Application
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Application Note 539

Routine, high-performance analysis of petrochemicals by GC×GC with simultaneous detection by FID and Tandem Ionisation TOF MS

Summary

This Application Note demonstrates the repeatability of a flow-modulated GC×GC–TOF MS system for the analysis of complex petrochemicals. The analytical approach described pushes the boundaries of hyphenated systems by simultaneously providing three information-rich datasets for each acquisition – namely, robust quantitation by FID, untargeted screening by TOF MS with electron ionisation (EI) at 70 eV, and confirmatory identification by TOF MS with soft EI.

Introduction

Precise characterisation of petrochemical samples is crucial for quality control, and also to understand the reactions that take place during refining processes. Comprehensive two-dimensional gas chromatography (GC×GC) offers significant advantages over conventional chromatography for such analyses, with its vastly expanded separation space and the added benefit of highly structured groupings of compounds.

Fast acquisition speeds make time-of-flight mass spectrometry (TOF MS) the ideal partner to GC×GC. Furthermore, the elimination of mass discrimination (unique to the design of Markes' BenchTOF), increased sensitivity and more compact instrument designs have made TOF MS much more appealing than previously. However, best-practice in the petrochemical industry recommends the use of flame ionisation detection (FID) for target compound quantitation.

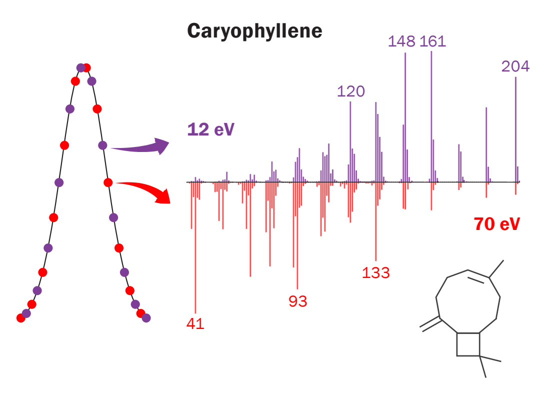
This study explores the use of dual-detection GC×GC to enable both targeted and non-targeted approaches to be performed simultaneously – with TOF MS for confident identification and FID for robust quantitation.

Within this workflow, we also investigate the use of Tandem Ionisation at conventional 'hard' (70 eV) *and* 'soft' ionisation energies to overcome the problem of certain compounds exhibiting weak molecular ions and similar spectra at 70 eV. In particular, we show how the soft EI spectra allow speciation of isomers (such as branched hydrocarbons) that would not have been discriminated at 70 eV – thus unlocking the fine detail of the sample composition.

Tandem Ionisation®

Exclusive to Markes, Select-eV® allows you to collect soft EI spectra down to 10 eV, with no inherent loss in sensitivity and full automation in TOF-DS software with no need for manual intervention.

Tandem Ionisation now adds unparalleled productivity for soft ionisation. Soft and hard ionisation spectra are obtained across every peak, in both GC and GC×GC analyses, for comprehensive sample characterisation in a single run.



One chromatographic peak, two complementary spectra. Tandem Ionisation using Select-eV enables 70 eV and soft EI spectra to be collected across every peak in a single run.

Background to BenchTOF systems

BenchTOF™ mass spectrometers are high-sensitivity time-of-flight instruments designed specifically for gas chromatography. In addition to the Tandem Ionisation capability available with BenchTOF-Select (see previous page), they are particularly appropriate for confident chemical fingerprinting of petrochemicals for the following reasons:

- **Spectral quality:** Unlike other TOF systems for GC, BenchTOF instruments deliver 'reference-quality' spectra that are a close match to those in commercial libraries (*e.g.* NIST or Wiley) and standard quadrupole spectra (*e.g.* in in-house archives). This enables quick and confident matching of analytes.
- **Speed:** The ability to record full-range mass spectra information to extremely high densities (10,000 transient spectral accumulations per second) enables BenchTOF systems to handle the narrowest peaks encountered in well-optimised GC×GC configurations.

Experimental

A schematic of the analytical system is shown in Figure 1.

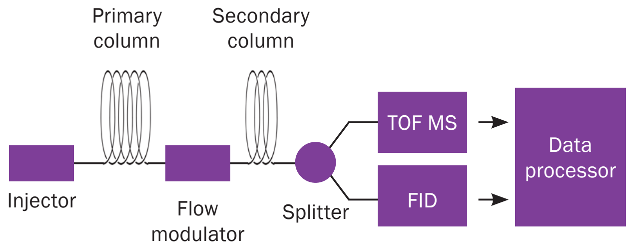


Figure 1: Schematic of the GC×GC–TOF MS/FID analytical system.

Sample:
Pump diesel (undiluted)

GC×GC:

Injector:	Split/splitless
Liner:	Single taper with wool, 4 mm (i.d.)
Carrier gas:	Helium, constant-flow at 0.5 mL/min
Mode:	Split 300:1
Temperature:	280°C
Septum purge:	On, 3 mL/min
Modulator:	Insight™ flow modulator (SepSolve Analytical)

2D column set (Repeatability study):

1st dimension:	BPX5™, 20 m × 0.18 mm × 0.18 µm
2nd dimension:	DB-17™, 2 m × 0.25 mm × 0.15 µm
Temp. program:	Main oven: 50°C (1 min), 3°C/min to 320°C (hold 10 min)
Loop dimensions:	30 cm × 0.32 mm i.d.
Loop volume:	24 µL
Fill time:	5800 ms
Flush time:	200 ms
P_M:	6.0 s

2D column set (Dual detection study):

1st dimension:	BPX5™, 25m × 0.15 mm × 0.25 µm
2nd dimension:	ZB-50™, 5 m × 0.25 mm × 0.15 µm
Temp. program:	Main oven: 50°C (1 min), 2.5°C/min to 320°C (hold 20 min)
Loop dimensions:	10 cm × 0.53 mm i.d. (loop volume: 22 µL)
Fill time:	3900 ms
Flush time:	100 ms
P_M:	4.0 s

TOF MS:

Instrument:	BenchTOF-Select™ (Markes International)
Filament voltage:	1.7 V
Ion source:	320°C
Transfer line:	300°C
Mass range:	m/z 45–450
Data rate:	100 Hz in Tandem Ionisation mode at 70 eV and 14 eV

FID:

H_2 flow:	30 mL/min
N_2 flow:	25 mL/min
Air flow:	400 mL/min
Data rate:	100 Hz
Software:	Instrument control and GC×GC data processing was carried out using TOF-DS™ with ChromSpace®

Results and discussion

Repeatability of flow modulation

A major advantage of flow-modulated GC×GC over thermally-modulated systems (aside from the reduction in running costs) is the superior repeatability that can be achieved. The precisely-defined microfluidic design allows identical configurations to be installed across multiple instruments, unlike in thermal devices, where small variations in column position can have a large impact on results.

In this study, the repeatability of the flow modulation device was first evaluated using GC×GC–FID for 24 replicate injections over the course of three days (Figure 2).

The results illustrate the excellent repeatability of the technique, with calculated RSDs less than 0.14%, 0.52% and 2.98% for ^1t_R, ^2t_R and peak abundance, respectively. This high precision of time response is a result of a dedicated EPC unit being used for each column, and enables simple comparison of large sample batches and confident interpretation of results.

Evaluation of GC×GC with simultaneous MS/FID detection

FID is the gold standard for quantitative GC and GC×GC applications in the petrochemical industry for many reasons, including negligible band broadening, wide linear range, fast data capture and mass-dependent response. At the same time, MS detection (especially high-performance TOF MS), offers the advantage of robust analyte identification, and options for peak deconvolution and retrospective data-searching.

The use of GC×GC with parallel detection by MS and FID is therefore an ideal approach for achieving qualitative and quantitative analysis of petrochemicals in a single run. Targeted quantitative analysis can be performed across the widest concentration ranges, with dual-detector cross-validation and confirmation of peak purity.

However, thermally-modulated systems can be troublesome to configure for such dual-detector setups, but this is not an issue with flow modulation. Figure 3 compares colour plots obtained by simultaneous detection by TOF MS and FID, with chromatographic conditions for optimum separation and alignment of retention times in both the first and second dimensions.

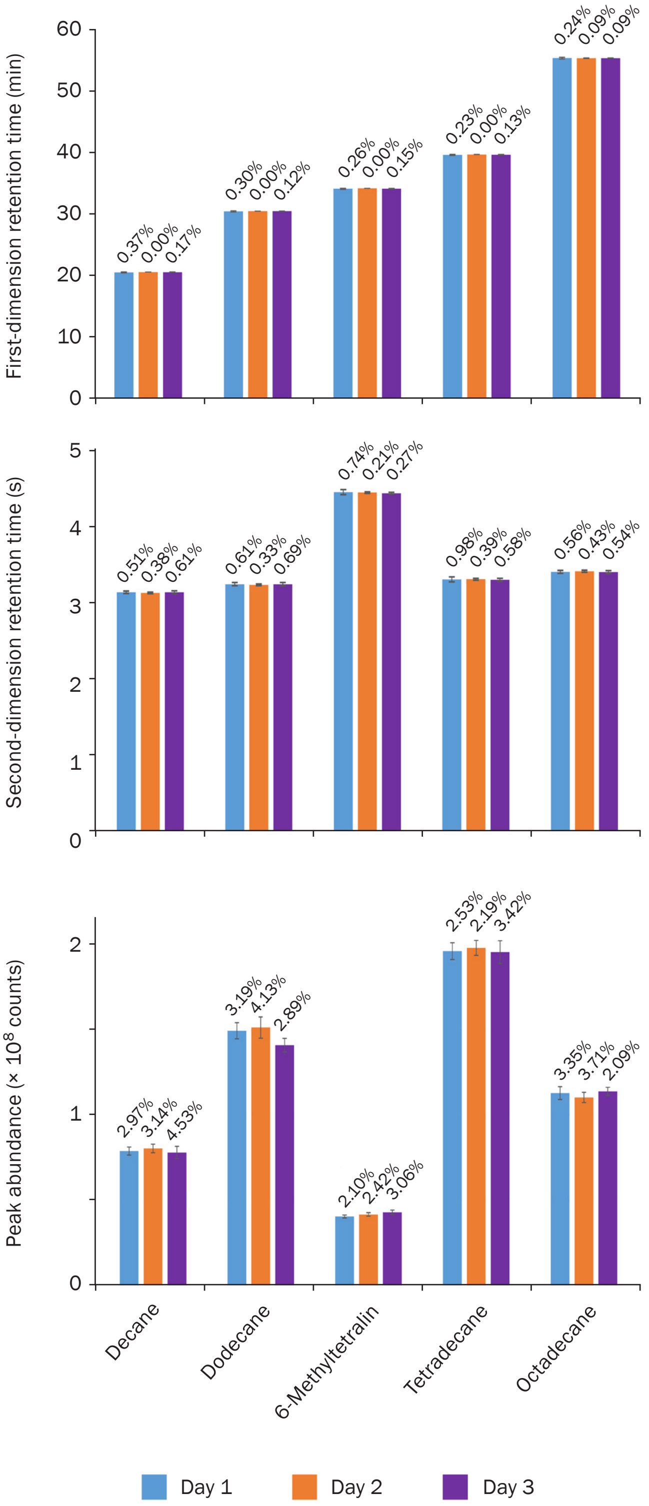


Figure 2: Repeatability of flow-modulated GC×GC–FID during a three-day study (n = 8 per day). The RSDs for each day are indicated.

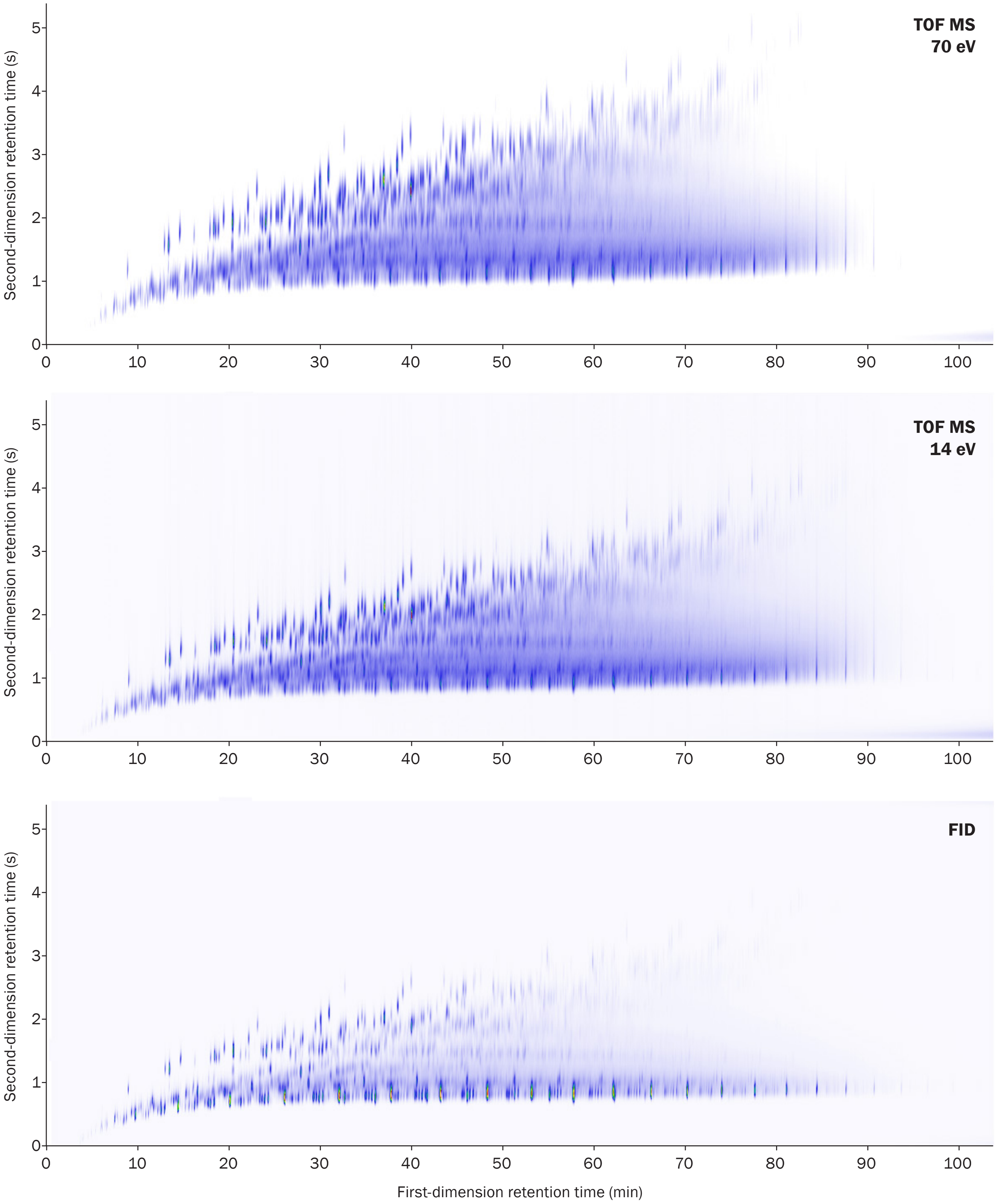


Figure 3: GC×GC colour plots of diesel, generated by simultaneous detection by TOF MS (with Tandem Ionisation at 70 eV and 14 eV) and FID.

Tandem Ionisation

The use of simultaneous detection by TOF MS and FID provides a wealth of information for petrochemical analyses, but the challenge of identifying individual hydrocarbon isomers still remains. At conventional 70 eV ionisation, the spectra of these isomers are virtually indistinguishable, meaning it is impossible to make confident compound assignments. Such identifications are of great commercial importance to the petrochemical industry, because individual isomers can provide different characteristics to the final fuel (*e.g.* octane number, flash point and viscosity).

Addressing this challenge, the use of soft electron ionisation (or soft EI) has been shown to provide increased confidence in the identification of branched alkanes,[1] by providing enhancement of the molecular ion and other structurally-significant ions. A further advance in this area is Tandem Ionisation, which involves fast switching between conventional 70 eV ionisation and Select-eV soft EI. This allows two complementary MS datasets to be simultaneously acquired, without impacting laboratory workflow and with perfectly aligned peaks for easy navigation of the soft EI data.

Figure 4 shows the speciation of three hydrocarbon isomers using soft EI. The 14 eV spectra exhibit clear spectral differences that enable confident identification – which would not have been achievable based solely on 70 eV analyses.

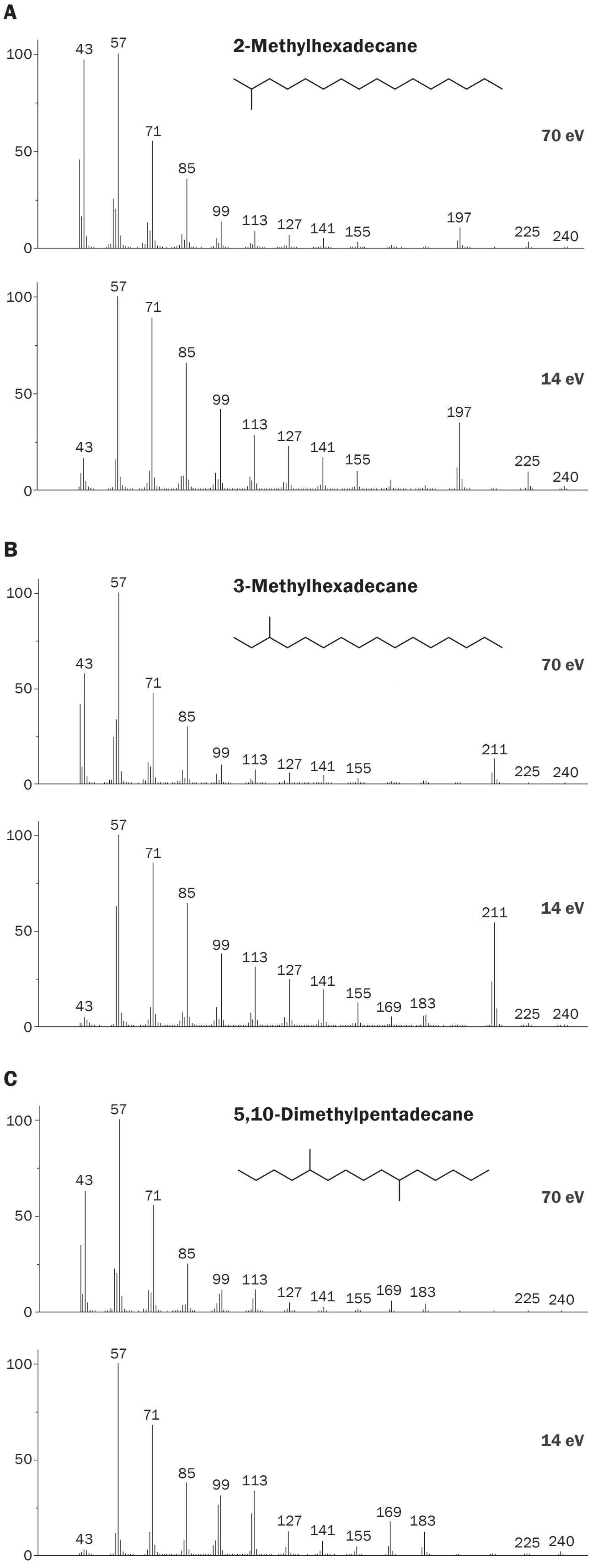


Figure 4: Spectral comparisons at 70 eV and 14 eV for three hydrocarbon isomers.

As another example of a challenging class of analytes, three alkylbenzenes are shown in Figure 5. The 70 eV spectra all share m/z 91 as the base peak, with relatively weak molecular ions at m/z 260. However, at 14 eV, the molecular ions and those ions indicating the branching positions of the alkyl chain are greatly enhanced.

As an additional qualifier for compound identification prior to sample quantitation and reporting, Tandem Ionisation can also be used to provide confirmatory ion ratios between low-eV and 70 eV spectra.

Conclusions

This Application Note has illustrated the power of flow-modulated GC×GC to provide structured chromatograms that greatly simplify the process of compound identification, as well as the ability of flow modulation to provide robust, repeatable analysis of petrochemicals, without the inconvenience or running costs associated with thermal modulation. In addition, the excellent retention-time repeatability in both dimensions enables fast and confident data processing of large sample batches, while the retention-time alignment between FID and TOF MS during parallel detection enables two-fold validation of measured peaks.

The analytical approach detailed here has also been shown to push the boundaries of hyphenated systems by providing three information-rich datasets per acquisition – namely, robust quantitation by FID, untargeted screening by TOF MS with electron ionisation (EI) at 70 eV, and confirmatory identification by TOF MS with soft EI.

References

1 M.S. Alam, C. Stark and R.M. Harrison, Using variable ionisation energy time-of-flight mass spectrometry with comprehensive GC×GC to identify isomeric species, *Analytical Chemistry*, 2016, 88: 4211–4220, http://dx.doi.org/10.1021/acs.analchem.5b03122.

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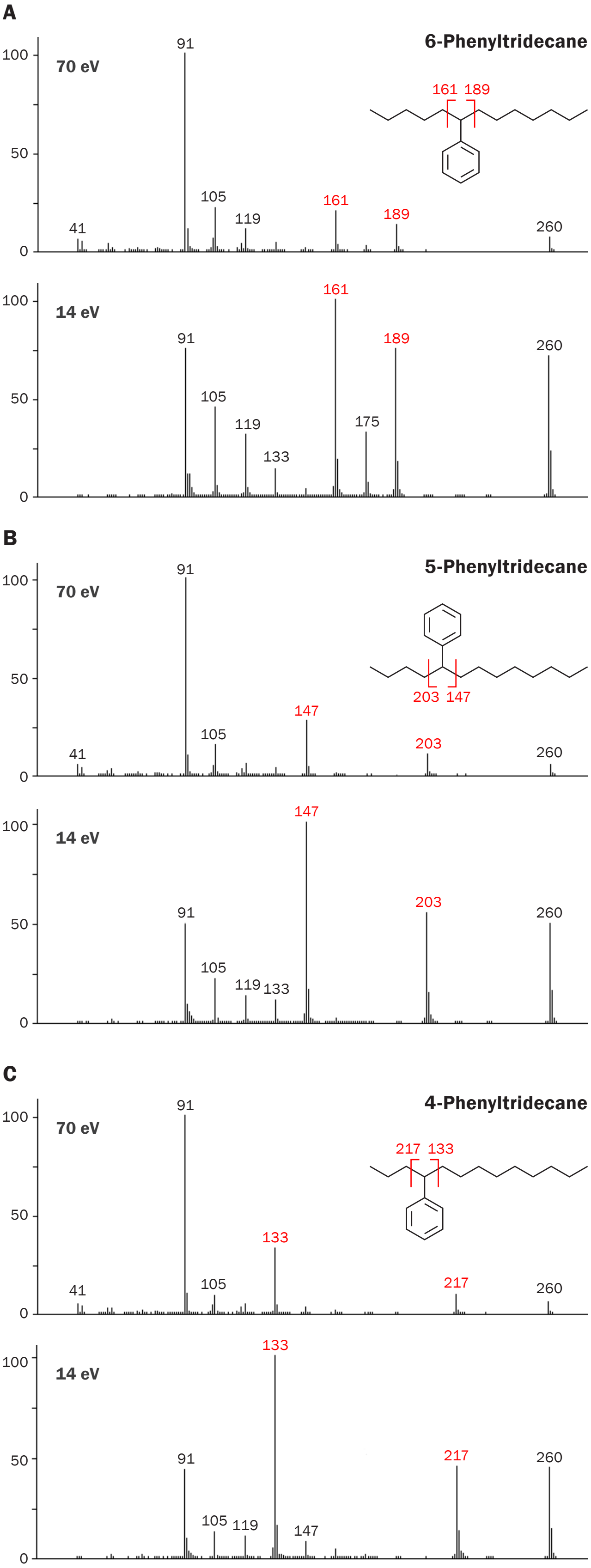

Figure 5: Spectral comparisons at 70 eV and 14 eV for three alkylbenzene isomers. Diagnostic ions resulting from fragmentation at the branching positions are indicated in red.