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Efficient Multidimensional GC Analysis of Complex Samples Using Low Thermal Mass Column Modules

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Abstract
Analysts often encounter complex real-world sample types such as petroleum fractions or volatile polymer components. Resolving all individual compounds using a single chromatographic separation can be quite challenging. Coupling columns with different polarities (multidimensional GC) can significantly improve the resolution of complex samples. We coupled two low thermal mass (LTM) GC column modules with dissimilar column phases using a valveless software-controlled column switching device to perform heartcutting 2D GC on polymer headspace samples. Headspace sampling with Twister stir bars was used to introduce sufficient analyte mass on column to identify odor causing compounds. The LTM GC uses resistive heating rather than a convection oven, allowing for rapid heating and cooling rates. Column modules can be independently programmed to achieve optimal separation and short analysis times on a single GC.

Introduction

The chemical composition of real-world samples such as plastics and polymers is usually very complex. Resolution of all the individual compounds by means of gas chromatographic separation can be challenging. Compounds present in these types of samples cover different ranges of polarity, boiling point, solubility, and may be responsible for malodors in the sample. It is therefore desirable to use innovative yet robust techniques that allow resolution of as many types of compounds as possible. When malodors are encountered it is also desirable to detect them simultaneously with an olfactometry detector and a mass spectrometer for rapid identification.

Chromatographic separation of individual components depends upon their interactions with the stationary phase of the column. Selection of the stationary phase is usually done with the familiar rule "like dissolves like". For complex samples, no single stationary phase can resolve all components of interest. Coupling columns with different polarities increases the resolution of complex samples. This approach is commonly known as multidimensional gas chromatography (GC).

In this study, we coupled two low thermal mass (LTM) GC columns with dissimilar phases using a valveless, software-controlled column switching device. The LTM GC has a resistive heating system rather than a convection oven which allows for independent control and rapid heating rates in a single 6890 GC. Using an innovative valveless heartcutting device, we monitor the pre-column signal with a flame ionization detector (FID) and the main column with a mass selective detector (MSD) and an olfactory detector port (ODP).

Experimental

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) equipped with a 5973 mass selective detector and a flame ionization detector, an olfactory detector port (ODP 2, Gerstel), a multi-dimensional column switching system (MCS 2, Gerstel) a PTV inlet (CIS 4, Gerstel) a Thermal Desorption unit with Autosampler (TDS 2 & TDS A, Gerstel) and an LTM A68 Retrofit GC System (RVM Scientific, Inc).

Analysis conditions.

TDS 2	splitless, 20°C, 60°C/min, 250°C (5 min)
PTV	solvent vent (50 mL/min), splitless -120°C (0.2 min), 12°C/s, 280°C (3 min)
Column A:	30m DB-5MS (Agilent), RVM d_i= 0.32mm, d_f= 1.0µm for single dimension / pre-column
Column B:	30m INNOWax (Agilent), RVM d_i= 0.25mm, d_f= 0.25µm for main column
Initial flows:	1.92 mL/min for single dimension 1.89 mL/min for pre-column 1.64 mL/min for main-column
Oven A:	40°C (2 min); 10°C/min; 280°C (5 min) for single dimension / pre-column
Oven B:	40°C (37 min); 10°C/min; 220°C (5 min) for main-column

MCS Cut Parameters- Shower curtain sample

	Time [min]	Cut-Flow [mL/min]	Pressure [kPa]	Rate [kPa/min]
Initial	0.00	On	125.70	0.00
	19.00	Off	0.00	0.00
	21.00	On	125.70	0.00
	37.00	On	125.70	4.40
Final	56.00	On	205.00	0.00

Sample preparation. Approximately 0.5g of sample was weighed into a 20ml headspace vial. A Twister stir bar was suspended above the sample and the vial was crimp capped. The sample was extracted at least 16hrs at room temperature. Following extractions the stir bars were removed and placed into conditioned thermal desorption tubes for analysis.

Results and Discussion

To illustrate the challenges associated with identification of trace volatile components contributing to odor in polymeric materials with a complex hydrocarbon background, we selected some common materials with distinctive odors: an inexpensive vinyl shower curtain and latex balloons.

The critical steps necessary to successfully identify trace odor components are:

- Introduction of sufficient mass of the compounds of interest into the column to obtain adequate response at the olfactory port and the analytical detector (MSD).
- Identification of the regions of the chromatogram in which odor-causing compounds elute using an olfactory detection port.
- Heart cut regions containing odor compounds and interfering matrix components onto a second, orthogonal GC column to separate matrix interferences from the compounds of interest.
- Identify the resolved components responsible for the odors using an ofactory detection port and MSD in parallel.

The instrumentation we used for this analysis is shown in Figure 1. This system includes a thermal desorber for sample introduction by either direct thermal extraction or preconcentration onto adsorbents or other adsorptive phases. Separations are performed on independently controlled low thermal mass ovens allowing optimization of the conditions for precolumn and main column separations. Detection consists of an olfactory detection port in parallel with a MSD for rapid identification of the components responsible for the odors. The pneumatic flow diagram for this system with the countercurrent flow “On” (no heart cut) is shown in Figure 2.

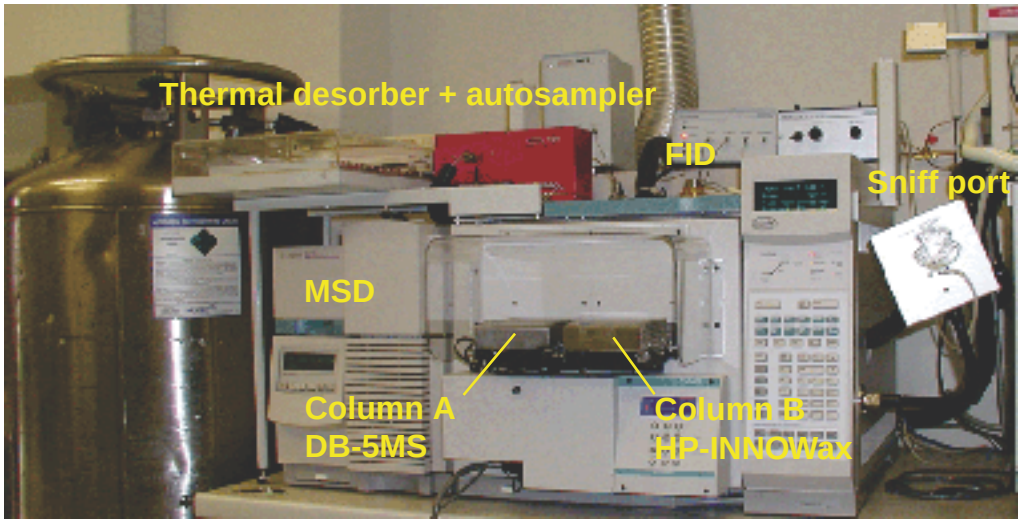

Figure 1. Multidimensional GC-GC instrument used for the study.

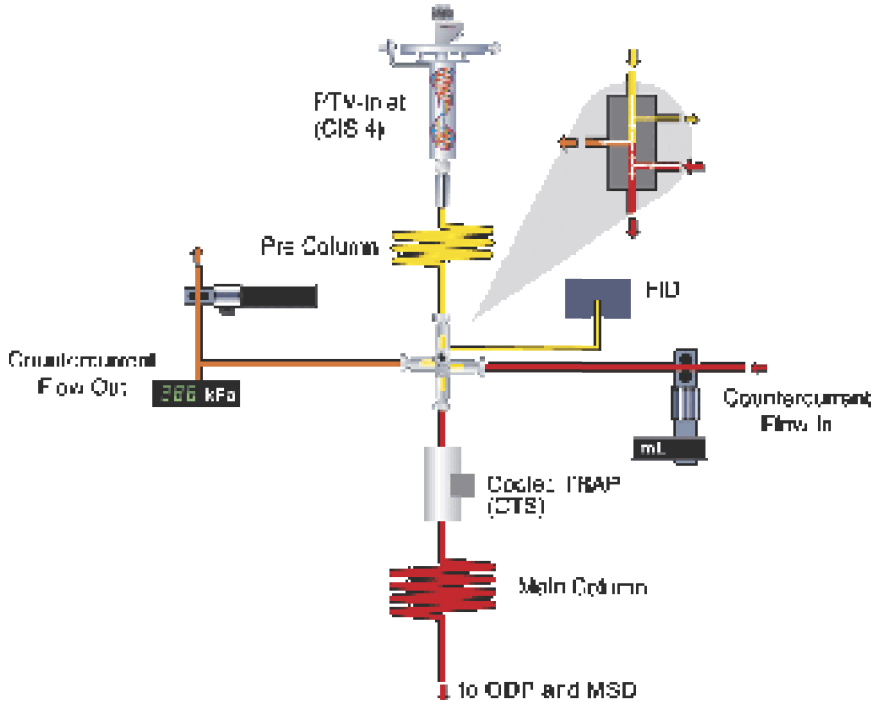

Figure 2. Pneumatic flow diagram for GERSTEL multidimensional system in venting condition, with countercurrent flow “On”.

Vinyl Shower Curtain Volatiles.

Step 1- Sample introduction. Previous experience had shown that direct thermal extraction of a small portion of a polymer sample gave insufficient response at the ODP sniff port. This illustrates the first critical step in odor identification: sufficient mass on column. The choice of an appropriate sample introduction technique is critical to all subsequent steps. In trace odor analysis, it is often necessary to heavily overload the GC column with the major matrix components to insure sufficient mass of the odor active components is available for detection.

It was therefore necessary to use a larger sample mass (hundreds of milligrams) and concentrate the headspace volatiles prior to sample introduction into the GC. For simplicity we chose to concentrate headspace volatiles onto the PDMS phase on a Twister stir bar, although dynamically purging the sample headspace onto a packed adsorbent tube is another option.

Step 2- Identification of odor regions. Figure 3 shows the TIC from the MSD from a single Twister desorption. The chromatogram is annotated to indicate the regions in which odors were detected using an olfactory detection port. At least 6 distinct regions containing odors were identified in the separation on the HP-5 column.

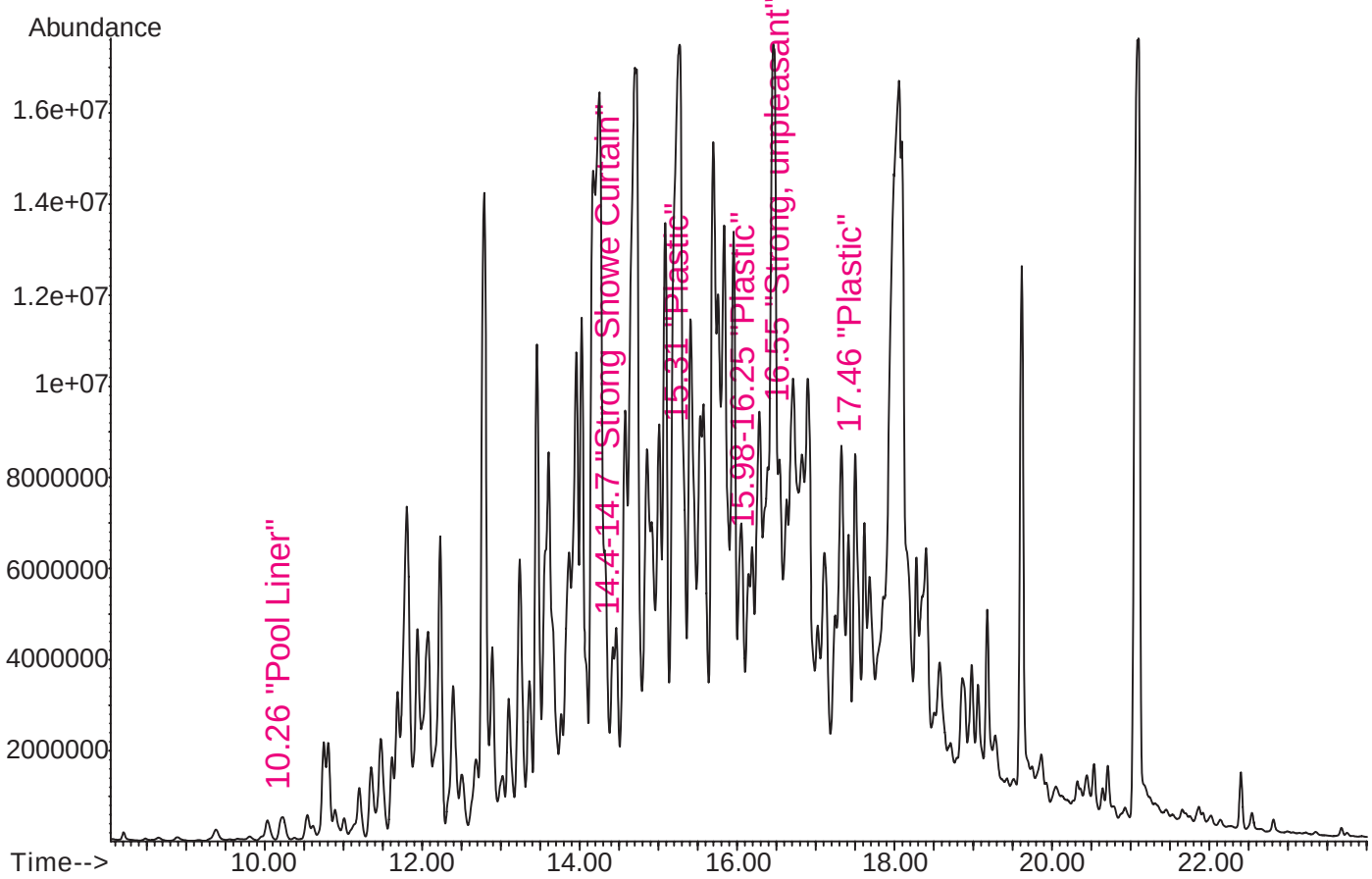

Figure 3. Single dimension TIC of vinyl shower curtain liner volatiles.

We focused on the region of the chromatogram where the strongest odor identified as “shower curtain” was located. Direct inspection of the data from the single dimension separation showed a large hydrocarbon background, and phenol and 2-ethyl hexanol were tentatively identified eluting in this region by matches with the NIST98 MS library. It was impossible to identify any other possible odor components due to the hydrocarbon background.

Step 3- Heart cut odor regions onto second column. We configured a multidimensional GC-GC system with heartcutting to further resolve the odor compounds from the interfering matrix. The precolumn separation was done with a 1µm film HP5 column, and we used a wax column for the main separation to resolve the hydrocarbon background from the odor causing components.

Figure 4a shows the precolumn separation under conditions similar to those used in Figure 3. Retention time shifts compared to Figure 3 were due to the higher absolute inlet and outlet pressures in the multidimensional configuration. Note that it is not necessary to completely resolve the peaks of interest if a second dimension separation will be performed. The region containing the distinctive odor causing compounds (19-21min) was cut into the main column without cold trapping. This allowed the hydrocarbon interference to move through the main column while the more polar components naturally refocused on the wax phase of the main column.

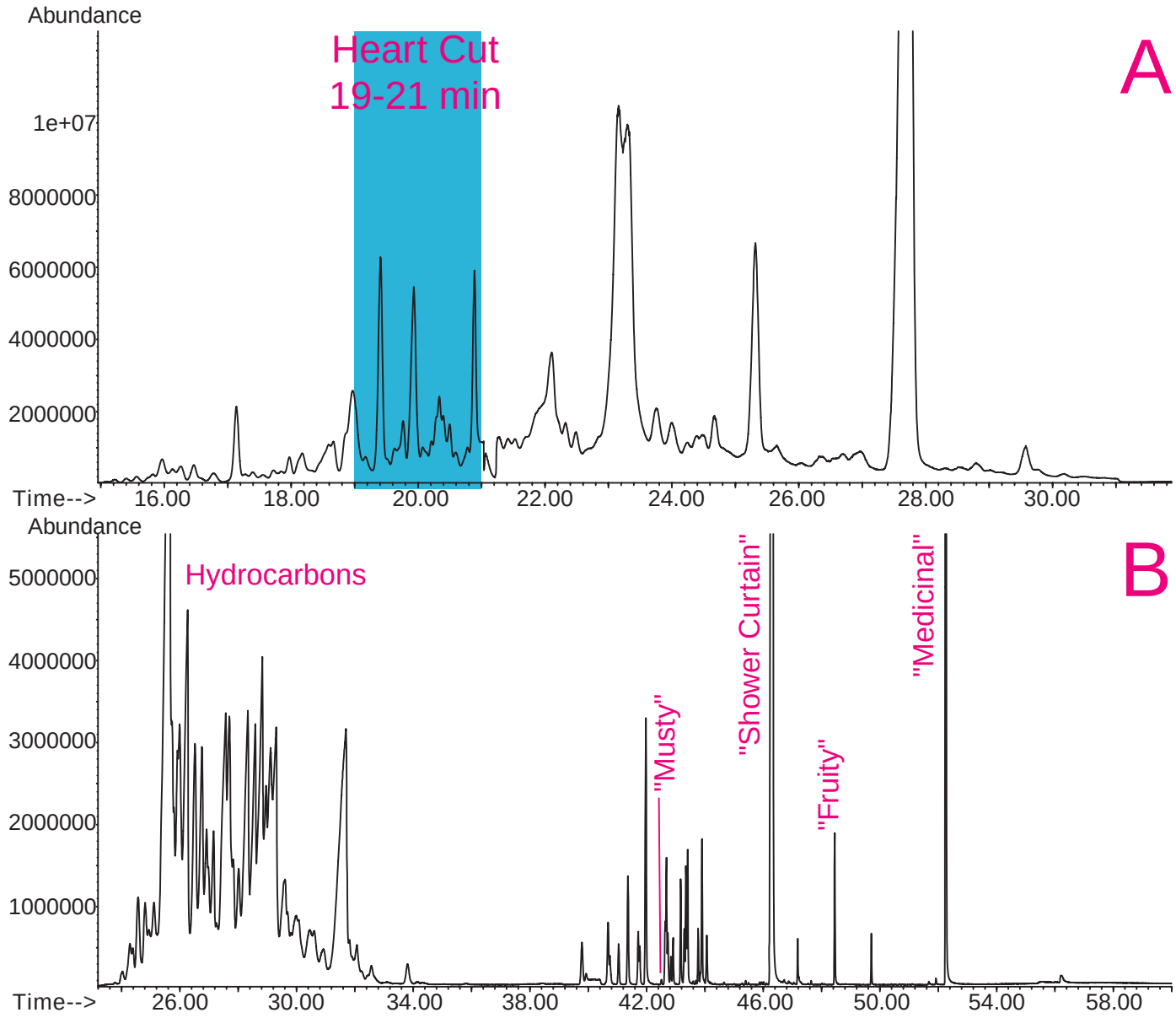

Figure 4. (A) FID trace from GC-GC precolumn separation of vinyl shower curtain liner volatiles. (B) TIC from GC-GC main column separation of 19-21min heart cut from precolumn.

Step 4- Identification of odor causing components. Figure 4b shows the chromatogram from the main column with four distinctly different odor descriptors identified. Note that the 2 minute heart cut from the precolumn transferred over 100 components to the main column. The components responsible for these odors are now nearly baseline resolved from any interference. Figure 5 shows the mass spectrum of the component identified as the most similar to the "shower curtain" smell and the NIST98 library match obtained with 2-ethyl hexanol. It is noteworthy that despite the intensity of this peak, it was impossible to unequivocally assign this compound as the odor causing component in the single-dimension separation due to the hydrocarbon interference from the matrix. A flavor database identified this component as having a rose or green odor.

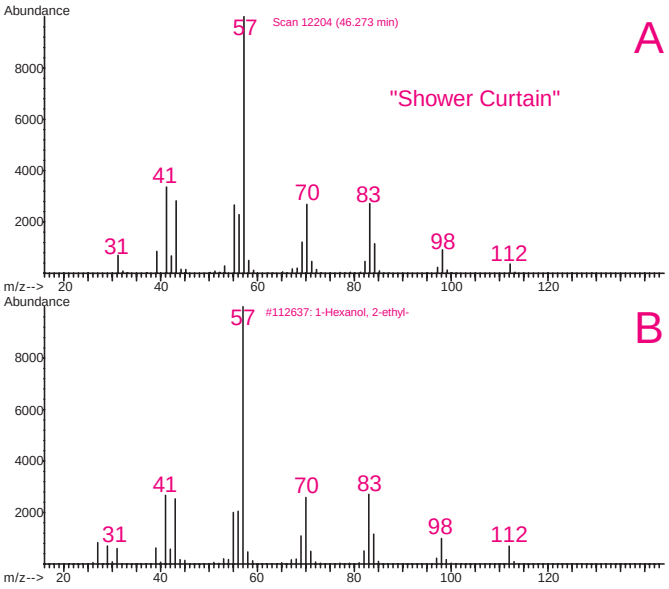

Figure 5. (A) MSD spectrum from "shower curtain" odor peak. (B) NIST98 MS library match with 2-ethyl-1-hexanol.

Figure 6 shows the mass spectrum of a very trace peak identified as having a "musty" odor, and the library match with 2-ethyl hexenal. This peak is less than 0.2% of the size of the 2-ethyl hexanol peak, yet it contributes a distinctly musty odor to the sample. A peak this size would clearly be impossible to identify in a single dimensional separation. The remaining components and descriptors from this cut are listed in Table 1. To fully characterize the odor from the sample, each odor region from the precolumn could be cut individually into the main column for further separation and identification.

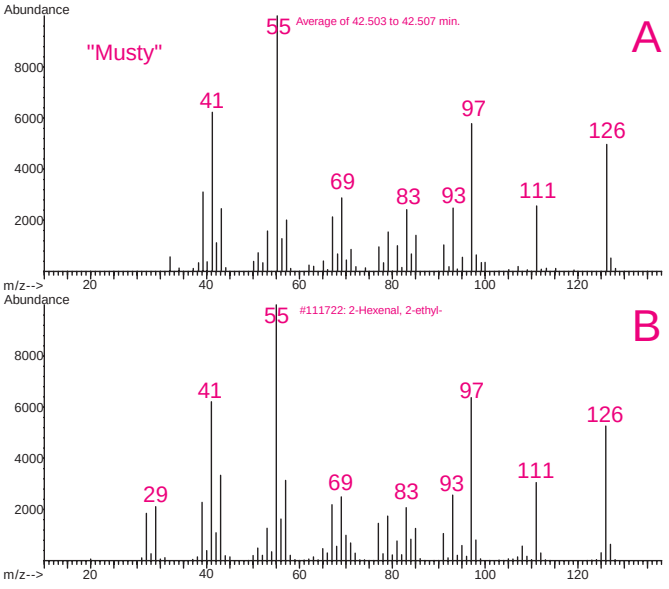

Figure 6. (A) MSD spectrum from "shower curtain" odor peak. (B) NIST98 MS library match with 2-ethyl-1-hexenal.

Table 1. Odor descriptors, tentative assignments and NIST98 library match quality for the four odor compounds from a single cut from shower curtain sample, Figure 4b.

Peak	Descriptor	Compound	MQ
1	Musty	2-Ethyl 2-hexenal	94
2	Shower curtain	2-Ethyl 1-hexanol	86
3	Plastic fruity	Acetophenone	94
4	Medicinal	Phenol	95

Latex Balloon Volatiles.

We applied the same approach to separate and identify volatiles responsible for the characteristic odor from latex balloons. Initial work had suggested that the compounds responsible for the balloon odor were present at very low levels. We therefore desorbed two Twister stir bars simultaneously to put more mass on column. Figure 7a shows the precolumn separation of volatiles from the balloon headspace with the regions with distinctive odors highlighted. The region containing the balloon odors (22.3-25min) was cut to the second column with cold trapping. Figure 7b shows the main column separation with 7 distinct odor descriptors identified. Note over 70 peaks were resolved on the main column from the 2.7 minute heart cut.

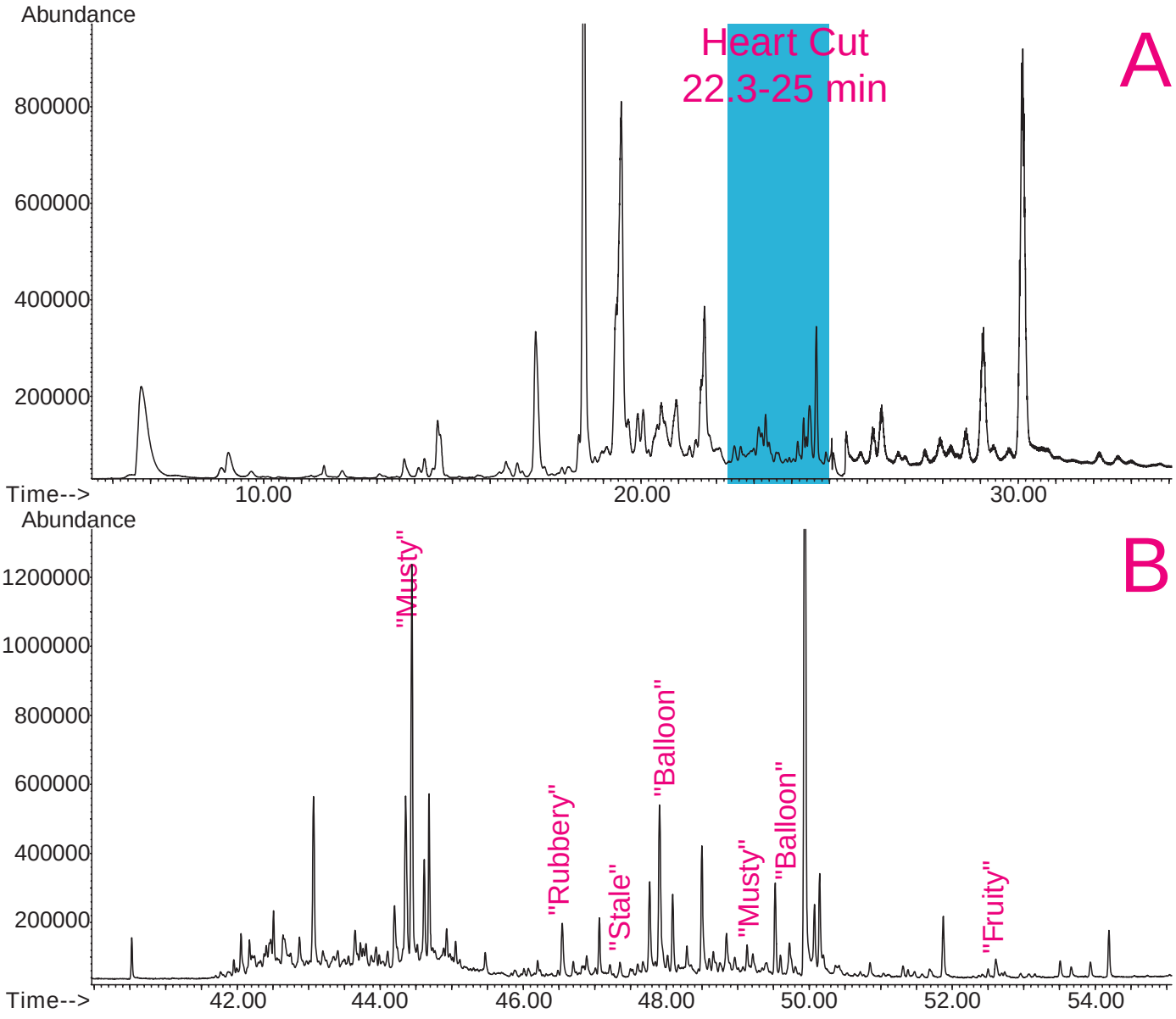

Figure 7. (A) FID trace from GC-GC precolumn separation of latex balloon volatiles (B) TIC from GC-GC main column separation of 22.3-25 min heart cut from precolumn.

The stale odor (peak 3) was tentatively identified as t-2-nonenal. All of the remaining odors were readily detectable at the olfactory detection port, but could not be unequivocally identified because of either low response in the MSD or coelution with similar compounds. This highlights the two critical issues in trace malodor analysis: analyte mass on column and resolution on the analytical column.

Increasing mass on column. To further increase analyte mass on column to improve MSD response and spectrum quality, several approaches are possible using the GERSTEL multidimensional system.

- Desorb up to 4 Twisters simultaneously.
- Perform multiple desorptions while retaining heart cut fraction in the cryotrap before transferring to the main column.
- Investigate selective adsorbents and larger sample sizes to trap and transfer more headspace volatiles into first dimension.
- Change 1:1 MSD:ODP split ratio to 4:1 to put more material into MSD.

Main column resolution. Once sufficient material is obtained on column, adequate resolution is necessary on the main column to resolve odor compounds from interferences. This may require:

- Slow temperature ramps
- Longer columns
- Different column phase

Conclusions

Identification of malodors in complex samples can be most effectively accomplished by multidimensional GC-GC/MS if an olfactometry detector using the human nose is used to help pinpoint the compounds responsible for the odor.

The four major steps to odor identifications are:

- Introduction of sufficient mass of the compounds of interest into the column to obtain adequate response at the olfactory port and the analytical detector (MSD).
- Identification of the regions of the chromatogram in which odor-causing compounds elute using an olfactory detection port.
- Heart cut regions containing odor compounds and interfering matrix components onto a second, orthogonal GC column to separate matrix interferences from the compounds of interest.
- Identify the resolved components responsible for the odors using an ofactory detection port and MSD in parallel.

Using this approach, we identified 2-ethyl-1-hexanol as one of the major contributors of the characteristic odor associated with vinyl shower curtains. Three other compounds contributing to the odor were also identified from a single heart cut.

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