

Vehicle interior air quality – (S)VOC emission from materials: Regulation, standard methods and analytical implementation

C. Widdowson, L. McGregor, S. Smith and N. Bukowski

Markes International, Gwaun Elai Medi-Science Campus, Llantrisant, RCT, CF72 8XL, UK

Introduction

Exposure to air pollutants has for many years been recognised as a major cause of health problems. Historically, pollutants from vehicle exhaust and the burning of fuels were of primary concern, but as urban air quality has generally improved, attention has shifted to vehicle interior air quality (VIAQ). Emissions of volatile and semi-volatile organic compounds from car interiors can have an adverse effect on VIAQ, raising concerns for passenger health and safety.

As a result of these concerns, VIAQ is of growing importance to the automotive industry, and has culminated in the development of harmonised methods (e.g. ISO 12219 series) to quantitate the release of chemicals from materials used in car manufacture. Methods generally specify the use of environmental chambers, vapour sampling onto sorbent tubes and analysis by thermal desorption (TD) with conventional GC-MS. However, the broad range of sample types and the presence of target compounds at ultra-trace levels, often within complex matrices, provide a challenge to analytical chemists.

Regulations and standard methods

The emission levels and potential impact of any given car trim component can be evaluated, and the levels of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs, *i.e.* fogging compounds) and specific malodorous compounds emitted under different conditions can be determined. Target compounds include formaldehyde, acetaldehyde, benzene, styrene, xylenes and phthalates, and limit levels have previously been specified by various automobile associations, including:

- Japan Automobile Manufacturers Association (JAMA).
- European Automotive Manufacturers' Association (ACEA).
- Global Automakers, formerly the Association of International Automobile Manufacturers (AIAM).
- Labelling organisations (e.g. TÜV Rhineland Group).

Over the years, hundreds of manufacturer-specific methods have been developed for the sampling and analysis of VOCs and SVOCs, and these employ numerous analytical techniques. Some widely-used methods are:

General Motors GMW15654: Full vehicle air sampling, VOC and SVOC analysis by GCMS.
General Motors GMW15634: Interior materials VOC and SVOC by TD-GCMS (direct sampling) thermal desorption.
BMW GS97014-3: Emission measurements with air exchange in a testing chamber.
Volkswagen PB VWL 709: Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermal desorption.
VDA 278: Thermal desorption analysis of organic emissions for the characterization of non-metallic materials for automobiles.
TSM0508G: Volatile component measurement method using sampling bag.

To simplify matters for the industry, the International Standards Organisation recently convened a technical committee (ISO/TC 146/SC 6) to develop harmonised methods. Seven methods have been developed by ISO/TC 146/SC 6 for sampling VOCs and SVOCs from vehicle interiors and the materials used in them:

ISO 12219-1: Interior air of road vehicles – Part 1: Whole vehicle test chamber – Specification and method for the determination of volatile organic compounds in cabin interiors.
ISO 12219-2: Interior air of road vehicles – Part 2: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials – Bag method.
ISO 12219-3: Interior air of road vehicles – Part 3: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials – Micro-scale chamber method.
ISO 12219-4: Interior air of road vehicles – Part 4: Method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials – Small chamber method.
ISO 12219-5: Interior air of road vehicles – Part 5: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials – Static chamber method.
ISO/AWI 12219-6: Interior air of road vehicles – Part 6: Method for the determination of the emissions of semi-volatile organic compounds from vehicle interior parts and materials – Small chamber method.
ISO/AWI 12219-7: Interior air of road vehicles – Part 7: Odour determination in interior air of road vehicles and test chamber air of trim components by olfactory measurements.

Thermal desorption

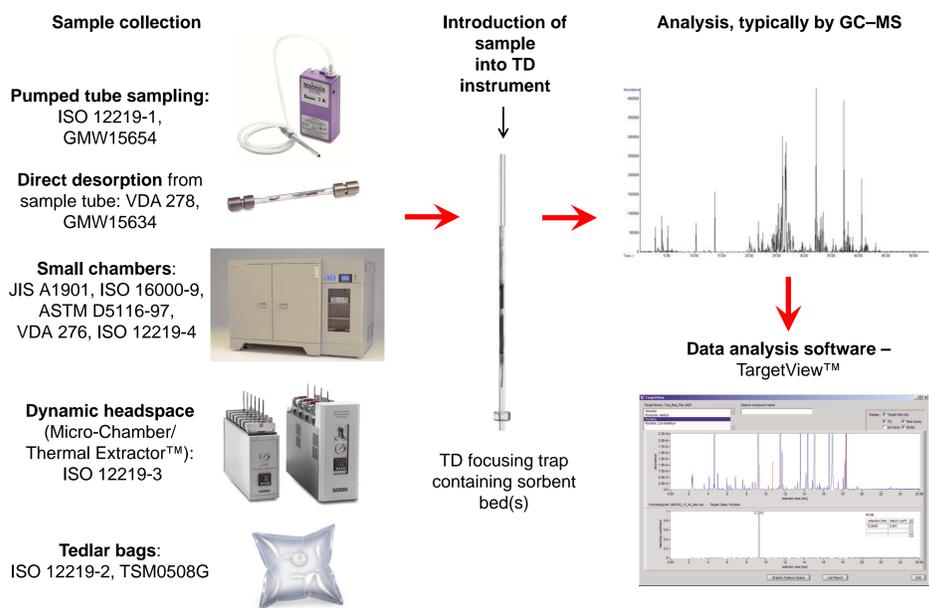


Figure 1: Overview of the multiple modes of sample introduction into TD systems.

TD is a versatile GC pre-concentration technology that is applicable to the analysis of VOCs and SVOCs in a wide range of sample matrices. As well as boosting sensitivity, it allows full automation of the processes of sample pre-concentration, 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. Focusing trap conditions (sorbents, gas flows and temperature) can be selected to allow quantitative retention of compounds of interest, while interferences 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 narrow band of vapour. This efficient two-stage desorption process optimises concentration enhancement and produces narrow chromatographic peaks, thus optimising sensitivity.

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. 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.

Beyond the standard methods...

While the harmonisation and implementation of the new ISO methods and the increased awareness of VIAQ has been a rapid process, there are still technical advances to be made. The standard methods and regulatory compound lists and limit levels cover a vast range of compounds, but there are now new techniques that now allow manufacturers to understand their materials in even greater depth. The use of techniques such as comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC-TOF MS) offers enhanced chromatographic separation with exceptional sensitivity. Here, Markes' BenchTOF-Select™ instrument (Figure 2) was used for all analyses. The innovative Select-eV® ion source extends the capabilities of GCxGC-TOF MS by enabling both hard and soft electron ionisation (from 70 eV down to 10 eV) with no loss in sensitivity.

The availability of full-fragmentation spectra for confident library matching is complemented by the ability of Select-eV to enhance the diagnostic ions that define compound identity and distinguish between similar compounds. Fragment ions that ordinarily dominate high matrix samples become greatly reduced, enhancing selectivity and further improving detection levels (Figure 3).

A GCxGC gas chromatograph (Agilent 7890GC with Zoex ZX1 modulator) was used in combination with the BenchTOF-Select for the following case study.



Figure 2: BenchTOF-Select with GCxGC.

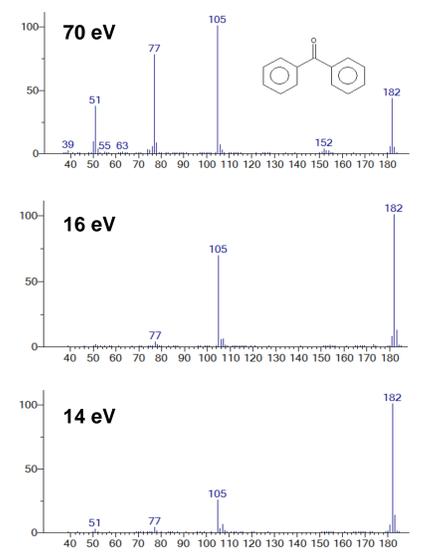


Figure 3: Comparison of mass spectra for benzophenone at 70, 16 and 14 eV using Select-eV.

Nitrosamines in vehicle interiors

There are a number of VOCs routinely monitored in the interiors of new cars due to the hazards they potentially pose to human health. Nitrosamines, which have the general formula R¹R²N=O, are one such group, and are found in rubber products. Because nitrosamines are known to be carcinogenic, it is important to be able to regulate the level in new vehicle interiors.

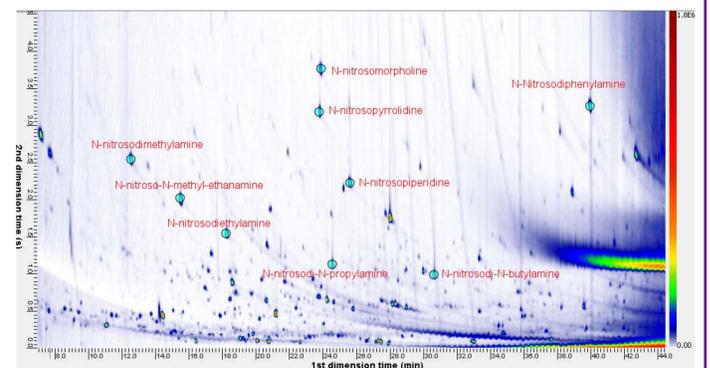


Figure 4: GCxGC-TOF MS contour plot of an EPA 8270 nitrosamine mix (1 µL of 20 ng/µL loaded on to a Tenax tube and split 100:1 on injection, 200 pg on-column).

Figure 4 shows the complete separation of all nine nitrosamines in the analysed standard, with each component having a NIST match factor >800. Select-eV ionisation complements the power of the TD-GCxGC-TOF MS system for the analysis of nitrosamines, by allowing soft electron ionisation with no loss in sensitivity in a fully automated method. Although the mass spectra of nitrosamines are generally quite simple at 70 eV, reducing the ionisation energy to 15 eV results in an increased intensity of the molecular ion (Figure 5), meaning detection limits can be extended.

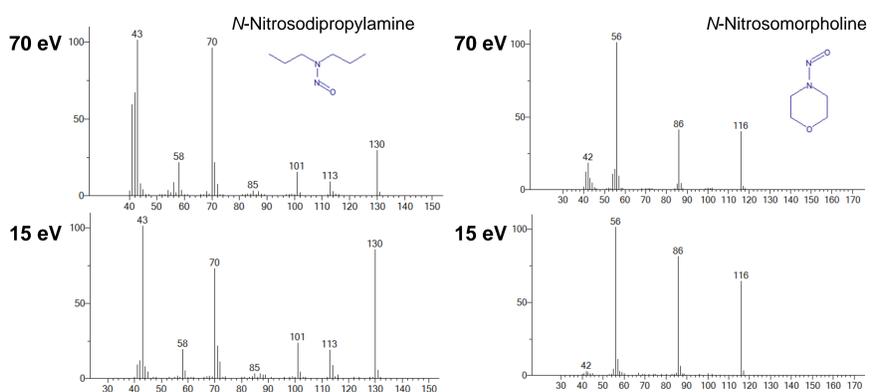


Figure 5: Spectral comparisons for two nitrosamines at 70 and 15 eV.

Moreover, background gases (such as carrier gas and CO₂) are not ionised at low ionisation energy, further increasing the selectivity of the technique. This is particularly useful for the detection and identification of low molecular weight compounds – for example, isopropanol and ethanol use m/z 45 for quantitation, which is an ion shared by CO₂.

Conclusions

Harmonised methods are now being used to quantitate releases of chemicals from the materials used inside vehicles, and assess the overall quality of in-vehicle air. Here, we have described how thermal desorption and related sampling methods that are stipulated in these methods can aid understanding of both the volatile content and emission profiles of car trim, as well as for analysis of in-vehicle air. In particular, we have shown how the scope of these methods can be broadened by using both two-stage thermal desorption and GCxGC-TOF MS, which enables reliable separation and identification of hundreds, if not thousands, of compounds in a single analysis. This combination overcomes selectivity and sensitivity issues, so allowing manufacturers to understand the emission profile of their materials in even greater depth.