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Ultra-inert low bleed GC columns with advanced silphenylene polymer technology

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Application benefits

- Thermo Scientific™ TraceGOLD™ silphenylene (SilMS)-based columns demonstrate 80% lower bleed compared to premium low bleed competitor columns.
- Column bleed variation across batches is 80% less than competitor ultra inert low bleed columns.
- Superior column inertness was demonstrated for the TraceGOLD TG-5 SilMS column compared to the market-leading UI column with a 50% improvement in inertness measured by the asymmetry value of 1,2-propanediol, a probe to measure silanol activity.

Goal

To compare the Thermo Scientific TraceGOLD TG-5SilMS column against the market-leading ultra-inert (UI) columns to determine relative inertness and column bleed across multiple batches.

Introduction

Trace analysis requires GC columns with excellent inertness, low column bleed, and excellent column-to-column reproducibility so that lower limits of detection and quantitation can reliably be achieved. Columns that require lengthy conditioning procedures to achieve stable baselines cause extended

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instrument down time and this reduces productivity. These problems are compounded with high bleed columns, where source contamination is accelerated and results in the need for more frequent preventative MS maintenance due to siloxane build up.

Many GC columns on the market contain original ‘pendent style’ polymer chemistry where functionality (usually mixtures of phenyl and methyl groups) are appended off the silicon as R groups (Figure 1).

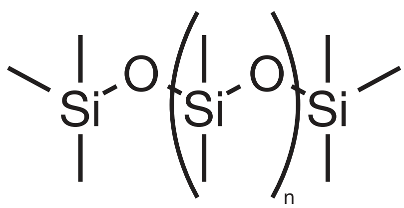


Figure 1. Original pendent and silphenylene based polymer chemistry.

This type of column chemistry is particularly prone to high bleed at elevated oven temperatures, which is caused by the breakdown of the column stationary phase. During the breakdown process the formation of characteristic cyclosiloxanes fragments occurs via a chemical reaction known as ‘back-biting’ (Figure 2) and is greatly accelerated by the presence of oxygen in the carrier gas. High column bleed is an issue to chromatographers as it can result in poor method sensitivity, reduced column lifetime, and higher frequency of MS maintenance. TraceGOLD SilMS columns however are based on newer advanced silphenylene polymer chemistry (Figure 3).

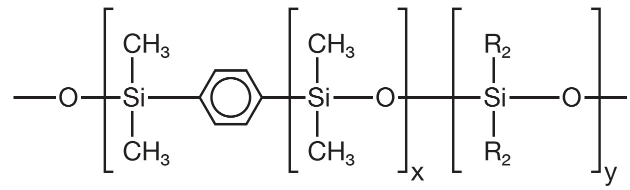


Figure 3. Advanced silphenylene based polymer chemistry.

The TraceGOLD SilMS column contains modern silphenylene-based chemistry incorporating the phenyl functionality fully integrated into the backbone of the siloxane polymer itself, which provides extra rigidity for enhanced chemical and thermal stability. This results in significantly reduced column bleed and extended useful column lifetime. Thermo Scientific TraceGOLD columns are also preconditioned prior to leaving the factory, which means that out of the box you can expect an exceptionally clean column that requires minimal conditioning prior to sample analysis.

The GC column accounts for greater than 90% of the exposed surface that the sample encounters during analysis; therefore, free silanol sites can cause poor peak shape, compound degradation, and adsorption. Improved inertness in the TraceGOLD SilMS column

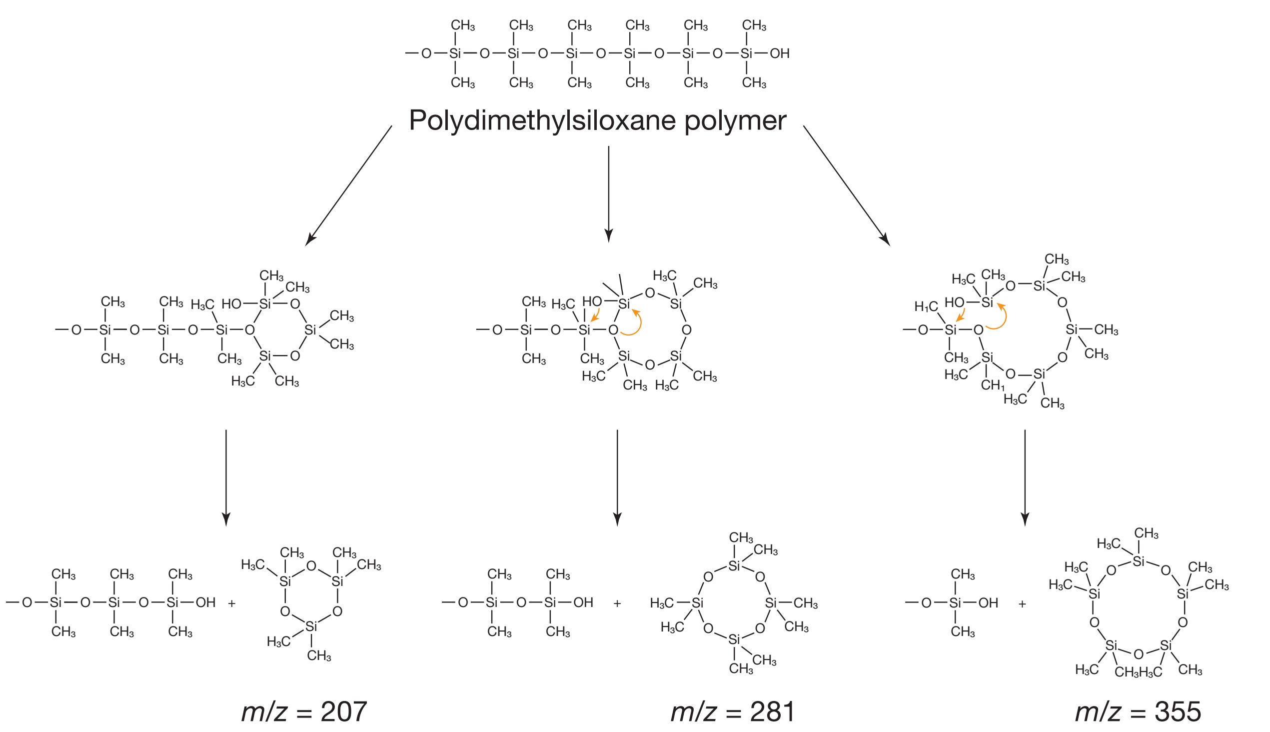
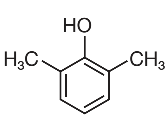


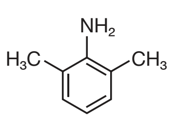
Figure 2. Back-biting reaction that occurs during siloxane polymer bleed process.

range is achieved by sterically hindering the access of active compounds to the fused silica surface, thereby reducing the likelihood of analyte interaction. The high efficiency and reproducibility of the TraceGOLD manufacturing process provides extensive surface coverage and maximizes the column inertness consistently between columns.

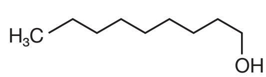
To compare the inertness of TraceGOLD columns, a demanding test mix containing strongly interacting compounds was chosen. The results for the TraceGOLD TG-5 SilMS column and leading competitor UI low bleed columns were then compared directly using the same method. The mix contained probes that measure stationary phase basicity, acidity, and silanol activity. These probes are more indicative of interaction than those used in the more familiar Grob style test mixes as they are more strongly interacting with the stationary phase (Figures 4 and 5). The individual functions of each probe are listed in Table 1.



Weak basicity probe 2,6-dimethyl phenol

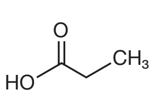


Weak acidity probe 2,6-dimethyl aniline

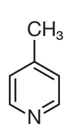


Weak silanol probe 1,2-pentanediol

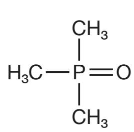
Figure 4. Structures for Grob style mix probes.



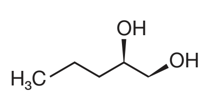
Strong basicity probe 1,2-propionic acid



Strong acidity probe 4-picolinic acid



Strong acidity probe trimethyl phophate



Strong silanol probe 1,2-pentanediol

Figure 5. Structures for Grob mix weak probes and Thermo Scientific UI GC-Mix strong probes.

Table 1. Components and functions for Thermo Scientific UI GC-Mix probes.

Probe		ng on column	Column functional test
1	**1-propionic acid**	**2.0**	**Basicity**
2	1-octene	1.0	Polarity
3	n-octane	1.0	Hydrocarbon marker
4	**4-picoline**	**2.0**	**Acidity**
5	n-nonane	2.0	Hydrocarbon marker
6	**trimethly phosphate**	**2.0**	**Acidity**
7	**1,2-pentanediol**	**2.0**	**Silanol**
8	n-propylbenzene	2.0	Hydrocarbon marker
9	1-heptanol	2.0	Silanol
10	3-octanone	2.0	Polarity
11	n-decane	2.0	Hydrocarbon marker

In addition to the problems associated with phase activity, the swapping and reconditioning of columns can be a problem for laboratories that wish to maximize their instrument up time and increase lab productivity. In general, this process is lengthy and may introduce contamination to the system that subsequently must be cleaned. The Thermo Scientific Thermo Scientific™ ISQ™, TSQ™, and Orbitrap™ series of GC-MS systems use a vent-free source removal tool that permits source removal during GC column conditioning, reducing the need for preventative source maintenance due to excessive siloxane contamination.

In this application note, the TraceGOLD 5 SilMS column is compared to leading competitor UI low bleed columns in terms of performance. The tests examined were out-of-the-box bleed, absolute column bleed, column-to-column variation in bleed, and inertness using a fit-for-purpose column test mix.

Experimental

Consumables

Column:	TraceGOLD TG-5 SilMS, 30 m × 0.25 mm × 0.25 µm (P/N 26096-1420)
Injection septum:	Thermo Scientific™ BTO™, 11 mm (P/N 31303215-BP)
Injection liner:	Thermo Scientific™ LinerGOLD™, Straight liner with glass wool (P/N 453A0164-UI)

Column ferrules: Thermo Scientific™ 15% Graphite/85% Vespel (P/N 290VA191)

Injection syringe: Thermo Scientific™ 10 µL fixed needle syringe (P/N 365D0291)

Solvent: Fisher Scientific™ HPLC grade dichloromethane (P/N 10784941)

Thermo Scientific™ Virtuoso™ vial, clear 2 mL kit with septa and cap (P/N 60180-VT402)

Thermo Scientific™ Virtuoso™ vial identification system (P/N 60180-VT100)

Sample pretreatment and preparation

10 mg/mL primary solution preparation

Individual 10.0 mg/mL solutions of probes 1–11 were prepared by weighing 100.0 mg into separate 10.0 mL volumetric flasks and diluting to volume with dichloromethane.

Mixed Thermo Scientific UI GC-Mix probe preparation

The test probe was prepared as outlined in Table 2.

Separation conditions

Instrumentation

- Thermo Scientific™ TRACE™ 1310 gas chromatograph (P/N 14800320)
- Thermo Scientific™ TriPlus RSH™ Autosampler (P/N 1 R77010-0100)
- Thermo Scientific™ Instant Connect Electron Flame Ionization Detector (FID) (P/N 19070001FS)
- Thermo Scientific™ ISQ™ LT Single Quadrupole GC-MS

Method conditions

Instrumentation: TRACE 1310 GC with TriPlus RSH Autosampler

Carrier gas: Helium

Split flow: 175.0 mL/min

Split ratio: 125:1

Column flow: 1.40 mL/min

Injector type: Split/Splitless

Injection volume: 2 µL

Injector mode: Split, constant flow

Injector temperature: 220 °C

Detector type: Flame ionization detector (FID)

Detector temperature: 250 °C

Detector air flow: 350 mL/min

Detector hydrogen flow: 35 mL/min

Detector nitrogen flow: 40 mL/min

Oven temperature profiles:

Inertness testing: 65 °C (15 min hold)

Bleed testing: 40 °C to 320 °C (4 °C/min, 30 min hold)
320 °C to 325 °C (4°C/min, 30 min hold)
325°C to 330 °C (4°C/min, 30 min hold)

Data processing

The Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) was used for data acquisition and analysis.

Table 2. Preparation of the Thermo Scientific UI GC-Mix.

Probe		Solution Used (mg/mL)	Volume pipetted (mL)	Final volume (mL)	Final Concentration (µg/mL)	Solvent
1	1-propionic acid	2.0	2	100	200	Dichloromethane
2	1-octene	1.0	1		100	
3	n-octane	1.0	1		100	
4	4-picoline	2.0	2		200	
5	n-nonane	2.0	2		200	
6	trimethly phosphate	2.0	2		200	
7	1,2-pentanediol	2.0	2		200	
8	n-propylbenzene	2.0	2		200	
9	1-heptanol	2.0	2		200	
10	3-octanone	2.0	2		200	
11	n-decane	2.0	2		200	

Results and discussion

Column conditioning

The chromatogram below (Figure 6) shows the differences in the bleed profile for the market-leading low bleed UI column versus the TraceGOLD TG-5 SilMS column. The black trace for the TraceGOLD TG-5 SilMS column shows negligible contamination peaks (compared with the competitor blue trace peaks 1-3), and the column quickly equilibrates to a point of a stable baseline. The TraceGOLD range of columns come preconditioned, meaning that they are quicker to condition, which reduces instrument downtime.

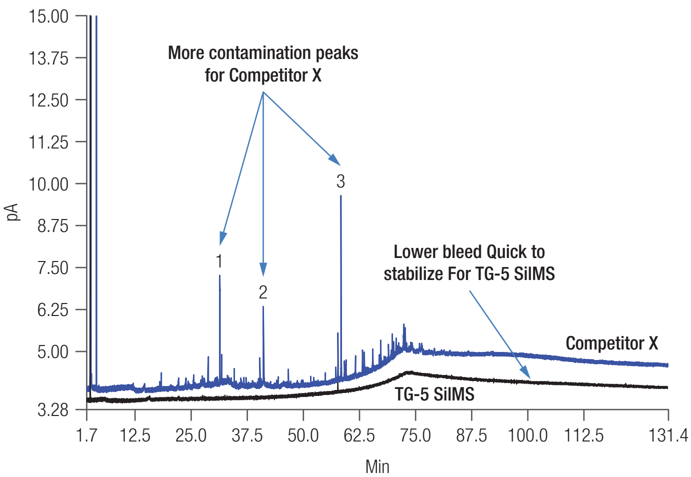


Figure 6. Chromatogram showing column bleed for TraceGOLD TG5-SilMS column and the leading competitor low bleed UI column following solvent injection directly out of the box.

Column bleed

The TraceGOLD SilMS columns exhibited exceptionally low bleed when compared to competitor columns following preconditioning as stated by the manufacturer (Figure 7). The bleed was calculated by subtracting the bleed at 40 °C from the bleed at 320 °C and 325 °C.

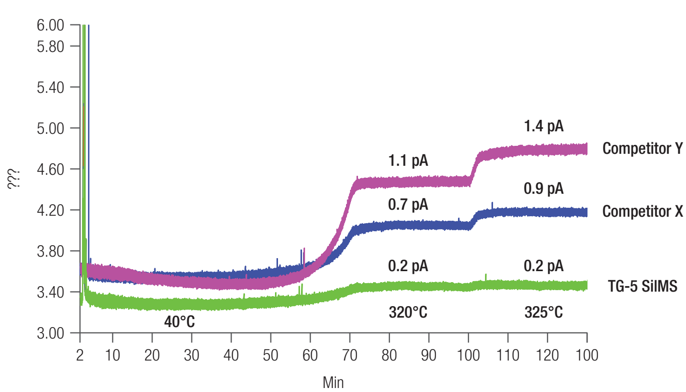


Figure 7. Overlay chromatogram showing column bleed for TraceGOLD TG5-SilMS column and leading competitor low bleed UI columns.

Batch reproducibility versus the competition

The TraceGOLD SilMS columns exhibited excellent batch-to-batch reproducibility compared to leading competitor low bleed columns (Figure 8). Another major advantage of using the TraceGOLD TG-5 SilMS column over some competitors' columns is that its top isothermal temperature is 330 °C, which means methods can be made faster, increasing lab productivity.

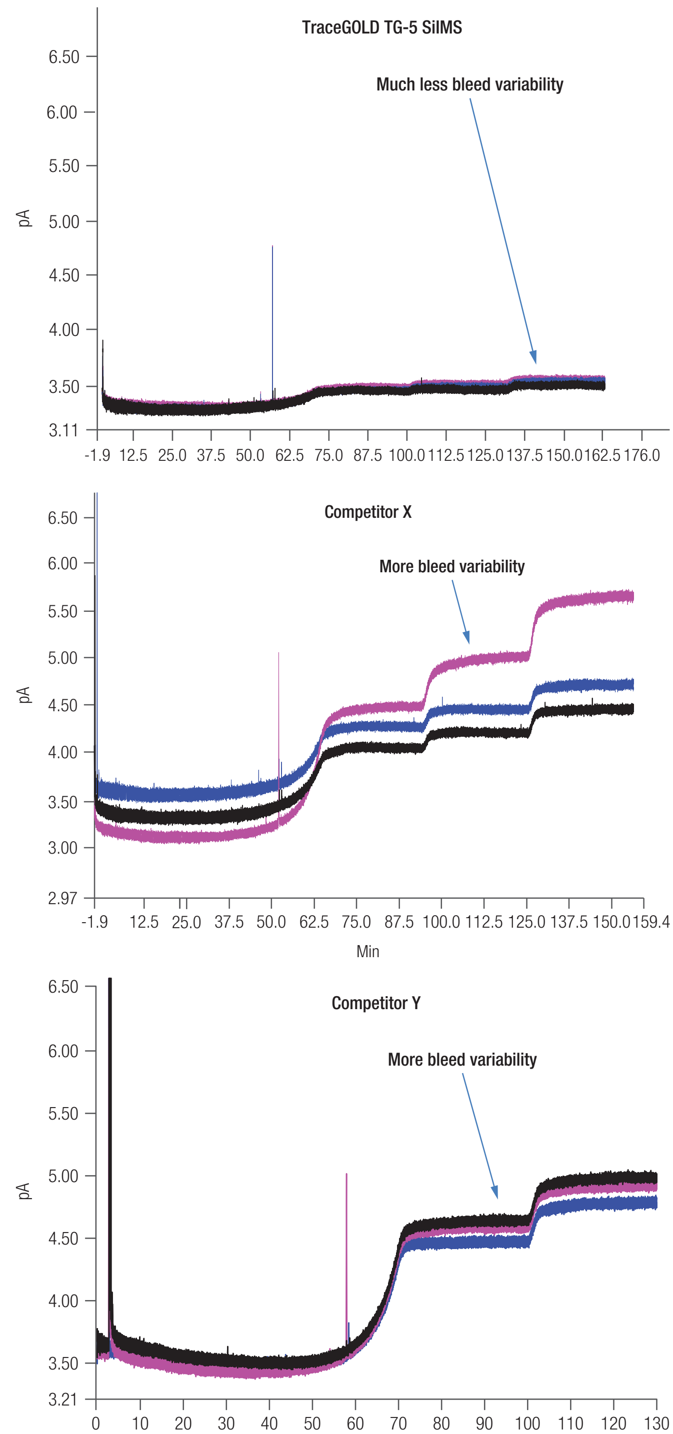


Figure 8. Overlaid column bleed for three lots from TraceGOLD TG5-SilMS, competitor X, and competitor Y columns.

The variation in column bleed for three separate lots of the TraceGOLD TG-5 SilMS, competitor X, and competitor Y low bleed columns were examined (Figure 9). The standard deviation for the TraceGOLD TG-5 SilMS columns was 0.02 pA, which demonstrates an adherence to tight controls in manufacture and quality control. Compared to the competitor columns, the variation in column bleed was 80% and 95% lower. The overall bleed was also found to be 80% lower than both competitors at 325 °C, which is the top isothermal temperature for these competitors. These are important factors as column-to-column performance is vitally important for generating robust and rugged analytical data.

Figure 10 shows components 4, 6, and 7 are significantly improved (30, 10, and 50% improved asymmetry values) on the TraceGOLD TG-5 SilMS column versus competitor X. Probes 4 and 6 test the column's acidity, whereas probe 7 is used to assess the column's free silanol activity. These probes are an excellent differentiator for assessing column performance due to their high polarity and modes of interaction. The TraceGOLD TG-5 SilMS column shows minimal differences in peak tailing across the remaining components compared to the competitor, indicating that overall the TraceGOLD column has superior inertness.

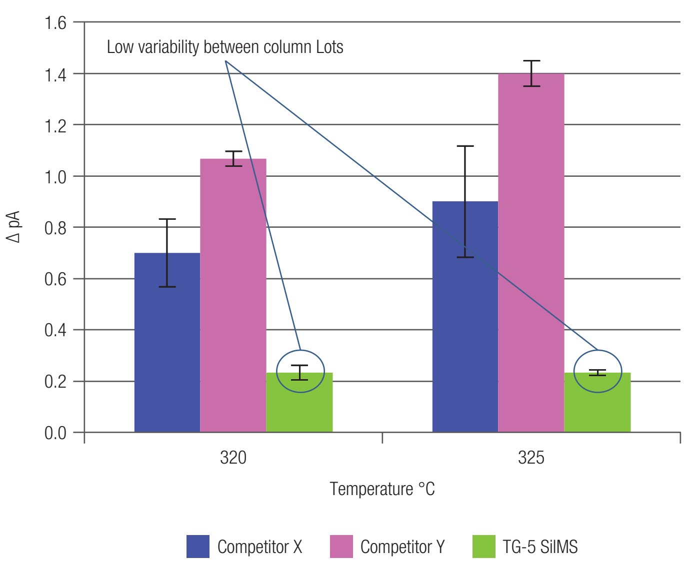


Figure 9. Variation in column bleed for three separate lots of columns tested identically Inertness compared to the market leader UI column.

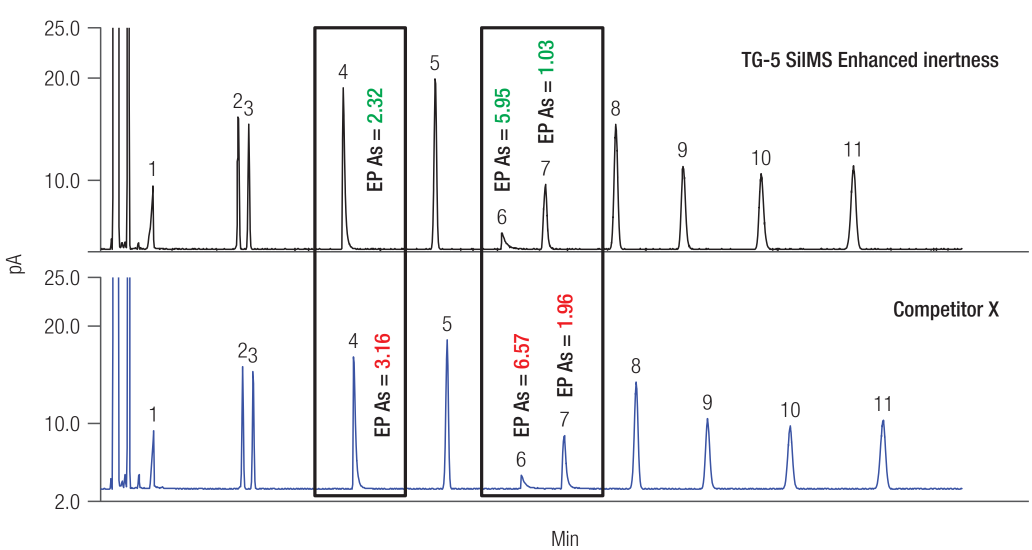


Figure 10. Chromatogram showing Thermo Scientific UI GC-Mix for TraceGOLD TG5-SilMS column and market-leading competitor column.

Conclusions

- Thermo Scientific silphenylene (SilMS)-based columns, such as the TraceGOLD TG-5 SilMS column, demonstrate up to 80% lower bleed compared to premium competitor low bleed columns.

- Column bleed variation across batches is 80% less than competitor ultra-inert low bleed columns.

- Superior column inertness was demonstrated for the TraceGOLD TG-5 SilMS column compared to the market-leading UI column with a 50% improvement in the asymmetry value in the case of the silanol probe 1,2-propanediol.

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