GC Analysis of Sulfur Compounds

Emphasis on refinery processes

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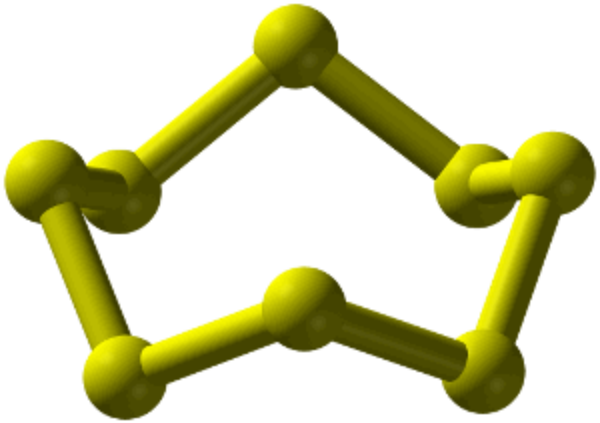
Why is there a focus on Sulfur?

Sulfur compounds are ubiquitous in refining and petrochemical products

- Variable in crude oils ranging from ppb level components to wt.% level S
- Sweet vs. Sour Crude oil
- Levels of sulfur in crude oil grow approximately 500 ppm per year, making sulfur management an ever increasing burden.

Sulfur compounds create processing problems for refiners, natural gas, companies, and petrochemical plants and have a negative impact on product quality



Why Focus on Sulfur Analysis 2

- Sulfur species cause corrosion
  - higher maintenance costs for pipe lines, reactors and furnaces

- Sulfur compounds in intermediates poison catalysts
  - may drastically reduce yield of final product
  - higher costs for catalysts
  - higher costs in catalysts regeneration
  - high costs in refinery down time

- All fuel sulfur pollutes the air. Environmental regulations aimed at reducing pollution are requiring lower levels of sulfur in fuels.

- Value of HPI products is related to the presence or absence of sulfur compounds.

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Challenges for Sulfur Analysis

Low levels often require maximum sensitivity

Matrix interference from the hydrocarbons present

Highly reactive and polar molecules

Detectors for Sulfur Analysis

Why not use an FID or MSD?

Sulfur Detection Portfolio

Detector	GC-FPD	GC-PFPD	GC-SCD
Supplier	Agilent	OI	Agilent
MDL Sulfur	3.6 pg/sec	1 pg/sec	<0.5 pg/sec
Selectivity	10^6	10^6	10^7
Dynamic Range	10^3	10^3	10^5
Quenching	yes	yes	no
Equimolar response	No	No	yes
Packed Col Compatible	yes	No, < 1ml/min	yes
Other Elements	P, Sn	P	N
Cost	$	$$	$$$

Sulfur related Analyzers based on PFD or SCD

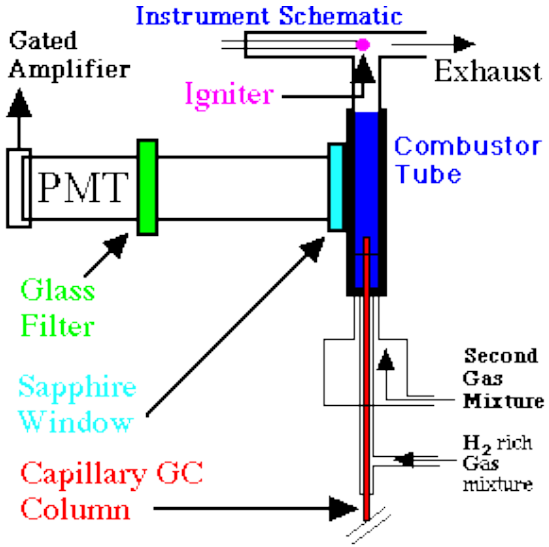
Method Description	Configuration for Published Methods	How to choose the right solution
Volatile Sulfur in C2, C3, C4 monomers and LPG Analyzer by FPD	ASTM D6228	•If the matrix is reasonably simple and sulfur levels are in the low ppm to 100 ppb range then the FPD will usually be a good choice. •Ease-of-use •The lowest cost of all detectors •Quenching can be an issue
Volatile Sulfur in NGA, fuel gas Analyzer by FPD	ASTM D6228	
Sulfur in gas fuels by SCD	ASTM D5504	•For samples where it is not feasible to completely separate sulfur components from the hydrocarbon matrix and low ppb sensitivities are required, the SCD can be considered if experienced users are available. •A good detector for low-level sulfur, reaching 10 ppb in ideal cases. • No quenching •Equimolar response
Sulfur in light petroleum liquids by SCD	ASTM D5623	

All are available as pre-configured analyzers from Agilent

Sulfur specific detectors and quenching

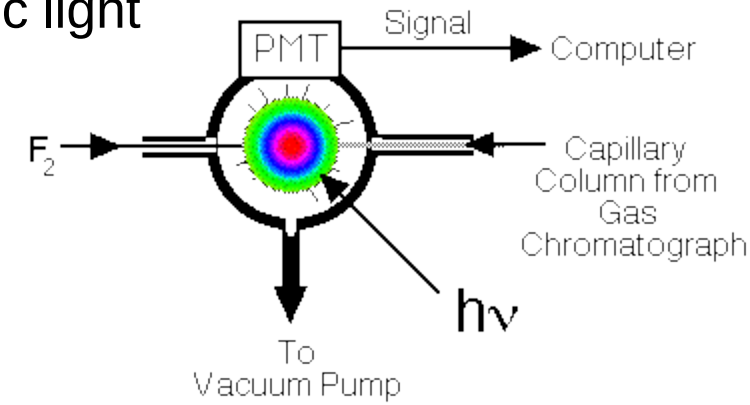
•PFPD

- Strong disturbance of carrier gas extinguishes flame
  - ie by large matrix peak
- Sensitivity to sulfur is reduced to zero



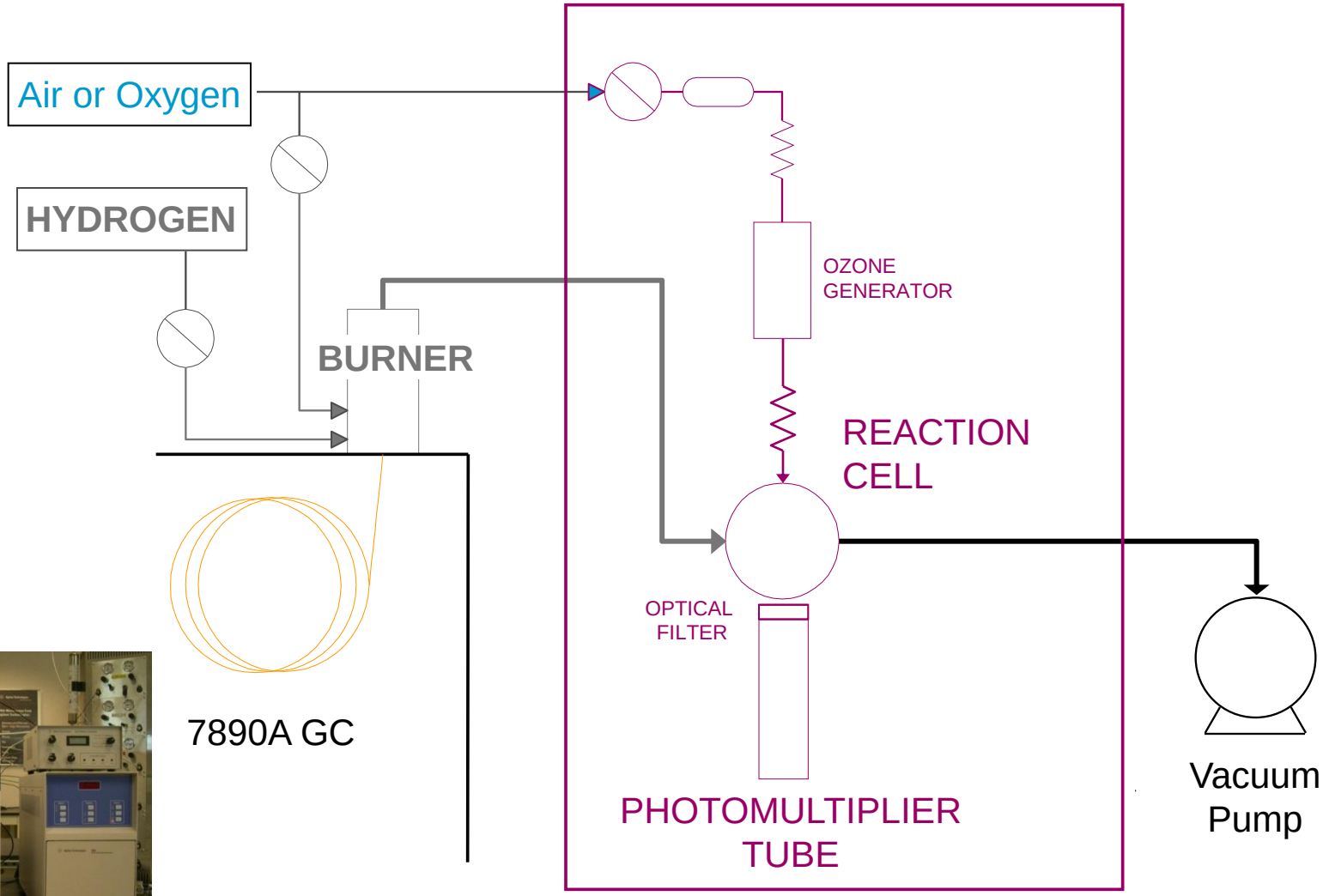
•SCD

- Detection based on emission of Sulfur specific light
  - Emitted by excited Sulfur dioxide
- Light is in UV range
  - Potentially absorbed by co-eluting peak
- Sensitivity is reduced, but not to zero
  - Typically 10-50% reduction

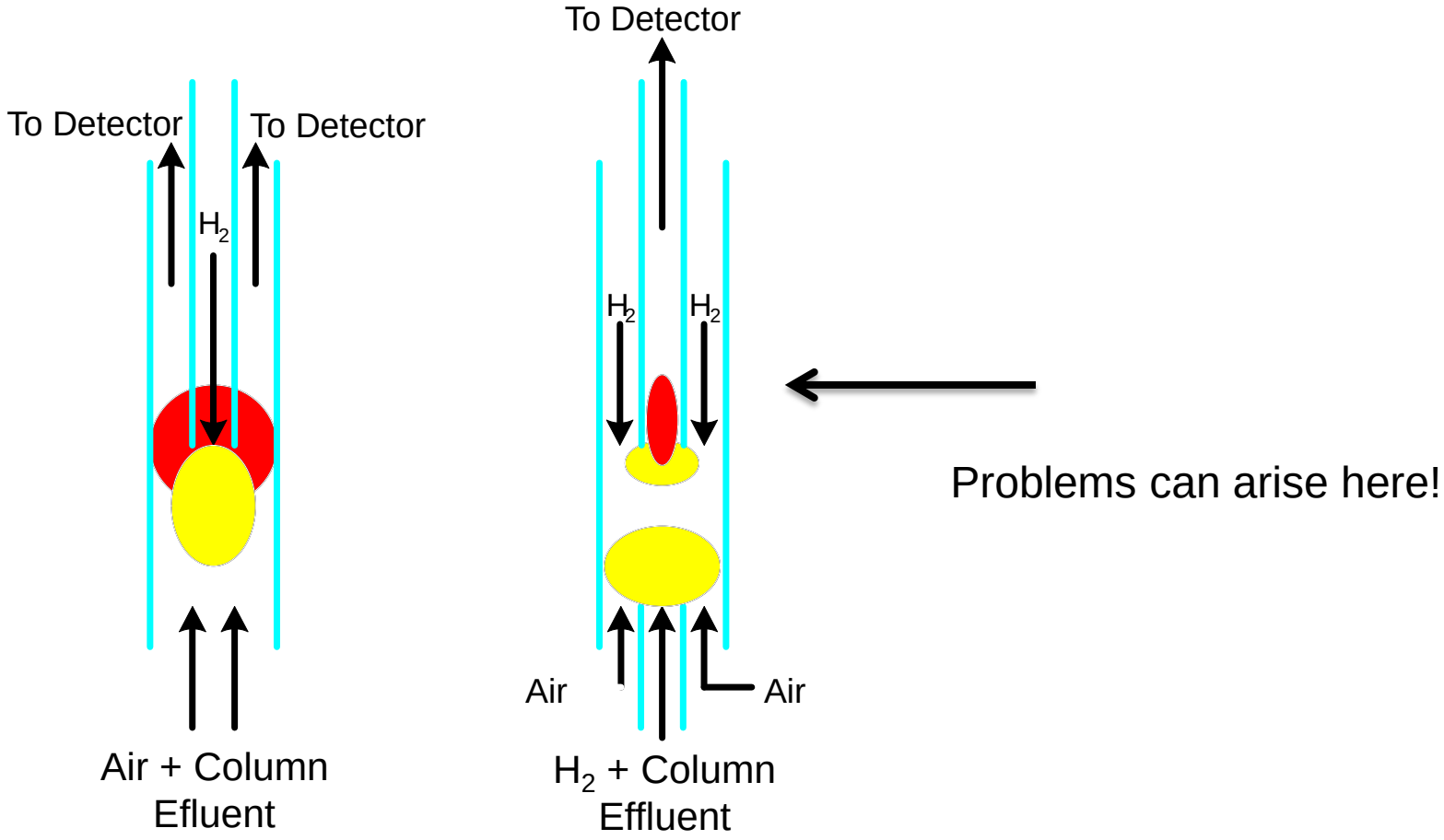


R-S-R+ O_2 → SO + Other Products
SO + O_3 → SO_2 + O_2 + Light (h*v*, 300-400 nm)

SCD/NCD Components



Burner Gas Flow Dynamics



Current SCD/NCD

Dual Plasma SCD

SCD for Sulfur Analysis

Basis for several ASTM methods

Very sensitive but….

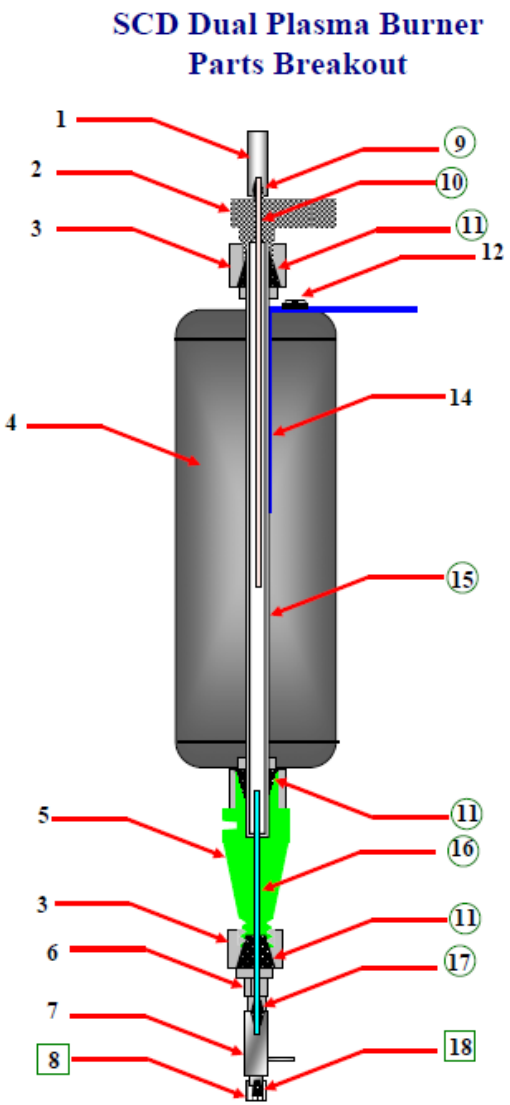
- slow to stabilize
- “tricky” to operate
- prone to “coking” in the ceramic reaction tubes with resulting costly maintenance and slow recovery (see above)

Method	Description
ASTM D6228	Volatile sulfur in C1, C2, C3 and C4 monomers and LPG
ASTM D6628	Volatile Sulfur in NGA, fuel gas
ASTM D5504	Sulfur in gas fuels by SCD
ASTM D5623	Sulfur in light petroleum liquids by SCD

About SCD Maintenance….

Ceramic reaction tube fouling/”coking”

- Price per incident preventative maintenance service call for GC-SCD is expensive.
- Cost of SCD ceramics: G6602-67000, G6602-60037 is also pricey. *Plus* the self repair time of 4 hours and several days to stabilize.



What is required of GC column for Sulfur Analysis?

Linearity of response from ppm – ppb

↓

100% sulfur recovery

Response

Stationary phase selectivity

Minimal detector quenching

↓

Low detection limits

Robust

No detector fouling

Loadability

Large injection volumes

↓

Low detection limits

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Introducing DB-Sulfur-SCD

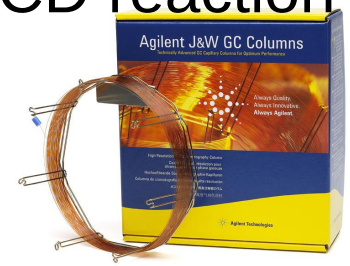
A novel optimized low polarity column with low bleed and exceptional inertness to sulfur.

Developed with Dow Chemical and other leading companies in these markets.

Excellent for a broad range of sulfur compounds from light sulfur gasses to sulfur containing hydrocarbons out to C24.

Designed for trace analysis

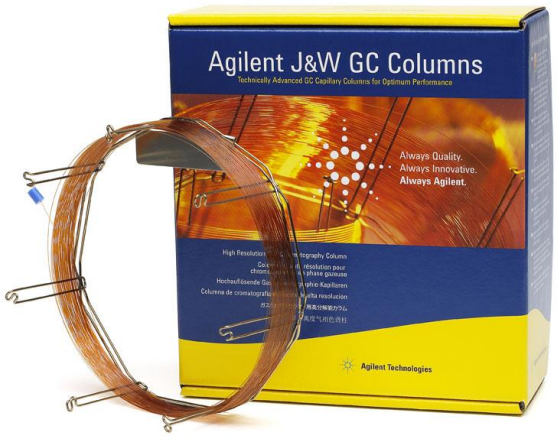
Optimized for the lowest possible contribution to SCD reaction tube fouling.



Introducing DB-Sulfur-SCD cont.

Easy to change from existing columns but with:

- greatly improved SCD performance
- increased stability
- less frequent burner tube maintenance



Part Number	Description	Temperature limits
G3903-63001	DB-Sulfur SCD 60m, 0.32mm, 4.2um	250°/270°C
G3903-63002	DB-Sulfur SCD 40m, 0.32mm, 0.75um	270°/290°C
G3903-63003	DB-Sulfur SCD 70m, 0.53mm, 4.3um	250°/270°C
G3903-63004	DB-Sulfur SCD 40m, 0.32mm, 3um	250°/270°C

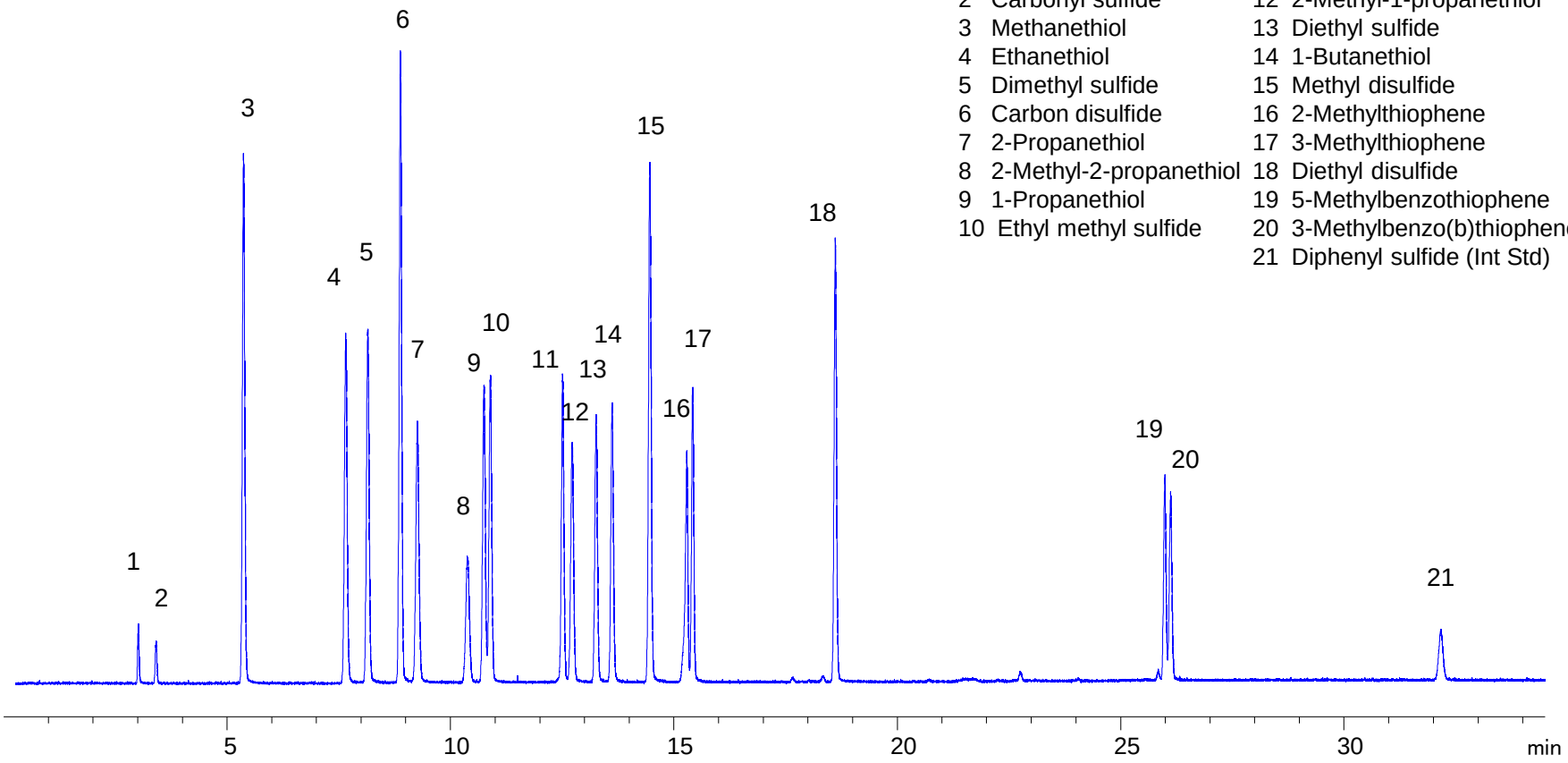
Other configurations are also available by request

DB-Sulfur SCD:

sulfur standards in Toluene

Good resolution of H2S and COS at room temperature

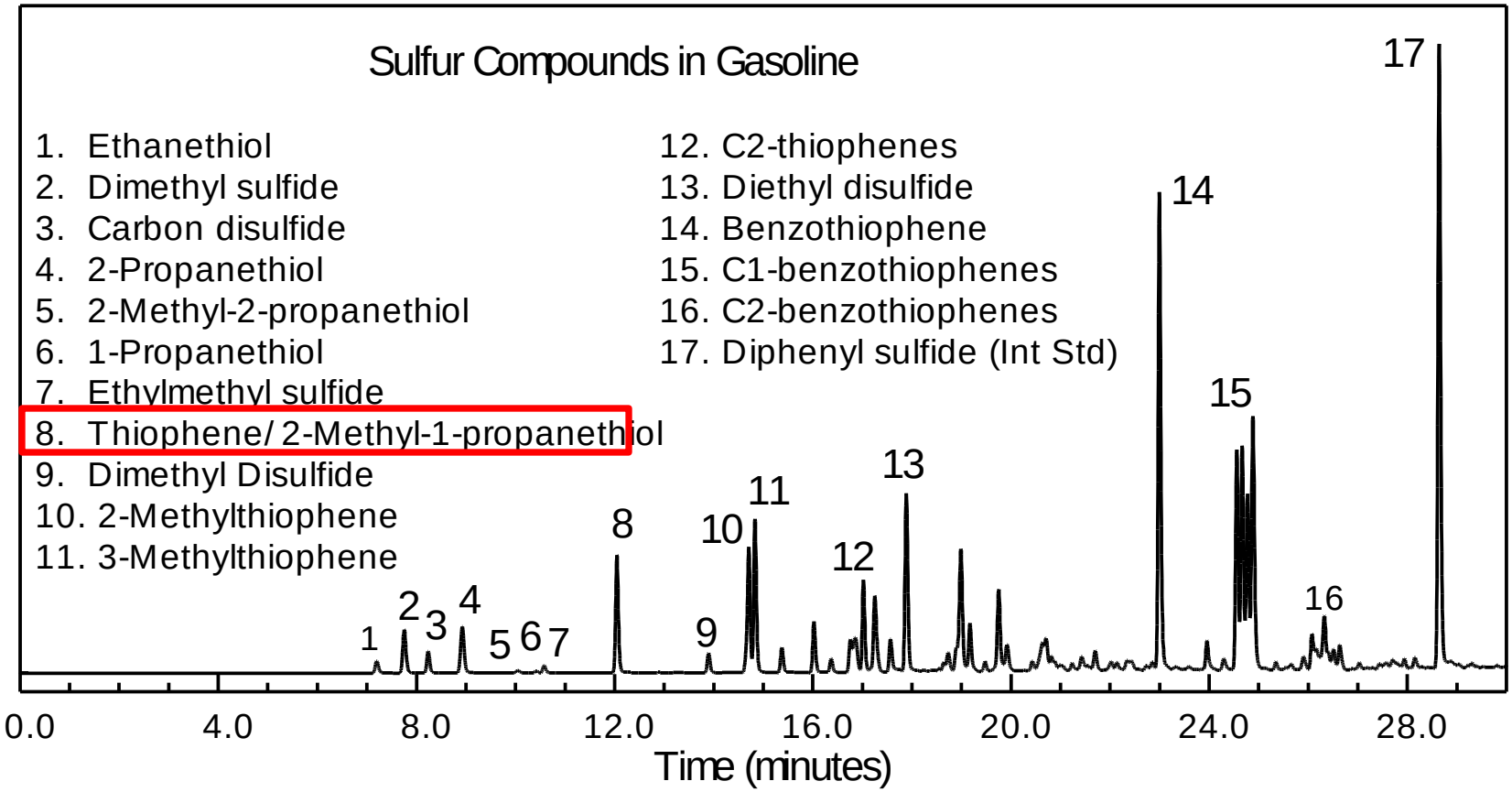
Thiophene and 2-Methyl-1-propanethiol can be baseline separated



1 Hydrogen sulfide
2 Carbonyl sulfide
3 Methanethiol
4 Ethanethiol
5 Dimethyl sulfide
6 Carbon disulfide
7 2-Propanethiol
8 2-Methyl-2-propanethiol
9 1-Propanethiol
10 Ethyl methyl sulfide
11 Thiophene
12 2-Methyl-1-propanethiol
13 Diethyl sulfide
14 1-Butanethiol
15 Methyl disulfide
16 2-Methylthiophene
17 3-Methylthiophene
18 Diethyl disulfide
19 5-Methylbenzothiophene
20 3-Methylbenzo(b)thiophene
21 Diphenyl sulfide (Int Std)

Column: Agilent J&W DB-Sulfur SCD, 60 m x 0.32 mm, 4.2 µm (p/n G3903-63001)

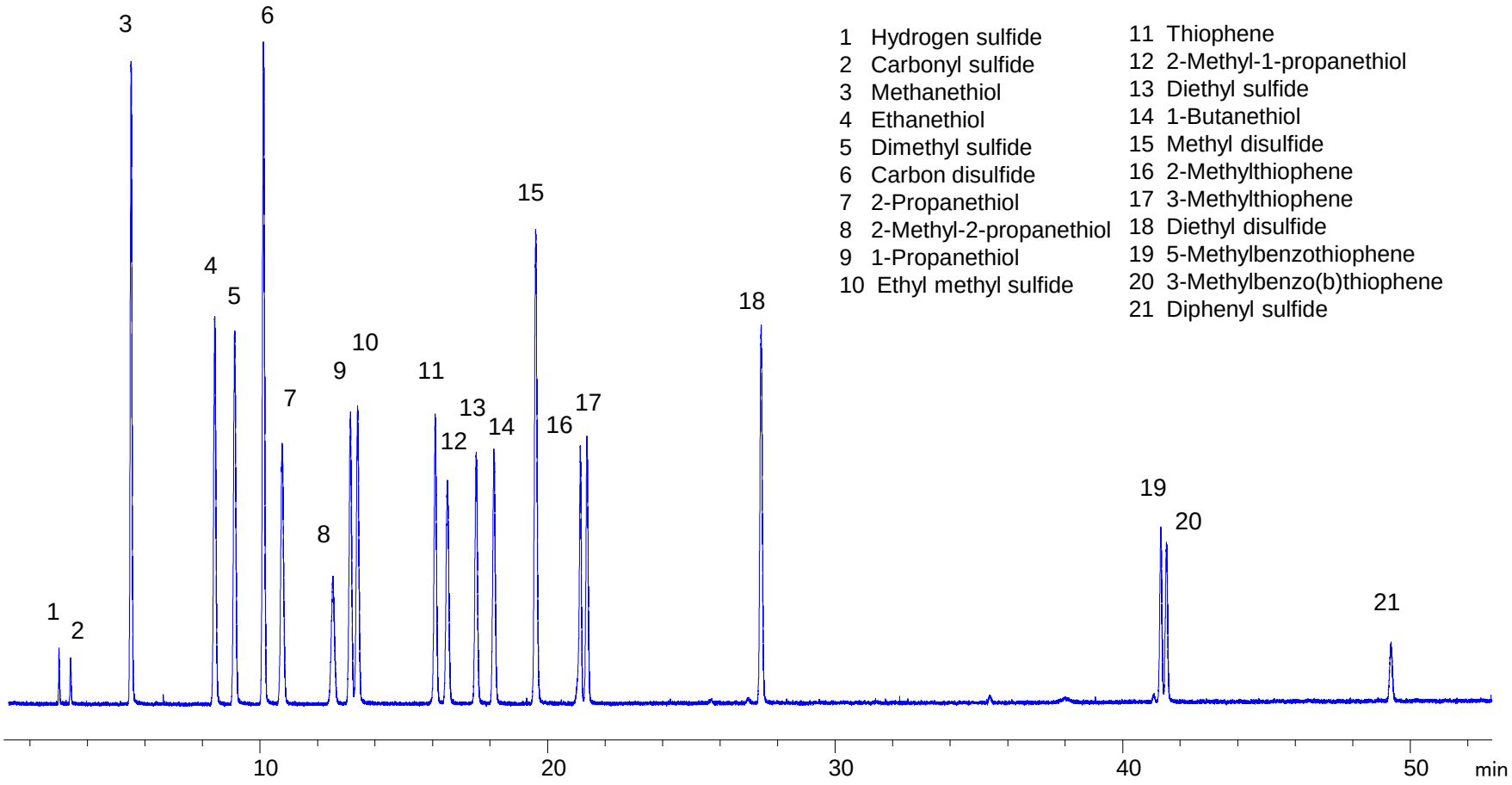
Typical chromatogram of Sulfur compounds in Light Petroleum Liquids by ATSM D5623



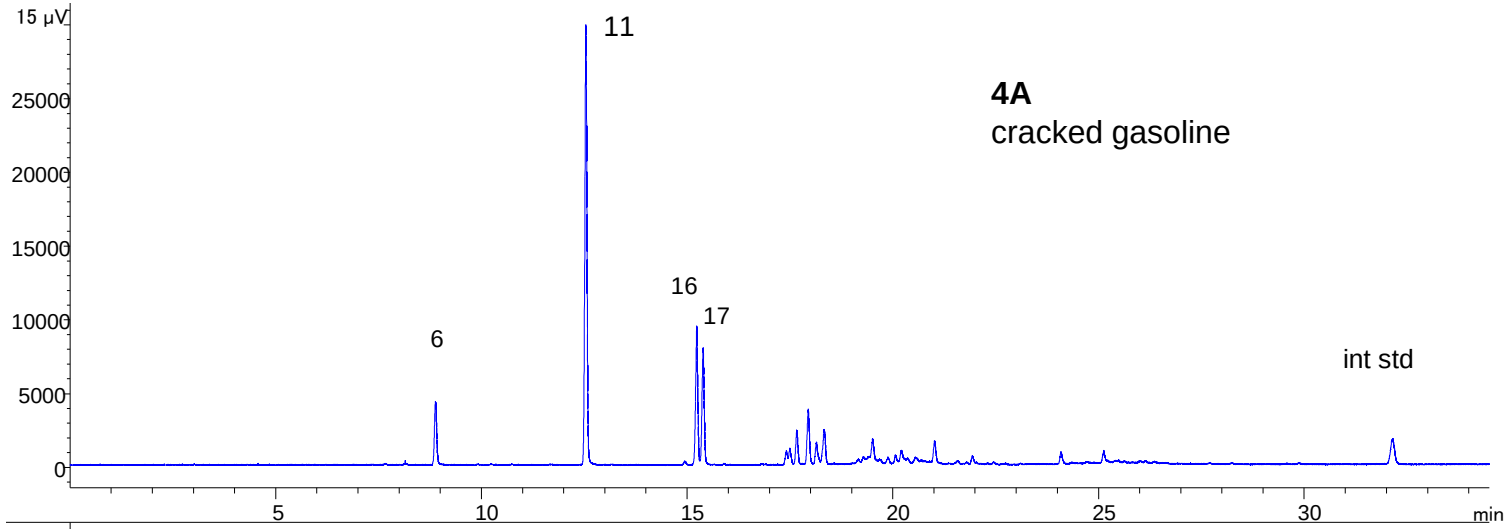
… the industry standard

Chromatogram of sulfur standards in Toluene with better Resolution

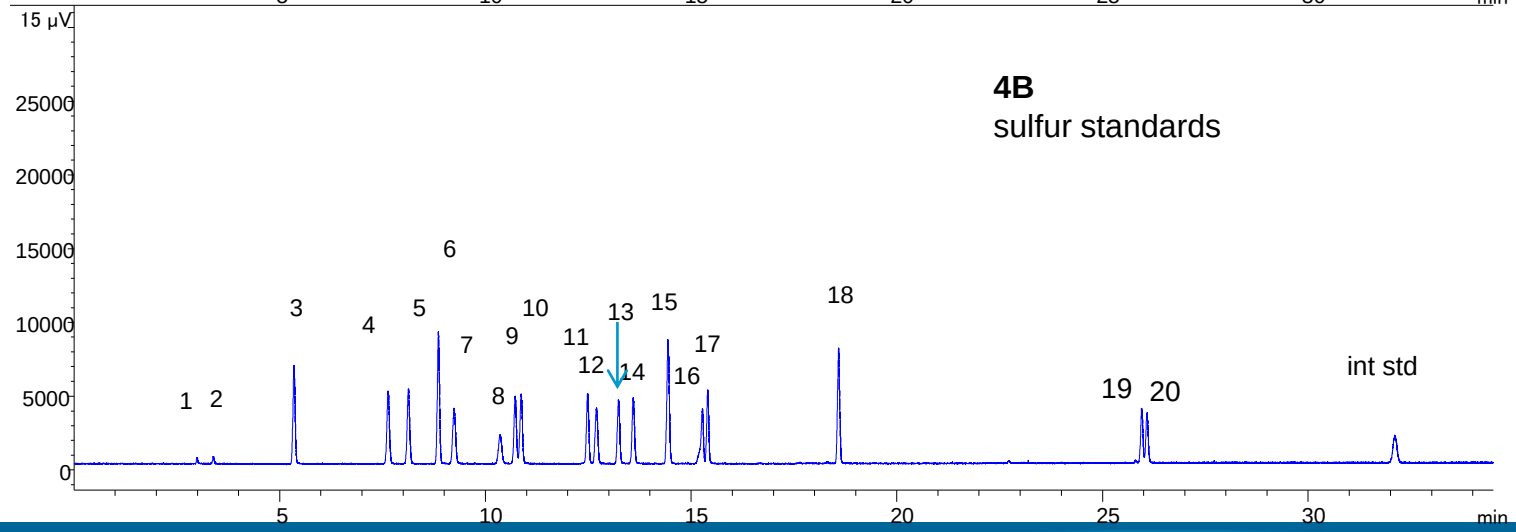
Oven: 35 ºC (3 min), 35 ºC -250 ºC @5 ºC /min, 250 ºC(10 min)



Cracked Gasoline Sample



4A
cracked gasoline



4B
sulfur standards

Individual sulfur compounds and Total S in cracked gasoline

Major individual sulfur compounds in cracked gasoline

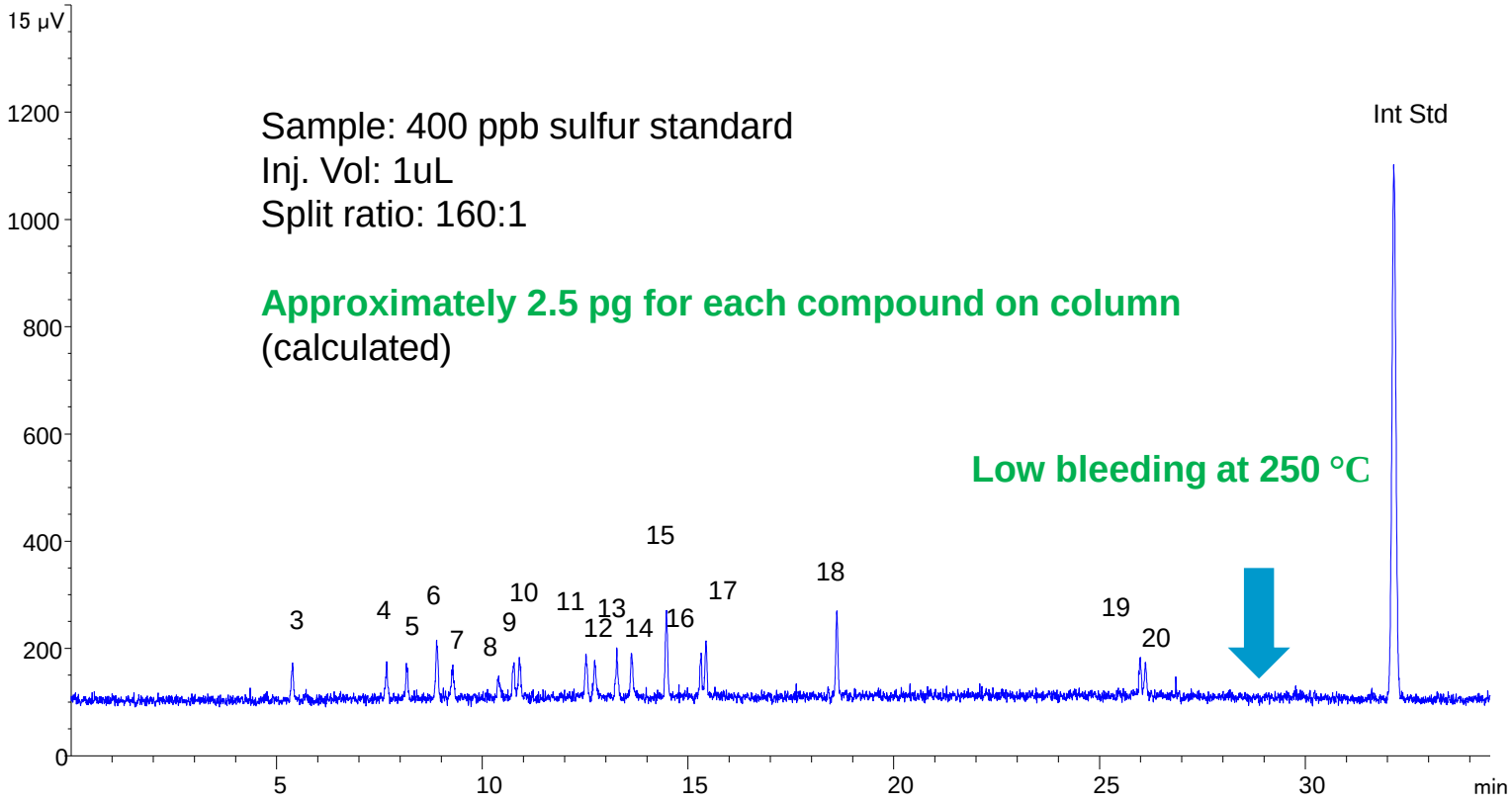
Major Sulfur compounds	Average content (mg/kg)	RSD% (n = 5)
Carbon disulfide	3.58	2.74
Thiophene	30.75	4.08
2-Methylthiophene	8.72	4.34
3-Methylthiophene	6.98	3.75

Repeatability data of total sulfur in cracked gasoline

Sample	Total sulfur (mg/kg)					Mean	RSD%
Cracked gasoline	91.46	91.60	100.60	94.89	100.88	95.89	4.84

DB-Sulfur-SCD: Sulfur Sensitivity

Peak No.	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
S/N	3.0	3.1	2.7	4.4	2.8	2.1	2.9	3.3	3.5	3.0	3.8	3.5	6.3	3.2	4.4	6.3	3.1	2.9

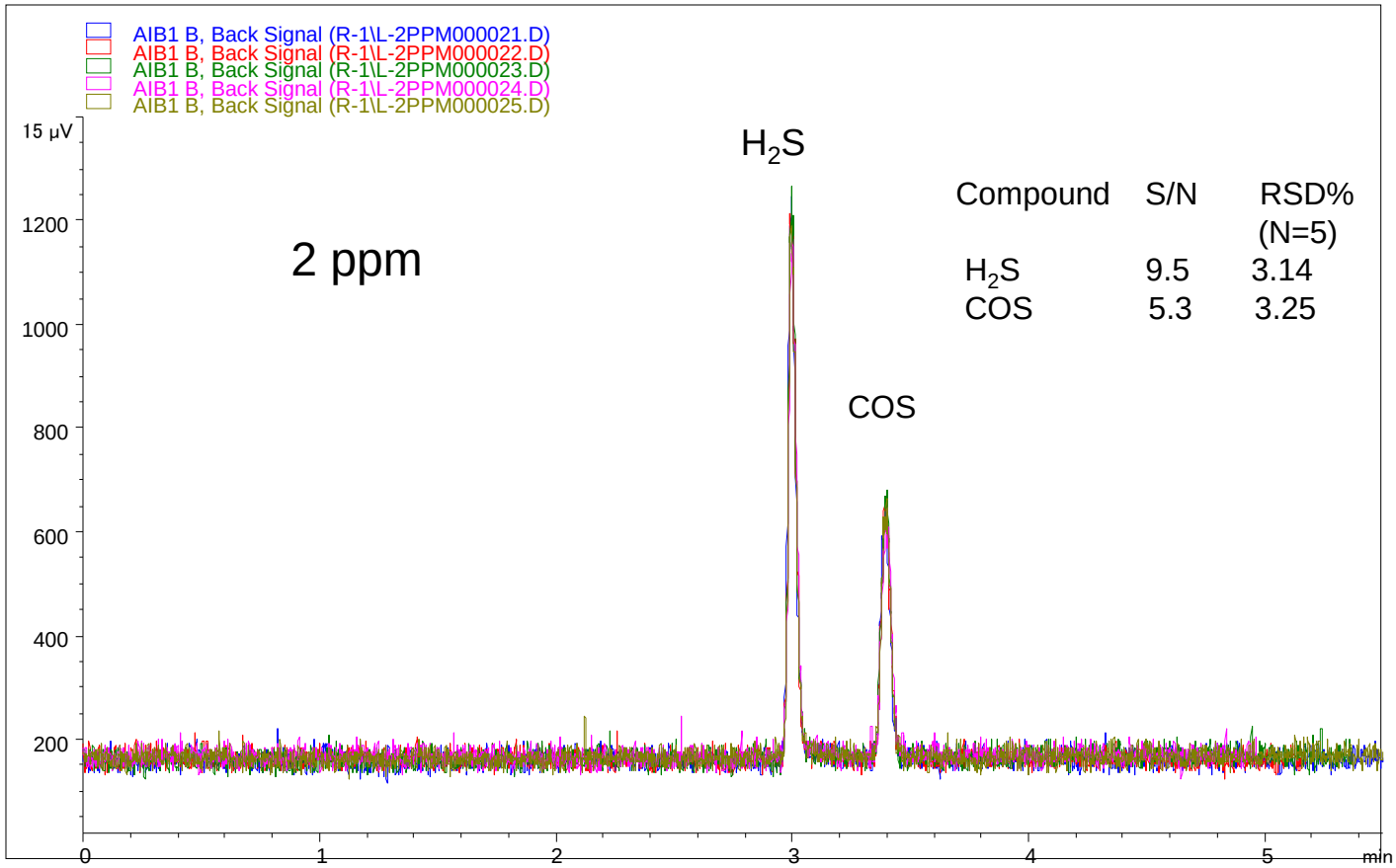


Repeatability

N=6

No	Compound	10 ppm RSD%	1ppm RSD%	0.1ppm RSD%
1	Methyl mercaptan	2.94	4.46	5.12
2	Ethyl mercaptan	2.53	3.00	4.38
3	Methyl sulfide	2.53	2.79	4.79
4	Carbon disulfide	2.13	3.29	5.43
5	2-Propanethiol	2.49	3.98	4.85
6	2-Methyl-2-propanethiol	2.89	4.47	4.41
7	1-Propanethiol	2.81	3.88	4.91
8	Ethyl methyl sulfide	2.34	4.17	5.24
9	Thiophene	2.24	3.06	3.49
10	2-Methyl-1-propanethiol	1.87	2.31	5.86
11	Diethyl sulfide	2.00	2.97	4.80
12	1-Butanethiol	2.46	3.36	6.47
13	Methyl disulfide	3.62	4.15	4.23
14	2-Methylthiophene	3.59	4.62	5.95
15	3-Methylthiophene	2.85	3.90	4.90
16	Diethyl disulfide	2.74	3.16	6.34
17	3-Methylbenzothiophene	2.48	4.87	5.29
18	5-Methylbenzo(b)thiophene	2.42	4.25	7.37

DB-Sulfur-SCD: Sulfur Sensitivity



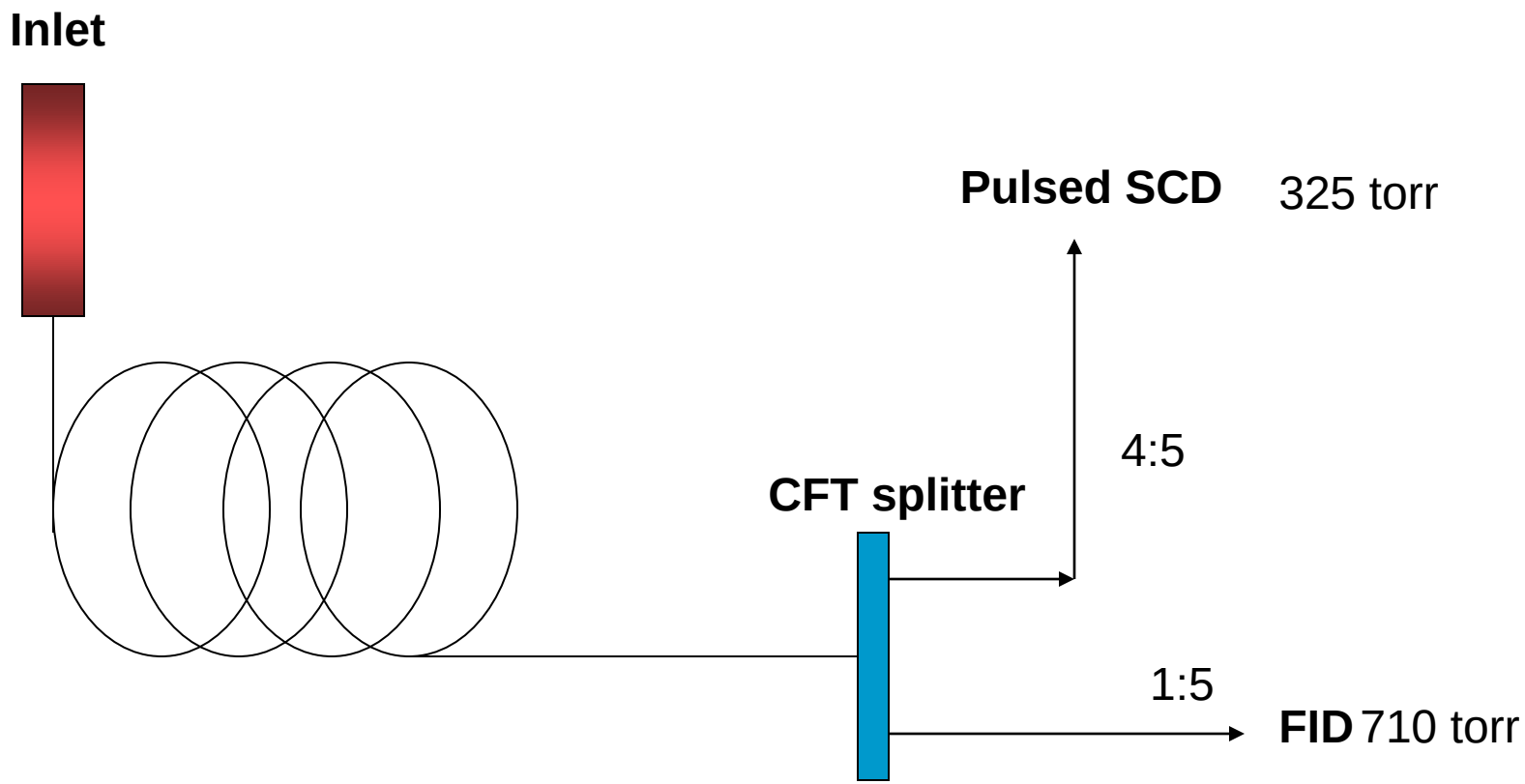
Compound	S/N	RSD% (N=5)
H_2S	9.5	3.14
COS	5.3	3.25

Linearity

Compound	Concentration Range	Linearity (R^2)
Hydrogen sulfide	2 -25 ppm	0.9976
Carbonyl sulfide	2 -25 ppm	0.9990
Methanethiol	0.1-10 ppm	0.9987
Ethanethiol	0.1-50 ppm	0.9998
Dimethyl sulfide	0.1-10 ppm	0.9991
Carbon disulfide	0.1-10 ppm	0.9990
2-Propanethiol	0.1-50 ppm	0.9999
2-Methyl-2-propanethio	0.1-10 ppm	0.9989
1-Propanethiol	0.1-10 ppm	0.9990
Ethyl methyl sulfide	0.1-50 ppm	0.9998

Compound	Concentration Range	Linearity (R^2)
Thiophene	0.1-50 ppm	0.9997
2-Methyl-1-propanethiol	0.1 -10 ppm	0.9991
Diethyl sulfide	0.1-10 ppm	0.9992
1-Butanethiol	0.1-10 ppm	0.9990
Methyl disulfide	0.1 -10 ppm	0.9987
2-Methylthiophene	0.1-50 ppm	0.9991
3-Methylthiophene	0.1-50 ppm	0.9996
Diethyl disulfide	0.1-10 ppm	0.9990
5-Methylbenzothiophene	0.1-10 ppm	0.9984
3-Methylbenzothiophene	0.1-50 ppm	0.9988

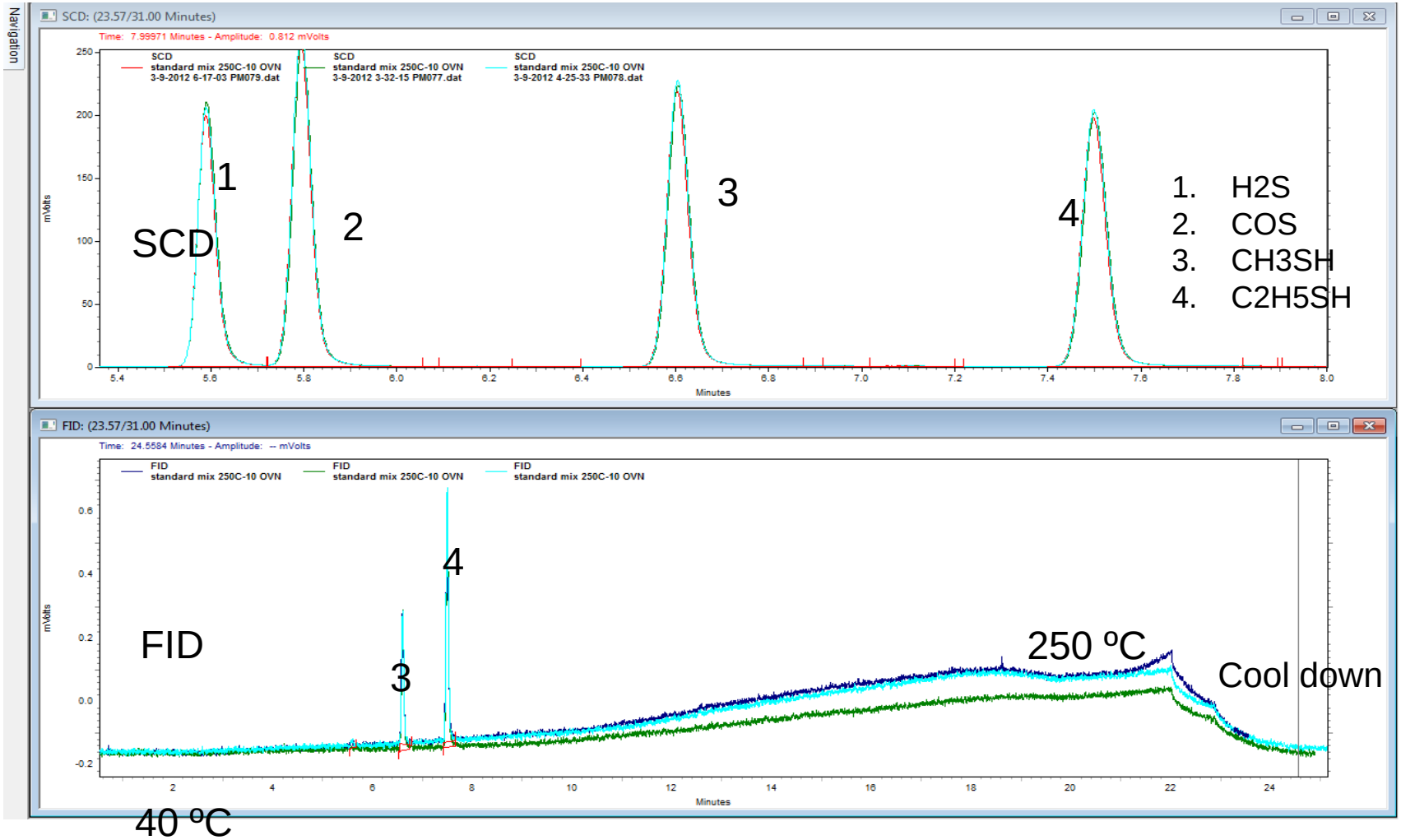
General SCD System Configuration for Chemical Analysis



60 m x 0.32 mm-id x 4.3 um DB-Sulfur-SCD

Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical*

Last Three Runs of the day (n=20, 100 ppmv std)



Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical*

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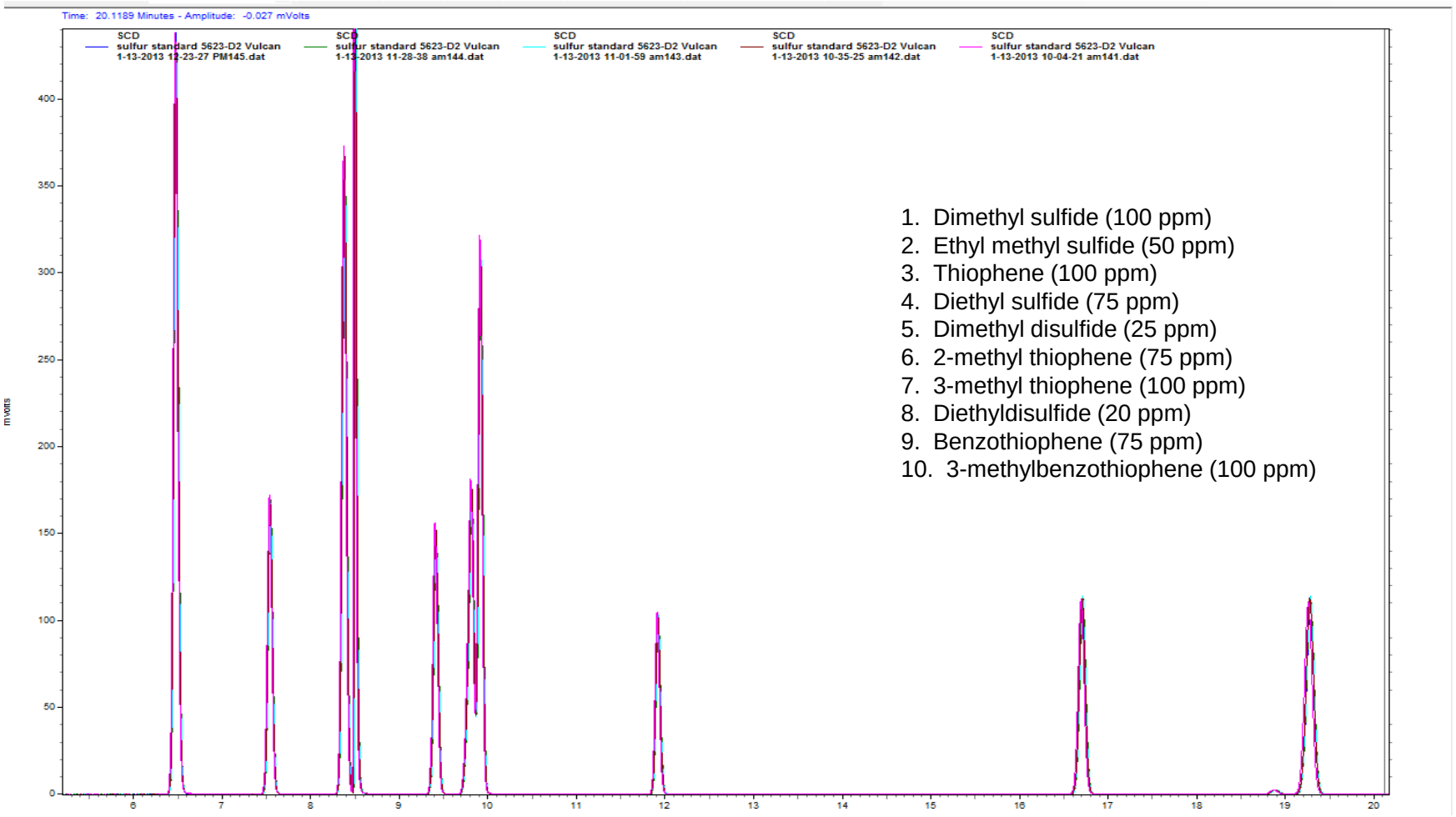
Sulfides and Thiophenes (n=5)



Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical*

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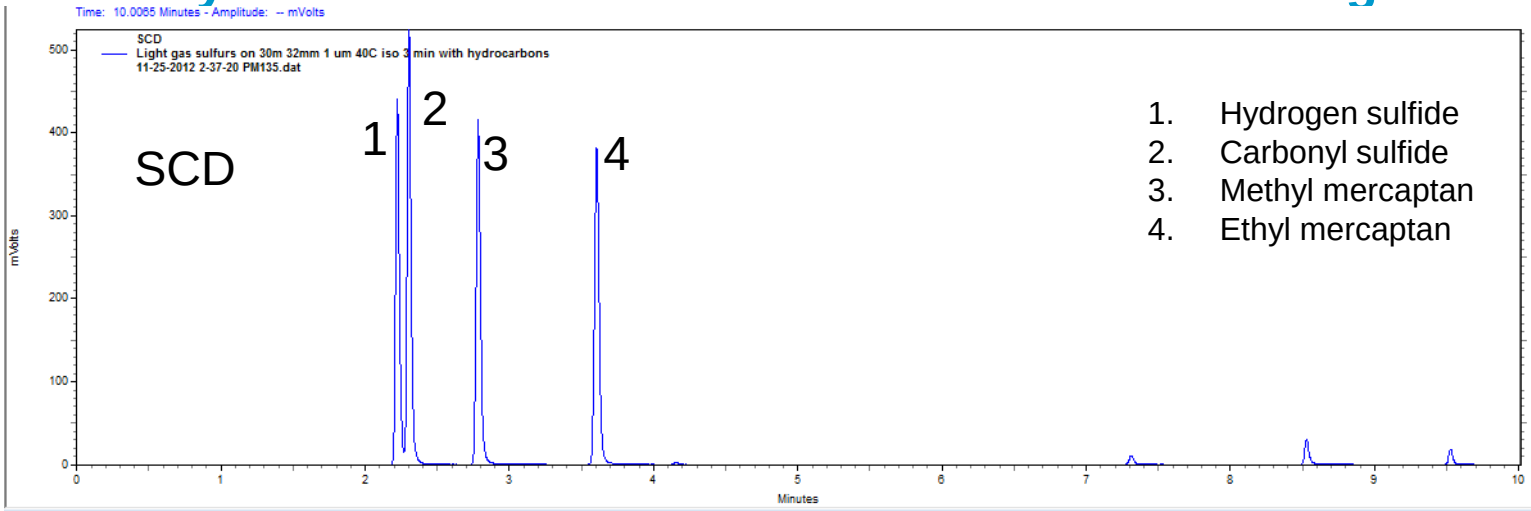
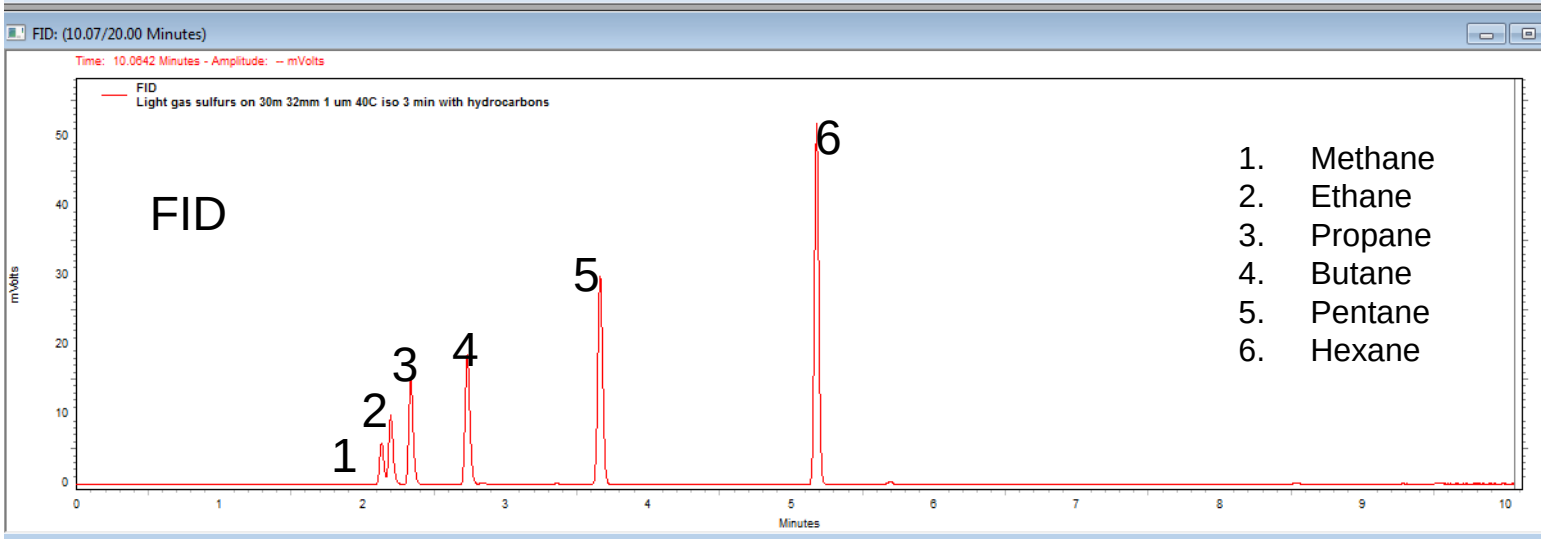
Overlay of chromatograms of 50 ppm_v each of hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan and 500 ppm_v each of hydrocarbons from methane to hexane in nitrogen





Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical*

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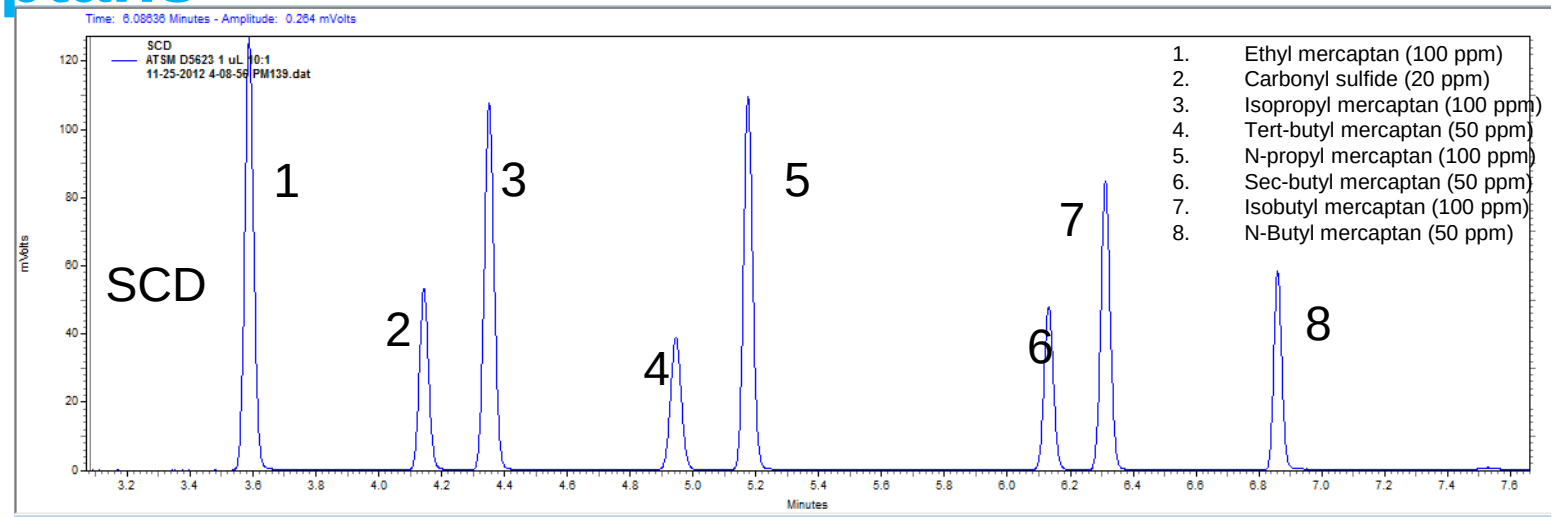
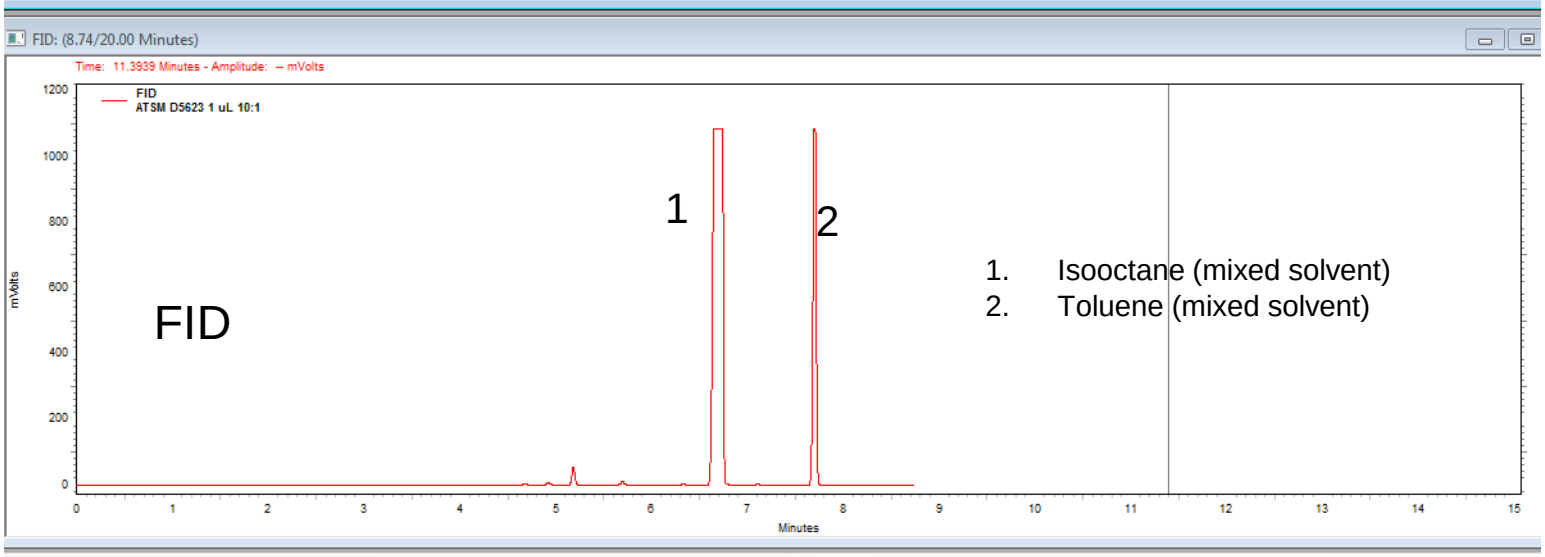
Chromatogram of carbon disulfide and alkyl mercaptans





Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical*

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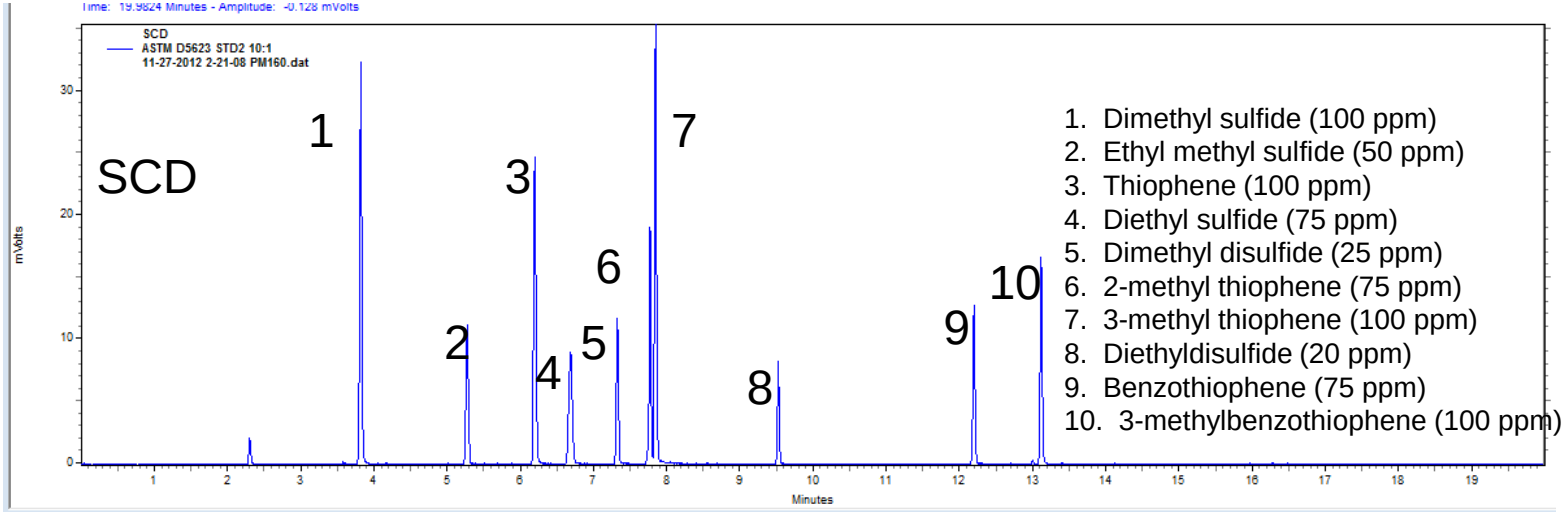
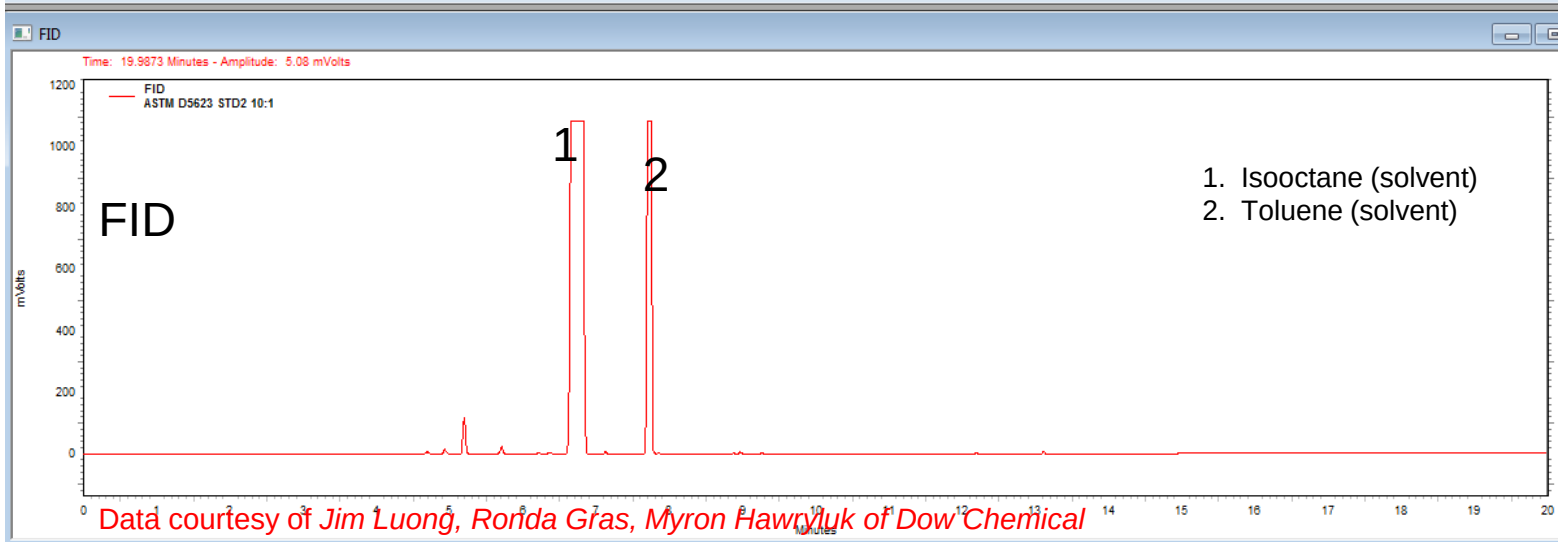
Chromatogram of sulfides, disulfides, thiophene, alkyl thiophenes, benzothiophene, and alkyl benzothiophenes





Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical*

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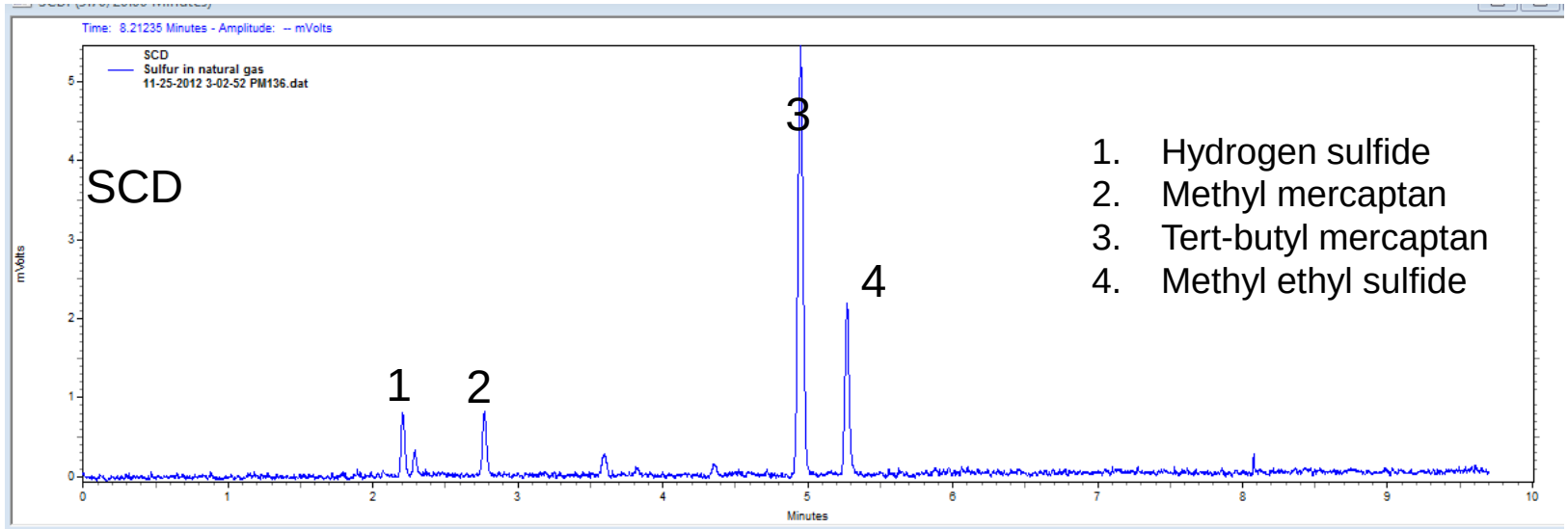
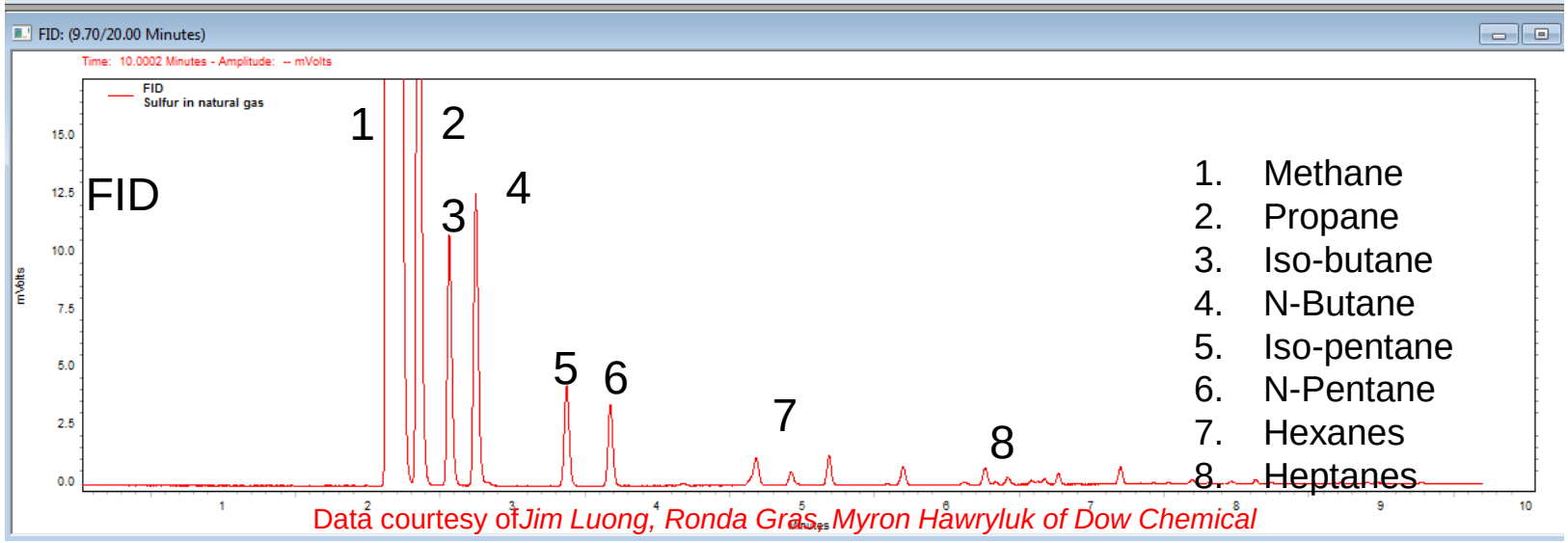
Chromatogram volatile sulfur odorants in commercially available natural gas





Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical*

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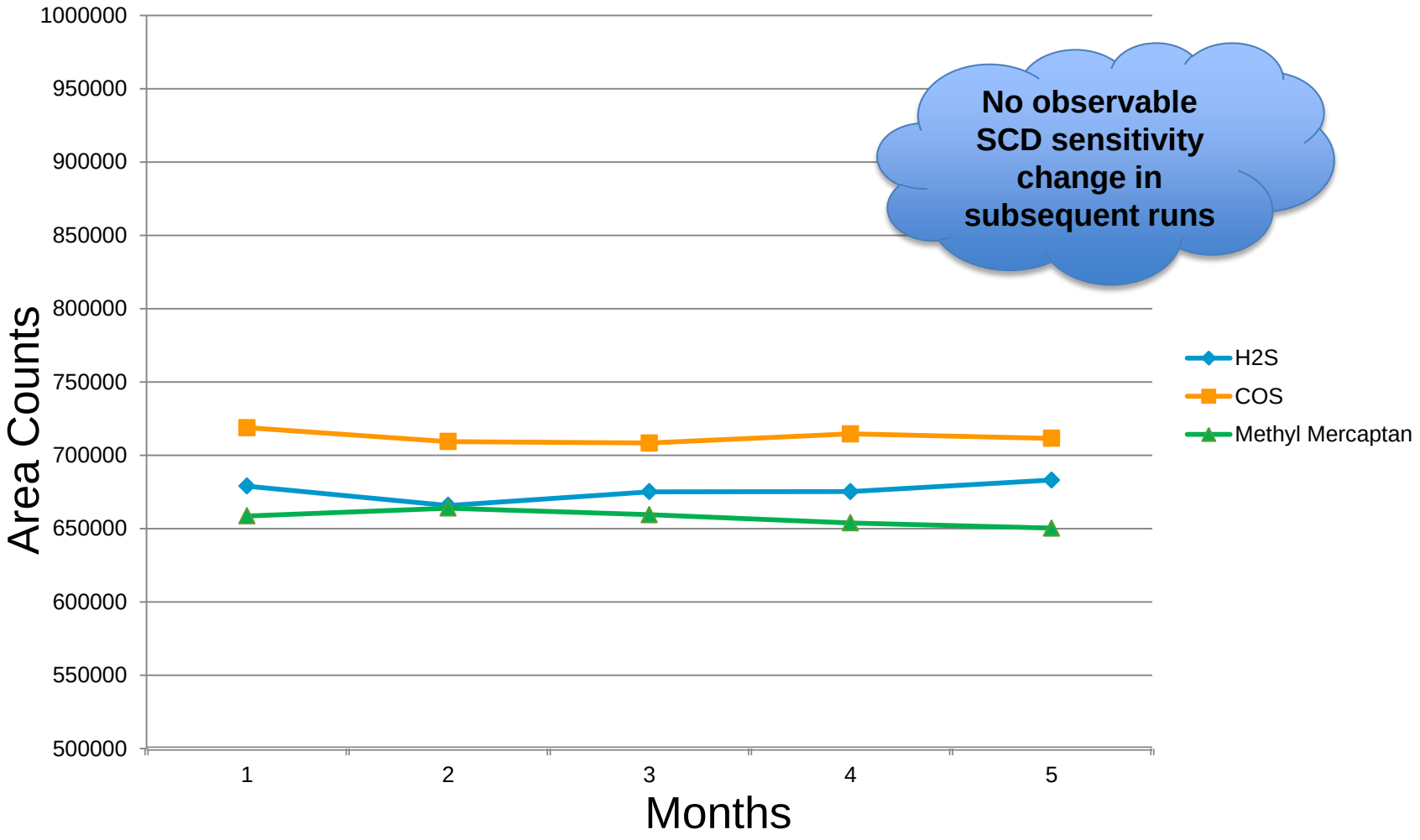
Long Term SCD Performance with DB-Sulfur-SCD



Data courtesy of *Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical* with permission

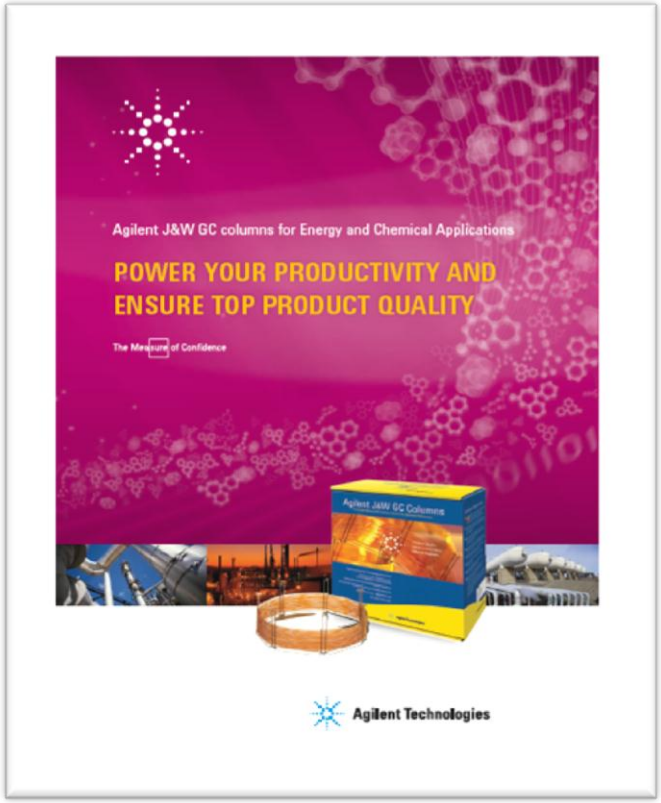
DB-Sulfur-SCD

Feature	Advantage	Customer Benefit
SCD Optimized lower bleed	Less ceramic tube fouling	• increased detector uptime and less maintenance • lower costs • improved S response and more accurate data
High column inertness	Improved linearity and sensitivity	Reliable and accurate ppb level measurements
Methyl silicone phase selectivity	Identical to standard columns	Easy method upgrade

Application Notes and Literature:

Applications for ASTM D5623 and ASTM D5504 Brochure

“The Analysis of Sulfur Compounds in Petroleum Fraction by Agilent J&W DB-Sulfur SCD Column”
Publication number: 5991-3108EN



Brochure number 5991-2977EN

Inert Flow Path for Trace Analysis with GC-SCD

The opportunity to sell the whole solution

Proprietary innovation in every component

Agilent Technologies

DB-Sulfur-SCD Summary

The new Agilent J&W DB-Sulfur-SCD with low bleed and inertness can provide:

- excellent resolution and peak shape
- excellent linearity at ppm to ppb levels
- best repeatability
- high sensitivity

All of which are required for dependable sulfur analysis.

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Sulfur in Refinery Feeds and Propylene

The boiling point range of the hydrocarbon matrix determines the scope of the sulfur species present.

Sulfur components of concern:

- H_2S, COS, Mercaptans, Thiophenes, Sulfides, Disulfides,

Example: H_2S, COS and Methyl Mercaptan in Propylene

Polypropylene catalysts are highly sensitive to sulfur poisoning:

Manufactures pay attention to sulfur components at *few ppb* in propylene

Introducing the Agilent J&W Select Low Sulfur GC Column

New PLOT column, especially engineered for trace level sulfur in Propylene matrix:

Inertness: 100% response for H2S, methylmercaptan

Selectivity: No quenching for COS because of the resolution from propylene

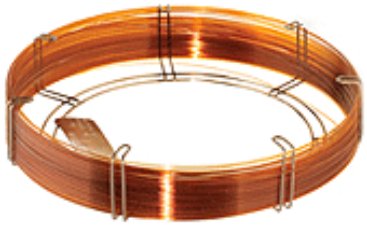
Stability: Zero particle shedding. Compatible with FPD, PFPD, SCD, AED

Dimensions: one dimension, 60 m x 0.32 mm id p/n CP8575

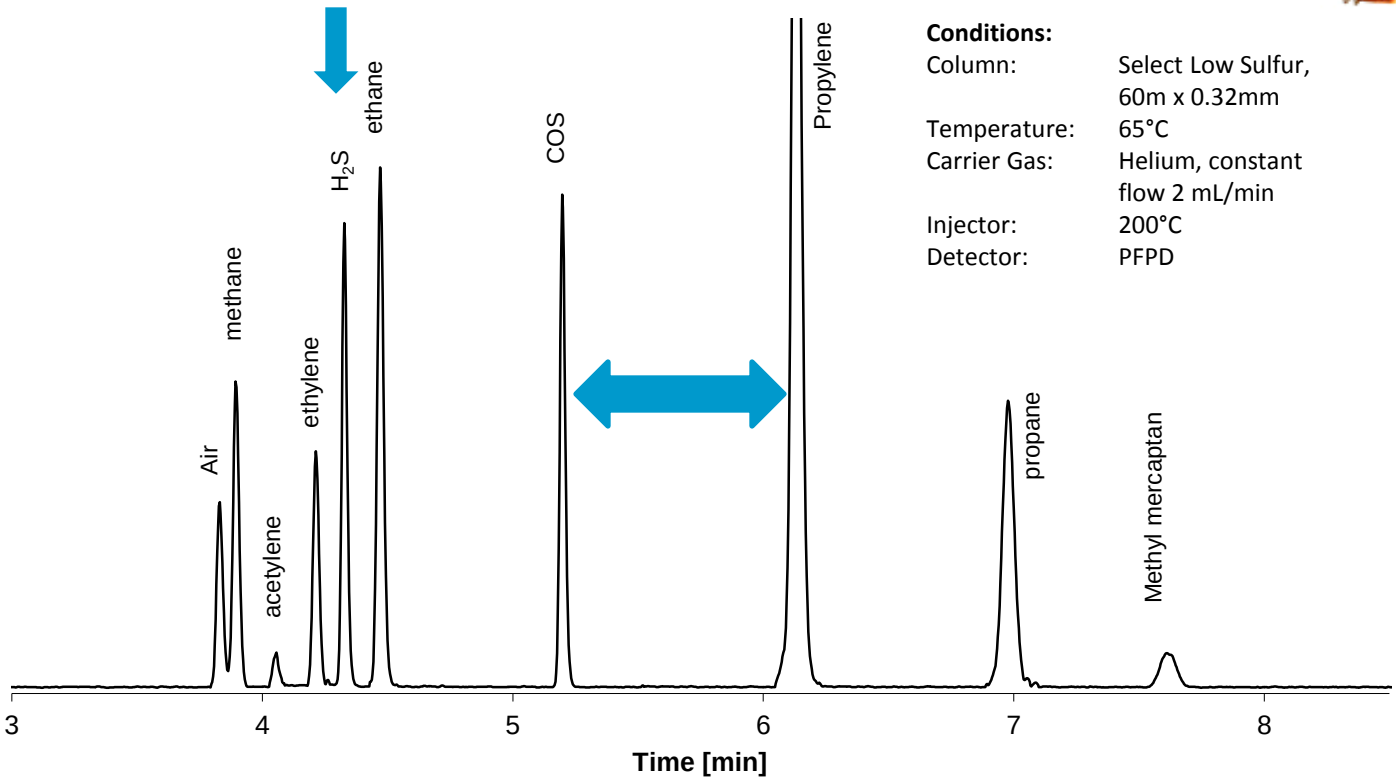
The new Select Low Sulfur PLOT column is designed to offer high inertness, sensitivity and linearity for low level detection of active sulfur and mercaptans in the HPI market.

The Select Low Sulfur improves data accuracy and can significantly improve propylene yields and reduce catalyst costs providing strong economic value and quality results for lab and process management.

Sulfurs & Propylene on Select Low Sulfur



Select Low Sulfur - 60m*0.32mm
Overlay of H_2S, COS and Methyl mercaptan with hydrocarbons



Conditions:

Column:	Select Low Sulfur, 60m x 0.32mm
Temperature:	65°C
Carrier Gas:	Helium, constant flow 2 mL/min
Injector:	200°C
Detector:	PFPD

Note that the hydrocarbon peaks are from the FID

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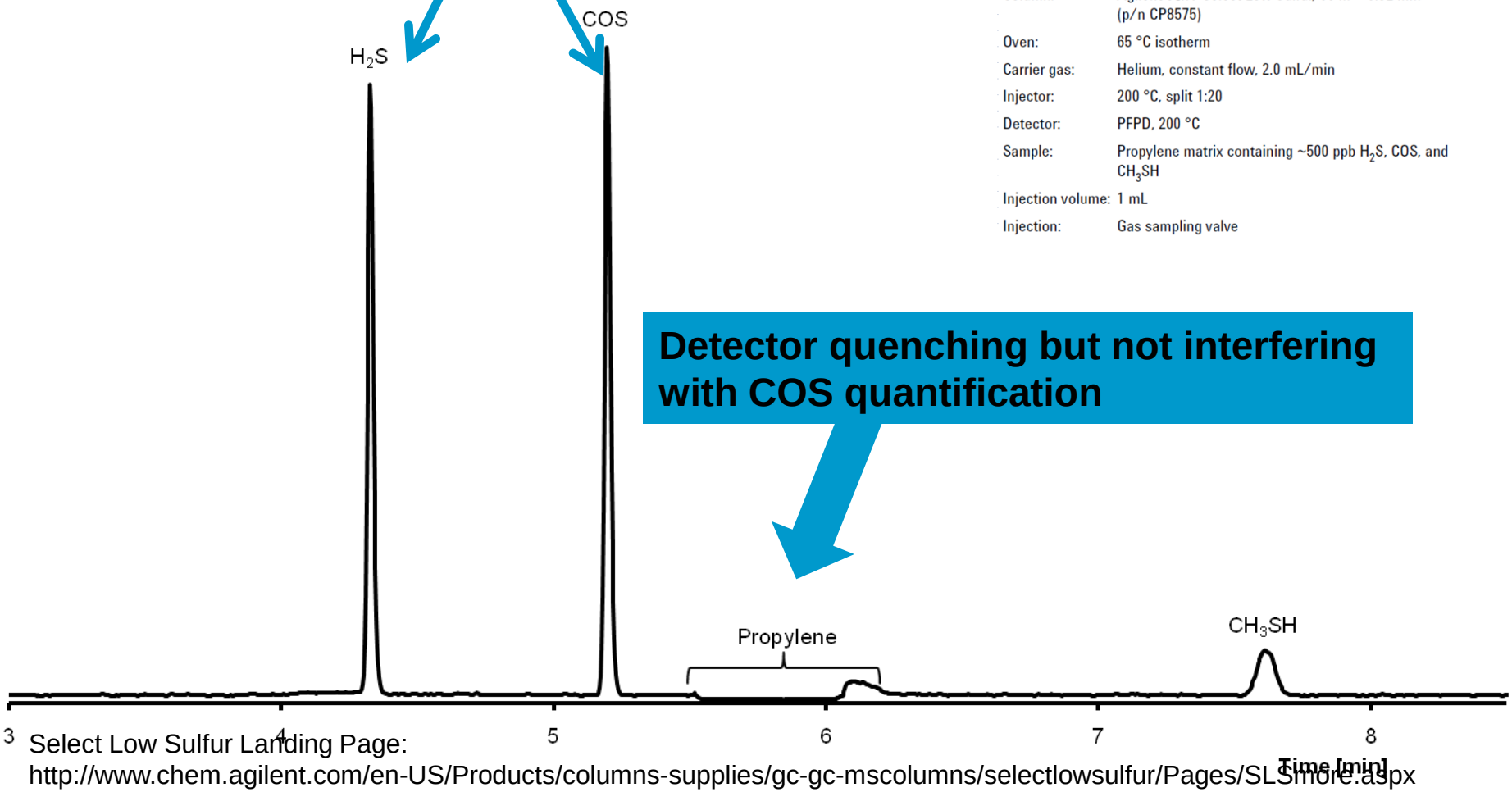
Sulfur components in Propylene using PFPD

500 ppbv H_2S and COS
same peak height
High response of H_2S

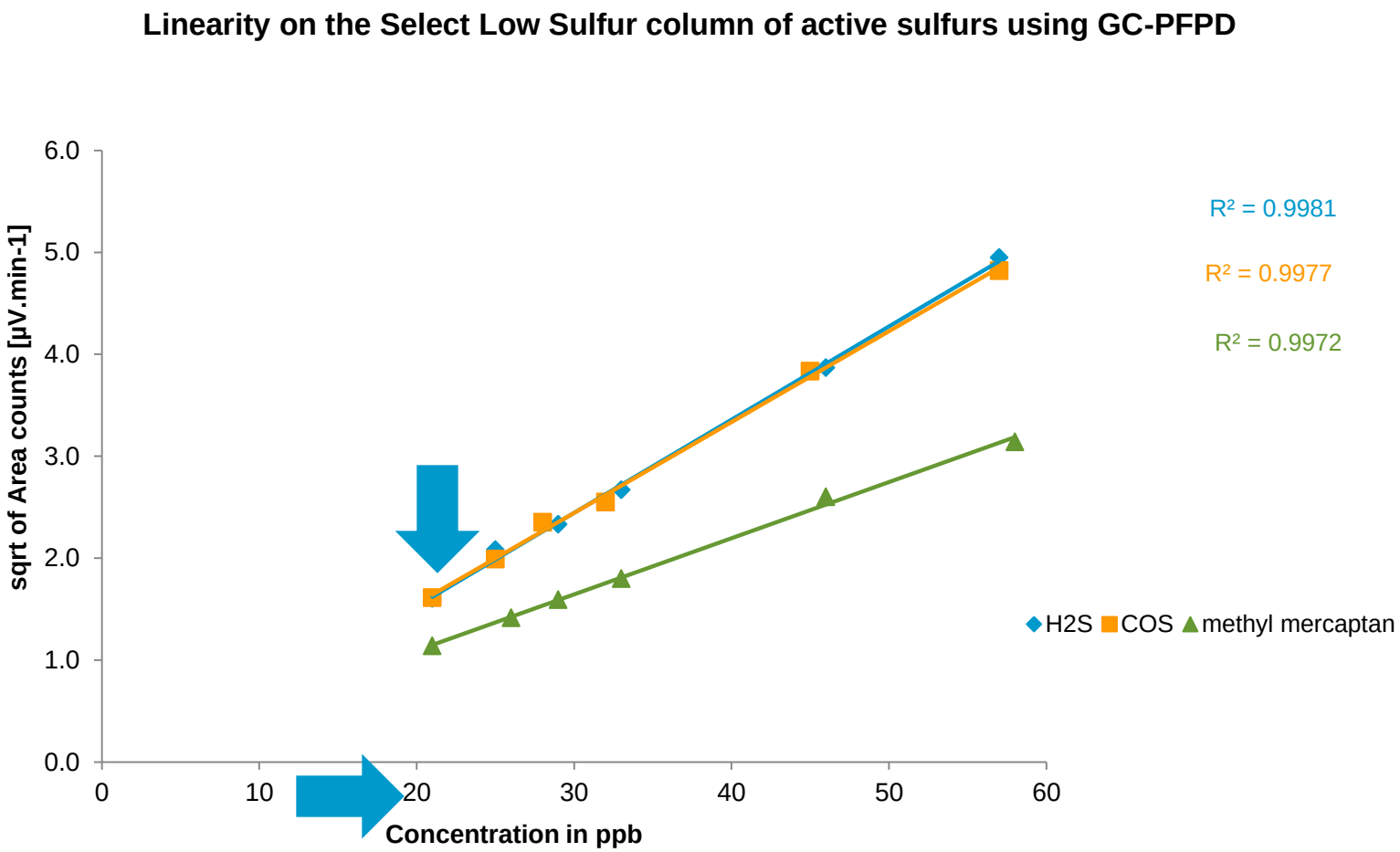
Technique:	GC-PFPD
Column:	Agilent J&W Select Low Sulfur, 60 m × 0.32 mm (p/n CP8575)
Oven:	65 °C isotherm
Carrier gas:	Helium, constant flow, 2.0 mL/min
Injector:	200 °C, split 1:20
Detector:	PFPD, 200 °C
Sample:	Propylene matrix containing ~500 ppb H_2S, COS, and CH_3SH
Injection volume:	1 mL
Injection:	Gas sampling valve

Detector quenching but not interfering with COS quantification



Select Low Sulfur Landing Page:
http://www.chem.agilent.com/en-US/Products/columns-supplies/gc-gc-mscolumns/selectlowsulfur/Pages/SLSmore.aspx

Linearity on Select Low Sulfur, PFPD



Select Low Sulfur Landing Page:
http://www.chem.agilent.com/en-US/Products/columns-supplies/gc-gc-mscolumns/selectlowsulfur/Pages/SLSmore.aspx

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Benefits of the Agilent J&W Select low Sulfur GC Column

Feature	Advantage	Benefit
Inert Sulfur column coating	Near 100% response for H2S and Methyl Mercaptan	• improved accuracy at low ppb levels for active sulfur compounds • more control of polymerization and refinery processes
Optimized separation between propylene and sulfur compounds	No quenching problems for S specific detectors	Better data for all sulfur compounds in propylene.
Every column is tested	Consistent column to column performance	• reliable and repeatable performance • less system downtime

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Summary

Sulfur compounds present challenges, even at low levels, for petroleum processers and downstream chemistry.

Agilent Technologies has introduced two new GC column technologies to improve trace level sulfur analysis

1. J&W DB-Sulfur-SCD. A columns engineered to improve sensitivity and linearity at very low levels while increasing uptime and reducing maintenance for the very selective and sensitive SCD.
2. J&W Select Low Sulfur. A PLOT column optimized for Propylene analysis with optimized selectivity and inertness to deliver reliable results at low levels.

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Select Low Sulfur Resources

Select Low Sulfur landing page

http://www.chem.agilent.com/en-US/Products/columns-supplies/gc-gc-mscolumns/selectlowsulfur/Pages/SLSmore.aspx

SCD application note:

5990-6989EN

http://www.chem.agilent.com/Library/applications/5990-6989EN.pdf

PFPD application note:

5990-6990EN,

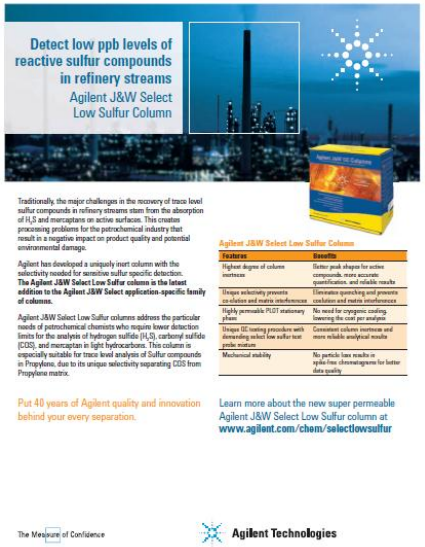
http://www.chem.agilent.com/Library/applications/5990-6990EN.pdf

Flyer 5990-7243EN

http://www.chem.agilent.com/Library/flyers/Public/5990-7243EN%20Select%20Low%20Sulfur%20Column%20Flyer.pdf

Workshop talk on Select Low Sulfur

http://www.chem.agilent.com/Library/posters/Public/Workshop_Talk2AM_Sulfur_Detection_PPB_Using_SuperPermeable_PLOT_Column.pdf



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Agilent resources for HPI and Sulfur analysis

Sulfur Chemiluminescence Detector

http://www.chem.agilent.com/en-US/products-services/Instruments-Systems/Gas-Chromatography/Sulfur-Chemiluminescence-Detector/Pages/default.aspx

Pulsed Flame Photometric Detector

http://www.tau.ac.il/chemistry/amirav/pfpd.shtml

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