Improved Performance in Capillary GC Columns

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The development of durable and inert stationary phases for GC has substantial benefits for the analysis of all compounds as it improves the sensitivity and reproducibility of the assay and increases the overall robustness of analysis. The introduction of a new range of capillary GC columns substantially reduces column bleed, increases inertness and offers unparalleled injection-to-injection and batch-to-batch reproducibility. The highly inert characteristics displayed, as well as the improved column performance, are outlined here in a series of tests and applications.

Column Bleed

Detection of low levels of compounds is a requirement of chromatographers in many different fields; to meet, in most cases, stringent reporting and testing requirements. Analysts rely on GC–MS and other GC methods to enable highly sensitive, low level detection. Extreme care must be taken when measurement is required at the ppb or even ppt level. Detection at these levels is severely hampered by 'noise', the major source of which is the introduction of unwanted chemicals, mostly as the result of column bleed, where traces of oxygen and water in the carrier gas contribute to degradation of the liquid phase. System noise hinders sensitivity by lowering the signal-to-noise ratio; therefore, if noise is reduced, sensitivity increases. Column bleed also leads to reduced column lifetime with excessive bleeding resulting in the need for regular maintenance and instrument downtime. When using GC–MS, column bleed is a source of non-solute fragment ions; if bleed is minimized, there is a better chance of mass spectral matching against a database of reference spectra. For this reason, today's analysts require capillary columns that exhibit a very low level of bleed, in addition to being inert towards the various analytes in the method.

Bleed can be minimized by introducing aromatic groups into the polysiloxane phase to improve stability at higher temperatures, as well as by cross-linking the phase and bonding this to the fused silica wall. Further measures also ensure minimization, such as reducing the presence of O_2, H_2O and other reactive species in the carrier gas and by correctly conditioning the column to remove any O_2 before use.

Ultra Low Bleed Columns

It is, therefore, clear that low bleed columns are essential for the integrity and sensitivity of analytical results. The amplitude of baseline noise associated with column bleed is indicative of stationary phase stability. Column phase material stability is essential in ensuring low bleed values across the operating temperature range of the column. Column inertness is ideal for highly active compounds.

Column Bleed Test

This test focuses on the high temperature range close to the operating limits of the columns used, where column bleed is most observable. Columns are held at 325 °C for 5 minutes and then the temperature is ramped to 350 °C where it is held for another 5 minutes. It can be seen from Figure 1 that the new column range shows very low bleed and good stability.

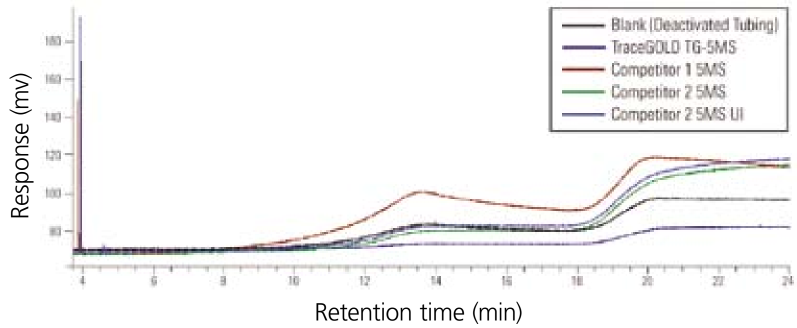
In a comparison of the bleed characteristics of a range of different 5% diphenyl/95% dimethyl polysiloxane columns under identical run conditions, the new column gave the lowest column bleed, particularly at the higher temperature of 350 °C.[1]

High Levels of Reproducibility

Run-to-run reproducibility is essential for all analytical laboratories. An advantage of low bleed columns is the superior reproducibility of the stationary phase over a period of time leading to greater run-to-run reproducibility. Figure 2 demonstrates that over a series of 100 injections using a mixture of phenol standards, the new column provided excellent run-to-run reproducibility.

It is also essential that there is column-to-column batch reproducibility. Failure to obtain the same high levels of performance for the same type of column can result in methods having to be revalidated and potential doubt being cast on the original data generated.

Figure 1: TraceGOLD TG-5MS. Comparison of bleed with three commercially available 5% diphenyl/95% polysiloxane phase columns.



Instrument: Thermo Scientific TRACE GC Ultra, TriPlus Autosampler
All column dimensions: 30 m × 0.25 mm i.d. × 0.25 µm
Sample: Dodecane in MeOH 1000 ppm
Injection: 1 uL injection (25 ng on column)
Split/splitless injector
Split flow: 100 mL/min (Split ratio 40:1)
Liner: 5 mm FocusLiner with glass wool insert
Injection temperature: 300 °C
Carrier gas: Helium, constant pressure 200 kPa
Oven programme: 70 °C, 20 °C/min to 325 °C hold 5 mins, 20 °C/min to 350 °C hold 5 mins
Detection: FID 350 °C

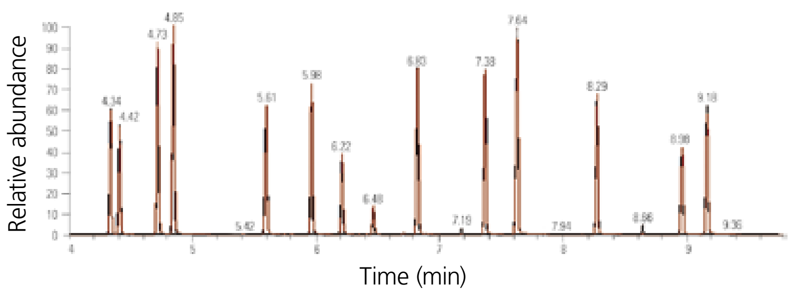
Analysis of Difficult Compounds

The acidic nature of the silanol groups prevalent within many GC columns can result in the adsorption of basic compounds, which frequently leads to peak tailing. Poor peak shape affects the sensitivity of an assay, as well as the robustness. Treatment of the analytical column by the bonding of basic functional groups onto the column surface reduces the effects of tailing and improves run-to-run reproducibility and sensitivity. Comparison of the chromatograms obtained for the analysis of 4-picoline and trimethyl phosphate demonstrates the substantially reduced tailing offered by the new amine base-deactivated column (Figure 3). The qualities of the new range can be seen in a typical application with the analysis of a standard tea tree oil sample (Figure 4).

Wide Range of Applications

The new series of columns are ideally suited to MS applications, offering exceptionally low bleed, even at maximum operating temperature, along with good stability and sensitivity. The non-polar 100% dimethyl polysiloxane offers equivalence to *United States Pharmacopeia* (*USP*) method G2, while the low polarity phase 5% diphenyl/95% dimethyl polysiloxane is equivalent to *USP* G27, offering the exceptional inertness necessary for the analysis of active compounds, such as semivolatiles, phenols, amines, residual solvents and solvent impurities, pesticides etc. The range includes a column optimized for system qualification, recommended for benchmark testing. The low-polarity 5% diphenyl/95% dimethyl polysiloxane amine column offers analysis of ppm levels of amines and other basic compounds, including alkylamines, diamines, triamines

Figure 2: TraceGOLD TG-5MS: An assessment of run-to-run reproducibility over 100 analytical runs.

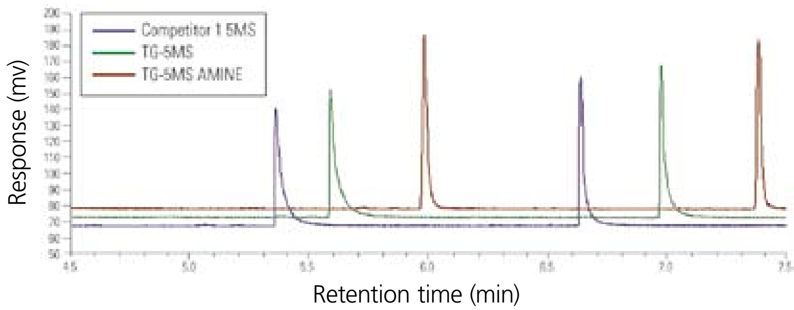


Instrument : TRACE GC Ultra, TriPlus Autosampler
Column dimensions: 30 m × 0.25 mm i.d. × 0.25 µm
Initial temperature: 45 °C, 1 minute
Rate 1: 15 °C/minute to 125 °C
Rate 2: 20 °C/minute to 205 °C
Injection: Split 50:1
Carrier : Helium 1.0 mL/min constant flow
Detection: DSQ
Source: 250 °C
Transfer line: 250 °C
Full scan: 50 to 650 *m/z*

and ethanolamines, without column priming. The tubing surface is chemically altered to reduce the tailing of active basic compounds and also allows analysis of neutral or weakly acidic compounds, such as phenols and compounds susceptible to hydrogen bonding.

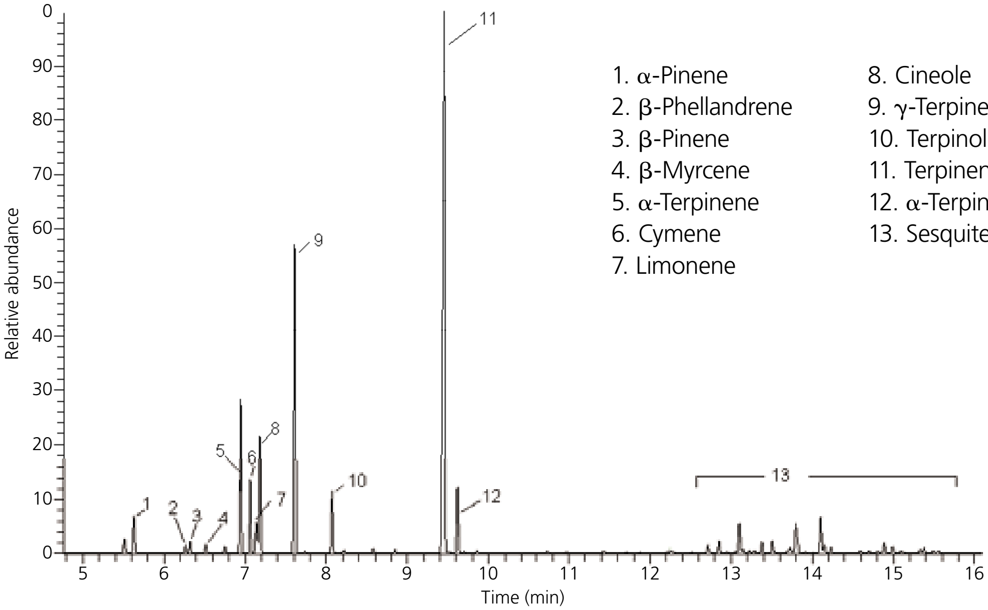
Other low polarity columns incorporate phenyl groups in the polymer backbone for improved thermal stability and outstanding inertness, and a special fused silica tubing design extends column lifetime by up to 40%, in addition to increasing the maximum operational temperature to 400 °C — ideal for high temperature extended GC applications. Mid-polarity phase columns of 35% diphenyl/65% dimethyl polysiloxane are equivalent to *USP* G42 phase and an amine version has been developed for the analysis of active basic compounds

Figure 3: TraceGOLD TG-5MS AMINE: Comparison of inertness with TraceGOLD TG-5MS and competitor.



Instrument: TRACE Ultra GC
All column dimensions: 30 m × 0.25 mm i.d. × 0.25 μm
Initial temperature: 40 °C, 1 minute
Rate 1: 15 °C/minute to 280 °C, hold 1 min
Inlet temperature: 250 °C
Injection: Split 10:1, split flow 50 mL/min
Carrier: Helium, constant pressure 200 kPa

Figure 4: Tea tree oil application on TraceGOLD TG-5MS.



Instrument: TRACE Ultra GC
Oven temperature: 40 °C hold 1.0 min
Ramp 1: 10 °C/min to 200 °C
Ramp 2: 30 °C/min to 250 °C
Carrier gas: Helium
Flow-rate: 1.1 mL/min
Injection volume: 1.0 μL
Injector mode: Split 1:30
Injector temperature: 250 °C
Detector: DSQ II Mass Spec
Transfer line: 250 °C
Source temperature: 200 °C

without derivatization. This enables analysis of neutral and adsorptive compounds with oxygen groups that are susceptible to hydrogen bonding. Low to mid-polarity phase 6% cyanopropylphenyl/94% dimethyl polysiloxane columns offer equivalence to *USP* G43 phase and 90+% resolution of the first six gases in EPA method 8260 and EPA Method 524.2 for volatile organics analysis. Mid-polarity phase columns are also available featuring a mix of cyano and phenyl groups equivalent to *USP* G46 phase and particularly suited to GC–MS applications that require more polarity than a 5% phenyl phase, as well as offering good thermal stability and reduced tailing. Additionally, the polar trifluoropropylmethyl polysiloxane solid phase offers an exceptionally inert mid-polarity column optimized for difficult separations — resolving compounds that phenyl and cyano phases cannot. Suitable for use with sensitive detectors, including ECDs, NPDs and MS, it is equivalent to *USP* G6 phase.

The higher polarity phase columns offer excellent thermal stability and resist damage from oxidative processes, as well as strongly acidic or basic volatiles, while giving excellent peak shapes for high MW acids. These are equivalent to USP G14, G15, G16, G25, G35 and G39 phases. Specifically designed polymer and surface treatment of the highly polar 90% biscyanopropyl/10% phenylcyanopropyl polysiloxane overcomes traditional problems with high polarity columns. Equivalent to *USP* G8 and G48, it offers strong dipole movement and high selectivity for *cis/trans* compounds or compounds with conjugated double bonds.

Improved performance

A low bleed, stable GC column produces consistent results, which combined with the low baseline noise, improves the limits of detection while enhancing the resolution of low level analytes. Column bleed also contributes to contamination of the MS; minimizing column bleed extends the interval between scheduled maintenance leading to higher productivity. A low bleed characteristic ensures preservation of the stationary phase over its working life assuring high levels of run-to-run reproducibility with greater sensitivity and a reduction in detector contamination.

A new GC capillary column range clearly shows improvements in capillary column performance. The inherent stability of the phase bonding provides a proven basis for chromatographic clarity, which is further enhanced by the low rate of bleed. The advances in phase resistance to temperature extremes and the durability of the column when used close to its operating limits are evidenced by the column bleed tests and the run-to-run comparability results. The inert nature of the stationary phase can be further augmented by chemical base deactivation and this is seen in the superior resolution and peak shape of basic compounds when using the amine column. The new range delivers low bleed and superior inertness and is ideally suited for an extensive range of MS applications.

Reference

1. P. Wheeler et al., *Improved Performance From The New Thermo Scientific TraceGOLD 5 Series GC Columns*, Poster 2420-14P presented at PITTCON 2010.

Luisa Pereira joined the Chromatography Columns and Consumables group of Thermo Fisher Scientific in 1999 after completing a PhD in LC–MS in the Mass Spectrometry Research Unit, University of Wales, Swansea, UK. Since then she has held a few different roles within the Applications and Technical Support team and currently holds the position of principal scientist. One of her key responsibilities is the investigation of the performance of new and innovative column phases.

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