

Focus on the Low-Emissions Display Case

Description of the BEMMA Investigative and Evaluative Procedure

BEMMA is the German abbreviation for a procedure for evaluating the emissions from materials used in museum displays. This procedure makes it possible to investigate and evaluate volatile organic compounds from modern materials that stand in indirect contact with the historical or modern materials of art or cultural goods. What is evaluated for emissions is not the display case or storage cupboard itself, but the corresponding building materials. (In the following, “display case” is used for both display cases and storage cupboards.)

Introduction

Museum display cases aim to protect art and cultural goods not only from theft and vandalism, but also from dirt and dust. But numerous examples show clearly that works of art are sometimes exposed to deleterious environmental influences not only outside of, but also inside museums, archives, etc. For example, constructions or decorations in exhibition spaces, storage containers in depot rooms, and exhibition display cases release volatile substances that lead to irreversible changes or, under certain circumstances, damage to the stored or displayed objects. Among these substances are organic acids like formic and acetic acid, but also compounds that contain sulfides. In response to this, when newly conceiving exhibitions, museums and archives increasingly call for display cases and construction and building materials free of harmful substances and emissions.



Fig. 1: The Court in Delhi on the Birthday of Grand Mogul Aureng-Zeb, 1701-1708, Johann Melchior Dinglinger, New Green Vault, Dresden; left: total view; right: damage to the enamel (photo: SKD)

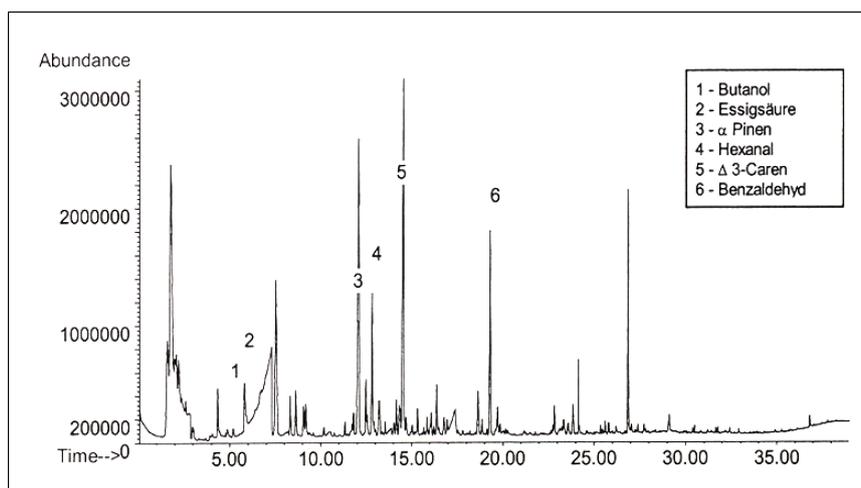


Fig. 2: Sample extracted on Tenax®, then thermodesorption and identification, quantification with GC/MS: damage to the enamel through acids (graphic: BAM)

Along with the absence of every impurity and damaging substance, today's demands also comprise strong sealing to ensure constancy of climate. These requirements are difficult to fulfill at the same time, since there is no universal emission-free material and almost every even minimal release of compounds leads to concentration within the display case. The question thereby arises how an evaluation schema can be established that makes it possible to evaluate museum display cases qualitatively and quantitatively in terms of their potential to damage exhibited cultural goods.



Fig. 3: Display case with VOC sample (photo: BAM)

The BEMMA Schema

Before we go into detail about the BEMMA schema, we should make it clear once more that successful evaluation by specialized evaluators and auditors using the **BEMMA schema** does not guarantee low-emission display cases. Rather, the procedure creates the preconditions for the choice of suitable materials to produce display cases as low in emissions as possible. It is a necessary, but at the same time not the sole precondition producers of display cases face to make their products BEMMA-compliant. In addition, producers who want a certificate for low-emission display cases will have to show that they comply with the requirements of the BAM certification office (BZS) regarding manufacturer supervision, control over supplier agreements, and adherence with the principles of the QMH of the BZS. Concrete craftsmanlike execution during construction, the requirements of seal tightness, and the conditions of placement (the surroundings of the display cases) influence the emission characteristics of

finished display cases in practice. A clean display case is useless in burdened surroundings, when later alterations are made with unchecked materials, or with display items that produce emissions.

The Evaluation Criteria of the BEMMA Schema have to do with the measurement methods to be carried out (dynamic concentration determination in the microchamber). These values cannot be applied to finished display cases, since the latter, once sealed, go into a static state. This can be avoided to a great degree by using a defined climate with low ventilation and with filtration.

In addition, these evaluation criteria (threshold values) were not set in accordance with experimental specifications as are known in, for example, medicine (for example, MAK values). Such threshold values cannot be determined for the field of art and cultural goods.

Crucial for the definition of two basic criteria were, first, knowledge of the potentially damaging effects of some substances (acids, oximes, etc.) and, second, the statistical survey of the total values of volatile organic compounds (VVOC: Very Volatile Organic Compounds, VOC: Volatile Organic Compounds; SVOC: Semi-Volatile Organic Compounds) from a wide variety of emission measurements. *

The key component of the BEMMA schema is the evaluation of all measurement results in accordance with the investigative and evaluative criteria presented in the following. A double determination is carried out for all investigated materials, from which the middle value for all results is individually calculated. Should these results diverge from each other by more than 20% in more than 25% of the components, a third determination must be carried out, due to the possible inhomogeneity of the sample. With divergences greater than 50%, the procedure must be determined anew in consultation with the respective commissioning party. As much as possible, inhomogeneities in the samples should be avoided.

* Hydrogene sulfide (H₂S), sulfur dioxide (SO₂) und ammonia (NH₃) can in principle also damage cultural goods. This compounds would not emit from typical materials used for the construction of show (see products that can be tested with BEMMA procedure / Page 4). At the beginning of the BEMMA scheme development these compounds were also discussed to be measured. Due do to needless measurements and increasing costs they were excluded from the BEMMA evaluation.

The BEMMA test can be applied to the following products:

- Coatings:
- Powder coatings (baking enamels)
 - Liquid coatings, for example for coating glass or metal surfaces
- Sealing materials:
- Joint sealants (injectable, moldable sealants in accordance with DIN EN 26 927 (joint sealing products): products that are inserted in joints to seal them by adhering to the sides of the joints.) These are categorized as:
 - Silicon sealants and
 - Polymer adhesives
 - Seal profiles (pre-assembled sealing strips, for example of silicon or rubber, which are customarily sold by the meter; with or without self-adhesive backings)
 - UV adhesives (reactive adhesives) / acrylic resins
- Plastics:
- Sheet plastics (for example, rear walls, shelf surfaces, acrylic glasses, etc.)
 - Plastic moldings
- Textiles:
- Textile skins for display case fixtures
- Other:
- for example, aluminum composite panels, cardboard-foam composite panels, etc.

Wood and wood-based materials can be tested with the same procedure; but they are excluded from the BAM certificate “Low-Emissions Materials for the Construction of Museum Display Cases”. These products can evince high inhomogeneity. Also, wood-based materials often contain carboxylic acids and formaldehyde, so that compliance with the BEMMA requirements cannot be expected.

All investigated materials will always be subjected to a double determination, which means that two chambers of the microchamber are loaded with the same material. The middle value for all results is calculated from this.

Sample Preparation

Determination of emissions for the BEMMA evaluation is carried out in microchambers (μ -CTE / μ -Chamber, Markes company). A crucial parameter for emissions tests is the surface-specific airflow rate q , which expresses the relationship between air exchange (n) and space loading (L): $q=n/L$. The dimensions and measuring parameters for the investigations are the following values: volume of the chamber 0.044 L or 0.000044 m³, air flow per chamber ca. 28 mL/min or 1.7 per L/h; n : air exchange rate (air exchange/hour) 38 1/h. Table 1 supplements these general values with sample-specific guidelines:

Tab. 1: Parameters for preparing and extracting samples in the microchamber at a volume stream of 28 ml/min (consisting of 6 small chambers each)

Parameter / Example for:	Flat samples	Sealants	Sealing profile	Unit
Surface of the sample	15.2	4		cm ²
Surface of the sample	0.00152	0.0004		m ²
L: Surface/volume	34.6	9.09		m ² /m ³
q = n/L	1.1	4.2		m ³ /(m ² *h)
Sample length			4	cm
Sample length			0.04	m
L _L : length/volume			909	m/m ³
q _L = n/L _L			0.042	m ³ /(m ³ *h)

The ISO 16000-11 standard is to be used to obtain the pieces to be tested. Wood-based materials, textiles, coated metals, and plastics are prepared for the microchamber by cutting out, die cutting, drilling, etc. The circular samples should have a diameter of 44 mm; to this end, a corresponding die punch, suitable band saw, or suitable hollow drill is used. The narrow or cut surfaces of the samples are not masked for the examinations.



Fig. 4: Micro-chamber (company Markes); left: sample preparation; right: emission measurement with Tenax[®] (photos: BAM)

For sealants, samples are prepared with a surface of 4 cm² by 6 mm bed depth, for example in a 4-cm aluminum U profile with an edge height of 7 mm, a width of 12 mm, and walls 1 mm thick[†]. The sealant is pressed into this U profile, for example with a cartridge pistol, and spread smooth at the edges; at the cut edges, the profile is sealed with self-adhesive low-emission aluminum tape (before being filled). When sample preparation was finished it should exhaust for a period. This duration will be given by the producer. A typical time span should be used between production and final close of the display case.

If several dimensions of sealants are available for the investigation, each of them should be chosen with the greatest use of material per unit of length. Pieces of these profiles 4 cm long are cut from

[†] For example, Alfer profile

these profiles (independent of the width, which is usually less than 4 cm; the cutting edges and narrow edges were not sealed) and placed in the microchamber.

Low-viscosity adhesives or coatings are spread evenly in accordance with the manufacturer's instructions on a round glass or metal plate with a diameter of $d=44$ mm and then, after the proper drying time (for example, 7 days at 23°C and 50% relative humidity), tested in the microchamber. Alternatively, flat materials or foils can be used, if their inertness has been checked. Correspondingly large samples can also be cut from larger, coated surfaces. In this case, attention should be paid to maintaining a high degree of cleanliness when cutting, to avoid unnecessarily contaminating the material.

Execution and Methods of Analysis:

- The following parameters apply when loading the microchambers with the samples to be tested: Flow: ca. 28 ml/min (note the precise values); 23 °C ± 2 K, ≈ 0 % relative air humidity, synthetic air, surface-specific air-flow rate: see Table 1 or values derived from the dimensions described above. With the aforementioned flows and sample-extracting times suitable for the analysis, the concentrations[‡] can then be calculated. Before leading, at least one Tenax[®] blind value must be extracted for each chamber; it is also recommended to regularly submit an unloaded chamber to the complete analysis procedure.
- Extract samples with Tenax[®] for VOCs (volatile organic compounds), SVOCs (semi-volatile organic compounds) (in accordance with ISO 16000-6) with the following parameters: 0.25 liters sample volume, 10 min. sample-extracting time. Quantification is performed with a GC-MS combination that detects amu: 28 to 550 with the scanning parameters. The evaluation of the individual peaks is carried out with the total ion chromatogram, which quantifies by toluene calibration. For quality control, an internal standard on the Tenax tube should be given before extracting the sample, whereby, first, a VOC and SVOC total value is determined from the sum of the individual components[§]. The summation is carried out for all components whose quantification through toluene equivalents equals or is greater than 5 µg/m³ (threshold for consideration). The resulting main components (≥ 5 µg/m³) are listed separately. Only the oximes^{**} and piperidine derivatives^{††} are collected with a second sampling tube with a sample-extraction time of 40 min. corresponding to ca. 1 liter of sample volume, and then quantified substance-specifically with a mass-selective analysis run and separately listed.
- Sample extraction with DNPH (dinitro-2,4-phenylhydrazine)-cartridges for aldehydes and ketones (in accordance with ISO 16000-3) with the following parameters: ca. 33 liters sample extraction volume; 20 h sample extraction time. At least formaldehyde and acetaldehyde should be listed separately. Additional aldehydes beyond a concentration of 5 µg/m³ should be noted.

[‡] Alternatively, the surface-specific emission rates can be used; but then the values for the determined total values must be correspondingly corrected.

[§] For VOC in the elution area of n-hexane to n-hexadecane and for SVOC in the elution area of n-hexadecane to docosane on a weakly polar GC column, for example DB-5,

^{**} For example, 5-methyl-2-hexanoneoxime, 4-methyl-2-pentanoneoxime, 2-butanoneoxime, should cover low-volatile oximes.

^{††} For example, 2,2,6,6-tetramethyl-4-piperidinol; Lit Newman and Hatchfield, 2015
1,2,2,6,6-pentamethyl-4-piperidinol, Diehl 2016

- Sample extraction for volatile, short-chain, organic acids, like formic and acetic acid, on silica gel cartridges with ca. 33 liters sample extraction volume, which corresponds to a sample extraction time of ca. 20 hours. After sampling, the silica gel cartridges, pre-cleaned with ca. 100 ml ultrapure water, are eluted with 1.5 ml of water and ion-chromatographically quantified. This procedure is carried out in accordance with VDI 4301 Sheet 7.
- Testing for isocyanates is not standard.** Inorganic gases (H₂S, SO₂, or NO_x, etc.) are not expected in construction products.

Examination Procedure

The concrete and closely clocked timing of the investigations is very important for the comparability of the results, so it is imperative that it be followed. The microchambers must be well cleansed when using: a blank value of the microchambers must be determined before loading. The sequence of a test in accordance with BEMMA is as follows:

1. Adjust the flow to the microchamber (warm-up phase ca. 2 hours)
2. Load the microchambers
3. Sampling of the volatile, short-chain, organic acids: start/duration of the sample extraction ca. 1 after loading for ca. 20 hours, ca. 33-liter sample extraction volume
4. Then: sampling of the VOCs with Tenax[®]: duration of sample extraction ca. 10 minutes, 0.25-liter sample extraction volume
5. Then: sampling of oximes and piperidine derivatives^{Fehler! Textmarke nicht definiert.} with Tenax[®]: duration of the sample extraction ca. 40 minutes, ca. 1.0-liter sample extraction volume
6. Then: sampling of the aldehydes and ketones: start/duration of the sample extraction of the VOCs for ca. 20 hours, ca. 33-liter sample extraction volume

Evaluation Criteria:

No substances with a high burden potential, like formic acid, acetic acid, formaldehyde, (isocyanates see above.), oximes, and piperidine derivatives, may be detectable.

This means that substances that have a known high burden potential already multiply discussed in the literature, like acetic acid, formic acid, and formaldehyde, must not be emitted from the materials later used to build display cases. Oximes and isocyanates** are highly reactive substances, so that they, too, have potential to do damage. In one case of damage, a piperidine derivative†† (light stabilizers, etc.) led to a white precipitate on waxed art objects in a display case. These substances, too, must not be emitted from the materials.

BEMMA generally calls for the exclusion of detection of these components, i.e., these substances may not be analytically detected. Since different laboratories can produce different evaluations, for these components threshold values are introduced that definitely can be detected with the described methods. But for these threshold values, a measuring uncertainty (MU) must be assumed, so that slight

** Materials are tested for isocyanates only if a specific suspicion arises in advance. The usual materials used to build display cases and the gassing-off times associated with this processing have provided no indications for their presence (Wirts 2003 and Wolff 2000). In certain cases, the following isocyanates – toluene-2,6-diisocyanate (2,6-TDI), hexamethylenediisocyanate (HDI), and toluene-2,4-diisocyanate (2,4-TDI) – could be checked for diisocyanates in accordance with OSHA Method Number 42 (derivatization, HPLC; 33 liters sample extraction volume; 20 h sample extraction time). These would then have to be carried out as the first examinations after loading the microchambers followed by a second loading with the typical examination procedure.

breeches within the MU interval are tolerable. This ensures that the display case construction materials may emit these substances only to the extent unavoidable with the current state of technology; this refers not only to the determination limits of the analytic procedures, but also to the currently customary materials.

Tab. 2: Minimum determination limits of some volatile organic compounds

Components	Minimum determination limit $\mu\text{g}/\text{m}^3$
Formaldehyde	5
Formic acid	15
Acetic acid	15
Piperidine derivative	10

Tab. 3: Minimum determination limits of some volatile organic compounds

Components	Minimum determination limit $\mu\text{g}/\text{m}^3$
Acetonoxime	25
2-Butanonoxime	10
4-Methyl-2-pentanoxime	10
Cyclopentanoxime	10
5-Methyl-2hexanonoxime	10
Cyclohexanonoxime	10
3-Methylbenzamidoxime	25
Benzaldehydoxime	10
Tetramethyl-4-piperidinol	10

Corresponding sum emission values for the VOC considered here are not to be exceeded. These values are:

- Σ VVOCs 100 $\mu\text{g}/\text{m}^3$
- Σ VOCs 500 $\mu\text{g}/\text{m}^3$ (2000 $\mu\text{g}/\text{m}^3$ see below)
- Σ SVOCs 100 $\mu\text{g}/\text{m}^3$
- For sealants (pasty silicones and polymer masses), a deviating value of 2000 $\mu\text{g}/\text{m}^3$ for Σ VOCs is valid, because of the markedly lower used surface or contact surface in the interior of the display cases. UV adhesives and sealing strips call for the application of the usual sum values.

Calculating the sum emission values from the results of the above measurement procedures:

- The VVOC sum (Σ VVOC) is calculated from the concentrations of formic acid, formaldehyde, acetaldehyde, acetone, and propanol (from the determination of the aldehydes and ketones by means of DNPH and of the organic acids by means of IC) and VOCs that are detected before n-hexane (C_6) on a weakly polar column (for a definition, see EN 16516) and by means of Tenax[®] (evaluated using toluene equivalents).
- The VOC sum (Σ VOC) is calculated from the concentrations (evaluated using toluene equivalents) of all substances whose retention times lie between that of n-hexane (C_6) and that of n-hexadecane (C_{16}) on a weakly polar column (for a definition, see EN 16516) (see above), in addition

to the DNPH-aldehydes and ketones from crotonic aldehyde to undecanal and in addition to the concentration of acetic acid, which are each detected substance-specifically. Consider that the corresponding values of these components were subtracted of the values received from VOC analysis with Tenax®.

- THE SVOC sum (Σ SVOC) is calculated from the concentrations of all substances whose retention time in the Tenax® tube analysis on a weakly polar column is greater than that of n-hexadecane (C₁₆) and smaller than that of docosane (C₂₂)^{§§}.

Quality Control

The standard deviations for the various determining procedures in accordance with the BEMMA schema are presented. In Tables 4 to 6, the relative standard deviations and associated relative measurement uncertainties are listed showing determining procedures and concentration areas. The respective thresholds of determination are to be set below the smallest concentration shown there.

Tab. 4: Concentration areas, relative standard deviations, and measurement uncertainties for determining formic and acetic acid

Formic acid			Acetic acid		
Concentration area [µg/m³]	Standard deviation [%]	Measurement uncertainty [%] for k=2	Concentration area	Standard deviation [%]	Measurement uncertainty [%] for k=2
10-50	15	30	10-50	15	30
50-140	10	20	50-400	10	20

Tab. 5: Concentration areas, relative standard deviations, and measurement uncertainties for determining VOC with Tenax® as adsorbent in accordance with ISO 16000-6

Concentration area [µg/m³]	Standard deviation [%]	Measurement uncertainty [%] for k=2
5-20	20	40
20-100	10	20
100-400	5	10
400-1000	10	20
1000-1500	15	30

Tab. 6: Concentration areas, relative standard deviations, and measurement uncertainties for the DNPH procedure in accordance with ISO 16000-3

Concentration area [µg/m³]	Standard deviation [%]	Measurement uncertainty [%] for k=2
5-1500	10	20

^{§§} The sum of isocyanates may have to be added here.

A calculation of the overall measurement uncertainty is necessary only with materials that would not clearly fulfill the criteria of the BEMMA schema. This is the case where the calculated measurement values minus the measurement uncertainty are greater than the values given in the criteria.

Literature:

ISO 16000-3, Innenraumluftverunreinigungen - Teil 3: Messen von Formaldehyd und anderen Carbonylverbindungen in der Innenraumluft und in Prüfkammern - Probenahme mit einer Pumpe, Berlin: Beuth-Verlag, 2013.

ISO 16000-6, Innenraumluftverunreinigungen - Teil 6: Bestimmung von VOC in der Innenraumluft und in Prüfkammern, Probenahme auf Tenax TA®, thermische Desorption und Gaschromatographie mit MS oder MS-FID, Berlin: Beuth-Verlag, 2012.

ISO 16000-9, Bestimmung der Emission von flüchtigen organischen Verbindungen aus Bauprodukten und Einrichtungsgegenständen - Emissionsprüfkammer-Verfahren, Berlin: Beuth-Verlag, 2008.

ISO 16000-11, Bestimmung der Emission von flüchtigen organischen Verbindungen aus Bauprodukten und Einrichtungsgegenständen - Probenahme, Lagerung der Proben und Vorbereitung der Prüfstücke, Berlin: Beuth-Verlag, 2006.

16516, Construction products - Assessment of release of dangerous substances - Determination of emissions into indoor air, Berlin: Beuth-Verlag, 2017

VDI 4301 Part 7- Measurement of indoor air pollution - Measurement of carboxylic acids, Berlin: Beuth-Verlag, 2018

Wirts, M. et al. 2003 Time course of isocyanate emission from curing polyurethane adhesives. *Atmospheric Environment* 37, 5467-5475

Wolff, T., Stirn, H., 2000. Richtwerte für die Innenraumluft: Diisocyanate. *Bundesgesundheitsblatt* 43, 505-512.

Newman, R., Derrick, M., Byrne, E., Tan, M., Chiantore, O., Poli, T., and Riedo, C., Strange Events Inside Display Cases at the Museum of Fine Arts, Boston, and Lessons To Be Learned From Them - Part 1, in *Conservation and Exhibition Planning: Material Testing for Design, Display, and Packing*, Lunder Conservation Center Nov. 2015

Hatchfield, P., Goppion, S., M., Chiantore, O., Poli, T., Riedo, C., Suslick, K. and Abraham, M., Strange Events Inside Display Cases at the Museum of Fine Arts, Boston, and Lessons To Be Learned From Them - Part 2 Beyond the Oddy Test - the Way Forward, in *Conservation and Exhibition Planning: Material Testing for Design, Display, and Packing*, Lunder Conservation Center Nov. 2015

Diehl, J., Stanek, S., Hanzer, H., Griesser, M., Goldmann, B. and Pitthard, V., 2016, Preventive conservation strategies in the reopened collection of the Kunstkammer of the Kunsthistorisches Museum Vienna: Theory versus Practice, *IAQ 2016; Heritage Research to Conservation Practice; 12th Conference Indoor Air Quality - in heritage and historic environment*, Birmingham