APPLICATION NOTE: AN2208
TECHNOLOGY: P+T VOC
INDUSTRY: ENV

# US EPA Method 524.4 Using the Teledyne Tekmar Atomx XYZ with Agilent 7890B GC/5977B MS and Hydrogen as an Alternative Carrier Gas

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## Abstract

As helium supplies become increasingly scarce and expensive, laboratories have begun seeking alternative carrier gases that are readily available and economical. This application note will evaluate hydrogen as the carrier gas for US EPA Method 524.4 to determine the concentration of volatile organic compounds (VOCs) in drinking water matrices. The Teledyne Tekmar Atomx XYZ purge and trap (P&T) VOC sample preparation system combined with an Agilent 7890B Gas Chromatograph (GC)/5977B Mass Spectrometer (MS) was used to create a working linear ($r^2$) calibration curve, method detection limits (MDL), a mid-point calibration check with accuracy and precision and minimum reporting level (MRL) confirmation for target compounds.

## Introduction

The Atomx XYZ is Teledyne Tekmar's most advanced P&T system and is based on the time-tested Atomx instrument platform. The concentrator's efficient trap cooling design reduces sample cycle time by as much as 14% over the previous model. Combined with its 84-position soil and water autosampler, the result is more samples tested per 12-hour period. An innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan. In addition to other refinements, the Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

## Sample Preparation

A 50 parts per million (ppm) calibration working standard was prepared in methanol from the following Restek® standards: 524.3 VOA Mega Mix® and 524.3 Gas Calibration Mix. In total, the standards contained 75 compounds.

An eight-point linear ($r^2$) calibration curve was prepared from 0.2 ppb to 40 parts per billion (ppb) for all compounds with regression value ($r^2$) ≥0.995. The relative response factor (RRF) was calculated for each compound using three internal standards: 1,4-Difluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Surrogate standards consisted of: Methyl-tert-Butyl Ether-d3, 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 12.5 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 12.5 ppb.

Seven 1 ppb standards were prepared to calculate the MDL and MRL confirmation calculations. Also, seven 10 ppb standards were prepared for the accuracy and precision calculations of the mid-point calibration check. All calibration, MDL, MRL and mid-point calibration check standards were analyzed with the Atomx XYZ conditions in Table I. GC-MS conditions are shown in Table II.



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## Experimental Instrument Conditions

| Table I Teledyne Tekmar Atomx XYZ Water Method Conditions | | | |
|---|---|---|---|
| **Standby** | **Variable** | **Desorb** | **Variable** |
| Valve Oven Temp | 140 ºC | Methanol Needle Rinse | Off |
| Transfer Line Temp | 140 ºC | Water Needle Rinse Volume | 7.00 mL |
| Sample Mount Temp | 90 ºC | Sweep Needle Time | 0.25 min |
| Water Heater Temp | 90 ºC | Desorb Preheat Temp | 245 ºC |
| Sample Vial Temp | 20 ºC | GC Start Signal | Begin Desorb |
| Soil Valve Temp | 50 ºC | Desorb Time | 2.00 min |
| Standby Flow | 10 mL/min | Drain Flow | 300 mL/min |
| Purge Ready Temp | 40 ºC | Desorb Temp | 250 ºC |
| **Purge** | **Variable** | **Bake** | **Variable** |
| Sample Equilibrate Time | 0.00 min | Methanol Glass Rinse | Off |
| Pre-sweep Time | 0.25 min | Water Bake Rinses | 1 |
| Prime Sample Fill Volume | 3.00 mL | Water Bake Rinse Volume | 7.00 mL |
| Sample Volume | 5.00 mL | Bake Rinse Sweep Time | 0.25 min |
| Sweep Sample Time | 0.25 min | Bake Rinse Sweep Flow | 100 mL/min |
| Sweep Sample Flow | 100 mL/min | Bake Rinse Drain Time | 0.40 min |
| Sparge Vessel Heater | Off | Bake Time | 2.00 min |
| Purge Time | 8.00 min | Bake Flow | 200 mL/min |
| Purge Flow | 55 mL/min | Bake Temp | 260 ºC |
| Purge Temp | 20 ºC | MCS Bake Temp | 180 ºC |
| MCS Purge Temp | 20 ºC | | |
| Dry Purge Time | 1.00 min | **Trap** | 9 |
| Dry Purge Flow | 100 mL/min | **Chiller Tray** | On |
| Dry Purge Temp | 20 ºC | **Purge Gas** | Nitrogen |



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| Table II Agilent 7890B GC/5977B MS System Conditions | |
|---|---|
| **Agilent 7890B GC Conditions** | |
| Column | Rtx® VMS, 20 m x 0.18 mm, 1µm Film, Column Flow – 0.8 mL/min |
| Oven Profile | 35 ºC, 2 min, 10 ºC/min to 85 ºC, 30 ºC/min to 225 ºC, 1 min Hold, Run Time 12.67 min |
| Inlet | 200 ºC, 80:1 Split, Septum Purge Flow 0.5 mL/min, Carrier Gas - Hydrogen |
| **Agilent 5977B MS Conditions** | |
| Temp | Transfer Line 250 ºC; Source 250 ºC; Quad 200 ºC |
| Scan | Range 35 *m/z* to 260 *m/z*, Solvent Delay 0.50 min, Normal Scanning |
| Current | Gain Factor 1.00, Extraction Source Tune |

## Results

The linear correlation coefficient of the calibration curve ($r^2$), MDL, mid-point calibration check and MRL confirmation data are shown in Table III. Figure 1 displays a 10 ppb standard, indicating excellent peak resolution with minimal water interference for all VOCs.

**Table III Method 524.4 Calibration, Method Detection Limit, Mid-Point Check, and Minimum Reporting Level Data**

| Compound | Calibration (0.2 ppb – 40 ppb) | | | | Method Detection Limits (n=7, 1 ppb) | | Mid-Point Check (n=7, 10 ppb) | | Minimum Reporting Level (n=7, 1 ppb) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ret. Time | Confirm. Ion | Linearity ($r^2$ ≥0.995) | Avg. RRF | MDL (ppb) | Precision (≤20%) | Precision (≤20%) | Accuracy (±30%) | LPIR (≥50%) | UPIR (≤150%) |
| Dichlorodifluoromethane | 0.788 | 85 | 0.998 | 0.566 | 0.14 | 4.8 | 5.8 | 106 | 75 | 110 |
| Chlorodifluoromethane | 0.809 | 51 | 1.00 | 0.896 | 0.13 | 4.2 | 7.1 | 107 | 82 | 116 |
| Chloromethane | 0.880 | 50 | 0.999 | 0.424 | 0.14 | 4.4 | 5.6 | 103 | 82 | 116 |
| Vinyl Chloride | 0.915 | 62 | 0.999 | 0.587 | 0.10 | 3.3 | 6.7 | 104 | 88 | 114 |
| 1,3-Butadiene | 0.924 | 54 | 0.999 | 0.606 | 0.17 | 5.2 | 6.7 | 104 | 81 | 123 |
| Bromomethane | 1.08 | 94 | 0.998 | 0.614 | 0.13 | 4.0 | 7.3 | 108 | 90 | 124 |
| Trichlorofluoromethane | 1.22 | 101 | 0.999 | 0.572 | 0.10 | 3.5 | 6.1 | 106 | 75 | 99 |
| Diethyl Ether | 1.40 | 59 | 0.999 | 0.319 | 0.13 | 3.8 | 4.5 | 106 | 89 | 121 |
| Carbon Disulfide[1] | 1.51 | 76 | 1.00 | 0.206 | 0.15 | 4.7 | 6.3 | 100 | 84 | 122 |
| 1,1-Dichloroethene | 1.51 | 96 | 1.00 | 0.288 | 0.08 | 2.7 | 7.0 | 103 | 90 | 111 |
| Iodomethane | 1.59 | 142 | 0.997 | 0.238 | 0.07 | 1.6 | 4.5 | 98 | 124 | 141 |
| Allyl Chloride | 1.81 | 76 | 1.00 | 0.172 | 0.16 | 5.2 | 6.1 | 99 | 79 | 119 |
| Methylene Chloride | 1.89 | 84 | 0.999 | 0.371 | 0.18 | 5.8 | 5.3 | 105 | 76 | 120 |



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**Table III Method 524.4 Calibration, Method Detection Limit, Mid-Point Check, and Minimum Reporting Level Data**

| Compound | Calibration (0.2 ppb – 40 ppb) | | | | Method Detection Limits (n=7, 1 ppb) | | Mid-Point Check (n=7, 10 ppb) | | Minimum Reporting Level (n=7, 1 ppb) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ret. Time | Confirm. Ion | Linearity ($r^2$ ≥0.995) | Avg. RRF | MDL (ppb) | Precision (≤20%) | Precision (≤20%) | Accuracy (±30%) | LPIR (≥50%) | UPIR (≤150%) |
| trans-1,2-Dichloroethene | 2.00 | 96 | 0.999 | 0.269 | 0.15 | 5.1 | 6.1 | 104 | 77 | 115 |
| Methyl-tert-Butyl Ether-d3 (SURR) | 2.09 | 76 | 1.26 | 1.05 | | 1.3 | 1.9 | 99 | 94 | 105 |
| Methyl Acetate | 2.10 | 43 | 0.999 | 1.94 | 0.17 | 5.3 | 5.6 | 107 | 79 | 121 |
| Methyl-tert-Butyl Ether | 2.11 | 73 | 0.999 | 1.12 | 0.08 | 2.9 | 4.5 | 107 | 82 | 103 |
| tert-Butyl Alcohol | 2.23 | 59 | 0.999 | 0.045 | 0.11 | 3.1 | 3.3 | 104 | 95 | 122 |
| Diisopropyl Ether | 2.42 | 45 | 0.999 | 1.27 | 0.13 | 4.2 | 5.2 | 107 | 84 | 118 |
| 1,1-Dichloroethane | 2.47 | 63 | 0.999 | 0.695 | 0.18 | 5.7 | 5.6 | 106 | 78 | 123 |
| tert-Butyl Ethyl Ether | 2.71 | 59 | 0.999 | 1.20 | 0.07 | 2.5 | 5.1 | 106 | 83 | 101 |
| cis-1,2-Dichloroethene | 2.91 | 96 | 1.00 | 0.380 | 0.15 | 4.9 | 5.5 | 108 | 78 | 117 |
| Bromochloromethane | 3.06 | 128 | 0.999 | 0.181 | 0.17 | 5.3 | 5.2 | 101 | 81 | 125 |
| Chloroform | 3.14 | 83 | 1.00 | 0.557 | 0.06 | 2.1 | 4.2 | 104 | 92 | 108 |
| Carbon Tetrachloride | 3.21 | 117 | 1.00 | 0.221 | 0.15 | 4.9 | 5.8 | 101 | 81 | 119 |
| Tetrahydrofuran | 3.28 | 72 | 0.999 | 0.048 | 0.09 | 2.9 | 3.6 | 94 | 90 | 114 |
| 1,1,1-Trichloroehane | 3.28 | 97 | 0.999 | 0.352 | 0.12 | 3.6 | 4.8 | 102 | 89 | 119 |
| 1,1-Dichloropropene | 3.38 | 75 | 0.999 | 0.417 | 0.15 | 5.0 | 5.0 | 105 | 78 | 116 |
| 1-Chlorobutane | 3.44 | 56 | 0.999 | 0.579 | 0.13 | 4.2 | 5.3 | 106 | 83 | 116 |
| Benzene | 3.59 | 78 | 0.999 | 1.60 | 0.18 | 5.8 | 4.9 | 107 | 77 | 124 |
| tert-Amyl Methyl Ether | 3.75 | 73 | 0.999 | 0.902 | 0.10 | 2.9 | 4.0 | 102 | 93 | 117 |
| 1,2-Dichloroethane | 3.78 | 62 | 0.999 | 0.489 | 0.13 | 4.2 | 3.8 | 105 | 82 | 115 |
| Trichloroethylene | 4.12 | 95 | 0.999 | 0.465 | 0.10 | 3.4 | 4.1 | 104 | 82 | 108 |
| 1,4-Difluorobenzene (IS) | 4.19 | 114 | | | | | | | | |
| tert-Amyl Ethyl Ether | 4.42 | 59 | 0.999 | 0.753 | 0.10 | 3.0 | 4.0 | 102 | 94 | 120 |
| Dibromomethane | 4.50 | 93 | 0.999 | 0.192 | 0.18 | 5.2 | 2.4 | 101 | 88 | 133 |
| 1,2-Dichloropropane | 4.61 | 63 | 0.999 | 0.378 | 0.06 | 1.9 | 4.0 | 104 | 100 | 116 |
| Bromodichloromethane | 4.70 | 83 | 0.999 | 0.285 | 0.10 | 2.9 | 3.6 | 101 | 100 | 126 |
| cis-1,3-Dichloropropene | 5.34 | 75 | 0.999 | 0.436 | 0.08 | 2.3 | 3.9 | 99 | 106 | 127 |
| Toluene | 5.57 | 92 | 0.999 | 0.942 | 0.09 | 2.7 | 4.6 | 106 | 93 | 115 |



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**Table III Method 524.4 Calibration, Method Detection Limit, Mid-Point Check, and Minimum Reporting Level Data**

| Compound | Calibration (0.2 ppb – 40 ppb) | | | | Method Detection Limits (n=7, 1 ppb) | | Mid-Point Check (n=7, 10 ppb) | | Minimum Reporting Level (n=7, 1 ppb) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ret. Time | Confirm. Ion | Linearity ($r^2$ ≥0.995) | Avg. RRF | MDL (ppb) | Precision (≤20%) | Precision (≤20%) | Accuracy (±30%) | LPIR (≥50%) | UPIR (≤150%) |
| Tetrachloroethylene | 5.95 | 166 | 0.999 | 0.493 | 0.08 | 2.7 | 4.9 | 100 | 86 | 107 |
| trans-1,3-Dichloropropene | 6.06 | 75 | 0.999 | 0.344 | 0.08 | 2.2 | 3.4 | 102 | 104 | 124 |
| 1,1,2-Trichloroethane | 6.22 | 83 | 0.999 | 0.245 | 0.09 | 2.7 | 3.7 | 102 | 90 | 112 |
| Ethyl Methacrylate | 6.32 | 69 | 0.996 | 0.325 | 0.14 | 3.6 | 3.6 | 98 | 108 | 144 |
| Dibromochloromethane | 6.38 | 129 | 0.999 | 0.175 | 0.17 | 5.0 | 4.2 | 102 | 85 | 126 |
| 1,3-Dichloropropane | 6.50 | 76 | 0.999 | 0.561 | 0.12 | 3.7 | 3.1 | 105 | 85 | 115 |
| 1,2-Dibromoethane | 6.59 | 107 | 0.999 | 0.213 | 0.14 | 3.8 | 3.5 | 99 | 97 | 131 |
| Chlorobenzene-d5 (IS) | 7.21 | 117 | | | | | | | | |
| Chlorobenzene | 7.22 | 112 | 0.999 | 1.02 | 0.06 | 2.0 | 4.2 | 105 | 88 | 103 |
| Ethylbenzene | 7.30 | 91 | 0.999 | 1.99 | 0.15 | 4.7 | 4.6 | 106 | 80 | 117 |
| 1,1,1,2-Tetrachloroethane | 7.32 | 131 | 0.999 | 0.188 | 0.11 | 3.2 | 3.7 | 102 | 97 | 125 |
| m,p-Xylene | 7.45 | 106 | 1.00 | 0.674 | 0.08 | 1.3 | 4.3 | 102 | 96 | 107 |
| o-Xylene | 7.83 | 106 | 0.999 | 0.647 | 0.09 | 2.8 | 4.2 | 102 | 93 | 116 |
| Bromoform | 7.87 | 173 | 0.997 | 0.101 | 0.11 | 2.9 | 3.4 | 98 | 105 | 132 |
| Styrene | 7.88 | 104 | 0.999 | 0.979 | 0.07 | 2.0 | 3.8 | 99 | 104 | 122 |
| Isopropylbenzene | 8.10 | 105 | 1.00 | 1.63 | 0.09 | 2.8 | 4.8 | 103 | 88 | 110 |
| 4-Bromofluorobenzene (SURR) | 8.30 | 95 | 4.01 | 1.14 | | 2.3 | 1.2 | 99 | 94 | 112 |
| Bromobenzene | 8.35 | 156 | 0.999 | 0.707 | 0.15 | 4.7 | 4.7 | 104 | 81 | 119 |
| n-Propylbenzene | 8.42 | 91 | 0.998 | 4.72 | 0.13 | 4.0 | 5.2 | 111 | 86 | 118 |
| 1,1,2,2-Tetrachloroethane | 8.50 | 83 | 0.995 | 0.438 | 0.12 | 4.6 | 3.8 | 102 | 114 | 143 |
| 2-Chlorotoluene | 8.51 | 91 | 0.999 | 2.61 | 0.14 | 4.6 | 5.3 | 110 | 77 | 111 |
| 1,2,3-Trichloropropane | 8.56 | 75 | 0.998 | 0.684 | 0.18 | 5.9 | 3.7 | 106 | 74 | 119 |
| 1,3,5-Trimethylbenzene | 8.58 | 105 | 0.999 | 3.38 | 0.16 | 5.8 | 5.2 | 109 | 69 | 110 |
| 4-Chlorotoluene | 8.63 | 91 | 0.999 | 2.65 | 0.12 | 4.0 | 4.8 | 108 | 82 | 113 |
| tert-Butylbenzene | 8.79 | 119 | 0.997 | 2.53 | 0.11 | 4.0 | 5.2 | 114 | 73 | 100 |
| Pentachloroethane | 8.79 | 167 | 0.999 | 0.063 | 0.17 | 5.4 | 6.1 | 102 | 78 | 120 |
| 1,2,4-Trimethylbenzene | 8.84 | 105 | 0.999 | 3.25 | 0.12 | 4.2 | 4.7 | 109 | 77 | 107 |



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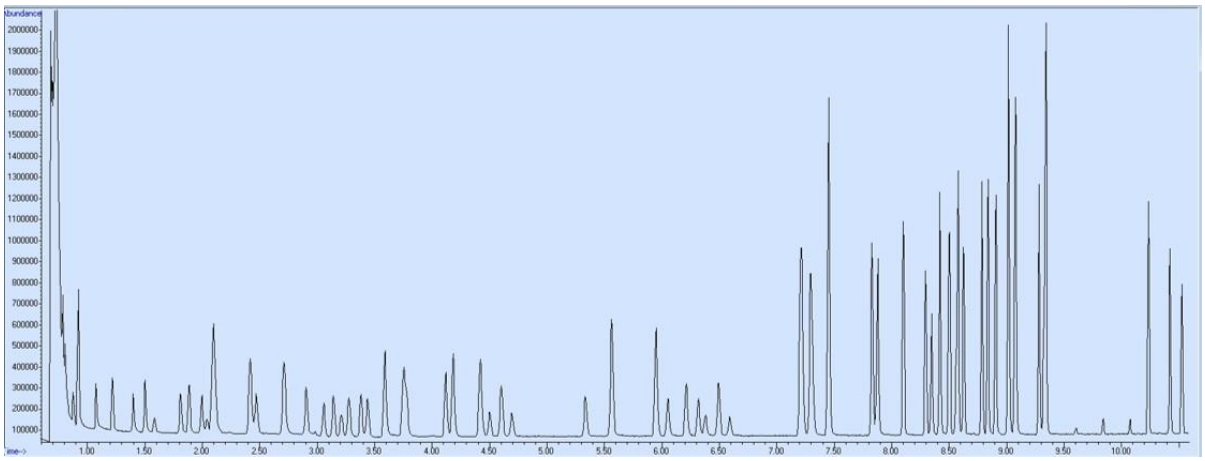
| Compound | Calibration (0.2 ppb – 40 ppb) | | | | Method Detection Limits (n=7, 1 ppb) | | Mid-Point Check (n=7, 10 ppb) | | Minimum Reporting Level (n=7, 1 ppb) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ret. Time | Confirm. Ion | Linearity ($r^2$ ≥0.995) | Avg. RRF | MDL (ppb) | Precision (≤20%) | Precision (≤20%) | Accuracy (±30%) | LPIR (≥50%) | UPIR (≤150%) |
| sec-Butylbenzene | 8.91 | 105 | 0.999 | 3.83 | 0.12 | 4.7 | 5.4 | 110 | 66 | 97 |
| p-Isopropyltoluene | 9.02 | 119 | 0.998 | 3.08 | 0.06 | 2.3 | 5.1 | 110 | 74 | 89 |
| 1,3-Dichlorobenzene | 9.02 | 146 | 0.999 | 1.44 | 0.07 | 2.1 | 4.5 | 104 | 95 | 112 |
| 1,4-Dichlorobenzene-d4 (IS) | 9.08 | 152 | | | | | | | | |
| 1,4-Dichlorobenzene | 9.09 | 146 | 0.999 | 1.44 | 0.08 | 2.5 | 4.6 | 105 | 88 | 107 |
| n-Butylbenzene | 9.28 | 91 | 0.998 | 3.44 | 0.15 | 4.9 | 4.9 | 111 | 80 | 118 |
| Hexachloroethane | 9.33 | 166 | 0.999 | 0.335 | 0.16 | 5.4 | 6.1 | 104 | 76 | 117 |
| 1,2-Dichlorobenzene-d4 (SURR) | 9.34 | 152 | 1.72 | 0.999 | | 1.5 | 1.3 | 99 | 92 | 103 |
| 1,2-Dichlorobenzene | 9.35 | 146 | 0.999 | 1.40 | 0.07 | 2.5 | 4.2 | 106 | 86 | 104 |
| 1,2-Dibromo-3-Chloropropane | 9.84 | 75 | 0.995 | 0.111 | 0.16 | 4.7 | 2.6 | 102 | 86 | 126 |
| Hexachlorobutadiene | 10.24 | 225 | 0.999 | 0.266 | 0.17 | 5.0 | 3.8 | 102 | 89 | 133 |
| 1,2,4-Trichlorobenzene | 10.24 | 180 | 0.999 | 0.861 | 0.08 | 2.2 | 3.4 | 99 | 106 | 126 |
| Naphthalene | 10.42 | 128 | 0.998 | 2.66 | 0.12 | 4.3 | 3.8 | 108 | 76 | 107 |
| 1,2,3-Trichlorobenzene | 10.53 | 180 | 0.998 | 0.817 | 0.06 | 1.7 | 3.5 | 99 | 107 | 123 |

1. Calibration range from 0.5-40 ppb.

**Figure 1** Total Ion Chromatogram (TIC) of a US EPA 524.4 Water Method 10 ppb VOC Standard Indicating Consistent Peak Shapes and Separation with Minimal Water Interference.





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## Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in drinking water samples following the US EPA Method 524.4 with detection by an Agilent 7890B GC/5977B MS. The linearity of the calibration curve from 0.2 ppb to 40 ppb passed all method requirements with no interference from excessive water. Furthermore, the average MDL for all compounds was 0.12 ppb with a 3.7% RSD. Seven 10 ppb mid-point calibration check standards averaged a 104% recovery with a 4.6% RSD. Both MDL, MRL and mid-point calibration check showed no interference from excessive water.

The Atomx XYZ and GC-MS conditions displayed in Table I and Table II allow for up to three samples to run, within one hour. By making additional, appropriate changes to the GC oven temperature program, the GC/MS cycle time may also be reduced, increasing laboratory throughput in a 12-hour period.

## References

1. US EPA. 2013. “Method 524.4: “Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas,” Cincinnati, OH. [Online] https://nepis.epa.gov/Exe/ZyPDF.cgi/P100J7EE.PDF?Dockey=P100J7EE.PDF (accessed April 29, 2022).



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