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Application

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Application Note 110

Rapid detection of chemicals emitted from museum display cases

Summary

This Application Note discusses assessment of volatile organic compounds emitted from the materials used in the manufacture of museum display cases, which can have a detrimental impact upon the condition of the artefacts within them. We describe how sampling devices such as Markes' Micro-Chamber/Thermal Extractor, used in conjunction with analysis by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) can allow rapid and convenient sampling of such chemicals from the wide range of construction materials used in these cases, and how new test schemes are being used by industry to certify these materials.

Introduction

Museum artefacts need to be protected against a range of environmental influences, including cigarette smoke, exhaust gases, spores, pollen, dust, smoke particles, excess moisture, and volatile organic compounds (VOCs) from skin and breath. To achieve this, airtight display cases are widely used, with very low air exchange rates. However, these low air exchange rates are only beneficial if the materials used to construct the display case are themselves low-emitting. If not, concentrations of undesirable VOCs can build up, resulting in damage to the artefact. The situation is made particularly complicated by the fact that some artefacts can themselves emit undesirable chemicals.

Chemicals of particular concern include formic acid, acetic acid, nitrogen dioxide and formaldehyde, which have been linked with the corrosion of metals, calcareous objects and cellulose-based artefacts such as paper. However, the need to detect chemicals also extends more widely, and includes highly volatile residual solvents in the materials used to construct the cases, and semi-volatile pesticides formerly used for pest control.

Given this situation and the large amount of research currently being conducted in this area, there has been considerable demand for rapid methods to test the materials used to construct display cases, and for a set of standards to apply when assessing them. An example of such a method is the BEMMA assessment scheme.

The BEMMA scheme

The German materials research institute BAM (Bundesanstalt für Materialforschung und -prüfung [The Federal Institute for Materials Research and Testing]) has recently developed a new scheme for assessing museum display case construction materials.

This scheme, known as BEMMA (Bewertung von Emissionen aus Materialien für Museumsausstattungen [Assessment of emissions from materials for museum equipment]),[1] comprises guidelines for carrying out analytical methods, and for applying limit levels for various chemical classes. As a result, it is expected to be an effective decision-making tool for curators, restorers and conservators involved in the selection and use of exhibition showcases, storage facilities and transport packaging for art and cultural artefacts, as well as those responsible for planning or specifying performance criteria for these materials.

Under the BEMMA scheme, individual materials are examined prior to construction of the display case, minimising the risk of having to resolve issues with a material after expensive manufacturing processes have been carried out.

Methods and materials covered under BEMMA

Five methods for sampling and analysis are specified under BEMMA:

- Micro-Chamber/Thermal Extractor™ and TD–GC–MS – For assessing VOCs and SVOCs from materials.
- Derivatisation and LC–MS – For formic acid and acetic acid.
- Pumped sampling onto Tenax® tubes and TD–GC–MS – For assessing VOCs and SVOCs from the cabinet air.
- DNPH cartridges and HPLC – For formaldehyde and other very volatile aldehydes and ketones.
- Derivatisation and HPLC – For isocyanates.

BEMMA is applicable to a wide range of materials, including:

- Textiles.
- Plastics.
- Sealants (*e.g.* silicone).
- Coatings.
- Other materials (*e.g.* glue).

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Criteria for passing the BEMMA test

The data resulting from the above analyses provides the basis of a test report, which defines whether or not the material has passed the scheme. The scheme sets out the following criteria:

- Substances with high pollution potential such as formic acid, acetic acid and formaldehyde must not be emitted from the materials, or be detected.
- Total very volatile organic compounds (∑VVOCs): 100 µg/m^3 maximum.
- Total volatile organic compounds (∑VOCs): 500 µg/m^3 maximum (with the exception of sealing materials, for which the value is 2000 µg/m^3 due to the significantly smaller application surface).
- Total semi-volatile organic compounds (∑SVOCs): 100 µg/m^3 maximum.

If the material fails any of these criteria, then it fails to pass the BEMMA test.

Overall, the benefit of the BEMMA scheme is that it combines methods for effective testing with criteria for assessing the outcome of those tests. The resulting certification marking makes it clear whether or not materials are suitably low-emitting to be considered for use in the construction of display cases.

Sampling and analysis methods

The Micro-Chamber/Thermal Extractor

As indicated above, Markes' Micro-Chamber/Thermal Extractor™ (µ-CTE™) (Figure 1) forms a key component of the sampling setup specified under BEMMA. It is a compact unit with four or six small cylindrical chambers, suitable for sampling chemical emissions both from finished products and from the corresponding raw materials.[2] In conjunction with thermal desorption (TD)–GC–MS analysis, it has become very popular for the fast, inexpensive screening of materials as part of the monitoring of compliance with industry regulations.

Figure 1: The Micro-Chamber/Thermal Extractor.

For planar materials, the sampling process involves first cutting or 'punching' out a circular piece of material, which is placed into the chamber (see Figure 2). Alternatively, small glass dishes can be used to hold samples of resins or adhesives.

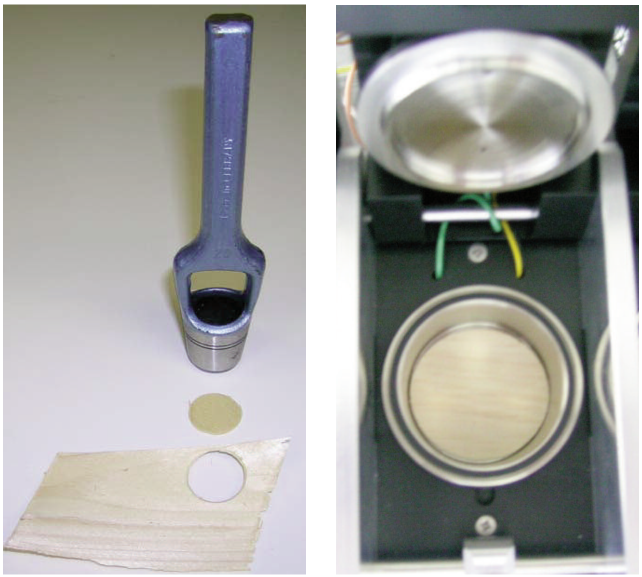

Figure 2: Preparing planar materials for sampling using the Micro-Chamber/Thermal Extractor.

The chamber lids are then closed, and a flow of pure air or nitrogen is applied, with the chambers being held at a set temperature. After an appropriate period of equilibration, a sorbent tube is attached to the outlet of each chamber to trap vapours released from the sample (Figure 3). After sampling is complete, the sorbent tubes are analysed off-line using TD–GC–MS. Alternatively, to assess formaldehyde, a DNPH cartridge can be attached to the outlet, the vapours sampled as before, and the cartridge then analysed by HPLC.

The availability of multiple chambers (four or six depending on which model is chosen) means that duplicate materials can be sampled in parallel under the same conditions (as specified under BEMMA), allowing rapid processing as well as the option of looking at multiple samples from the same material.

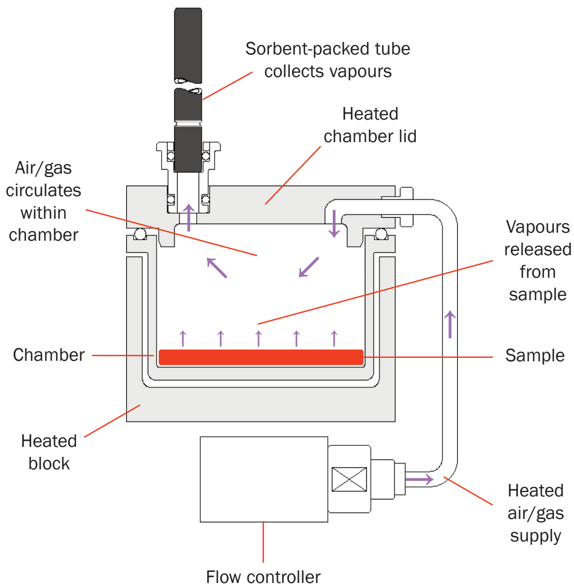

Figure 3: Operation of the Micro-Chamber/Thermal Extractor for sampling emissions of volatile chemicals from flat samples.

As far as the BEMMA scheme is concerned, sampling is usually carried out at room temperature. However, higher temperatures can be also useful to simulate and/or accelerate conditions in display cases, and also to force higher-boiling SVOCs into the gas phase. In these situations the temperature of the microchambers can be raised.

Pumped sampling onto sorbent tubes

Pumped sampling onto sorbent tubes is one of the most versatile TD sampling methodologies. By allowing precise volumes from 20 mL to several hundred litres to be drawn through the tubes, it ensures compatibility with a huge concentration range (sub-ppt to high ppm).

Within the BEMMA scheme, pumped sampling can be used to assess VOC levels within the cabinets themselves. A TD sampling pump is simply attached to the end of a sorbent tube packed with Tenax TA, and cabinet air drawn through the tube using a sampling rate and time appropriate for the expected concentration of analytes in the cabinet atmosphere.

Markes' ACTI-VOC™ pump is particularly well-suited for TD applications because it provides constant flow rates irrespective of sorbent tube impedance – meaning that the system does not have to be recalibrated each time a different sorbent tube is used.

Analysis of sorbent tubes by thermal desorption

The thermal desorption technique referred to above is a versatile 'front-end' technology for GC and GC–MS that is applicable to the analysis of VVOCs, VOCs and SVOCs in a wide range of samples – gases, liquids and solids. It combines pre-concentration, desorption/extraction and GC injection into one sensitive and fully automated operation.

The sorbent tubes used to collect the emitted vapours are heated in a flow of inert gas, with the released components being transferred to an electrically cooled narrower 'focusing' trap within the TD system. After completion of the primary (tube) desorption stage, the focusing trap is itself desorbed very quickly by heating it rapidly in a reverse flow of carrier gas. This transfers/injects the organic compounds into the GC–MS analytical system. This two-stage process optimises concentration enhancement and produces narrow chromatographic peaks, thus optimising sensitivity across a broad volatility range.

Markes' thermal desorption systems are designed so that, during injection into the GC–MS, the split effluent can be quantitatively transferred to a second sorbent tube. This split effluent can then be desorbed onto the same trap for re-analysis. This offers the capability to analyse the same sample under identical or different analytical conditions. One example of this is conducting the initial analysis under high-split conditions (appropriate to components at high concentrations) and subsequently by desorption of the re-collected VOCs under low-split conditions (for optimum detection of trace compounds), thus potentially increasing the dynamic range of the analysis.

Example application: Analysis of pumped air from a museum case

The value of TD–GC–MS to identify problem contaminants is illustrated by Figure 4, which shows the analysis of air pumped from a museum case containing an artefact showing enamel decay. The significant response from acetic acid indicates high levels that are likely to be responsible for degradation of the artefact.

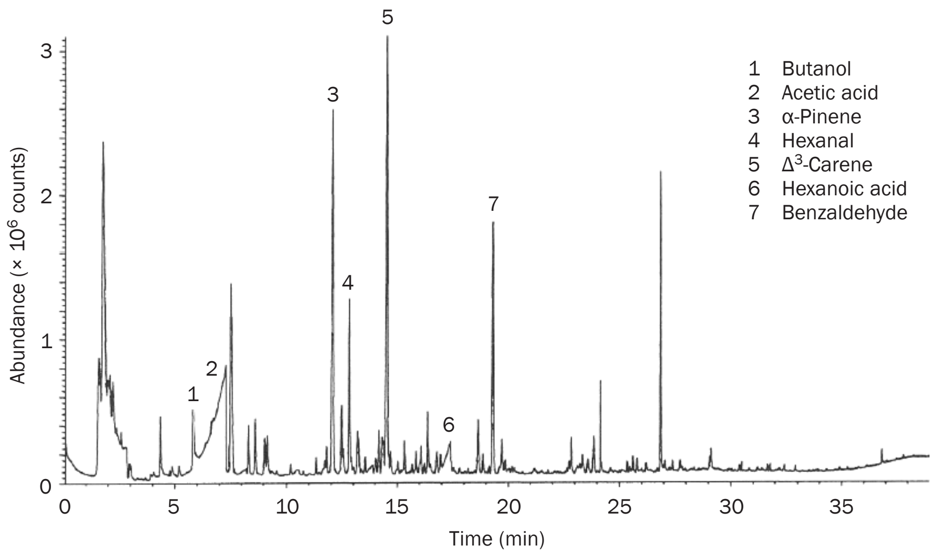

Figure 4: Analysis of air pumped from a museum case, with sampling onto Tenax TA and analysis by TD–GC–MS.

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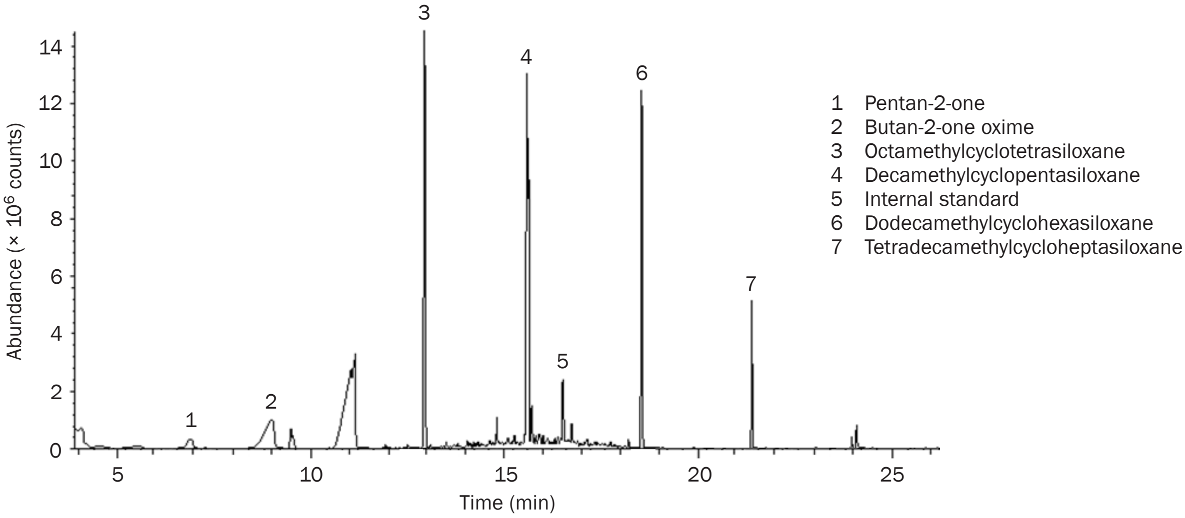

Figure 5: Analysis of emissions from a sealant typically used to join together glass panels, with sampling using the Micro-Chamber/Thermal Extractor and analysis by TD–GC–MS.

Example application: Analysis of a glass sealant

This example (Figure 5) shows analysis of a piece of silicone sealant used to join together glass panels used to construct museum cases. The presence of butan-2-one oxime means that this material would fail the BEMMA criteria, as it is one of the components listed as having 'high pollution potential'.

Conclusion

In conclusion, a number of technologies, including TD–GC–MS, will be of value in helping the museums sector to protect artefacts from damage due to volatile chemicals. In particular, Markes' Micro-Chamber/Thermal Extractor, by being cited in the BEMMA method, is expected to play a key role, by providing a fast, reliable and versatile means for assessing volatile emissions from display case materials.

Acknowledgement

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References

1. BEMMA is described in: K. Wiegner, M. Farke, W. Horn, O. Jann and O. Hahn, Den Schadstoffen auf der Spur – Das BEMMA-Schema [Tracing contamination – The BEMMA scheme], *Restauro*, April/May 2012, pp. 38–44. Available at http://www.callwey-shop.de/restauro-3-2012.html?SID=7eb1639d216e423aa971f68e93d1ac00.
2. For an example of the Micro-Chamber/Thermal Extractor (with TD–GC–MS analysis) being used to sample VOCs from polymers used in display cases, see: G. Mitchell, C. Higgitt and L.T. Gibson, Emissions from polymeric materials: Characterised by thermal desorption-gas chromatography, *Polymer Degradation and Stability*, 2013, http://dx.doi.org/10.1016/j.polymdegradstab.2013.12.003.

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