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

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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 quantify 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 a 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, can be measured. Several methods have been developed by standards and organisations to quantify the release of chemicals from materials used in vehicles, to provide a unified assessment of chemical content and emission profiles of car trim, as well as for analysis of in-vehicle air. Here, we have shown how the desorption and related sampling methods that are stipulated in these methods can aid understanding of both the volatile compounds 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 GC×GC-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.

Beyond the standard methods...

The availability of full-spectrum fragmentation for confident library matching is complemented by the ability to selectively 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 GC×GC chromatograph (Agilent 7890GC with ZeeX ZX1 modulator) was used in combination with the BenchTOF-Select™ for the sake of brevity.

Figure 2: BenchTOF-Select with GC×GC.

The development 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 (GC×GC-TOF MS) offers enhanced chromatographic separation with exceptional sensitivity. Here, Markes’ BenchTOF-Select™ instrument (Figure 2) was used for all analyses. The innovative Select+ ion source extends the capabilities of GC×GC-TOF MS by enabling both hard and soft electron ionisation (from 70 eV down to 10 eV) with no loss in sensitivity.

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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–N=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 shows the complete separation of all nine nitrosamines in the analysed standard, with each component having a NIST match factor >90. Select+ ionisation complements the power of the TD-GC×GC-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.

However, 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.

Harmonised methods are now being used to quantify releases of chemicals from the materials used inside vehicles, and assess the overall quality of in-vehicle air. Here, we have described how the desorption and related sampling methods that are stipulated in these methods can aid understanding of both the volatile compounds 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 GC×GC-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.