GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

TechNote 3/2002

The Use of Different PTV Inlet Liner Types for Trapping Alkanes, Aromatics and Oxygenated Compounds During Thermal Desorption

Bita Kolahgar
Gerstel GmbH & Co. KG, Eberhard-Gerstel-Platz 1, D-45473 Mülheim an der Ruhr, Germany

Edward Pfannkoch
Gerstel, Inc., Caton Research Center, 1510 Caton Center Drive, Suite H, Baltimore, MD 21227, USA

Keywords
Thermal desorption, PTV, Inlet liner, sample introduction

Abstract
PTV inlets are often used for cryo-focussing and trapping of analytes for large volume, headspace, and thermal desorption applications. Selecting and optimizing trapping conditions for thermal desorption applications can be challenging, since often a wide variety of analytes spanning a broad boiling point range are present in each sample. For efficient, high flow thermal desorption systems such as the Gerstel TDS 2, a variety of inlet liner configurations with different trapping characteristics are available.

This study was conducted to qualify the best type of liner for the determination of alkanes, aromatics and oxygenated compounds by thermal desorption GC. Inlet liners packed with materials of different trapping strengths ranging from glass wool to adsorbents (Carbotrap™ or Tenax TA™) to special purpose multi-bed liners were used to cryo-focus test mixtures of alkanes, aromatics and oxygenates thermally

desorbed from air sampling adsorbent tubes. The parameters trapping temperature and desorption flow were optimized for the best trapping efficiency. Guidelines are given for choosing appropriate trapping conditions for these analyte classes.

Introduction

A number of GC sample introduction techniques benefit by a pre-focussing step prior to separation on the analytical column. Although this can sometimes be accomplished by using a cryogenic cooling device on the head of the column itself, this technique has several limitations. First, the flow through the cooled region is limited to column flow, therefore sample introduction techniques that benefit by high flow (such as thermal desorption, purge and trap and online sampling) require a significant split of the sample flow ahead of the column. This severely limits sample load on-column. Second, trapping at sub-zero temperatures in a narrow-bore capillary is prone to blockage due to freezing of water. Third, trapping on the column will also trap contaminants, impurities and other undesirable materials on the analytical column, often necessitating cutting sections from the head of the column to eliminate this interfering material.

A programmed temperature vaporizing inlet (PTV) can be used to refocus analytes before introduction onto the analytical column. Using this technique, the entire sample stream, whether it be headspace injection or high gas flow from thermal desorption, purge and trap or online sampling, is passed through the trapping region in the inlet prior to the split vent. If trapping conditions are properly chosen then the entire sample will be trapped in the inlet liner before the high gas flow exits via the split vent. Since trapping is done in the inlet liner which has a much larger internal diameter than a GC column it is much less prone to blockage due to freezing. Also, any low-volatility contaminants that may be trapped along with the sample accumulate in the easily replaced inlet liner, protecting the integrity of the analytical column.

The first step in selecting appropriate trapping conditions is the choice of inlet liner. Several types of inlet liners are commercially available, ranging from inert supports (glass or quartz wool) to chemical adsorbents (Tenax TA™ or Carbotrap™). Custom combinations of adsorbents can also be prepared to meet special application needs. Once a liner type is chosen, trapping conditions (flow and temperature) must be optimized for the analyte range of interest. This study provides a set of guidelines for selecting inlet liner type and trapping conditions for aliphatic, aromatic and oxygenated organic compounds with boiling points between 80°C and 290°C.

Experimental

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) with mass selective detection (5973, Agilent Technologies) equipped with a Thermal Desorption system with autosampler (TDS2 & TDSA, Gerstel) and a PTV inlet (CIS4, Gerstel).

Analysis Conditions.

TDS 2	Tube Tenax TA™, 60/80 mesh splitless 20°C, 60°C/min, 280°C (5 min)
PTV	insert type: see figures solvent vent flow: see figures, split ratio 30:1 initial temp: see figures, 12°C/s, 280°C (3 min)
Column	30m HP-5 (Agilent), d_i= 0.25mm, d_f= 0.25mm
Pneumatics	He, constant flow = 1.0 mL/min
Oven	40°C (1 min), 10°C/min, 300°C
MSD	scan, 35-300 amu

All data were analyzed by using target ions in the extracted ion mode. The molecular ions of the compounds are used as target ions (see Table 1).

Standard preparation. A standard mixture of 14 compounds (alkanes, aromatics and oxygenated VOCs) at a concentration of 2 mg/mL in hexane was prepared for this study. The compounds investigated in this study are listed in table 1.

Sampling. Gas sampling TDS tubes filled with Tenax TA™ were spiked with the standard mixture. For this purpose, 1 µL of the standard was injected through a Gerstel septumless sampling head on the Tenax bed. The tubes were purged 8 min with a helium flow of 400 mL/min during and after the injections. Afterwards the tubes were placed in the TDS autosampler for thermal desorption and the subsequent GC/MS analysis.

Table 1. Investigated compounds.

Compound	BP [°C]	Target Ion
Benzene	80	78
Heptane	98	43
Toluene	110	91
Acetic acid butyl ester	125	43
Octane	126	43
o-Xylene	144	91
Nonane	151	43
Decane	174	43
1,2,3-Trimethylbenzene	175	105
Acetophenone	202	105
Dodecane	216	57
Tetradecane	252	57
Pentadecane	270	57
Hexadecane	287	57

Note: Throughout the following figures, aliphatics are shown in black; aromatics in blue , and oxygenates in red.

Figure 1 shows a total ion chromatogram of the standard mixture.

Variation of cryo-focussing temperature. All spiked Tenax TDS tubes were desorbed using the same desorption conditions. The cryo-focussing of the compounds during thermal desorption was performed at 3 different temperatures (-150°C, -40°C, 10°C). In the case of CIS liners filled with Tenax TA™, cryo-focussing was performed at -40°C and 10°C. The cryo-focussing temperature yielding the highest peak area was judged to be the best.

Variation of desorption flow. Using the optimized cryo-focussing temperature, the desorption flow was varied: 70 mL/min, 50 mL/min, and 30 mL/min. The desorption flow yielding the highest peak area was judged to be the best.

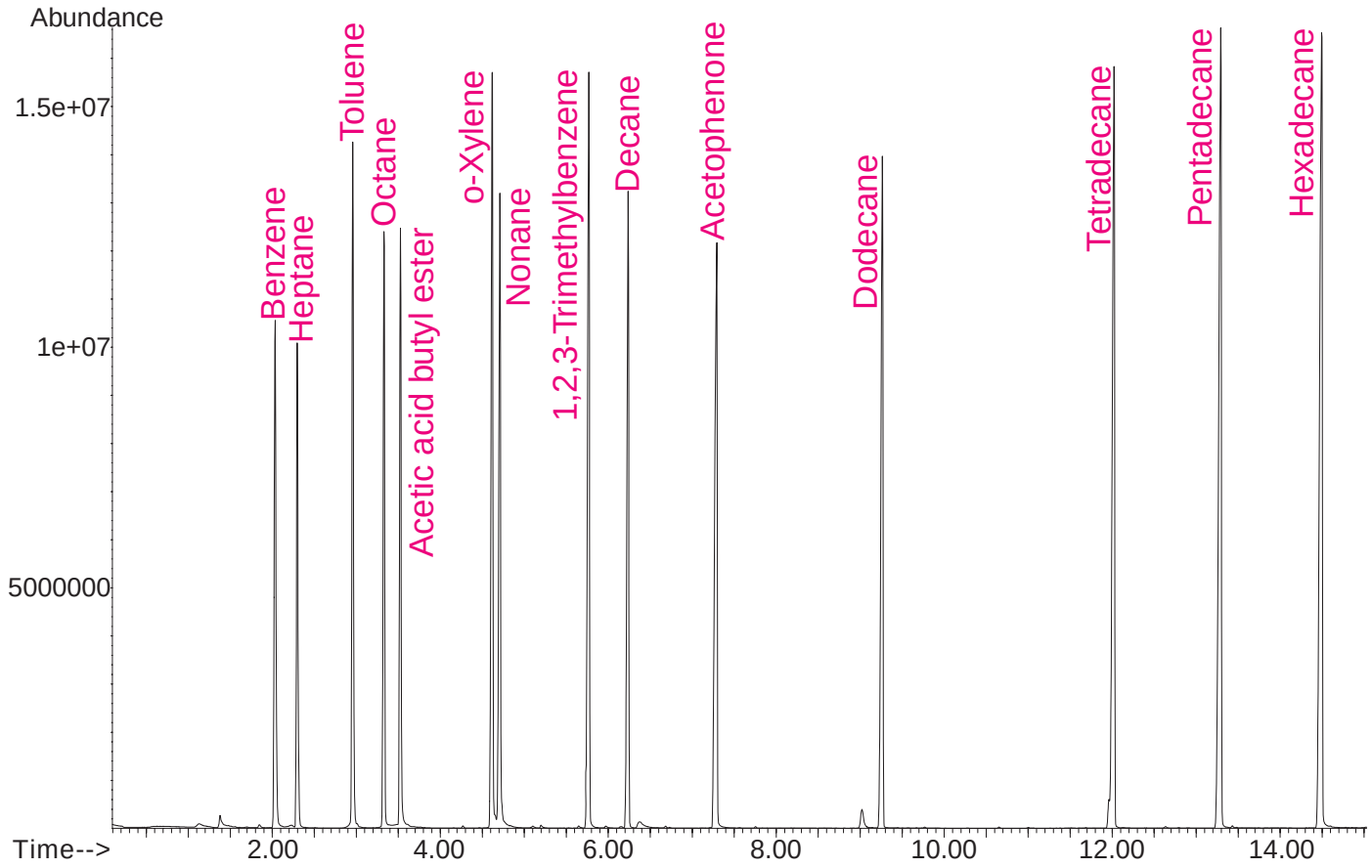

Figure 1. Total ion chromatogram of the standard mixture.

Results and Discussion

Cryotrapping on inert supports. The simplest approach to pre-focussing analytes in a PTV inlet is to cryotrap onto inert supports. Glass wool and quartz wool packed inlet liners provide sufficient surface area to trap volatile analytes when cooled cryogenically. Quartz wool contains fewer impurities than glass wool, and therefore may be more inert toward some analyte types. Both glass and quartz wool are deactivated by silanization to further passivate the surfaces. Pesticide grade glass wool packed inlet liners are specially deactivated after the glass wool is inserted into the liner.

The results of cryotrapping on inert supports with different cryo-focussing temperatures and different desorption flows are shown in figures 2 – 4. The columns in the diagrams are averages of 3 measurements and the error bars indicate the standard deviations.

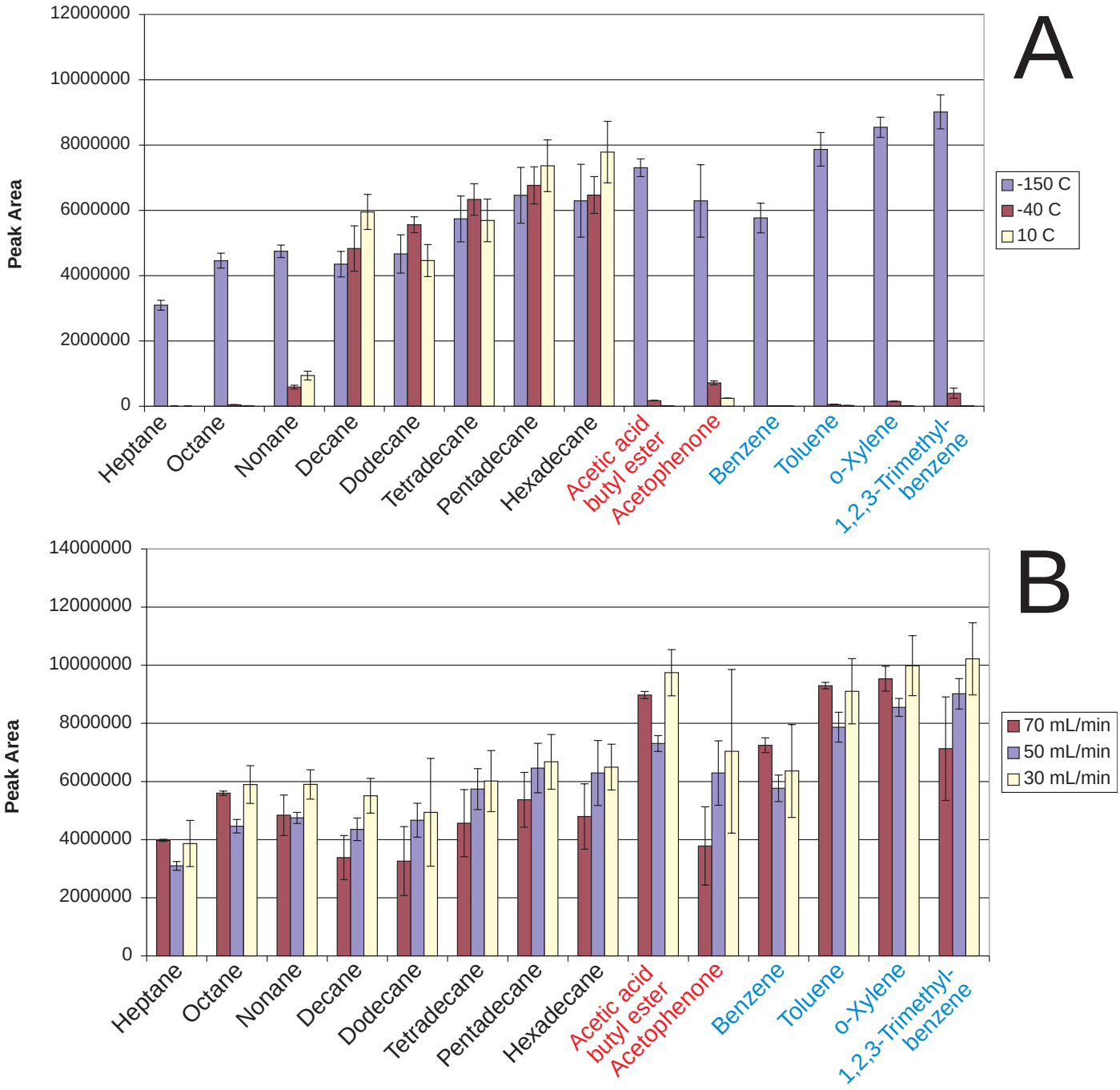

Figure 2. Variation of cryo-focussing temperature (A) and desorption flow (B) using a deactivated glass wool liner.

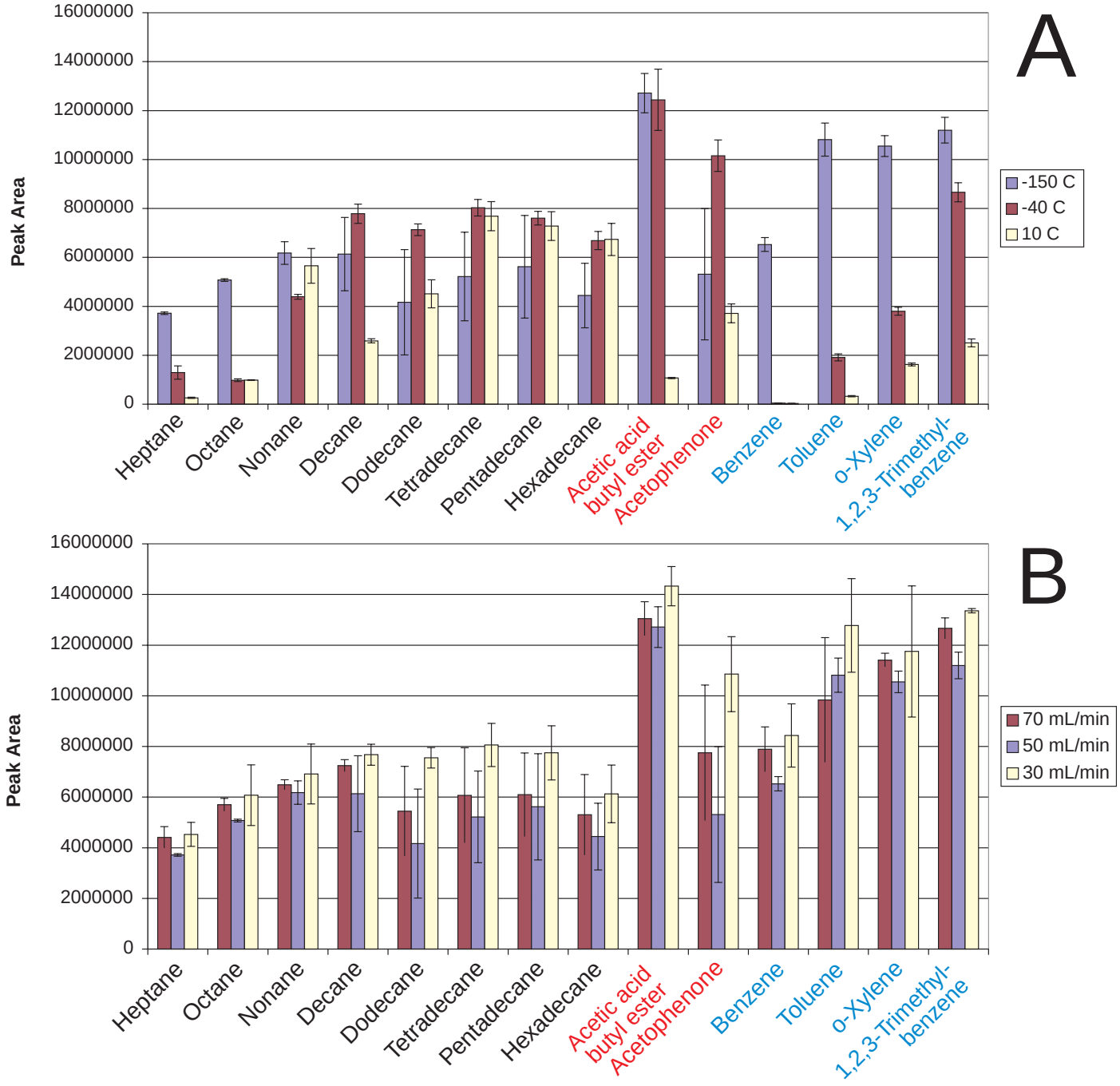

Figure 3. Variation of cryo-focussing temperature (A) and desorption flow (B) using a quartz wool liner.

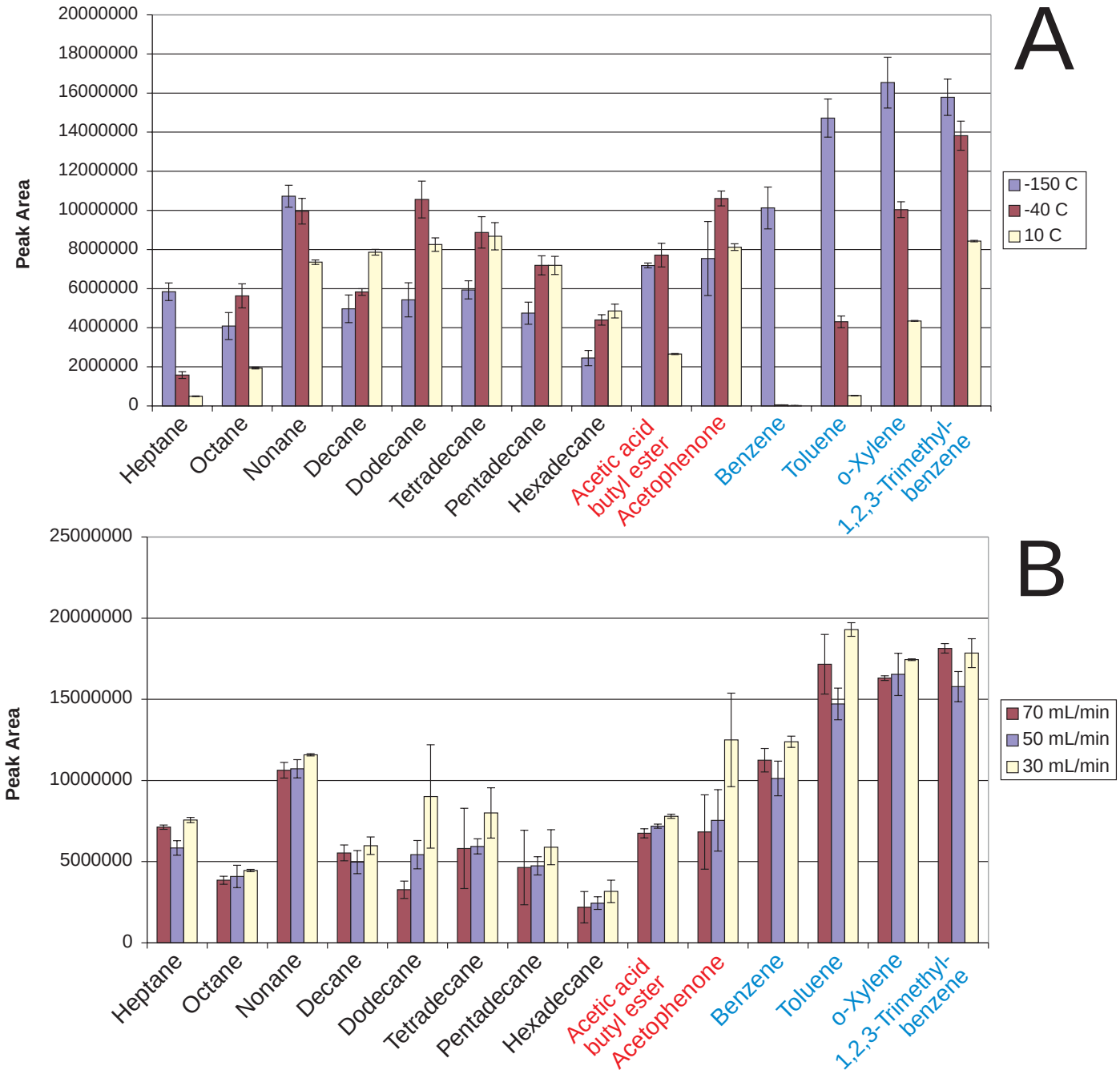

Figure 4. Variation of cryo-focussing temperature (A) and desorption flow (B) using a silanized glass wool liner.

As might be expected, the coldest temperature (-150°C) provided the best cryotrapping on inert supports for the wide range of test compounds. A slight tendency toward better trapping with low flow (30 mL/min) was seen, although the amount of improvement was marginal. In general, the inert supports gave reasonably consistent trapping efficiency for oxygenates, aromatics, and C10 and higher alkanes.

Interestingly, both quartz wool and silanized glass wool showed better trapping efficiency at higher temperatures than seen for the deactivated glass wool, particularly for shorter chain alkanes, oxygenates and aromatics. One possibility to explain this difference is that the pesticide-grade deactivated glass wool liner is treated after the wool is packed into the liner therefore all surfaces are more completely passivated. For the other liners, the quartz and glass wool is silanized with a different process before packing, which may result in slightly different coating density or thickness. The pesticide-grade deactivated glass wool liner gave the best peak shapes of all liners tested (Figure 9).

Focussing on chemical adsorbents. If no cryogenic liquids are available, or if samples contain high moisture levels or very low boiling organics then an inlet liner packed with an adsorbent may be necessary. Tenax TA™ is a porous polymer designed to trap C5-C26 organics without retaining water. Carbotrap™ is a non-porous graphitized carbon black designed to trap C5-C12 organics. Both are available as prepacked inlet liners for the PTV inlet.

The results of cryotrapping on adsorbent-packed inlet liners with different cryo-focussing temperatures and different desorption flows are shown in figures 5-7. The columns in the diagrams are averages of 3 measurements and the error bars indicate the standard deviations.

The lower temperature limit for Tenax TA™ is about -50°C therefore trapping was only tested at 10°C and –40°C. Using a Tenax liner, the best results were obtained at a cryo-focussing temperature of -40°C and a desorption flow of 70 mL/min (Figure 5). Neither trapping temperature nor desorption flow made a significant difference in the range tested. Similar trapping efficiency for the oxygenates and aromatics was seen for Tenax TA™ and cryotrapping on inert supports.

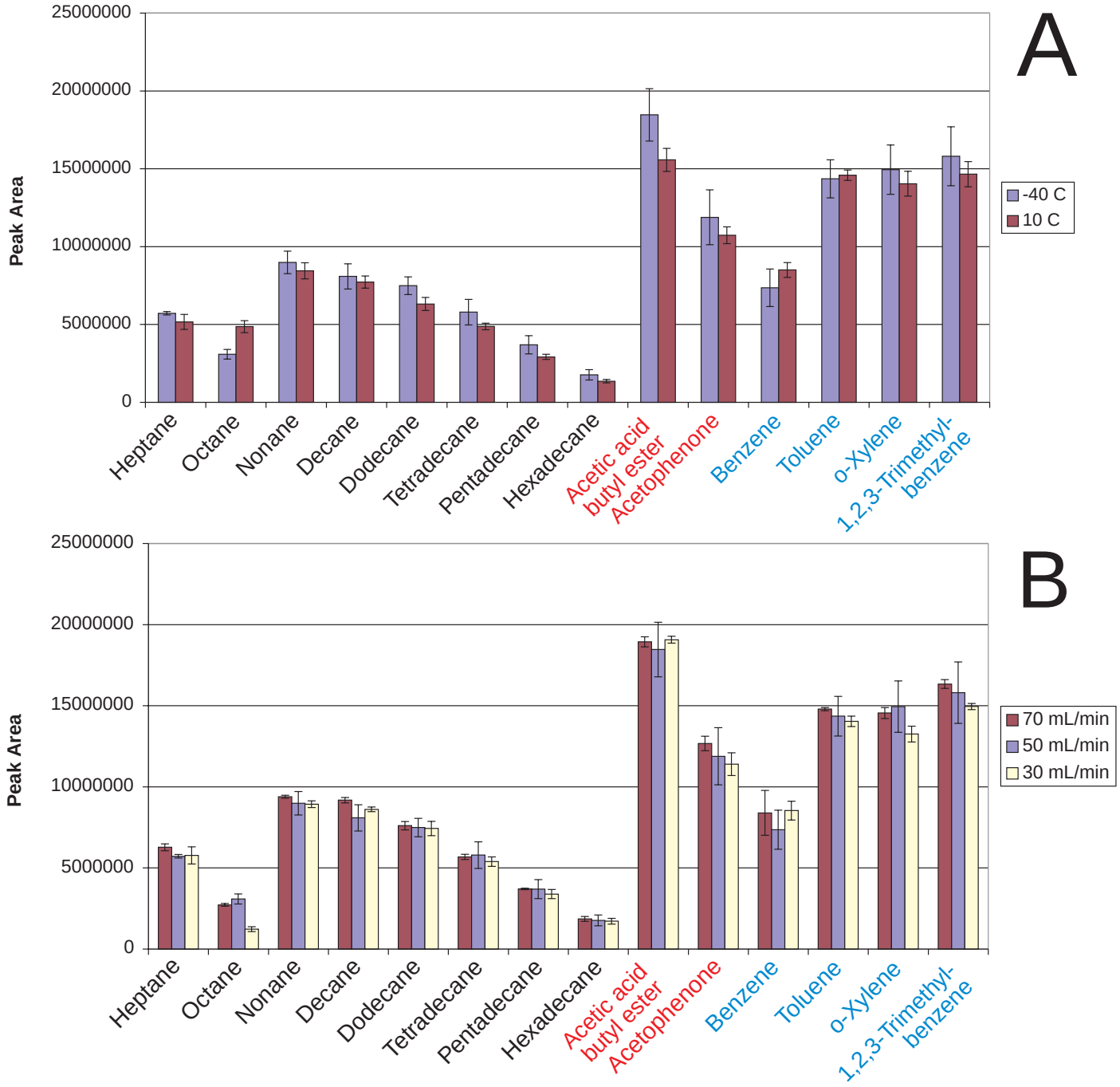

Figure 5. Variation of cryo-focussing temperature (A) and desorption flow (B) using a Tenax liner.

A significant difference was seen for the long chain alkanes, however. On the inert adsorbents the long chain alkanes were generally more efficiently trapped than the short chain alkanes, but on Tenax TA™ the response for long chain (C14 and higher) alkanes was poorer than the short chain alkanes. This is due to insufficient desorption of these compounds from the porous Tenax TA™ at a desorption temperature of 300°C used in this study. It should be mentioned that 300°C is nearly the temperature limit for Tenax. The low peak size for C14-C16 on Tenax is more likely due to poor recovery of these compound on Tenax. This was manifested by carryover problems.

The Carbotrap™ liner performed well for nearly all compounds in the study (Figure 6) at all trapping temperatures used. Long chain alkane trapping and recovery was better than for Tenax TA™, although a slight drop in response for hexadecane was seen, particularly at -150°C. The better performance for the long chain alkanes compared to Tenax TA™ is probably due to the improved recovery from the nonporous particles compared to the porous polymer.

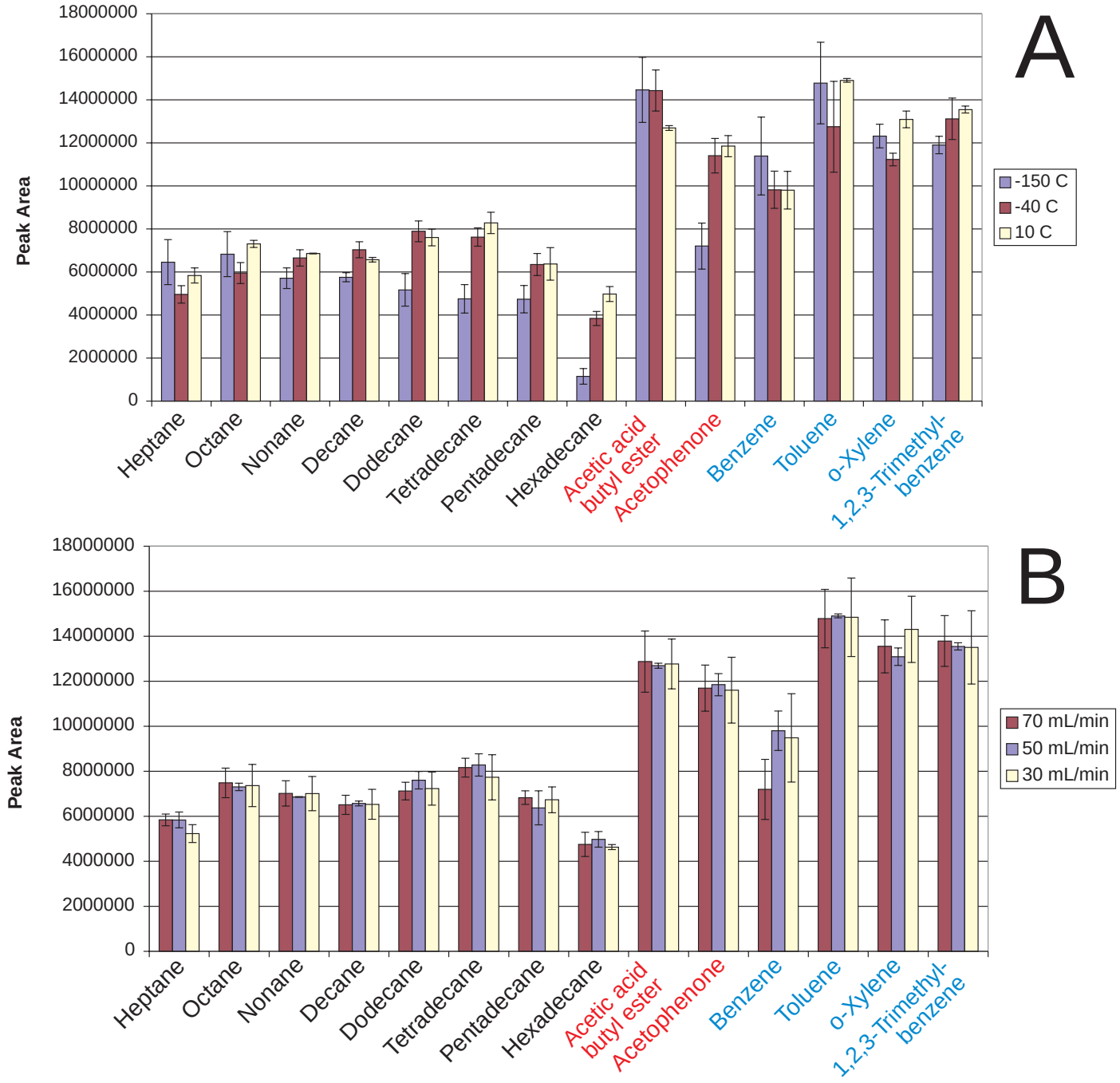

Figure 6. Variation of cryo-focussing temperature (A) and desorption flow (B) using a Carbotrap liner.

When a mixed-bed liner (Tenax TA™ + Carbotrap™) was prepared and tested, the results closely paralleled the results for Tenax TA™ alone (Figure 7). Since Tenax is the first adsorbent on the liner in the carrier gas flow direction, the adsorption of the compounds during trapping is dominated by Tenax giving results similar to using pure Tenax TA™ (compare figures 5 and 7).

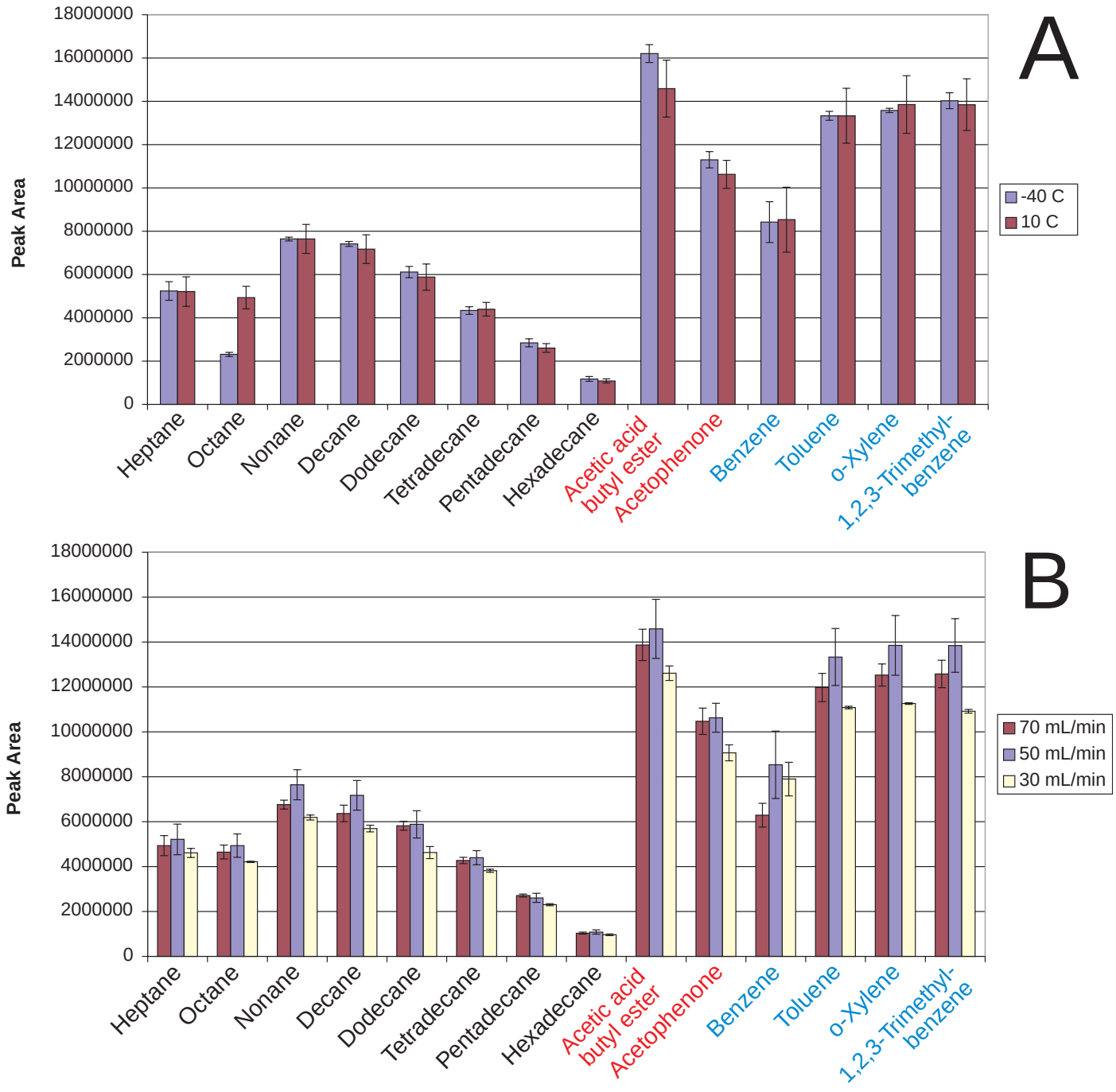

Figure 7. Variation of cryo-focussing temperature (A) and desorption flow (B) using a Tenax & Carbotrap

Figure 8 shows the comparison of the results of the measurements performed with optimized parameters using different liners. In general, all the liners employed in this study are more efficient for trapping of the oxygenated and aromatic compounds than for trapping alkanes.

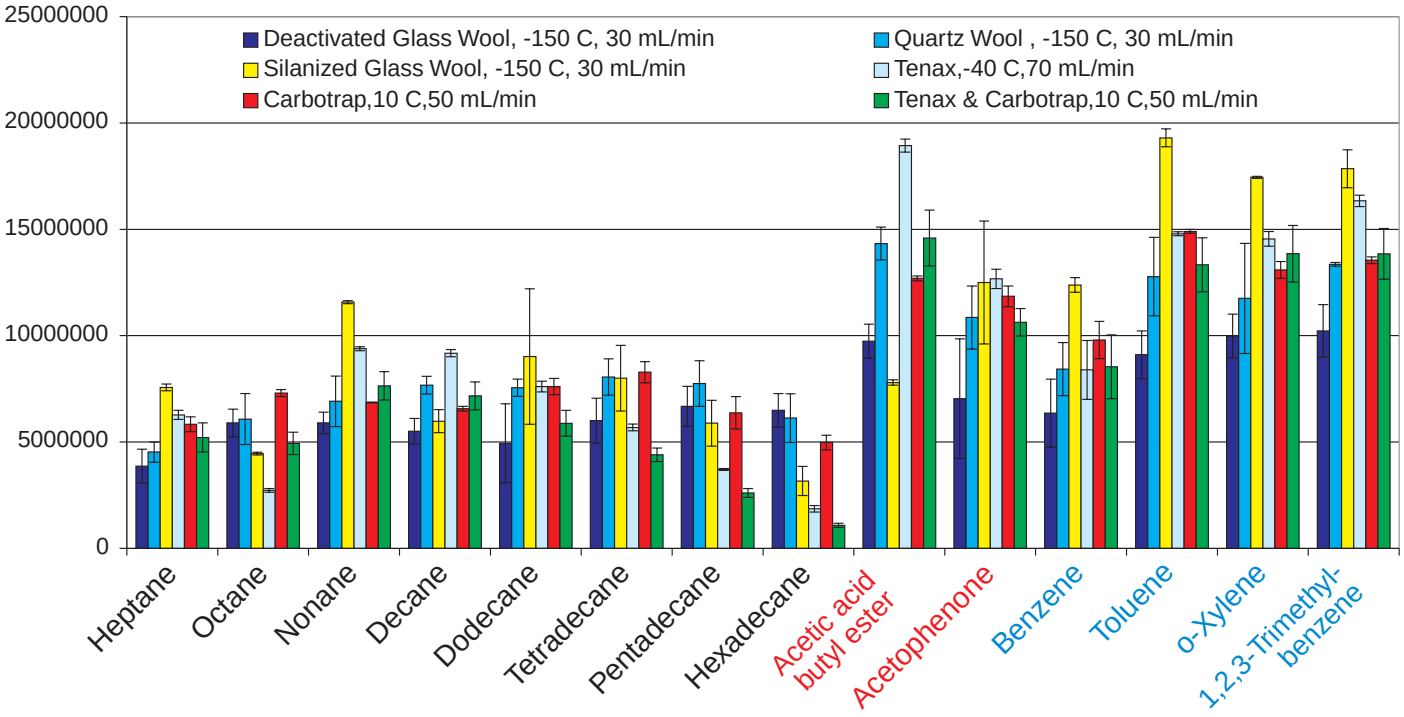

Figure 8. Summary of the results obtained with different liner.

Based on the recovered peak areas, the best results were obtained as follows:

- benzene, heptane, toluene, o-xylene, nonane, 1,2,3-tri-methylbenzene, and dodecane using a silanized glass wool liner at –150°C and 30 mL/min.
- octane and tetradecane using a carbotrap liner at 10°C and 50 mL/min.
- acetic acid butyl ester, acetophenone and decane using a Tenax liner at -40°C and 70 mL/min.
- pentadecane using a quartz wool liner at –150°C and 30 mL/min.
- hexadecane using deactivated glass wool at –150°C and 30 mL/min.

Liner effect on chromatography. Looking into the chromatograms and the peak shapes (see Figure 9) we can see that the best peak shape is obtained using the deactivated glass wool liner. The strong adsorption of the compounds on Tenax TA™ and Carbotrap™ lead to inefficient desorption of the analytes during injection, which leads to peak broadening and/or peak splitting. This might be the reason for the poor recovery of octane on the Tenax TA™ liner. Peak broadening and splitting make integration of the peaks more difficult and can lead to misinterpretation of the data.

It should be mentioned that a quite high split ratio (30:1), which provides a high carrier gas flow through the injector liner, is used for the measurements performed in this study. Using the splitless injection mode, the carrier gas flow through the injector would be below 5 mL/min, which leads to a slow transfer of the compounds to the column and to an even greater deterioration of the peak shape when using adsorbents for trapping.

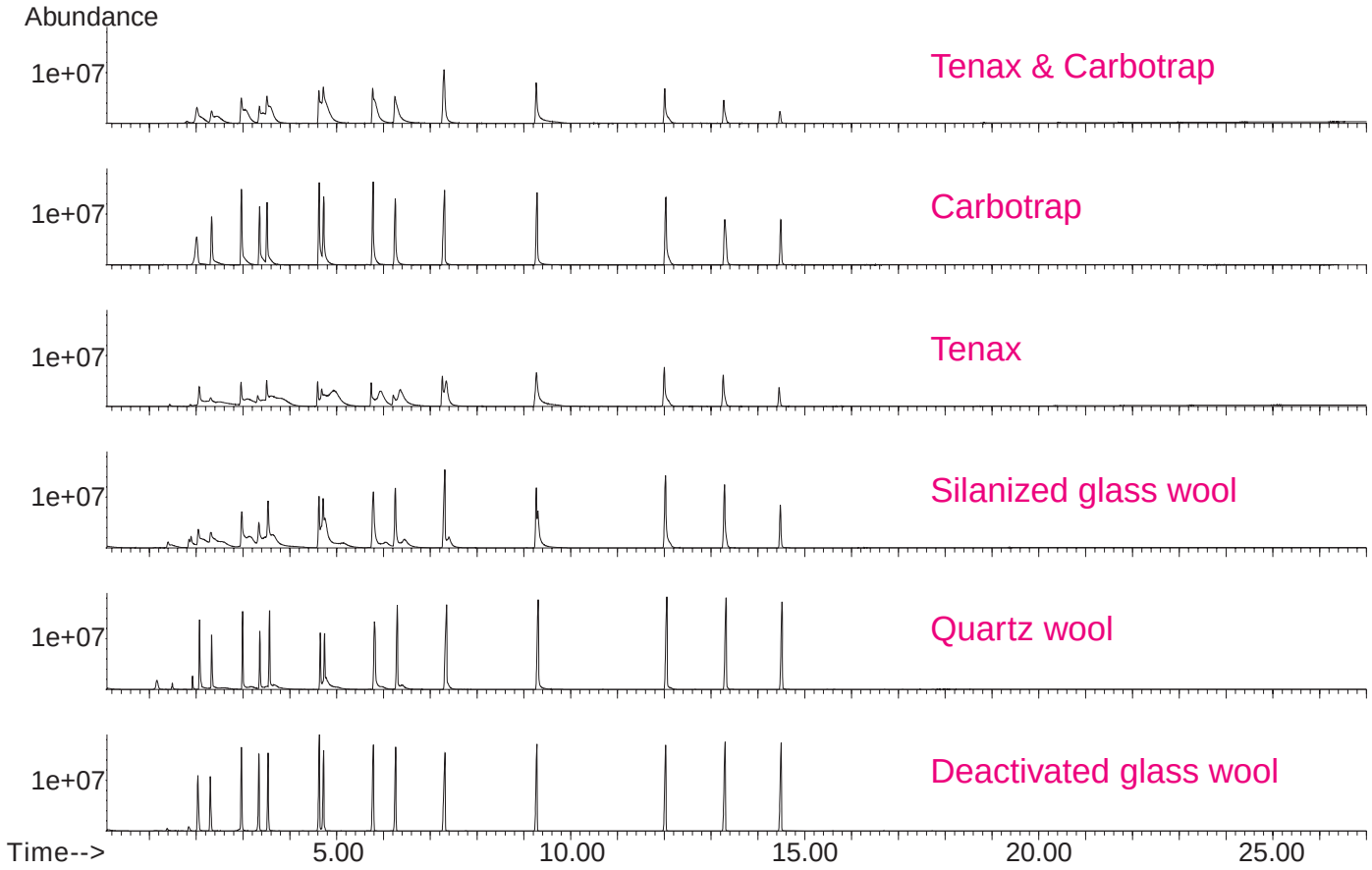

Figure 9. Chromatograms of the measurements performed with different liner and the optimized cryo-focussing temperature and desorption flow.

If adsorbent packed liners are used to trap low boiling compounds, then the best strategy is to use a thick film column to provide adequate focussing on the head of the column after transfer from the inlet. This also will provide better retention and resolution of the low boiling compounds.

Conclusions

The best results concerning both peak shape and recovery throughout all compounds were achieved using the pesticide-grade deactivated glass wool liner. Using this liner type a cryo-focussing temperature of –150°C is required to trap aromatics, and alkanes down to C7.

If CIS systems with cryostat (temperature limit: -40°C) or Peltier cooling (temperature limit: 10°C below room temperature) are used, Tenax TA™ or Carbotrap™ filled liner should be applied. Using adsorbent packed liners, adequate flow (>6 mL/min) through the liner during heating is necessary to obtain good peak shapes.

If the sample contains moisture or other polar impurities, Tenax TA™ might be the more appropriate packing material. Tenax does not adsorb water and polar impurities and therefore prevents freezing of the CIS during trapping.

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
+41 (41) 9 21 97 25
swiss@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
10 Science Park Road
#02-18 The Alpha
Singapore 117684
+65 6779 0933
+65 6779 0938
SEA@gerstel.com
www.gerstel.com

GERSTEL (Shanghai) Co. Ltd
Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District
Shanghai 201206
+86 21 50 93 30 57
china@gerstel.com
www.gerstel.cn

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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