EVALUATION OF RUBBER PROFILES USING DICHLOROMETHANE EXTRACTION BY GCXGC-TOFMS

APPLICATION NOTE AS-301

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Abstract

The extracts produced when extracting rubbers or plastics into solvent as part of an extractables study often produce complex chromatograms that can be difficult to interpret when using traditional one-dimension gas chromatography. In this work, the use of comprehensive two-dimensional gas chromatography (2D GC) to provide enhanced separation with time-of-flight mass spectrometry (TOFMS) providing required data acquisition rates for deconvolution for analysis of rubber samples extracted in dichloromethane to simulate an extractables study. The resulting chromatograms showed a complex mixture containing multiple chemical species which were separated using orthogonal column chemistries. The conclusion of which demonstrates how use of 2D GC can be a powerful tool when used in extractables studies.

INTRODUCTION

Extractables and Leachables (E+L) studies involve the analysis of extracts of complex matrices such as rubbers and plastics, used in drug storage and delivery devices as well as medical devices. The resulting chromatograms can be complex and present difficulties with spectral deconvolution, which needs to be used to ensure that no potentially harmful extractable or leachable species are missed. Orthogonal separation, using two-dimensional gas chromatography (2D GC), provides greater chromatographic separating power which can be combined with time-of-flight mass spectrometric (TOFMS) detection to provide the necessary acquisition rate to generate adequate numbers of data points for reliable deconvolution.

In 2D GC, peaks are modulated and peaks eluting from the first column (dimension) are 'cut' into smaller peaks which are then separated in a second column, typically of a different phase chemistry. This provides chromatographically efficient peaks, fractions of a second in width, in addition to the improved selectivity provided by the second dimension column[1].

In this work, extracts produced from an extractables study of a rubber are analysed using GCxGC-TOFMS to highlight the benefits when using 2D GC for the analysis of complex matrices and chromatograms.

EXPERIMENTAL

Instrumentation

Gerstel MultiPurposeSampler MPS DualHead Robotic/Robotic^{Pro}

LECO Pegasus BT 4D GCxGC-TOFMS

ChromaTOF®

First dimension: RXi-5SilMS 30 m x 0.25 mm x 0.25 µm

Second dimension: DB-17MS 0.7 m x 0.18 mm x 0.18 µm

Figure 1: *GERSTEL MPS and LECO Pegasus BT 4D*

METHOD

5 mL of dichloromethane was used to extract rubber samples at 30°C for 7 hours. The extract was then analysed by 2D GC for untargeted analysis using a 1 µL splitless injection.

A C10-C35 alkane ladder was also injected to provide retention indices for assistance in compound identification along with an extractables and leachables test mix containing several compounds covering a range of classes such as alkanes, and a range of polar and non-polar aromatics, that may be encountered in these scenarios.

The resulting data files were processed using peak finding deconvolution within ChromaTOF® with Target Analyte Finding (TAF) enabled to identify compounds contained within a test mixture.

RESULTS

A high number of compounds were separated in the second dimension, illustrating the power of the 2D chromatographic separation, figure 2. Extracting m/z 57, a common ion for alkane related species, shows a large number of components which would co-elute in traditional 1D chromatography without use of extended run times, figure 3.

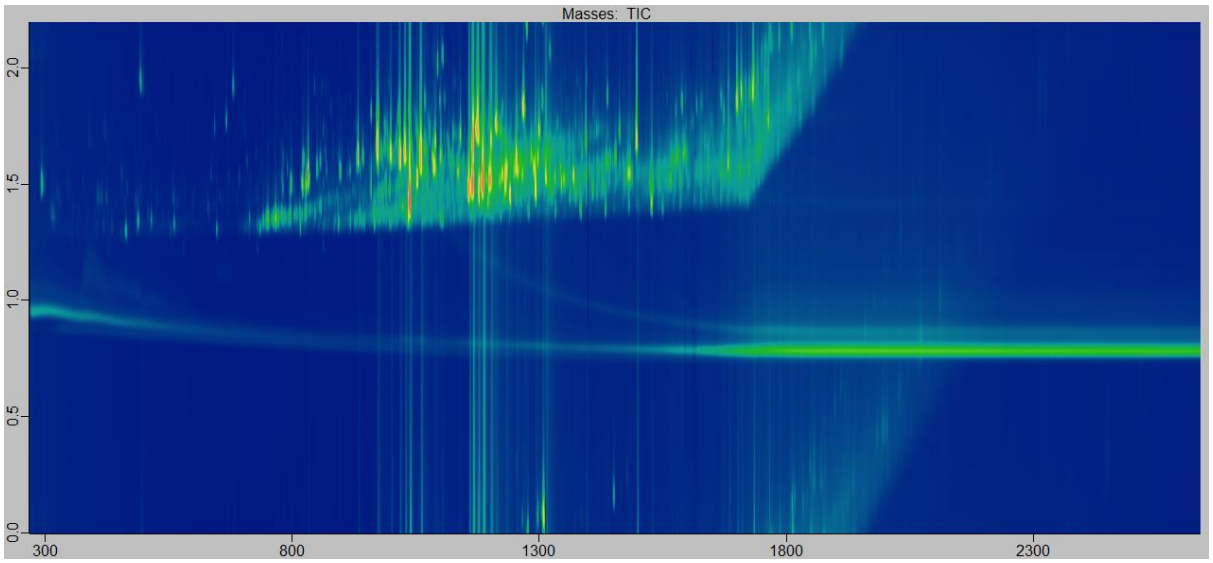


Figure 2: *Representative Total Ion Chromatogram Contour Plot of DCM extract of a rubber.*

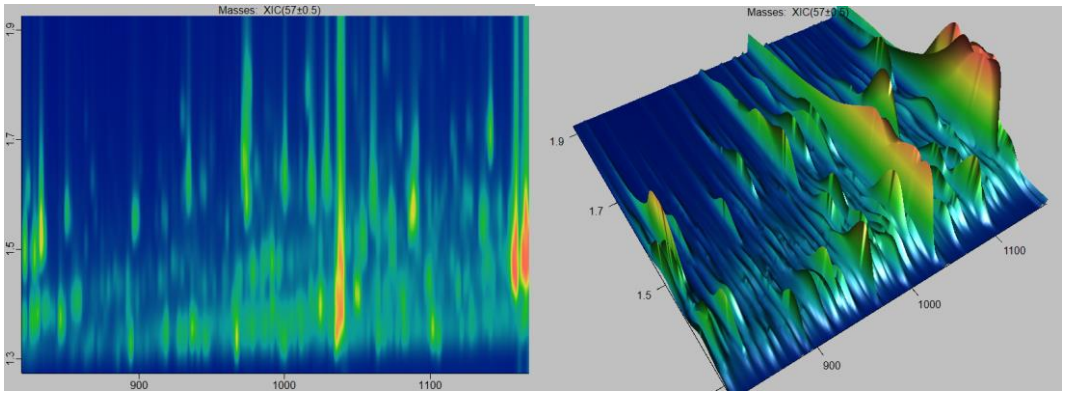
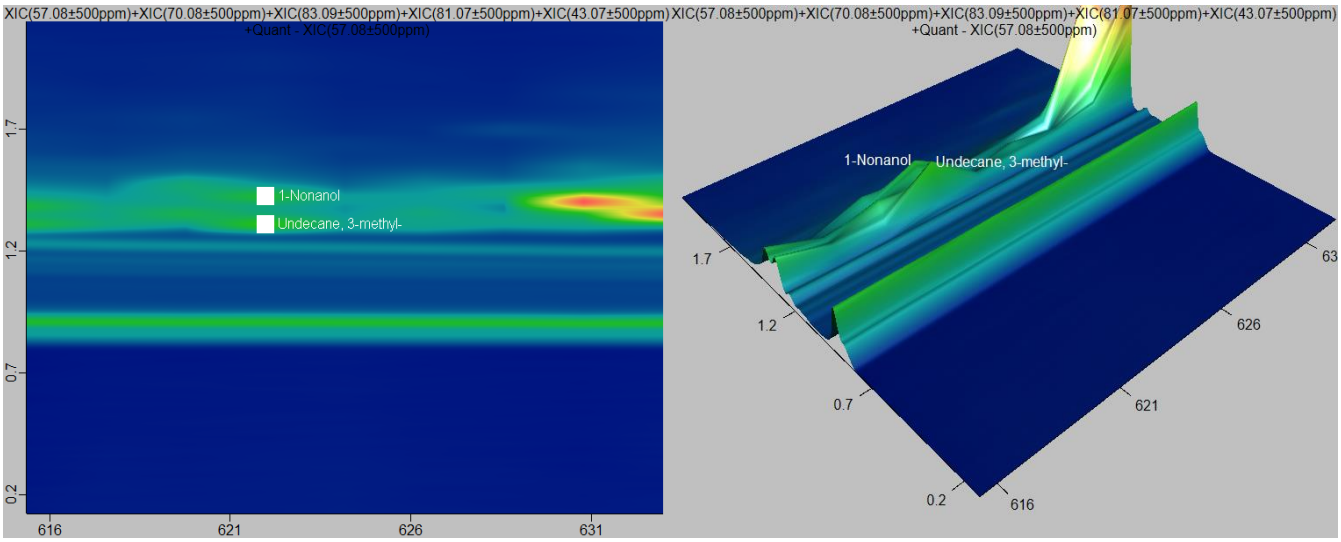


Figure 3: *Left: Extracted Ion Chromatogram (XIC) contour plot of m/z57. Right: 3D plot of same area. 1st Retention time: 800-1150 seconds, 2nd dimension retention time: 1.3 – 1.9 seconds.*

With GCxGC extremely highly efficient peaks are produced during the modulation process, with typical full-width half-height peak widths of 200 milliseconds in this analysis. With higher flow rates and use of hydrogen as a carrier gas, these peak widths can be narrower still. It is for this reason time-of-flight mass spectrometers are used for GCxGC work as these instruments can provide fast data acquisition, with 200 spectra/s used in this work. This provides 40 data points across the peak, which ensures accurate modelling of the peak shape which is highly important for peak deconvolution.

Figure 4 clearly shows the benefit of using a GCxGC-TOFMS approach combined with retention time indexing (RI). Without the orthogonal separation of 2D GC, both compounds would co-elute in the first dimension, both having a 1D retention time of 621.977 seconds. Comparing the library and sample spectra for both compounds, figure 5 shows that without further separation on the second dimension it would be very difficult to identify both compounds due to the similarity of spectra, both containing linear alkyl chain moieties.



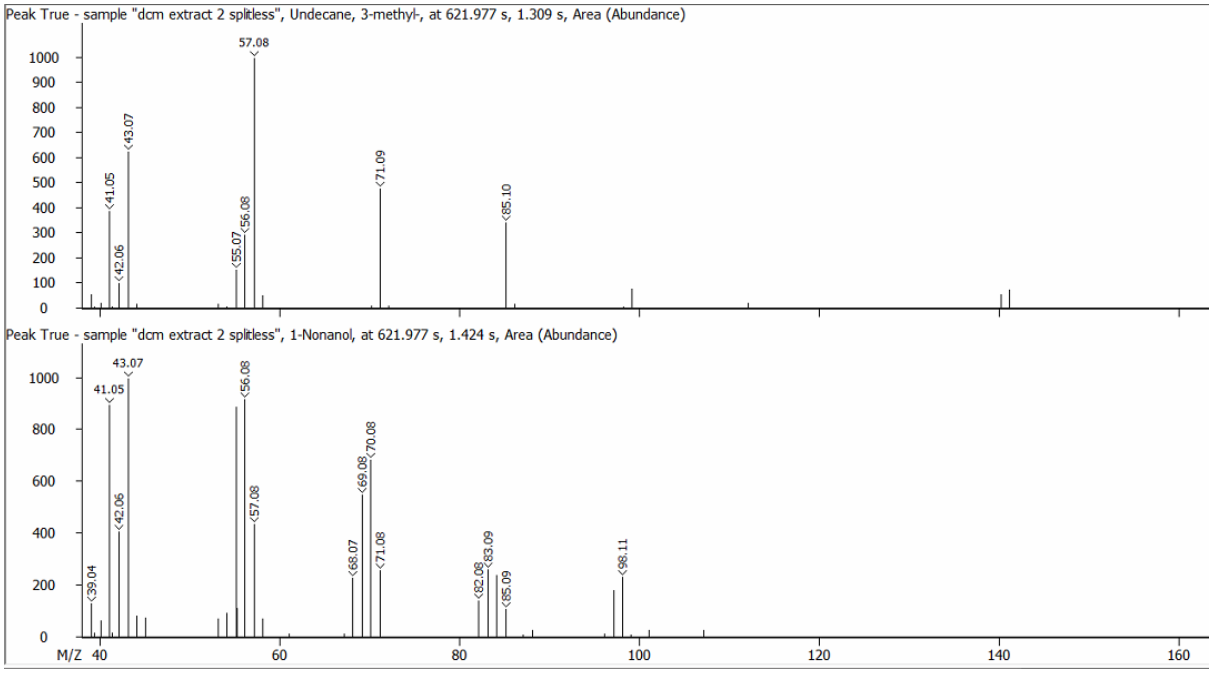


Figure 5: *Experimentally obtained spectra for 3-methylundecane, top and 1-nonanol, bottom.*

Table 1 shows the similarities and RI for both compounds. Use of RI in this case has provided additional confidence in the library hit. Alkanes and their derivatives are notoriously difficult to identify without RI due to lack of molecular ion in their spectra and similarity of ions between different species.

Table 1: *Similarity and RI values for tentatively identified compounds*

Compound	Retention time (1D, 2D)	Similarity	RI	Library RI
3-methylundecane	621.977, 1.309	894	1171.4	1170±1(14)
1-nonanol	621.977, 1.424	880	1171.4	1173±2(66)

Further benefits of utilising orthogonal separation are shown in figure 6, with two compounds again having identical 1D retention times with very different separation chemistries enabling separation in the second dimension. By using a mid-polarity column as the second column, DB-17ms, both components are fully resolved and identifiable, again with RI confirmation for tentative identification.

CONCLUSION

This work has shown how use of GCxGC-TOFMS instrument can be used to comprehensively evaluate sample profiles through enhanced chromatographic separation and increased numbers of spectral data points to provide deconvoluted data for tentative identification

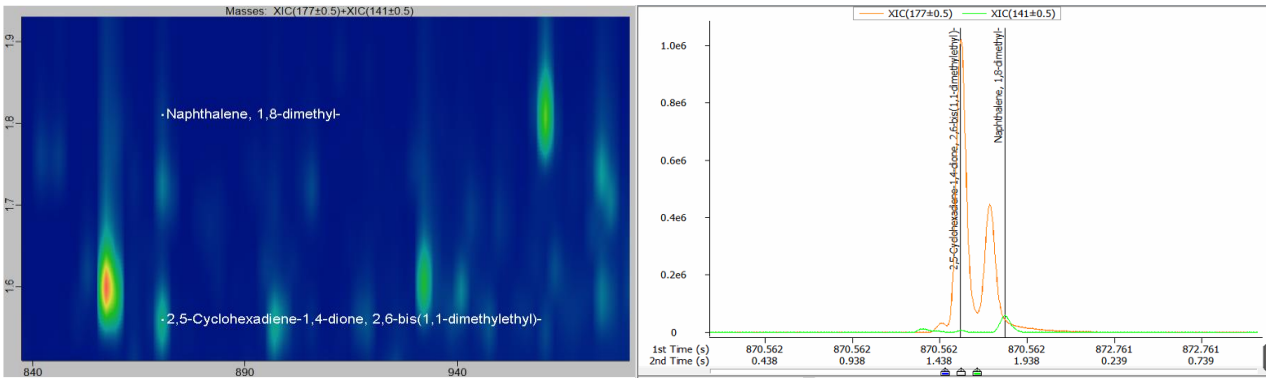


Figure 6: *XIC contour plot (left) and chromatogram (right) of 1,8-dimethylnaphthalene and 2,6-bis(1,1-dimethylethyl-2,5-cyclohexadiene-1,4-dione.*

Of the compounds that were included as part of a target analyte screening data processing method, eight were tentatively identified, see table 3. RI confirmation from the library is also listed where values are present with figure 7 showing their location within the chromatogram. Creation of a library through injection of standards would be preferrable to provide absolute confirmation. Both targeted and untargeted analysis has been performed, highlighting that TOFMS instruments can perform complex analyses without subsequent loss of sensitivity which would be experienced using traditional quadrupole SIM/SCAN methods.

with use of features within ChromaTOF® software such as Target Analyte Finding.

REFERENCES

1. Research Hype To Practical Analysis: Benefits of Comprehensive Two-Dimensional Gas Chromatography (GCxGC) for a Routine Laboratory https://knowledge.leco.com/papers/gcxgc-benefits-white-paper-209-281-003/viewdocument/1823?submissionGuid=4442a775-64ec-43d7-8e5b-63eade5323be

To discuss implementing this application solution for Extractables + Leachables, contact us and we will be delighted to work with you from conception to method transfer into your laboratory.

We also offer fully validated methods, according to your validation protocol, where required.

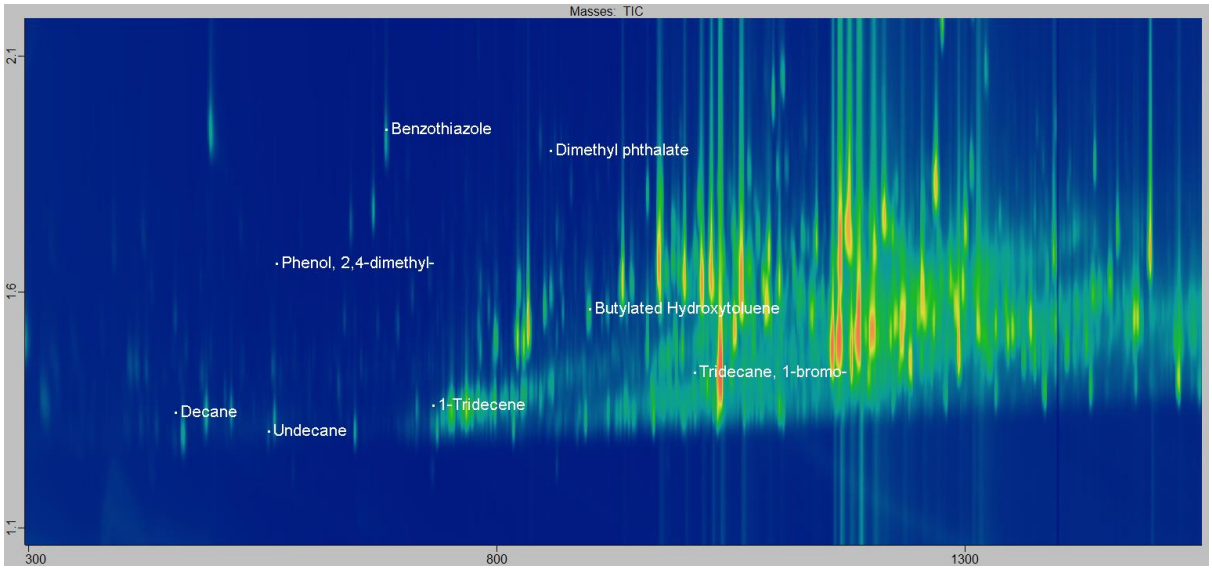


Figure 7: *Target compounds overlaid on TIC contour plot.*

Table 2: *Target compounds tentatively identified.*

Compound	RI	Library RI	Similarity
Decane	1002	1000	762
Undecane	1100	1100	814
2,4-Dimethylphenol	1109	1108±6(33)	746
Benzothiazole	1237	1228	822
1-Tridecene	1295	-	721
Dimethyl phthalate	1451	1454±4(24)	732
Butylated hydroxytoluene	1506	1514±5(17)	886
1-bromo-tridecane	1664	1664±1(9)	789