Screening emission analysis of construction materials and evaluation of airborne pollutants in newly constructed display cases

A. Schieweck, D. Markewitz and T. Salthammer

Abstract

Emissions of materials currently used for constructing show cases have been studied by means of thermal extraction. The most abundant compounds in the broad spectrum of identified substances were n-butyl acetate, ethoxypropylacetate, 1-methoxy-2-propylacetate and ethyl-3-ethoxypropionate. These are used as solvents and additives in coating and adhesive formulations. Additionally, ketoximes, cross-linking agents in neutral curing silicones, were conspicuous compounds. Materials, whose emissions cause adverse health effects, were detected and should be used with caution.

Introduction

The effects of indoor air pollutants on cultural heritage have been a topic in conservation science for several decades. In the beginning, the focus of most field studies was on inorganic compounds, organic acids and formaldehyde as well as on their risk potential to museum collections [1-4, 19]. Currently, the focal point has increasingly shifted to volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) in the museum environment as well as to biocides in dust deposits [16, 17]. During these studies it became obvious that the selection of materials for use in the direct surrounding of artefacts has to be carried out with caution in order to keep the emission potential as low as possible to avoid pollution induced damage. Most cultural artefacts are stored and exhibited today in showcases, storage boxes, cabinets and envelopes to preserve them against mechanical and climatic impact. At the request of conservators and exhibition technicians, storage containers and showcases are designed with an air exchange rate reduced to a minimum. The sealed boxes allow the creation of a microclimate, which is independent of the surrounding room and which can be suited to the individual requirements of the specific artefact. However, this construction promotes the accumulation of airborne pollutants. In addition to primary emissions, a number of organic compounds present in indoor air are not in the material composition from the beginning. They result from secondary reactions during production or use [11, 20]. Construction and packaging materials with a proved low emission potential under normal use and with adequate ventilation (about one air exchange per hour($n \approx 1 h^{-1}$)) are not necessarily suitable for the museum environment because of the almost static conditions inside the show cases, their low volume and the often high surface-to-volume ratio. Therefore, it is recommended that materials with a well-known emission potential of hazardous compounds, e.g. wood-based products, wet lacquer finishes and cover fabrics, must be replaced by so-called inert materials like metal, glass and powder coatings. However, a change of material does not inevitably result in a decrease of emissions. This circumstance was shown in preliminary investigations carried out by the authors, were a summed concentration of volatile organic compounds (∑VOC) of up to 26 mg m^{-3} could be detected. Moreover, complaints about odorous containers and visible changes in the appearance of an exhibit are commonly reported by conservators. However, the prediction of the damage potential of specific construction materials or a specific type of showcase is very difficult without adequate investigation. Thus, it was considered necessary to study emissions from products currently used for the construction of display cases. The paper presents the first results of screening emission analysis with focus on volatile and semi-volatile organic compounds (VOC/SVOC). The preliminary results enable first conclusions about the emission potential of different material classes and their application for museum purposes.

Materials and methods

In close cooperation with manufacturers of furnishings and equipments for museums, products of the following material classes were chosen as representative for screening emission analysis: 1) lacquers/coatings, 2) adhesives/sealants, 3) wood-based products, 4) other construction materials (e.g. aluminium board, ceramic and plastic plates) and 5) textiles. A screening of organic vapour emissions was accomplished using thermal extraction

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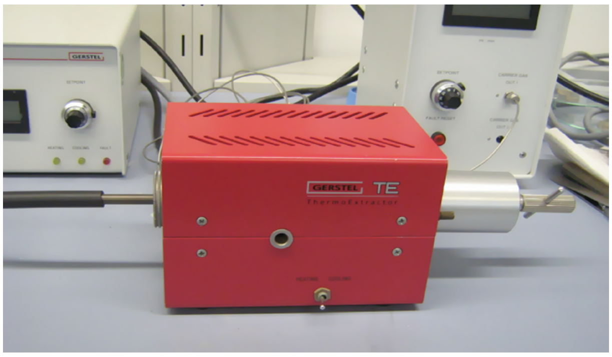

Figure 1a. Thermal Extractor TE2

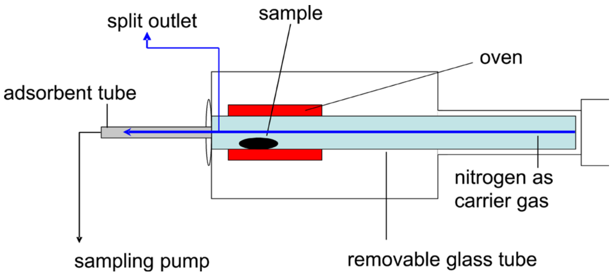

Figure 1b. Thermal Extractor TE2, schematic. Source: Scherer et al. [15]

(Thermal Extractor TE2, Gerstel, Mühlheim an der Ruhr/Germany). This new device allows quick emission measurements and therefore time-efficient and low-cost analysis [14, 15].

The Thermal Extractor TE 2 is shown in Figure 1a. Figure 1b illustrates the mode of operation schematically. The Thermal Extractor consists of an adjustable oven (temperature range: 23°C-350°C) heating a glass tube (length 178 mm, diameter 13.6 mm) with the sample inside. The sample size is limited both by the diameter of the tube and by the heatable length of the oven to a maximum of 73 mm x 10 mm. Nitrogen flows through the glass tube. In normal use, the whole gas flow passes over the adsorbent material (Tenax TA®). At heightened concentrations, the gas can be partly led off through a split outlet. To pass a defined volume over the adsorbent at an open split outlet, a sampling pump is used (FLEC Air Pump 1001, Fa. Chematec) [15]. Substances, which are emitted by the sample are transported with the gas flow over the adsorbent. Operating conditions were chosen according to the emission potential of the material classes. All materials were tested at room temperature (25°C) except lacquers and coatings. Some of these

material class	**T**[°C]	**V** [l]	**t** [min]	**n** [h^{-1}]
lacquers/coatings	65	6	40	233
sealants/adhesives	25	1	10	233
wood-based materials	25	6	40	233
construction materials	25	9	60	233
textiles	25	6	40	233

Table 1 Parameters during thermal extraction.

samples showed low emissions at room temperature, so a higher temperature for the whole material class was used (65°C) to detect all generated compounds. Depending on the emission potential of each material class, the sampling volume varied between 1 l and 9 l. Samples with high emissions were sampled with 1 l to prevent contamination during analysis. For low emissive materials, a sampling volume of 6 l – 9 l was necessary to achieve good results. Air sampling was performed with a flow rate of 100 ml min^{-1} and 150 ml min^{-1}, respectively, so that sampling time ranged from 10 min. to 60 min. Due to the low volume of the glass tube and the high nitrogen gas flow, the air exchange rate is 233 h^{-1}.

After sampling, the Tenax TA® tubes (60/80 mesh, Chrompack) were thermally desorbed (Perkin Elmer ATD 400) into a GC/MS system (Agilent 6890/5970). The compounds were separated on a HP-5 MS column (60 m x 0.25 mm, 0.25 µm). Identification was based on a PBM library search. Mass spectra and retention data were compared with those of reference compounds. All identified compounds were quantified using their own response factors. The limit of detection was < 1 µg m^{-3}. All investigation parameters are summarized in Table 1.

Results

Summed VOC(∑VOC) concentrations varied between 12000 µg m^{-3}, emitted by a cellulose nitrate coating on metal, to 2 µg m^{-3}, generated by a plastic plate. The emissions of representative materials of each product class are shown on linear (Figure 2a) and logarithmic scale (Figure 2b). Lacquers on metal and on glass, as well as sealants and adhesives, showed the highest emission potential among the investigated product categories. Other construction materials, wood based products and textiles were in general low-emissive unless they had an additional surface treatment. Coatings such as finishings on particle boards or linen coated with adhesives, caused increased emissions. Although the emission potential varied in a wide range between the material classes and the individual products, the dominating gaseous products were similar in each category. For lacquers and coatings, characteristic compounds were identified as carboxylic esters and glycol esters like n-butyl acetate, ethoxypropylacetate, 1-methoxy-2-propylacetate and ethyl-3-ethoxypropionate. These substances are widely used as solvents and additives in coatings (see Figure 3). Further conspicuous compounds were dicarboxylic esters generated by a cellulose nitrate coating. Mixtures

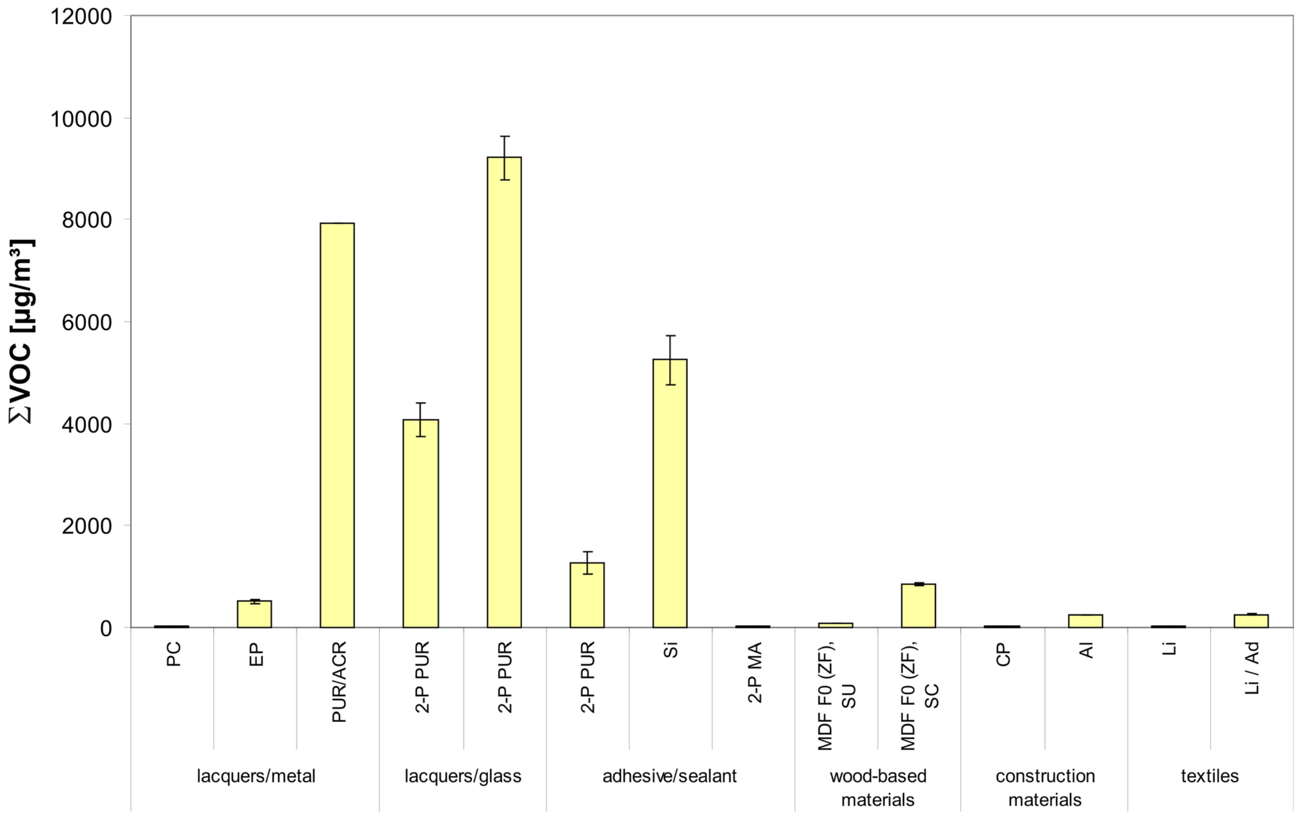

Figure 2a. Total VOC emissions of representative products of each material class, linear scale. Abbreviations: PC: powder coating, EP: epoxy resin, PUR: polyurethane, ACR: acrylic lacquer, Si: silicone, MA: methacrylate, MDF: medium density fibre board, SU: surface uncoated, SC: surface coated, CP: ceramic plate, Al: aluminium composite board, Li: linen; Ad: adhesive; 2-P: two-pack system

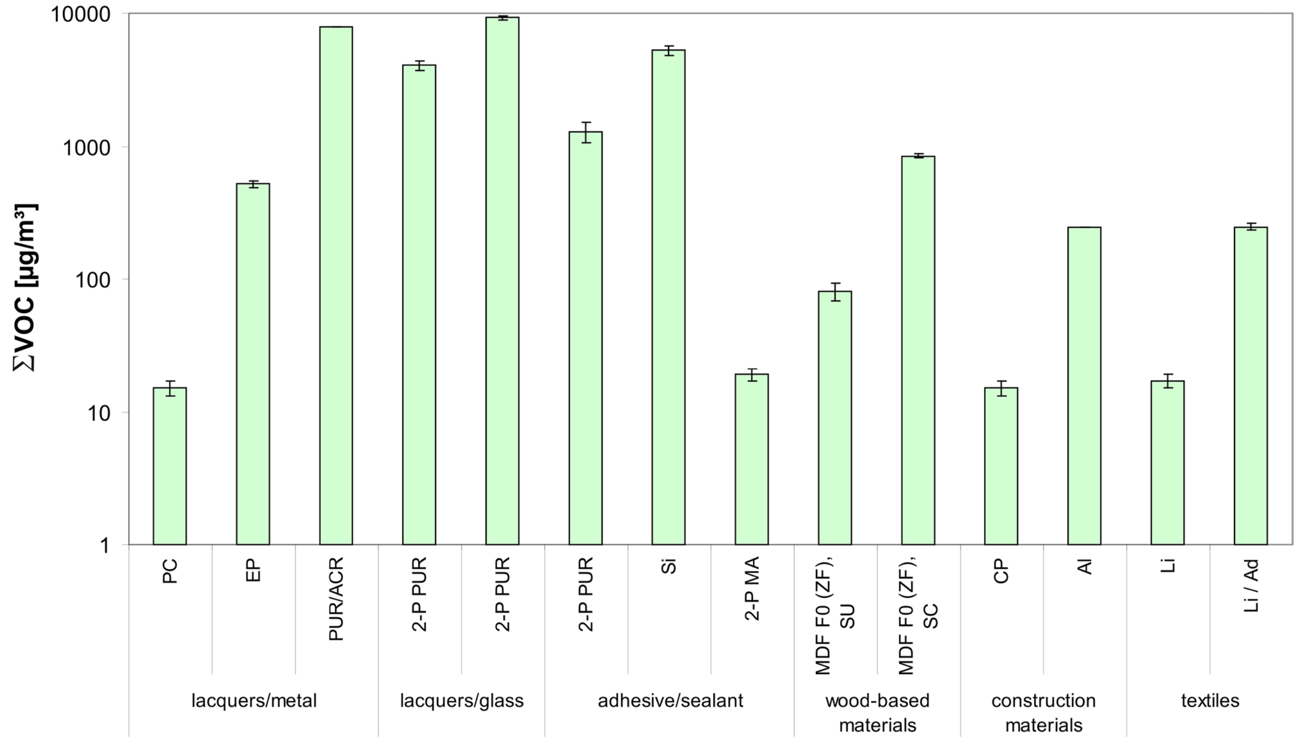

Figure 2b. VOC sum values of representative products of each material class, logarithmic scale. Abbreviations: PC: powder coating, EP: epoxy resin, PUR: polyurethane, ACR: acrylic lacquer, Si: silicone, MA: methacrylate, MDF: medium density fibre board, SU: surface uncoated, SC: surface coated, CP: ceramic plate, Al: aluminium composite board, Li: linen; Ad: adhesive; 2-P: two-pack system

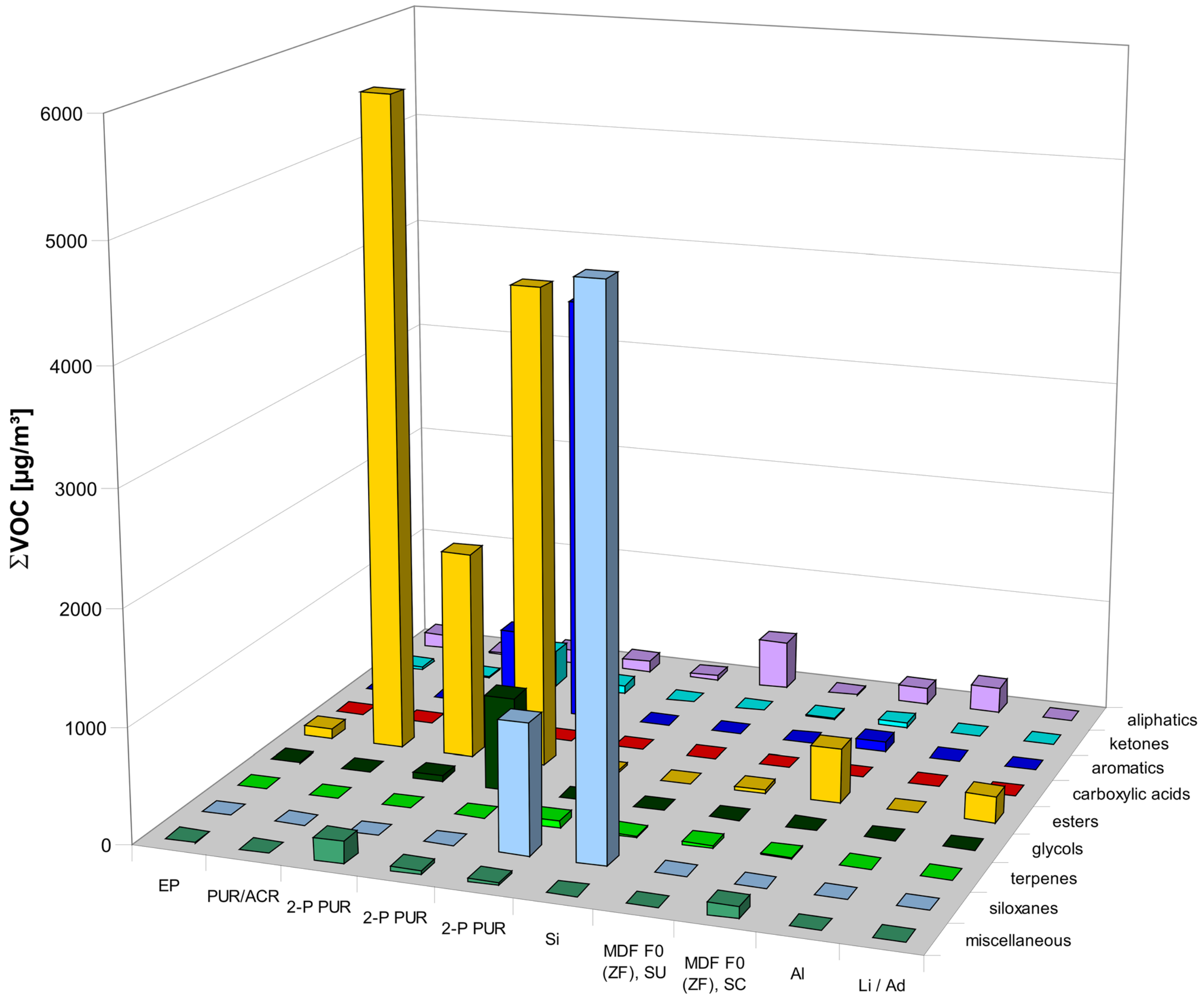

Figure 3. Substance groups identified during screening emission analysis by means of thermal extraction. The figure shows representative materials. Abbreviations: PC: powder coating, EP: epoxy resin, PUR: polyurethane, ACR: acrylic lacquer, Si: silicone, MA: methacrylate, MDF: medium density fibre board, SU: surface uncoated, SC: surface coated, CP: ceramic plate, Al: aluminium composite board, Li: linen; Ad: adhesive; 2-P: two-pack system

of dimethylglutarate, dimethylsuccinate and dimethyladipate are used as filming agents. They can also substitute for chlorinated or hazardous solvents. Moreover, different C3-/C4-benzenes and aromatic compounds such as ethylbenzene and xylene could be identified, which are also used as solvents for a large variety of lacquer systems. An exception among the lacquers was a solvent-free powder coating with nearly no emissions during thermal extraction.

Most of the adhesives and sealants were neutral curing silicones, which are today of industrial importance due to the well-known adverse effects of acid curing formulations on cultural artefacts. Prevalent compounds were therefore siloxanes and ketoximes. Especially siloxanes, which are separated from the polymer matrix, can reach very high concentrations. Ketoximes are fragmentation products, which act as neutral cross linking agents. They decompose during the curing process by reaction with water vapour and form specific fragmentation products. Characteristic fragmentation products of neutral curing sealants were 2-butanone oxime (MEKO: methylethylketone oxime) and 4-methyl-2-pentanone oxime.

Predominant volatiles from wood-based products were acetic acid and terpenes like alpha-terpineol, borneol and verbenone. Among the construction materials only an aluminium composite board showed an increased solvent emission due to the lacquered cover plates, in comparison to ceramic and plastic plates. Characteristic emissions were the same as detected in lacquers and coatings.

Raw textiles without any surface treatment showed nearly no emissions. The increased emission from a textile treated with an adhesive are attributed to the release of maleine acid di-butyl ester, a key precursor for adhesives (see Figures 2a and 2b).

Discussion

A broad spectrum of substances could be identified by thermal extraction. The most abundant compounds were in general similar to those found in recent studies of building products [8, 10-12, 21]. They were primary fragmentation products of additives and solvent residues released by the polymeric matrix. Alcohols, carboxylic esters as well as glycol esters and glycol ethers are today widely used in formulations of lacquers and sealants. In some adhesives and coatings, substances with adverse heath effects could be identified. 2-Butanone oxime (MEKO) is classified as carcinogenic category II and III and teratogenic category III [7, 18]. Moreover, some C3-/C4-benzenes are known to be irritants. Adhesives and sealants with high emissions of MEKO should therefore be avoided for health reasons. Also, product formulations containing large amounts of C3-/C4-benzenes should be used cautiously. Typical emissions from wood and wood-based materials are acetic acid and terpenes. The damage caused by acetic acid is described in the literature [5, 6, 9, 13]. Terpenes are known for their irritant effects on human health. Textiles are mostly used to decorate show cases. If they are untreated, without dyes or additives such as flame retardants, plasticizers, stabilizers and antioxidants, they can be regarded as not hazardous to cultural artefacts.

Conclusion and outlook

The results of screening emission analysis show that air pollution inside showcases is not limited to formaldehyde, formic acid and acetic acid. In newly constructed display cases, glycol esters, glycol ethers, ketoximes and siloxanes are the most abundant volatile organic compounds emitted by construction materials.

In the future, further investigations of emission behaviour of selected materials will be carried out. In a second step the indoor air quality in complete show cases will be assessed, and finally we will study the influence of secondary emissions, reaction products and possible contributions from the exhibits themselves.

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