Introduction
Contaminants in high purity propylene and propane/propylene mixtures can have detrimental effects on the polymerization product, including clarity and odor, and can shorten the lifetime of the catalysts used in the process. It is important to quantitate the levels of these impurities approaching 1 part per billion (ppb) in order to predict catalyst lifetimes as well as control product quality. The contaminants of concern include phosphine (PH$_3$), Arsine (AsH$_3$), Hydrogen Sulfide (H$_2$S), and Carbonyl Sulfide (COS). Ideally it would be desirable to perform this analysis using a single column and a single tune mode, however, due to interferences two columns have traditionally been utilized.

The first, a mega-bore (0.53 mm) boiling point column has been useful for this analysis with the exception that COS elutes with the propane/propylene matrix. Second, an Agilent PLOT U (0.53mm) column works well for the COS analyte in propylene, but the presence of ethane at significant levels will result in a false positive peak for phosphine. It has been determined that the Agilent Select Low Sulfur column satisfies the separation problems of each of the previous columns (Table 1) allowing for the use of one column. Additionally, using oxygen in the Octopole Reaction System (ORS) in MS/MS mass shift mode, all contaminants of interest can be detected with excellent sensitivity while minimizing interferences (e.g. m/z 32 interference of OO+ with S+) and lowering overall background noise without the need of changing tune modes or cell gas.

Abstract
There are a number of impurities that are of consequence in propylene products. These include hydrogen sulfide, carbonyl sulfide, phosphine, and arsine. Using the Agilent Select Low Sulfur column these components can be measured in a single analysis using the Agilent 7890B GC and 8800 triple quadrupole ICP-MS.

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<table>
<thead>
<tr>
<th>Analyte</th>
<th>RRT, Ethane = 1.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.964</td>
</tr>
<tr>
<td>Acetylene</td>
<td>1.000</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.898</td>
</tr>
<tr>
<td>Phosphine</td>
<td>0.840</td>
</tr>
<tr>
<td>Germane</td>
<td>0.964</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.936</td>
</tr>
<tr>
<td>Arsine</td>
<td>1.173</td>
</tr>
<tr>
<td>Carbonyl Sulfide</td>
<td>1.343</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.797</td>
</tr>
<tr>
<td>Propane</td>
<td>2.239</td>
</tr>
</tbody>
</table>

Table 1. Relative retention times of Agilent select low sulfur column

<table>
<thead>
<tr>
<th>Analyte</th>
<th>RRT, Ethane = 1.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier</td>
<td>Helium @ 20 psig</td>
</tr>
<tr>
<td>Column</td>
<td>Select Low Sulfur 60 meter X 0.32 mm</td>
</tr>
<tr>
<td>Oven</td>
<td>35 oC Isothermal</td>
</tr>
<tr>
<td>Sample size</td>
<td>400 ul</td>
</tr>
<tr>
<td>Split</td>
<td>~ 5:1</td>
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</tbody>
</table>

Table 2. Agilent 7890 GC conditions

<table>
<thead>
<tr>
<th>Analyte</th>
<th>RRT, Ethane = 1.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Power (W)</td>
<td>1450</td>
</tr>
<tr>
<td>Sample depth (mm)</td>
<td>7.6</td>
</tr>
<tr>
<td>Argon carrier (dilution) gas flow (L/min)</td>
<td>0.85</td>
</tr>
<tr>
<td>Extract 1 (V)</td>
<td>-147</td>
</tr>
<tr>
<td>Extract 2 (V)</td>
<td>-208</td>
</tr>
<tr>
<td>Kinetic Energy Discrimination (V)</td>
<td>-4</td>
</tr>
<tr>
<td>Cell gas/flow, Oxygen (mL/min)</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 3. Agilent 8800 ICP-QQQ operating conditions

**Experimental**

Instrumentation: An Agilent 7890B Gas Chromatograph was coupled to an Agilent 8800 ICP Triple Quad (ICP-QQQ) using the Agilent GC-ICP-MS interface.

Acquisition conditions: MS/MS mass-shift mode using oxygen as the cell gas for the measurement of P, S, and As. Sampling rates for H2S and COS were 0.4 seconds (m/z 32→48), for PH3 was 0.4 seconds (m/z 31→47), and for AsH3 was 0.1 seconds (m/z 75→91).

**Reagents and sample preparation:** Gas standards of phosphine and arsine (balance hydrogen) and hydrogen sulfide and carbonyl sulfide (balance argon) were supplied by Custom Gas Solutions at a nominal value of 10 ppmv. These standards were diluted dynamically using a fixed restrictor based dilution system supplied by Merlin MicroScience (Pasadena, TX). A real world sample containing methane and ethane was supplied by a customer. A Valco (Houston, TX) 10 port gas sampling valve (GSV) was used to simultaneously inject the sample and standard addition as shown (Figure 1). The 10-port GSV allows for a standard addition or ‘spike’ to determine the actual retention time of analytes in the matrix.

A high flow Deans switch was employed to vent the matrix gas while still supplying ~ 800 cc/minute of Argon as make-up gas to the torch. This venting configuration was required to minimize the propylene matrix entering the torch and to prevent the build-up of carbon on the sampling and skimmer cones.

Figure 1. 10-port valve diagram
RESULTS AND DISCUSSION

Detection limits

The goal of work was to determine if a single column and single tune mode could be used to determine the concentration of the analytes of interest at ppb levels and to evaluate the detection limits that could be practically achieved. A simple 3x signal to noise (S/N) was used to determine detection limits (DLs) as illustrated in table 4.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>DL, ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbonyl Sulfide</td>
<td>1.9</td>
</tr>
<tr>
<td>Arsine</td>
<td>0.05</td>
</tr>
<tr>
<td>Phosphine</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 2. Agilent 7890 GC conditions

Figure 2 illustrates a chromatogram of hydrogen sulfide (H₂S) and carbonyl sulfide (COS) in propylene. What is remarkable in this chromatogram is the fact that hydrocarbon impurities at percent levels depress the sulfur signal (m/z 32→48). The opposite happens when analyzing phosphine (m/z 31→47, Figure 4); the hydrocarbon produces a positive response or interference. It is believed this is an effect on the plasma stoichiometry or disruption rather than the inability of the spectrometer to deal with mass interferences.

Figure 3. Hydrogen sulfide and carbonyl sulfide (m/z 32→48) in propylene.
Matrix effects
It has been observed that the propylene matrix temporarily displaces the carrier gas to a large degree and can have a significant effect on the retention time of the analytes. Figure 5 depicts the effect the matrix has on the H$_2$S and COS elution time. For this reason, it is useful to have the ability to make a standard addition via the 10 port valve to properly identify the matrix induced shift and to properly determine the vent time needed to prevent the propylene matrix from entering the torch.

Conclusion
The 8800 ICP-QQQ provides excellent detection limits for all contaminants using a single tune while minimizing atmospheric/isobaric interferences and reducing overall noise.

The Select Low Sulfur column solves the separation issues other columns experience with respect to possible matrix interferences that would otherwise prevent the ppb level quantitation of PH$_3$ and COS in propylene using GC-ICP-MS.

The detection limits could also be improved by using a mega-bore column and un-split sample, but the Select Low Sulfur column is currently not available in 0.53 mm dimension.