Chemical fingerprinting of tobacco and related products by TD–GC–TOF MS

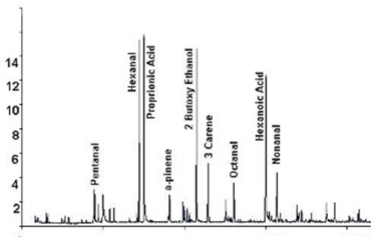
Nick Bukowski[1], Caroline Widdowson[1], Pete Grosshans[2], Kevin Collins[1], Steve Smith[1] and Laura McGregor[1]

[1] Markes International Ltd, Gwaun Elai Medi-Science Campus, Llantrisant, RCT, UK; [2] Markes International, Inc., 11126-D Kenwood Road, Cincinnati, Ohio 45242, USA.

Introduction

The hazardous constituents of cigarette smoke have attracted considerable media attention, especially with increasing regulation around the world limiting or banning smoking in public places – and even in private cars if children are present.

Furthermore, the recent surge in tobacco-replacement devices, such as e-cigarettes, is driving the development of fast and efficient quality control procedures. E-cigarette solutions may contain potentially harmful chemicals, including nitrosamines and polycyclic aromatic hydrocarbons (PAHs). The presence of such chemicals naturally gives rise to some concern, and confident chemical fingerprinting is required for both research & development and regulatory purposes.



Although e-cigarettes emit less particulate matter than regular tobacco cigarettes (since no combustion takes place), they still produce a wide range of compounds at trace levels. Organic constituents of tobacco smoke have historically been analysed by gas chromatography (GC) coupled with quadrupole mass spectrometry (MS).

However, quadrupoles are mass filters, with a high percentage of ions being wasted, which limits sensitivity. Moreover, in selected ion monitoring (SIM) mode, only target compounds can be monitored, meaning that full characterisation of the sample is not possible in a single run and retrospective searching of data is limited.

This presentation explores the use of a multi-functional thermal desorption (TD)–GC–TOF MS system to capture and identify whole e-cigarette emissions using a single, highly-automated platform.

Thermal desorption

Thermal desorption (TD) is a versatile GC pre-concentration technology that is applicable to the analysis of volatile and semi-volatile organic compounds (VOCs and SVOCs) in a wide range of sample matrices. As well as boosting sensitivity, it allows full automation of the processes of sample preconcentration, desorption/extraction and GC injection, greatly improving sample throughput. The typical two-stage TD process involves the relatively gentle heating of sampled sorbent tubes in a flow of inert carrier gas. The released components are then swept into an electrically-cooled 'focusing' trap within the TD system.

Figure 1: Overview of the multiple modes of sample introduction into TD systems for analysis of tobacco products.

Focusing trap conditions (sorbents, gas flows and temperature) can be selected to allow quantitative retention of compounds of interest, while interferents such as water are selectively purged prior to analysis. Once sample tube desorption is complete, the focusing trap is heated rapidly in a reverse flow of carrier gas to inject the organic compounds into the GC column as a sharp band of vapour. This efficient two-stage desorption process optimises concentration enhancement and produces narrow chromatographic peaks, thus optimising sensitivity.

TD provides enhanced sensitivity for a wide range of analytes, enabling comprehensive material emissions profiling and allowing the potential hazard to human health to be thoroughly assessed.

Experimental

In this work, we use Markes' fully automated TD-100™ thermal desorber, which can accommodate up to 100 sorbent tubes. A key advantage of the TD-100 is that it provides the option of sample splitting during primary (tube) desorption and secondary (trap) desorption, giving the system an exceptionally wide dynamic range. It also offers quantitative re-collection of split flow for repeat analysis and method validation.

Figure 2: Workflow for the analysis of e-cigarette aerosol.

E-cigarette aerosol was sampled directly on to a sorbent tube and analysed by GC–TOF MS, with the TOF-DS software suite providing full instrument control and near-real-time data processing (including background subtraction, deconvolution and library-searching). The high degree of automation increases sample throughput and removes any analyst subjectivity.

Results

Analysis of e-cigarette aerosols

The use of time-of-flight mass spectrometry (TOF MS) overcomes the issues associated with GC–quadrupole MS, by providing highly sensitive detection whilst acquiring full-range mass spectra, to allow both target and unknown identification in a single, rapid analysis. The combination of TD preconcentration and GC–TOF MS enables sensitivity compatible with toxicological levels of interest or potential concern.

Figure 3 shows the GC–TOF MS chromatograms obtained for the analysis of three e-cigarette aerosols. High-loading peaks for (**A**) allyl alcohol, (**B**) glycidol, (**C**) propylene glycol and (**D**) nicotine were found across many samples, and in one case (**E**) ethyl maltol. It is worth noting that allyl alcohol is associated with the thermal degradation of glycerol and propylene glycol (humectants in e-cigarette liquid).

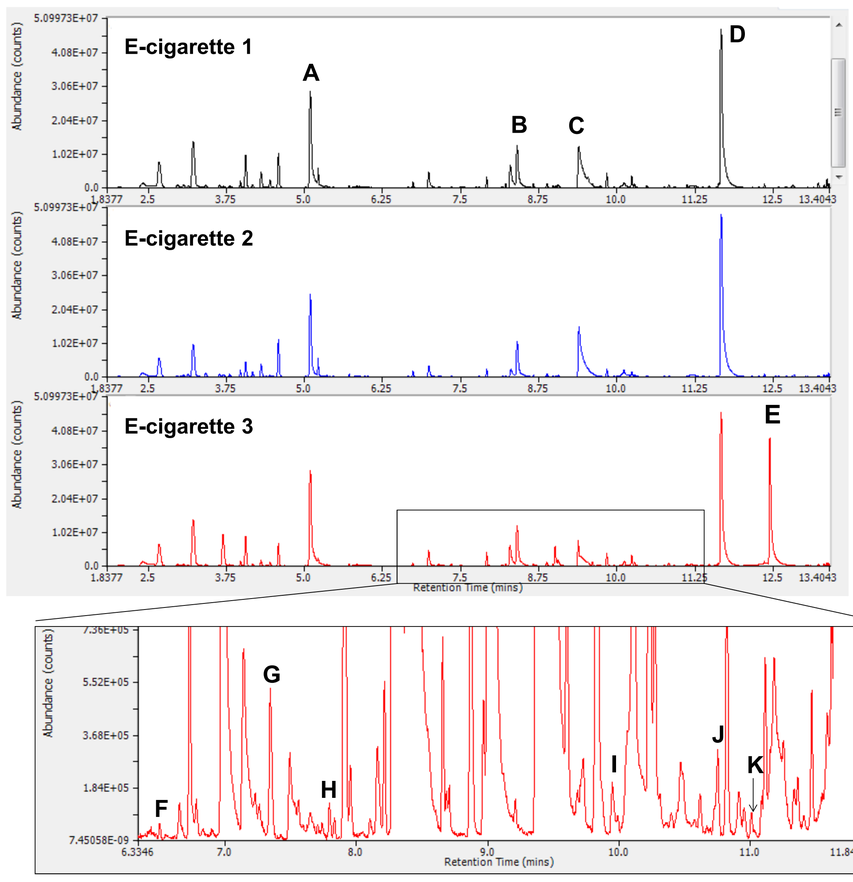


Figure 3: GC–TOF MS chromatograms (TIC) for the analysis of three e-cigarette aerosols.

A: Allyl alcohol
B: Glycidol
C: Propylene glycol
D: Nicotine
E: Ethyl maltol

F: *o*-Cymene
G: Ethoxyethene
H: Butyl glycol
I: γ-Butyrolactone
J: α-Cumyl alcohol
K: 2-Pyranone

Considering the potential for formation of such degradants as artefacts of the thermal desorption process, the ability for secure sample re-collection on the Markes' TD systems enables thorough monitoring of their formation and excellent quality control. Many trace constituents were also detected, as shown in the expansion, enabling full characterisation of the sample in a single run.

Analysis of cigarette smoke by TD–GC×GC–TOF MS

This preliminary study also investigated the use of TD coupled with comprehensive two-dimensional gas chromatography (GC×GC) for the analysis of cigarette smoke. Figure 4 shows the enhanced separation achieved over 1D analyses, by coupling non-polar (BPX5) and mid-polar (BPX50) columns.

Although further work is required to optimise the separation, this initial study enabled the separation of >1000 peaks, showing the great potential of the technique.

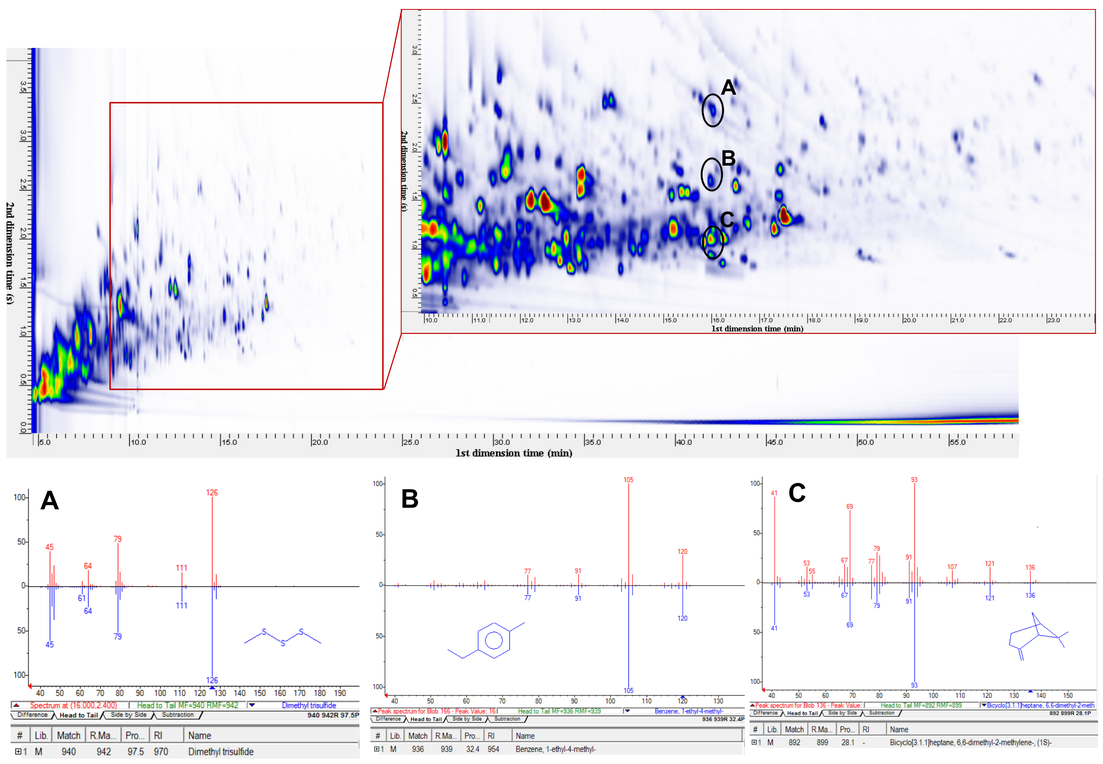


Figure 4: Colour plot generated by TD–GC×GC–TOF MS of cigarette smoke, with spectral matches against the NIST library for three compounds that would have co-eluted in conventional 1D GC–MS.

Conclusion

This work has demonstrated the versatility of TD in combination with GC–TOF MS and GC×GC–TOF MS, for pre-concentrating VOCs to allow confident quantitation of ultra-trace analytes. Markes' splitting and re-collection technologies are particularly valuable, because they aid analysis of samples over a wide dynamic range by allowing repeat analysis with different split ratios.

Complementing this capability, the high sensitivity of BenchTOF mass spectrometers delivers detection limits better than quadrupoles in SIM mode, enabling detection of ultra-trace targets and unknowns. In addition, the 'classical', library-searchable spectra mean confident assignment of trace-level analytes in a single run, for robust quality control of tobacco products.

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T: +44 (0)1443 230935 **F:** +44 (0)1443 231531 **E:** enquiries@markes.com **W:** www.markes.com