Using a Novel Heartcut Device for Multidimensional GC Peak Sectioning to Reveal Small Peaks Otherwise Obscured by Large Peaks in Mass Chromatograms

Daniel Pentek, Andrew Tipler, William D. Goodman, Adam J. Patkin, PerkinElmer Life and Analytical Sciences, Shelton, CT, United States .

1 Introduction

Solvents are widely used in the pharmaceutical and food industries for a variety of purposes. It is important that such solvents are carefully QC tested prior to use to ensure that no unsafe levels of impurities are present.

GC is normally the preferred technique for the determination of impurities in solvents. The inclusion of a mass spectrometric detector enables the identities and quantification of trace-level impurities to be established.

Because many solvents are produced by fractional distillation, their impurities will have similar boiling points to that of the solvent. Thus in GC, the retention times will be similar to that of the solvent and the risk of co-elution can be high. Furthermore, if the MS is kept active during solvent elution, contamination of the ion source or analyzer may result and the risk of filament damage is greatly increased.

This poster describes a heartcutting technique that allows the entire injected sample to reach the detector and yet resolve the issues with solvent peak resolution and potential detector damage.

2 Deans' Switch

For this work, a D-Swafer™ microchannel pneumatic switch was used as shown in Figures 1 to 4. This device is about the same size as a nickel coin. The internal microchannels are fabricated using laser etching. They are fully chemically deactivated to handle reactive analytes.

In this instance the wafer was configured in a classical heartcutting configuration (Deans' switch) to enable sample cuts to be directed from the effluent of the first column into the inlet of the second column as shown in Figures 5 and 6. The cutting operation is controlled through a solenoid valve programmed by GC timed events to apply a switching gas to direct the primiary column effluent between the wafer two outlets.

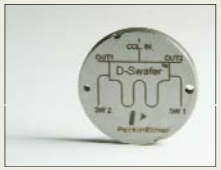

Figure 1. The D-Swafer Deans' switching microchannel wafer

Figure 2. Installing the wafer in the holder

Figure 3. Wafer mounted in the threaded holder

Figure 4. The holder containing the wafer mounted inside the GC oven

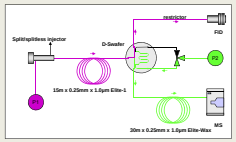

Figure 5. Wafer heartcut system with effluent from primary column directed to mid-point FID.

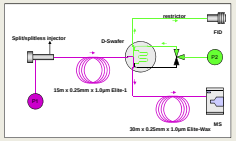

Figure 6. Wafer heartcut system with effluent from primary column cut to secondary column.

3 Experimental Conditions

Tables 1 and 2 give details of the analytical system and method applied to examine 5 samples of dichloromethane (DCM).

Table 1. Analytical System.

Component	Description
GC	Clarus 600
Heartcut device	D-Swafer in D4 configuration
Injector	Split/Splitless
Detector 1	Flame Ionization
Detector 2	Clarus 600 MS
Column1	15m x 0.25mm x 1.0m Elite-1
Column 2	30m x 0.25mm x 1.0µm Elite Wax
Restrictor	50cm x 0.10mm deactivated fused silica

Table 2. Analytical Conditions.

Setting	Value
Oven Temperature	80°C isothermal for 8 minutes
Carrier Gas	Helium
Injector Temperature	225°C
Carrier Gas Pressure (IP1)	23psig (159kPa)
Split Flow	100mL/min
Midpoint Pressure (P2)	16psig (110kPa)
Detector 1 (FID) Temperature	250°C
Air Flow rate	450mL/min
Hydrogen Flow Rate	45mL/min
Range	x20
Attenuation	x64
Detector 2 (MS) Temperature	200°C
Mass Range	35 to 150 Da
Scan Time	0.2s
Interscan delay	0.1s
Sample Injection	1µL by Autosampler in Fast Mode
Swafer Switching Valve (V4) Timed Events	See Results Section

4 Solvent Sidecutting

In Figures 7 and 8 we see the solvent peak dominates the chromatography around it and probably obscures some smaller peaks. The large amount of solvent entering the MS system also raises some concerns.

A run was made with the heartcut switched to the second column at the start of the run and switched to the FID during the solvent peak elution then switched back again. This sidecutting technique has the effect of removing a large fraction of the solvent yet allowing the rest of the sample to enter the second column and the MS detector. Figure 9 shows a chromatogram run this way.

Inspection of Figure 9 shows that much of the solvent has been removed by the sidecutting method. This removal is better illustrated by Figure 10 which shows the two chromatograms at a larger scale. This is a highly effective technique for keeping solvent away from the MS detector.

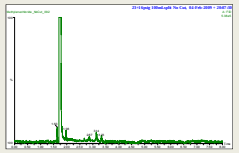

Figure 7. FID chromatogram of DCM Sample 3 showing small impurity peaks.

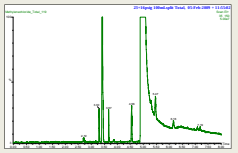

Figure 8. MS total ion chromatogram (TIC) of DCM Sample 3.

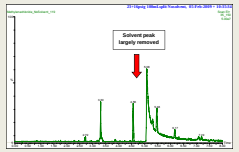

Figure 9. MS TIC with DCM solvent peak sidecut. The switching valve was turned off between 1.68 and 1.80 minutes but was on for the rest of the run.

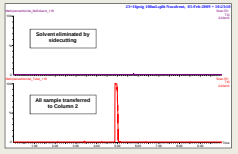

Figure 10. Chromatograms shown in Figures 8 and 9 plotted together at a larger scale to show the efficacy of sidecutting for solvent removal.

5 Solvent Sectioning

Although this sidecutting technique allows the sample to be processed on the MS without the potential damage and interference from the solvent peak, it does not take into account any peaks which will co-elute with the solvent on the primary column – these peaks would not enter the secondary column or be seen by the MS.

Close examination of Figure 9 reveals that two peaks are missing from this chromatogram at approximately 3.42 and 3.67 minutes that were present in Figure 8. These clearly must co-elute with the solvent on the primary column.

To enable these (and possibly other) peaks that co-elute with the solvent to be transferred to the second column for separation, a peak sectioning technique was used to deliver time-incremented narrow heartcuts of the solvent peak from successive runs of the same DCM sample. Figure 11 shows how the solvent peak was sectioned into six 0.02-minute heartcuts that each produced chromatograms shown in Figure 12. This approach allows the area under the solvent peak on the first column to be fully mapped by the second without exposing the MS detector to large amounts of solvent.

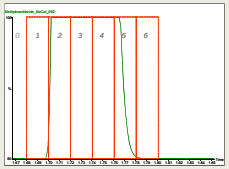

Figure 11. Sectioning the DCM solvent peak into six 0.02-minute heartcuts.

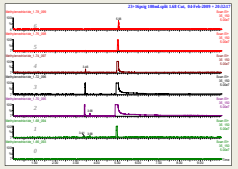

Figure 12. Chromatograms from successive 0.02-minute heartcuts

The final analytical data is obtained by combining the results from all the chromatograms shown in Figures 10 and 12. Table 3 lists each impurity detected in each of the 5 DCM samples. In each case there would have been co-elution of some peaks if the sidecutting and heartcut sectioning techniques were not deployed.

Table 3. Tentative MS assignment of compound identities in DCM samples using the solvent side cutting and heartcut sectioning technique.

Retention Time, min	MS Identification	DCM Sample 1	2	3	4	5
3.30	2-methylbutane			√		
3.41*	branched chain pentene*	√		√	√	√
3.66+	dichloroethylene*	√	√	√	√	√
3.75	branched chain hexane*				√	
3.87	acetone	√		√		
3.90	branched chain hexane*				√	
4.56	branched chain hexene*				√	√
4.56	dichloroethylene*	√	√	√	√	
4.65	ethanol				√	
4.70	isopropanol				√	
4.91#	trimethyl oxirane				√	
5.31	1-chlorobutane			√		
5.48	2-chloro-2-methylbutane	√		√		
5.79	cyclohexene		√		√	
6.02	acetonitrile				√	
6.17	2-butanone			√		
7.08	hexyl alcohol*			√		√
7.19	chloroform		√	√	√	

+ Peak co-eluting with solvent in Column 1
# Peak co-eluting with solvent in Column 2
* Isomer not determined

6 Summary

This side-cut and heartcut technique provides a comprehensive and reliable method of revealing the low-level impurities of solvents using MS as the detection system. Although the solvent peak sectioning process entails several repeat chromatograms of the same sample, these runs are fairly short and isothermal and so the total analytical time is just 50 minutes.

This time would be needed to fully map the obscured components. In the samples examined here, only two additional peaks were found in the sectioned chromatograms and so the method could be optimized just to apply heartcuts to the affected sections and so reduce the number of runs necessary.

Although we have shown the application of this technique just to samples of dichloromethane, the same approach could be extended to other solvents or any sample where there is an interest in identifying and quantifying compounds at low levels that co-elute with other relatively large peaks.