Analysis of Arsine and Phosphine in Ethylene and Propylene Using the Agilent Arsine Phosphine GC/MS Analyzer with a High Efficiency Source

Application Note

Petrochemical

Authors

Angela Smith Henry and Bruce Quimby
Agilent Technologies Inc.
Wilmington, DE

Abstract

The Agilent Arsine Phosphine GC/MS analyzer enables detection at single-digit parts per billion (ppb) concentrations and long-term signal stability of arsine, phosphine, and other contaminants in ethylene and propylene, with relative standard deviations of ~5 % or less.

Agilent Technologies

Introduction

Developments in the area of metallocene catalysts have significantly 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 can potentially shut down the production 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. Low-level parts per billion (ppb) detection limits also require excellent system sensitivity, which can be achieved using a high efficiency source (HES). Analysis using gas chromatography/mass spectrometry (GC/MS) must provide high resolution, high capacity, high sensitivity, and an inert sample flow path.

To achieve the required chromatographic resolution and capacity, a thick film column is required. The addition of 150 µL/min of H_2 into the source during data acquisition provides continuous source cleaning, and eliminates dropping peak responses that arise from higher column bleed introduced by the thick film. The Agilent Arsine Phosphine GC/MS analyzer with the HES and Self Cleaning Ion Source (SCIS) enables quick start-up for the analysis of arsine and phosphine at low ppb concentrations with high precision, stability over time, and ease-of-use.

Experimental

Reagents and standards

Polymer grade ethylene (grade 3.0, 99.9 % pure) was sourced from Praxair, and industrial grade propylene was sourced from Keen Compressed Gas. Individual G-Cal permeation tubes of AsH_3, PH_3, H_2S, and COS were purchased from VICI Metronics. The permeation tubes were placed in a dilution system to dilute these standards to concentrations in the range of 5–50 ppb. Ethylene and propylene were used, separately, as a matrix gas with the four standards.

Instruments

The Agilent Arsine Phosphine GC/MS analyzer (G3440B with option SP1 7890-0667) uses the Agilent 7890B GC and the Agilent 5977B Series GC/MSD System HES with hydrogen cleaning (Figure 1). Thick film columns provide resolution of the four contaminants in ethylene and three contaminants (PH_3, AsH_3, and H_2S) in propylene. Table 1 lists the analysis conditions.

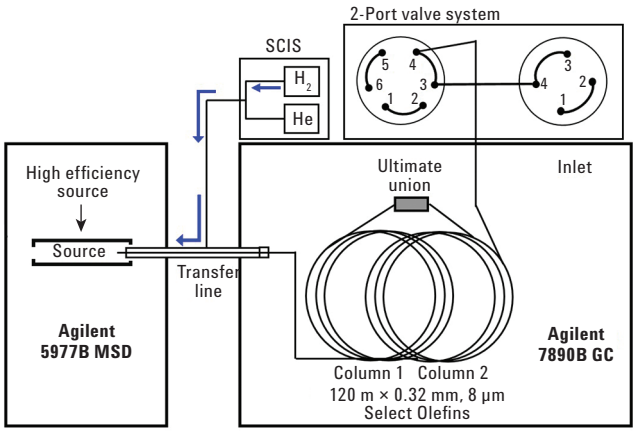

Figure 1. Schematic of the Agilent Arsine Phosphine GC/MS analyzer.

Table 1. Phosphine Analyzer Analysis Conditions

GC conditions	
Column	120 m × 0. 32 mm, 8.0 µm Select Olefins (p/n CP8580)
Sample introduction	2 valve system
Carrier gas	Helium, constant flow at 1.2 mL/min
Oven program	35 °C for 22 minutes
MS conditions	
Transfer line temperature	60 °C
Source temperature	120 °C
Quadrupole temperature	100 °C
Solvent delay	8.00 minutes
SIM ions	33, 34, 60, 75, 76
Tune	HES_atune.u
EM gain	1
Hydrogen cleaning	
H_2	40 psi (150 µL/min)

Results and Discussion

Calibration standards of the four contaminants were run in ethylene and propylene matrices. At single-digit ppb concentrations in matrix, these contaminants were successfully detected and quantified. Only three contaminants were detected in propylene, since carbonyl sulfide coelutes with propylene. Precision over time was tested with 300 runs over 4.5 days with calibration standards at ~5 ppb level. Figure 2 shows the overlay of every 50th total ion chromatogram (TIC), and Table 2 lists the statistics for linearity, repeatability (%RSD), and instrument detection limit (IDL) of each contaminant in ethylene. All %RSD values were below 6 %, and the IDL values were lower than 1 ppb. The repeatability and IDL values were calculated from 50 runs of ~5 ppb concentrations in ethylene.

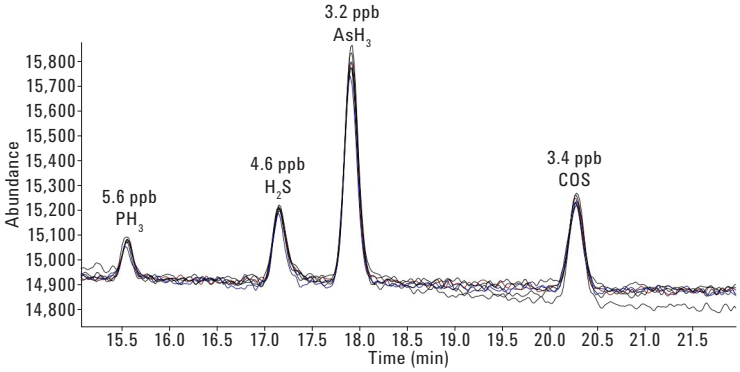

Figure 2. Overlay of TICs for every 50th run out of 300 runs completed over 4.5 days. Runs 1, 50, 100, 150, 200, 250, and 300 are shown.

Table 2. Statistics for Detected Analytes in Ethylene

	Linearity (R_2)*	% RSD† (~5 ppb, 50 runs)	IDL (ppb)‡	IDL (fg)‡
Phosphine (PH_3)	0.9996	5.14	0.715	21.2
Hydrogen sulfide (H_2S)	0.9995	3.96	0.456	29.9
Arsine (AsH_3)	0.9999	0.62	0.063	17.6
Carbonyl sulfide (COS)	0.9987	5.06	0.575	18.8

* Calculated from 5 to 50 ppb

† Percent relative standard deviation

‡ Instrument detection limit, 99 % confidence Interval; fg = femtograms

Conclusion

The Agilent Arsine Phosphine GC/MS analyzer with HES and continuous hydrogen cleaning detects single-digit ppb concentrations of contaminants in ethylene and propylene with high precision and stability over time. This hardware configuration enables excellent linearity, %RSD, and IDL values for samples in matrix.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

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

© Agilent Technologies, Inc., 2016
Printed in the USA
May 13, 2016
5991-6967EN

Agilent Technologies