Using GC/MSD with High Efficiency Source and Hydrogen Cleaning to detect low level contaminants in ethylene and propylene

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Introduction

Developments with metallocene catalysts have increased productivity for the polymerization of ethylene and propylene; however, these catalysts can also be more susceptible to impurities, such as arsine (AsH_3), phosphine (PH_3), hydrogen sulfide (H_2S), and carbonyl sulfide (COS). This sensitivity to contaminants has driven a need to monitor impurities at the lowest possible detection levels. Contaminants can degrade a polymerization catalyst sooner than desired and shut down the process for catalyst replacement. Precise, low level detection of these contaminants during the production process offers the ability for olefin producers to take steps to mitigate these contaminants.

The challenge for analysis is resolving significant matrix peaks from low level, active contaminants, which necessitates an inert pathway. Analysis with a GC/MSD must have high chromatographic resolution, high capacity, and an inert sample flow path. These detection limits require a system to have excellent sensitivity to detect sub-picogram amounts of AsH_3 and PH_3, which can be achieved with the High Efficiency Source (HES). In order to achieve the required resolution and capacity, a thick film column is required. However, it introduces higher column bleed, which results in source fouling with a dropping response. Using the JetClean self-cleaning ion source (JetClean) provides continuous source cleaning and assures consistent response.

Experimental

G-Cal permeation tubes of the 4 calibrants (=) are connected to a 2-stage dilution system that connects to a sample loop in a 10 port valve, where all tubing and fittings are deactivated to maintain an inert flow path. The dilution system is built to dilute the calibrants in the range of 5 ppb to 50 ppb. The sample loop pressure is controlled by a back-pressure regulator at 2 psi for better precision across calibration and sample concentration range.

The 7890B Agilent GC is configured with a 10 port valve with 2 sample loops for easier method development and sample introduction. Diluted calibrant gases are introduced through one sample loop and the 2nd sample loop introduces the matrix gas, such as helium, polymer grade ethylene, or polymer grade propylene, which creates a sandwich-like injection. The diluted calibrants are directly injected by switching the valve onto a 120 m x 0.32 mm id x 8.0 µm Select Olefins capillary column.

The 5977B is operated in EI (electron ionization) mode with selected ion monitoring (SIM) acquisition. Hydrogen was introduced at a constant rate of 0.15 mL/min, during data acquisition into the MS source to minimize effects of column bleed and retain good signal repeatability. Method parameters are found in the following table and the schematic of the GC/MSD system is in Figure 1.

Table 1. Method Parameters for Detection of Contaminants in Ethylene, Propylene (or Helium for calibration).

| GC conditions	
Column	120 m x 0.32 mm x 8.0 µm Select Olefins
Sample loop	50 µL
Run Time events	Valve 1 On — 1.5 min
	Valve 1 Off — 1.7 min
Valve Box	120 °C
Carrier gas	Helium, constant flow 1.2 mL/min
Oven program	Temp °C — Hold Time (min)
Initial Temp Setpoint	35 — 22
MS transfer line temperature	60 °C
MS conditions	
Solvent Delay	8.00 min
Tune	HES_atune.u
EM gain	1.0
SIM ions	34, 60, 76
Dwell time	200 ms
Source temperature	120 °C
Quad temperatures	100 °C
	JetClean
H_2 flow	150 µL/min
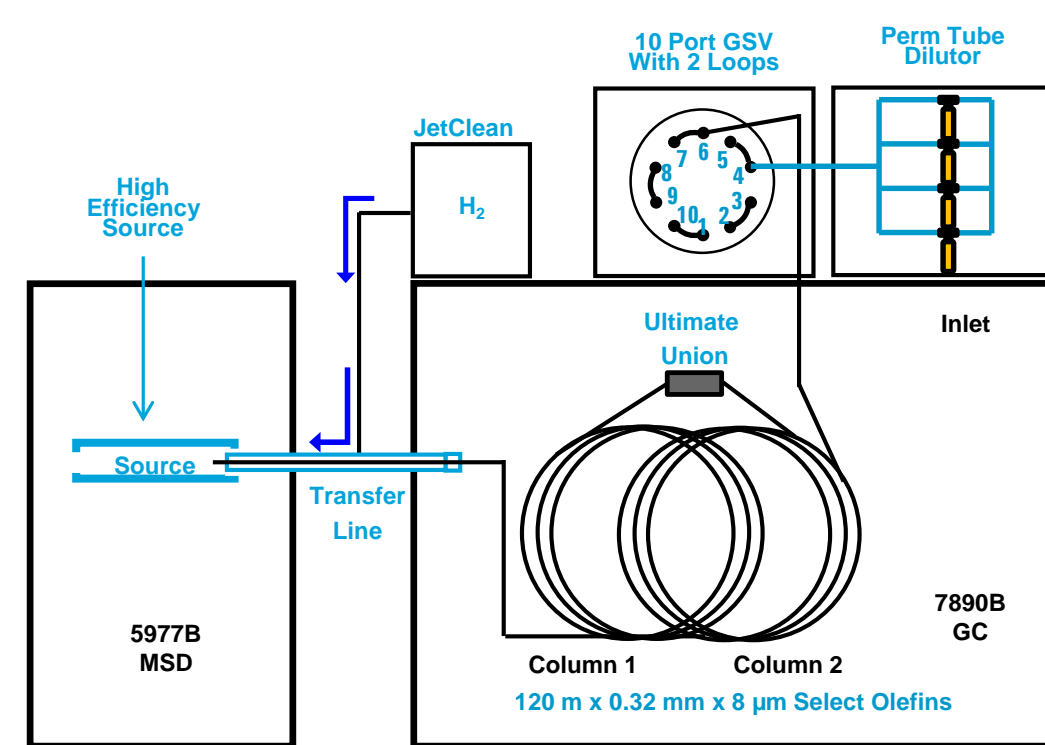
Figure 1. Schematic of 7890B/5977B GC/MSD for contaminants in ethylene and propylene analysis.
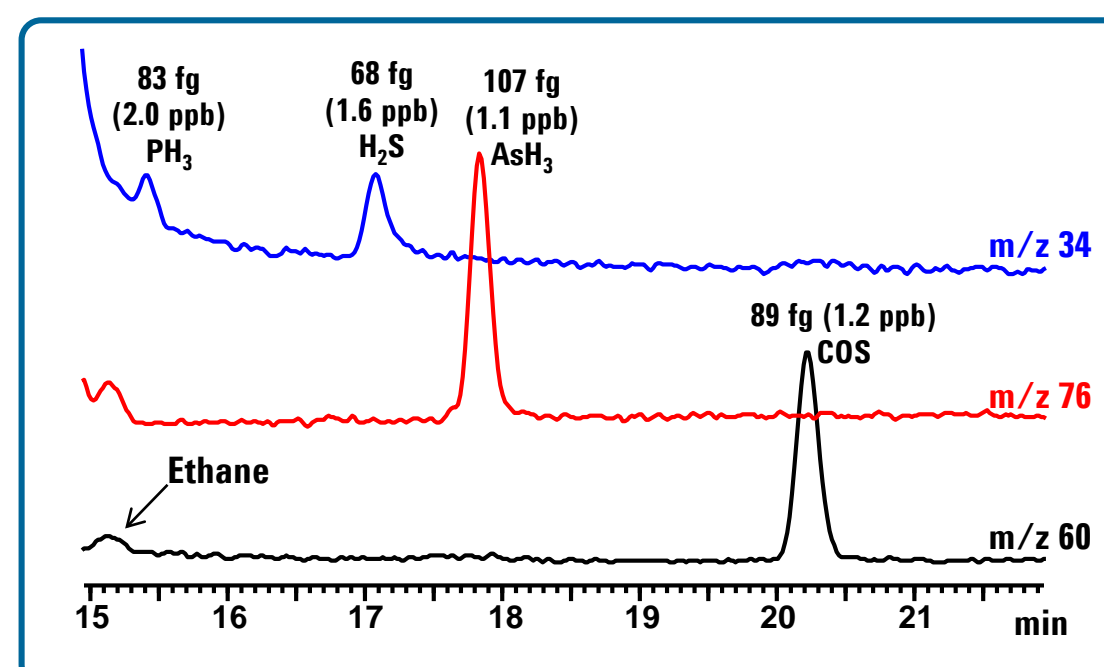
Sub-Picogram Level Detection in Matrix

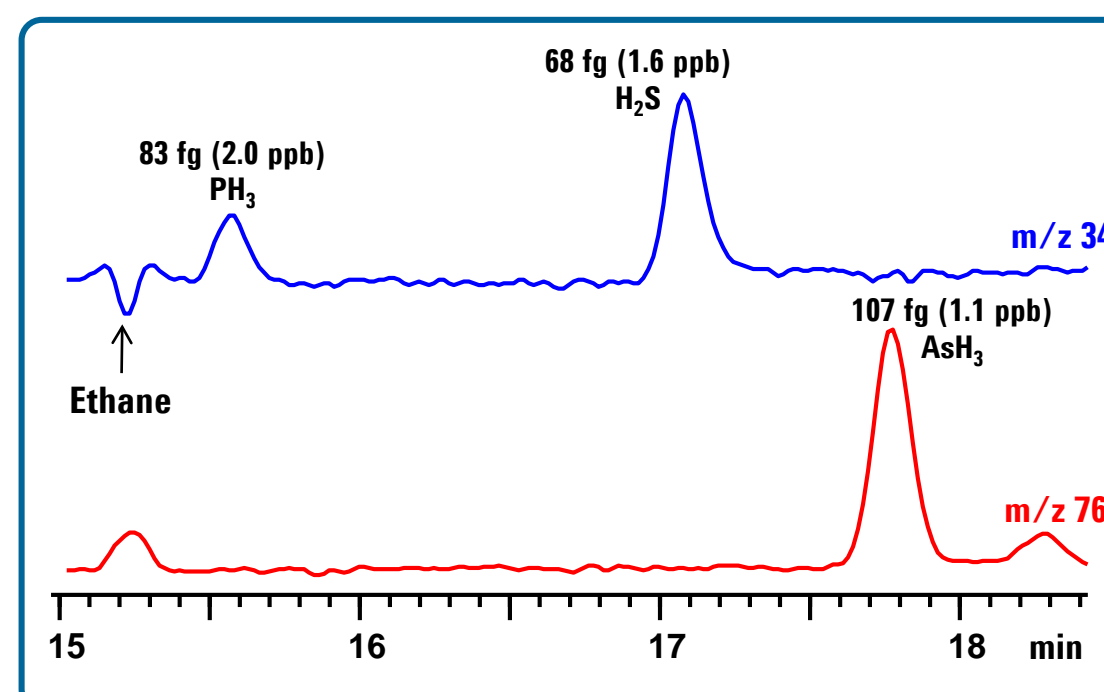Figure 2. EICs of ~1.5 ppb calibrants in polymer grade ethylene matrix.

Figure 3. EICs of ~1.5 ppb calibrants in polymer grade propylene matrix.

Table 2. Statistics of 4 calibrants in ethylene and propylene.

	R^2 (Linearity, 5-50 ppb)	% RSD (~5ppb)	IDL (in ppb, 99% CI)	IDL (in fg, 99% CI)
Ethylene Matrix				
PH_3	0.9996	5.14	0.715	21.2
H_2S	0.9995	3.96	0.456	29.9
AsH_3	0.9999	0.62	0.063	17.6
COS	0.9987	5.06	0.575	18.8
Propylene Matrix				
PH_3	0.9993	4.83	0.673	31.9
H_2S	0.9998	2.54	0.292	20.3
AsH_3	0.9999	0.58	0.045	6.0

"Contaminant" detection in matrix

Calibration standards of the 4 contaminants were run in ethylene and propylene to test for resolution, precision and instrument detection limits with real matrices. At ~1.5 ppb concentrations in ethylene, all 4 contaminants were resolved from the matrix; the extracted ion chromatograms (EICs) are shown in Figure 2. PH_3 is on the shoulder of the ethylene peak, but is best resolved on this 8 µm thick film column, compared to other tested columns.

Three contaminants are detected in propylene, since carbonyl sulfide co-elutes with propylene; Figure 3 displays the EICs for PH_3, H_2S, and AsH_3 at ~1.5 ppb concentrations. The ethylene and propylene matrices were run without calibrants (matrix only), and small amounts of H_2S and COS were detected. In ethylene, 30 fg (0.3 ppb) COS was detected and quantified; 25 fg (0. 43 ppb) H_2S and 63 fg (0. 62 ppb) COS were detected and quantified in propylene.

Figure 4. Permeation tubes of 4 calibrants in the dilution block.

Table 2 lists the statistics for linearity, repeatability (%RSD), and instrument detection limit (IDL) of each contaminant in ethylene and propylene, shown in both ppb and femtograms. This hardware configuration contributes to excellent linearity, repeatability (% RSD) and IDL values for samples in matrix, where the repeatability and IDL are calculated from 50 runs of ~5ppb concentration in matrix. All % RSD values are below 6% and the IDL values are lower than 1 ppb.

5977B HES MS Instrument Detection Limit (IDL$_{RSD}$) in fg

$$IDL_{RSD} = \frac{t_{n,n-1} \times RSD \times c}{100}$$

$t_{n,n-1}$ = t value (coefficient) at the level of α with the sample size of n-1

c = concentration of the std sample injected
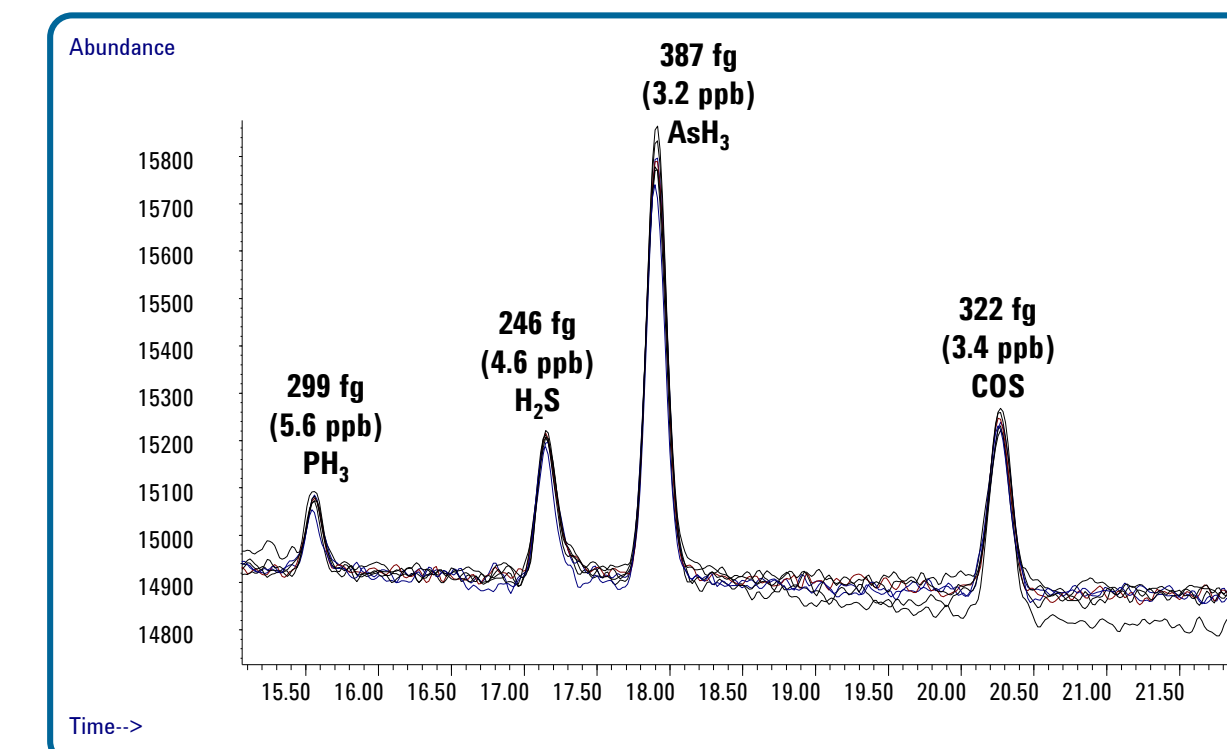
Maintaining Long-Term Stability

Figure 5. Long-term repeatability: Overlays of every 50th TIC of 300 runs over 4.5 days (4 calibrants in helium matrix).
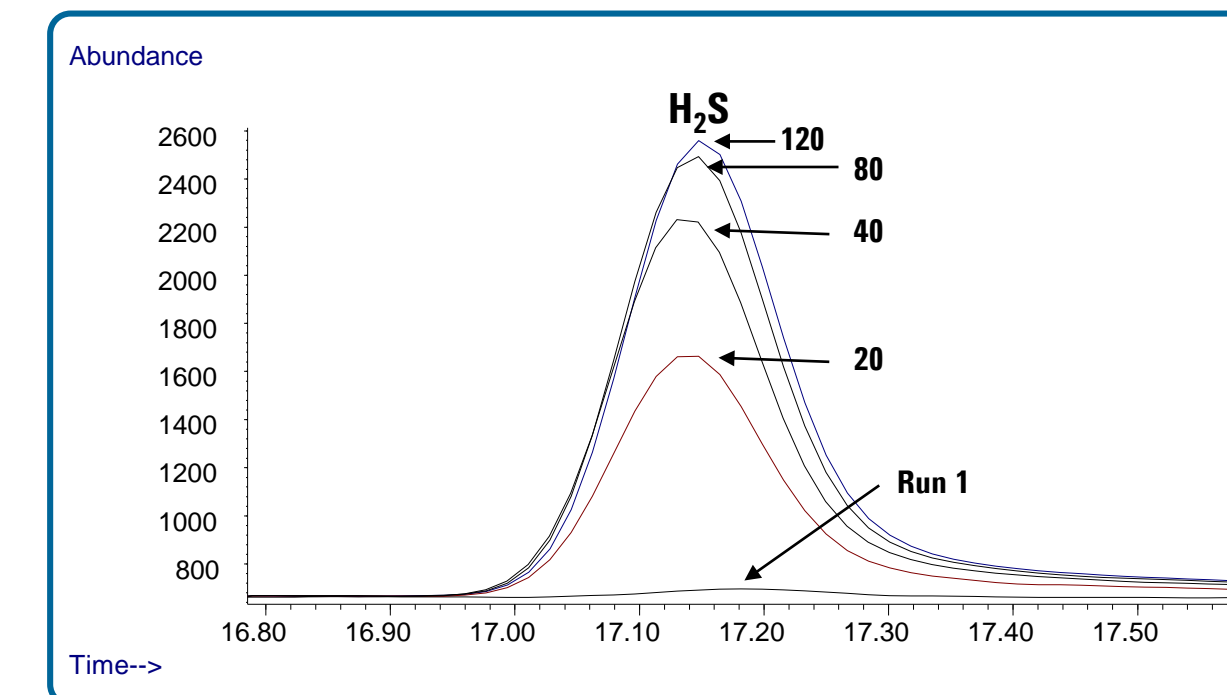

Figure 6. Inert Flow Path is key: In-situ deactivation of untreated stainless steel pathway with high concentrations of H_2S over 120 runs.

Table 3. Repeatability, in % RSD, for 4 calibrants (in He matrix) for 300 runs, completed in 4.5 days.

	% RSD (~5ppb)
PH_3	4.22
H_2S	1.91
AsH_3	3.64
COS	4.14

Signal Stability and Inert Flow Path

Precision over time was tested with 300 runs over 4.5 days with calibration standards at ~5ppb level in helium matrix. Figure 5 overlays every 50th total ion chromatogram (TIC) and Table 3 contains the repeatability of the 300 runs, which are all below 5% RSD. The High Efficiency Source and continuous hydrogen cleaning provide the ability to detect the calibrations at ~5ppb concentrations in helium for 300 runs with excellent repeatability.

Precision and sensitivity also benefit from the use of an inert flow path. Figure 6 shows the results of running high concentration H_2S samples through non-deactivated stainless steel, where the H_2S peak is nearly indistinguishable from the baseline in the first 10 runs. Over time, the high concentrations of H_2S will passivate the stainless steel pathway, but passivation takes ~100 runs. An inert pathway eliminates the need for 100 extraneous conditioning runs.

Conclusions

In both matrices, the long, thick film column provides resolution of PH_3 from ethylene and ethane. Hydrogen cleaning during data acquisition, and pressure regulation in the sample loop provide high precision. The HES MS provides sub-picogram detection of contaminants in the olefin matrices.

G-Cal permeation tubes — No isothermal oven needed for excellent repeatability
Back Pressure Regulation — High precision
Inert Flow Path — Sensitivity and precision for active compounds
120 m Select Olefins— Resolution of arsine and phosphine
HES MS — Sensitivity of sub-picogram level detection in olefin matrix
JetClean— Low maintenance and high precision

The Arsine Phosphine GC/MS analyzer detects sub-picogram concentrations of contaminants in ethylene and propylene with high precision and stability over time.