New high temperature PEG GC column with ultra-low bleed level

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Introduction

"WAX columns" based on 100% Polyethylene Glycol (PEG) stationary phase have been commonly used for years for the analysis of a wide variety of compounds in numerous applications, such as flavor & fragrance and industrial chemical quality control. These columns often suffer from a limitation of upper temperature limit (Tmax), mainly up to 250°C/260°C and high bleed level resulting in low sensitivity, low reproducibility, poor column lifetime and increased analysis time in conventional GC and GC/MS applications. Moreover, having current PEG-based column as 2nd dimension column in comprehensive GC×GC encounters a significant drawback of separation capacity reduction because of its limited Tmax compared to 1st dimension non-polar column.

Here, we present a new High-Temperature WAX (HT-WAX) GC column, where a combination of inertness, bleed level and upper temperature limits of the column was investigated [1,2]. Inertness testing was evaluated via rigorous procedures using strong test probes in most demanding GC and GC/MS applications at critical levels. Moreover inertness thermal stability was tested during a longevity test at different upper temperature limits. Bleed level was measured at different upper temperature limits and compared to current WAX columns.

The first results on the HT-WAX suggest the column may present a new step in the search for a tempearture stable WAX columns. Its good inertness and ultra-low bleed level are suitable for the most sensitive GC and GC/MS applications and can be used as 2nd dimension polar column with extended upper temperature limits in comprehensive GC×GC applications.

Experimental

Inertness testing

Table. 1 DB-WAX UI test mix in Dichloromethane

Peak No.	DB-WAX UI	Amount on column (ng)
1	5-Nonanone	3.3
2	Decanal	3.3
3	Propionic acid	3.3
4	Ethylene glycol	3.3
5	Heptadecane	1.65
6	Aniline	3.3
7	Methyl dodecanoate	3.3
8	2-Chlorophenol	3.3
9	1-Undecanol	3.3
10	Nonadecane	1.65
11	2-Ethylhexanoic acid	6.6
12	Ethyl maltol	6.6

Analytical conditions for DB-WAX UI test mix : Injector temp: 250 °C, split 1:75, injection volume 1 µL, Carrier gas flow rate 1.1 mL/min, H_2. Oven temp: 130 °C isothermal; FID detector: temp 260 °C

Table 2. Modified Grob test mix in Dichloromethane

Peak No.	Modified Grob	Amount on column (ng)
1	Decane	2.5
2	Dodecane	2.5
3	Decanal	2.5
4	2,3-Butanediol*	5
5	1-Octanol	2.5
6	C10 FAME	2.5
7	*n*C11-FAME	2.5
8	Dicyclohexylamine	5
9	*n*C12-FAME	2.5
10	2,6-Dimethylaniline	2.5
11	2,6-Dimethylphenol	2.5
12	2-Ethylhexanoic acid	5
13	Ethyl maltol	5

**2,3-Butanediol is present as two isomers, RR/SS and meso isomers respectively.*

Analytical conditions for modified Grob test mix: Injector temp: 250 °C, split 1:100, injection volume 1 µL; Carrier gas flow rate 1.35 mL/min, H_2. Oven temp: initial temp 60 °C, ramp 3 °C/min, final temp 200 °C; FID detector: temp 260 °C.

Bleed measurement

Bleed was measured at different upper temperature limits in the range of 250 °C and 290 °C. Columns were conditioned for 11 hours at each upper temperature limit to measure the bleed. Detail method for bleed measurement was found in [2].

Results and Discussion

Bleed level of HT-WAX at different upper temperature limits

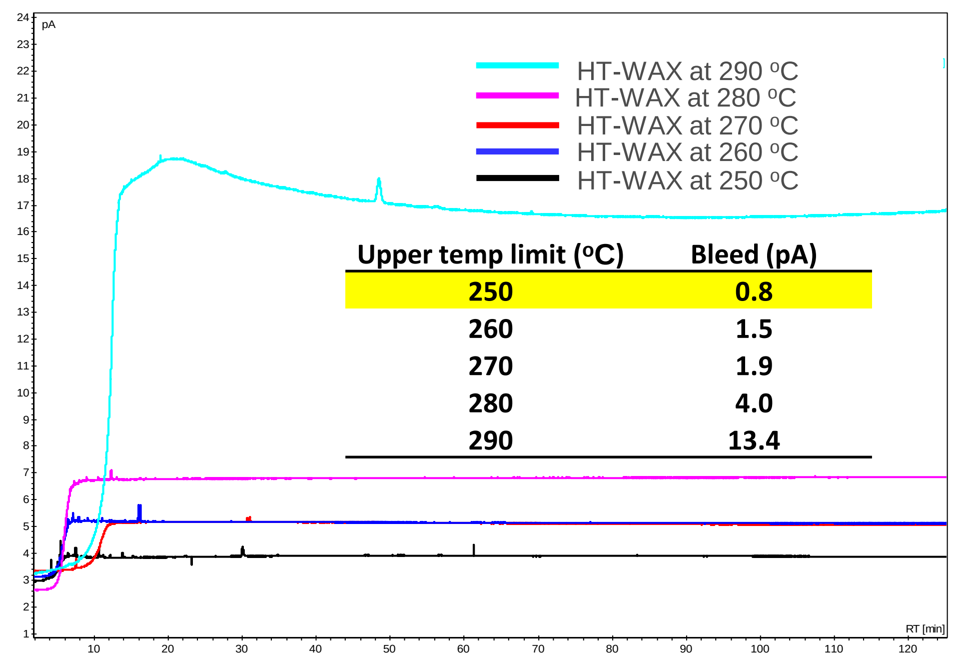

Fig.1 Bleed level measured on HT-WAX prototypes after conditioning 11 hours at different upper temperature limits in a range of 250 °C and 290 °C. Column: 30 m x 0.25 mm id, 0.25 µm.

Good and stable inertness at 280 °C on HT-WAX

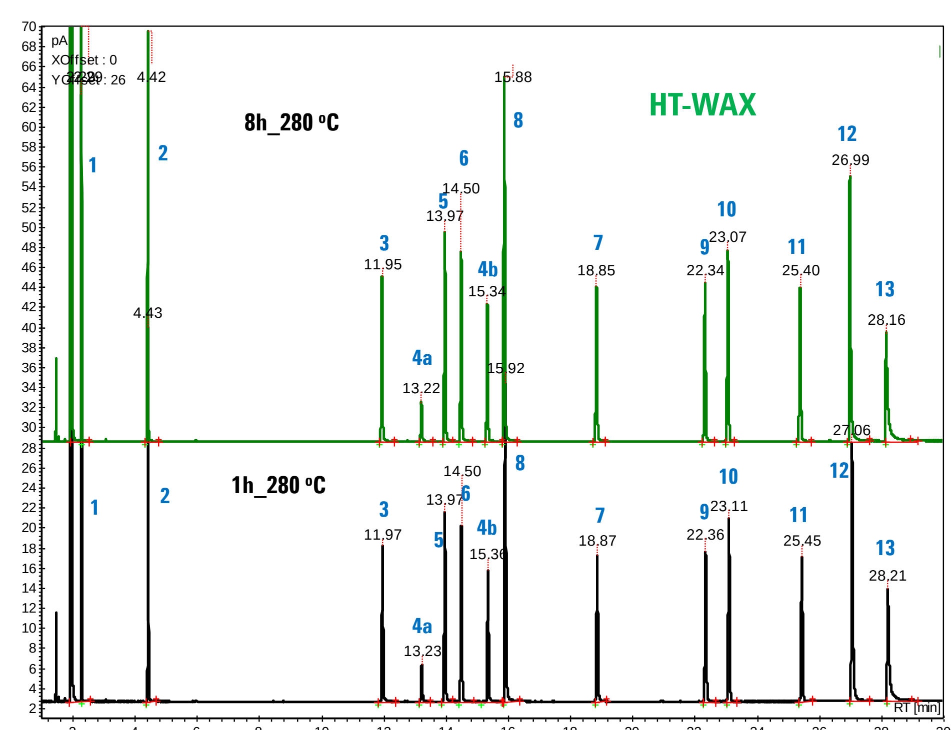

Fig. 2 Example of FID chromatograms of the modified Grob test mix on HT-WAX after conditioning 1 hour and 8 hours at 280 °C. See Table 2 for GC conditions and peak identifications. Column: 30 m x 0.25 mm id, 0.25 µm.

Improve detection limit for analysis of phenol test mix on HT-WAX using 5977B High Efficiency Source GC/MSD

A phenol test mix containing 32 critical components at approximately 45pg/component on-column was analyzed on both HT-WAX and "lowest bleed level" non-Agilent WAX using GC/MS.

Results and Discussion

Bleed comparison of WAX columns at 250 °C

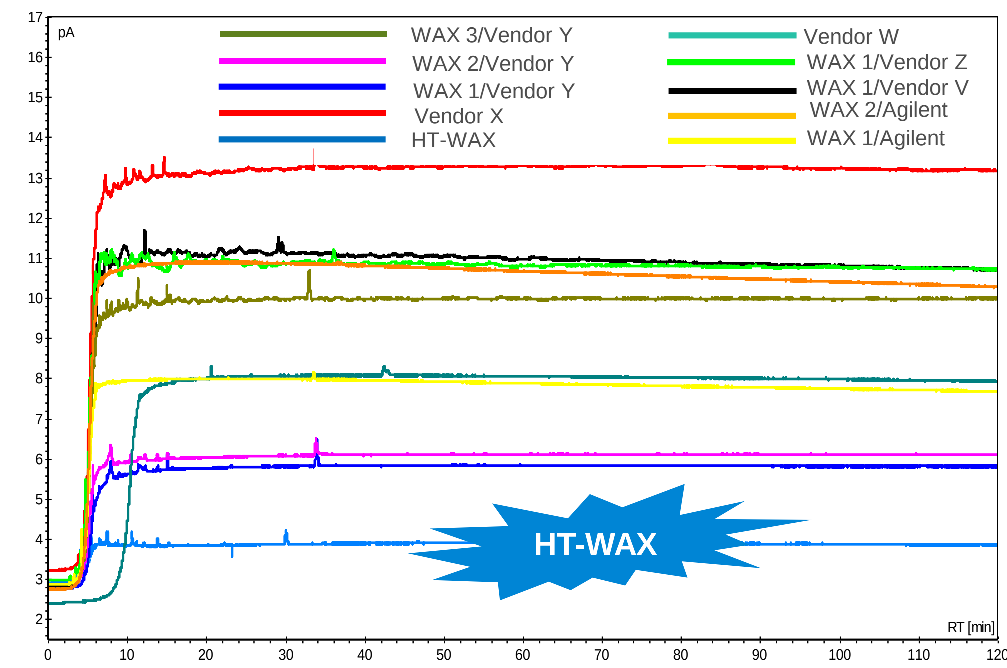

Fig.4 Bleed level measured on HT-WAX compared to current WAX columns after conditioning 11 hours at 250 °C. Column: 30 m x 0.25 mm id, 0.25 µm.

Inertness comparison after 50 hours conditioning at 250 °C

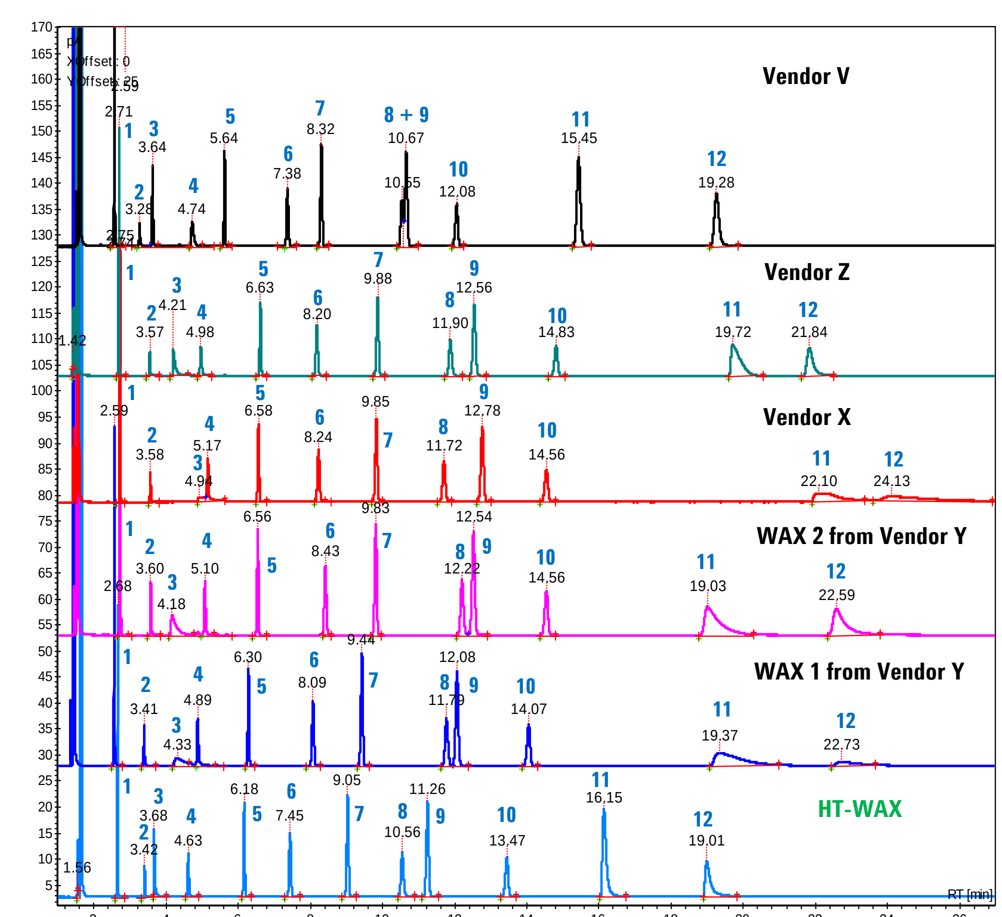

Fig. 5 Example of FID chromatograms of the DB-WAX UI test mix on HT-WAX and non-Agilent WAX columns after conditioning 50 hours at 250 °C. See Table 1 for GC conditions and peak identifications. Column: 30 m x 0.25 mm id, 0.25 µm.

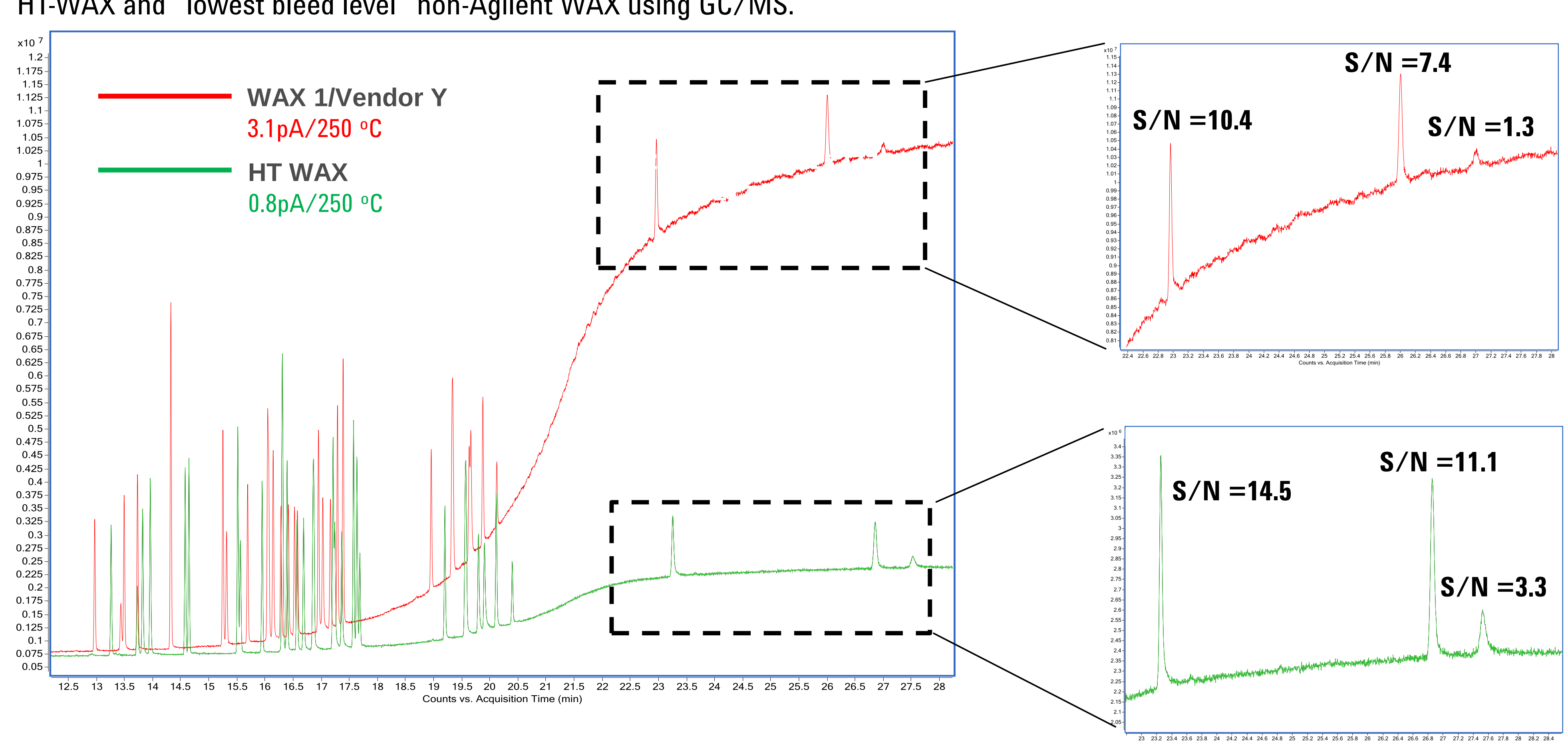

Fig. 3 Example of GC/MS chromatograms of phenol test mix on HT-WAX and "lowest bleed level" non-Agilent WAX column. GC conditions: Column: 30 m x 0.25 mm id, 0.25 µm, Column flow 1.2 ml/min with He carrier gas, Split ratio 50, Oven temperature: 40 °C, 0.5 min, 10 °C/min to 250 °C, 4 min hold. MS full scan mode in a range of 35 and 550 m/z values.

Conclusions

HT-WAX prototype shows promise as a valuable addition to the WAX column family because of its good inertness and ultra-low bleed level. This contributes to significant improvement of detection limit and column lifetime. Moreover an extended column's upper temperature limit to approximately 280 °C/290 °C provides significant benefits for conventional GC, GC/MS and comprehensive GC×GC applications. Furthermore, a similar selectivity to existing WAX columns allows a simple switch to this column due to minimal method modification and re-validation.

References

[1] Biermans F., Duvekot J. Patent Chromatography columns US 9034186 B2 (2005).

[2] J Oostdijk, NA Dang. Poster B.02 "New definition for maximum allowable operating temperature of WAX GC columns", 40th ISCC (2016).