CONTAMINANTS IN ETHYLENE AND PROPYLENE
ULTRA TRACE LEVEL DETECTION

Technology Advantage: Agilent HES and Agilent JetClean Self-Cleaning Ion Source

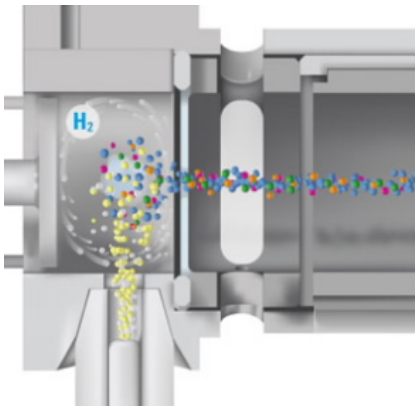

Figure 1. Agilent JetClean Self-Cleaning Ion Source.

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 (pure ethylene or propylene) from low level, active contaminants. Analysis with a GC/MSD must have high chromatographic resolution, high capacity, and an inert sample flow path. The ultra-low detection limits require a system to have excellent sensitivity to detect subpicogram amounts of AsH_3 and PH_3, which can be achieved with the High Efficiency Source (HES). To achieve the required chromatographic resolution and capacity, a long, thick film column (120 m, 8 µm film) is required. However, it introduces significant column bleed, which results in source fouling and unstable response. Using the Agilent JetClean self-cleaning ion source at 0.2 mL/min provides continuous source cleaning, removal of column bleed, and ensures consistent responses.

For more information, visit:
www.agilent.com

Agilent Technologies

Instrumentation

- Agilent 7890B GC, Agilent 5977B Series Mass Selective Detector(MSD), with an Agilent High Efficiency Source
- Column: 120 m × 0.32 mm, 8.0 µm Select Olefins
- Agilent JetClean self-cleaning ion source with continuous H_2 flow

Sampling

Sample introduction was completed with a gas sampling valve. Calibration standards of the four contaminants were analyzed in ethylene and propylene to test for chromatographic separation, response precision, and instrument detection limits with real matrices.

Results and Discussion

Chromatographic separation

The long column with 8 µm film provided adequate resolution of the four contaminants: AsH_3, PH_3, H_2S, and COS in ethylene. 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, providing very good and highly repeatable quantitative results (Figure 2). Three contaminants were detected in propylene, since COS coelutes with propylene; Figure 3 displays the EICs for PH_3, H_2S, and AsH_3 at ~1.5 ppb concentration in propylene.

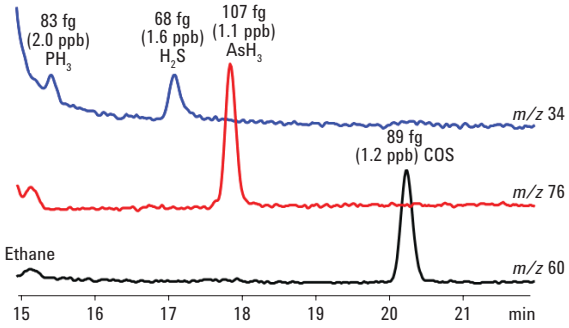

Figure 2. EICs of ~1.5 ppb calibrants in polymer-grade ethylene matrix.

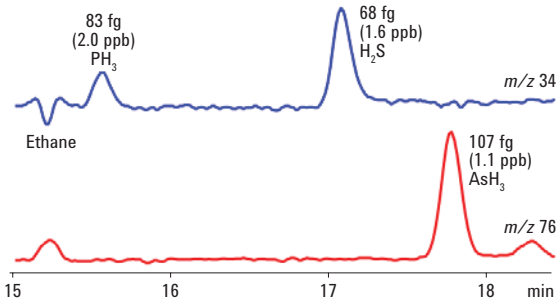

Figure 3. EICs of ~1.5 ppb calibrants in polymer-grade propylene matrix.

The ethylene and propylene matrices were also tested without calibrants (matrix only), and small amounts of H_2S and COS were detected. In ethylene, 0.3 ppb COS was detected and quantified; 0.43 ppb H_2S and 0.62 ppb COS were detected and quantified in propylene.

Linearity, precision, and detection limits

Table 1 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 inert hardware configuration contributes to excellent linearity, %RSD, and IDL values for samples in matrix, where the %RSD and IDL were calculated from 50 runs of ~5 ppb concentration in matrix. All %RSD values were below 6 %, the IDL values were lower than 1 ppb, and MDL values were lower than 2 ppb.

Table 1. Statistics of four calibrants in ethylene and propylene (n = 50).

	R^2 (Linearity, 5–50 ppb)	% RSD (~5 ppb)	IDL (ppb, 99 % CI)	MDL (ppb, S/N =3)
Ethylene matrix				
PH_3	0.9996	5.14	0.715	1.31
H_2S	0.9995	3.96	0.456	0.858
AsH_3	0.9999	0.62	0.063	0.391
COS	0.9987	5.06	0.575	0.081
Propylene matrix				
PH_3	0.9993	4.83	0.673	1.30
H_2S	0.9998	2.54	0.292	0.798
AsH_3	0.9999	0.58	0.045	0.306

Precision over time was tested with 300 runs over 4.5 days with calibration standards at ~5 ppb level in helium matrix. Figure 4 overlays every 50th total ion chromatogram (TIC), and the table inset contains the %RSD of the 300 runs, which were all below 5 %RSD. The inert flow path, HES, and JetClean provide the ability to detect the contaminants at ~5 ppb concentrations in helium for 300 runs with excellent %RSD.

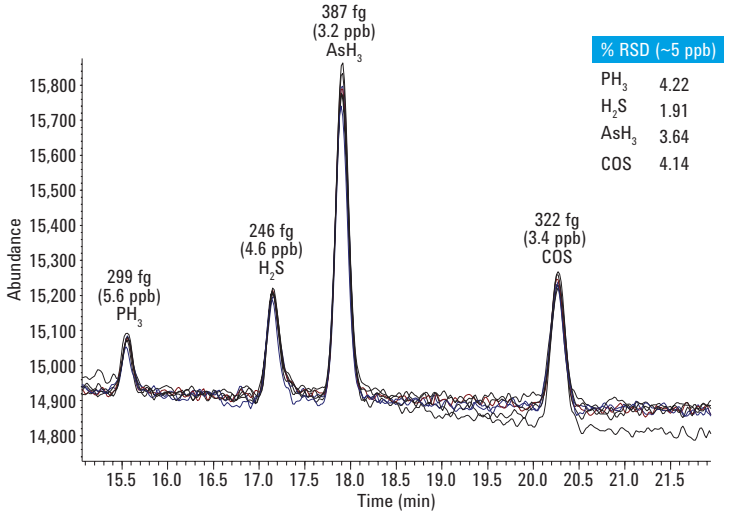

Figure 4. Long-term repeatability: Overlays of every 50th TIC of 300 runs over 4.5 days (4 calibrants in helium matrix).

Conclusions

In both matrices, the long, thick film column provides adequate chromatographic resolution of AsH_3, PH_3, and H_2S from ethylene and ethane. The Agilent JetClean source eliminates column bleed during analysis, and provides high precision. The Agilent HES MS delivers subpicogram detection of contaminants in the olefin matrices.

www.agilent.com
Information, descriptions and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc. 2016
Published in USA, November 29, 2016
5991-7690EN

Agilent Technologies