Mount Royal University team uses GC×GC–TOF MS to gather data to increase conviction rates in wildfire arson cases

Wildfires are common in Canada. In the province of Alberta alone, 3269 hectares of land were burned during the 704 wildfires that occurred over the wildfire season in 2020. Gwen O'Sullivan and Nadin Boegelsack at Mount Royal University, Canada, use GC×GC–TOF MS to identify ignitable liquid residues from complex wildfire debris samples.

Professor Gwen O'Sullivan and Nadin Boegelsack, environmental forensics researchers at Mount Royal University in Alberta, Canada, investigate the causes of wildfires by searching for ignitable liquid residues (ILRs) – remnants of accelerants – in wildfire debris samples. Determining the presence of an ILR and the type and source of accelerant used in arsonous fires can provide key evidence for conviction in arson cases.

However, identifying an ILR and the type and source of accelerant can be challenging with one-dimensional gas chromatography (1D GC) analysis. This is because wildfire debris will consist of hundreds of compounds from different types of wood and soil, tree bark and other vegetation, together with by-products of combustion and pyrolysis. The ILRs will also consist of hundreds of compounds. The challenge with 1D GC is that many compounds can co-elute, and combined with lower sensitivity, false negatives can occur.

> " GC×GC–TOF MS is better for us in terms of identifying and separating our targets from our non-targets. "

CUSTOMER:
Mount Royal University, Canada

APPLICATION:
Analysis of ignitable liquid residues (ILRs) from fire debris

CHALLENGE:
To improve separation of target compounds from complicated matrices and characterise potential source of ILRs

SOLUTION:
GC×GC with TOF MS

RESULTS:
Greater separation and characterisation of ILRs to provide more information for improved decision-making during arson investigations

Overcoming barriers to peak separation

To overcome the challenge with peak separation, O'Sullivan's team uses two-dimensional gas chromatography–time-of-flight mass spectrometry (GC×GC–TOF MS) using the INSIGHT® flow modulator and BenchTOF™ mass spectrometer. 2D GC separates the compounds that usually co-elute, so they can all be seen clearly on the resulting chromatogram. "We always have matrix issues and complex contaminants so GC×GC–TOF MS is better for us in terms of identifying and separating our targets from our non-targets," says O'Sullivan.

## Improving the certainty of source identification

The presence of target compound classes prescribed by the American Society of Testing and Materials (ASTM) will corroborate the presence of an ILR, which can then be identified by comparison with an ASTM data table.[1]

"However, the ASTM method is all about visual comparison," says Boegelsack. This means that while analysts can identify an accelerant, they are less likely to be able to distinguish between accelerants of the same type, which would enable them to trace the source (such as a particular petrol station). "We're trying to move away from the visual comparison and make it more quantifiable."

Library of GC×GC data to increase conviction rates

To gather quantitative data, the team used GC×GC to devise a new system to build a reference library of ILRs using retention time data from both the first and second dimensions. [2] Using retention time indices (RI, a unitless constant calculated from the retention times), the team was able to distinguish between compounds that had been indistinguishable with RI data from 1D GC.

Now, the team is collecting and analysing samples of ignitable liquids from as many sources as possible, including traditional (e.g. gasoline and diesel) and non-traditional (e.g. plant and animal oil and fat accelerants) sources to populate their reference library with the goal of increasing the amount of information available to arson investigators to increase conviction rates.
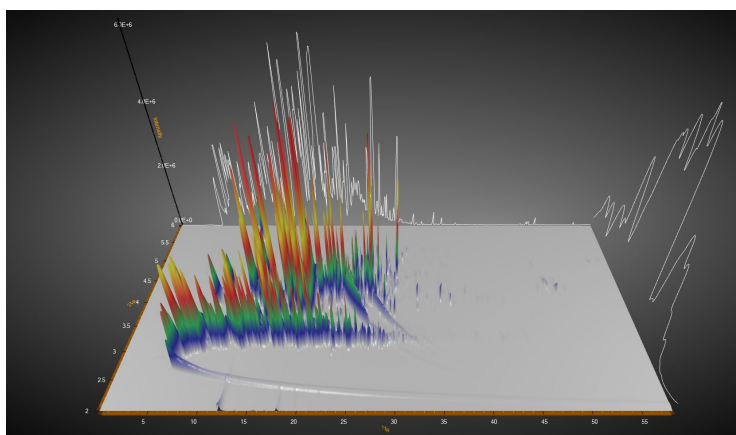
The GCxGC chromatogram shows the enhanced separation of peaks that would normally co-elute in 1D GC (shown here by the unresolved hump in the white trace).

Preventing cross-contamination

Currently, the team extracts compounds from samples using passive headspace sampling, in which a carbon strip is attached to the inside of a sealed can containing a sample. Over time, volatile compounds from the sample are adsorbed onto the strip and these are then extracted using carbon disulfide and the solution is injected into the GC.

However, the cans, which are similar to paint cans, can sometimes leak, causing cross-contamination. O'Sullivan plans to reduce this by switching from cans to sampling tubes for thermal desorption (TD), which can be capped securely for transportation to a lab and do not leak. She plans to use TD with GC×GC–TOF MS to analyse samples, not only for wildfire debris investigations but also for their work on air toxics analysis. The tubes can also provide stable long-term storage and don't take up much space. "This would solve a current storage challenge where we require lots of fridge and freezer space to store sample cans and extracts. This can be very challenging for cases that may take months or years to go to court," she says.

References

[1] ASTM E1618 – 19, Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry, https://www.astm.org/Standards/E1618.htm.

[2] N. Boegelsack, C. Sandau, D.W. McMartin, J.M. Withey and G. O'Sullivan, Development of retention time indices for comprehensive multidimensional gas chromatography and application to ignitable liquid residue mapping in wildfire investigations, *Journal of Chromatography A*, 2021, 1635: 461717, https://www.sciencedirect.com/science/article/pii/S0021967320309912.

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