Olefin Analyzer
Solutions for Polymer
Grade Ethylene and
Propylene

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Kelly Beard
George Gonzalez
Analysis of contaminants in ethylene and propylene

• Trace impurities can foul the process units and product quality
• Frequently used metallocene catalysts are susceptible to impurities
  - Contaminants can degrade a polymerization catalyst and can potentially shut down the production process for catalyst replacement
• Impurities need to be monitored at lowest possible detection limits
Outline

- Arsine Phosphine GC/MS Analyzer
  - ASTM Work Item #56896 – Arsine and Phosphine in Ethylene
- GC-FID
  - D6159 – Trace Level Hydrocarbons in Ethylene
  - D7212 – Trace Level Hydrocarbons in Propylene
  - D7423 – Oxygenates in Ethylene
- GC-PDHID
  - ASTM Work Item #55889 – Fixed gases in Ethylene with PD-HID
Arsine Phosphine Analyzer: Detect low level contaminants in ethylene and propylene

Applications Chemists
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Bruce Quimby, Ph.D.
Arsine/Phosphine GC/MS Analyzer - Overview

Excellent analytical performance

- Single digit ppb detection limits, RSDs of ~5% or less
- Inert Flow Path for robust operation
- **High Efficiency Source** for highest sensitivity and **JetClean Self Cleaning Ion Source** for long-term precision
- Hands-free **multi-level Calibration** – Automated calibration sequence

Provides ability of in-house routine monitoring for contaminants

- Detection at this level previously only achievable with GC/ICP-MS
  - GC/ICP-MS is still more sensitive than GC/SQ
Arsine Phosphine GC/MS Analyzer

Fully automated multi-level calibration system with PCM modules and pre-made methods

Agilent designed and manufactured inert dilution system for built-in calibration

Use a GC-controlled back pressure regulator on valve system: High precision

HE Source: Improved IDL for single ppb detection

JetClean: Low maintenance, high precision

Agilent deactivation for inert flow path

Novel column: Resolution of contaminants in olefin matrix
Schematic of Arsine Phosphine GC/MS Analyzer

Blue lines (or outline) indicate deactivated stainless steel tubing
GC-Integrated Calibration with G-Cal Permeation Tubes

- Dilution controlled with GC flow modules
- Performs automated, multi-level calibration runs in same sequence as samples
  - User sets up sequence with calibration and sample runs
  - Press OK and let the GC/MS do the work
Permeation Tube Dilution System: GC-controlled 2-stage dilution

Section in gray is incorporated into permeation tube fixture design
GSV 1: 4 port valve to select calibrants or customer sample
GSV 2: 6 port valve to send selected gases (from GSV 1) onto column for analysis (or vent)

*PCM 1B is modified with a split vent valve to handle higher flows.
ANALYTICAL PERFORMANCE

Ethylene and propylene matrices with permeation tube dilution system
Analytes in Ethylene Matrix: Below 1ppb Detection limits

<table>
<thead>
<tr>
<th>Analyte</th>
<th>R² Linearity 5-50 ppb</th>
<th>% RSD 50 runs, ~5ppb</th>
<th>IDL in ppb, 99% CI</th>
<th>IDL in fg, 99% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH₃</td>
<td>0.9996</td>
<td>4.40</td>
<td>0.671</td>
<td>38.6</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.9997</td>
<td>2.66</td>
<td>0.256</td>
<td>14.9</td>
</tr>
<tr>
<td>AsH₃</td>
<td>0.9999</td>
<td>1.33</td>
<td>0.128</td>
<td>16.9</td>
</tr>
<tr>
<td>COS</td>
<td>0.9999</td>
<td>0.77</td>
<td>0.097</td>
<td>9.83</td>
</tr>
</tbody>
</table>

* IDL = (t* RSD* concentration)/100
(t for 99% confidence level, n-1 degree of freedom)
Propylene Matrix: Below 1ppb Detection Limits

Propylene Matrix: ~5 ppb analytes

<table>
<thead>
<tr>
<th>Analyte</th>
<th>R² Linearity 5-50 ppb</th>
<th>% RSD 50 runs, ~5ppb</th>
<th>IDL in ppb, 99% CI</th>
<th>IDL in fg, 99% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH₃</td>
<td>0.9998</td>
<td>3.16</td>
<td>0.541</td>
<td>31.2</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.9996</td>
<td>3.92</td>
<td>0.431</td>
<td>24.7</td>
</tr>
<tr>
<td>AsH₃</td>
<td>0.9998</td>
<td>1.39</td>
<td>0.153</td>
<td>20.0</td>
</tr>
</tbody>
</table>

*IDL = (t*RSD*concentration)/100
(t for 99% confidence level, n-1 degree of freedom)
Liquid propylene sampling: Micro Gasifier

- Can be connected to the Arsine Phosphine Analyzer
- < 1% sample carryover
- Max inlet pressure of 1000 psi
- Pre-set to 100°C and outlet pressure of 10 psi
- Sample and vent flows are user controlled
- Excellent repeatability: < 5% RSD for 50 runs at 5ppb
Unmatched Long Term Precision

<table>
<thead>
<tr>
<th>Compound</th>
<th>% RSD (5ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphine</td>
<td>4.23</td>
</tr>
<tr>
<td>H₂S</td>
<td>2.76</td>
</tr>
<tr>
<td>Arsine</td>
<td>2.30</td>
</tr>
<tr>
<td>COS</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Overlays of Total Ion Chromatograms (TIC) for every 50th run out of 300 runs completed over 4.5 days. Runs 2, 50, 100, 150, 200, 250, and 300 are shown for 5ppb compounds in helium.
Using Scan mode to identify other impurities in ethylene

- Compared spectra of peaks to NIST library
- Identified ethane and propylene impurities in ethylene
- Let’s take a closer look around the propylene peak….
Impurities in ethylene matrix near propylene peak: Scan mode

RTs: Propylene (20.383 min), water (20.465 min) and COS (20.697 min)

Closely eluting compounds can be separated and identified with Scan mode
Early eluting compounds in propylene:
Extracted Ion Chromatograms from Scan

Identify low level hydrocarbon impurities with Scan Mode
Arsine/Phosphine GC/MS Analyzer - Summary

• Robust solution for routine monitoring of olefin impurities
• Single digit ppb detection limits for AsH\textsubscript{3} & PH\textsubscript{3} in monomer grade ethylene and propylene
• High efficiency source and JetClean for highest sensitivity and long-term precision
• Gas or liquid sampling possible
• Applicable to other low-boiling point matrices (e.g. H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2})

**In-house routine monitoring allows fast mitigation and cost savings**
FID and PDHID
Olefin Solutions
Ethylene Monomer Purity with GC-FID – D6159

Contaminant detection in ethylene matrix

- Trace level hydrocarbon detection
- IDL less 1 ppm
- Repeatability, less than 4 % RSD
- Excellent linearity in matrix

[Graph showing gas chromatography peaks for various compounds, with labels and concentrations indicated.]

Conc.: 16ppm
Propylene Monomer Purity with GC-FID – D2712

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Cyclopropane
6. Propylene
7. iso-Butane
8. n-Butane
9. Propadiene
10. Acetylene
11. trans-2-Butene
12. 1-Butene
13. neo-Pentane
14. iso-Butylene
15. iso-Pentane
16. cis-2-Butene
17. n-Pentane
18. 1,3-Butadiene

concentration: 1ppm
Oxygenates in Ethylene with GC-FID – D7423

Contaminant detection in matrix
- IDL less 1 ppm
- Repeatability, less than 5 % RSD
- Excellent linearity in matrix
Non-condensable Gases with GC-PDHID
ASTM Work Item #55889

<table>
<thead>
<tr>
<th>Gas</th>
<th>ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>11.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>14.6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>25.4</td>
</tr>
<tr>
<td>Methane</td>
<td>11.1</td>
</tr>
<tr>
<td>CO</td>
<td>11.4</td>
</tr>
</tbody>
</table>
Plumbing diagram
Linear calibration curve in ethylene

**CO2**  
$R^2 = 0.9929$

**Hydrogen**  
$R^2 = 0.9875$

**Oxygen**  
$R^2 = 0.9835$

**Nirtorgen**  
$R^2 = 0.9981$

**Methane**  
$R^2 = 0.9936$

**CO**  
$R^2 = 0.9899$
Summary

Agilent Olefin Analyzer Suite provide a complete polymer grade ethylene and propylene contaminant testing capability.

Agilent’s GC-MS provides lowest detection for arsine and phosphine in the industry.

<table>
<thead>
<tr>
<th>Description</th>
<th>ASTM Method</th>
<th>Agilent Instrument Capability</th>
<th>Agilent Analyzer Product Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsine / Phosphine</td>
<td>ASTM Work Item #56896</td>
<td>GC-MS</td>
<td>M7474AA / M7484AA</td>
</tr>
<tr>
<td>Ethylene monomer purity</td>
<td>D6159</td>
<td>GC-FID</td>
<td>7890-0138 (D6159)</td>
</tr>
<tr>
<td>Propylene monomer purity</td>
<td>D2712</td>
<td>GC-FID</td>
<td>7890-0138 (D2712)</td>
</tr>
<tr>
<td>Oxygenates</td>
<td>D7423</td>
<td>GC-FID</td>
<td>7890-341</td>
</tr>
<tr>
<td>Non-condensable Gases</td>
<td>ASTM Work Item #55121</td>
<td>GC-PDHID</td>
<td>7890-0237</td>
</tr>
</tbody>
</table>
Linear working range calibration curve in ethylene - AsP

PH$_3$ Linearity

$R^2 = 0.9996$

H$_2$S Linearity

$R^2 = 0.9997$

AsH$_3$ Linearity

$R^2 = 0.9999$

COS Linearity

$R^2 = 0.9999$
Deactivation is key:
Testing untreated stainless steel with hydrogen sulfide

Stainless steel permeation tube dilution block **WITHOUT** deactivation:
Takes ~1 day for “in situ” deactivation with hydrogen sulfide samples
Deactivation is key:
Testing deactivated stainless steel dilution block

Stainless steel permeation tube dilution block WITH deactivation:
Takes ~3 runs to reach a stabilized response
## Conditions

<table>
<thead>
<tr>
<th><strong>GC conditions</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>Select Olefins (CP8580)</td>
</tr>
<tr>
<td>Sample introduction</td>
<td>2 valve system</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium, constant flow at 1.1 mL/min</td>
</tr>
<tr>
<td>Oven program</td>
<td>35 °C for 23 min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>MS conditions</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Transfer line temperature</td>
<td>60 °C</td>
</tr>
<tr>
<td>Source temperature</td>
<td>120 °C</td>
</tr>
<tr>
<td>Quadrupole temperatures</td>
<td>100 °C</td>
</tr>
<tr>
<td>Solvent delay</td>
<td>8.00 min</td>
</tr>
<tr>
<td>SIM ions</td>
<td>33, 34, 60, 75, 76</td>
</tr>
<tr>
<td>Tune</td>
<td>HES_atune.u</td>
</tr>
<tr>
<td>EM gain</td>
<td>1</td>
</tr>
</tbody>
</table>

### Hydrogen Cleaning

| JetClean H₂                | 0.20 mL/min                           |

Data acquired on **prototype** equipped with fully automated calibration system.
Detection limits and S/N ratio (5ppb, 50 runs)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration (ppb)</th>
<th>ASTM S/N (average)</th>
<th>S/N Detection Limit (ppb)</th>
<th>% RSD</th>
<th>IDL (ppb, 99% CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH₃</td>
<td>6.4</td>
<td>33.5</td>
<td>0.510</td>
<td>1.75</td>
<td>0.300</td>
</tr>
<tr>
<td>H₂S</td>
<td>4.1</td>
<td>25.1</td>
<td>0.431</td>
<td>2.62</td>
<td>0.287</td>
</tr>
<tr>
<td>AsH₃</td>
<td>4.1</td>
<td>120.9</td>
<td>0.089</td>
<td>1.07</td>
<td>0.118</td>
</tr>
<tr>
<td>COS</td>
<td>5.3</td>
<td>281.7</td>
<td>0.050</td>
<td>0.75</td>
<td>0.106</td>
</tr>
</tbody>
</table>

ASTM S/N ratio calculated in MassHunter Quantitative Analysis.