SELECTIVE ANALYSIS OF TRACE LEVEL CARBONYL SULPHIDE IN PROPYLENE BY GAS CHROMATOGRAPHY AND CHEMILUMINESCENCE AS ALTERNATIVE DETECTION FOR ASTM D5303

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Introduction

TRACE LEVEL CARBONYL SULFIDE IN PROPYLENE BY GAS CHROMATOGRAPHY AND
INTRODUCTION

• Introduction
• Standardization
• Analytical Challenge
• SCD VS PFPD/FPD
• Recent development
• Application COS in Propylene
INTRODUCTION
COS IN PROPYLENE

• Catalyst Poisoning / degenerate

• Product Quality / conversion
Sulfur Speciation

STANDARDIZATION
<table>
<thead>
<tr>
<th>Method</th>
<th>Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D5303</td>
<td>Flame Photometric Detection (PFPD)</td>
</tr>
</tbody>
</table>

- Limited in scope
  - 0.5 - 4 mg/Kg
COS in Propylene

ANALYTICAL CHALLENGE
ANALYTICAL CHALLENGE

- COS in Propylene (Boiling point column)
- CO-ELUTION of COS in Propylene
- Selectivity
- Detection Limit
COS IN Propylene

SCD VS PFPD/FPD
## DETECTOR CHARACTERISTICS

### SULFUR DETECTOR COMPARISON

<table>
<thead>
<tr>
<th></th>
<th>SCD</th>
<th>PFPD</th>
<th>FPD+</th>
</tr>
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<tbody>
<tr>
<td><strong>Response Stability</strong></td>
<td>≤2% RSD 2 hrs ≤3% RSD 24 hrs</td>
<td>≤ 3%</td>
<td>≤ 3%</td>
</tr>
<tr>
<td><strong>Minimum Detectability</strong> (pg S/s)</td>
<td>≤ 0.3</td>
<td>≤ 1.0</td>
<td>≤ 2.5</td>
</tr>
<tr>
<td><strong>HC Selectivity (S/C Ratio)</strong></td>
<td>≥ 5.0 e7</td>
<td>≥ 1.0 e6</td>
<td>≥ 1.0 e6</td>
</tr>
<tr>
<td><strong>Linear response</strong></td>
<td>≥ 1.0 e4</td>
<td>1.0 e3 (approximate)</td>
<td>≥ 1.0 e3 (not linear)</td>
</tr>
<tr>
<td><strong>Equimolar Response</strong></td>
<td>≤ 10%</td>
<td>≤ 8%</td>
<td>Non equimolar</td>
</tr>
<tr>
<td><strong>High Column Flow</strong></td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Compatible with GC*GC</strong></td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td><strong>Simultaneous Multi-element Response</strong></td>
<td>S&amp;N</td>
<td>Multi</td>
<td>S&amp;P</td>
</tr>
</tbody>
</table>
PRO’s vs. CON’s FPD

Advantages FPD:
- Low Cost
- High flow rates

Disadvantages FPD:
- Non Equimolar
- Non Linear response
- Quenching of hydrocarbons

- Single component
- Low Cost solution
PRO’s vs. CON’s PFPD

Advantages PFPD:

• Long term stability of the PFPD
• Consumes less gas
• Uses Air

Disadvantages PFPD:

• HC Quenching
• Linear range limited

• Stable
• Permeation device recommended
Advantages SCD:

• Larger dynamic range
• Less prone to quenching / hydrocarbon interference
• Best sensitivity

Disadvantages SCD:

• Requires high quality gasses

• No matrix effects
• Single level calibration
Sulfur Speciation

RECENT DEVELOPMENTS
RECENT DEVELOPMENTS
SENSE

- NEW Sulphur Chemiluminescence Detector (SCD)
- Replaces existing Antek 7090

Research focus:
- Stability
- Fast start-up times
• Research
  – Complete redesign of the detector
  – Changed probe design
  – Optimized flow settings
  – Hardware redesign for easy septum / column change
  – Implementation of automated vacuum check procedure
  – Uses air instead of oxygen
• 72 hour response stability check
Sulfur Speciation

COS IN PROPYLENE
Trace Carbonyl Sulfide (COS) in Propylene

- GSV injection
- LDL <30 ppb

**Parameter** | **Setting**
--- | ---
Column | 60 m x 0,53 mm x 4 µm methylsilicone
Sample size | 1 ml loop
Split | N.A.
Injector | Direct injection
Carrier gas | Helium
Carrier flow | 10 ml/min
SCD gasses | Air / H2
COS IN PROPYLENE
EXAMPLE CHROMATOGRAM

- 100 ppb Mol COS in Propylene Matrix
COS IN PROPYLENE QUENCHING

- Sulfur standard in Propylene
- Propylene Matrix

LDL of <20 ppbM
COS in Propylene

OVERVIEW
Sulfur Chemiluminescence
Best in market for COS in Propylene