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# A Comparison of Volatile Organic Compound Response When Using Nitrogen as a Purge Gas

**Application Note**

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## Abstract

For many years Helium has been the gas of choice for purging Volatile Organic Compounds (VOCs). However, in the past few years, the price and demand for helium gas has increased substantially, thus making the use of Helium for the purge gas in Purge and Trap (P&T) very expensive. The expense of Helium has provoked interest in finding a viable alternative purge gas. This application note investigates VOC compound responses when purged using Helium and Nitrogen in order to validate Nitrogen as a possible alternative to Helium for P&T applications.

## Introduction

Teledyne Tekmar developed a combination P&T Concentrator/ Vial Autosampler, the Atomx. The Atomx was developed to fully automate water, soil, and methanol extraction in accordance with the USEPA methods for volatile analyses. One of the beneficial features of the Atomx highlighted in this study is the use of an electronic mass flow controller that is calibrated for either Nitrogen or Helium. The controller is employed for both fritted glass sparging used for aqueous samples and in vial sparging used in soil applications. Since the mass flow controller is electronic, flow rates can be programmed via the software interface for various modes of operation. This patent pending ability allows for the end user to simplify the potential switch by simply changing the configuration rather than manually adjusting pressures and flows as seen in traditional regulator/needle flow controller systems.

In this study, data was collected to evaluate compound response when using Nitrogen as a purge gas as opposed to the traditional Helium purge gas. Furthermore, as water samples are purged in the sparge vessel and soils are purged in the sample vial, an additional comparison was done to see if the analytes responded differently when purged in the vial with Nitrogen in contrast to a Helium purge.

## Experimental-Instrument Conditions

The Atomx, an Agilent 7890A GC and a 5975C inert XL MSD were used for this analysis. The Atomx was equipped with a #9 adsorbent trap. Tables 1 and 2 display the GC, MSD conditions while Tables 3 and 4 display the P&T Concentrator/Autosampler conditions for water and soil matrices respectively.

| GC Parameters | |
|---|---|
| GC: | Agilent 7890A |
| Column: | J&W Scientific DB-VRX 30m x 0.250mm x1.4um |
| Oven Program: | 35°C for 4 min; 16°C/min to 85°C for 0 min; 30°C /min to 210°C for 3 min, 14.29 min runtime |
| Inlet: | 220°C |
| Column Flow | 1.2mL/min |
| Gas: | Helium |
| Split: | 80:1 |
| Pressure: | 9.3 psi |
| Inlet | Split/Splitless |

| MSD Parameters | |
|---|---|
| MSD: | 5975C Inert XL |
| Source: | 230°C |
| Quad: | 150°C |
| Solvent Delay: | 0.5 min |
| Scan Range: | m/z 35-300 |
| Scans: | 4.51 scans/sec |
| Threshold: | 400 |
| MS Transfer Line Temp. | 230°C |

*Tables 1 & 2: GC and MSD Parameters*

| Atomx Water Parameters | | | |
|---|---|---|---|
| **Variable** | **Value** | **Variable** | **Value** |
| Valve Oven Temp | 140°C | Dry Purge Flow | 100mL/ min |
| Transfer Line Temp | 140°C | Dry Purge Temp | 20°C |
| Sample Mount Temp | 90°C | Methanol Needle Rinse | Off |
| Water Heater Temp | 90°C | Methanol Needle Rinse Volume | 3.0mL |
| Sample Vial Temp | 20°C | Water Needle Rinse Volume | 7.0mL |
| Sample Equilibrate Time | 0.00 min | Sweep Needle Time | 0.50 min |
| Soil Valve Temp | 125°C | Desorb Preheat Temp | 245°C |
| Standby Flow | 10mL/ min | GC Start Signal | Start of Desorb |
| Purge Ready Temp | 40°C | Desorb Time | 2.00 min |
| Condensate Trap Standby | 45°C | Drain Flow | 300mL/min |
| Presweep Time | 0.25 min | Desorb Temp | 250°C |
| Prime Sample Fill Volume | 3.0mL | Methanol Glass Rinse | On |
| Sample Volume | 5.0mL | Number of Methanol Glass Rinses | 1 |
| Sweep Sample Time | 0.25 min | Methanol Glass Rinse Volume | 3.0mL |
| Sweep Sample Flow | 100mL/min | Number Of Bake Rinses | 1 |
| Sparge Vessel Heater | Off | Water Bake Rinse Volume | 7.0mL |
| Sparge Vessel Temp | 20°C | Bake Rinse Sweep Time | 0.25 min |
| Prepurge Time | 0.00 min | Bake Rinse Sweep Flow | 100mL/min |
| Prepurge Flow | 0mL/min | Bake Rinse Drain Time | 0.40 min |
| Purge Time | 11.00 min | Bake Time | 4.00 min |
| Purge Flow | 40mL/min | Bake Flow | 250mL/min |
| Purge Temp | 20°C | Bake Temp | 280°C |
| Condensate Purge Temp | 20°C | Condensate Bake Temp | 200°C |
| Dry Purge Time | 0.50 min | | |

*Table 3: Atomx Water Parameters (Parameters highlighted in yellow were not used.)*

| Atomx Soil Parameters | | | |
|---|---|---|---|
| **Variable** | **Value** | **Variable** | **Value** |
| Valve Oven Temp | 140°C | Purge Time | 11.0 min |
| Transfer Line Temp | 140°C | Purge Flow | 40mL/min |
| Sample Mount Temp | 90°C | Purge Temp | 20°C |
| Water Heater Temp | 90°C | Condensate Purge Temp | 20°C |
| Sample Vial Temp | 40°C | Dry Purge Time | 1.00 min |
| Prepurge Time | 0.00 min | Dry Purge Flow | 100mL/ min |
| Prepurge Flow | 0mL/min | Dry Purge Temp | 20°C |
| Preheat Mix Speed | Off | Methanol Needle Rinse | On |
| Sample Preheat Time | 0.00 min | Methanol Needle Rinse Volume | 3.0mL |
| Soil Valve Temp | 125°C | Water Needle Rinse Volume | 7.0mL |
| Standby Flow | 10mL/min | Sweep Needle Time | 0.25 min |
| Purge Ready Temp | 40°C | Desorb Preheat Temp | 245°C |
| Condensate Temp Standby | 45°C | GC Start Signal | Start of Desorb |
| Presweep Time | 0.25 min | Desorb Time | 2.00 min |
| Water Volume | 10mL | Drain Flow | 300mL/min |
| Sweep Water Time | 0.25 min | Desorb Temp | 250°C |
| Sweep Water Flow | 100mL/min | Bake Time | 4.00 min |
| Sparge Vessel Heater | Off | Bake Flow | 250mL/min |
| Sparge Vessel Temp | 20°C | Bake Temp | 280°C |
| Purge Mix Speed | Medium | Condensate Bake Temp | 200°C |

*Table 4: Atomx Soil Parameters (Parameters highlighted in yellow were not used.)*

## Calibration

A 50ppb working calibration stock standard was prepared in methanol. Calibration standards were prepared in a 50mL volumetric flask and filled to volume with de-ionized water. In this study, a linear calibration was performed for both the water and the soil matrices for 95 analytes. The range for the water study was 0.5-200ppb and the soil range was 1.0-200ppb. The water standards were transferred to headspace free 40mL vials for analysis while the soil standards were transferred to 40mL vials in 5mL aliquots. A 5.0 milliliter (mL) purge volume was used for the water curve. For the soil curve, a 5g sample with 10mLs of reagent water was simulated. Conditions and specifications outlined in USEPA Method 8260 were utilized for both matrices.

The calibration data was analyzed using Agilent Chemstation software. The average compound response for the water and soil matrices with the Helium and Nitrogen purge gases is outlined in Table 5. The relative response factors of all of the analytes of interest were evaluated for linearity and response and the average %RSD of the respective curves are summarized in Table 6.

## Method Detection Limit (MDL)

A statistical determination of the MDL's was determined for all of the compounds by analyzing seven replicate standards of a low calibration standard. The average detection limits are provided in Table 6.

| Compound | Water | | Soil | |
|---|---|---|---|---|
| | Ave. Response N2 Purge | Ave. Response He Purge | Ave. Response N2 Purge | Ave. Response He Purge |
| Pentafluorobenzene (IS) | N/A | N/A | N/A | N/A |
| Dichlorodifluoromethane | 0.337 | 0.517 | 0.807 | 0.507 |
| Chloromethane | 0.551 | 0.655 | 0.993 | 0.692 |
| Vinyl Chloride | 0.675 | 0.620 | 1.194 | 0.763 |
| Bromomethane | 0.379 | 0.393 | 0.717 | 0.660 |
| Chloroethane (Ethyl Chloride) | 0.461 | 0.415 | 0.693 | 0.501 |
| Trichlorofluoromethane | 0.962 | 0.735 | 1.526 | 1.035 |
| Diethyl Ether | 0.604 | 0.484 | 0.783 | 0.540 |
| 1,1-Dichloroethene | 0.839 | 0.686 | 1.416 | 0.528 |
| Carbon Disulfide | 1.069 | 1.417 | 2.423 | 1.111 |
| 1,1,2-Trichlorofluoroethane (Freon ) | 0.283 | 0.349 | 0.805 | 0.366 |
| Iodomethane | 0.469 | 0.475 | 0.801 | 0.462 |
| Allyl Chloride | 0.713 | 0.615 | 0.859 | 0.441 |
| Methylene Chloride | 0.694 | 0.614 | 1.067 | 0.377 |
| Acetone | 0.263 | 0.203 | 0.252 | 0.194 |
| trans-1,2-Dichloroethene | 0.675 | 0.712 | 0.874 | 0.768 |
| Methyl Acetate | 0.493 | 0.494 | 0.336 | 0.187 |
| MTBE | 1.507 | 1.827 | 2.721 | 1.780 |
| TBA | 0.088 | 0.078 | 0.098 | 0.046 |
| Diisopropyl Ether | 1.394 | 1.668 | 1.711 | 1.565 |
| Chloroprene | 0.671 | 0.851 | 0.945 | 0.878 |
| 1,1-Dichloroethane | 0.874 | 0.953 | 1.996 | 1.119 |
| Acrylonitrile | 0.308 | 0.263 | 0.299 | 0.104 |
| Vinyl acetate | 0.855 | 0.636 | 1.146 | 1.025 |
| ETBE | 1.462 | 1.776 | 1.520 | 1.596 |
| cis-1,2-Dichloroethene | 0.617 | 0.704 | 1.390 | 0.855 |
| 2,2-Dichloropropane | 0.682 | 0.485 | 0.928 | 0.915 |
| Bromochloromethane | 0.397 | 0.392 | 0.476 | 0.422 |
| Chloroform | 0.915 | 1.005 | 1.094 | 0.974 |
| Carbon Tetrachloride | 0.571 | 0.727 | 0.710 | 0.715 |
| 1,1,1-Trichloroethane | 0.726 | 0.892 | 0.880 | 0.844 |
| THF | 0.143 | 0.169 | 0.105 | 0.125 |
| Dibromofluoromethane (Surrogate) | 0.464 | 0.502 | 0.502 | 0.510 |
| Methyl Acrylate | 0.511 | 0.576 | 0.438 | 0.466 |
| 1,1-Dichloropropene | 0.614 | 0.706 | 0.740 | 0.807 |
| 2-Butanone (MEK) | 0.209 | 0.217 | 0.208 | 0.158 |
| Benzene | 1.977 | 2.214 | 2.316 | 2.243 |
| Propionitrile | 0.591 | 0.637 | 0.612 | 0.567 |
| tert Amyl Methyl Ether (TAME) | 1.449 | 1.787 | 1.216 | 1.524 |
| 1,2-Dichloroethane | 0.729 | 0.815 | 0.777 | 0.728 |
| Isobutyl Alcohol | 0.451 | 0.193 | 0.458 | 0.148 |
| Isopropyl Acetate | 0.931 | 1.134 | 0.813 | 0.873 |
| Trichloroethene | 0.482 | 0.617 | 0.588 | 0.619 |
| 1,4-Difluorobenzene (IS) | N/A | N/A | N/A | N/A |
| Dibromomethane | 0.160 | 0.197 | 0.148 | 0.172 |
| 1,2-Dichloropropane | 0.253 | 0.300 | 0.275 | 0.270 |
| Bromodichloromethane | 0.330 | 0.466 | 0.391 | 0.393 |
| Methyl Methacrylate | 0.227 | 0.317 | 0.180 | 0.238 |
| n-Propyl Acetate | 0.347 | 0.411 | 0.270 | 0.323 |
| 2-Cleve | 0.162 | 0.192 | 0.110 | 0.149 |

*Table 5: Average Compound Response Summary*

| Compound | Water | | Soil | |
|---|---|---|---|---|
| | Ave. Response N2 Purge | Ave. Response He Purge | Ave. Response N2 Purge | Ave. Response He Purge |
| cis-1,3-Dichloropropene | 0.377 | 0.460 | 0.370 | 0.444 |
| Toluene-d8 (surr) | 0.830 | 1.092 | 0.790 | 1.089 |
| Toluene | 0.999 | 1.249 | 1.034 | 1.276 |
| 2-Nitropropane | 0.339 | 0.425 | 0.270 | 0.323 |
| Tetrachloroethene | 0.266 | 0.493 | 0.235 | 0.300 |
| 4-methyl2-pentanone | 0.036 | 0.050 | 0.068 | 0.034 |
| 1,1,2-Trichloroethane | 0.230 | 0.301 | 0.205 | 0.235 |
| Ethyl Methacrylate | 0.192 | 0.255 | 0.124 | 0.177 |
| Dibromochloromethane | 0.207 | 0.329 | 0.213 | 0.248 |
| 1,3-Dichloropropane | 0.420 | 0.506 | 0.354 | 0.410 |
| 1,2-Dibromoethane | 0.230 | 0.301 | 0.187 | 0.233 |
| n-Butyl Acetate | 0.361 | 0.463 | 0.272 | 0.339 |
| 2-Hexanone | 0.174 | 0.213 | 0.128 | 0.149 |
| Chlorobenzene-d5 (IS) | N/A | N/A | N/A | N/A |
| Chlorobenzene | 0.739 | 0.908 | 0.803 | 0.949 |
| Ethylbenzene | 1.207 | 1.550 | 1.321 | 1.573 |
| 1,1,1,2-Tetrachloroethane | 0.242 | 0.336 | 0.270 | 0.287 |
| M&P Xylene | 0.961 | 1.264 | 1.042 | 1.300 |
| Ortho Xylene | 1.014 | 1.314 | 1.115 | 1.290 |
| Styrene | 0.675 | 0.920 | 0.747 | 0.913 |
| Bromoform | 0.131 | 0.240 | 0.143 | 0.164 |
| Isopropylbenzene | 1.200 | 1.502 | 1.218 | 1.541 |
| n-Amyl Acetate | 0.471 | 0.533 | 0.399 | 0.401 |
| BFB (surr) | 0.364 | 0.501 | 0.390 | 0.501 |
| n-Propylbenzene | 1.335 | 1.720 | 1.452 | 1.924 |
| trans-1,4-Dichloro-2-Butene | 0.104 | 0.116 | 0.085 | 0.091 |
| Nitrobenzene | 0.016 | 0.041 | 0.017 | 0.020 |
| Bromobenzene | 0.536 | 0.675 | 0.555 | 0.661 |
| 1,1,2,2-Tetrachloroethane | 0.413 | 0.429 | 0.381 | 0.366 |
| 1,3,5-Trimethylbenzene | 0.917 | 1.260 | 0.972 | 1.262 |
| 2-Chlorotoluene | 0.869 | 1.113 | 0.914 | 1.127 |
| cis-1,4-Dichloro-2-Butene | 0.143 | 0.152 | 0.109 | 0.125 |
| 4-Chlorotoluene | 0.886 | 1.113 | 0.933 | 1.223 |
| Tertbutylbenzene | 0.756 | 1.035 | 0.813 | 1.050 |
| 1,2,4-Trimethylbenzene | 0.930 | 1.259 | 0.961 | 1.260 |
| sec-Butylbenzene | 1.216 | 1.578 | 0.388 | 1.717 |
| p-Isopropyltoluene | 0.992 | 1.281 | 1.081 | 1.367 |
| 1,3-Dichlorobenzene | 0.506 | 0.629 | 0.546 | 0.671 |
| 1,4-Dichlorobenzene-d4 (IS) | N/A | N/A | N/A | N/A |
| 1,4-Dichlorobenzene | 0.552 | 0.678 | 0.580 | 0.691 |
| n-Butylbenzene | 0.936 | 1.159 | 1.127 | 1.360 |
| 1,2-Dichlorobenzen | 0.507 | 0.642 | 0.481 | 0.600 |
| 1,2-Dibromo-3-Chloropropane | 0.070 | 0.097 | 0.049 | 0.061 |
| Hexachlorobutadiene | 0.125 | 0.169 | 0.157 | 0.199 |
| 1,2,4-Trichlorobenzene | 0.313 | 0.439 | 0.293 | 0.413 |
| Naphthalene | 1.098 | 1.461 | 0.685 | 1.026 |
| 1,2,3-Trichlorobenzene | 0.318 | 0.442 | 0.264 | 0.364 |

*Table 5:  Average Compound Response Summary (cont.)*

| Matrix | Average %RSD N2 Purge | Average %RSD He Purge | Average MDL N2 Purge | Average MDL He Purge | Average Compound Response N2 Purge | Average Compound Response He Purge |
|---|---|---|---|---|---|---|
| Water | 10.08 | 8.30 | 0.32 | 0.33 | 0.602 | 0.708 |
| Soil | 10.30 | 8.10 | 0.48 | 0.53 | 0.718 | 0.689 |

*Table 6: Experimental Results Summary*

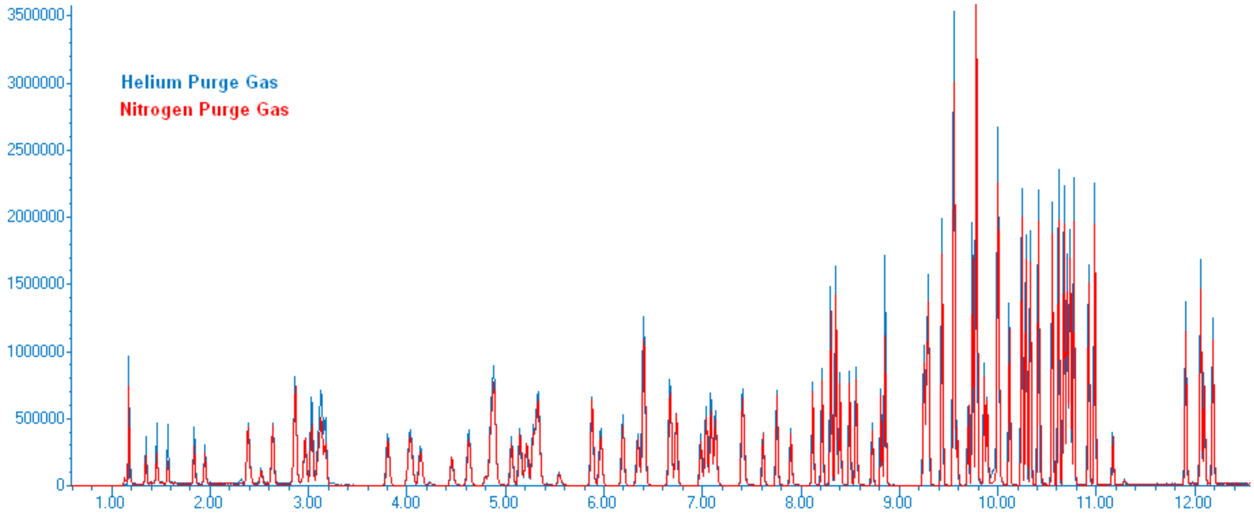

*Figure 1: Overlay of 50ppb water standard purged in Helium and in Nitrogen*

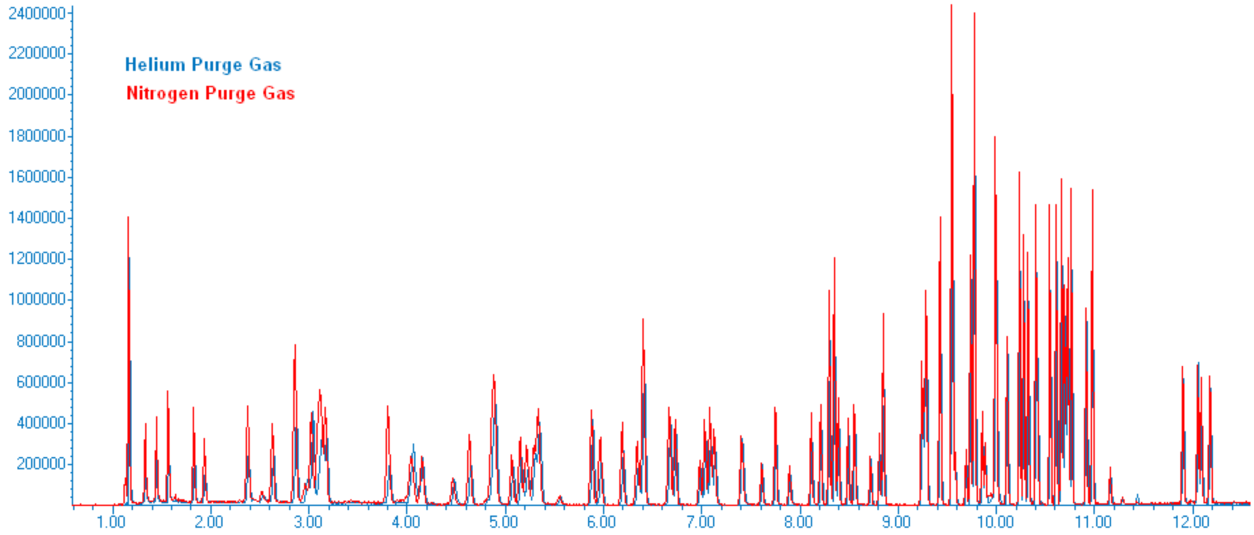

*Figure 2: Overlay of 50ppb soil standard purged in Helium and in Nitrogen*

## Conclusions

The Atomx Purge and Trap Concentrator Multi-Matrix Autosampler in conjunction with an Agilent GC/MS system performed very well for both the water and the soil calibration range. These findings support the option of moving to Nitrogen as an alternative to Helium. Considering Helium can cost as much as three times the price of Nitrogen, this switch can save companies performing typical USEPA methodologies considerable amounts of costs over the long term. In addition the use of Nitrogen generators capable of producing 99.999 or greater purity offer yet another solution to the cost associated with the analysis by removing the need for cylinders.