Column Optimization and Chemiluminescence Detector Enhancements for Improved Sulfur Analysis

KVCV – GC studiedag

Remko van Loon
GC & GCMS product specialist

October 12, 2017

Why so much focus on Sulfur analysis?

Sulfur compounds

- corrosive to equipment, pipe lines, reactors
- inhibit or destroy catalysts employed in downstream processing
- undesirable odors or off-flavour to products
- pollutes the air (fuels)

Analytical challenges:

- Low levels often require maximum sensitivity
- Matrix interference from the hydrocarbons present
- Highly reactive and polar molecules

Importance of Sulfur analysis

- Environmental air monitoring (e.g. paper plant odors)
- Beverage grade CO2
- Alcoholic beverages, beer/wine/whisky/cognac
- Non alcoholic beverages, flavors/aroma’s
- Fragrances
- Breath analysis, diagnostic biomarkers

- **Hydrocarbon Processing Industry**

GC Columns for Sulfurs

PoraPLOT Q / HP-PLOT Q (PT)

Low boiling sulfurs, H_2S absorption <100ppm

100% PDMS, CP-Sil 5 CB Sulfur, 1 > df < 5µm

poor matrix selectivity, SCD fouling

SilicaPLOT, GasPro

Low SCD fouling, No higher boiling sulfurs

Select for Low Sulfur

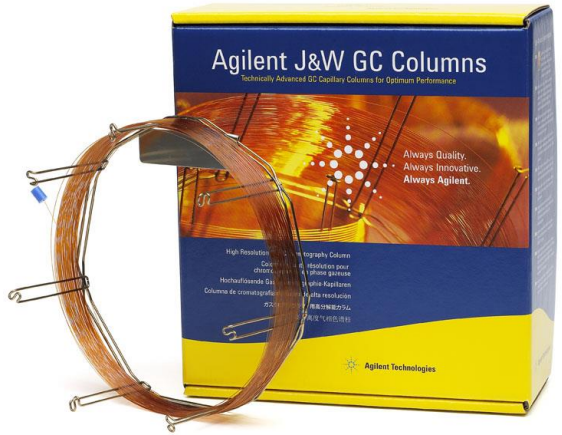
Excellent recovery < 10 ppb

Limited Max T, Prone to SCD fouling at high temperature

DB-Sulfur SCD

Excellent recovery < 10 ppb

Wide matrix range, Low SCD fouling



What detectors can we use for Sulfur?

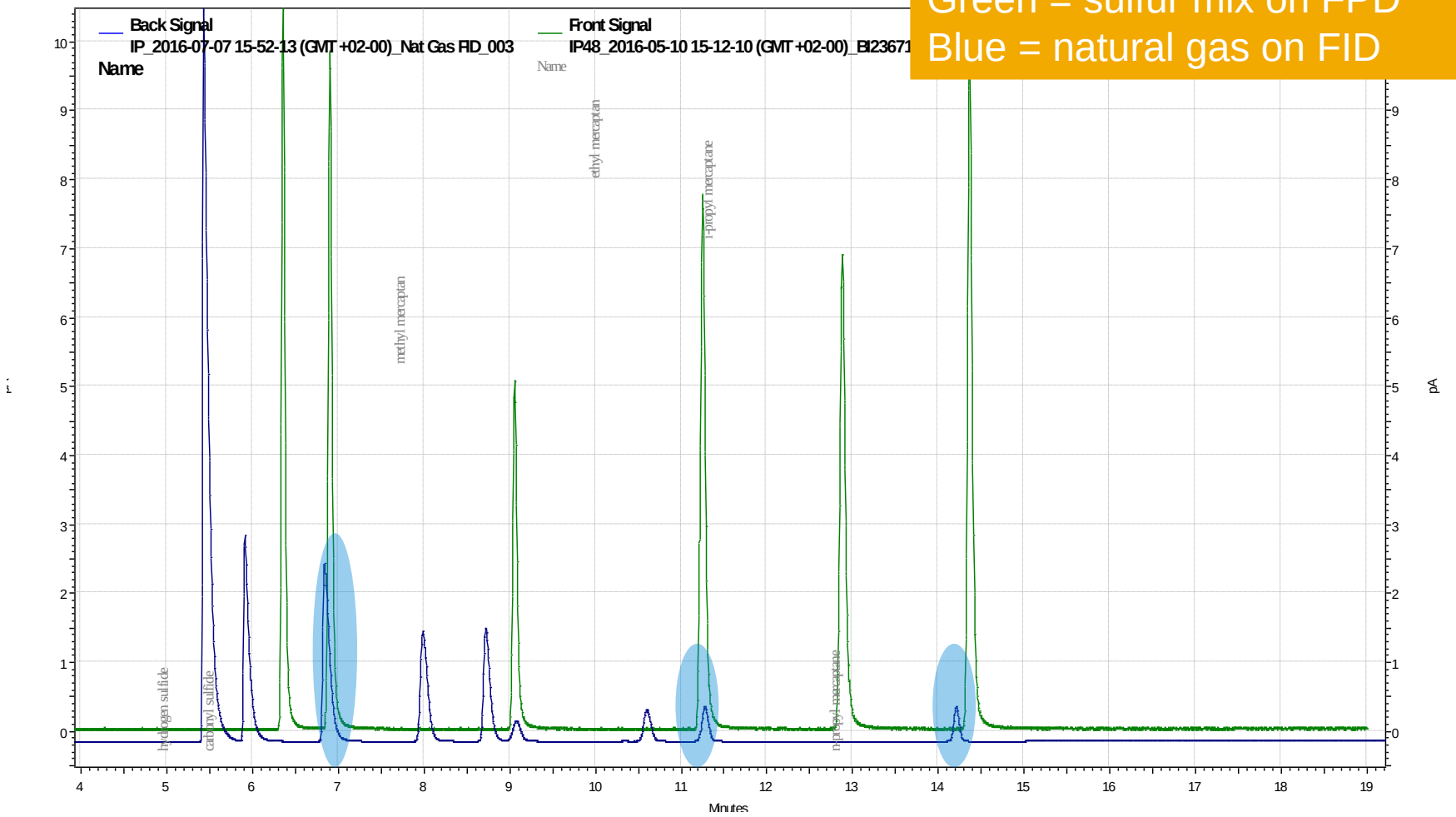
	FPD+	PFPD	SCD
MDL spec for sulfur	2.5 pg/sec	1 pg/sec	0.5 pg/sec
Dynamic range	10^3	10^3	10^5, linear
Quenching	Yes	Yes	No
Equimolar response	Quadratic response	Yes	Yes
Packed column compatible	Yes	No, 1 ml/min	Yes
Other elements	P, Sn	P	N
Relative cost	$	$$	$$$

Flame Photometric Detector

Signal quenching

Co-elution of Sulfur compounds and high concentration matrix

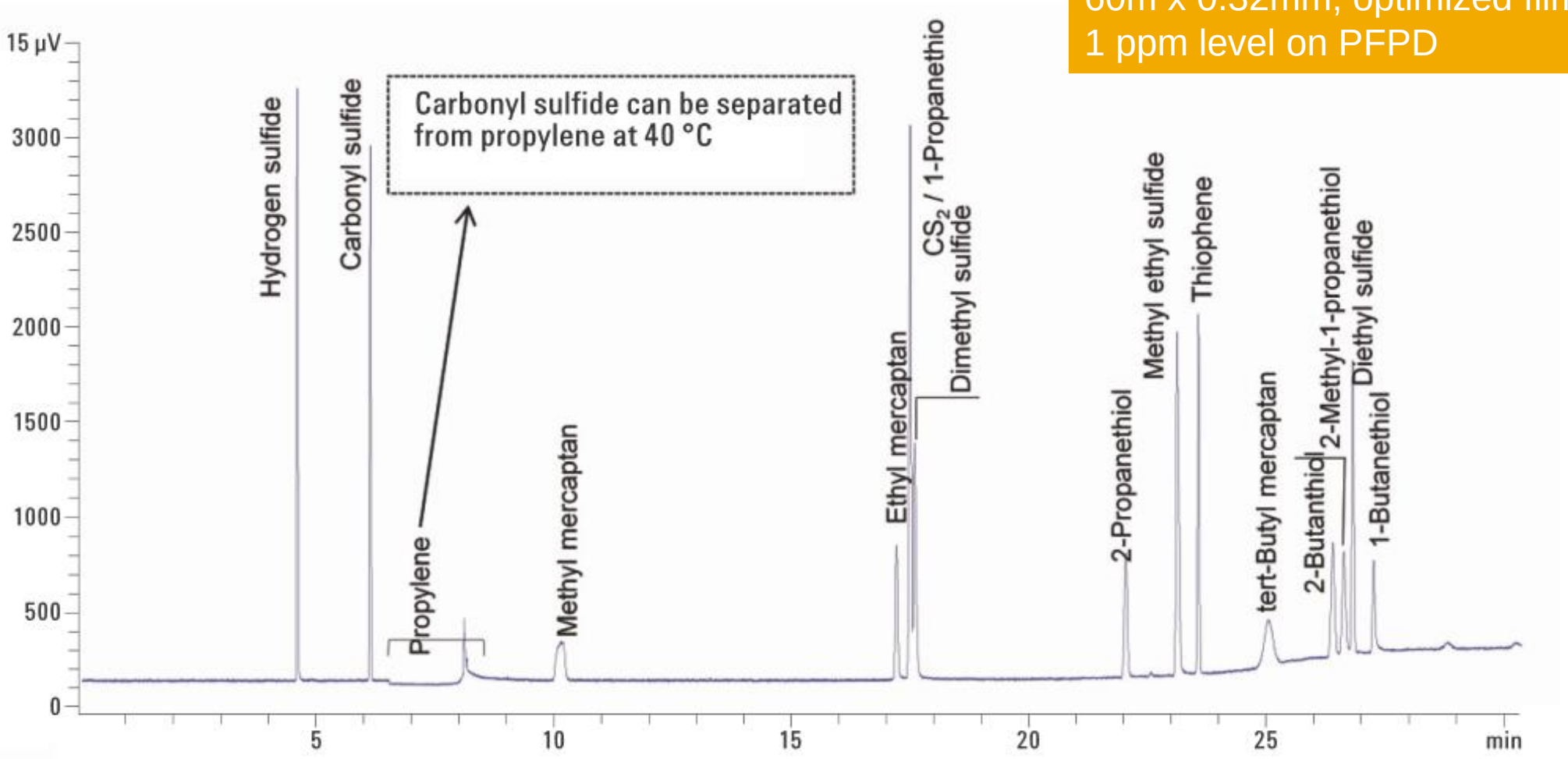
Potential signal quenching



Select for Low Sulfur

Column optimized for propylene matrix

Select for Low Sulfur
60m x 0.32mm; optimized film thickness
1 ppm level on PFPD



Sulfur Chemiluminesence Detector

Principle of Operation

Chemically transforming of sulfur compounds

- Combustion in plasma (S to SO)
- Followed by reaction with ozon (SO to SO2*)
- Emitted light is detected by photo multiplier tube

$$\text{Sulfur compound (analyte)} \rightarrow SO + H_2O + \text{other products}$$

$$SO + O_3 \rightarrow SO_2 + O_2 + h\nu\ (< 300\text{-}400\ nm)$$

Sulfur Chemiluminesence Detector

Principle of Operation

Reducing complexity improves uptime readiness

Pathway connections
Reduced ~ 40%

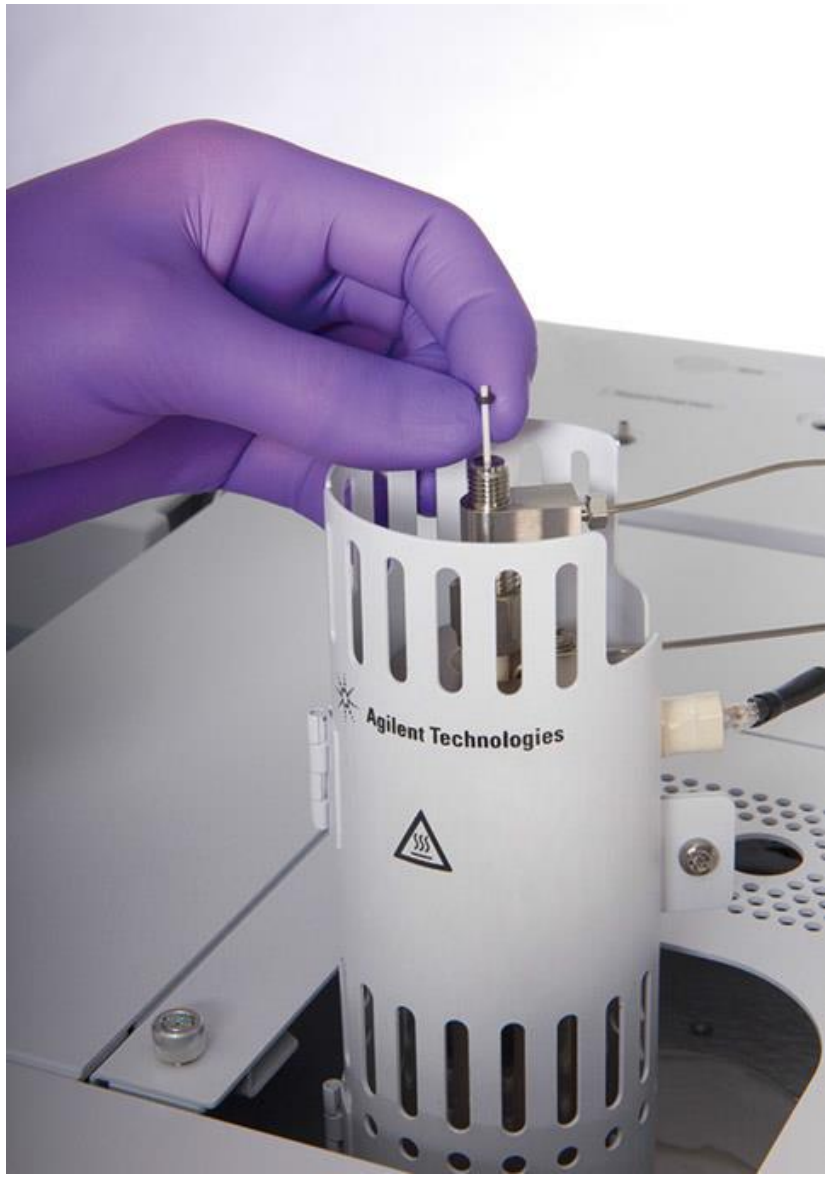
Significantly decreasing the number of potential leak points compared to model 355.

Burner components
Reduced ~ 50%

Making the inner ceramic tube easier to replace.

Inner tube change time
Reduced ~ 92%

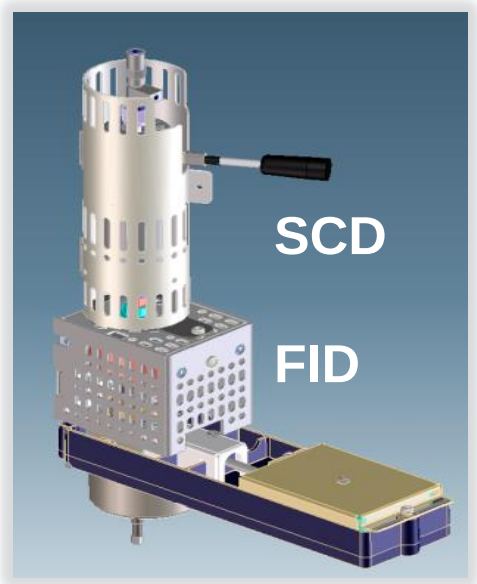
Change the inner ceramic tube in as little as 10 minutes, as opposed to 2 hours.



System Integration

Hardware Integration

- Intergrate version (7890 GC) - support all parameters on GC front panel
- Standalone version for old/third party GC's
- FID / SCD combi poissble



Software Integration

- Full dynamic range data (integrated version only)
- Support all parameters in CDS
  - ✓ Gas Flows
  - ✓ Temperature
  - ✓ Pressure

DB-Sulfur SCD

Optimized for use with SCD

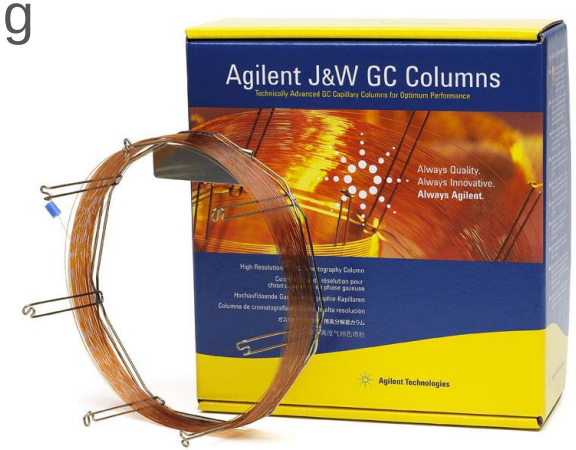
New optimized low polarity column with low bleed and exceptional inertness to sulfur even at trace levels

Developed with Dow Chemical and other leading companies

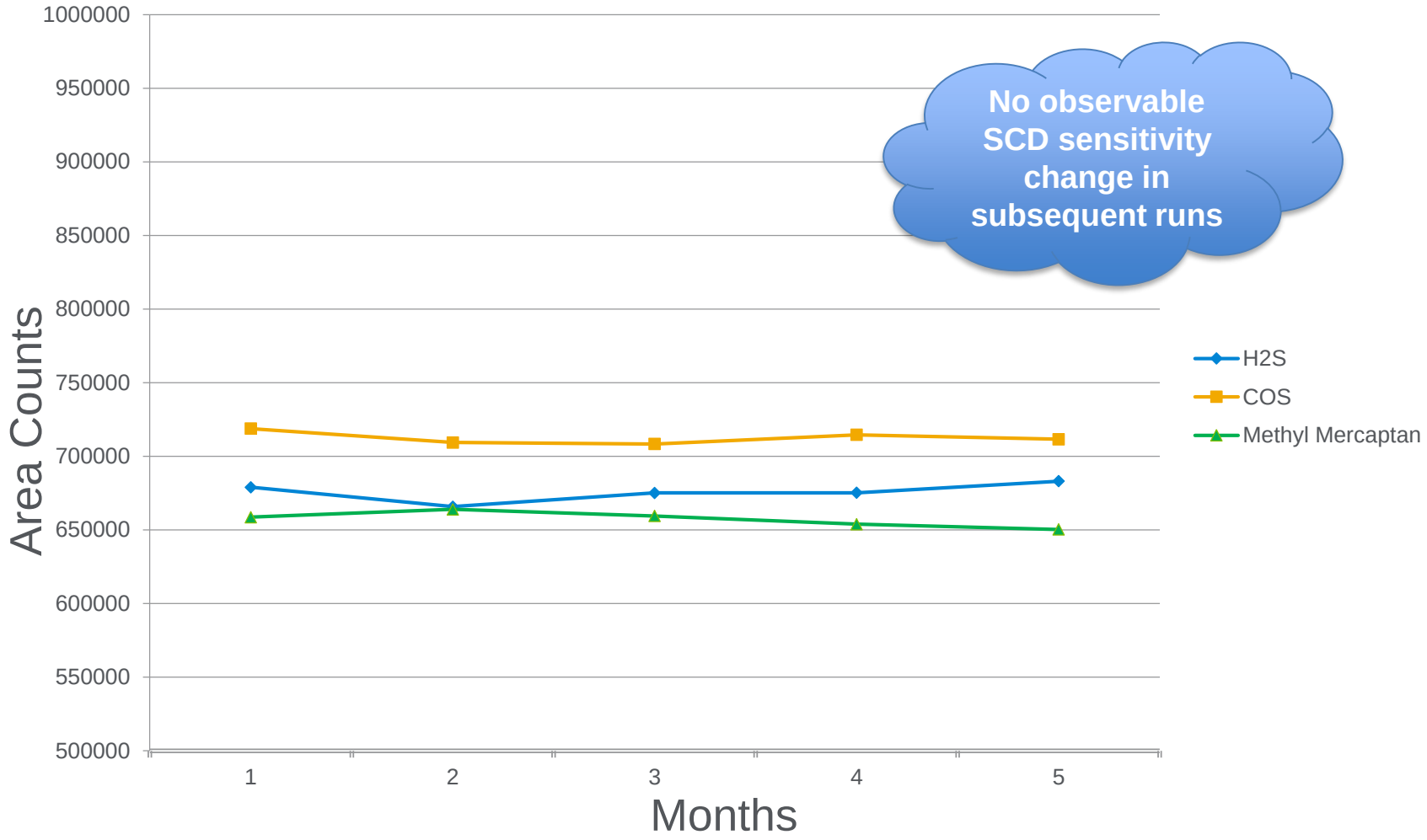
Excellent for a broad range of sulfur compounds from light sulfur gasses to sulfur containing hydrocarbons out to C24

Optimized for the lowest possible contribution to SCD reaction tube fouling

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



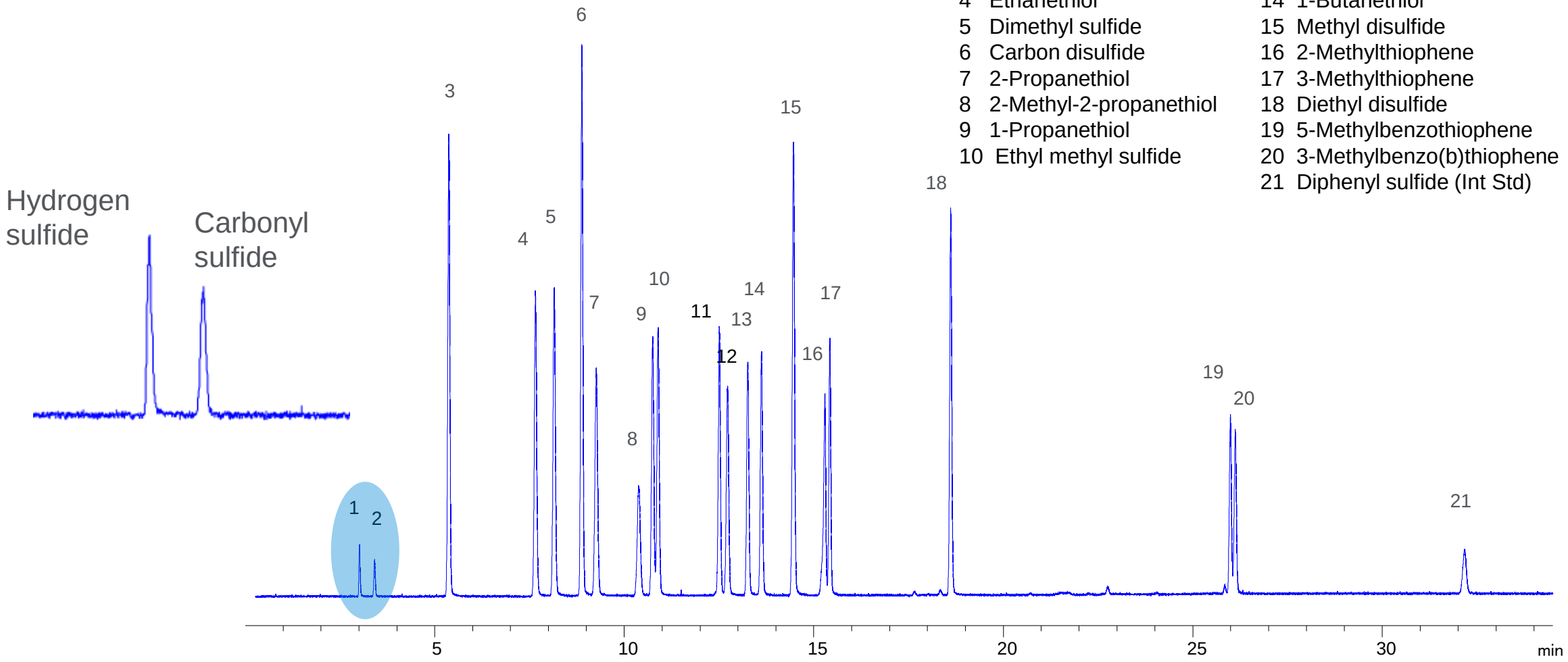
Long Term SCD Performance with DB-Sulfur SCD



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

DB-Sulfur SCD

Baseline separation of H_2S and COS



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)

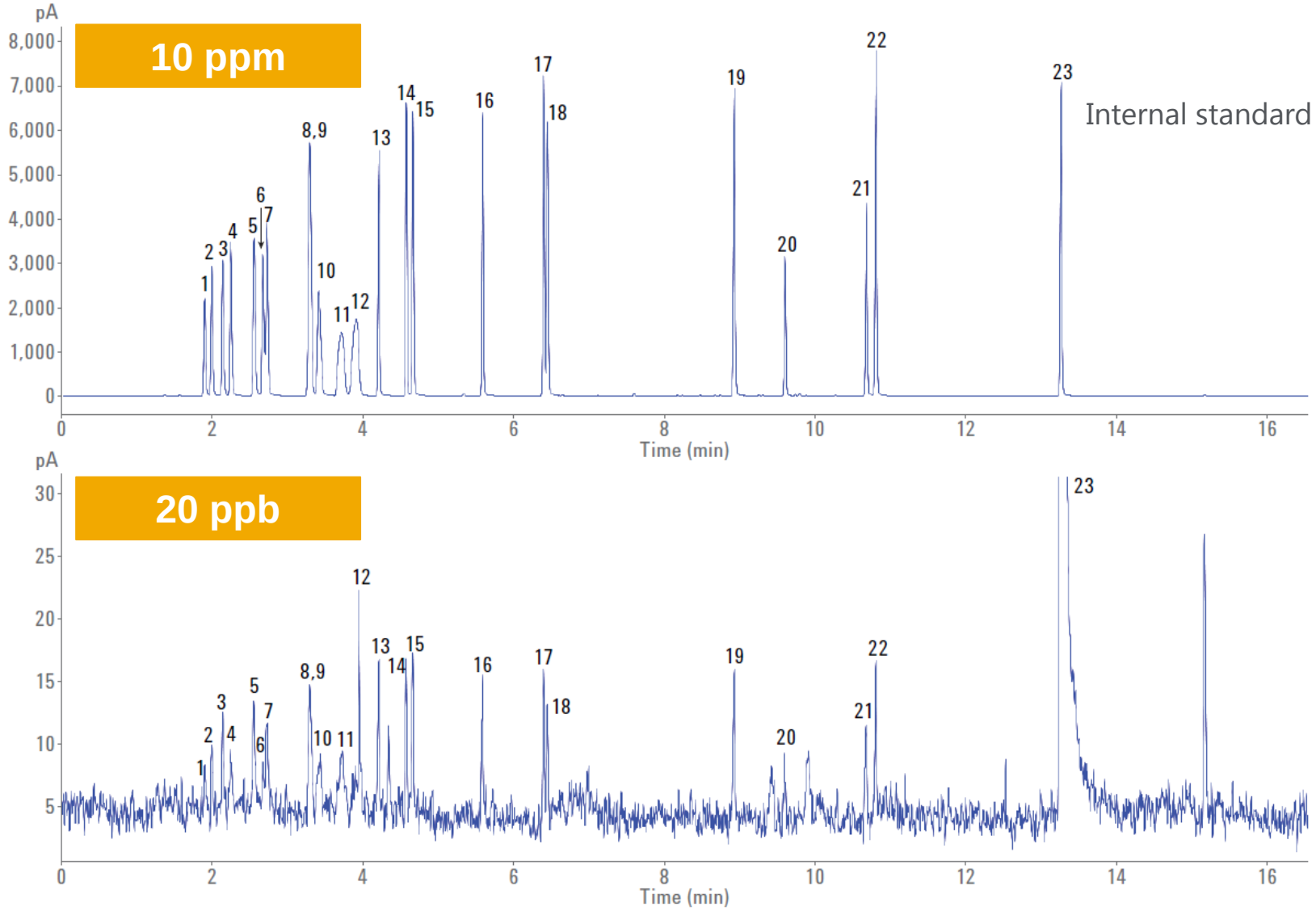
Column: Agilent J&W DB-Sulfur SCD, 60 m x 0.32 mm, 4.2 µm (p/n G3903-63001)

35 °C for 3 min --10 °C/min → 250 °C for 10 min

Sulfur Compounds Analysis

Intuvo GC / SCD

	Compound
1	Ethanethiol
2	Dimethyl sulfide
3	Carbon disulfide
4	2-Propanethiol
5	2-Methyl-2-propanethiol
6	1-Propanethiol
7	Ethylmethyl sulfide
8	2-Butanethiol
9	Thiophene
10	2-Methyl-1-propanethiol
11	Diethyl sulfide
12	*n*-Butanethiol
13	Dimethyl disulfide
14	2-Methylthiophene
15	3-Methylthiophene
16	3-Chlorothiophene
17	2-Bromothiophene
18	Diethyl disulfide
19	Di-*tert*-butyl disulfide
20	Thianaphthene
21	2-Methylbenzothiophene
22	3-Methylbenzothiophene
23	Diphenyl sulfide



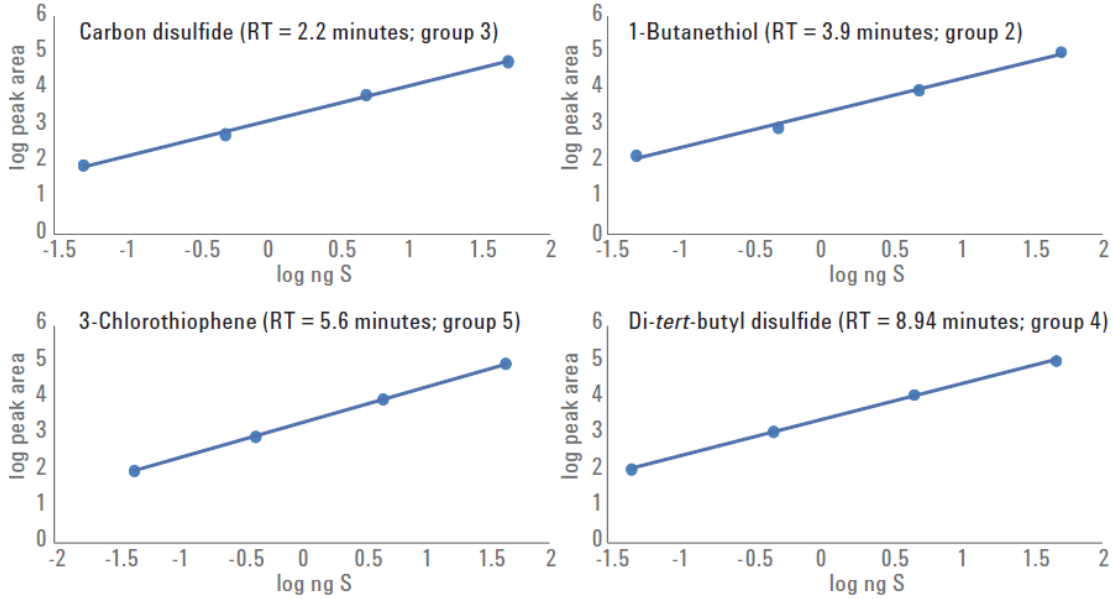
Sulfur Compounds Analysis

Intuvo GC with SCD

Repeatability (RSD%) and linearitity

Analyte	0.1 ppm (%)	1 ppm (%)	10 ppm (%)	100 ppm (%)	R^2
Ethanethiol	8.5	4.6	5.4	3.9	0.998
Dimethyl sulfide	5.5	5.9	6.9	4.1	0.997
Carbon disulfide	3.9	6.8	4.0	7.3	0.997
2-Propanethiol	3.1	3.6	3.9	3.7	0.999
2-Methyl-2-propanethiol	4.3	2.6	1.6	1.0	0.999
1-Propanethiol	6.7	2.2	5.3	2.9	0.999
Ethylmethyl sulfide	3.8	5.3	5.1	3.0	0.999
2-Butanethiol	3.1	4.2	2.4	3.8	0.999
Thiophene	3.9	3.6	4.5	4.0	0.999
2-Methyl-1-propanethiol	3.0	3.2	1.4	1.1	0.999
Diethyl sulfide	6.9	2.6	3.7	1.9	0.999
n-Butanethiol	4.0	3.7	3.7	1.9	0.994
Dimethyl disulfide	3.3	3.5	2.2	4.0	0.999
2-Methylthiophene	2.8	3.5	2.7	1.7	0.999
3-Methylthiophene	4.4	3.3	1.5	0.9	0.999
3-Chlorothiophene	4.7	3.2	1.2	0.8	0.999
2-Bromothiophene	2.8	0.9	2.30	0.5	0.999
Diethyl disulfide	3.1	1.20	1.60	0.56	0.999
Di-*tert*-butyl disulfide	2.5	1.9	0.66	0.74	0.999
Thianaphthene	4.7	0.7	1.2	0.54	0.999
2-Methylbenzothiophene	2.7	1.4	1.20	0.6	0.998
3-methylbenzothiophene	1.5	2.4	0.6	0.2	0.999

Calibration plots, 5 data points for each calibration



Innovating a New Path to GC Productivity

Intuvo GC - A whole new way to GC

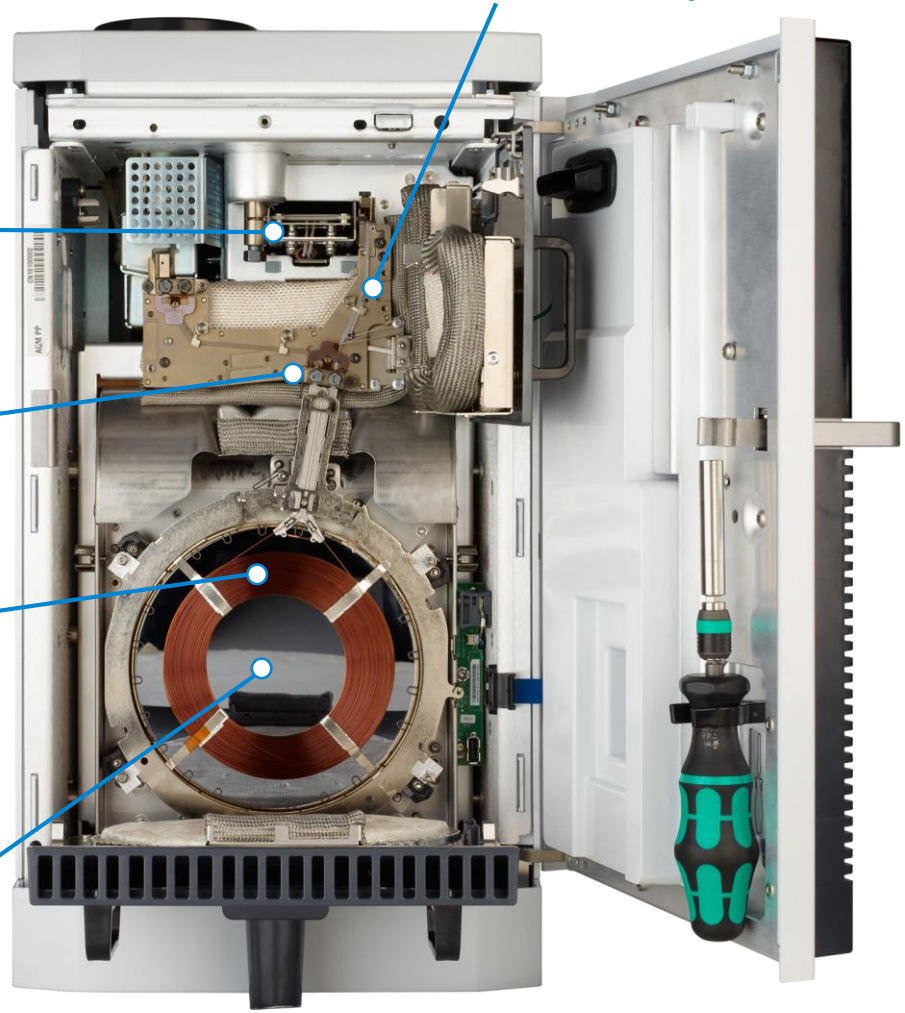
Disposable
Guard chip

Ferrule-free click-and-run
connections

No-trim
column

Direct fast
heating

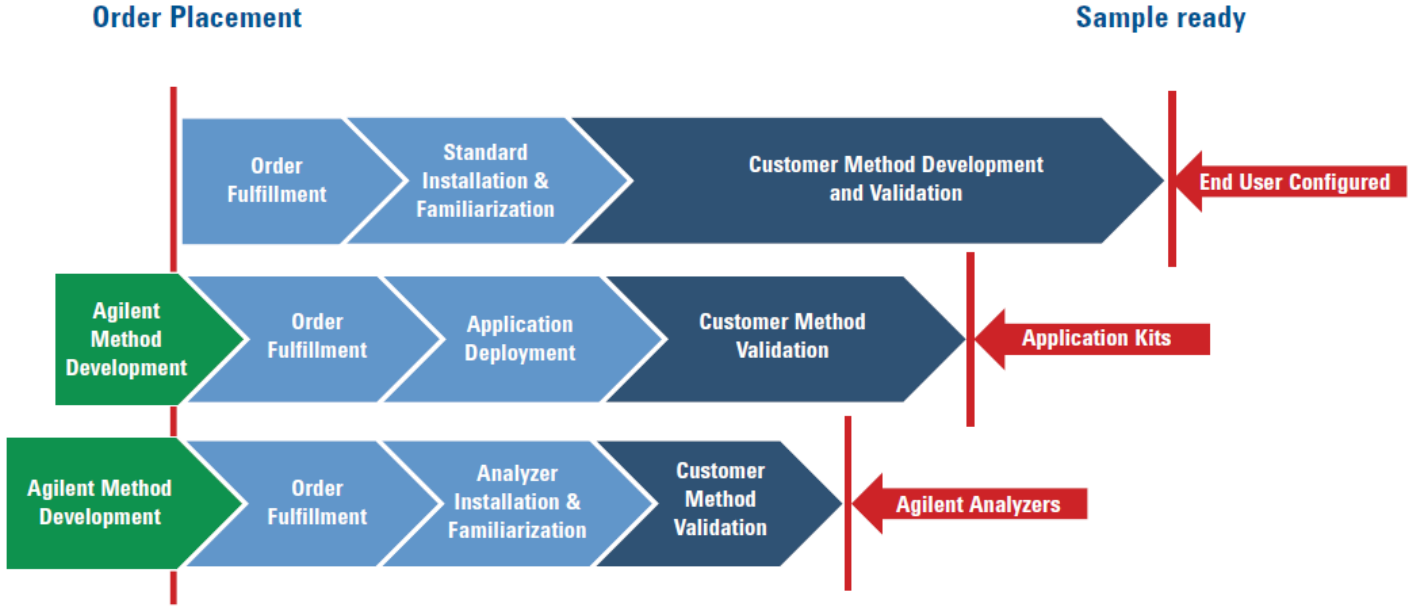
Modular
Intuvo flow chips



GC and GC-MS analyzers

- Pre-configured system
- Factory tested
- Shipped with method, manual and check-out mix

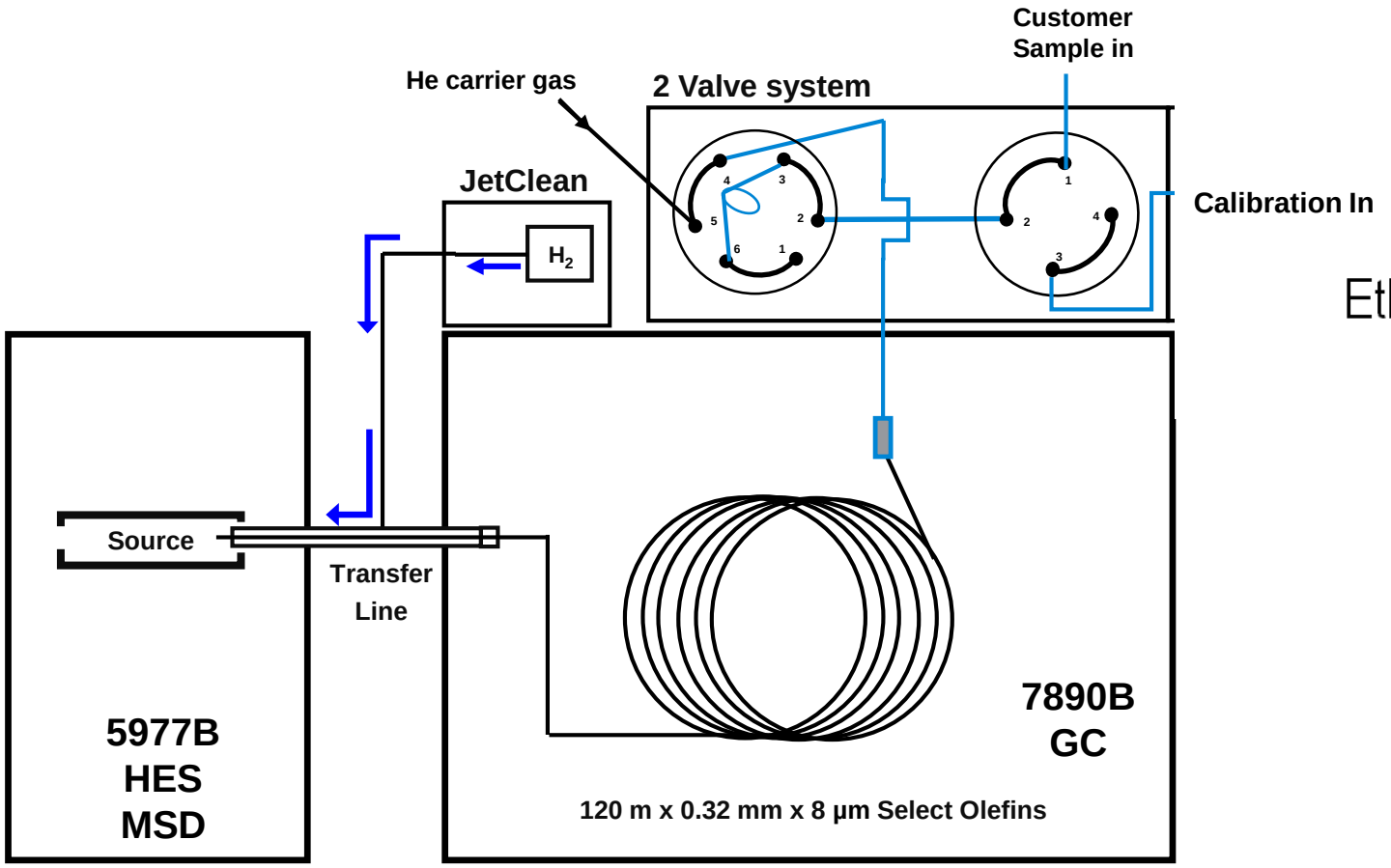
Analyzers and Application Kits reduce your method development time



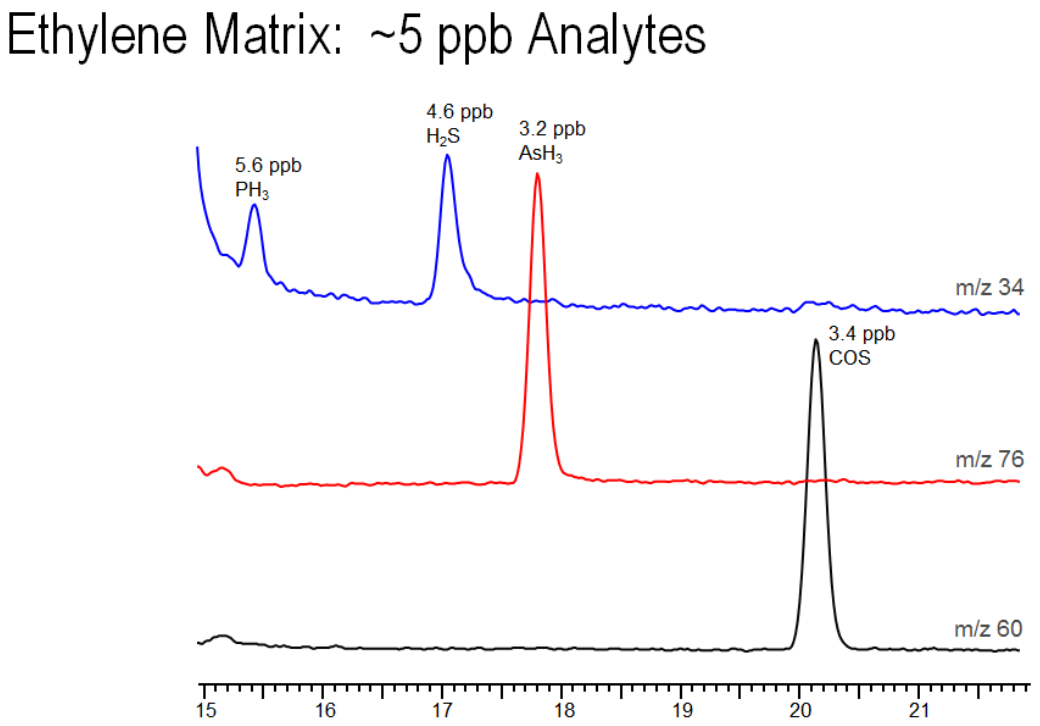
Sulfur analyzers
Three Channel Fast RGA + H2S with Five Valves
Extended RGA with high H2 and H2S 100ppm to 5%
Analyzer for sulfur in liq Nat Gas and LPG
Sulfur Comp. in Nat. Gas or gas fuels by GC-SCD ASTM D5504
Sulfur Comp. in Light Petroleum Liquids by GC-SCD ASTM D5623
Sulfur Comp. in Gas or Liquids by chemiluminescence as per ASTM D5504, D5623 and UOP 791
Parallel splitter analyzer for liquefied and gas samples through SCD-FID
Parallel splitter analyzer for gaseous samples through SCD-FID
NGA Analyzer with PFPD Sulfur Channel
Light sulfur species and light hydrocarbons in fuels or heavy matrices with CFT backflush and FID-SCD
Fast Refinery Gas Analyzer (RGA) with hydrogen sulfide and oxygen
Dual Channel trace sulfur analyzer for Natural Gas and Fuel Gas streams
Dual Channel trace sulfur analyzer for Ethylene, Propylene and C4 streams
Dual channel Natural Gas Analyzer with H2, He and % level H2S capability
Analyzer for ppm traces of tiophene in benzene by Deans Switch (2-D GC)
GCMS single quadrupole analyzer for arsine, phosphine, hydrogen sulfide and carbonyl sulfide

GC-MS analyzers

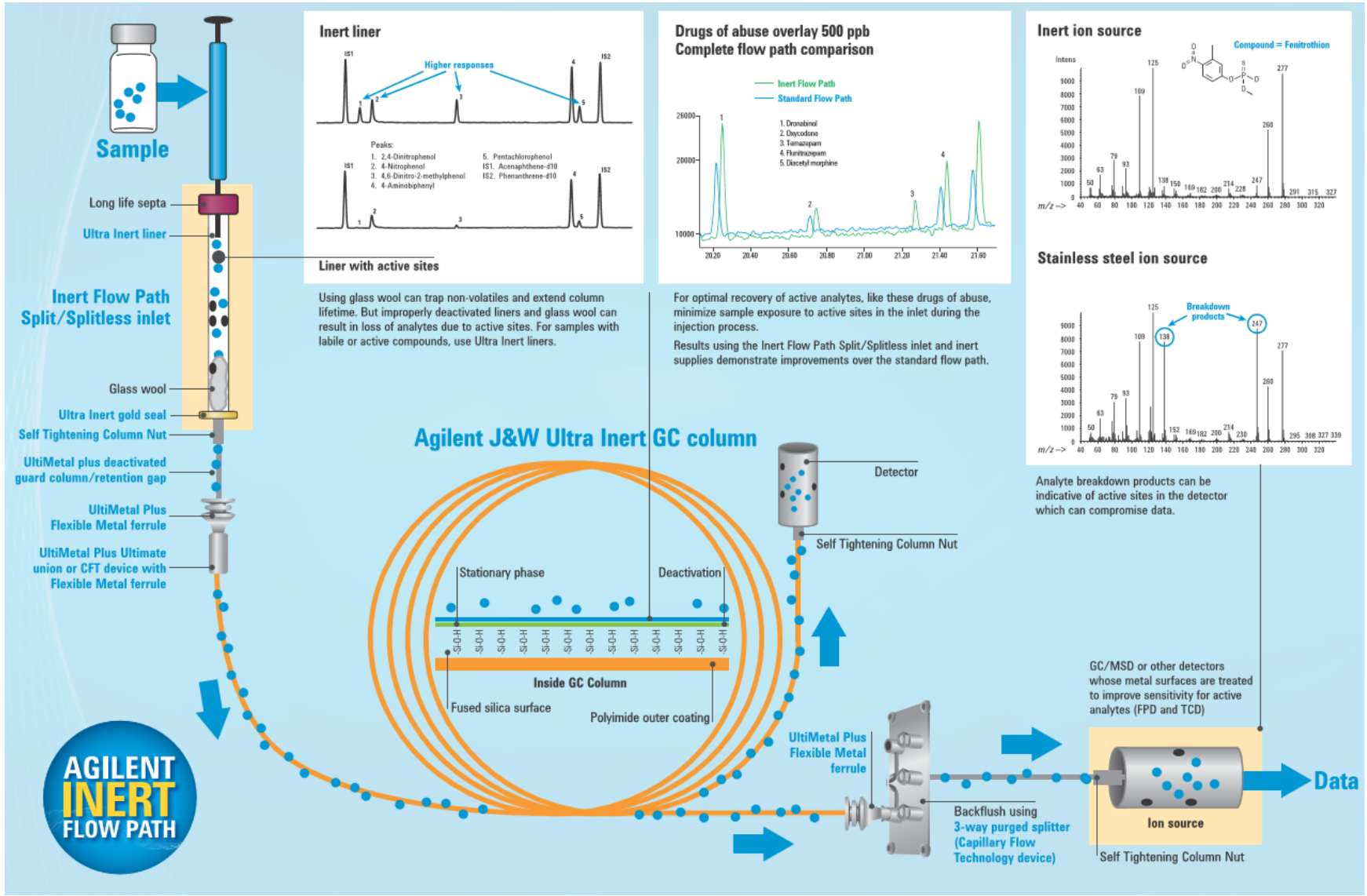
Arsine, phosphine, H2S & COS in ethylene and propylene



Blue lines (or outline) indicate deactivated stainless steel tubing



Inert GC Flow Path



Inert GC flow path

- Sample introduction
- Liner/gold seal
- Ultra Inert columns
- Capillary flow technology / connectors
- Deactivated injector/ detector weldment
- Gas clean filters

Sulfur Analysis

To summarize

- Multiple detectors for sulfur detection
  - Required sensitivity
  - Sample type/matrix
- Optimized columns available
  - DB-Sulfur SCD - low bleed, inert and minimizes detector fouling
  - J&W Select Low Sulfur – for Propylene streams
- Inert flow path
  - Prevent adsorption of active compounds
- Sulfur Chemiluminesense Detector
  - Enhanced detector design – robustness and simplified maintanence
  - Avialable for 7890 GC, Intuvo GC and standalone version for other GC’s