CHEMICAL & ENERGY ANALYSIS

ANALYSIS OF PROPYLENE IMPURITIES USING SELECT LOW SULFUR COLUMN AND SINGLE TUNE WITH GC-ICP-MS QQQ ORS

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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.

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_2S), 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.

Agilent Technologies

Analyte	RRT, Ethane = 1.000
Ethylene	0.898
Acetylene	0.840
Ethane	1.000
Phosphine	0.964
Germane	1.036
Hydrogen Sulfide	0.936
Arsine	1.173
Carbonyl Sulfide	1.343
Propylene	1.797
Propane	2.239

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

Analyte	RRT, Ethane = 1.000
Carrier:	Helium @ 20 psig
Column:	Select Low Sulfur 60 meter X 0.32 mm
Oven:	35 oC Isothermal
Sample size:	400 ul
Split:	~ 5:1

Table 2. Agilent 7890 GC 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 H_2S and COS were 0.4 seconds (m/z 32⟶48), for PH_3 was 0.4 seconds (m/z 31⟶47), and for AsH_3 was 0.1 seconds (m/z 75⟶91).

	O2 mode
RF Power (W)	1450
Sample depth (mm)	7.6
Argon carrier (dilution) gas flow (L/min)	0.85
Extract 1 (V)	-147
Extract 2 (V)	-208
Kinetic Energy Discrimination (V)	-4
Cell gas/flow, Oxygen (mL/min)	0.27

Table 3. Agilent 8800 ICP-QQQ operating conditions

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.

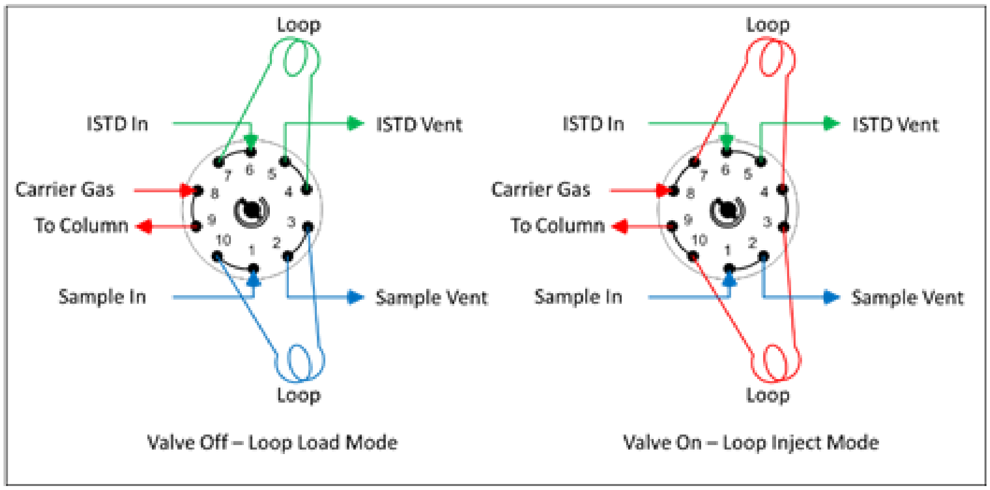

Figure 1. 10-port valve diagram

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.

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.

Analyte	DL , ppbv
Analyte	DL , ppbv
Hydrogen Sulfide	2.5
Carbonyl Sulfide	1.9
Arsine	0.05
Phosphine	0.15

Table 2. Agilent 7890 GC conditions

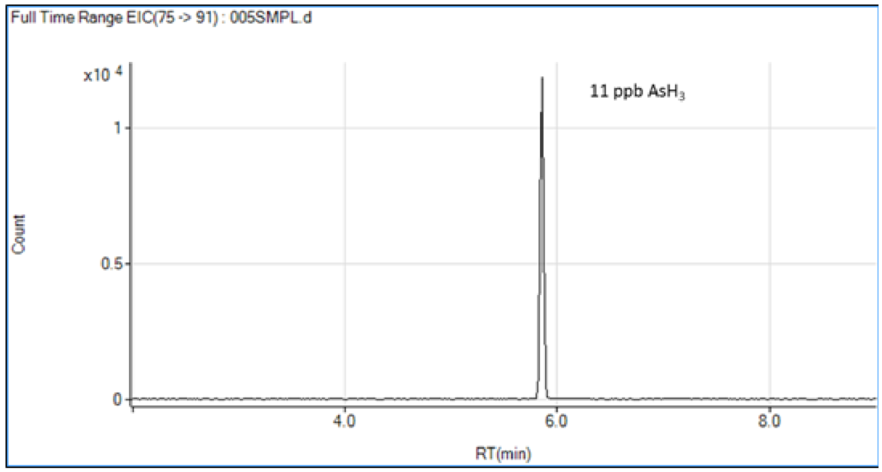

Figure 2. Arsine (m/z 75 ⟶ 91) in propylene.

Figure 3 illustrates a chromatogram of hydrogen sulfide (H_2S) 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.

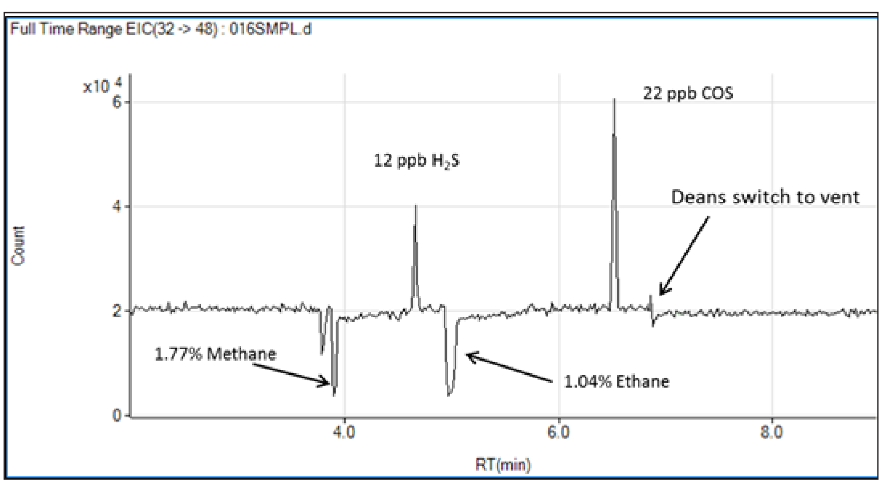

Figure 3. Hydrogen sulfide and carbonyl sulfide (m/z 32 ⟶ 48) in propylene.

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_2S 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.

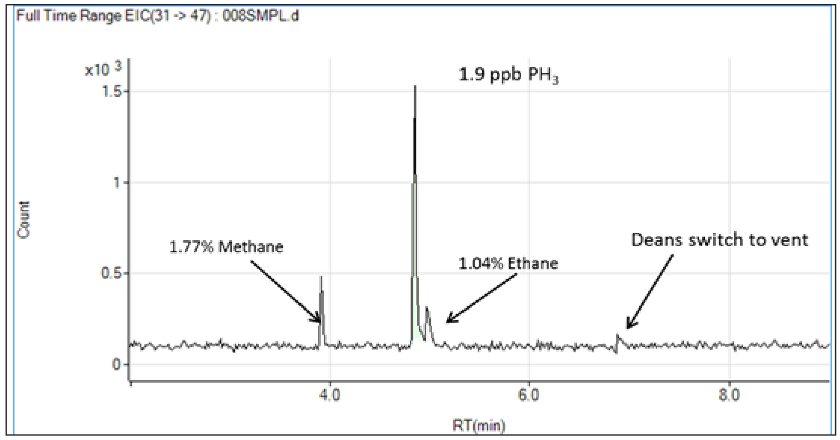

Figure 4. Phosphine (m/z 31 -> 47) in propylene.

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.

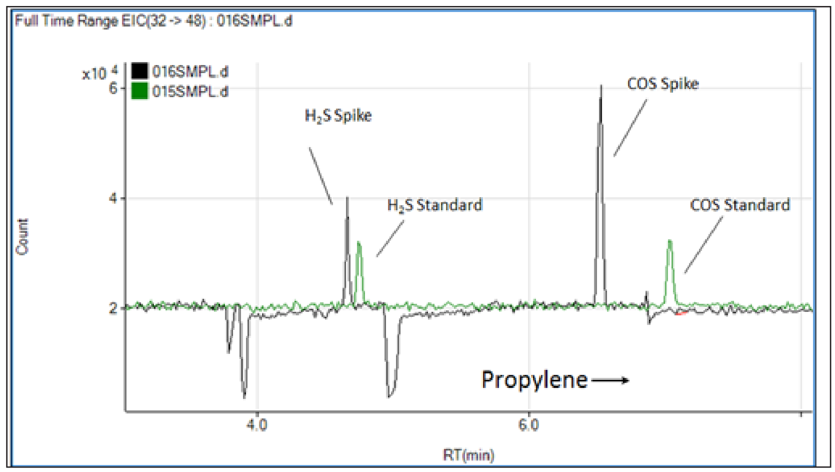

Figure 5. Matrix effect on retention time.

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.

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