

Uncovering trace additives in gasoline

This study demonstrates the use of GC×GC coupled with BenchTOF2™ and Tandem Ionisation® to identify trace additives in gasoline, with time-saving workflows in ChromCompare+ software utilising all of the tandem data in a single workflow to automatically uncover differences between gasoline blends.



Introduction

Fuel additives are used to improve the properties of the particular fuel, for example to boost the octane rating or reduce corrosiveness. However, they can also have an impact on exhaust emissions, and as such, are subject to environmental regulations such as the US Clean Air Act,^[1] which requires that fuel manufacturers must register all additives used in their products.^[2]

Conventional additives, such as benzene, toluene, ethylbenzene and xylenes (BTEX) and methyl *tert*-butyl ether (MTBE) are now heavily controlled due to their impact on the environment and human health, causing a drive to find new environmentally-friendly additives. The composition of gasoline is therefore constantly evolving and many proposed additives have already faced bans in several countries due to their unknown ecological impact and potential risk to humans, so it is important to be able to detect illegal additives.

This is a challenging prospect, as gasoline itself is a complex mixture, making it difficult to identify trace differences between blends. To tackle this challenge, we employ comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC–TOF MS) for improved separation and detection of trace additives or adulterants. Moreover, the BenchTOF2-TI™ mass spectrometer used in this study incorporates innovative Tandem Ionisation technology for simultaneous acquisition of hard (70 eV) and soft (10–20 eV) electron ionisation (EI) spectra. The complementary nature of hard and soft EI spectra has been shown to improve chemical selectivity when identifying trace additives in complex mixtures such as petrochemicals.^[3]

In this study, we show the value of GC×GC–TOF MS with Tandem Ionisation for comprehensive chemical fingerprinting of neat and spiked gasoline samples. Importantly, we will also demonstrate the use of new data mining tools to uncover the key differences between the gasoline samples using the tandem data to confirm positive hits. Here, the tandem data is utilised in a single, automated workflow to improve discovery of subtle differences by reducing the rate of false positives for review.

Experimental

Samples: Neat and spiked gasoline. The neat gasoline was spiked with three different mixes at 30 ppm (labelled as Mix A, B and C, respectively). The composition of each mix is provided in Table 1. Mix A contained all compounds, while Mix B and Mix C contained a sub-set of eight compounds each.

Injection: Split 5:1, 0.1 µL.

GC×GC: INSIGHT® flow modulator (SepSolve Analytical); Modulation period (P_M): 4.2 s.

MS: Instrument: BenchTOF2-TI (SepSolve Analytical); Mass range: m/z 35–500; Acquisition rate: 100 Hz in Tandem Ionisation mode at 70 and 14 eV.

Software: Full instrument control and data processing by ChromSpace® with ChromCompare+ (SepSolve Analytical) for automated, untargeted comparisons.

Please contact SepSolve for full analytical parameters.

Compound	1t_R (min)	2t_R (s)	Mix A	Mix B	Mix C
Acetone- d_6	2.818	0.542	✓	✓	✓
2-Methylfuran	3.095	0.667	✓	✓	✓
Ethyl acetate	3.2640	0.869	✓	✓	✓
2-Butanone	3.323	0.699	✓	✓	✓
Benzene- d_6	3.665	0.881	✓	✓	✓
2-Pentanone	4.009	0.891	✓	–	–
4-Methyl-2-pentanone	4.282	1.040	✓	✓	–
3-Hexanone	4.830	1.157	✓	✓	–
Cyclopentanone	6.560	1.005	✓	✓	–
Anisole	8.610	0.994	✓	–	✓
Methylcyclopentadienyl manganese tricarbonyl (MMT)	13.930	1.020	✓	–	✓
Ferrocene	14.770	1.307	✓	–	✓

Table 1

List of compounds included in the three mixes used to spike neat gasoline.

Results and discussion

In this study, neat and spiked gasoline samples were compared using GC×GC–TOF MS with Tandem Ionisation. Figure 1 shows example chromatograms for the neat gasoline and that of gasoline spiked with Mix A, containing all twelve spiking compounds. A visual comparison of the chromatograms (Figure 1) shows that three of the spiking compounds could be observed easily, despite their trace levels, as they elute in sparse regions of the chromatogram, well-separated from the gasoline matrix. However, the other nine spiking compounds were masked by the gasoline matrix, meaning that powerful instrumentation and smart data analysis workflows are required to find the differences between such complex samples.

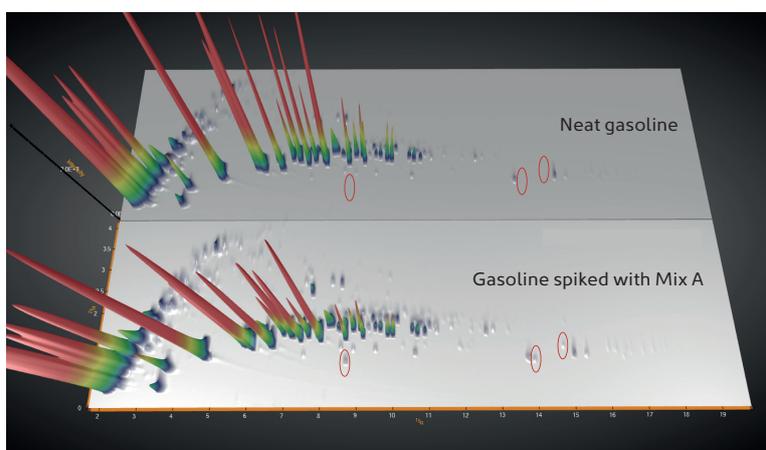


Figure 1

Example GC×GC–TOF MS surface charts for the neat gasoline and the gasoline spiked with Mix A. Circled regions indicate spiking compounds that could be visually observed.

Here, the GC×GC–TOF MS system utilised Tandem Ionisation to further improve selectivity in such analyses, by simultaneously acquiring both hard and soft EI spectra for complementary chemical information with no added analysis time. Figure 2 shows examples of the complementary spectra for two of the spiking compounds, with clear enhancement of the higher m/z ions using soft EI (14 eV, in this case).

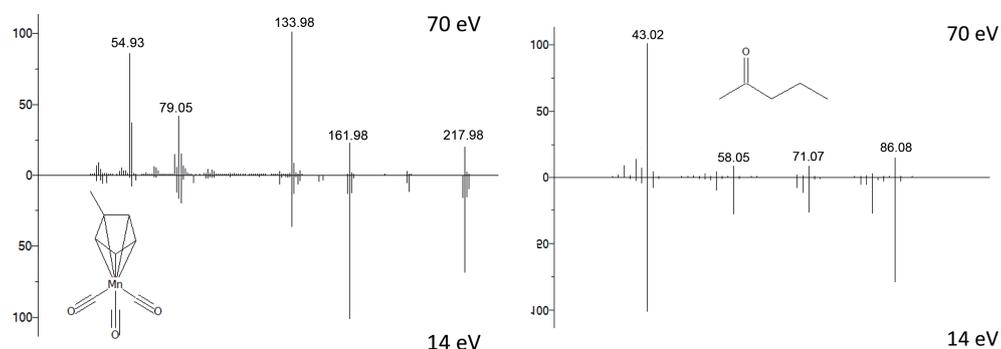


Figure 2

Examples of the enhanced selectivity obtained through the complementary nature of Tandem Ionisation spectra for (A) MMT and (B) 2-pentanone.

Novel automated workflows were utilised in ChromCompare+ software to make use of all of the raw tandem data. This approach divides the chromatogram into small tiles, and sums the signal for every individual m/z channel in each tile for comparison between samples. Time-consuming pre-processing steps, such as integration and identification, are eliminated and it ensures that all of the raw data is used, minimising the risk of missing important details.

By utilising both sets of MS data in a single workflow, discovery of true differences is improved through reduction of false positives. Find out more about these tandem workflows in our technical note [‘Improving discovery workflows using Tandem Ionisation data’](#).

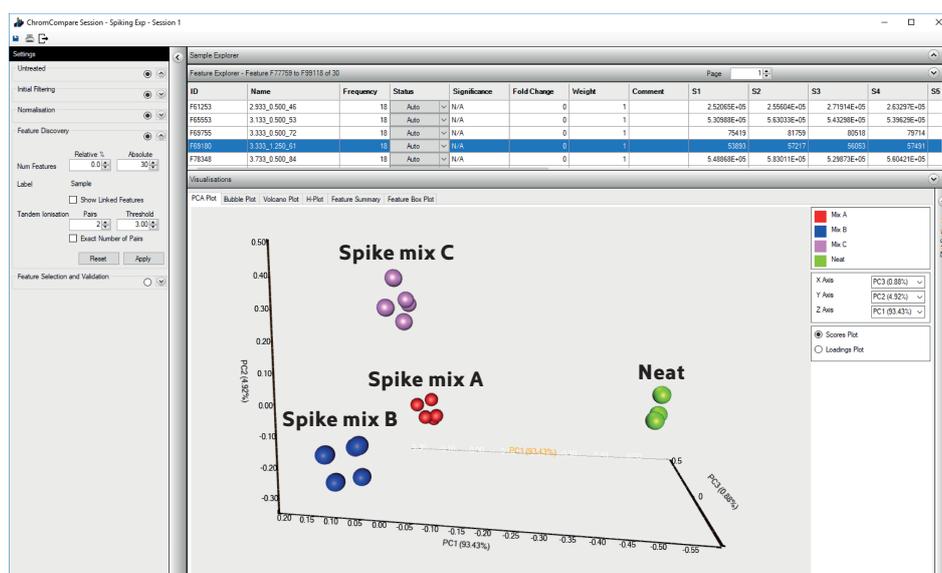


Figure 3

Principal components analysis (PCA) score plot in ChromCompare+ software for the comparison of neat and spiked gasoline samples using tandem data.

The resulting PCA score plot is provided in Figure 3 and shows clear clustering of the gasoline samples, with the neat gasoline well-separated from the spiked samples along principal component 1 (PC1). In fact, the software was able to identify every spiking compound when using the tandem data.

However, when the same processing workflow was applied to the 70 eV data alone, fewer positive hits were achieved (Table 2). The spiking compounds ethyl acetate, 4-methyl-2-pentanone, 3-hexanone and cyclopentanone were not identified as top differentiators in the 70 eV-only dataset.

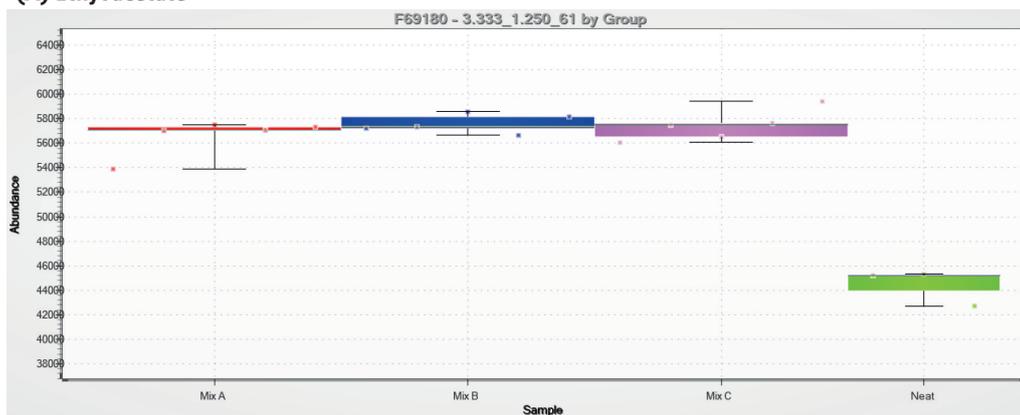
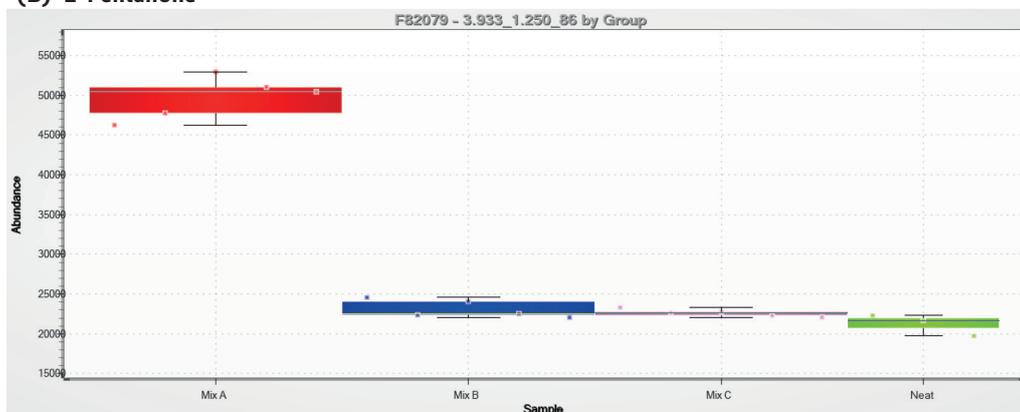
Spiking compounds	Datasets	
	70 eV only	Tandem (70/14 eV)
Acetone-d ₆	✓	✓
2-Methylfuran	✓	✓
Ethyl acetate	x	✓
2-Butanone	✓	✓
Benzene-d ₆	✓	✓
2-Pentanone	✓	✓
4-Methyl-2-pentanone	x	✓
3-Hexanone	x	✓
Cyclopentanone	x	✓
Anisole	✓	✓
Methylcyclopentadienyl manganese tricarbonyl (MMT)	✓	✓
Ferrocene	✓	✓

Table 2

The compounds identified as key differentiators between the neat and spiked gasoline samples using tandem data (70 eV and 14 eV) and 70 eV-only.

Using tandem data in discovery workflows therefore provides greater confidence that the true differences are identified, instead of false positives. For example, Figure 4(A) shows the box and whisker plot for ethyl acetate, which was identified as a top differentiator using the tandem data, despite being present at an intensity four orders of magnitude lower than the highest-loading features. While it is clearly present in all three spiked samples and not in that of the neat samples, it was not identified as a significant difference in the 70 eV-only dataset, due to being overshadowed by false positives. Furthermore, the compositional differences between the spiking mixes were also easily identified, such as for 2-pentanone shown in Figure 4(B), which was only present in Spiking Mix A.

It is clear from this study that the powerful combination of GC×GC–TOF MS, Tandem Ionisation and smart data analysis tools in ChromCompare+ provides an ideal approach to identifying trace additives or adulterants in complex petrochemical samples.

(A) Ethyl acetate**(B) 2-Pentanone****Figure 4**

Box and whisker plots in ChromCompare+ showing two significant differences between the neat and spiked gasoline samples, which were identified as the spiking compounds ethyl acetate and 2-pentanone, respectively.

Conclusions

This study has shown that the described GC×GC–TOF MS system is ideal for detection and identification of trace adulterants in complex petrochemicals, including:

- ▶ Enhanced separation by GC×GC using INSIGHT® consumable-free flow modulation to discover more in petrochemical samples.
- ▶ BenchTOF2-TI provides sensitive detection and confident identification of trace adulterants in complex samples.
- ▶ Tandem Ionisation provides complementary hard and soft ionisation data for enhanced chemical selectivity with no added analysis time.
- ▶ Fully untargeted data analysis in ChromCompare+ automatically finds the significant differences between complex samples.
- ▶ Tandem data can be utilised in streamlined workflows to improve discovery of subtle, trace differences by suppressing false positives in untargeted comparisons.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

References

- [1] United States Clean Air Act, 42 U.S. Code § 7545 – Regulation of fuels, Section 211.
- [2] United States Environmental Protection Agency (US EPA), List of Registered Gasoline Additives, <https://www3.epa.gov/otaq/fuels1/ffars/web-gas.htm> (as accessed on 1 March 2021).
- [3] C.E. Freye, N.R. Moore and R.E. Synovec, Enhancing the chemical selectivity in discovery-based analysis with tandem ionization time-of-flight mass spectrometry detection for comprehensive two-dimensional gas chromatography, *Journal of Chromatography A*, 2018, 1537: 99–108.

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