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**Application Note 32610109**

# Can You Use Nitrogen as an Alternate Purge Gas for Analysis of Volatile Organic Compounds (VOCs)?


**Keywords**
Helium (He)
Nitrogen ($N_2$)
Purge Gas
Eclipse 4660 Purge-and-Trap (P&T) Sample Concentrator
Volatile Organic Compounds (VOCs)
U.S. EPA Method 524.2
U.S. EPA Method 502.2
U.S. EPA Method 8021



*Presented at the 2009 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, Illinois March 8–March 13, 2009*


## Introduction

In environmental laboratories, compressed gases such as helium, hydrogen, and air, are consumables that must be purchased on a regular basis and make up a large portion of the laboratory's operating budget. Because commercial laboratories operate on a slim margin, even a moderate increase in the price of compressed gases can have a negative impact on profitability. A recent increase in the demand for helium, coupled with low production levels worldwide has led to a global helium shortage, a dramatic increase in price for this commodity, and a search for alternatives in some applications.

Most U.S. Environmental Protection Agency (U.S. EPA) methods for analysis of volatile organic compounds (VOCs) call for extraction of the analytes by purging with helium for 11 minutes at 40 mL/minute, making purge-and-trap (P&T) one of the biggest consumers of helium in a laboratory. Any reduction in helium consumption could represent a significant savings. Compared to helium, nitrogen is abundantly available, inert and safe to use, and can be purchased at affordable prices.

This application note presents data comparing the relative response of typical VOCs when using helium (He) and nitrogen ($N_2$) as the purge gas in U.S. EPA, P&T methods. Data presented includes a calibration curve, method detection limit (MDL) study, and accuracy and precision study using $N_2$ as the purge gas and optimized P&T conditions.

## Instrumentation

Instrumentation used for this study included an OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator equipped with a patented [1] Infra-Sparge® sample heater, a 4551A Vial autosampler with Standard Addition Module (SAM) (Figure 1), and an Agilent 7890A/5975C
GC/MS.


Figure 1. Eclipse Purge-and-Trap Sample Concentrator with 4551A Autosampler and SAM

## Experimental

Standard P&T analytical conditions were defined as a helium purge flow rate of 40 mL/minute for 11 minutes, the OI #10 Trap (Tenax®/silica gel/carbon molecular sieve), sample temperature of 40 °C, and a 1-minute Desorb time. Variables tested included the OI #11 Trap (VOCARB® 3000), nitrogen purge gas at 40 mL/minute for 11 minutes, and modified Purge and Desorb times. The purge gas flow rate was measured and adjusted if necessary before each series of tests. Full instrument configuration and operating conditions, including the variables tested, are shown in Table 1.

For each series of tests, four 5-mL aliquots of the test standard were analyzed (refer to Table 2). Each peak was integrated using the quantitation ions recommended by U.S. EPA Method 524.2, and the average peak area over the four replicate analyses was used to evaluate the performance of the variable under examination.

Table 1. Instrument Configuration and Operating Conditions for Evaluation of Nitrogen as a Purge Gas

| Purge–and–Trap | Eclipse 4660 P&T Sample Concentrator |
|---|---|
| Autosampler | OI Analytical 4551A Vial Autosampler with Standard Addition Module (SAM) |
| Traps | Standard Conditions: #10 Trap, Tenax®/silica gel/CMS<br>Variable Tested: #11 Trap VOCARB® 3000 |
| Purge Gas | Standard Conditions: Helium at 40 mL/minute<br>Variable Tested: Nitrogen at 40 mL/minute |
| Purge Time | Standard Conditions: 11 minutes<br>Variable Tested: 7 minutes |
| Sample Temperature | 40 °C |
| Desorb Time | Standard Conditions: 1 minute<br>Variable Tested: 2 minutes |
| Bake Time | 5 minutes |
| OI #10 Trap Temperatures | 20 °C (ambient) at Purge<br>180 °C at Desorb Preheat<br>190 °C at Desorb<br>210 °C at Bake |
| OI #11 Trap Temperatures | 20 °C (ambient) at Purge<br>230 °C at Desorb Preheat<br>240 °C at Desorb<br>250 °C at Bake |
| Water Management | 110 °C at Purge<br>0 °C (ambient) at Desorb<br>240 °C at Bake |
| Transfer Line Temperature | 110 °C |
| Six-port Valve Temperature | 110 °C |
| Autosampler Gas | Nitrogen for vial pressurization and sample transfer |
| **Gas Chromatograph** | **Agilent 7890** |
| Column | Rtx-624, 30–m x 0.250–mm I.D. x 1.40–$\mu$m film |
| Carrier Gas | Helium |
| Inlet Temperature | 220 °C |
| Column Flow rate | 0.8 mL/minute |
| Split Ratio | 35:1 |
| Oven Program | 45 °C for 4.50 minutes<br>12 °C/minute to 100 °C<br>25 °C/minute to 240 °C (hold 1.32 minutes)<br>Total GC Run 16 minutes |
| **Mass Spectrometer** | **Agilent 5975C** |
| Mode | Scan 35–260 |
| Scans/Second | 3.25 |
| Solvent Delay | 1.40 minutes |
| Transfer Line Temperature | 240 °C |
| Source Temperature | 230 °C |
| Quad Temperature | 150 °C |

Table 2. Description of Test Standard

| Analyte Mix | USEPA Method 502.2 Mix, 60 compounds |
|---|---|
| Internal Standards | Fluorobenzene and 1, 2–dichlorobenzene–$d_4$ |
| Surrogates | Dibromofluoromethane, Toluene-$d_8$ and 1, 4–Bromofluorobenzene |
| Sample Size | 5 mL |
| Concentration | 25 ppb |

## Results and Discussion

The initial series of tests compared the absolute response for each compound on the OI #10 Trap and the OI #11 Trap using helium as a purge gas and the standard P&T conditions defined in Table 1. Compound responses were comparable on the two traps, indicating that either trap can be used for VOC analyses using standard conditions, with equally good results. Refer to Figure 2.

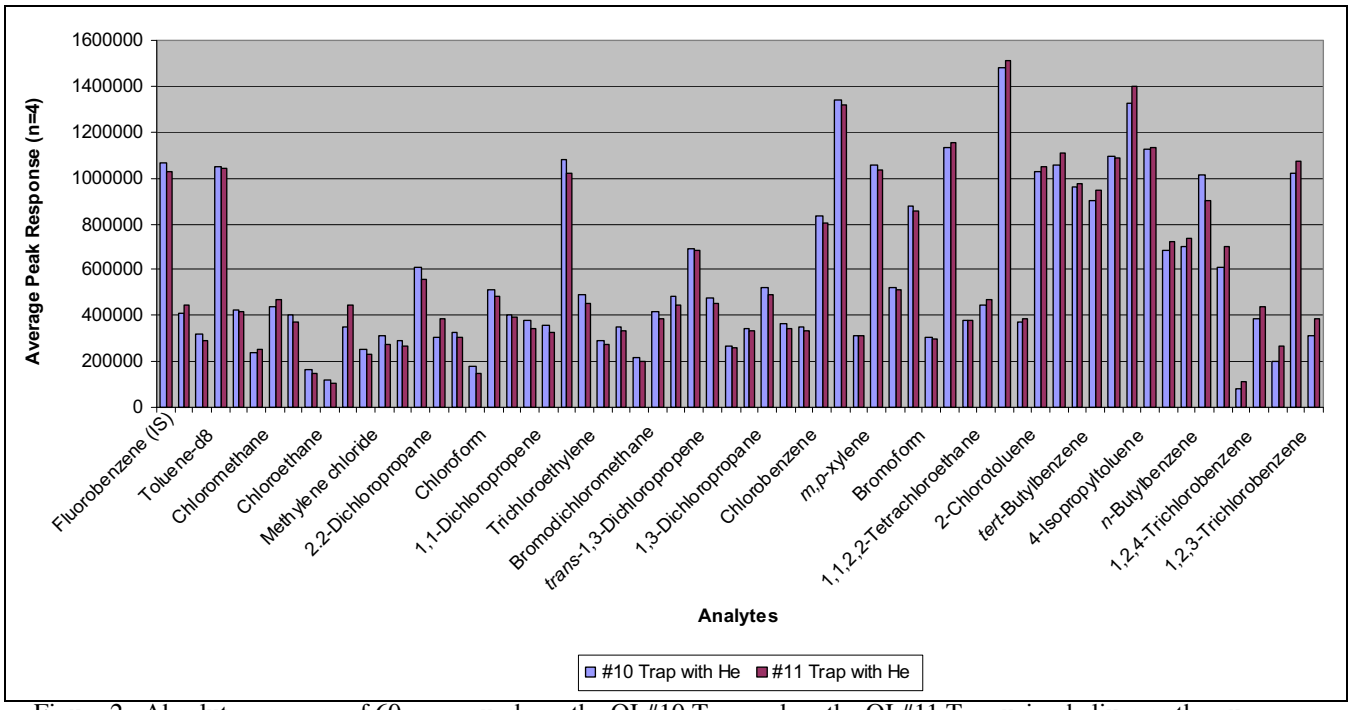


Figure 2. Absolute response of 60 compounds on the OI #10 Trap and on the OI #11 Trap using helium as the purge gas (40 mL/minute for 11 minutes). The full list of all 60 compounds is shown in Tables 4 and .

The next series of tests was designed to evaluate the relative response of each compound on the two traps when using nitrogen versus helium as the purge gas. With the OI #11 Trap (VOCARB), the average relative response of some compounds varied slightly between the two purge gases, but overall, performance using nitrogen as the purge gas was comparable to using helium. In Figure 3, the average compound responses using helium and the OI #11 Trap were normalized to 100% and compound responses with nitrogen are shown relative to the helium response. The percent Relative Standard Deviation (%RSD) of the responses for the four replicate analyses were under 5% for the majority of the compounds.

With the Tenax®/silica gel/carbon molecular sieve trap, the early eluting compounds had equivalent responses using nitrogen and helium as the purge gas; however, many of the mid-range and heavy compounds had reduced responses when nitrogen was used. Therefore, when the application calls for a low-level calibration standard of 5 ppb or higher, nitrogen can be used with either the OI #10 or #11 Trap, but if the low-level calibration standard is below 5 ppb, the #11 Trap is recommended because of the higher responses for mid- and heavy-range compounds.

A similar study was performed using the OI Analytical tandem PID/ELCD detector to confirm that nitrogen can be used as a purge gas for the U.S. EPA Methods 502.2 and 8021, and the results were identical to the MS results for nitrogen and the OI #11 Trap.

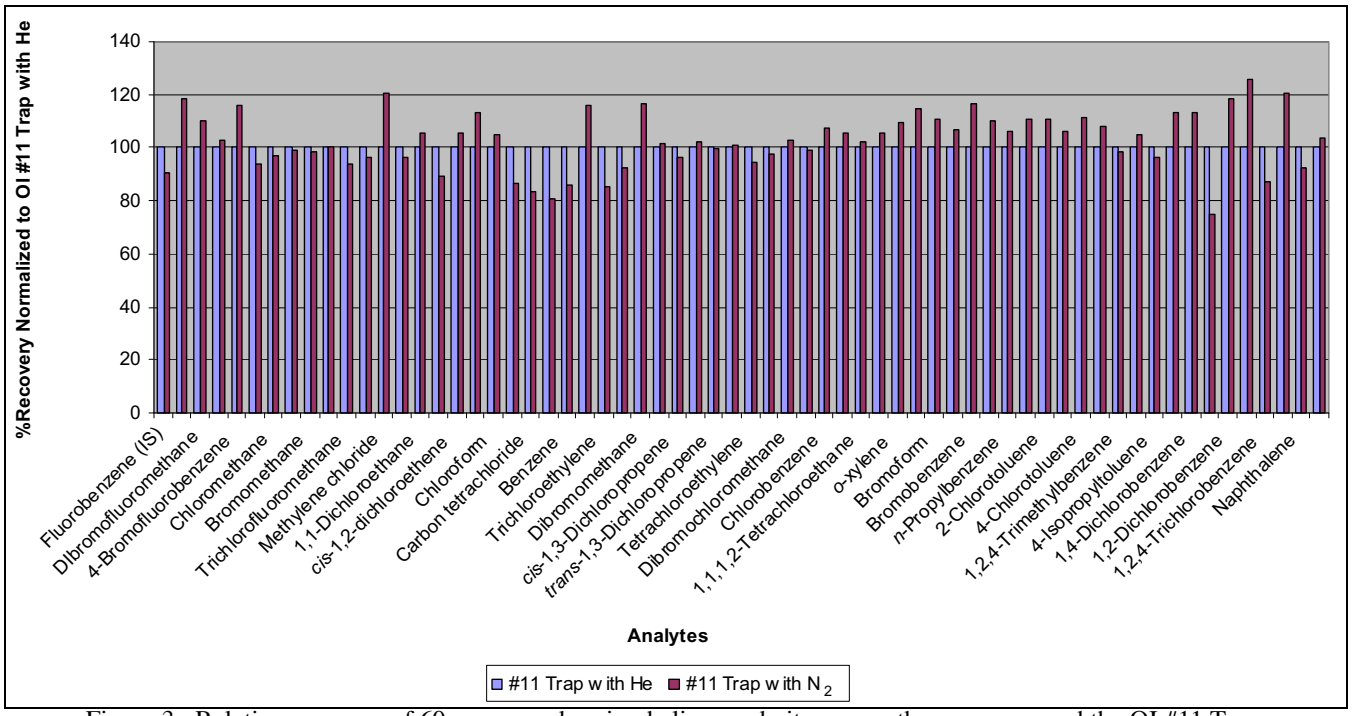

Figure 3. Relative response of 60 compounds using helium and nitrogen as the purge gas and the OI #11 Trap. Responses with helium are normalized to 100%.

Previous studies have shown that reduced purge gas volumes (e.g. using shorter purge times) will produce results equivalent to the standard conditions [2, 3]. To determine the effect of shorter purge times when using nitrogen as the purge gas, four replicate standards were analyzed using a 7-minute nitrogen purge, a 2-minute Desorb, and the OI #11 Trap.

Average compound responses with the 11-minute nitrogen purge were normalized to 100% and compound responses with the 7-minute nitrogen purge are shown relative to the 11-minute response. Most compound responses were comparable using a 7-minute nitrogen purge, and responses for the heaviest compounds improved significantly using the 2-minute Desorb. Refer to Figure 4.

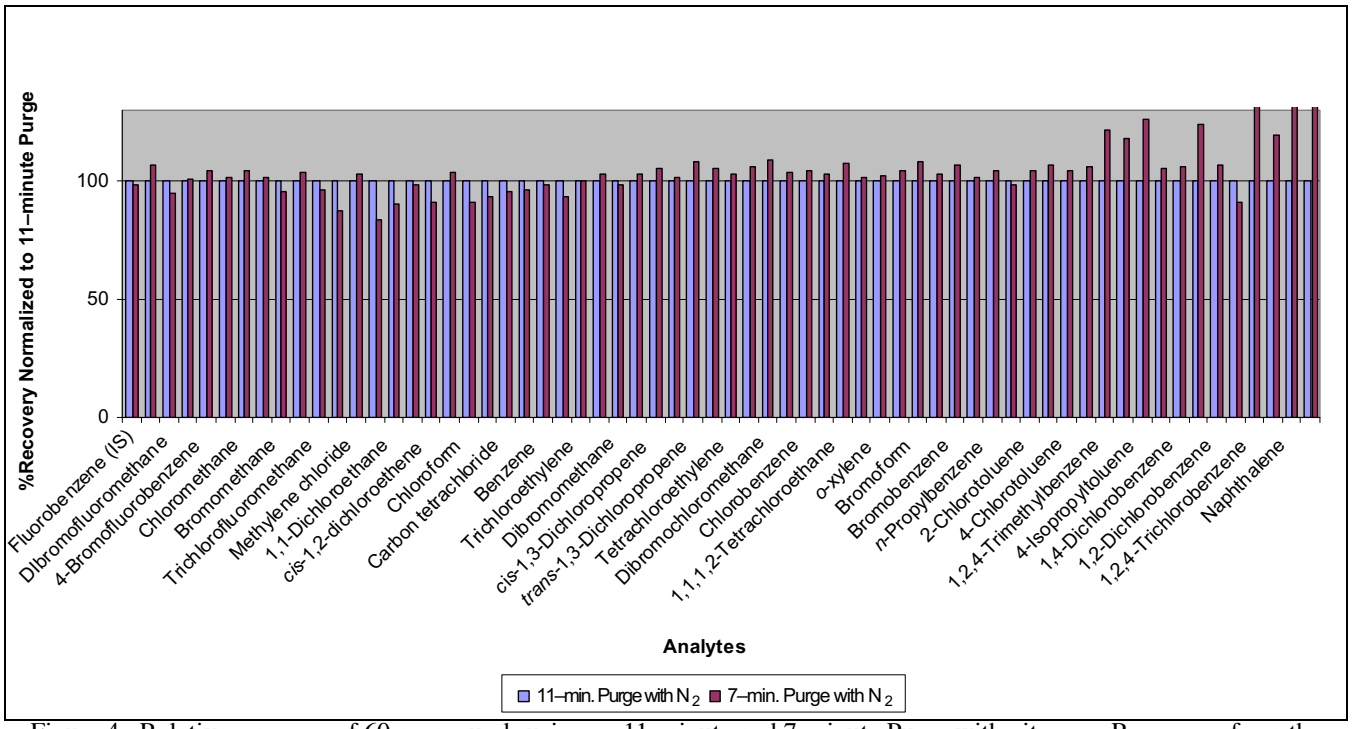


Figure 4. Relative response of 60 compounds using an 11-minute and 7-minute Purge with nitrogen. Responses from the 11-minute nitrogen Purge are normalized to 100%. (The 7–minute Purge included a 2–minute Desorb.)

## Calibration Curve and Method Detection Limit (MDL) Study

These data suggest that nitrogen can be used to replace helium as a purge gas when using the OI #11 Trap without compromising analytical performance, and that either an 11-minute or a 7-minute Purge can be used. To evaluate the performance of the system using nitrogen as a purge gas, a full proficiency study was run for each set of recommended operating conditions. See Table 3 for a summary of the P&T conditions.

Table 3. P&T Operating Conditions for the Proficiency Study

| Purge–and–Trap | Eclipse 4660 P&T Sample Concentrator |
|---|---|
| Trap | OI #11 Trap (VOCARB® 3000) |
| Purge Gas | Nitrogen at 40 mL/minute |
| Purge Time | Standard Conditions: 11 minutes<br>Alternate Conditions: 7 minutes |
| Sample Temperature | 40 °C |
| Desorb Time | Standard Conditions: 1 minute<br>Alternate Conditions: 2 minutes |
| Bake Time | 10 minutes |
| OI #11 Trap Temperatures | 20 °C (ambient) at Purge<br>230 °C at Desorb Preheat<br>240 °C at Desorb<br>250 °C at Bake |
| *All other P&T conditions were as described in Table 1.* | |

A 7-point calibration curve ranging from 0.5 to 100 ppb was run using both the Standard and Alternate conditions. Method detection limits were determined for all analytes using the student's *t* test and the standard deviation from eight replicates analyses as described in Appendix B to Part 136 in the Federal Register [(4)].

Results from the calibration curve and MDL study using Standard and Alternate Conditions are shown in Table 4. All compounds met calibration criteria established by all U.S. EPA methods, with response factor %RSD well below 10% for most compounds. All MDLs were found to be well below the target concentrations cited in U.S. EPA regulations when using instrument conditions described in Table 4.

Table 4. Calibration and MDL results using the Standard and Alternate Conditions

| Analytes | Calibration %RSD 7–point Calibration 0.5 to 100 ppb | | Method Detection Limits (ppb) | |
|---|---|---|---|---|
| | Standard Conditions | Alternate Conditions | Standard Conditions | Alternate Conditions |
| Dichlorodifluoromethane | 9.1 | 8.2 | 0.19 | 0.17 |
| Chloromethane | 4.3 | 7.1 | 0.15 | 0.15 |
| Vinyl chloride | 6.9 | 6.2 | 0.15 | 0.14 |
| Bromomethane | 5.5 | 6.4 | 0.20 | 0.23 |
| Chloroethane | 6.7 | 8.2 | 0.19 | 0.30 |
| Trichlorofluoromethane | 9.8 | 6.8 | 0.09 | 0.11 |
| 1, 1-Dichloroethene | 9.4 | 7.4 | 0.10 | 0.23 |
| Methylene chloride | 8.5 | 5.3 | 0.13 | 0.12 |
| *trans*-1, 2–dichloroethane | 3.0 | 5.5 | 0.23 | 0.20 |
| 1, 1–Dichloroethane | 5.2 | 3.7 | 0.14 | 0.17 |
| 2, 2–Dichloropropane | 5.1 | 6.1 | 0.20 | 0.28 |
| *cis*–1, 2–dichloroethene | 2.1 | 2.4 | 0.17 | 0.16 |
| Bromochloromethane | 6.0 | 7.1 | 0.42 | 0.13 |
| Chloroform | 2.5 | 4.9 | 0.12 | 0.08 |
| 1, 1, 1–Trichloroethane | 7.9 | 3.1 | 0.18 | 0.13 |
| Carbon tetrachloride | 1.6 | 3.3 | 0.17 | 0.21 |
| 1, 1–Dichloropropene | 10.0 | 3.8 | 0.20 | 0.12 |
| Benzene | 7.8 | 6.7 | 0.11 | 0.07 |
| 1, 2–Dichloropropene | 3.8 | 3.1 | 0.11 | 0.16 |
| Trichloroethylene | 3.7 | 3.4 | 0.14 | 0.19 |
| 1, 2–Dichloropropane | 4.2 | 3.4 | 0.12 | 0.14 |
| Dibromomethane | 3.1 | 3.8 | 0.13 | 0.07 |
| Bromodichloromethane | 3.4 | 3.7 | 0.13 | 0.12 |
| *cis*–1, 3–Dichloropropene | 5.9 | 4.1 | 0.08 | 0.16 |
| Toluene | 11.0 | 8.7 | 0.14 | 0.12 |
| *trans*–1, 3–Dichloropropene | 3.5 | 2.2 | 0.10 | 0.19 |
| 1, 1. 2–Trichloroethylene | 2.6 | 3.0 | 0.17 | 0.10 |
| Tetrachloroethylene | 10.6 | 6.3 | 0.16 | 0.12 |
| 1, 3–Dichloropropane | 3.7 | 5.1 | 0.13 | 0.15 |
| Dibromochloromethane | 5.0 | 7.3 | 0.08 | 0.15 |
| 1, 2–Dibromoethane | 2.1 | 2.6 | 0.14 | 0.08 |
| Chlorobenzene | 9.2 | 3.0 | 0.14 | 0.13 |
| Ethylbenzene | 4.0 | 3.5 | 0.16 | 0.18 |
| 1, 1, 1, 2–Tetrachloroethane | 2.0 | 2.5 | 0.14 | 0.18 |
| *m, p*–xylene | 2.9 | 6.8 | 0.12 | 0.21 |
| *o*–xylene | 3.3 | 4.1 | 0.13 | 0.20 |
| Styrene | 3.2 | 7.6 | 0.13 | 0.20 |
| Bromoform | 3.6 | 7.2 | 0.05 | 0.14 |
| Isopropylbene | 3.3 | 10.8 | 0.11 | 0.23 |

Table 4. Calibration and MDL results using the Standard and Alternate Conditions

| Analytes | Calibration %RSD 7–point Calibration 0.5 to 100 ppb | | Method Detection Limits (ppb) | |
|---|---|---|---|---|
| | Standard Conditions | Alternate Conditions | Standard Conditions | Alternate Conditions |
| Bromobenzene | 11.0 | 6.7 | 0.15 | 0.15 |
| 1, 1, 2, 2–Tetrachloroethane | 4.6 | 7.6 | 0.18 | 0.11 |
| *n*–Propylbenzene | 3.8 | 2.1 | 0.14 | 0.22 |
| 1, 2, 3–Trichloropropane | 6.2 | 5.2 | 0.09 | 0.13 |
| 2–Chlorotolene | 8.6 | 8.3 | 0.12 | 0.19 |
| 1, 3, 5–Trimethylbenzene | 3.7 | 3.6 | 0.16 | 0.19 |
| 4–Chlorotoluene | 7.9 | 7.1 | 0.15 | 0.23 |
| *tert*–Butylbenzene | 2.4 | 3.3 | 0.15 | 0.20 |
| 1, 2, 4–Trimethylbenzene | 3.6 | 6.4 | 0.14 | 0.13 |
| *sec*–Butylebenzene | 2.5 | 2.4 | 0.17 | 0.17 |
| 4–Isopropyltoluene | 4.0 | 6.1 | 0.15 | 0.12 |
| 1, 3–Dichlorobenzene | 8.2 | 8.2 | 0.10 | 0.20 |
| 1, 4–Dichlorobenzene | 6.2 | 7.0 | 0.13 | 0.19 |
| *n*–Butylbenzene | 8.0 | 9.0 | 0.18 | 0.13 |
| 1, 2–Dichlorobenzene | 5.9 | 4.4 | 0.12 | 0.10 |
| 1, 2–Dibromo–3–chloropr | 5.0 | 3.5 | 0.14 | 0.21 |
| 1, 2, 4–Trichlorobenzene | 4.8 | 7.0 | 0.22 | 0.12 |
| Hexachlorobutaadiene | 3.3 | 2.3 | 0.20 | 0.13 |
| Naphthalene | 7.9 | 8.1 | 0.13 | 0.13 |
| 1, 2, 3–Trichlorobenzene | 5.3 | 5.4 | 0.20 | 0.15 |

## Precision and Accuracy Study

The same analytical conditions were used to determine the precision and accuracy of the Standard and Alternate conditions by analyzing 10 aliquots of a 10-ppb test standard. Fluorobenzene and 1,2-dichlorobenzene-$d_4$ were used as internal standards at 20 ppb, and analyte concentrations were determined using the associated calibration curve. Accuracy is reported as average percent recovery compared to the expected concentration, and precision is reported as the %RSD for compound concentrations over the 10 replicate analyses.

The average recovery of the analytes was 100.4% and 99.7% for the Standard and Alternate conditions, respectively. Refer to Table .

Table 5. Precision and Accuracy Results using the Standard and Alternate Conditions

| Analytes | Precision as %RSD (n=10) | | Accuracy as %Recovery | |
|---|---|---|---|---|
| | Standard Conditions | Alternate Conditions | Standard Conditions | Alternate Conditions |
| Dichlorodifluoromethane | 4.9 | 3.9 | 96.6 | 100.9 |
| Chloromethane | 5.5 | 5.2 | 92.8 | 93.4 |
| Vinyl chloride | 6.7 | 5.4 | 93.9 | 102.0 |
| Bromomethane | 4.6 | 9.6 | 106.1 | 93.1 |
| Chloroethane | 4.8 | 8.0 | 97.2 | 89.6 |
| Trichlorofluoromethane | 7.6 | 6.7 | 98.7 | 96.3 |
| 1, 1-Dichloroethene | 9.3 | 4.5 | 97.6 | 90.0 |
| Methylene chloride | 6.7 | 2.7 | 94.8 | 105.1 |
| *trans*-1, 2–dichloroethane | 5.9 | 4.8 | 98.8 | 87.4 |
| 1, 1–Dichloroethane | 5.9 | 3.9 | 102.0 | 92.7 |
| 2, 2–Dichloropropane | 7.3 | 8.1 | 100.7 | 93.8 |
| *cis*–1, 2–dichloroethene | 4.3 | 3.6 | 100.3 | 93.6 |
| Bromochloromethane | 4.6 | 4.2 | 88.1 | 102.1 |
| Chloroform | 4.0 | 3.5 | 99.4 | 92.9 |
| 1, 1, 1–Trichloroethane | 5.4 | 4.8 | 99.7 | 93.7 |
| Carbon tetrachloride | 5.1 | 5.0 | 99.4 | 92.2 |
| 1, 1–Dichloropropene | 7.1 | 5.9 | 97.9 | 97.2 |
| Benzene | 4.3 | 3.9 | 99.2 | 98.0 |
| 1, 2–Dichloropropene | 2.4 | 3.7 | 98.2 | 95.0 |
| Trichloroethylene | 5.0 | 4.9 | 101.2 | 96.0 |
| 1, 2–Dichloropropane | 4.1 | 3.2 | 99.5 | 97.1 |
| Dibromomethane | 2.4 | 2.9 | 98.7 | 96.3 |
| Bromodichloromethane | 3.8 | 3.0 | 95.8 | 98.6 |
| *cis*–1, 3–Dichloropropene | 4.2 | 3.1 | 104.7 | 105.8 |
| Toluene | 4.3 | 4.9 | 102.4 | 98.3 |
| *trans*–1, 3–Dichloropropene | 3.6 | 2.8 | 106.2 | 106.3 |
| 1, 1. 2–Trichloroethylene | 4.0 | 2.4 | 101.1 | 99.9 |
| Tetrachloroethylene | 5.3 | 4.8 | 106.3 | 95.0 |
| 1, 3–Dichloropropane | 3.6 | 2.2 | 100.3 | 101.6 |
| Dibromochloromethane | 4.4 | 1.8 | 99.5 | 104.0 |
| 1, 2–Dibromoethane | 3.4 | 1.7 | 103.0 | 101.8 |
| Chlorobenzene | 4.4 | 3.9 | 102.2 | 101.5 |
| Ethylbenzene | 5.1 | 4.6 | 104.4 | 106.7 |
| 1, 1, 1, 2–Tetrachloroethane | 4.1 | 2.9 | 101.0 | 99.7 |
| *m, p*–xylene | 4.5 | 3.9 | 104.9 | 108.2 |
| *o*–xylene | 4.3 | 4.1 | 105.0 | 107.6 |
| Styrene | 4.1 | 4.1 | 102.7 | 111.5 |
| Bromoform | 4.8 | 2.3 | 98.5 | 108.9 |
| Isopropylbene | 5.0 | 4.5 | 106.2 | 105.7 |
| Bromobenzene | 4.1 | 3.3 | 102.9 | 99.1 |
| 1, 1, 2, 2–Tetrachloroethane | 4.5 | 1.6 | 99.3 | 104.2 |
| *n*–Propylbenzene | 4.8 | 4.8 | 105.0 | 101.7 |
| 1, 2, 3–Trichloropropane | 5.9 | 2.3 | 100.7 | 98.5 |

Table 5. Precision and Accuracy Results using the Standard and Alternate Conditions

| Analytes | Precision as %RSD (n=10) | | Accuracy as %Recovery | |
|---|---|---|---|---|
| | Standard Conditions | Alternate Conditions | Standard Conditions | Alternate Conditions |
| 2–Chlorotolene | 4.2 | 4.2 | 104.2 | 103.6 |
| 1, 3, 5–Trimethylbenzene | 4.8 | 4.1 | 105.0 | 106.3 |
| 4–Chlorotoluene | 4.2 | 4.0 | 103.2 | 102.6 |
| *tert*–Butylbenzene | 4.5 | 4.4 | 104.9 | 104.6 |
| 1, 2, 4–Trimethylbenzene | 6.8 | 4.7 | 97.4 | 107.0 |
| *sec*–Butylebenzene | 6.0 | 5.0 | 103.5 | 103.8 |
| 4–Isopropyltoluene | 8.2 | 5.0 | 96.0 | 105.7 |
| 1, 3–Dichlorobenzene | 3.7 | 3.5 | 102.8 | 100.3 |
| 1, 4–Dichlorobenzene | 3.8 | 3.1 | 102.8 | 100.7 |
| *n*–Butylbenzene | 7.2 | 7.9 | 98.1 | 98.0 |
| 1, 2–Dichlorobenzene | 3.1 | 2.7 | 103.8 | 99.2 |
| 1, 2–Dibromo–3–chloropr | 6.9 | 2.8 | 91.0 | 98.5 |
| 1, 2, 4–Trichlorobenzene | 4.8 | 5.1 | 98.7 | 99.3 |
| Hexachlorobutaadiene | 5.2 | 4.5 | 105.7 | 94.8 |
| Naphthalene | 5.6 | 3.1 | 96.2 | 107.3 |
| 1, 2, 3–Trichlorobenzene | 4.9 | 5.1 | 96.2 | 99.0 |

## Summary and Conclusions

This study demonstrates that nitrogen can completely replace helium for analysis of VOCs using P&T methods. Using nitrogen as an alternative to helium will significantly reduce the operating costs for VOC methods. The study also confirms that the Alternate Conditions used here (7-minute Purge and 2-minute Desorb) produced improved analytical results while shortening the overall P&T cycle time by a full 3 minutes on each sample.

Laboratories are advised to review their analytical method and consult with their regulating agency prior to making modifications to the P&T operating conditions.

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Publication 32610109