



solid partners  
proven solutions

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

MARIJN VAN HARMELEN

Introduction

# TRACE LEVEL CARBONYL SULFIDE IN PROPYLENE BY GAS CHROMATOGRAPHY AND

- 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

## Standardization

Method	Detection
ASTM D5303	Flame Photometric Detection (PFPD)

- Limited in scope  
0.5 - 4 mg/Kg

COS in Propylene

# ANALYTICAL CHALLENGE

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





COS IN Propylene

# SCD VS PFPD/FPD

## SULFUR DETECTOR COMPARISON

	SCD	PFPD	FPD+
Response Stability (%RSD in 24 hrs)	≤2% RSD 2 hrs ≤3% RSD 24 hrs	≤ 3%	≤ 3%
Minimum Detectability (pg S/s)	≤ 0.3	≤ 1.0	≤ 2.5
HC Selectivity (S/C Ratio)	≥ 5.0 e7	≥ 1.0 e6	≥ 1.0 e6
Linear response	≥ 1.0 e4	1.0 e3 (approximate)	≥ 1.0 e3 (not linear)
Equimolar Response	≤ 10%	≤ 8%	Non equimolar
High Column Flow	Yes	No	Yes
Compatible with GC*GC	Yes	No	No
Simultaneous Multi-element Response	S&N	Multi	S&P

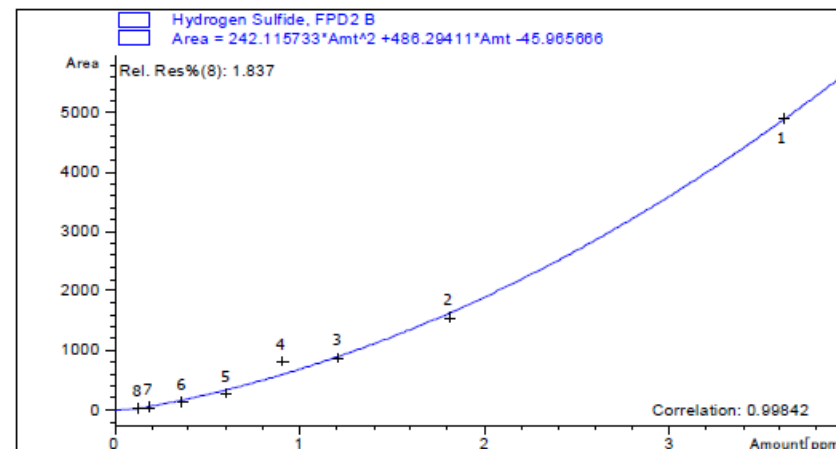
## Advantages FPD:

- Low Cost
- High flow rates

## Disadvantages FPD:

- Non Equimolar
- Non Linear response
- Quenching of hydrocarbons

- Single component
- Low Cost solution



## 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

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

## Research focus:

- Stability
- Fast start-up times



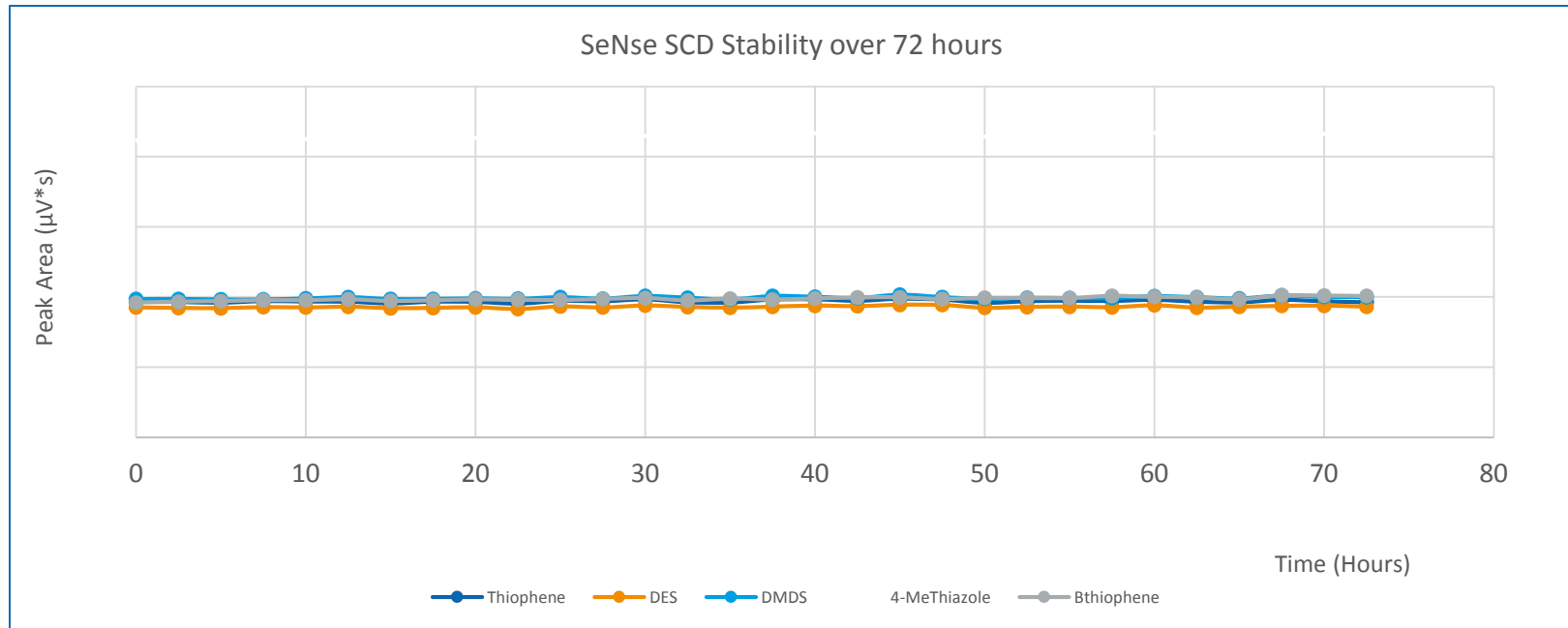
- Research
  - Complete redesign of the detector
  - Changed probe design
  - Optimized flow settings
  - Hardware redesign for easy septum / column change
  - Implementation of automated vacuum check procedure
  - Uses air instead of oxygen





# RESPONSE STABILITY

## SENSE DETECTOR CHECK STANDARD



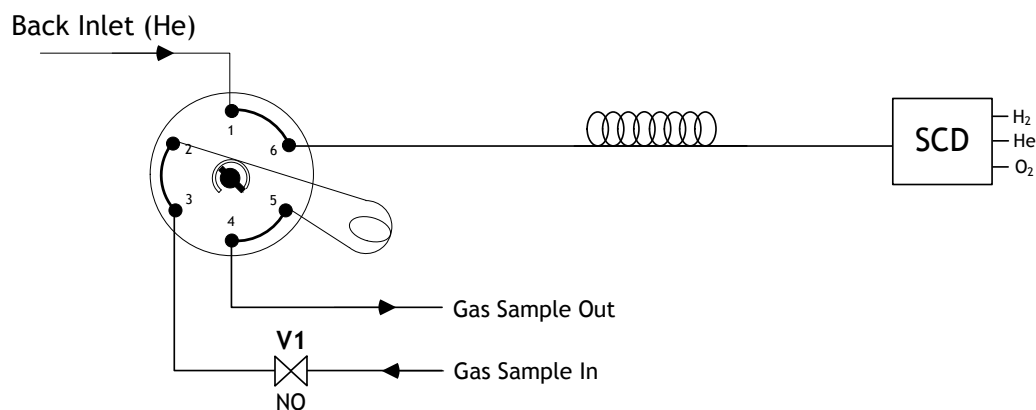
- 72 hour response stability check

Sulfur Speciation

# COS IN PROPYLENE

## Trace Carbonyl Sulfide (COS) in Propylene

- GSV injection
- LDL <30 ppb

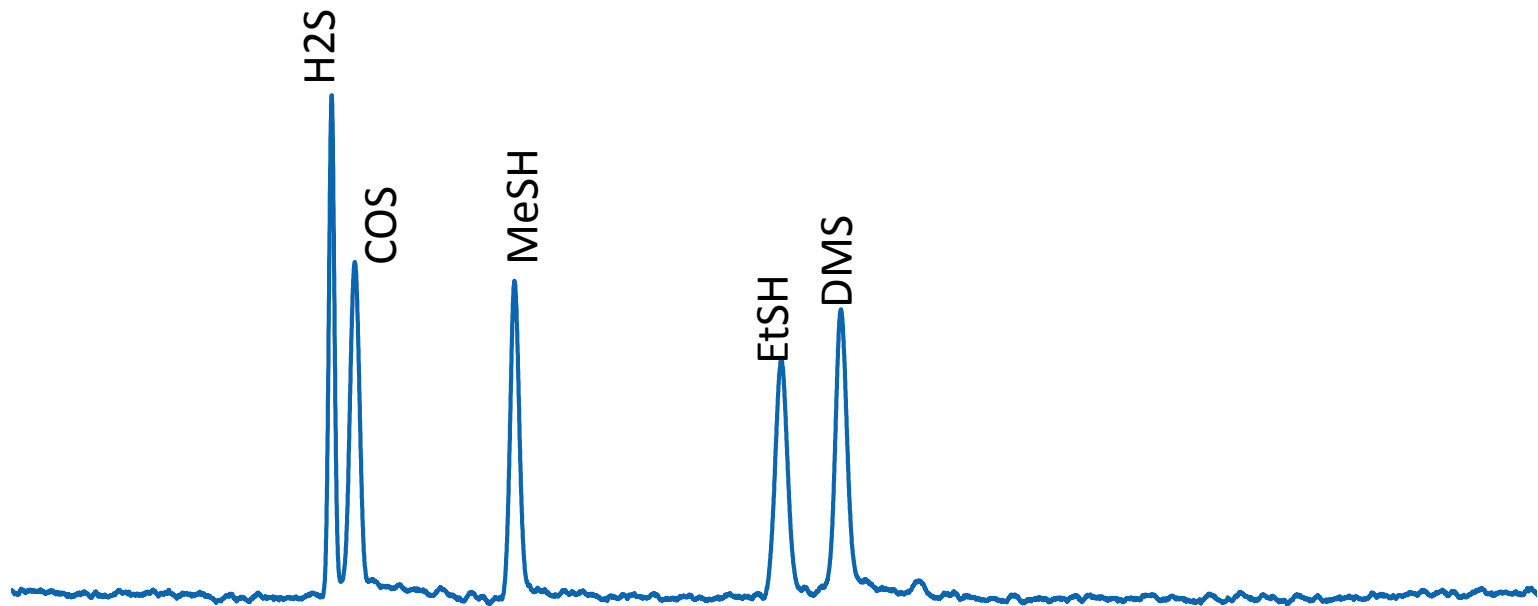


Parameter	Setting
Column	60 m x 0,53 mm x 4 $\mu$ m methylsilicone
Sample size	1 ml loop
Split	N.A.
Injector	Direct injection
Carrier gas	Helium
Carrier flow	10 ml/min
SCD gasses	Air / H <sub>2</sub>

# COS IN PROPYLENE EXAMPLE CHROMATOGRAM



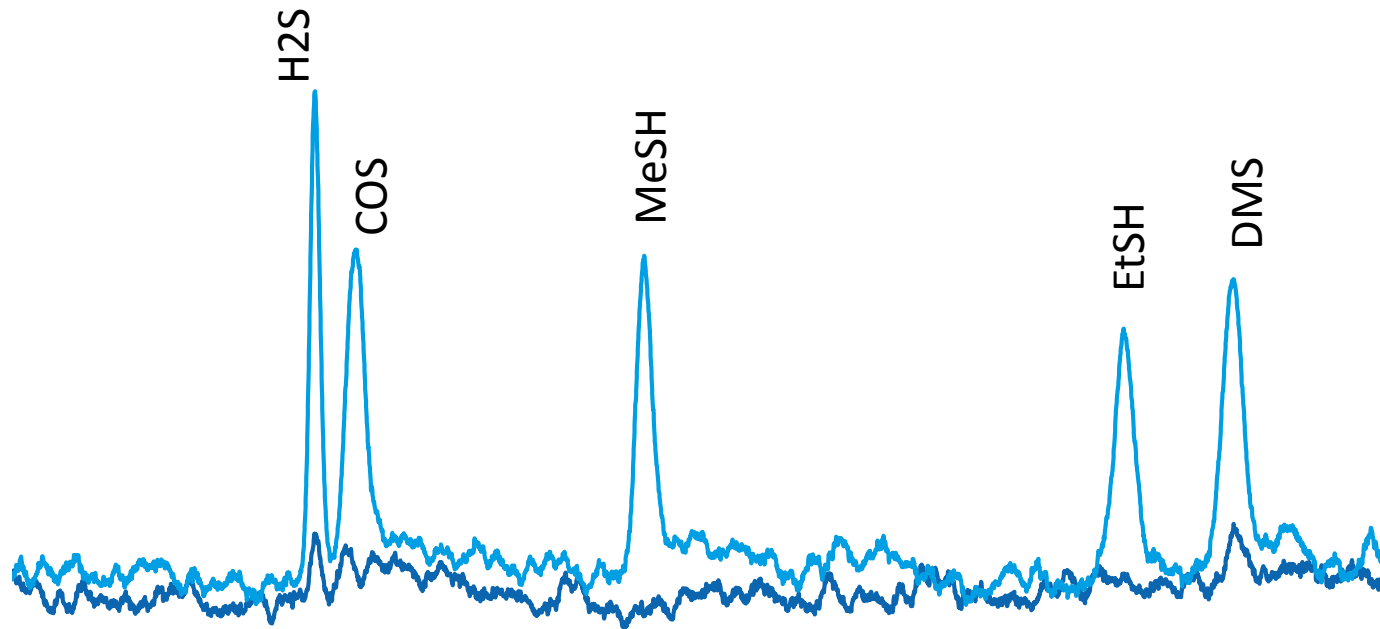
- 100 ppb Mol COS in Propylene Matrix



# 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



