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Thermal Desorption GC Analysis of High Boiling, High Molecular Weight Hydrocarbons

Edward A. Pfannkoch, Jacqueline A. Whitecavage, and Jeffrey Christenson
Gerstel, Inc., 701 Digital Drive, Suite J, Linthicum, MD 21090, USA

Summary

Thermal desorption is a valuable and versatile GC sample introduction technique for a wide variety of solid, liquid, and gaseous samples that are not amenable to direct injection into the GC instrument. Gas-phase samples can be collected and concentrated onto adsorbent tubes from the atmosphere or from the headspace over liquid or solid samples, and volatiles trapped onto the tubes are thermally desorbed and introduced onto the GC column. Direct thermal extraction of volatiles and semivolatiles in solid materials allows simplified trace GC analysis of volatiles and semivolatiles in such samples as polymers, waxes, powders, pharmaceutical formulations, foods, and cosmetics. For liquid samples, the Gerstel Twister stir bar sorptive extraction technique combined with thermal desorption enables trace and ultra-trace GC or GC/MS analysis.

The basic design and flow path of a thermal desorption system can strongly influence the ability to transfer high boiling compounds from the sample to the GC column. Quantitative transfer of high boiling, high molecular weight compounds is quite challenging for some thermal desorption

instruments that incorporate long transfer lines, valves, and various cold spots; such instruments typically fail for high-boiling compounds corresponding to C_{26} and higher. The GERSTEL Thermal Desorption System (TDS) is a direct-transfer thermal desorption instrument with no valves or septa seals in the flow path, and a very short, highly inert transfer line. These design features ensure leak-free operation and provide for extremely efficient transfer of both very low and very high boiling analytes, including C_{40} and higher.

High boiling hydrocarbons were introduced into a GC by either liquid injection or thermal desorption using a GERSTEL TDS. An Agilent test mix of C_5-C_{40} hydrocarbons with boiling points ranging from approximately 35°C to 566°C was used. For the thermal desorption test, the hydrocarbons were spiked into empty glass tubes. TDS conditions were optimized for trapping the hydrocarbons in the C_{15}-C_{40} range.

A standard desorption flow of 50 mL/min was sufficient to give complete transfer of hydrocarbons up to C_{32}, whereas 80 mL/min desorption flow was necessary to completely transfer all hydrocarbons up to C_{40}. Under optimized conditions, peak areas for C_{15}-C_{40} hydrocarbons were similar whether introduced by liquid injection or by thermal desorption.

A previous study (GERSTEL TechNote – Thermal Desorption of High boiling Diesters) showed that trapping efficiency in the inlet for high boiling diesters was the same between 100°C and -70°C, suggesting that for high boiling hydrocarbons in the C_{15}-C_{40} range, satisfactory trapping would be achieved at temperatures that are easily provided by Peltier-based cooling of the CIS 4 (40°C), eliminating the need for liquid cryogenic cooling.

Instrumentation

GERSTEL Automated Thermal Desorption System (TDS 2/TDS A) with temperature programmable cooled injection system (CIS 4) using LN2 cooling or Peltier cooling; Agilent 6890 GC with FID.

Experimental

Sample.

Agilent boiling point calibration sample #1 (5080-8716) diluted 1:100 in methylene chloride

Sample preparation.

The sample was sonicated with heat prior to dilution. It was necessary to warm the methylene chloride to completely dissolve all components in the sample.

Sample introduction.

Liquid Injection. 1 uL of sample was injected manually into a CIS 4 inlet heated at 300°C with a septumless sampling head installed.

Thermal Desorption. 1 uL of sample solution was spiked onto clean empty glass TDS tubes and loaded onto the autosampler magazine. Samples were desorbed in the splitless mode under either 50 or 80 mL/min helium flow at 300°C for 10 minutes. Analytes were cold trapped in the CIS 4 inlet on a glass wool liner. When desorption was complete, analytes were transferred to the column by heating the inlet rapidly to 400°C. A 3:1 sample split was used for the transfer.

Analysis conditions.

TDS 2	splitless, 20°C, 60°C/min, 300°C (10 min)
PTV	insert type: glass wool solvent vent (50 mL/min), split 3:1 -120°C, 12°C/s, 400°C (3 min)
Column	15m HP-1 (Agilent) d_i= 0.53mm, d_f= 0.15µm
Pneumatics	He, constant flow=15.2mL/min
Oven	35°C (1 min); 7.5°C/min; 325°C (6 min)
Detector	FID

Results & Discussion

Transfer of high boiling hydrocarbons from the TDS to the inlet was compared to a direct liquid injection into a hot inlet to assess the transfer efficiency of the thermal desorption step. Figure 1 shows an overlay of the chromatograms obtained for a 1 uL sample injected into a hot inlet or into an empty glass TDS tube. Note that there is a slight peak retention time difference between the hot liquid and thermal desorption sample introduction due to the time necessary for the inlet to heat after thermal desorption. Excellent agreement was seen for peak areas in the sample range between C_{15}-C_{40} for these two introduction techniques.

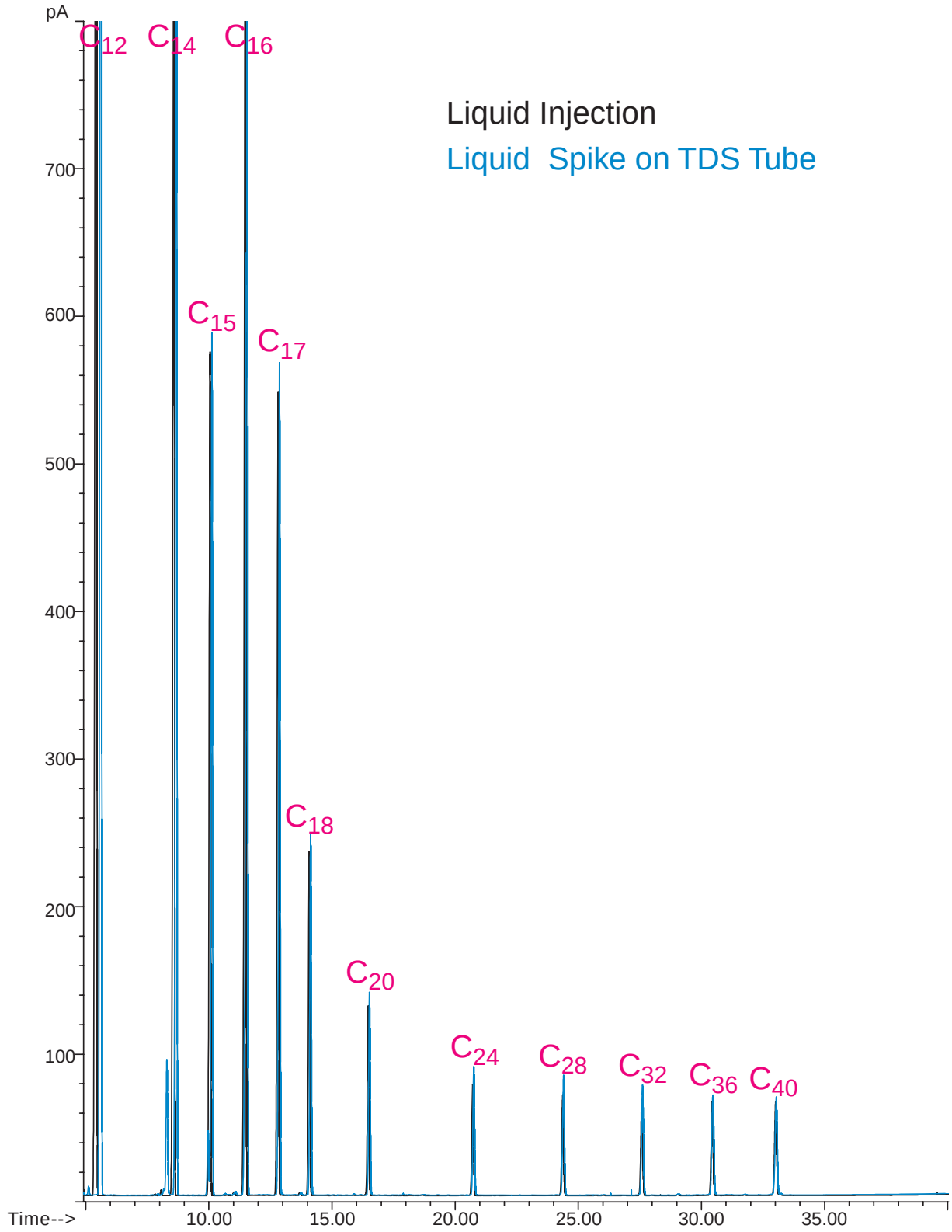

Figure 1. Overlay of 1 uL liquid injection and 1 uL liquid spike on TDS tube.

The study of high boiling diesters showed good compound transfer (up to C_{26}) using 50 mL/min desorption flow. Since this study used hydrocarbon standards up to C_{40}, two different desorption flows were tested on the TDS (50 mL/min and 80 mL/min) to see whether an improvement in very high boiler ($>C_{26}$) transfer could be obtained.

Table 1 shows the raw data for the mean peak areas from these runs. No significant drop off of peak area was seen with the standard 50 mL/min desorption flow, except perhaps for the highest boiling ($>C_{36}$) components. It appears that a higher desorption flow of 80 mL/min may provide a slight improvement if very high boiling components are present.

Table 1. Peak areas for liquid injection and liquid spike on TDS tube using different vent flows.

Compound	Wt%	Peak Area		
		TDS[1] [50 mL/min]	TDS[2] [80 mL/min]	Manual Injection[3]
C15	5.11	2143	2341	2249
C16	10.28	4582	5103	4598
C17	5.17	2231	2497	2248
C18	2.21	969	1091	974
C20	1.30	562	636	555
C24	0.9	384	436	362
C28	0.9	382	435	357
C32	0.9	370	423	351
C36	0.91	365	421	367
C40	0.92	336	404	386

[1] Peak Area at TDS Vent Flow, n=2
[2] Peak Area at TDS Vent Flow, n=3
[3] Peak Area at Manual Injection, n=2

Figure 2 shows a chromatogram obtained for the hydrocarbon mix using 80 mL/min desorption flow, followed by desorption of a blank tube. No significant carryover of any high boiling components is seen in the system. This is a direct result of the valveless, highly inert, direct flow path design of the GERSTEL TDS.

Under conditions optimized for complete high boiler transfer, trapping efficiency of lower hydrocarbons is expected to decrease. It is therefore advisable to optimize the desorption and trapping conditions for the particular analyte range of interest, rather than using an extreme set of time, temperature, and flow conditions for all samples.

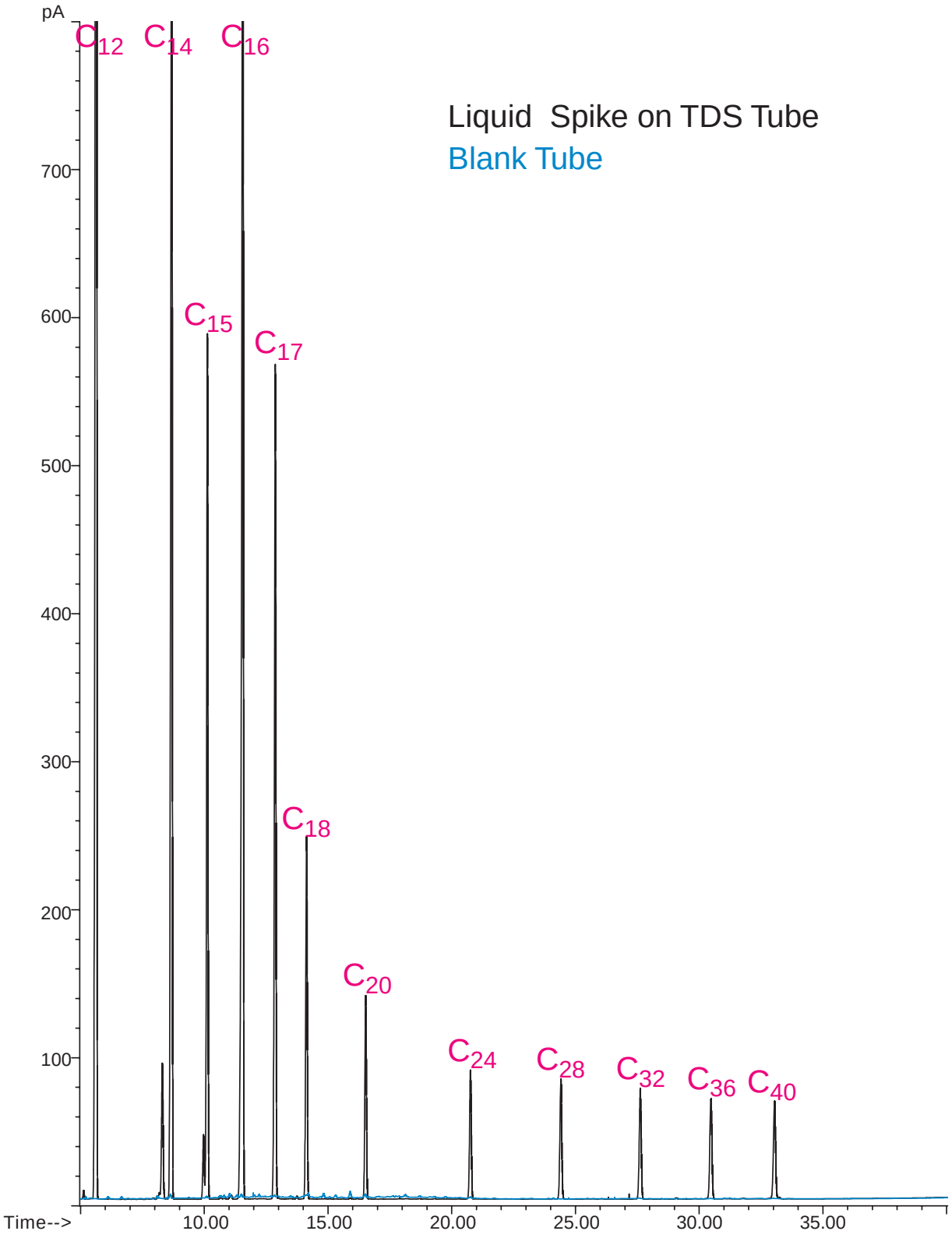

Figure 2. Overlay of 1ul liquid spike on TDS tube and following blank tube run.

Conclusions

By using a very short direct transfer line, an integrated cold trap/inlet, and no valves or septa seals in the flow path, the GERSTEL TDS is able to transfer a very wide boiling point range of compounds onto a GC column. Compounds with boiling point equivalents equal to or greater than C_{26} can be transferred onto the GC column as efficiently as with standard hot split injection. This capability significantly extends the range of compounds that can be quantitatively transferred onto the GC column, enabling the applicability of thermal desorption sampling to a far wider range of compounds.

GERSTEL GmbH & Co. KG
Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany
+49 (0) 208 - 7 65 03-0
+49 (0) 208 - 7 65 03 33
gerstel@gerstel.com
www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.
701 Digital Drive, Suite J
Linthicum, MD 21090
USA
+1 (410) 247 5885
+1 (410) 247 5887
sales@gerstelus.com
www.gerstelus.com

GERSTEL AG
Wassergrabe 27
CH-6210 Sursee
Switzerland
+41 (41) 9 21 97 23
gerstelag@ch.gerstel.com
www.gerstel.ch

GERSTEL K.K.
1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan
+81 3 5731 5321
+81 3 5731 5322
info@gerstel.co.jp
www.gerstel.co.jp

GERSTEL LLP
Level 25, North Tower
One Raffles Quay
Singapore 048583
+65 6622 5486
+65 6622 5999
SEA@gerstel.com
www.gerstel.com

GERSTEL Brasil
Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
+55 (11)5665-8931
+55 (11)5666-9084
gerstel-brasil@gerstel.com
www.gerstel.com.br

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