

# Improved GC Columns for the Petroleum Industry

by Daron Decker

GC Columns Technical Specialist, Agilent Technologies, Inc. Wilmington, Delaware USA

Petroleum analysis makes extensive use of specialised columns for gas chromatography, with continuous expectations from the industry for better columns that improve analytical performance and chromatographic efficiency. In this article we discuss two new developments in GC column technology that improve petroleum analyses, while reducing instrument downtime and maintenance costs.

The first of these approaches is based on PLOT (porous layer open tubular) columns which have previously been a challenge to use because of particle shedding, which can lead to detector spikes, instrument/column flow restriction, or plugging of switching valves. A new approach is to use PLOT columns that include integrated particle traps on both ends, in one continuous length of fused silica capillary.

The second development looks at the development of a new column for use with sulfur analysis. Thick film polydimethylsiloxane phases are commonly used for analysis of volatile sulphur compounds using sulphur chemiluminescence detection (SCD). The inherent bleed of these thick film columns can contribute to rapid fouling of SCD ceramic reaction tubes. This causes a fast decline in detector stability and frequent need for detector maintenance. A new column has been optimised specifically for use with SCD to enhance stability for improved results and instrument uptime.

## PLOT Column Problems

PLOT columns are commonly used for samples that have very high vapour pressures, or for gases, i.e. analytes that are difficult to retain chromatographically due to their very low boiling points. Gas-solid chromatography in the form of PLOT columns is therefore used to achieve the required retention.

These columns work through a very strong mechanism of adsorption, with excellent selectivity and retention. PLOT columns are less useful for high boiling compounds.

These less volatile analytes are too highly retained on this type of column. Even so, PLOT columns work very well for certain specific types of analysis.

However, the adsorbents that are immobilised on the inner surface of the fused silica in a PLOT column can shed particles that can reach the detector, causing signal spikes and potentially impacting results. These particles can accumulate in any kind of valve or union in the system which can also cause obstruction. This reduces instrument control and causes instrument tuning issues. This material can also fly into column switch valves or small capillary flow technology devices, causing flow restrictions or scoring valve rotors.

Although there have been advancements in PLOT stationary phase coating techniques,

stationary phase particle shedding is still problematic, at varying degrees, for the widely used porous polymer, alumina and molecular sieve phases.

It is for these reasons that PLOT columns are not usually used with mass spec, to avoid the risk of source damage or contamination. Traditional solutions have involved installing a particle trap at the end of the column or using inline filters to trap particles. This installation procedure can be time consuming, adding to labour costs. Unions are also a potential source of leaks, and, of course, the material can still leave the column and clog the union. Inline filters are also prone to clogging and flow restriction. Faced with all these potential issues, many analysts simply hope for the best and address issues as and when they arise.

**2.5-m  
integrated  
particle trap at  
front and rear  
of the column**

**PLOT  
column  
part**



Figure 1: Integral 2.5-m particle traps at both ends of the GC column.

## PLOT Columns with Integral Particle Traps

PLOT columns with particle traps integrated during manufacture are a better solution than add-on particle traps or inline filters (Figure 1).

With integrated particle traps, a thin film of polydimethylsiloxane type stationary phase is coated on both ends of the column, so that no matter what direction of flow is used, particulates are very unlikely to get past the 2.5- $\mu$ m particle trap without adhering to its wall. The advantage of this approach is the absence of unions or other fittings that are extra sources of possible leaks, or sites of accumulation. What's more, particles are trapped along the surface and no plugging problems are observed. This allows for the opportunity to use these columns with mass spec detection, without running the risk of particulates entering the MS, damaging its source or causing other problems. The integrated particle traps also remove the worry of valves rotors becoming damaged, or of capillary flow technology (CFT) components becoming plugged.

## Reliable Particle Trapping

An experiment was performed to ramp the temperature of a standard PLOT column from 150°C to 250°C at 20°C a minute, with this cycle repeated 15 times (Figure 2). Fifteen different increases in the signal are evident, due to column bleed. The column was then pressurised at three times the optimum pressure, turning the pressure on and off 10 times. This gave rise to the characteristic signal trace shown in Figure 2 with small hash marks 'eyelashes' on each of those individual 15 ramps. However, the biggest difference between the two chromatograms was the absence of spikes in the bottom one. When using the integrated particle trap column some bleed is evident, as is flow fluctuation that changes the detector signal. Even so, there is no evidence of particles leaving the column and spiking at the detector with such a demanding procedure.

## Selectivity is Maintained

Figure 3 demonstrates the absence of major selectivity differences - all the peaks emerge in the same order on both chromatograms, with or without a particle trap. Slightly more retention was observed with the integrated particle trap columns. Nonetheless, these differences between the standard

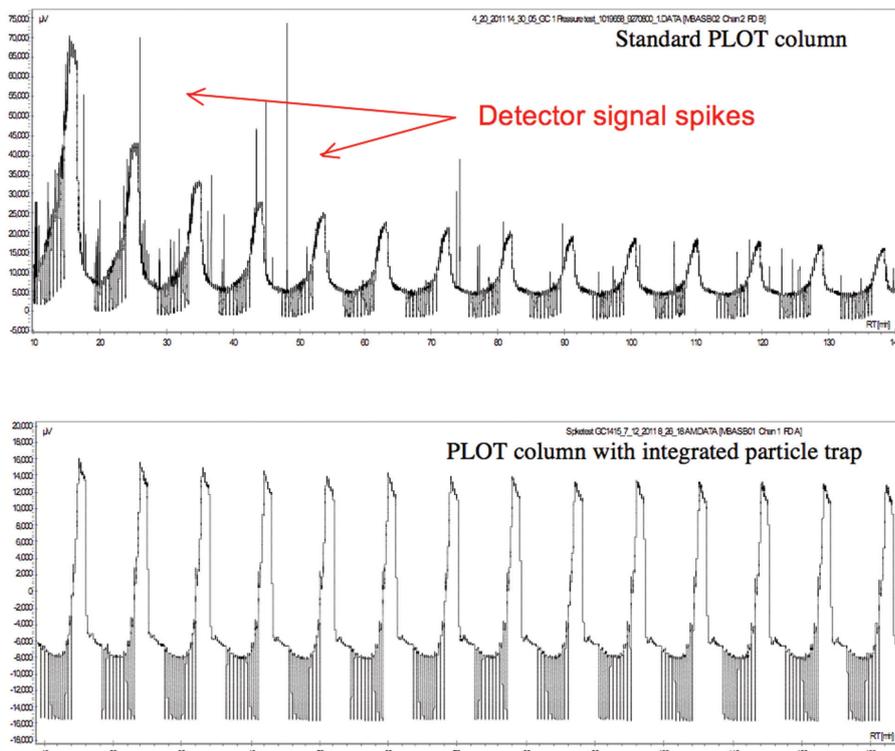


Figure 2: No detector spikes observed on the particle trap columns (below), even after repeated temperature and pressure cycling.

Carrier: Helium, 5.25 mL/min  
Oven: 150°C  
Inlet: 200°C, split ratio 60:1  
Detector: FID 250°C  
Inj. vol: 0.2  $\mu$ L

- |                       |                     |
|-----------------------|---------------------|
| 1. Methanol           | 7. 1-Propanol       |
| 2. Ethanol            | 8. Trichloromethane |
| 3. Acetonitrile       | 9. Ethyl acetate    |
| 4. Acetone            | 10. Hexane          |
| 5. Methylene chloride | 11. Benzene         |
| 6. Diethyl ether      | 12. Heptane         |

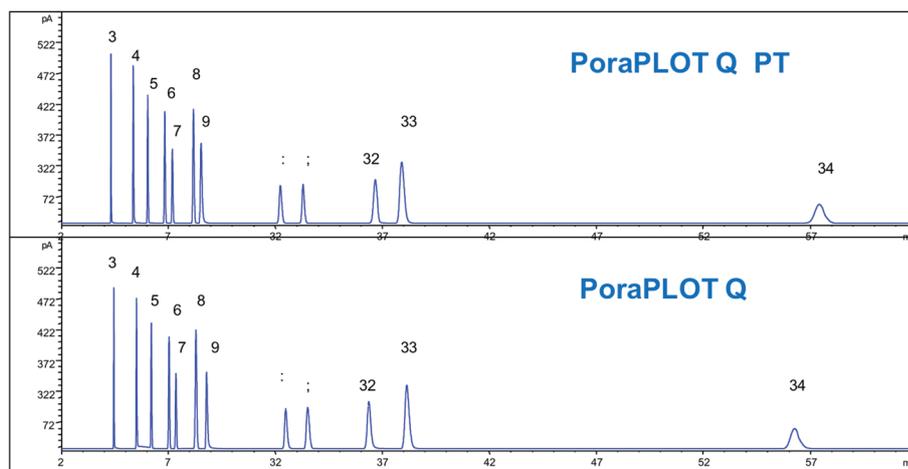


Figure 3: Differences observed between PLOT columns with (PoraPLOT Q PT) and without (PoraPLOT Q) integrated particle traps shows that variability is generally within the column-to-column reproducibility range for PLOT column manufacturing.

PLOT column and the PLOT PT column (the column with the particulate trap) are generally within the normal column-to-column reproducibility that is evident during manufacture of PLOT columns.

Figure 3 shows an example of the effect that the particulate trap has on the retention of volatile compounds, using PoraPLOT Q and a PoraPLOT Q PT. The analysis of the compounds containing 3 or fewer carbons in

particular is of great importance in residual solvent analysis and is often associated with the use of PLOTGC columns. In both cases, retention order is exactly the same with or without particle traps.

It is possible to argue that using the integrated particle trap column gives a slightly better separation, but for most applications the results are the same.

Column: Agilent J&W PoraPLOT Q PT, 25 m x 32 mm, 10  $\mu$ m (30 m total length)  
 Carrier: Helium, 42 cm/s at 55°C  
 Oven: 55°C for 5 min, 55 to 200°C at 12 /min, 200°C for 10 min  
 Injection: 250°C, splitless, 0.2 min purge  
 Detector: MSD, transfer line 280°C, full scan at m/z 45 to 185  
 Sample: 1  $\mu$ L

- |   |   |
|---|---|
| 1. Fluoroform (Freon-23)                    | 12. Fluorodichloromethane (Freon-21)                    |
| 2. 1,1,1-Trifluoroethane (Freon-143a)       | 13. Trichloromonofluoromethane (Freon-11)               |
| 3. Pentafluoroethane (Freon-125)            | 14. 1,1-Dichloro-1-fluoroethane (Freon-141)             |
| 4. Bromotrifluoromethane (Freon-13b1)       | 15. 2,2-Dichloro-1,1,1-trifluoroethane (Freon-123)      |
| 5. 1,1,1,2-Tetrafluoroethane (Freon-134a)   | 16. 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon-113)   |
| 6. 1,1-Difluoroethane (Freon-152a)          | 17. 1,2-Dibromo-1,1,2,2-tetrafluoroethane (Freon-114b2) |
| 7. Difluorochloromethane (Freon-22)         | 18. Trichloromethane (Freon-20)                         |
| 8. 1,1,2,2-Tetrafluoroethane (Freon-134)    | 19. 1,2-Dichloroethane                                  |
| 9. 1-Chloro-1,1-difluoroethane (Freon-142)  | 20. 1,1,1-Trichloro-ethane                              |
| 10. Bromochlorodifluoromethane (Freon-12b1) | 21. Trichloroethylene                                   |
| 11. Ethyl chloride (Freon-160)              | 22. 1,1,2-Trichloroethane                               |

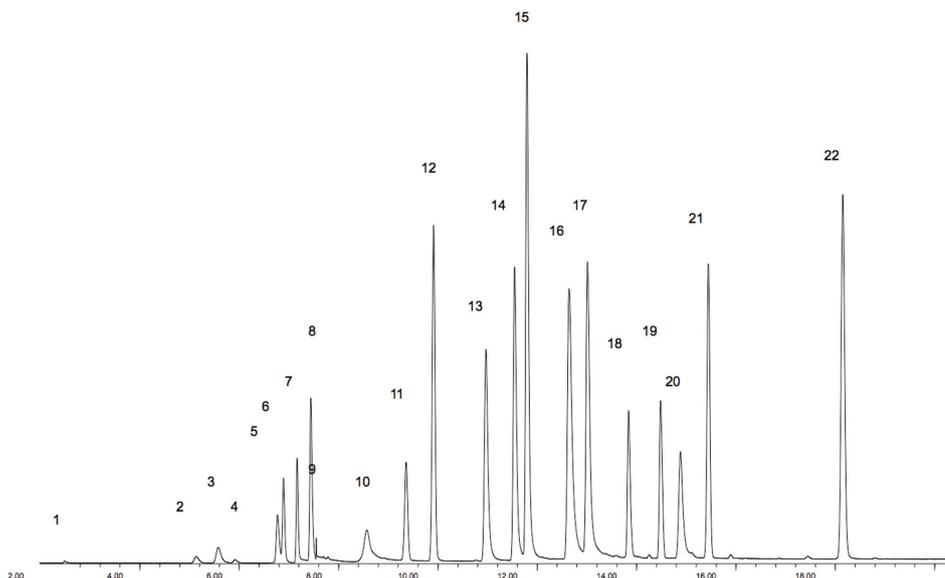


Figure 4: Using an integrated particle trap GC column to analyse halocarbons without risk of damage to the MSD.

Column: Agilent J&W HP-PLOT Q PT, 30 m x 0.32 mm, 20  $\mu$ m (35 m total length)  
 Carrier: Helium, 1 mL/min  
 Oven: 32°C for 3 min, 32 to 180°C at 15°C /min  
 Injection: 170°C, split 5:1  
 Detector: MSD, transfer line 280°C, full scan at m/z 10 to 100  
 Sample: 250  $\mu$ L

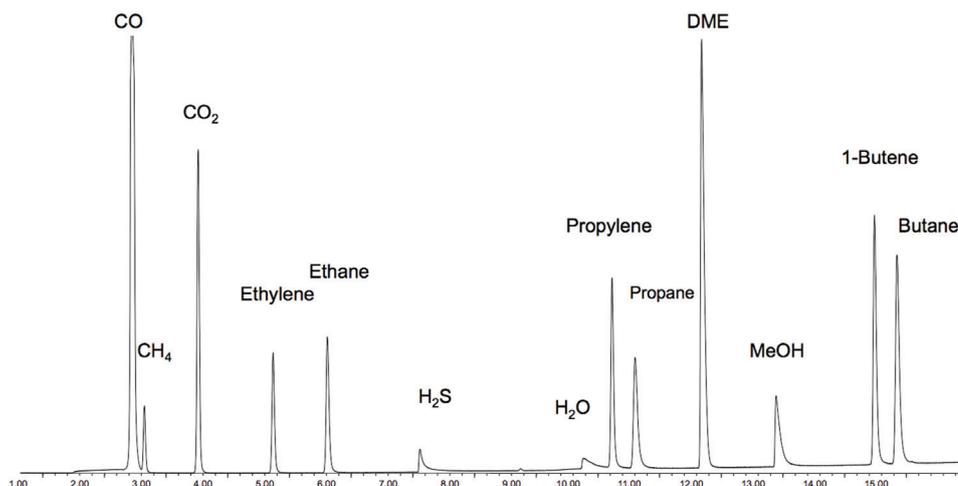


Figure 5: Coal-to-chemical process gas analysis with MSD using a GC column with integrated particle traps.

## Integrated Particle Traps and MS

Let's consider the use of integrated particle traps with MS detectors. Figure 4 is a chromatogram of halocarbons using mass spec detection. These freons and light chlorinated solvents are of interest to analysts looking at priority pollutants in volatiles' analysis. Peak shapes look good with only slight tailing, the separation is maintained, and the mass spec could be used without fear of detector contamination from the PLOT column stationary phase.

The final example (Figure 5) is a process gas analysis obtained from coal-to-chemical processing. Once again, the power of mass spec is available without the worry that is generally associated with the use of PLOT columns.

It is evident that integrated particle trap technology for PLOT columns provides a similar selectivity to the non-particle trap PLOT column, and so these can be exchanged without the worry of altering the analytical results. Even better, problems due to particle shedding are virtually eliminated, allowing the use of powerful mass spectrometry detection with confidence.

## New Approaches to Volatile Sulphur Analysis

Why is there so much focus on sulphur? Sulphur compounds can be very corrosive to equipment, pipelines, and reactors. Analysts may experience problems analysing these compounds because they are typically reactive. Specifically, sulphur compounds can inhibit or destroy expensive catalysts. Catalysts are used for downstream processing of many hydrocarbon streams that contain these sulphur compounds, and so it can be very expensive to have to replace poisoned catalysts. Sulphur compounds also impart an undesirable odour to many products, and in fuel they cause air pollution due to the oxidation products and other reactive species formed during the combustion process. Sulphur and the byproducts are monitored by environmental agencies with specified guidelines on the detection limits.

Analysing sulphur brings its own problems, in that very low detection levels are required. Matrix interferences are often present, because hydrocarbon streams contain many hydrocarbons but only trace amounts of sulphur components. These sulphur compounds can also be highly reactive and polar, which can also interfere with the desired sensitivity.

Flame ionisation or mass spec detectors are not typically used for sulphur GC analyses. FID works on the principle of burning a hydrocarbon in a flame. However, some sulphur compounds have very little hydrocarbon character, and so there is a sensitivity issue. Due to the low detection limits required by the regulatory authorities.

Mass spec, again, does not usually deliver sufficient sensitivity for the kinds of levels that are needed. That's why sulphur detection tends to be accomplished by other types of detectors, using a flame photometric detector (FPD), or a version of FPD called the pulsed flame photometric detector (PFPD), or, in many cases, a sulphur chemiluminescence detector, SCD. SCD measures down to very low levels and has very good selectivity against other constituents of the matrix, in particular hydrocarbons that do not contain sulphur are invisible to the SCD as it specifically measures only sulphur-containing compounds.

The SCD has good dynamic range, and good sensitivity, and is therefore the basis for several ASTM methods (Figure 6). In particular, ASTM D5504 and D5623 identify the SCD as the detector of choice. However, even though SCD is very sensitive and performs excellently, it can be slow to stabilise at start-up and a little tricky to operate. Coking or coating (desensitising) of the ceramic reaction tubes can also be an issue, which causes down time of the instrument.

Desensitisation of the SCD results from the use of very thick film columns, when analysing volatile sulphur-type compounds. Thick film columns are used as they help with inertness, and retention of the volatile sulphur compounds. However, very thick films operated at higher temperatures bleed much more than standard film columns. This bleed enters the SCD coating the reaction tubes, causing problems. When it comes to SCD maintenance, reaction-tube fouling can be expensive to rectify with replacement parts, and can cause down time of up to four hours. More importantly, the SCD can take several days to stabilise.

What sort of column is required to address these points? First and foremost, it should enable the system to provide good linear response across a wide concentration range. An inert stationary phase is also important to avoid losing the sulphur components due to activity. The stationary phase has to have good retention and selectivity because some sulphur compounds are very volatile



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

Figure 6: SCD for Sulphur Analysis is the basis for several ASTM methods.

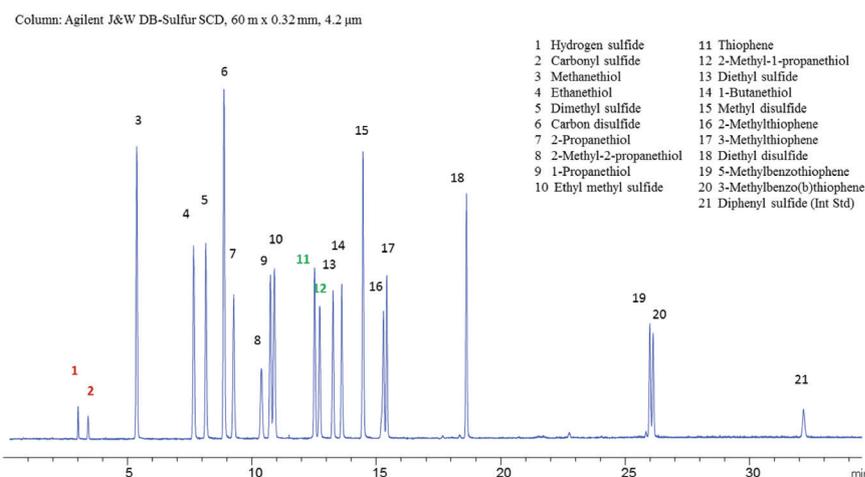


Figure 7: Sulphur standards in toluene, with good resolution of  $H_2S$  and  $COS$  at room temperature and baseline separation of thiophene and 2-methyl-1-propanethiol.

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

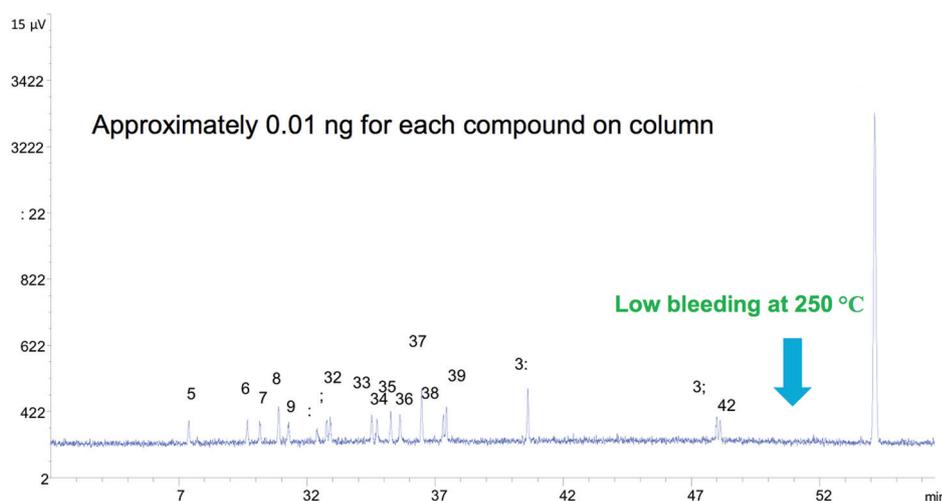
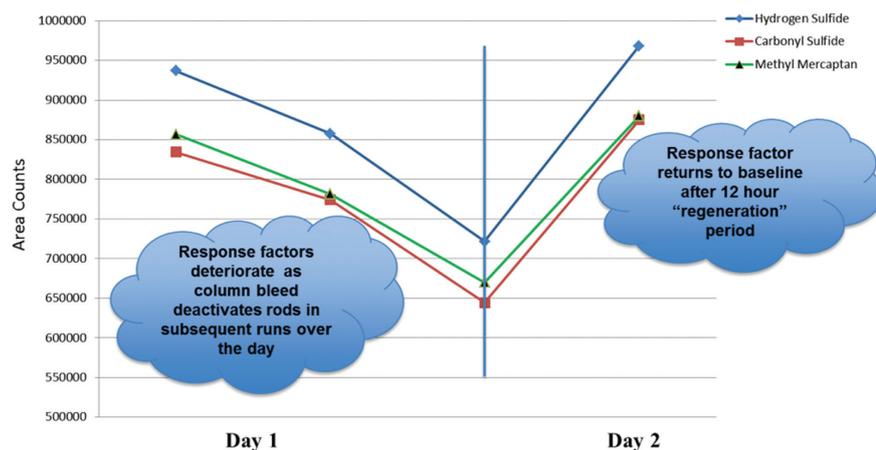
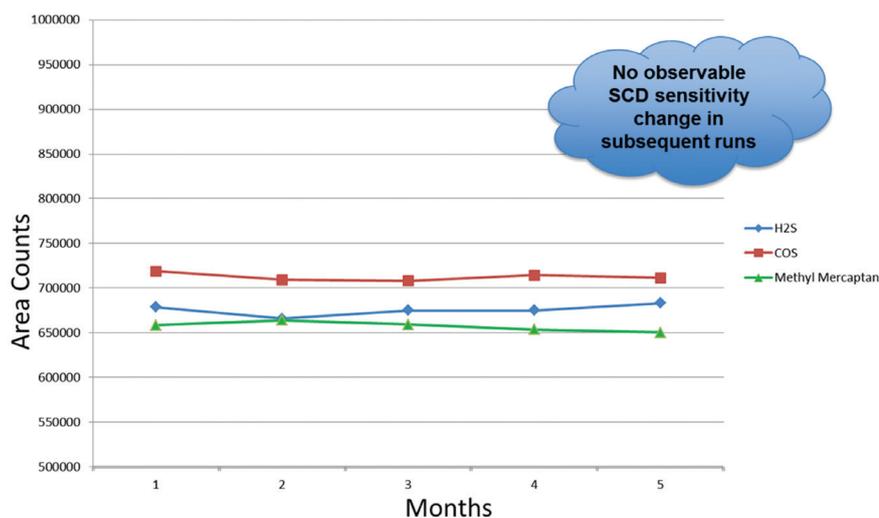


Figure 8: Good signal-to-noise, low bleed, and very low levels of a 400 ppb sulphur standard.



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

Figure 9: Traditional PDMS column—SCD rod deactivation



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

Figure 10: Long-term SCD performance with the Agilent J&W DB-Sulfur SCD GC column.

and need to be separated from other compounds of interest to avoid coelution. Also, as low detection limits are desirable, it is essential to minimise detector quenching at higher temperatures.

Loadability/capacity is also necessary, which is one of the reasons that smaller dimensions of this type of column are not applicable, because large injection volumes are required to provide very low detection limits. Finally, the column must be robust. It must have low bleed, so the ceramic reaction tubes in the SCD are not fouled, and it must deliver a very stable detector response that lasts a long time, so that detector maintenance is minimised.

To meet these requirements, a new column was specifically designed and developed for volatile sulphur compound analysis by GC/SCD. This optimised low polarity column, the Agilent J&W DB-Sulfur SCD, is very similar to other types of polydimethylsiloxane (PDMS) type stationary phase typical of DB-1 type column. It has very low bleed and exceptional inertness to sulphur, even at trace levels. The column permits analysis of a broad range of sulphur compounds from very light sulphur gases, through to C24 in the sulphur-containing hydrocarbons. Most importantly, it is optimised to make the lowest possible contribution to the fouling of the reaction tubes in the SCD.

Because it is designed for this type of analysis, it becomes a seamless operation to exchange it for an existing column, with greatly improved performance on the SCD, increased stability, and reduced burner tube maintenance.

Figure 7 is a chromatogram of sulphur standards in toluene. Resolution of H<sub>2</sub>S and COS at room temperature is excellent and so no cryogenics are needed. Even thiophene and 2-methyl-1-propanethiol are separated to baseline. This is better than the industry standard column specified in ASTM D5623 where these two peaks co-elute.

Good signal-to-noise is evident in Figure 8 for all the peaks in this sulphur standard.

Customers (Dow Chemical, Canada) tested a typical PDMS-type column against the DB-Sulfur SCD column (Figure 9).

With the traditional PDMS column throughout the day, the customer observed deterioration of the signal on the SCD as progressively more samples were analysed, and column bleed deactivated the rods and the ceramics in the SCD. Figure 9 covers hydrogen sulphide, carbonyl sulphide and methyl mercaptan only, but more sulphur based compounds were identified.

Over a six month period, the customers saw no SCD sensitivity change (Figure 10) and additionally, no maintenance was required replacing SCD ceramics. In contrast, the traditional method that Dow had used required detector maintenance around every three weeks.

## Conclusions

It is clear that mass spec can be used safely with PLOT columns that incorporate integrated particle traps, because the traps virtually eliminate particle shedding. There is no need for concern regarding scored valves or plugged capillary flow technology devices. All of the different PLOT types (U, Q, Alumina and Molsieve) benefit from integral particle traps and have very similar selectivity to their non-PT counterparts.

A similar rethink has led to marked developments in sulphur GC column technology. Improvements in sulphur analysis are now available that can greatly reduce the running costs of sulphur chemiluminescence detectors, while preserving analytical sensitivity, resolution and peak shape.