TECHNICAL TRACK: VOC EMISSIONS FROM PRODUCTS AND MATERIALS: REGULATIONS, STANDARD METHOD AND ASSOCIATED TECHNOLOGIES.

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Abstract

The release of chemicals from products and materials has been the subject of various mandatory regulations and 'green codes' for many years. REACH, European Construction Product Regulation (CPR) and US building codes are key examples of regulatory developments that increase the need for chemical emissions testing as part of product labelling. Vehicle Interior Air Quality has now become a key focus, with new upcoming Chinese mandates dictating the worldwide response to health concerns and off odour complaints. The ever-expanding list of target compound has grown creating additional challenges for those responsible for carrying out sampling and analysis of target and non-target compounds. This has led to a need for innovative sampling and analytical techniques to be created and validated to respond to the pressures being placed on manufacturers, researchers, test laboratories alike. During the presentation we will discuss the status of regulations and associated standard methods effecting suppliers of construction and vehicle interior products, how to carry out sampling and analysis in accordance with current and impending standard methods, as well as introduce some innovative techniques for advanced analysis.

Indoor Air Quality

Increased awareness of the potential health risks associated with poor indoor air quality has led to calls for the regulation and labelling of construction materials, decorative products and consumer goods used indoors. As a result, regulatory requirements relating to emissions of potentially harmful chemicals from these products into the indoor environment are currently undergoing major review in many parts of the world.

These regulations impact many manufacturers, with producers of flooring, furniture, wood-based products, insulation materials, spray polyurethane foam, coatings, adhesives, sealants, vehicle trim, domestic goods, cleaning products and even medical devices being affected, together with all their suppliers.

Europe

The European Construction Products Regulation (CPR[1] has arguably the biggest worldwide impact on construction product manufacturers. The series of events that led to the CPR began in 1989, when its predecessor, the Construction Products Directive (CPD), was introduced with its 'Essential Requirement 3' (ER3) requiring that chemical emissions from products used indoors must not adversely affect the indoor environment or the health and comfort of occupants. A wide range of structural and decorative materials were covered by this legislation; however, ER3 was never properly implemented under the CPD, largely due to the lack of suitable and broadly applicable ('horizontal') test methods.

This has now been rectified under the CPR with the finalisation of EN 16516 as a horizontal method for testing chemical emissions from materials (publication expected September 2017) and the development of a harmonised list of safe levels for over 100 organic compounds (so-called ‘lowest concentrations of interest’ or LCIs[2]). Use of the new test method and LCI list is being embedded in relevant European product standards and will be implemented as a mandatory part of the CE marking process for any affected construction material made or sold within the European Union. Chemical emission testing is expected to be required both for initial product certification by an accredited third-party laboratory and for in-house ‘factory production control’ of emissions at specified intervals. The list of harmonised LCIs will also be continually maintained and is expected to be updated annually.

Work on these requirements has also been driven by the promulgation of German,[3,4] French,[5,6] and Belgian[7] national regulations, which require emissions testing of certain construction and decorative products and which establish performance criteria for product approval or classification. European national regulations like these will be superseded by the CPR, as it is rolled out across all relevant trades and European member states.

Over and above the CPR, European legislators have also enacted important legislation on the evaluation and authorisation of chemicals under ‘REACH’,[8] which came into force in June 2007, and is being phased-in gradually. Under REACH, chemical manufacturers, importers and downstream users need to prepare technical dossiers and/or ‘Chemical Safety Reports’ depending on tonnages. If a consumer product contains a potentially hazardous chemical at a level above 0.1%, and if it is possible for that chemical to be emitted under normal usage conditions (intentional or unintentional release), this must be assessed. Current guidance on implementation of emissions testing for articles and preparations (general consumer goods) under REACH specifies many of the methods developed for construction products.

US

Concern relating to product emissions and their potential impact on indoor environments and human health are driving similar regulatory developments in the US. One example is Standard 189.1,[9] developed by a consortium of American agencies including the national standards agency ANSI and the indoor air quality interest group ASHRAE. In parallel with this, another US agency, the International Code Council, is collaborating with ASTM and the American Institute of Architects to incorporate the International Green Construction Code (IGCC) into a regulatory framework for new and existing buildings, establishing minimum green requirements for buildings and complementing voluntary rating systems. One other relevant regulation is the LEED ‘green buildings’ program.[10]

China

‘Chinese REACH’[11] makes similar requirements to the European equivalent, and was initiated in 2010. As the world’s foremost manufacturing centre, Chinese companies are also likely to be impacted by European and US regulations that control chemical emissions from construction materials, decorative products and other consumer goods used indoors.

Procedures and standard methods for assessing chemical emissions

The various standard methods for testing emissions or release of VOCs and SVOCs from products and materials are usually broken down into multiple sections covering sample collection and preparation, emissions testing and vapour analysis. The vast majority of released chemicals are collected on adsorbent-packed tubes (‘sorbent tubes’) and analysed by thermal desorption (TD) with gas chromatography (GC) and detection by mass spectrometry (MS) and/or flame ionisation detection (FID). Relevant international standard methods include EN 16516,[12] ISO 16000-series standards[13] and a number of ASTM standards such as D5116[14] and D6196.[15] Method selection depends on geography and the regulation being adhered to.

Overall, the test procedure involves placing representative material or product samples into test chambers under prescribed conditions of temperature, humidity and clean air flow rate. Emitted organic vapours are then trapped on sorbent tubes at prescribed times and under specified sampling conditions. Note that alternative samplers and test methods are used for a few compounds such as ammonia and formaldehyde.

There are a wide range of test chamber options for measuring material emissions. Reference methods for initial product certification carried out by accredited third-party laboratories generally require the use of small environmental chambers (typically stainless steel or glass, 50 to 1000 L volume) with tests that take 3–28 days. Complementary screening methods for routine verification of product performance and factory production control usually use quicker tests with micro-chambers (see ASTM D7706[16] and EN 16516[12]).

Small environmental chambers

Procedures for final product certification typically involve placing a representative sample of the material in a 50–1000 L ‘small’ chamber (Figure 2) under simulated real-use conditions and with only the relevant surfaces exposed. Samples of chamber air, including any emitted chemical vapours, are collected onto sorbent tubes at specific times (typically 3, 10 or 28 days), and analysis is carried out using TD–GC–MS-based techniques as described above. Before a reference method can be implemented by a laboratory, it must be accredited by the relevant approval process or a ‘notified body’.

Microchambers

Microchamber devices speed up emission testing for routine screening, by using micro-scale chambers to sample air or gas from representative samples of materials onto sorbent tubes. Subsequent analysis is by TD–GC–MS in the normal way. Microchambers generate emission screening data (typically within 30–40 minutes of sample preparation) that correlates well with the results of extended small chamber tests. This makes them suitable for screening incoming raw materials, routine product quality control and for testing emission levels from products under development. Microchambers can also be used to estimate the results from longer-term certification tests and may be operated at elevated temperatures to speed up equilibration – SVOC emissions are particularly of interest.

Analysis

Whichever small-chamber or microchamber option is selected for emission testing, most organic vapours are collected in sorbent tubes (Figure 1), typically packed with Tenax TA or a combination of sorbents, prior to TD–GC–MS analysis in accordance with standard methods.

Before being analysed, the sampled tubes are unsealed, fitted with analytical caps and placed into a thermal desorber. They are then integrity-checked before being heated in a flow of pure inert ‘carrier’ gas to release the retained compounds and transfer them onto a narrow, electrically-cooled internal focusing trap. This is the first of a two-stage thermal desorption process.

Subsequent rapid heating of the TD instrument’s internal focusing trap, in a reverse flow of carrier gas, transfers (injects) the VOCs and SVOCs to the GC column in a narrow band, which ensures sharp peaks and high levels of sensitivity.

Vehicle Interior Air Quality

Vehicle interior air quality (VIAQ) has been a topic of interest since the late 1970s, when concern over the effect of volatile and semi-volatile organic compounds (VOCs and SVOCs) on the indoor environment began to be replicated in the automotive industry. The release of VOCs and SVOCs from vehicle trim materials (including plastics, polyurethane, foam, wood, carpets, textiles and adhesives) is the major factor causing poor VIAQ,[17] and the consequent negative effect on health is the primary driver for regulations in this area. However, in China concerns largely relate to consumers' dislike of off-odours in vehicle cabins, which has risen to be the most complained-about quality issue in that country.[18]

Regulations relating to VIAQ

As a result of concerns over VIAQ, voluntary guidelines had been developed to control acceptable levels of VOCs allowed in vehicle interiors. However, most manufacturers are now preparing to adhere to the mandatory Chinese regulation GB/T 27630.[19] Like its less rigorous equivalent guidelines in Japan[20] and Korea,[21] this is government-led, in contrast to the EU and US, where limit levels have largely been defined by manufacturers or industry/regulatory bodies. As is typical for VIAQ regulations, GB/T 27630 requires the concentration of a number of VOCs to be determined, and in this case eight VOCs are listed (Table 1).

Table 1: Limit levels for VOCs defined within Chinese regulation GB/T 27630. The changes proposed for the 2017 release also include changes to sampling conditions and reporting details.

	Limit level (mg/m3)		
	Prior to January 2016	**January 2016**	**May 2017**
Benzene	≤0.11	≤0.06	≤0.05
Toluene	≤1.10	≤1.00	≤1.00
Xylenes	≤1.50	≤1.00	≤1.00
Ethylbenzene	≤1.50	≤1.00	≤1.00
Styrene	≤0.26	≤0.26	≤0.26
Formaldehyde	≤0.10	≤0.10	≤0.10
Acetaldehyde	≤0.05	≤0.20	≤0.20
Acrolein	≤0.05	≤0.5	≤0.5
TVOC	≤8	≤6	Removed
Ranking	A–E	A–C	Removed

Previously, it also stated the need for a total VOC (TVOC) concentration to be reported, and defined a strict ranking system – but it is now proposed to remove both these requirements. Irrespective of the country of manufacture, the responsibility for demonstrating conformance with specified limits for VOC levels in vehicle cabins (whether voluntary or mandatory) rests with the car manufacturer. However, in general a failure to meet these requirements is passed successively down the manufacturing chain to component manufacturers and raw material suppliers. This means that suppliers at all stages of the manufacturing chain need to be able to carry out testing of their products and materials in order to identify components causing high chemical emissions, and also to facilitate the development of low-emitting alternatives.

The development of standard methods relating to VIAQ

Over the years, hundreds of manufacturer-specific methods have been developed for the sampling and analysis of VOCs and SVOCs from car interiors. This proliferation of methods has become a major inconvenience for manufacturers, with regulators also challenged by the fact that the results from different protocols often cannot be meaningfully compared.

To simplify matters for the industry, the International Organization for Standardization (ISO) has been working on the development of harmonised methods, through technical committee ISO/TC 146/SC 6 (Indoor Air). This has led to the release of six standards for sampling and analysis of VOCs and SVOCs from vehicle interiors and the materials used in them, with three further methods currently under development (Table 2).

Table 2: Standard ISO methods relating to sampling of VOCs and SVOCs relevant to VIAQ. [a]Within the scope of ISO 12219, VOCs are defined as those with a boiling point above that of n-hexane (n-C_6H_{14}, 68°C) but below that of n-hexadecane (n-$C_{16}H_{34}$, b.p. 287°C); SVOCs are those boiling above the latter temperature.

Sample	**Analyte scope[a]**	**Sampling method**	**Method**	**Released**
Cabin air	VOCs	Environmental chamber	ISO 12219-1	2012 (2020 under review)
Car trim	VOCs	Small sampling bag	ISO 12219-2	2012
Car trim	VOCs	Microchamber	ISO 12219-3	2012
Car trim	VOCs	Small chamber	ISO 12219-4	2013
Car trim	VOCs	Static chamber	ISO 12219-5	2014
Car trim	SVOCs	Small chamber	ISO 12219-6	2017
Car trim	VOCs	Large sampling bag	ISO 12219-9	2019
Cabin air (Trucks & Buses)	VOC	Environmental chamber	ISO12219-10	In progress

However, in 2012, shortly before the release of the first of the ISO 12219 methods, it became apparent that the move for global harmonisation might not be straightforward, due to the introduction of the mandatory Chinese regulation GB/T 27630.[19] This regulation cites standard method HJ/T 4007 (which had previously been voluntary), and states the need to carry out VIAQ testing of all vehicles imported into China. This was viewed by many as a considerable barrier to trade, not only due to the initial strict limit levels but also the logistics of shipping prototype cars to be tested in China at one of the few certified laboratories. Discussions are ongoing as to whether the regulation will allow self-certification, or whether certified laboratories outside China will be able to run the method. A further difficulty is that, although HJ/T 400 is broadly similar to ISO 12219-1 – namely, pumped sampling of cabin air within a large environmental chamber – differences in the conditions under which sampling takes place mean that the results from the two methods cannot be correlated with each other. A similar situation arises with the widely-used Japanese and Korean methods. Although not addressing this problem directly, the situation for manufacturers will be alleviated somewhat in 2017 by proposed changes to GB/T 27630 (see Table 1), which are a result of US and EU negotiations with the Chinese regulators.

Sampling apparatus used in standard methods

The various standard methods used to assess VIAQ, or analyse VOC and SVOC emissions from component parts, all use thermal desorption (TD) to concentrate the vapours to a point where they can be detected by gas chromatography (GC), with detection by mass spectrometry (MS) and/or flame ionisation detection (FID).

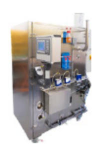
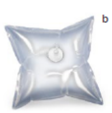
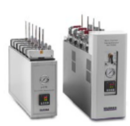
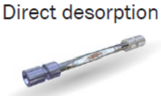
Purpose	Sampling method	Description of analytical process	Methods
Overall VIAQ	Environmental chamber	• Air sampled from a chamber enclosing the whole car. • Sampling onto a sorbent-packed TD tube. • Tube desorbed and vapours collected on a focusing trap. • Trap desorbed and vapours injected into GC.	• ISO 12219-1. • China: HJ/T 400. • Japan: JASO Z125. • South Korea: Article 33-3.
Emissions from assembly parts	Small chambers  [a]	• Air sampled from a (typically) 1 m^3 chamber. • Sampling onto a sorbent-packed TD tube. • Tube desorbed and vapours collected on a focusing trap. • Trap desorbed and vapours injected into GC.	• ISO 16000-9. • ISO 12219-4. • ISO 12219-6. • VDA 276. • JIS A1901. • BMW GS 97014-3 ('Summer test'). • ASTM D5116-97.
	Sampling bags  [b]	• Air sampled from bags of various sizes from 10 L to 2000 L. • Sampling directly into a focusing trap. • Trap desorbed and vapours injected into GC.	• Japan: JASO M902. • MS300-55 (Hyundai-Kia). • NES M0402 (Nissan). • ATSM 0508G (Toyota). • DWG 0094Z SNA 0000 (Honda). • ISO 12219-2 (10 L bag). • ISO 12219-9 (2000 L bag).
Emissions from components	Microchambers 	• Air/gas sampled from micro-scale chambers (44 or 114 cm^3). • Sampling onto a sorbent-packed TD tube. • Tubes desorbed and vapours collected on a focusing trap. • Trap desorbed and vapours injected into GC.	• TPJLR.52.104 (Jaguar Landrover). • ISO 12219-3. • ASTM D7706. • GMW17082 (General Motors).[10] • RNES-B-20116 (Renault/Nissan).
	Direct desorption 	• Small sample (up to ~50 mg) heated in an empty TD tube. • Vapours collected on a focusing trap. • Trap desorbed and vapours injected into GC.	• VDA 278.

Figure 2: Sampling approaches used for monitoring VIAQ and related emissions from vehicle components and materials. All GC analyses are carried out in accordance with ISO 16000-6,11 which stipulates either MS or FID for detection. [a] Image credit: SP Technical Research Institute of Sweden. [b] Image credit: Equipco.

Chemical release from products and materials: Innovations to simplify chemical emission testing for industry.

The use of these innovative technologies for certification and for fast screening of chemical emissions from products and raw materials within manufacturing industry is becoming more common place. With the advent of new regulations all over the world the impact on manufactures has been great. Simple, indirect methods harnessing efficient tools for speeding up chemical emission screening have been developed to simplify factory production control. Microchamber thermal desorption GC/MS can be used for routine quality control of production (e.g. for 'attestation of conformity'), industrial R&D – to aid development of new, low-emitting products, comparing emissions across a product range, checking raw materials, addressing customer complaints and comparing products against best-in-class competitors. These indirect methods have been correlated to longer term reference tests for a wide range of materials and product types and can be applied in routine industrial quality control.

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