 |
| 31 | Bromoform | 7.5 | 0.10 | 4.2 | 0.12 |
| 33 | 4-Bromofluorobenzene (Surr) | 0.7 | 0.21 | 1.3 | 0.39 |
| 34 | 1,1,2,2-Tetrachloroethane | 5.4 | 0.08 | 3.9 | 0.12 |
| 35 | 1,3-Dichlorobenzene | 4.8 | 0.07 | 8.5 | 0.26 |
| 36 | 1,4-Dichlorobenzene | 5.1 | 0.08 | 8.5 | 0.26 |
| 37 | 1,2-Dichlorobenzene | 5.6 | 0.08 | 8.7 | 0.26 |

Precision and Accuracy Study

A Precision and Accuracy (P&A) study was conducted to gauge the expected performance of the method at different concentration levels. Eight replicate aliquots each of the 0.5, 1.0, and 20 µg/L standards were analyzed using the operating conditions shown above. Table 5 lists the detailed results of the P&A study, reporting the average concentration reported for each compound (n = 8), the percent recovery, and the %RSD for all compounds at all three levels.

Internal standard response remained stable during the entire study at ≤ 4%, and Surrogate recoveries fell within the 80 – 120 % method criteria for all analyses. IS and Surr results from a representative 12-hour sequence are shown in Figures 4 and 5, respectively.

Table 5: Precision and Accuracy (P&A) Study Results

| Peak # | Compound Name | Precision and Accuracy at 0.5 µg/L n = 8 | | | Precision and Accuracy at 1.0 µg/L n = 8 | | | Precision and Accuracy at 20 µg/L n = 8 | | |
|--------|-----------------------------------|---|----------|------|---|----------|------|--|----------|------|
| | | Mean Concentration (µg/L) | Recovery | %RSD | Mean Concentration (µg/L) | Recovery | %RSD | Mean Concentration (µg/L) | Recovery | %RSD |
| 1 | Chloromethane | 0.55 | 110% | 8.6 | 0.98 | 98% | 4.3 | 16.35 | 82% | 2.8 |
| 2 | Vinyl chloride | 0.52 | 103% | 5.5 | 0.95 | 95% | 3.7 | 16.83 | 84% | 5.0 |
| 3 | Bromomethane | 0.61 | 122% | 11.5 | 1.15 | 115% | 15.0 | 16.55 | 83% | 3.5 |
| 4 | Chloroethane | 0.53 | 106% | 4.8 | 1.00 | 100% | 5.1 | 17.14 | 86% | 3.7 |
| 5 | Trichlorofluoromethane | 0.56 | 112% | 8.2 | 0.99 | 99% | 1.9 | 17.19 | 86% | 4.9 |
| 6 | 1,1-Dichloroethene | 0.51 | 102% | 5.4 | 0.98 | 98% | 7.4 | 18.07 | 90% | 4.8 |
| 7 | Methylene chloride | 0.55 | 110% | 6.2 | 1.09 | 109% | 8.8 | 18.25 | 91% | 3.0 |
| 8 | <i>trans</i> -1,2-Dichloroethene | 0.52 | 104% | 8.0 | 1.05 | 105% | 9.5 | 18.12 | 91% | 4.2 |
| 9 | 1,1-Dichloroethane | 0.50 | 100% | 4.8 | 0.98 | 98% | 5.2 | 18.66 | 93% | 3.5 |
| 10 | Bromochloromethane (IS) | 30.00 | NA | NA | 30.00 | NA | NA | 30.00 | NA | NA |
| 11 | Chloroform | 0.52 | 104% | 4.6 | 1.04 | 104% | 5.7 | 18.59 | 93% | 3.3 |
| 12 | Pentafluorobenzene (Surr) | 9.86 | 99% | 1.1 | 9.67 | 97% | 1.8 | 9.91 | 99% | 2.4 |
| 13 | 1,1,1-Trichloroethane | 0.46 | 91% | 8.1 | 0.95 | 95% | 5.8 | 18.69 | 93% | 3.8 |
| 14 | Carbon tetrachloride | 0.41 | 81% | 4.6 | 0.91 | 91% | 9.1 | 19.31 | 97% | 3.8 |
| 15 | Benzene | 0.50 | 99% | 2.8 | 0.98 | 98% | 5.1 | 18.67 | 93% | 3.6 |
| 16 | 1,2-Dichloroethane | 0.52 | 105% | 3.8 | 1.06 | 106% | 6.9 | 18.49 | 92% | 2.0 |
| 17 | Fluorobenzene (Surr) | 9.77 | 98% | 1.4 | 9.80 | 98% | 1.2 | 9.93 | 99% | 2.0 |
| 18 | Trichloroethene | 0.52 | 104% | 3.3 | 1.02 | 102% | 8.6 | 18.64 | 93% | 4.1 |
| 19 | 1,2-Dichloropropane | 0.53 | 105% | 3.1 | 1.02 | 102% | 3.6 | 18.76 | 94% | 1.4 |
| 20 | Bromodichloromethane | 0.49 | 98% | 7.1 | 1.01 | 101% | 7.3 | 19.20 | 96% | 1.6 |
| 21 | 2-Chloroethylvinyl ether | 0.47 | 93% | 12.4 | 0.87 | 87% | 5.3 | 20.40 | 102% | 1.2 |
| 22 | <i>cis</i> -1,3-Dichloropropene | 0.46 | 92% | 4.8 | 0.95 | 95% | 9.7 | 18.72 | 94% | 1.4 |
| 23 | Toluene | 0.47 | 93% | 5.7 | 0.92 | 92% | 4.7 | 19.35 | 97% | 2.1 |
| 24 | <i>trans</i> -1,3-Dichloropropene | 0.45 | 90% | 7.6 | 0.97 | 97% | 9.2 | 18.87 | 94% | 1.0 |
| 25 | 2-Bromo-1-chloropropane (IS) | 30.00 | NA | NA | 30.00 | NA | NA | 30.00 | NA | NA |
| 26 | 1,1,2-Trichloroethane | 0.54 | 108% | 3.6 | 1.06 | 106% | 3.0 | 18.94 | 95% | 1.5 |
| 27 | Tetrachloroethene | 0.52 | 104% | 4.6 | 1.02 | 102% | 8.0 | 18.08 | 90% | 2.7 |
| 28 | Dibromochloromethane | 0.49 | 98% | 5.4 | 1.05 | 105% | 5.4 | 19.96 | 100% | 1.3 |
| 29 | Chlorobenzene | 0.50 | 100% | 4.7 | 0.99 | 99% | 5.2 | 19.63 | 98% | 1.5 |
| 30 | Ethylbenzene | 0.41 | 83% | 3.6 | 0.85 | 85% | 8.2 | 20.57 | 103% | 2.4 |
| 31 | Bromoform | 0.46 | 93% | 7.5 | 0.97 | 97% | 4.2 | 20.10 | 100% | 1.7 |
| 32 | 1,4-Dichlorobutane (IS) | 30.00 | NA | NA | 30.00 | NA | NA | 30.00 | NA | NA |
| 33 | 4-Bromofluorobenzene (Surr) | 10.15 | 101% | 0.7 | 10.10 | 101% | 1.3 | 9.99 | 100% | 1.4 |
| 34 | 1,1,2,2-Tetrachloroethane | 0.51 | 103% | 5.4 | 1.07 | 107% | 3.9 | 19.31 | 97% | 1.3 |
| 35 | 1,3-Dichlorobenzene | 0.51 | 102% | 4.8 | 1.03 | 103% | 8.5 | 19.82 | 99% | 0.5 |
| 36 | 1,4-Dichlorobenzene | 0.51 | 101% | 5.1 | 1.03 | 103% | 8.5 | 20.51 | 103% | 1.6 |
| 37 | 1,2-Dichlorobenzene | 0.50 | 101% | 5.6 | 1.01 | 101% | 8.7 | 20.55 | 103% | 1.2 |

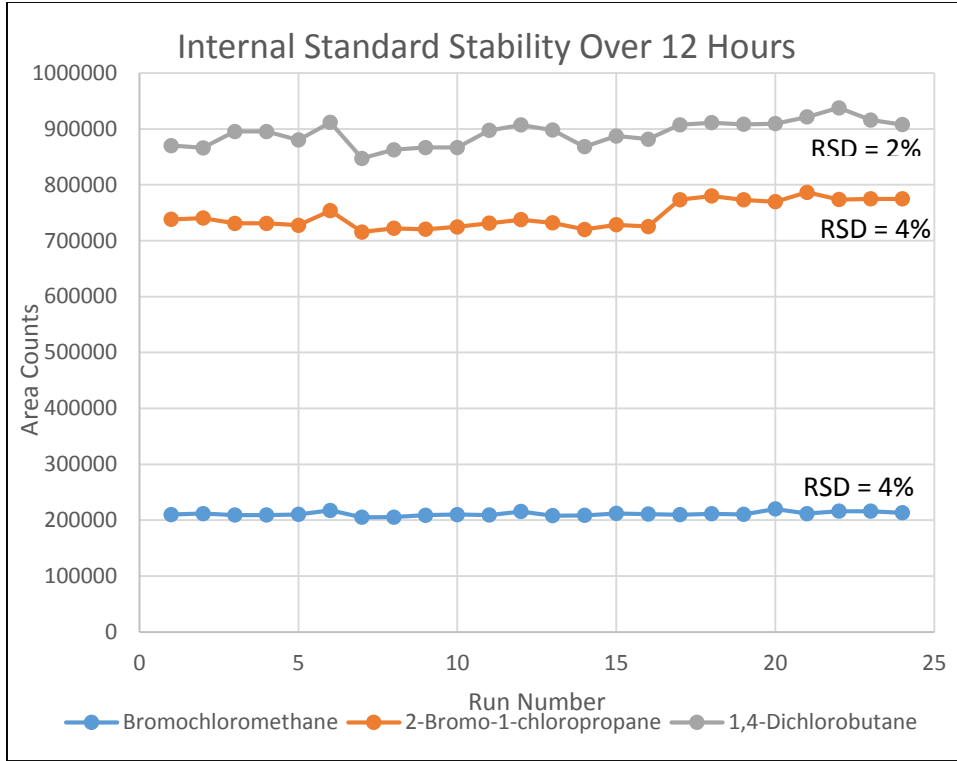


Figure 4: Internal Standard Response over a Representative 12-Hour Tune Period during This Study

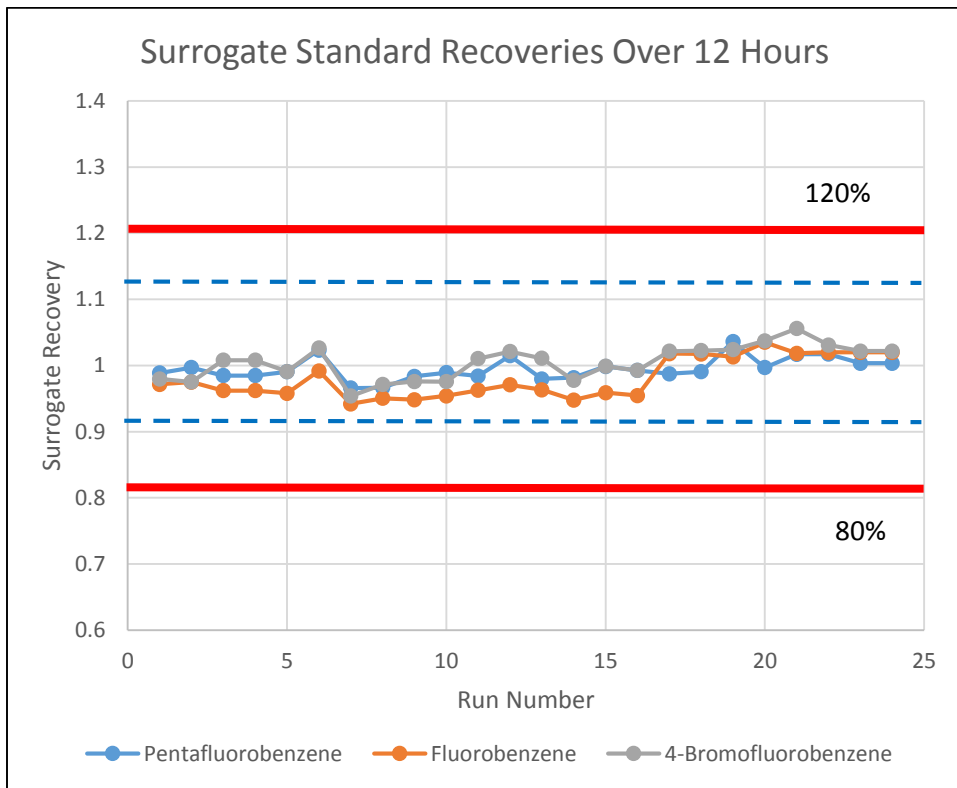


Figure 5: Surrogate Standard Recoveries over a Representative 12-Hour Tune Period during This Study

Analysis of Reference Material and Real-world Samples

An analytical standard from a second source was obtained and analyzed as a Reference Material. It was spiked at 100 µg/L and analyzed in triplicate. Repeatability across the three replicates yielded %RSD between 0.2 and 5.4% for all compounds, average %RSD of 1.8%, and average recovery of 109 to 111% for all compounds.

Three real-world wastewater samples were also analyzed in triplicate. Most compounds were either

not detected or were detected at concentrations below the calibration range (coded J). One compound, chlorobenzene, was detected in all three samples at concentrations ranging from 300 to 400 µg/L and had to be diluted. The EST Centurion Water/Soil Autosampler has an optional syringe that provided auto-dilution capability and produced repeatable results. Results from analysis of the Reference Material and the three real-world samples are summarized in Table 6.

Table 6: Summary of Results from Triplicate Analyses of One Second Source Reference Material and Three Real-World Samples

| Peak # | Compound Name | 2nd Source | Sample #1 | | | | Sample #2 | | | | Sample #3 | | | |
|-------------------------|------------------------------|------------|--------------|-----------------|--------------|-----------------|--------------|-----------------|--------------|-----------------|--------------|-----------------|--------------|-----------------|
| | | | Original | | 1:5 Dilution | | Original | | 1:5 Dilution | | Original | | 1:5 Dilution | |
| | | | %RSD (n = 3) | Avg Conc (µg/L) | %RSD (n = 3) | Avg Conc (µg/L) | %RSD (n = 3) | Avg Conc (µg/L) | %RSD (n = 3) | Avg Conc (µg/L) | %RSD (n = 3) | Avg Conc (µg/L) | %RSD (n = 3) | Avg Conc (µg/L) |
| 1 | Chloromethane | 1.3 | J | J | J | J | J | J | J | J | J | J | J | J |
| 2 | Vinyl chloride | 1.0 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 3 | Bromomethane | 5.4 | J | J | J | J | J | J | J | J | J | J | J | J |
| 4 | Chloroethane | 0.2 | ND | ND | ND | ND | J | J | J | J | J | J | J | J |
| 5 | Trichlorofluoromethane | 1.1 | J | J | J | J | J | J | J | J | J | J | J | J |
| 6 | 1,1-Dichloroethene | 1.7 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 7 | Methylene chloride | 1.7 | 5.8 | 1.9 | 5.2 | 2.3 | 14.4 | 0.7 | 9.6 | 2.9 | 9.0 | 2.5 | 8.8 | 1.3 |
| 8 | trans-1,2-dichloroethene | 1.1 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 9 | 1,1-Dichloroethane | 0.8 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 10 | Bromochloromethane (IS) | | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA |
| 11 | Chloroform | 0.9 | J | J | J | J | 3.0 | 3.8 | 3.8 | 7.8 | 6.1 | 4.9 | 5.9 | 2.6 |
| 12 | Pentafluorobenzene (Surr) | 1.4 | 10.0 | 2.5 | 13.0 | 0.8 | 9.5 | 0.7 | 13.1 | 1.8 | 9.4 | 1.8 | 13.5 | 2.4 |
| 13 | 1,1,1-trichloroethane | 1.2 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 14 | Carbon tetrachloride | 1.3 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 15 | Benzene | 0.6 | 0.6 | 3.5 | 0.6 | 5.8 | 1.3 | 2.0 | 0.8 | 2.5 | 0.9 | 2.0 | 0.6 | 3.8 |
| 16 | 1,2-Dichloroethane | 1.1 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 17 | Fluorobenzene (Surr) | 2.9 | 9.9 | 0.8 | 11.9 | 0.6 | 10.1 | 1.4 | 11.9 | 1.5 | 10.2 | 3.3 | 12.0 | 1.0 |
| 18 | Trichloroethene | 0.6 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 19 | 1,2-Dichloropropane | 2.2 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 20 | Bromodichloromethane | 2.1 | J | J | J | J | J | J | J | J | 2.9 | 1.6 | 2.7 | 2.5 |
| 21 | 2-Chloroethylvinyl ether | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 22 | cis-1,3-Dichloropropene | 2.0 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 23 | Toluene | 2.2 | 2.3 | 1.8 | 1.5 | 20.1 | 4.6 | 2.0 | 3.2 | 1.9 | 3.2 | 6.5 | 2.2 | 4.4 |
| 24 | trans-1,3-dichloropropene | 2.0 | J | J | J | J | ND | ND | ND | ND | ND | ND | ND | ND |
| 25 | 2-Bromo-1-chloropropane (IS) | | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA |
| 26 | 1,1,2-Trichloroethane | 2.0 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 27 | Tetrachloroethene | 4.4 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 28 | Dibromochloromethane | 2.6 | ND | ND | ND | ND | ND | ND | ND | ND | 1.9 | 5.0 | ND | ND |
| 29 | Chlorobenzene | 1.5 | 418.9 | 0.8 | 85.8 | 22.4 | 347.3 | 0.9 | 71.3 | 1.2 | 302.7 | 2.1 | 63.8 | 3.4 |
| 30 | Ethylbenzene | 1.7 | J | J | J | J | J | J | J | J | J | J | J | J |
| 31 | Bromoform | 1.7 | J | J | J | J | J | J | J | J | J | J | J | J |
| 32 | 1,4-Dichlorobutane (IS) | | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA | 30.0 | NA |
| 33 | 4-Bromofluorobenzene (Surr) | 3.1 | 9.8 | 1.1 | 9.1 | 0.9 | 9.5 | 1.1 | 9.3 | 0.9 | 9.8 | 2.1 | 9.5 | 1.8 |
| 34 | 1,1,2,2-Tetrachloroethane | 1.2 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 35 | 1,3-Dichlorobenzene | 3.1 | J | J | J | J | J | J | J | J | J | J | J | J |
| 36 | 1,4-Dichlorobenzene | 2.9 | J | J | J | J | J | J | J | J | J | J | J | J |
| 37 | 1,2-Dichlorobenzene | 1.9 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Average %RSD | | 1.8% | | | | | | | | | | | | |
| Average Recovery | | 109-111% | | | | | | | | | | | | |

■ Summary and Conclusions

The instrumentation and analytical conditions shown here have been demonstrated to provide outstanding results for US EPA Method 624, far exceeding all existing method criteria. The narrow-bore capillary column and Constant Linear Velocity mode provided outstanding chromatography for all compounds, including the early-eluting light gases, in less than 10 minutes. Calibration curves over narrow or wide ranges can be used to meet the project or contract needs. MDLs are easily 10-fold lower than the MDLs cited in the method, and a high level of precision and accuracy can be expected across any calibration range, particularly at the lower concentrations.

■ Ordering Information for Replacement Consumables

The consumables used in this application note are shown in the table below. To order any of these items please contact Customer Service at Shimadzu Scientific Instruments at 1-800-477-1227, or visit our web store at <http://store.shimadzu.com>.

| Part Number | Item Name | Photo | Item Description |
|--------------|--|---|---|
| 221-75962-30 | Capillary Column |  | SH-RXI-624 SIL MS, 30 m x 0.25 mm x 1.40 µm |
| 220-90784-10 | Inlet Liner |  | Low-volume Liner, 1.0 mm ID, Straight, 5/Pkg (Restek) |
| 220-94775-10 | VOA Tuning Compound |  | 1-Bromo-4-fluorobenzene (BFB), 5,000 µg/mL in P&T MeOH, 1 mL/ampule, CAS #: 460-00-4 (Restek) |
| 220-94775-11 | 624 Internal Standard Mix (3 Components) |  | 1,500 µg/mL each in P&T MeOH, 1 mL/ampule (Restek) |
| 220-94775-12 | 624 Surrogate Standard Mix (3 Components) |  | 2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek) |
| 220-94775-13 | 624 Volatiles Standard Mix (26 Components) |  | 2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek) |
| 220-94775-14 | 502.2 Calibration Mix #1, Gases (6 Components) |  | 2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek) |
| 220-94775-00 | n-Alkane Mix |  | AART Standard for determination of Retention Index (RI) and Retention Times (RT) |
| 220-94594-00 | Electronic Flow Meter |  | ProFLOW 6000 Electronic Flow Meter (Restek) |
| 220-94594-01 | Electronic Leak Detector |  | Electronic Leak Detector With Hard-Sided Carrying Case and Universal Charger Set (Restek) |

■ **References**

- I. Appendix A to Part 136, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 624 – Purgeables.
- II. Shimadzu Guide to BFB Tuning for Analysis of Volatile Organic Compounds, GCMS Application News No. GCMS-1405.
- III. Definition and Procedure for the Determination of the Method Detection Limit. *Fed. Regist.* **1984**. 49 (209), Appendix B to Part 136.

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