Sulfur Chemiluminescence Detectors for Gas Chromatography

Wenmin Liu, Mario Morales, Thomas F Daniels. **Agilent Technologies**

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Introduction

Petroleum feeds and products contain varying amounts and types of sulfur compounds. Many sulfur compounds can be corrosive to equipment, inhibit or destroy catalysts employed in downstream processing, and impart undesirable odors to products.

Analysis of sulfur compounds is difficult because they are polar, reactive and present at trace level. They pose problems both in sampling and analysis.

Gas chromatography with sulfur chemiluminescent detection (SCD) provides a rapid and highly specific means to identify and quantify various sulfur compounds that may be present in miscellaneous petroleum feeds and products, such as gasoline, natural gas. Agilent technologies has further enhanced 355 SCD performance and ease of use by developing the dual plasma (DP) technology with its patented detection method. The key features of DP SCD are as follows:

- **Highest selectivity over carbon**
- **Little or no quenching**
- **Linear and equimolar response**
- **Simultaneous serial FID response is available**
- **Fast amplifier available for comprehensive GC X GC**

This poster shows the results of two ASTM sulfurs analysis methods (ASTM5504, ASTM5623) developed on Agilent 7890 GC DP SCD.

Experimental

Method 1 (ASTM 5623) Experimental conditions of sulfur compounds in gasoline

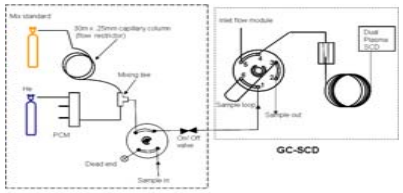
GC conditions			
Front Inlet	SS Sulfinert® treated capillary inlet system	**Mode**	Split
Pressure	10.951 psi	**Split Ratio**	10 :1
Oven	30°C (1min) 10°C/min 250°C (1min)	**Column**	HP-1 30m×0.32mm × 4um
SCD Conditions			
Burner temperature	800°C	**H2**	40 ml/min
Vacuum of burner	372 torr	**Air**	53ml/min
Vacuum of reaction cell	5 torr		

Method 2 (ASTM 5504) Experimental conditions of sulfur compounds in natural gas

GC conditions			
Front Inlet SS	Sulfinert® treated capillary inlet system	**Sample loop**	1 ml
Pressure	On 14.5 psi	**Oven**	30°C (1.5min) 15°C/min 200°C (3min)
Septum Purge Flow	On 3 mL/min	**Column**	HP-1 60m×0.53mm × 5um
Mode	Splitless	**Injection mode**	Static flow & dynamic flow mode
SCD conditions			
Burner temperature	800°C	H2	40 ml/min
Vacuum of burner	372 torr	Air	53 ml/min
Vacuum of reaction cell	5 torr		

Diagram of on-line gas blending-GC-SCD

- On-line gas blending system
- Sample injection valve
- Two injection mode realized by On/Off valve (dynamic and static injection modes)



Results

Method 1 (ASTM 5623) Results of sulfur analysis in gasoline

Peak identification
1.Ethyl Mercaptan; 2.Dimethyl Sulfide; 3. Carbon Disulfide; 4. Iso-Propylpropyl Mercaptan; 5. t-Butyl Mercaptan; 6. n-Propyl Mercaptan ; 7. Methylethl Sulfide ; 8. Thipphene ; 9. Sec-butyl Mercaptan; 10. n-Butyl Mercaptan ; 11.Dimethyl Disulfide; 12. 2-Methyl Thiophene; 13.3-Methyl Thiophene; 14.Diethyl Disulfide; 15. Benzo(B)thiophene.

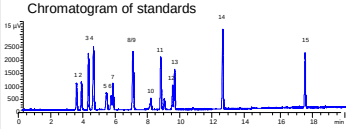
Method repeatability of sulfurs at different concentrations.

	1	2	3	4	5	6	7	8	10	11	12	13	14	15
Con. ppm	1.16	1.79	1.78	3.42	1.13	0.59	1.19	3.80	0.59	1.47	1.43	2.14	2.80	4.0
RSD (%)	2.8	3.6	3.1	1.9	3.0	2.7	3.9	3.9	2.9	2.1	2.2	2.9	0.4	3.7
Con. ppm	0.12	0.18	0.18	0.34	0.11	0.06	0.12	0.38	0.06	0.15	0.14	0.21	0.28	0.4
RSD (%)	5.7	7.4	3.4	3.7	6.6	4.8	5.7	4.8	8.0	4.0	3.3	4.7	7.3	3.1

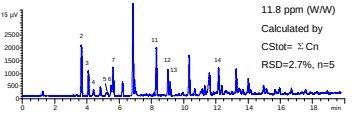
S/N of sulfurs at 20 ppb

Peak No.	1	2	3	4	5	6	7	8/9	10	11	12	13	14	15
S/N	2.0	2.5	5.0	4.6	1.8	1.6	2.4	5.0	1.5	3.6	2.0	4.6	3.2	5.2

Chromatogram of standards



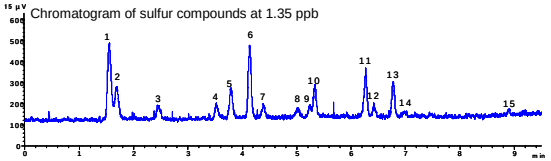
Chromatogram of standard real sample



Method 2 (ASTM5504) Results of sulfurs analysis in natural gas

Peak Identification
1. Hydrogen Sulfide; 2.Carbonyl Sulfide; 3. Methyl Mercaptan; 4. Ethyl Mercaptan; 5. Dimethyl Sulfide; 6. Carbon Disulfide; 7. 2-Propanethiol; 8. tert-Buthyl Mercaptan; 9. 1-Propanethiol; 10. Thiophene; 11. n-Butanethiol; 12. Diethyl sulfide; 13.Methyl ethyl Sulfide14 2-Methyl-1-Propanethiol; 15. 1-Methyl-1-Propanethiol.

Chromatogram of sulfur compounds at 1.35 ppb



S/N of sulfurs at 1.35 ppb

Peak No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
S/N	12.0	5.0	2.1	2.6	4.9	11.5	4.0	2.7	3.7	9.1	7.6	2.3	5.7	1.0	1.1

Method stability of long term and short term

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
20.79 ppb	2.7	2.6	2.9	3.0	0.9	1.4	2.8	4.0	2.6	1.7	1.7	3.3	3.2	8.6	7.9
S.T. RSD (%)															
L.T. RSD (%)	3.0	2.7	2.4	2.5	1.4	1.5	2.6	4.3	3.8	2.7	2.0	4.9	3.2	7.9	6.9
1.38 ppb	6.6	10.1	11.7	22.8	30.4	4.1	6.9	18.7	10.7	25.1	5.1	11.1	5.8	29.6	24.1
S.T. RSD (%)															
L.T. RSD (%)	14.4	7.5	16.3	20.8	21.7	4.6	6.1	27.7	23.7	25.3	12.2	24.6	6.1	35.7	38.4

S.T.: Short term (8h); L.T.: Long term (72h)

Summary

- The compact DP advances the established technology by improving performance;
- GC-SCD provides a highly sensitive, selective, and linear response to sulfur compounds in different matrix.
- The detection limits for the trace sulfurs detection are down to ppb level;
- On-line dilutor combining with GC DP SCD is suitable for the gaseous sulfurs analysis especially for the low level components