AIRBORNE POLLUTANTS IN MUSEUM SHOWCASES

– Material emissions, influences, impact on artworks –

genehmigte

Dissertation

zur Erlangung des akademischen Grades
Doctor rerum naturalium
(Dr. rer. nat.)

Im Lehrgebiet Kunsttechnologie, Konservierung und Restaurierung
von Kunst- und Kulturgut
der
Hochschule für Bildende Künste Dresden

vorgelegt von
Alexandra Schieweck

geboren am 29.08.1977 in Wolfenbüttel

Betreuer: Prof. Dr. rer. nat. Christoph Herm

Prof. Dr. rer. nat. Tunga Salthammer

Gutachter: 1. Prof. Dr. rer. nat. Christoph Herm

2. Prof. Dr. rer. nat. Tunga Salthammer

3. Prof. Dr. phil. Michael Graf von der Goltz

Tag der Einreichung der Dissertation bei der Hochschule für Bildende Künste Dresden:

22. September 2008

Tag der öffentlichen Verteidigung:

23. Januar 2009

Druckjahr 2009

For information contact: alexandraschieweck@gmx.net

„Telemachus, we must get out the armour together and take it down inside. Make some excuse when the suitors ask you why you have to removed it. Say that you have taken it to be out of the way of the smoke, inasmuch as it is no longer what it was when Ulysses went away, but has become soiled and begrimed with soot.“

Homer, The Odyssey, Book XIX

Dedicated to my parents

IN MEMORIAM Angelika Schieweck

Ulrich Schieweck

Teilergebnisse aus dieser Arbeit wurden mit Genehmigung der Hochschule für Bildende Künste Dresden (HfBK Dresden), Studiengang Kunsttechnologie, Konservierung und Restaurierung von Kunst- und Kulturgut, in folgenden Beiträgen vorab veröffentlicht:

Publikationen (*Peer reviewed articles*)

Schieweck, A., Lohrengel, B., Siwinski, N., Genning, C. and Salthammer, T., 2005a. Organic and inorganic pollutants in storage rooms of the Lower Saxony State Museum Hanover, Germany. Atmospheric Environment 39, 6098-6108.

Schieweck, A., Hoffmann, J., Genning, C. und Salthammer, T., 2005b. Organische und anorganische Schadstoffe – Untersuchungen in Magazinen des Niedersächsischen Landesmuseums Hannover. RESTAURO 111, 354-361.

Schieweck, A., Delius, W., Siwinski, N., Vogtenrath, W., Genning, C. and Salthammer, T., 2007. Occurrence of organic and inorganic biocides in the museum environment. Atmospheric Environment 41, 3266-3275.

Schieweck, A., Markewitz, D. and Salthammer, T., 2007. Chemical substances in newly constructed showcases. ZKK – Zeitschrift für Kunsttechnologie und Konservierung 21, 48-54.

Tagungsbeiträge (*Peer reviewed proceedings*)

Salthammer, T., Lohrengel, B., Siwinski, N. and Schieweck, A., 2005. Organic and inorganic pollutants in the Lower Saxony State Museum Hanover, Germany. Proceedings of the 10th International Conference on Indoor Air and Climate, INDOOR AIR 2005, Beijing/China, 782-786.

Salthammer, T., Siwinski, N., Vogtenrath, W. and Schieweck, A., 2006. Occurrence of formaldehyde and organic acids in the museum environment. Proceedings of the 8th Healthy Buildings Conference, HB2006, Lisboa/Portugal, 4-8 June 2006, Vol. II, 283-286.

Schieweck, A., Markewitz, D. and Salthammer, T., 2007. Screening emission analysis of construction materials and evaluation of airborne pollutants in newly constructed display cases. In: Padfield, T. and Borchersen, K. (ed.), Museum Microclimates, Contributions to the conference in Copenhagen 19-23 November 2007. Copenhagen/Denmark, 67-72.

Schieweck, A. and Salthammer, T., 2008. Primary and secondary emissions in museum showcases – Impact on exhibits. Proceedings of the 11th International Conference on Indoor Air Quality and Climate, INDOOR AIR 2008, Copenhagen/Denmark.

Schieweck, A., Uhde, E. and Salthammer, T., 2008. Influence of artificial lighting on emissions of volatile organic compounds (VOC) in enclosed spaces. Proceedings of the 11th International Conference on Indoor Air Quality and Climate, INDOOR AIR 2008, Copenhagen/Denmark.

Abstract

Main emission sources of volatile organics in indoor atmospheres are furnishings, building products and decoration materials. The comparison of the indoor environment as a *"reaction vessel"* as stated by Weschler and Shields (1997) comes to a head in museum showcases. In contrast to occupied indoor rooms, the air exchange with the outer air is almost completely cut off ($n \leq 0.01\ h^{-1}$). This circumstance causes accumulation of primary emissions and promotes secondary reactions. Concentrations of indoor air pollutants under nearly static conditions, reaction processes and their impact on artefacts are not clarified so far. Thus, primary and secondary emissions of building products for museum enclosures (lacquers, sealants, UV-curing systems, textiles, and construction materials) have been studied in emission test chambers and inside of constructed showcases. The focal point was on analysing volatile and semi-volatile organic compounds (VOC/SVOC), formaldehyde and organic acids (formic acid, acetic acid) to point out dominating emissions and reactive compounds. The role of artworks as emission sources themselves as well as influences of air exchange rates and artificial lighting on indoor air quality within museum enclosures was also investigated. The results were evaluated concerning possible adverse effects on cultural assets.

Zusammenfassung

Als Hauptemissionsquellen im Innenraum sind Einrichtungsgegenstände, Bauprodukte und Dekorationsmaterialien anzusehen. Der von Weschler und Shields (1997) aufgestellte Vergleich eines Innenraumes als „Reaktionsgefäß“ spitzt sich in Museumsvitrinen zu, da in diesen im Gegensatz zu bewohnten Innenräumen der Luftaustausch mit der Umgebung nahzu komplett unterbunden ist. Es ist bisher unbekannt, welche Schadstoffkonzentrationen sich unter diesen Bedingungen einstellen und ob Reaktionsprozesse der Schadgase untereinander und in Wechselwirkung mit dem Exponat ablaufen. In der vorliegenden Studie wurden daher Materialien, die im Vitrinenbau eingesetzt werden, auf ihr Emissionspotential untersucht und darüber hinaus Raumluftmessungen in Vitrinen durchgeführt. Der Fokus der Analysen lag auf der Erfassung von flüchtigen und schwerflüchtigen organischen Verbindungen (VOC/SVOC), Formaldehyd und organischen Säuren (Ameisensäure, Essigsäure), um Hauptemissionsquellen und reaktive Verbindungen zu identifizieren. Darüber hinaus wurden auch die Exponate als potentielle Emissionsquelle berücksichtigt und mögliche Einflüsse auf die Luftqualität mit Schwerpunkt auf Luftwechselraten und künstliche Beleuchtungsquellen untersucht. Die Ergebnisse wurden abschließend in die Diskussion um mögliche Auswirkungen auf museales Sammlungsgut gestellt.

Acknowledgements

I want to acknowledge Prof Dr Christoph Herm (HfBK Hochschule für Bildende Künste Dresden – Academy of Fine Arts Dresden) for his great interest in this subject and his supervision of this work. Great thanks go to Prof Dr Tunga Salthammer (Fraunhofer Wilhelm-Klauditz-Institute (WKI) Braunschweig) who provided me the opportunity to work as an *exotic conservator* amongst chemists and who opened a lot of doors. I also would like to thank Prof Dr Michael Graf von der Goltz (HAWK University of Applied Sciences and Arts Hildesheim/Holzminden/Göttingen) for his unrestricted support.

Special thanks go to my colleagues: to Frank Fuhrmann for funny official journeys, his professional help and a plenty of cynical comments at the right time, to Astrid Schwarz for supporting me with evaluating and interpreting lots of chromatograms and to Nortje Siwinski for her assistance with analytical equipment. Great thanks also to Manuela Lingnau for various cups of coffee, for preparing lovely posters and supporting me also during her vacation. I want to thank Dr Erik Uhde, Dr Michael Wensing and Peter Meinlschmidt for kindly and helpful discussions.

My special thanks go to Dr Simon Francis Watts (Office of the Parliamentary Commissioner for the Environment, Wellington/New Zealand) for taking the voluntary task to fight through my *German English* and to Dr Marianne Odlyha (Birkbeck, University of London/UK) and David Thickett (English Heritage, London/UK) for enabling me a one month stay in London within the COST Action D 42 [Chemical Interactions between Cultural Artefacts and Indoor Environment (ENVI^{ART})].

Financial support by the Stiftung Industrieforschung Köln (Project # S 727) to perform experimental work is gratefully acknowledged. Special thanks go to the Studienstiftung des deutschen Volkes for a dissertation fellowship and kind support.

I am also grateful to Vitrinen- und Glasbau Reier, Lauta/Germany, for providing pictures.

From my family background it was not taken for granted to start a scientific profession. My parents did without much in life in order to enable me to go this long way of education. My deepest thanks go to them.

I wish also to thank Stefan Hoffmann who gave me the impact to start my PhD.

Contents

1 **Introduction** **1**

2 **Indoor air pollution in the museum environment** **4**

2.1 Current state of the art 4

2.1.1 A short review about previous and current researches 4

2.1.2 Known adverse effects of gaseous air pollutants on artworks 7

2.2 The museum environment 9

2.2.1 Museum showcases 10

2.2.2 Emission sources 14

2.2.2.1 Classification of pollutants 15

2.2.2.2 Emission mechanisms 17

3 **Fundamentals of emission analysis** **20**

3.1 Devices for emission testing 20

3.1.1 Emission test chambers 20

3.1.2 Emission screening devices 23

3.1.3 Sink effects 25

3.1.4 Modelling of kinetic emission test chamber results 25

3.2 Analysis of organic indoor air pollutants 28

3.2.1 Continuous analytical devices 28

3.2.2 Discontinuous sampling techniques 29

3.2.3 Sorbent materials and analytical procedures 30

4 **Introduction to experimental series** **32**

4.1 Experimental approach 32

4.1.1 Material emission tests 32

4.1.2 Indoor air quality in museum showcases 33
4.1.3 Influences on indoor air quality 34

5 Experimental series I – Material emission tests 36

5.1 Sample selection 36
5.1.1 Construction and decoration materials 36
5.1.1.1 Coating materials 37
5.1.1.2 Adhesives and sealants 41
5.1.1.3 UV-curing systems 44
5.1.1.4 Wood-based materials 45
5.1.1.5 Construction and other materials 47
5.1.1.6 Cover fabrics 47

5.1.2 Conservation and restoration materials 48
5.1.2.1 Natural products 48
5.1.2.2 Synthetic products 49

5.2 Sample preparation and investigation parameters 51
5.2.1 Screening emission analysis 51
5.2.2 Chamber emission tests 52
5.2.3 Air sampling and analysis 54
5.2.3.1 Volatile organic compounds (VOCs) 54
5.2.3.2 Formaldehyde 55
5.2.3.3 Organic acids (formic acid, acetic acid) 55

5.3 Results and discussion 56
5.3.1 Emissions from construction and decoration materials 58
5.3.1.1 Lacquers and coatings 64
5.3.1.2 Adhesives and sealants 70
5.3.1.3 UV-curing systems 74
5.3.1.4 Wood-based products 80
5.3.1.5 Construction and other materials 83
5.3.1.6 Cover fabrics 83
5.3.1.7 Summary of the results 84

5.3.2 Emissions from conservation and restoration materials 85
5.3.2.1 Natural products 87
5.3.2.2 Synthetic products 89

5.3.2.3 Summary of the results 93

6 Experimental series II - Indoor air quality within museum showcases 94

6.1 Parameters of investigation 94
6.1.1 Air sampling and analysis 95
6.1.2 Air exchange rate measurements 96

6.2 Showcases directly after production 97
6.2.1 Volatile organic compounds (VOCs) 98
6.2.2 Formaldehyde, organic acids (formic acid, acetic acid) 101
6.2.3 Comparison of chamber test results and pollution levels inside of showcases 102

6.3 Showcases in museum use 103
6.3.1 Modern-type showcases 103
6.3.1.1 Volatile organic compounds (VOCs) 106
6.3.1.2 Formaldehyde and organic acids 108

6.3.2 Old-type showcases 110
6.3.2.1 Volatile organic compounds (VOCs) 112
6.3.2.2 Formaldehyde and organic acids 114

6.4 Artworks as emission sources 116
6.4.1 Biocide treatments 116
6.4.2 Semi-volatile organic compounds (SVOCs) - "*Fogging effect*" 120

6.5 Summary of the results 122

7 Experimental series III - Influences of artificial lighting 125

7.1 Experimental set-up and investigation parameters 125

7.2 Results 127

7.3 Discussion 129

7.4 Air flows and temperature distribution within showcases 130
7.4.1 Passive thermography 130
7.4.2 Test procedure 130
7.4.3 Results 132

7.5 Summary of the results 135

8 Evaluating potential damage to artwork materials – a theoretical approach 136

9 Conclusions 143

10 References 149

11 Appendix 164

1 Introduction

The identity of a population group is affected by previous historical events and is reflected by contemporary currents. To collect and to investigate evidence of these ages, to preserve them as well as to hand them on to future generations, are the basis and the primary responsibilities for cultural heritage institutions. The International Council of Museums (ICOM) defines them as

"... a non-profit making permanent institution in the service of society and of its development, open to the public, which acquires, conserves, researches, communicates and exhibits, for purposes of study, education and enjoyment, the tangible and intangible evidence of people and their environment." (ICOM International Council of Museums, 2006).

During the last decades, the effort to eliminate adverse environmental influences at a very early stage by optimizing the surrounding conditions of museum collections in order to prevent the occurrence of damages on artworks has become a major part among restoration work. This conservation approach termed as "*Preventive conservation*" is defined as effort to decelerate the deterioration of cultural heritage, to preserve its integrity and to reduce the necessity of restoration treatment to a minimum (Charta of Vantaa, 2000).

In order to achieve a most comprehensive control of the surrounding conditions, many museum institutions are using today progressive containment as an underlying strategy to preserve artefacts in an ideal way. In order to minimize environmental influences (climate fluctuation, entry of polluted outer air), climatic requirements within (i) the museum building and (ii) inside of galleries, exhibition areas and storage rooms are closely defined. To prevent furthermore mechanical damage (theft, attacks) and to ensure a microclimate inside, which is independent of the surrounding room to suit the individual requirements of the specific artefact, mobile cultural assets are stored and displayed in showcases, cabinets and envelopes; paintings are glazed. This kind of nested prevention strategy is referred to as a so-called *"box in a box-model"* (Camuffo et al., 2000).

In order to meet these conditions, cases are predominantly constructed as airtight as possible at the request of conservators and exhibition technicians which implies that the air exchange rate should be lowered to a minimum. It is to be assumed that the high surface to volume ratio, which characterizes especially smaller enclosures, combined with unsuitable construction materials and extremely lowered air exchange rates, enhance the accumulation of chemical compounds, which contribute to a bad indoor air quality. Hence, the comparison of the indoor environment as a *"reaction vessel"*, as stated by Weschler and Shields (1997), comes to a head in museum showcases.

Problems linked with hazardous emissions generated by building products installed in the showcase causing macroscopically observable damages on artworks were early observed. Thus, especially formaldehyde and organic acids (formic acid, acetic acid) were focussed in the past due to their corrosion potential. Facing this problem, responsible persons both of the conservators and the manufacturer's site made efforts to minimize potential emission sources. Specific materials known for emitting corrosive compounds were increasingly substituted in the last decades by so called inert substances. Nevertheless, complaints are still expressed by conservators. A special problem seems to be a significant odorous load and high pollution levels.

Even though building products of modern showcases are also used in occupied indoor environments, there is no knowledge about their emission profile under museum conditions. This is of particular relevance as substances with a proved low emission potential regarding indoor scenarios under normal use and with adequate ventilation conditions are not mandatory qualified for the application in the museum environment due to differing boundary conditions, especially the considerably reduced ventilation rates. Furthermore, the exhibits are in close or direct contact to building materials and decoration products within showcases.

Among medical and chemical science, indoor hygiene has become an independent advanced branch of research. Over time, a substantial state of knowledge has been gained, e.g. regarding health hazards due to formaldehyde and wood preservatives within prefabricated houses, chemical load through asbestos and polychlorinated biphenyls (PCB) in kindergardens, schools and office buildings and actual problems such as sick-building syndrome, fogging effects and fine particles.

In order to determine indoor air quality and individual substances precisely and exactly, such sophisticated measuring methods are necessitated. Museum institutions do not possess corresponding possibilities neither to control emission potentials of building and decoration materials nor to evaluate indoor air quality within constructed enclosures. In most cases museums renounce professional analyses due to financial reasons. Thus, there is a lack of knowledge so far resulting in a high uncertainty both on the part of museum staff and of manufacturers about the emission profile from newly applied products under almost static conditions and about the selection of appropriate materials. The consequences due to the static design of showcases and material emissions have not been basically investigated so far. Fundamental investigations are missing.

Objectives and scientific approach

The present study targets to create a comprehensive picture of the current situation of indoor air quality in modern-type museum showcases by means of sophisticated analytical techniques, which were transferred from environmental chemistry.

Facing the current lack of knowledge and missing basic investigations, main emission sources have to be revealed. Reactive compounds have to be identified concerning undesired chemical reactions which might proceed under museum conditions. It is further to clarify how high air pollution levels inside of showcases are. Moreover, no investigations were accomplished so far concerning correlations and/or differences between modern showcases and traditional construction types, particularly regarding the question if the shift in material selection has contributed to lower indoor air pollution levels. In this context, influencing factors such as air exchange rates, artificial lighting and the exhibits themselves are of importance.

The present study gives at first a short overview of the current state of the art regarding indoor air pollution in the museum environment (chapter 2), before introducing in fundamentals of emission analysis (chapter 3). Standardized analytical methods are presented which are predominantly unknown in the conservation field, but were utilized in the conducted experimental series (chapter 4 - 7). In order to obtain information about the emission potential and the spectrum of released substances, fundamental emission analyses of materials for production purposes were carried out (chapter 5). To reveal correlations and/or differences to material emission tests, indoor air analyses in different museum showcase types were accomplished (chapter 6). Influences on indoor air quality by museum exhibits themselves (chapter 6) as well as air exchange rates and light sources directly installed inside the case (chapter 7) were also considered. The thesis concludes by highlighting the results concerning possible interactions between gaseous volatiles as well as concerning the evaluation of corrosive potentials on cultural assets (chapter 8).

2 Indoor air pollution in the museum environment

2.1 Current state of the art

2.1.1 A short review about previous and current researches

Even though pollution is not a phenomenon just of modern times, it is intimately connected with the dawn of the industrial age with which the effects of gaseous air pollutants on precious cultural assets became obvious. The high atmospheric load caused strong soiling as well as corrosion and erosion of artworks located outdoors. The assumption that these would be protected inside of museums and archives was disproved by visible damage or loss.

A first detailed insight into conservation problems entailed by gaseous outdoor pollutants is delivered by Saunders (2000) giving a comprehensive literature research about pollution in the London National Gallery during the early nineteenth century. Due to the coal-burning industries and the close vicinity of several large chimneys and the Thames with its steamboats, the air in the exhibition halls was dusty; frames and paintings were soiled and lead white as well as copper corroded, which required daily cleaning. As a means of temporary protection, paintings were glazed and the backs were covered. The difficulty to provide healthy climate conditions for museum staff and visitors and similarly to protect artworks became evident even in these early times as it was decided not to cut off totally the entry of outer air facing the poor indoor air quality resulting from that, in particular at high numbers of visitors. An attempt to counteract against first signs of damages on panel paintings, which were caused by the overheated air, was undertaken by positioning zinc troughs filled with water over the air outlets of the heating system (Saunders, 2000 and citations therein).

Whereas this report refers to indoor air pollution due to exogenous pollutants and damages resulting from inappropriate climatic conditions, one of the first documentations regarding adverse effects on objects as result of unsuitable showcase materials is bequeathed from the end of the nineteenth century. Byne (1899) documented efflorescence on sea shells. His interpretation that this powdery coating is formed on the items surface and encroaches on adjacent exhibits similar to a contagious disease coined the term *Bynes disease*. The reaction mechanism was not clarified until several decades later. The deterioration of lead and mollusc shells by acidic exposure due to wooden display materials (especially oak) belongs now to the most popular examples for damages on museum objects as proved by the abundance of publications, amongst others Grzywacs and Tennent (1994), Brokerhof and van Bommel (1996), Tétreault et al. (1998) and Niklasson et al. (2005).

First scientific approaches

However, the main concern of conservation scientists was on climatic influences through fluctuations in temperature and relative humidity as well as on light intensities (Padfield, 1966; Michalski, 1993; Saunders and Kirby, 1996; Camuffo, 1998; Brimblecombe et al., 1999; Camuffo et al., 1999). Detailed interactions between gaseous substances and artwork materials remained unknown. A first scientific basis of indoor air quality in the museum field was set out by Thomson (1965), who gave a basic review of atmospheric chemistry for conservators and dealt with parameters affecting the museum environment by involving the fundamentals of air pollution. In 1978 the first edition of his popular standard work *The museum environment* was published (Thomson, 1986). At nearly the same time, Hackney (1984) gave a first comprehensive survey of the distribution of gaseous air pollutants in the museum environment.

Previous main topics

Due to such basic publications and observable damages on museum collections, indoor air quality gained growing awareness in the restoration community. The emphasis of these studies in the last five decades was clearly dedicated to (i) the field of inorganic substances entering the indoor environment by outdoor pathways, such as ozone (O_3), nitrogen oxides (NO_x), sulfurous gases (SO_2, H_2S, OCS) (Hackney, 1984; Brimblecombe, 1990; Druzik et al., 1990; Blades et al., 2000; Ankersmit et al., 2005), (ii) formaldehyde and organic acids (formic acid, acetic acid) (Grzywacz and Tennent, 1994; Raychaudhuri and Brimblecombe, 2000) and (iii) impact of known corrosive compounds on artworks (Franey et al., 1985; Grosjean et al., 1988; Whitmore and Cass, 1988, 1989; Williams et al., 1992; Brokerhof and van Bommel, 1996; Dupont and Tétreault, 2000; Ankersmit et al., 2005). A special concern was thereby on carbonyl compounds and there effects on artefacts due to inappropriate construction materials (Grzywacz and Tennent, 1994; Tétreault, 1994, 1999; Tétreault et al., 1998). All these investigations contributed to the understanding of basic mechanisms.

Beneath these main topics other subjects have been ignored for a long time. The multiplicity of organic volatiles released by the furnishing of museum interiors was elucidated just in the last few years (Schieweck et al., 2005a,b; Schieweck und Salthammer, 2006; Hahn et al., 2007).

Particles and dust

Also the field of airborne particles in museums has not attracted as much attention as outdoor pollutants and carbonyl compounds. However, some basic researches have been published under consideration of protection strategies and mathematical approaches for modelling particle dynamics (Nazaroff and Cass, 1991; Nazaroff et al., 1993). Other investigations are focussing on the correlation of particulate matter with heating systems, air flows and ventilation rates in museums and historic buildings (Gysels et al., 2002; Bencs et al., 2007; Samek et al., 2007; Spolnik et al., 2007). The influence of visitors on the amount and distribution of dust and particles is especially a question regarding historic interiors with objects on open display (Yoon and Brimblecombe, 2001; Lloyd et al., 2002; Lithgow and Brimblecombe, 2003; National Trust, 2005; Worobiec et al., 2008).

Pesticides

Another main focus is on biocides (Glastrup, 1987; Krooß and Stolz, 1993; Schieweck et al., 2007), which are outgassing especially from wooden objects and ethnological collections due to previous prevention treatments. Unger et al. (2001) published a comprehensive overview and literature research about wood preservatives formerly applied in museum collections. A special focus is currently on the handling of contaminated artworks and decontamination possibilities (Unger, 1998; Winkler et al., 2002; Tello et al., 2005; Odegaard and Sadongei, 2005; Tello, 2006).

Monitoring and prevention strategies

As most museum institutions do not possess an own laboratory and sufficient funds to commission fundamental and comprehensive investigations, many researches are dealing currently with the developing of simple monitoring methods and low-cost prevention strategies.

Recently, several books have been dedicated to this sector (Blades et al., 2000; Hatchfield, 2002; Tétreault, 2003; Grzywacz, 2006).

2.1.2 Known adverse effects of gaseous air pollutants on artworks

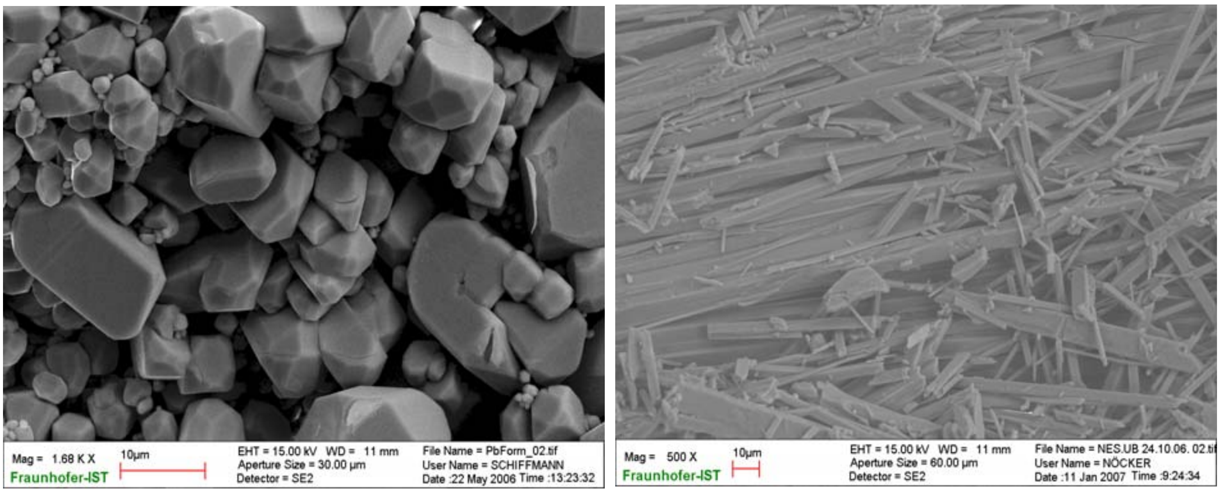
The increasing attraction on indoor air pollutants in the museum environment and associated investigations contributed to the understanding of basic mechanisms. The fact that gaseous substances are involved in deterioration processes and ageing mechanisms was not realized until macroscopic observable damages occurred which gave the starting point for scientific investigations. Due to the main topics in previous research high emphasis regarding adverse effects of pollutants on artwork materials were on (i) inorganic compounds and (ii) formaldehyde, formic acid and acetic acid due to obvious damages.

I Inorganic compounds

One main topic were inorganic substances, which enter the indoor environment by outdoor pathways, such as ozone (O_3), nitrogen oxides (NO_x) and sulphurous gases (SO_2, H_2S, OCS) due to their oxidation potential. Organic fibres from textiles and papers corrode resulting in loss of strength durability. Moreover, it is reported that oxidizing gases cause the formation of tiny red spots on photographic silver images. The image appears consequently brown-yellow and might entirely bleach out at high pollution levels (Feldman, 1981; Ryhl-Svendsen, 1999, 2001). Oxidizing gases also damage colorants by attacking functional groups (Grosjean et al., 1988; Whitmore and Cass, 1988, 1989; Williams et al., 1992; Salmon and Cass, 1993; Ye et al., 2000). Silver tarnishes under influence of sulphurous gases. The strongest corrosion potential is attributed to hydrogen sulphide (H_2S) (Franey et al., 1985). It is also known that rubber is oxidized by ozone exposure (Jaffe, 1967; Shashoua, 1999).

II Formaldehyde and organic acids (formic acid, acetic acid)

Formaldehyde and organic acids (formic acid, acetic acid) belong to the most discussed pollutants in the museum environment as they cause characteristic white efflorescence on surfaces of metals and calcareous materials. The corrosion potential increases in the following order: formaldehyde < formic acid < acetic acid. Corrosion products on calcareous materials consist in general of hydrated calcium acetate in different forms and appear in combination with chlorides and nitrates (Ryhl-Svendsen, 2001). Brokerhof and van Bommel (1996) considered that efflorescence on calcareous materials is formed by a direct reaction of acetic acid and an indirect reaction of formaldehyde. The most remarkable circumstance is that the efflorescence composition does not inevitably mirror the pollutant composition in the surrounding atmosphere (Grzywacs and Tennent, 1994). Even in a single display case it is possible that different corrosion products are formed (Tennent and Baird, 1985). Efflorescence on metal items, notably on lead, is formed as lead formate and basic lead carbonate. Lead formate is characterized by its orthorhombic structure, whereas lead acetate forms spicular structures, as illustrated in Figures 2.1-1a and 2.1-1b. Both salts are often identified together on the same artefact. Due to its instability, lead acetate is not normally detected as a corrosion product (Grzywacs and Tennent, 1994).



Figures 2.1-1a and b. Lead formate [$Pb(HCOO)_2$] and lead acetate [$Pb\,(CH_3COO)_2$]. SEM micrographs.

Further materials which are also susceptible to organic acids are inorganic specimens such as glass, stone and enamels as well as organic items like cellulose and leather. Cellulose materials depolymerize due to acid hydrolysis notably at long term exposure. Molecular chains are cleaved randomly causing a shortening and decreasing strength durability of the fibres (Dupont and Tétreault, 2000). The deterioration process of vitreous materials will be significantly increased by carbonyl pollutants. Sodium methanoate and sodium ethanoate can be detected as corrosion products (Bradley and Thickett, 1999; Torge et al., 2000; Müller et al., 2000).

Table 2.1-1 summarizes characteristic deterioration processes, which are linked with airborne pollutants.

Table 2.1-1. Known effects on artwork materials induced by airborne pollutants (Bear and Banks, 1985; Brimblecombe, 1990; Pietsch, 1994).

Pollutant	Material	**Adverse effect**
Ozone (O_3)	Rubber	Embrittlement
	Metals	Corrosion
	Textile dyes	Fading
	Photographic materials	Deterioration
	Papers, textiles	Cracking
Nitrogen oxides (NO_x)	Rubber	Embrittlement
	Photographic materials, plastics, metals	Deterioration
Sulphur dioxide (SO_2)	Metals	Tarnishing
	Paints, dyes, photographic materials, leather	Deterioration
	Papers, textiles	Embrittlement
	Inorganic materials, e.g. glass, stone, lime plaster, fresco	Discolouration
	Organic materials, e.g. cellulose, proteins, plant fibres	Corrosion
Hydrogen sulphide (H_2S)	Metals	Tarnishing
	Paints	Dying
	Lead pigments	Blackening
	Photographic materials	Deterioration
Formaldehyde (HCHO)	Paper, metallic oxide pigments	Dying, discolouration
	Leather, parchment, wool, silk, paper	Embrittlement
Formic acid (HCOOH) Acetic acid (CH_3COOH)	Metals, calcareous materials, papers, textiles, protein-containing materials	Corrosion
Hydrogen peroxide (H_2O_2)	Iron	Corrosion
	Photographic materials	Discolouration
Ammoniac (NH_3)	Metals	Corrosion, tarnishing

2.2 The museum environment

Air quality indoors differs from the outer area by creating an own confined atmosphere. With increasing ventilation rates and, thus, increased exchange with the outer air, indoor and outdoor climate equates. However, the supply of fresh outer air is drastically reduced especially due to heat insulating measures to lower the energy consumption in buildings and leads therefore to an accumulation of chemical substances generated in the interior itself (Salthammer, 1994).

The museum environment differs from normal indoor environments under residential or office use in one fundamental aspect: it has to protect cultural assets beneath providing a healthy indoor climate for museum staff and visitors. As preventive conservation tries to ensure appropriate conditions for the stability of exhibited and stored items, high demands are required on climatic conditions. In order to eliminate external environmental influences, especially climatic fluctuations and entry of outdoor pollutants, indoor climate parameters are defined in very close spaces, which results in a drastic reduction of unhindered infiltration of outdoor air supply. Whereas in occupied rooms and offices the continually entering of outdoor pollutants and the exiting of indoor generated substances is allowed by structural leakages and by the opening of windows and doors, this air exchange is almost completely cut off in museum institutions. However, the strict climatic requirements might just be insufficient achieved. The needs of preservation and security require therefore the storage and exhibition of artworks inside of cases, which constitute today the main element of museum exhibition areas. Showcases form self-contained indoor rooms and are even more separated from the outdoor environment.

2.2.1 Museum showcases

Museum showcases shall provide increased protection of the stored or displayed artworks against undesired environmental influences, such as climatic fluctuations, irradiation, entry of dust and against touching by visitors. Due to increasing assault on exhibits (e.g. acid attacks, mechanical damages and theft) showcases are meanwhile also a kind of security boxes.

Even though the specific dimensions, construction and decoration materials are custom-made, several showcase types can be distinguished in general (see Figure 2.2.-1).

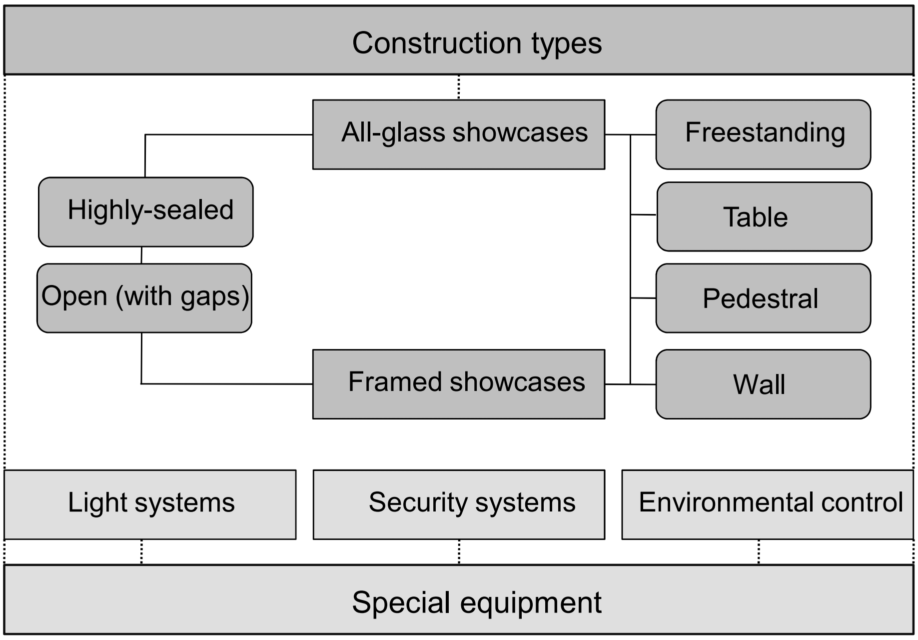
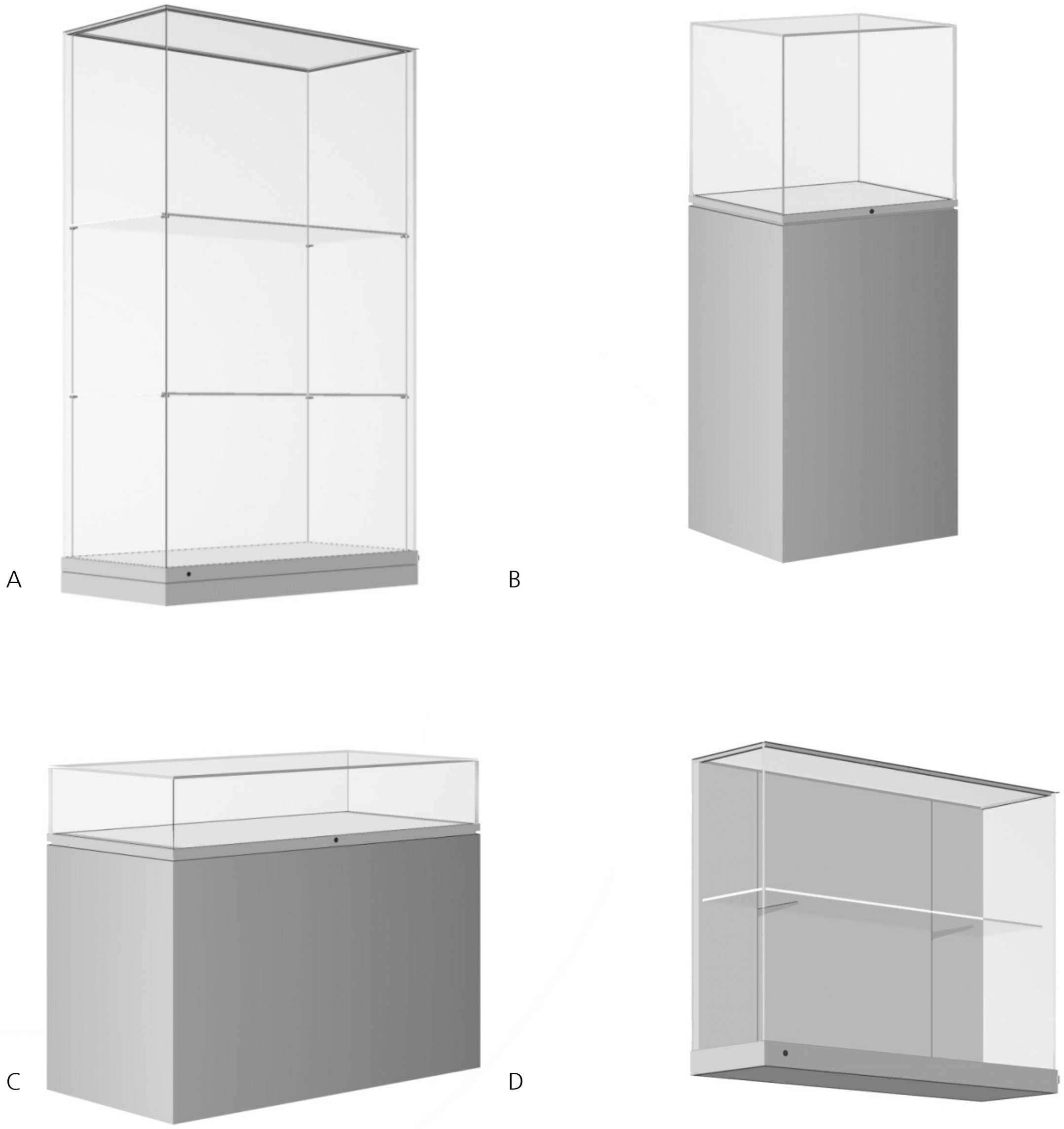


Figure 2.2-1. Overview of common showcase construction types and special equipment.

The term “showcase” comprises enclosures from a few litres up to several cubic metres. All-glass showcases allow an unhindered view on the exhibit without apparently construction elements, such as framed profiles at vertical and horizontal glass edges (framed showcases). For the all-side view objects are mostly displayed in freestanding cases, whereas wall cases are either attached on a wall or are self-supporting. Tables are primarily used for exhibiting small, two-dimensional objects such as coins, graphics or textiles. Pedestal display cases are mostly also of the free-standing type but with a high pedestal zone and a glass hood. Those pedestal zones are generally used for hiding special equipment, such as buffer and/or adsorption materials or dust filters for environmental control or security systems (e.g. alarm device, security locks, tremor detectors). Some manufacturers also offer the installation of a pump inside of the pedestal to ensure an active air circulation within the showcase, which leads the air stream in specific time intervals over an adsorbent. Some special showcases might also be purged with nitrogen to create an inert atmosphere for the prevention of oxygen sensible artwork materials, to protect the exhibit against insect attack as well as against entry of dust and pollutants by maintaining slight over pressure. The purchase of special equipped showcase types is primarily a financial question and in most cases not possible for middle- and low-sized museum institutions.

The range of available light systems, which are installed directly within the case, comprises LED-light, fibre optics, halogen spotlights as well as fluorescent lamps. Lights can also be installed inside a hood to prevent influences of irradiation and/or heating by separation from the case interior. Beneath this, some museums prefer no light equipment inside the case and illuminate the collection just by the room lighting. Construction types might be highly sealed to cut off any air exchange with outer air to prevent undesired influences or might be constructed open with gaps. The latter type is currently not in great demand in Germany due to the entry of dust and outdoor pollutants. Moreover, security arrangements seem to be lowered.

Figures 2.2-2a–d demonstrate common showcase construction types.



Figures 2.2-2a-d. Four main showcase construction types: freestanding (A), pedestal (B), table (C) and wall (D) [©Vitrinen- und Glasbau Reier, Lauta/Germany].

As damages caused by formaldehyde, formic acid and acetic acid are intimately connected with unsuitable showcase construction materials, which release acidic gases, efforts were made by museum staff to improve these building products (Miles, 1986; Eremin and Wilthew, 1996; Tétreault, 1994, 1999). Showcase manufacturers took this opportunity to substitute certain materials which are known for acidic emissions, especially particle boards, wood, felt and acid curing silicone rubber. Most of the showcases constructed today consist of *modern* materials which mean glass, stainless steel, lacquered metals/wood-based products and neutral curing silicones. Figure 2.2-3a shows a showcase built of *traditional* materials nearly twenty years ago, whereas Figure 2.2-3b illustrates a new showcase constructed with modern materials.

Figures 2.2-3a and b. (a) Showcase constructed with traditional materials, e.g. wood-based products and felt; (b) modern showcase mainly consisting of glass and lacquered metals/wood-based products. Examples [Figure 2.2-3b: ©Vitrinen- und Glasbau Reier, Lauta/Germany].

2.2.2 Emission sources

Emission sources in the museum environment can be generally assigned to three main categories (i-iii) according to normal indoor environments under residential or office use (Moriske, 2000). Considering the special position of interiors for museum use, a fourth class (iv) can be added:

i Environmental effects (external air, ground)
ii Human activities (breathing, transpiration, particles/dust)
iii Building products, furniture and fixtures
iv Exhibits (object-inherent materials and products used for conservation and/or restoration purposes)

With the external air inorganic and organic substances enter the building through windows, doors, fissures and structural leakages. Particularly inorganic compounds are associated with outer air. Characteristic pollutants are ozone (O_3), sulphur dioxide (SO_2), nitrogen oxides (NO_x) as well as carbon monoxide (CO) and carbon dioxide (CO_2). Ozone is formed in the atmosphere as photochemical reaction product from nitrogen oxides and hydrocarbons; concentrations are increased especially during summer months (Schieweck und Salthammer, 2006). In the indoor environment, electronical devices and photocopiers were potential emission sources in previous times. However, such emissions are today of secondary importance by equipping these tools with ozone absorbers (Moriske, 2000; Seifert und Salthammer, 2003). Nitrogen oxides, sulphur dioxide and carbon monoxide are mainly released by combustion processes and can be analysed in heightened concentrations in particular on crossroads and in urban centres due to exhaust fumes. The same applies for carbon dioxide, which is also released indoors by human respiration. In this regard, particles and dust inserted by streams of visitors are of main concern (Lloyd et al., 2002; National Trust, 2005).

Beneath this, indoor environments are characterized by furnishings and a broad variety of materials applied for decoration and construction purposes, whose emission potential depends on the age and climatic parameters (Salthammer, 2004). Especially materials of large areas, such as floorings, wall coverings and sealants as well as furnishings exert strong influence on indoor air quality. Moreover, also cleaning and sanitary products as well as materials for office use and work-related products contribute to indoor air pollution. Additionally, also the artefacts themselves are to be considered as own emission source in the museum environment either due to their composition or by emitting previously applied conservation and restoration products (Horie, 1987; Mills and White, 1994). A special attention has to be paid on previous biocide treatments as these release active agents into indoor air for long-term (Unger et al., 2001). Hence, indoor air pollution in museum collections has always to be regarded concerning both risk to the collection and adverse effects on human health. Emission sources, main pollutants as well as influences and interactions in the museum environment are shown in Figure 2.2-4.

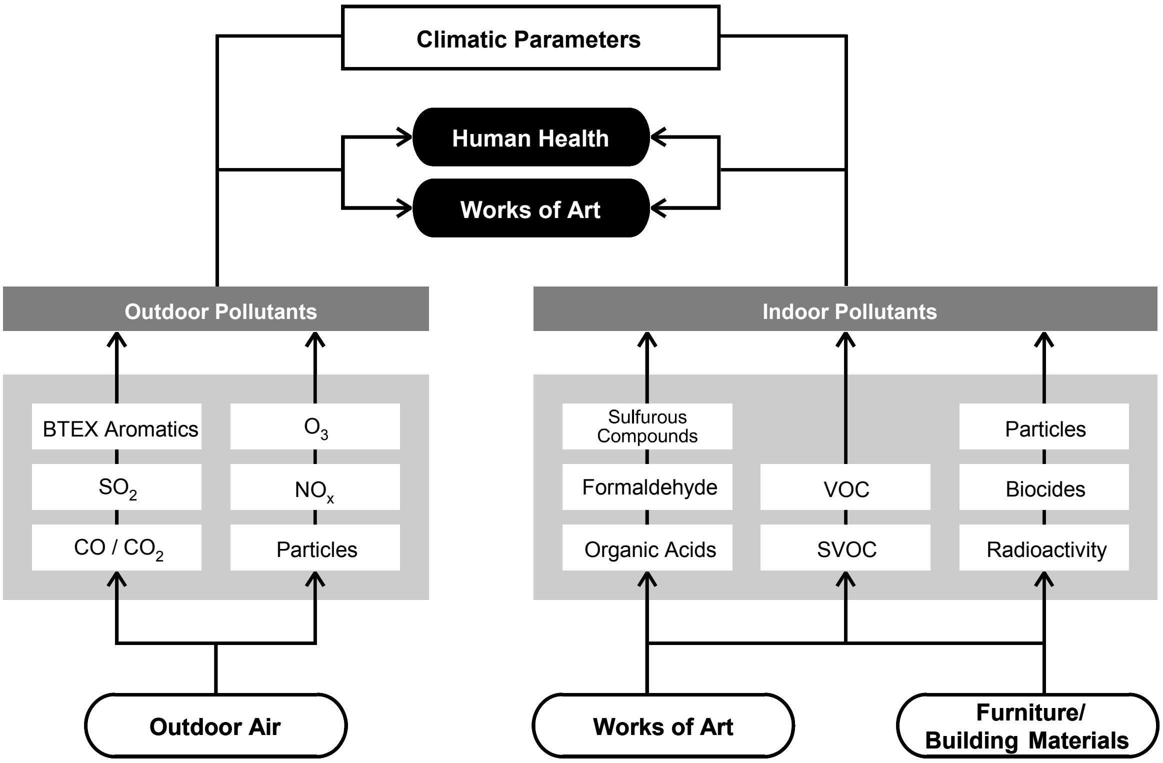


Figure 2.2-4. Outdoor and indoor emission sources affecting works of art and human health [reprinted from Schieweck et al., 2005a with permission from Elsevier].

2.2.2.1 Classification of pollutants

Pollutants are in general distinguished in inorganic and organic compounds. Organic substances are classified by the World Health Organisation (WHO, 1989) according to their boiling points into *very volatile organic compounds* (VVOC; *bp* ≥ 60°C), *volatile organic compounds* (VOC; *bp* = 60°C–290°C), *semi-volatile organic compounds* (SVOC; *bp* = 290°C–400°C) and *particulate* *organic compounds* or *organic compounds associated with particulate matter* (POM), as illustrated in Figure 2.2-5. The classification of the European Union is in contrast oriented towards retention data, in which a substance is eluted in gas chromatography with hexane (C_6) and hexadecane (C_{16}) as marking substances (ECA Report No. 19, 1997).

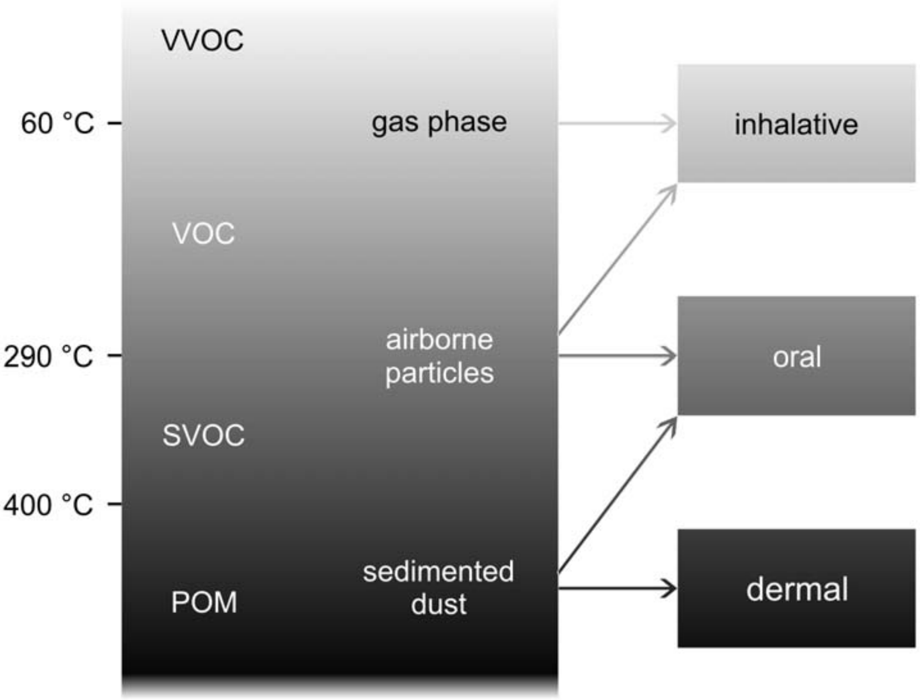


Figure 2.2-5. Classification of organic compounds on the basis of boiling points, accumulation in indoor compartments and personal exposure pathways [reprinted from Wensing et al., 2005 with permission from Elsevier].

In order to simplify control and monitoring strategies for the reduction and prevention of indoor air pollution in museums, the conservation community tends towards defining *key airborne pollutants*. Tétreault (2003) has designated seven pollutants, namely hydrogen sulphide (H_2S), nitrogen dioxide (NO_2), ozone (O_3) and sulphur dioxide (SO_2) as well as acetic acid (CH_3COOH) as indoor pollutant. Moreover, also particles ($PM_{2.5}$) and water vapour (H_2O) are amongst those key airborne pollutants. By controlling these most significant compounds, the majority of further airborne pollutants may also be controlled as these do not require the same level of control (Tétreault, 2003). This strong focus shall enable effective risk assessment strategies and monitoring campaigns.

2.2.2.2 Emission mechanisms

As mentioned above, materials for indoor use release in general a variety of volatile and semi-volatile organic compounds (VOCs/SVOCs) into the atmosphere. The particular emission potential depends on several use- and environment-related parameters and is furthermore affected by climatic parameters, which alter permanently under conditions of habitation and work (Salthammer, 2004). Material emissions are furthermore influenced by the total amount and volatility of constituents in the material, the distribution of these constituents between the surface and the interior of a material and are also affected by the time (e.g. ageing of the material) and the loading factor (ratio of mass or surface area of a material to the room volume) (Tucker, 2001). Furthermore, temperature, relative humidity, air velocity as well as moisture content of the material and in the air play therein an important role (Gunnarsen, 1997). Due to the different formation mechanisms following from this, a distinction is drawn between primary and secondary emissions (Wolkoff, 1995; Salthammer and Kephalopoulos, 2000).

Primary emissions

Primary emissions are non-bound or free VOCs, which are from origin present in the formulation of a new product, e.g. accelerators, additives, monomers, plasticizers, solvents and unreacted raw materials (Knudsen et al., 1999). Primary emissions are mainly controlled by two mechanisms: (i) the internal diffusion of VOCs within the material to the surface and (ii) the evaporation or desorption from the material surface to the ambient air, provided that inside a product no internal chemical reactions occur (Van der Wal et al., 1997; Knudsen et al., 1999). Primary emissions decay relatively fast and can furthermore be classified as *reactive* or *non-reactive* compounds due to their tendency to undergo chemical reactions under environmental conditions (Wolkoff et al., 1997; Salthammer et al., 1999).

Secondary emissions

Secondary emissions are VOCs which are not present in the formulation of a new product, but formed in the material itself or in the indoor environment by chemical reactions. Secondary emissions are developed delayed and may continue for the entire life of a product (Wolkoff and Nielsen, 1997).

Uhde and Salthammer (2007) defined three cases in which undesired chemical reactions occur:

i During the production of the material, whereas the reaction products are released at the customer's site. Formation processes may result from inadequate conditions during the production process or an inadequate product formulation.

ii At the material surface or in different materials at the customer's site, e.g. between layers of different materials (concrete – adhesive – flooring).

iii Unwanted reactions of primary compounds with primary emissions from other sources and/or with reactive gases in the gas phase at the customer's site.

In the complex system of emission mechanisms, primary and secondary emissions may interfere with each other in time-dependent fractions (Clausen et al., 1991; Wolkoff, 1995; Knudsen et al., 1999). Formation processes of primary and secondary emissions are visualized in Figure 2.2-6.

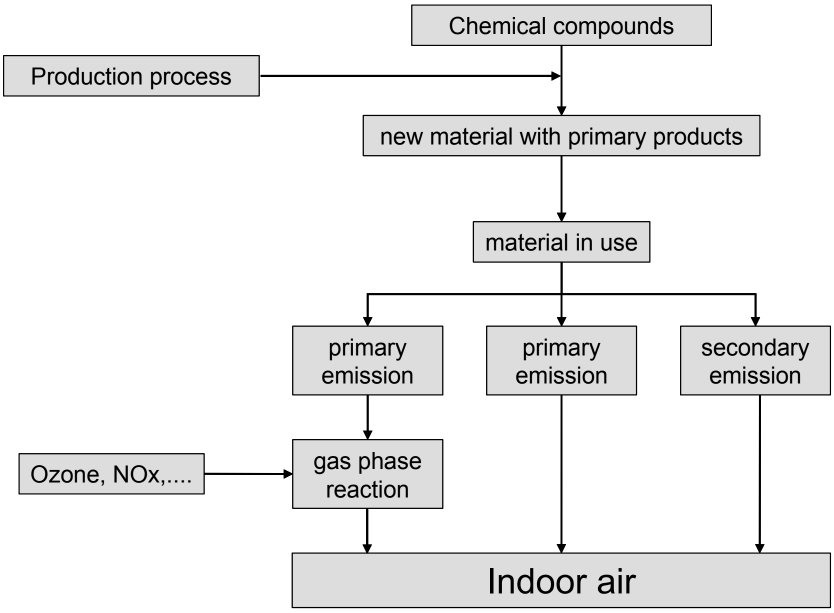


Figure 2.2-6. Formation of primary and secondary emissions from materials under indoor use [reprinted from Uhde and Salthammer, 2007 with permission from Elsevier].

Emissions of a test specimen are also influenced by material immanent processes. Those emission control mechanisms are mainly of physical type. Emissions of dry and deep sources are predominantly diffusion limited, whereas emissions of thin wet film coatings are mostly subjected to evaporation controlled mechanisms (Dunn, 1987; Li et al., 2006). Thus, emissions of a building product might be limited by these two control mechanisms or a combination of them (Yu and Crump, 1998). In the latter case, proportions of both mechanisms may be subjected to time-dependent variations. The diffusion of (S)VOCs within a material is given by the diffusion coefficient of the specific compound and is highly dependent on its physical properties (e.g. molecular size, boiling point, polar charges). Moreover, the process is influenced by the temperature and the material's structure, within which the diffusion proceeds. In a material mixture, the diffusivity is also affected by the composition and by any inhomogeneity in the material itself (Yu and Crump, 1998). Several researchers have dealt with the developing of mathematical models for fitting emission control mechanisms and time-dependent data, amongst others Clausen et al. (1991), Clausen (1993) and Tichenor et al. (1993).

3 Fundamentals of emission analysis

An important step in evaluating immission scenarios and minimizing organic emissions is the identification of emission sources and their specific contribution to indoor air pollution. Several devices for testing material emissions have been developed. The current chapter introduces fundamental principles of examination methods and indoor air sampling, which became routinely utilized techniques within chemical science and which were used in the present study.

3.1 Devices for emission testing

In order to identify and quantify organic emissions and to obtain additional information about emission spectra and source strength of test specimens, various methods with different expenditures of time exist. Standardized conventional methods are utilizing emission cells and emission test chambers under defined reproducible boundary conditions. Those kinetic experiments allow the investigation of emissions *versus* time in dependence of loading factors and environmental parameters, such as temperature, relative humidity and air exchange rate. Due to the necessity not only to test end products, but also to observe all stages of production, fast methods are beneficial. Further reliable devices for quick emission monitoring were developed recently (*screening methods*).

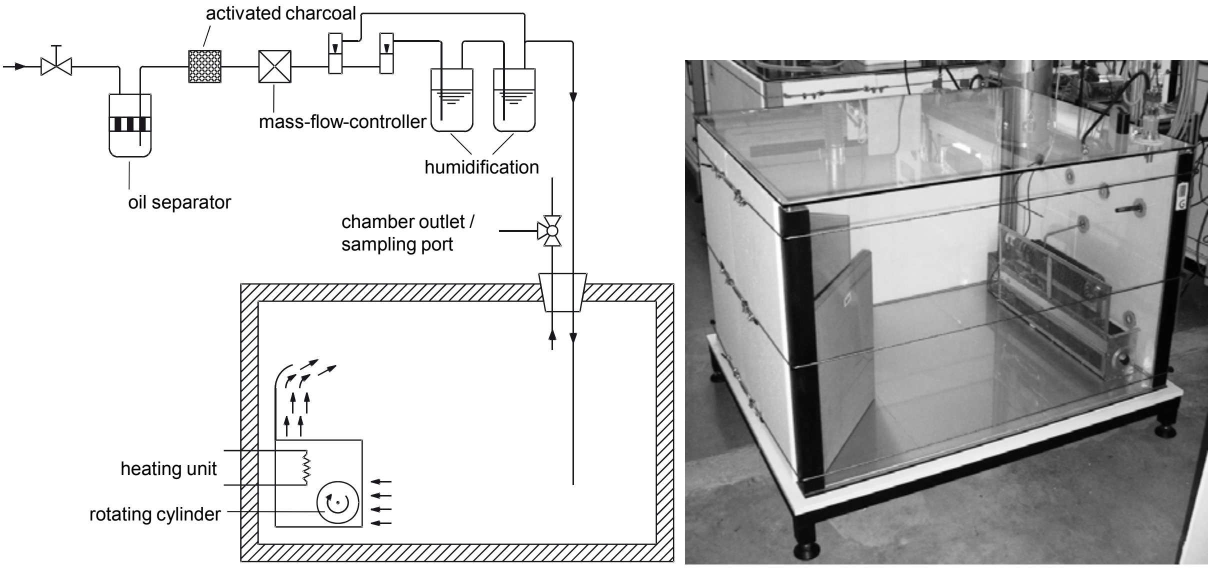
3.1.1 Emission test chambers

Emission tests are established to clearly attribute released volatiles to their sources and to determine the emission profile of a specific material without interfering uncontrollable outside influences, such as weathering, illumination and climatic conditions. Kinetic analysis of emission rates from building materials under indoor-related conditions (concentration *versus* time) has become the most important research method carried out with the following goals (Tichenor, 1989; Sollinger et al., 1993):

- to screen materials for indoor use in order to classify them according to their emission potential
- to obtain compound-specific data on various sources as necessary basis for field studies and for evaluating indoor air quality
- to identify environmental parameters which are influencing the concentration of (S)VOCs emitted from a source
- to simulate as close as possible real indoor conditions which allows conclusions about the degree of contribution of a given source to indoor air quality
- to obtain emission data to develop and verify mathematical models for prediction of indoor air concentrations
- to provide emission data to manufacturers and end-users to improve products, select materials and/or develop control options for environmental risk assessment
- to rank products according to their emission profiles and to develop labelling schemes

In order to investigate time-dependent material emissions with regard to temperature, relative humidity, air exchange rate, air velocity and product loading factor (ratio of exposed material surface area to the test chamber volume) under standardized conditions, the test specimen is placed into an emission test chamber. After loading with the sample, the emission test chamber is sealed off from the outside atmosphere and is purged with a constant flow of purified supply air, which ensures low background values and regulates the air exchange rate. Supply air is purified by passing an oil separator and activated charcoal. The required relative humidity is obtained by mixing dry and wet air. A stable air exchange rate is maintained by a mass-flow-controller. Enriching sampling is performed at the chamber outlet to detect chemical compounds of the exhaust air stream. A rotating cylinder, which also contains the heating unit, circulates the air inside the test chamber and ensures a homogeneous mixing. In this case, the air sample represents the test chamber atmosphere (Salthammer und Wensing, 1999; Wensing, 1999).

The design and operating principle of a well-mixed, environmentally controlled 1m³ test chamber is visualized in Figure 3.1-1a. Figure 3.1-1b shows a 1m³ glass test chamber in the Fraunhofer Wilhelm-Klauditz-Institute, Braunschweig.



Figures 3.1-1a and b. (a) Scheme of the design and operation principle of the environmental 1m³ test chamber, (b) 1m³ glass chamber in the Fraunhofer Wilhelm-Klauditz-Institute.

Environmental conditions (temperature, relative humidity and air exchange rate), which are influencing material emissions, can be exactly controlled and kept constant inside emission test chambers over the testing time. By aligning these parameters to the realistic indoor environment the specimen will be used in, experimental data sets supply valuable information about its emission profile, e.g. source strength, most abundant compounds and curve progression. If emission test chamber investigations are undertaken to simulate a real-life scenario, experiments under dynamic conditions (with air exchange) are required. Such an experimental set-up allows kinetic emission analysis. Most test samples show exponentially decreasing emission curves over time. Equilibrium concentrations are determined under static conditions with no air exchange (Sollinger et al., 1993). However, a simulation of a complex indoor scenario with different emission sources, secondary reactions and sink effects (see section 3.1.3) can hardly be achieved.

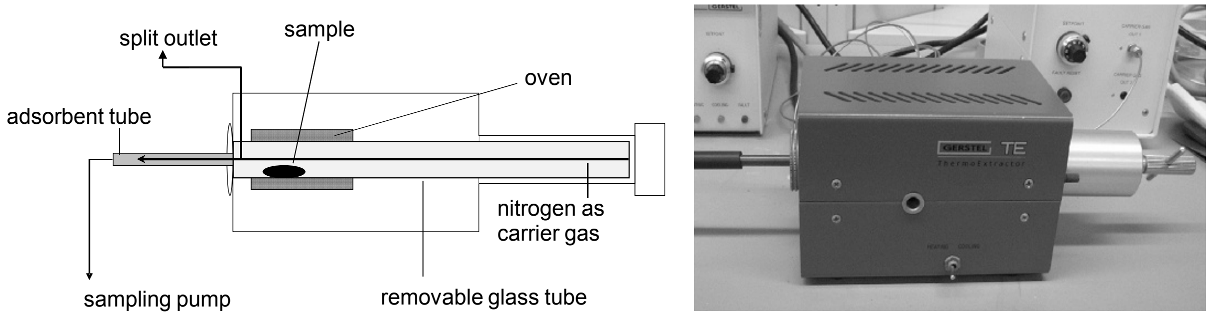
Sizes of emission test chambers range from a few litres (0.003 m³) to several cubic meters (80 m³). In general two different chamber types are to distinguish: room-size large scale chambers (*"walk-in" type*) with volumes typically between 12 m³ and 80 m³, which are constructed for examination of whole interiors, constructional systems or suites and so called small scale chambers with sizes ranging from a few litres up to a few cubic metres and room (EC, 1989; Gunnarsen et al., 1994; Destaillats et al., 2006). For investigating single materials or products, small scale chambers made of glass or stainless-steel with sizes ≤ 1 m³ are commonly used. The emission test chamber method is specified in DIN EN ISO 16000 Part 9 (2008).

The performance of chamber emission tests demands specific sample sizes in order to meet predetermined loading factors. Consequently, cutting of the material to be tested might be required. Due to the necessity not only to test end products, but also to observe all stages of production, fast methods are beneficial. In order to lower operational costs and to enable non-destructive emission testing of definite sources in situ during research and/or production, emission test cells as portable devices were developed. In contrast to conventional emission test chambers, in which the sample is put in, the cell is placed directly on the top of a planar material. Hence, the test specimen itself forms the bottom of the cell and becomes an integral part of it (Wolkoff et al., 1991, 1993; Wolkoff, 1996; Uhde, 1998). The main advantages of emission cells are the ease of use, the high loading factor (i.e. the small internal volume and relatively large emitting surface) and the associated improvement in analytical sensitivity. Other benefits include shorter equilibration times, higher sample throughput and better recovery of SVOCs (Gustafsson, 1999). The emission test cell method is specified in DIN EN ISO 16000 Part 10 (2006). Further reliable devices for quick emission monitoring were developed recently (*screening methods*).

3.1.2 Emission screening devices

Conventional fast methods to determine emissions of a sample material are direct thermal desorption or equilibrium headspace with coupled gas chromatography/mass spectrometry (GC/MS) or gas chromatography/flame ionisation detection (GC/FID). In a small vial emissions from solid or liquid samples are allowed to reach equilibrium under controlled temperature. Volatile compounds are then transferred from the headspace to the analytical device (GC/MS).

Recently, test methods based on thermal extraction were developed for quick meaningful emission analysis of small sample portions in order to produce fast information about the emission spectrum and concentration levels of materials before or during production. The Thermal Extractor TE2 (Gerstel, Mühlheim an der Ruhr/Germany) is such a new device. It consists in general of an adjustable oven (temperature range: 23°C – 350°C) heating a glass tube (length l: 178 mm; diameter d: 136 mm) with the sample inside. The sample size is limited both by the diameter of the tube and by the heatable section of the oven to a maximum of 73 mm x 10 mm. The specimen is extracted over a specific period at defined temperature in an inert gas flow. The inert carrier gas flows through the glass tube and transports volatiles released by the sample over a solid adsorbent material which retains target compounds. At increased emissions and in order to prevent pressure build-up in the glass tube, the gas can be partly led off through a split outlet during sampling. To pass a defined volume over the adsorbent at an open split outlet, a calibrated sampling pump with a gas flow counter is required (Scherer et al., 2006b). Figure 3.1-2a illustrates the mode of operation schematically, Figure 3.1-2b shows a photograph of the Thermal Extractor TE2.



Figures 3.1-2a and b. (a) Scheme and (b) photograph of the Thermal Extractor TE2 [Scheme according to: Scherer et al., 2006b].

By comparing results obtained via thermal extraction and conventional test chambers, it was shown that vapour concentrations are not directly comparable because of the higher loading factor in the screening device. Moreover, a higher susceptibility of the Thermal Extractor TE2 to SVOCs and great deviations in quantification of identified substances comparing to those obtained by chamber tests were observed. However, qualitative results show a good comparison and may therefore provide a useful basis for further emission analysis required for product certification (Schripp, 2005; Scherer et al., 2006b).

Emission screening by means of the Thermal Extractor TE2 offers essential information about whether and which pollutants are emitted by a specific material at all and gives first indications if the sample is high, moderate or low emissive. Emission test chamber measurements are though required to achieve information about concentration *versus* time profiles.

3.1.3 Sink effects

Sink effects characterize the fact that released substances may adsorb within an emission test chamber system (Sollinger and Levsen, 1993) which might contribute to lower (S)VOC concentrations measured at the chamber outlet and which might prolong the presence of (S)VOCs in the system (Meininghaus et al., 1999). Under dynamic conditions, sinks within test chamber systems extend the emission duration as they are acting as secondary emission sources, which desorb the compounds again as soon as the real emissions are decreasing. In contrast to this, equilibrium will be formed between surface-adsorbed and airborne compounds in a static system (Uhde and Salthammer, 2006).

Sink effects originate either from a material present in the system, which is able to uptake chemical substances via adsorptive processes and subsequent delayed release into the system, or from an insufficient mixed zone where substances have moved by diffusion (Uhde and Salthammer, 2006). Chamber-inherent sinks are in most cases e.g. sealants, gaskets, and tubes, which are influencing each measurement inside the test chamber. Moreover, it was shown that also the test sample itself may act as sink, especially porous structures and materials with high surface areas (*"fleece factor"*) (Colombo et al., 1993; Uhde, 1998; Jørgensen et al., 1999). In dependence of the physical properties of both chemical substances and building materials inside the system and the strength of the sink effect, duration of interaction may last just for a certain period of time or may be irreversible (Tichenor et al., 1991). Further comprehensive studies were carried out amongst others by Sollinger and Levsen (1993), Uhde (1998) and Meininghaus et al. (1999, 2000).

To avoid chamber-inherent sink effects, appropriate materials for constructing emission test chambers and the guarantee of a good recovery rate are necessitated. According to DIN EN ISO 16000 Part 9 (2008), the mean recovery for target VOCs such as toluene and n-dodecane shall be greater than 80%.

3.1.4 Modelling of kinetic emission test chamber results

For a better comparability of test results obtained by chamber emission tests, specific emission rates (SER) are indicated as these are independent from loading factors and air exchange rates.

Time-dependent emission rates can be calculated using the following balance equation (3-1):

$$\frac{dC}{dt} = L \cdot SER(t) - n \cdot C(t) \tag{3-1}$$

C (t) = chamber concentration, µg/m³, L = loading factor, m²/m³ and n = air exchange rate, h^{-1}.

At equilibrium state with $\frac{dC}{dt} = 0$ Equation (3-2) is obtained:

$$SER(t) = \frac{n \cdot C(t)}{L} \tag{3-2}$$

By introducing a difference quotient, the following Equation is derived from Equation (3-2) for decreasing emission sources:

$$SER(t) = \frac{\left(\frac{\Delta C}{\Delta t} + n \cdot C(t)\right)}{L} \tag{3-3}$$

The specific emission rate relates in most cases to the surface area (SER_A = area specific emission rate) or to the weight (SER_m = mass specific emission rate). Further indices may be chosen in relation to the volume (SER_V) or the length (SER_l). The dimension depends on the reference value, e.g. SER_A [µg/(m²*h)] or SER_m [µg/(g*h)].

Besides this balance equation, several mathematical approaches for modelling emission concentrations and/or sink effects inside an emission test chamber have been developed. A first all-embracing model which decouples the particular emission characteristics of a source from the effects caused by the surrounding climate chamber was introduced by Dunn and Tichenor (1988) and is shown in Figure 3.1-3. The estimation of concentration progresses and wall adsorption/desorption equilibria is based on a compartment model with first order rate constants k_i which physically characterize fundamental mass transfer processes between the four chamber sections *source*, well-mixed homogeneous *chamber air*, *sink* and *exit*. The linear kinetic constants $k_{1\text{-}5}$ are describing the flow among these compartments. The model was modified by De Bortoli et al. (1996) by introducing two reversible sinks (a *"fast"* and a *"slow"* sink).

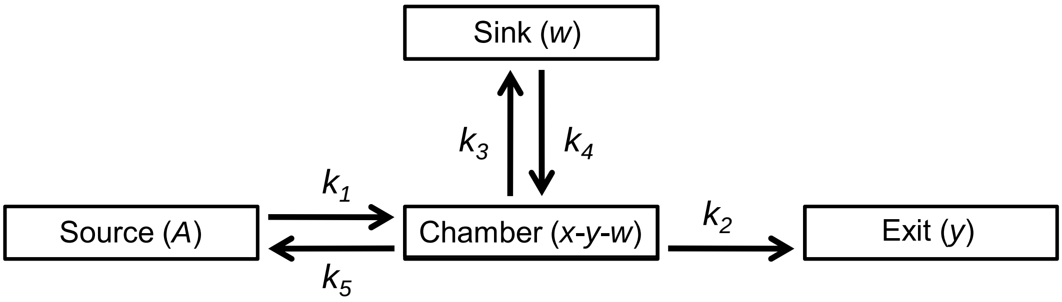


Figure 3.1-3. Four compartment model after Dunn and Tichenor (1988).

With A = initial mass to be emitted by the source described, $x = x(t)$ mass emitted to the chamber by time t described by k_1 indicating the emission rate constant and k_5 as the rate of mass transfer back to the source. $y = y(t)$ is the mass exiting from the chamber by time t so that k_2 is the air exchange rate per unit time and, thus, a known rate constant. $w = w(t)$ is the mass in the sink at time t characterized by k_3 as rate of movement to the sink and k_4 as rate of release from the sink. The time-dependent chamber concentration C (t) is given by $C(t) = (x\text{-}y\text{-}w)\ V^{-1}$ where V is the chamber volume.

Dunn and Tichenor (1988) provided several solutions of this model. The simple "*dilution model*" assumes no sink effects (k_3=0 and k_5=0) and was described for constant emission sources (Equation 3-4) and decreasing emission sources (Equation 3-5), repectively.

$$C(t) = \frac{k_1}{(k_2V)}\left(1 - e^{-k_2 t}\right) \tag{3-4}$$

$$C(t) = \frac{k_1 SER}{(k_1 - k_2)V}\left(e^{-k_2 t} - e^{-k_1 t}\right) \tag{3-5}$$

3.2 Analysis of organic indoor air pollutants

Concentrations of organic pollutants in indoor air normally range within a broad interval between few µg/m³ to several hundred µg/m³. In the museum environment, an evaluation of risk potentials both for museum collections and for human health is required. As sensitivities and, thus, risk levels of museum objects are mostly low, the detection of chemical contaminants even at a small scale is of high importance. Therefore, a precise identification of emission sources, their strength and emission profile (concentration *versus* time) as well as resulting indoor air values are essential. Hence, sophisticated analytical procedures with high resolution are necessitated.

The general mechanism of indoor air sampling is drawing an air sample either into the measurement chamber of the analytical device (direct-reading instrument) or over an appropriate sorbent matrix (active or passive sampling) with subsequent analysis of the target compounds. Whereas the former strategy enables a continuously real-time monitoring, the latter technique offers the discontinuous detection of airborne pollutants.

3.2.1 Continuous analytical devices

Direct-reading instruments can be applied for real-time monitoring to record temporal pollution concentration variations and, thus, to study influences of varying environmental conditions, such as outdoor pollution concentration, ventilation rate or the day-dependent usage pattern. In order to determine concentration profiles with high time-resolution or in order to reveal peak values, continuously analytical devices are necessitated which record data in short time segments of a few minutes or even of a few seconds. Furthermore, differences in concentration between various positions within a room or building can be revealed. It is also possible to utilize direct-reading instruments in order to record decaying emission rates during kinetic material emission analysis (see also section 3.1.1). Continuously measuring methods are unifying air sampling and air analysis in one instrument. Measuring principles of direct reading instruments are utilizing specific molecular properties, e.g. absorption or emission characteristics. By measuring the absorption of specific wavelength in the infrared, gases can be detected by nondispersive infrared spectroscopy (NDIR). This technique is applied for air exchange rate measurements utilizing tracer gases, e.g. carbon dioxide (CO_2) and nitrous oxide (N_2O). Devices for the detection of hydrocarbon sum values are of great importance, e.g. photo acoustic detectors

(PAD) or flame ionization detectors (FID). The output signal is the total concentration of volatile organic compounds (TVOC). The used detection principle is indicated in the index (e.g. $\mathrm{TVOC}_{\mathrm{PAS}}$). The TVOC-value obtained by one detector is expressed as an equivalent of one single compound, which is used for its calibration (Ekberg, 1999). Consequently, TVOC-values measured by several devices using different detection principles are not mandatory comparable due to different response factors for volatile organics (Massold et al., 2005). As real-time monitoring devices for TVOC are not selective, they give rather first indications of the degree of indoor air pollution than to allow identification and quantification of individual VOCs (Ekberg, 1999). Therefore, supplementary analysis by means of discontinuous sampling techniques may be needed.

3.2.2 Discontinuous sampling techniques

At discontinuous methods air sampling and analysis are separated. Organic volatiles are in general enriched on appropriate sorbent matrices as collecting phase. The analysis of retained target compounds is conducted afterwards in the laboratory. Air sampling can be accomplished by using either a pump to draw the air sample actively through a sorbent filled cartridge or tube (*active sampling*) or by simply letting volatile compounds diffuse through a well-defined sorbent bed (*diffusive passive sampler*) (Uhde, 1999).

Active versus passive sampling

As passive sampling seems more convenient and easier to perform without analytical equipment and due to lower associated costs, it is often applied by laypersons by means of commercial available diffusion tubes. The application is characterized by long sampling times, which last for several days or weeks. As uptake rates are influenced by the air flow rate, this strategy is not convenient for low volumes and nearly static conditions which entail starvation effects (Crump, 1999). Moreover, the hindered penetration may cause an underestimation of VOC concentration in comparison with active sampling methods. Also the risk that VVOCs may not be trapped on the sorbent sufficiently due to low interactions (Uhde, 1999) contributes to lower results. Such reverse diffusion is especially encouraged by weaker adsorbents (Crump, 1999). As the principle of diffusive passive sampling is based on gradient-driven diffusion, results are depending on temperature. However, it is stated that errors due to changes in temperature are acceptable in comparison to other sources of error (Crump, 1999; Hafkenscheid, 2006).

Knowing about these lacks, Ferm et al. (2002) proposed not to interpret the results quantitatively, but to discuss the obtained emission rate of specific compounds, given in µg/sampling duration.

In comparison to diffusive passive sampling, active air sampling is a faster measuring method of high accuracy, reproducibility and precision. The sampling process is performed by drawing the air actively through the sorbent by means of a pump. Thus, electric power supply is necessary. The strategy offers to detect short-term peak values with low limits of detection (LOD). The accuracy is thereby dependent by the air volume, whose correctness is controlled by calibrated pumps or mass flow controllers. Due to the high sensitivity, discontinuous active sampling is the preferred method regarding VOCs to study kinetic processes in comparison to continuous techniques, if the needed sample volume is small and therefore the sampling time short (Uhde, 1999). The required sample volume depends on the analytical method and can range from few litres up to several cubic meters of air. It also determines the expenditure of time, which is limited to several minutes up to few hours.

3.2.3 Sorbent materials and analytical procedures

Using active sampling techniques, chemical substances of an air sample may be generally trapped either (i) by adsorption on a porous solid material or (ii) by absorption into a liquid. For the selective detection of substance groups or specific compounds several sorption substrates are considered, which are analysed on the basis of standard analytical procedures.

Preferred solid sorbents for sampling VOCs (C_6 – C_{16}) are carbon blacks, e.g. activated charcoal and Carbotrap®, a graphitized carbon black, or the porous oxide polymer Tenax TA® (2,6-diphenyl-*p*-phenylenoxide). Both material sorbents retain all VOCs of thermal stability and show good reproducibility and accuracy as well as low background or blank values. A known difficulty is that the adsorbents themselves may decompose under specific conditions and/or that adsorbents may decompose some chemicals (e.g. decomposition of bromoalkanes by Carbotrap®) (De Bortoli et al., 1992; Clausen and Wolkoff, 1997). Multibed tubes (two or three different sorbents in one tube) may be utilized to overcome the limitations of a certain sorbent material by adding a second one (Uhde, 2003).

As air sampling and analysis are commonly separated regarding discontinuous techniques, the trapped compounds have to be transferred into an analytical device after collecting an air sample. If sampling into liquids was performed, complex formation or concentration steps might be required before analysis in order to meet the desired sensitivity. Conventional sample preparation methods for solid sorbents are either solvent based (extraction or elution) or heating the sorbent in a flow of inert carrier gas to extract trapped volatiles into the vapour stream (TD: thermal desorption). TD with subsequent analysis via GC/MS or GC/FID is nowadays the preferred method as solvent based techniques always have a certain risk of contamination during handling and transferring target compounds into the liquid and solvents causing false results. Furthermore, the pre-concentrated sample is diluted again. For the sake of completeness it should be noted that Massold et al. (2005) have proven that also liquid standards used on solid sorbent materials can influence the accuracy and quality of calibration curves.

4 Introduction to experimental series

4.1 Experimental approach

Techniques of emission analysis introduced in chapter 3 have been utilized for scientific investigations of material emissions and indoor air quality within museum showcases. The research was conducted in various experimental series in consecutive steps.

4.1.1 Material emission tests

In a first step, emission analyses of various individual materials were accomplished.

(a) Construction and decoration materials

A broad range of materials, which are widely-used for construction and decoration showcases was subjected to a screening on (S)VOC emissions via thermal extraction to value if an individual material is high, moderate or low emissive and to identify most abundant substances.

On the basis of these results, products were selected representatively for further investigations in emission test chambers to study time-dependent emission profiles and to distinguish primary emissions and secondary reactions. The focal point was on analysing (S)VOCs and in addition formaldehyde and organic acids (formic acid, acetic acid) due to their known corrosive potential.

(b) Conservation and restoration materials

Given that also the exhibits themselves act as potential emission sources, thermal extraction of various conservation and restoration materials was carried out in a second test series.

4.1.2 Indoor air quality within museum showcases

As it is assumed that the range of detectable volatile organics within showcases may differ compared to single emission tests concidering various materials emitting under nearly static conditions, investigations of indoor air quality within completed showcases were performed in a second step. Emphasizes was again on concentrations of (S)VOCs, formaldehyde and organic acids (formic acid, acetic acid).

During this investigation step, two main showcase construction types were distinguished: (i) modern-type showcases under use of modern materials, such as e.g. glass, powder coated or lacquered metals, neutral curing sealants and rarely wood-based products and (ii) old-type showcases, which had been constructed under use of traditional materials, such as e.g. wood, wood-based products, felt and acid curing silicone rubber; these types were mostly constructed before the 1990s.

(a) Modern-type showcases directly after production

In a first test series, analyses of indoor air quality within modern showcases immediately after production were carried out. These examinations provided direct comparison to material emission tests conducted in the lab and elaboration of correlations and differences.

(b) Modern-type showcases in museum use

Indoor air analyses within modern-type showcases in museum use since few months up to several years were performed in a second test series in order to clarify the question of long-term emissions.

(c) Old-type showcases in museum use

The third test series focussed on so called old-type showcases, which have been in museum use for nearly ten to twenty years at the time of measurement. The series was performed to obtain a direct comparison with modern-type showcases in museum use in order to reveal differences and/or correlations between the spectrum of individual substances and the range of pollution levels. Results should answer the question if any improvement has been achieved by material changes.

Within these test series, attention was also directed to the displayed and/or stored artworks as independent emission sources.

4.1.3 Influences on indoor air quality

Moreover, factors which might influence indoor air quality were emphasized in a third step. Air exchange rate measurements were performed considering different construction types - especially highly sealed *versus* open construction types. These results are discussed linked with the respective showcase to improve the readability.

As exhibited artworks might be illuminated by the room lighting or by lighting systems, which are directly installed inside the showcase, possible effects due to artificial lighting were additionally considered in the last test series.

The following chapters are denoted according to these experimental series. In each chapter, the purpose of investigation, selected samples/subjects of investigation, utilized analytical devices and sampling methods are outlined in the mentioned order before entering the discussion of the results.

A first overview of the experimental series is given in Table 4.1.

Table 4.1 Overview of samples/subjects of investigations, consecutive investigations and applied analytical procedures.

Test series no.	Samples/subject of investigation	Number of samples	Type of investigation	Analytical device	Analytical methods	Purpose
I	Construction/decoration materials	80	Screening emission analyses	Thermal extraction	Active sampling on VOCs/SVOCs	Emission strength Identification of lead compounds
		28	Time-dependent emissions	Emission test chambers	Active sampling on VOCs/SVOCs HCHO HCOOH/CH_3COOH	Concentration vs. time profile Primary and secondary emissions
	Conservation/restoration products	14	Screening emission analyses	Thermal extraction	Active sampling on VOCs/SVOCs	Emission strength Identification of lead compounds
	Museum objects	3	Time-dependent emissions	Emission test chambers	Active sampling on VOCs/SVOCs HCHO HCOOH/CH_3COOH	Emission strength Identification of lead compounds Concentration vs. time profile
II	Newly constructed showcases	5	Indoor air analyses	-	Active sampling on VOCs/SVOCs HCHO HCOOH/CH_3COOH Air exchange rate measurements	Indoor air quality directly after production Correlations/differences between results of I and II
	Showcases in museum use	26	Indoor air analyses	-	Active sampling on VOCs/SVOCs HCHO HCOOH/CH_3COOH Air exchange rate measurements	Indoor air quality under museum conditions Correlations/differences between results of I and II
	Artworks as emission sources	-	Material analyses	-	Sampling on SVOCs Sampling on biocides	Contribution of museum exhibits to indoor air quality
III	Showcases from test series II	5	Influence of artificial lighting	-	Active sampling on VOCs/SVOCs HCHO HCOOH/CH_3COOH Air exchange rate measurements	Comparison of indoor air quality within showcases without/with artificial lighting Correlations/differences to results of II

5 Experimental series I

Material emission tests

The present chapter introduces first in selected samples for emission testing and examination methods before discussing the obtained results of each material category.

5.1 Sample selection

5.1.1 Construction and decoration materials

In total, 80 test specimens of construction and decoration materials for museum showcases were chosen for emission analyses. Table 5.1-1 gives an overview of the individual material categories and the particular number of test specimen.

Table 5.1-1. Number of test specimen from different material categories for emission analysis.

Material category	Number of test specimen
Lacquers and coatings	16
Adhesives and sealants	18
UV-curing systems, thereof	9
Printer’s inks	4
Adhesives	5
Wood-based materials	17
Construction and other materials	5
Cover fabrics	6

5.1.1.1 Coating materials

Coating materials are generally based on organic binders. They may be classified according to different aspects, e.g. formulation, kind of use, application method, drying behaviour or processing state as well as the usage in the surface coating system or the substrate to be coated (Stoye, 1993; Baumann und Muth, 1997). In the following text, the selected coating materials are distinguished according to the chemical nature of the binder. The individual components of a lacquer system may be divided in several sub-categories as shown in Table 5.1-2.

Table 5.1-2. Subdivision of coating material components according to: Stoye (1993).

<table>
<tr><td rowspan="3">Ingredients of coating materials</td><td>Film-forming substances
Resins
Plasticizers</td><td>Binders</td><td rowspan="2">Varnishes</td><td rowspan="3">Paints</td></tr>
<tr><td colspan="2">Solvents
Coalescing agents
Additives
Dyes</td></tr>
<tr><td colspan="3">Pigments
Extender pigments</td></tr>
</table>

Film-forming substances can either be macromolecular substances or low molecular mass compounds forming macromolecules during the curing process. Most of the film-forming raw materials are resins, e.g. alkyd resins or epoxy resins. Plasticizers improve the flexibility and flow of the binder to which they are added by lowering the softening temperature range. Plasticizers act physically and do not undergo chemical reactions with the binder. Additives are auxiliary substances to improve the coating properties even in low quantities. They are defined according to their effects, i.e. driers, antiskinning agents, curing and levelling agents, wetting and dispersion agents, matting agents. Paints are achieved by adding pigments which define the colouring, the hiding power and may improve the coating resistance, e.g. against corrosion. Extender pigments are lower cost substrates as they are not of that high quality than pigments (Stoye, 1993).

Coating systems selected for material emission analysis are listed in Table 5.1-3. Most of them were multilayer composite materials consisting of primers and top coats, which again consisted of several layers, e.g. fillers, matting agents, hardeners, reducers and thinners. If more than one abbreviation is listed, the first abbreviation indicates the primer and the second the top coat.

Table 5.1-3. Coating materials selected for emission analysis via thermal extraction (screening) and/or emission test chambers.

Sample no.	Formulation	Remarks	Thermal extraction	Chamber test
L-1	PVB/2-P ACR	Solvent borne	+	-
L-2	PUR/2P-ACR	Solvent borne	+	-
L-3	2-P PE/2 P-ACR	Solvent borne	+	+
L-4	EP+ 2-P PUR/2-P ACR	Solvent borne	+	-
L-5	EP/EP	Solvent borne	+	+
L-6	PE	Powder-coating	+	-
L-7	PVB	Solvent borne	+	-
L-8	2-P ACR	Solvent borne	+	+
L-9	2-P ACR	Solvent borne	+	+
L-10	EP/2-P PUR	Solvent borne	+	-
L-11	PVB	Solvent borne	+	-
L-12	EP	Solvent borne	+	-
L-13	2-P PUR	Solvent borne	+	+
L-14	2-P PUR/ACR	Solvent borne	+	+
L-15	CN	Solvent borne	+	+
L-16	2-P PUR/ACR	Solvent borne	+	+

2-P	two-pack	EP	epoxy resin
ACR	polyacrylate	PVB	polyvinyl butyral
PUR	polyurethane	CN	cellulose nitrate
PE	polyester		

All coating systems were solvent borne which means that the formulation contains a relatively high solvent content in which the solids are dissolved. Just one of the investigated samples was a powder-coating system (L-6). Moreover, it becomes clear that polyurethane lacquers and acrylic resins are today the most commonly used top coats for varnishing metals within museum showcases.

Polyurethane coatings

Polyurethane resin (PUR) is characterized by a so called urethane linkage [-NH-CO-O-], which is produced by reacting an isocyanate group [-N=C=O] as hardener with a hydroxyl (alcohol) group [-OH] as resin component (diols and polyols, respectively). Commonly applied polyisocyanates are toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), methylene diphenyl diisocyanate (MDI) and methylene-bis(4-cyclohexylisocyanate) (HMDI). As curing proceeds by polyaddition no cleavage products appear, not even at a later stage.

All investigated PUR-lacquers were two-pack systems. The hydroxyl compounds and the polyisocyanates are kept separated and are mixed together immediately before application.

Curing takes place at ambient temperature, but can be accelerated by adding catalysers or heat (Stoye, 1993).

Acrylic coatings

Binders of polyacrylate coatings consist primarily of copolymers of acrylate and methacrylate esters. Other unsaturated monomers, such as styrene, vinyltoluene or vinylester may also be incorporated into this synthetic resin, but commonly for a lesser extent. Acrylic resins are divided into polyacrylates without and with functional groups (intrinsically or extrinsically crosslinking binders). Investigated acrylic coatings were extrinsically crosslinked binders, which are formed by hydroxyl-containing acrylates and aliphatic polyisocyanates as hardeners [e.g. hexamethylene diisocyanate (HDI) and methylene-bis(4-cyclohexylisocyanate) (HMDI)]. As the reaction proceeds slowly at ambient temperature, investigated samples contained metal salts (e.g. zinc octoate) as catalysers (Stoye, 1993; Baumann und Muth, 1997).

The two-pack acrylic coating, applied in samples 1-4, as well as the two-pack acrylic top coat of sample L-8 contained lead chromate pigments, namely lead sulfochromate yellow and lead chromate molybdate sulfate red according to the material safety data sheet.

Epoxy resin coatings

Epoxy resins are synthetic systems, which are crosslinked by polyaddition and which are characterized by the epoxy group. Selected epoxy resin coatings consisted of bisphenol-A, a condensation product of bisphenol A and epichlorohydrin. Crosslinking at the hydroxyl groups of a bisphenol-A resin may proceeds either (i) by aliphatic polyisocyanates or (ii) by polyamido-amine/polyamine adducts at elevated temperatures via the epoxy groups.

Cellulose nitrate coatings

Main components of cellulose nitrate coatings are binders, plasticizers and, if applicable, pigments dissolved in organic solvents. The solid film is formed by physical evaporation of the solvents (Stoye, 1993).

Polyester coatings

Fillers consisting of unsaturated polyester (UP) resin were one part of all investigated solvent borne coating systems. Unsaturated polyester resins are linear structures which are partly dissolved in monomers and which are composed of hardening (curing) agents, a range of additives (e.g. accelerators, promoters, stabilizers), pigments and extenders. UP resins might partially be dissolved in monomers which are suitable for copolymerisation (reactive diluents). The most important comonomer is styrene (Stoye, 1993). As UP resins are cured by free-radical polymerisation, peroxide was added for generating free radicals (conventional curing) in sample L-3 (benzoyl peroxide).

Polyvinylbutyral coatings

Among all tested coating materials, just sample L-7, an anti-rust priming coat, was based on polyvinylbutyral (PVB) as this is a preferred application of this resin. Raw materials for PVB coatings are polyvinylalcohol and butyraldehyde. PVB may be used alone or in combination with other resins, e.g. amino resins or epoxy resins. It might contain plasticizers in low concentrations (Baumann und Muth, 1997).

Powder coatings

Due to the high portion of volatile components in these solvent-borne systems (active and latent solvents as well as extenders and additives), manufacturers begin to apply increasingly powder coatings as these formulations do not require a solvent to keep the binder and filler parts in a liquid suspension form. Just one powder coating with polyester resin as binder was investigated during this study (sample L-6).

Powder coatings are commonly applied electrostatically with subsequent baking on the substrate.

5.1.1.2 Adhesives and sealants

Adhesives and sealants presented in this section are applied for sealing the edges of showcases. Table 5.1-4 compiles the sealant material samples selected for emission testing. It becomes clear that silicone rubber is the most applied sealant material.

Table 5.1-4. Sealant materials selected for emission analysis via thermal extraction (screening) and/or emission test chambers.

Sample no.	Formulation	Thermal extraction	Chamber test
S-1	Alkoxy curing silicone rubber	+	-
S-2	Alkoxy curing silicone rubber	+	-
S-3	Polybutadiene rubber	+	+
S-4	Homopolymeric polyvinylacetate dispersion	+	-
S-5	Two-pack alkoxy curing silicone rubber	+	+
S-6	Two-pack alkoxy curing silicone rubber	+	+
S-7	One-pack ketoxime curing silicone rubber	+	+
S-8	Two-pack alkoxy curing silicone rubber	+	+
S-9	Two-pack alkoxy curing silicone rubber	+	-
S-10	Polyurethane rubber	+	+
S-11	One-pack ketoxime curing silicone rubber	+	-
S-12	Two-pack methacrylate	+	-
S-13	Silane terminated polymer	+	+
S-14	Silicon adhesive tape	+	-
S-15	Polyester (100%)	+	-
S-16	Foam rubber adhesive tape	+	-
S-17	Book linen adhesive	+	-
S-18	Polyurethane cold glue	+	-

Silicone rubbers

Silicones are inorganic-organic polymers with the chemical formula $[R_2SiO]_n$ and are therefore characterized by a silicon-oxygen bonding (siloxane linkage). Manufacturers employ nowadays almost exclusively neutral curing silicones during the production process due to the well-known damage potential of acetic acid to collection property, which splits off during curing of acid curing silicone rubbers.

Silicone rubber types are predominantly linear, long-chained polysiloxanes. They are available in one-pack and two-pack room-temperature vulcanizing systems (RTV-1, RTV-2). Both systems were among the samples investigated during this study.

RTV-1 systems

RTV-1 systems are ready to use and react with atmospheric humidity to form flexible rubbers. Most common compounds are linear polydimethylsiloxanes (PDMS). In order to prevent early polymerisation and to render curing with humidity (H_2O), crosslinking agents (X) are blocking terminal hydroxyl groups (-OH) of the polysiloxane. During the curing process, the terminal OH-groups react with the crosslinking agents by separation of specific fragmentation products and by simultaneously crosslinking siloxane chaines via oxygen bonding (~Si-O-Si~), as illustrated in Figure 5.1-1.

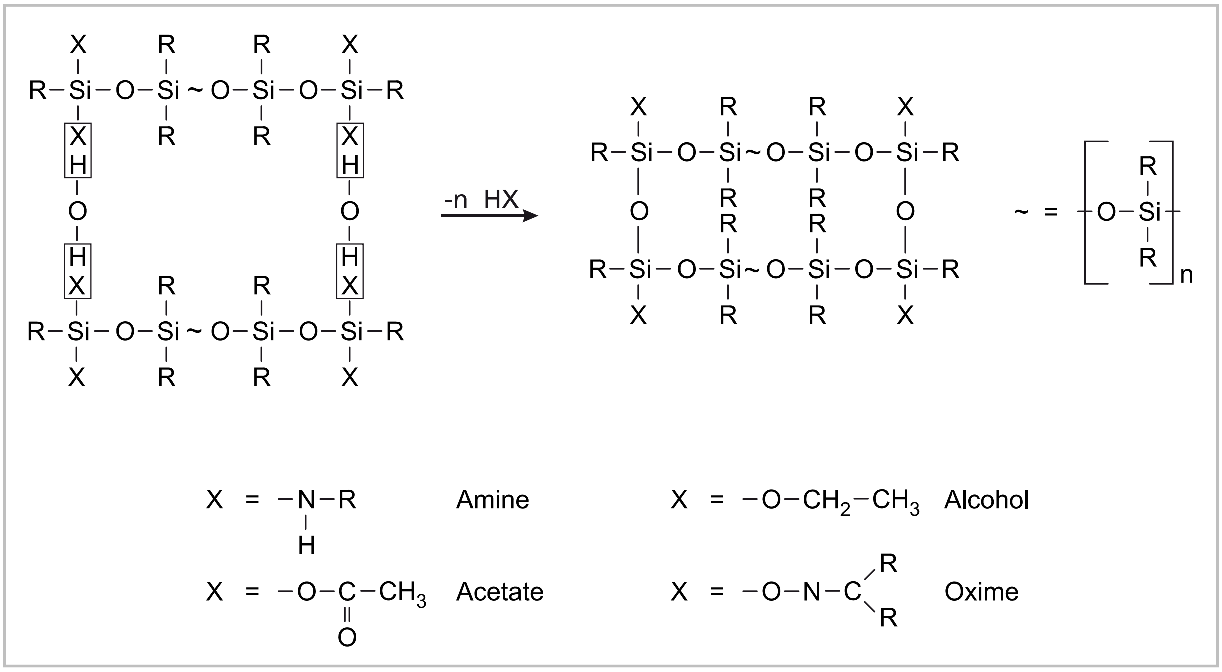


Figure 5.1-1. Condensation curing of RTV-1 silicone rubber.

Depending on the crosslinking agents, silicone rubbers are differentiated into three groups (see Table 5.1-5):

Table 5.1-5. Classification of silicone rubbers according to crosslinking agents (Habenicht, 1997).

System	Crosslinking agents	Fragmentation products
Alkaline	Primary amino groups [$-NH_2$]	Amines
Acidic	Acetoxy group [$-OOC-CH_3$]	Acetic acid
Neutral	Alkoxy groups [-O-R]	Alcohol
Neutral	Acid amide groups [-NH-CO-R]	Amides
Neutral	Ketoxime groups [$–O-N=C^{-R}_{-R}$]	Ketoximes

Addition curing RTV-2 silicone rubbers

Systems denoted as RTV-2 are especially applied in those cases, in which curing processes of RTV-1 systems are hindered or are too slow proceeding due to low atmospheric moisture. Investigated 2-P silicone rubbers were addition curing RTV-2 silicone rubbers. These materials consist of the two components A and B, whereas A is a siloxane with a terminal vinyl group and B is a siloxane with a silicium-hydrogen-bonding. The catalyzed addition curing proceeds without formation of any byproducts. Si-H groups are attached to the double bonds of the terminal vinyl group, as shown in Figure 5.1-2. The crosslinking process is highly temperature dependent (Habenicht, 1997).

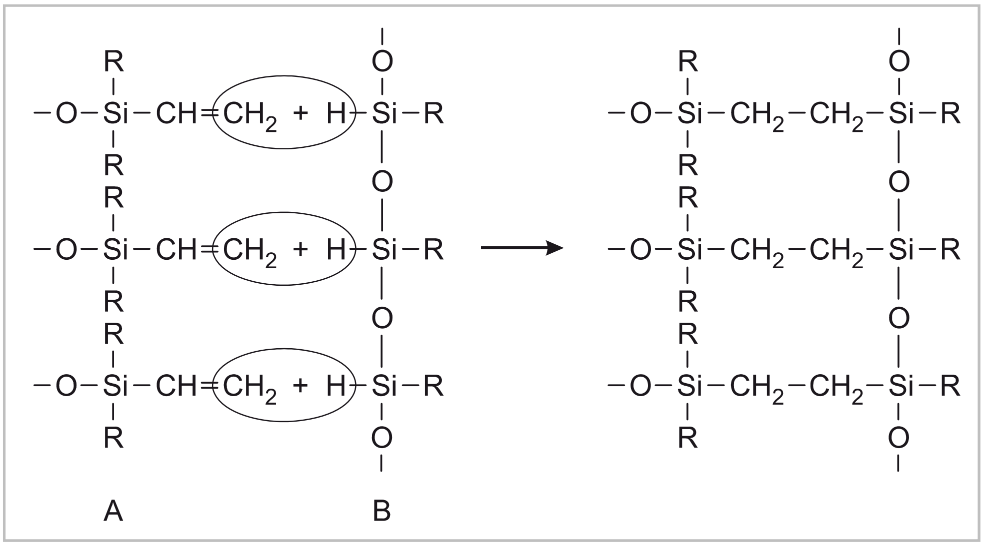


Figure 5.1-2. Mechanism of addition curing RTV-2 silicone rubber.

Also physically drying sealants on polymeric basis, which are ready to use, such as polybutadiene, methacrylate, polyurethane and polyvinylacetate, were investigated during emission testing.

As alternative to these materials, which are liquid in their initial condition, manufacturers are thinking also about the use of silicon adhesive tape (sample S-14) or foam rubber adhesive tape (sample S-16).

5.1.1.3 UV-curing systems

UV-curable acrylated systems are primary applied in showcase manufacturing as adhesives for non-visible bonding and they are currently also under testing as alternative to solvent borne glass lacquer systems. Investigated UV-curing coatings were printer's inks which remain similar to UV-curing adhesives in a liquid state after application by an inject printer. The polymerisation process proceeds under UV-radiation by radical photopolymerisation.

Photopolymerisation or photocrosslinking processes of acrylated systems are initiated by efficient photoinitiators to crosslink solvent monomers and prepolymers to solid resistant films. The basic mechanism of UV-curing formulations is the formation of free radical species through absorption of ultraviolet radiation by a photoinitiator (Allen et al., 1999). The generated active radicals add to the monomers and induce chain growth polymerisation/crosslinking with final termination (radical addition) (Allen, 1996). By means of diluent monomers the viscosity of the liquid prepolymer is controlled and therefore also the film properties, such as speed of cure, application, adhesion and degree of flexibility (Allen, 1996).

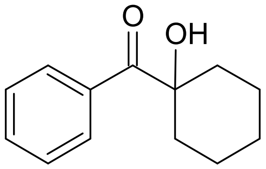
Diluent monomers/prepolymers and photoinitiators applied in investigated UV-curing systems are summarized in Table 5.1-6. Acrylate compounds were simple mono- and difunctional structures, namely methacrylate (MA), methyl methacrylate (MMA), butyl methacrylate (BMA), 2-hydroxyethyl methacrylate (HEMA) and isobornyl acrylate (IBOA) as well as 1,6-hexanediol diacrylate (HDDA) as multifunctional monomer and 2-phenoxyethyl acrylate (POEA). Photoinitiators contained in investigated formulations were 1-hydroxycyclohexyl phenyl ketone (HCPK), 2-hydroxy-2-methyl-1-phenyl-propane-1-one (HMPP), 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) and benzophenone (BP). The molecular structures are presented in Figure 5.1-3.

Table 5.1-6. Acrylate monomers and photoinitiators applied in investigated UV-curing systems. Sample selection for emission analysis via thermal extraction (screening) and/or emission test chambers.

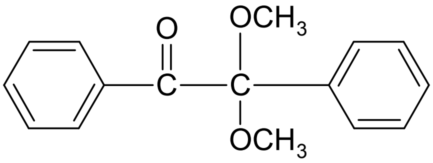
Sample no.	Acrylate monomers	Photoinitiators	Thermal extraction	Chamber tests
Printer's inks				
PI-1	-	HCPK	+	-
PI-2	POEA/HDDA	HMPP/HCPK	+	+
PI-3	POEA	HCPK/BP	+	-
PI-4	IBOA/HDDA/POEA	HMPP	+	+
UV-curing adhesives				
UV-1	MA/MMA/BMA/HEMA	HCPK/DMPA	-	+
UV-2	MA/MMA/HEMA	HCPK/HMPP	-	+
UV-3	IBOA	-	-	+
UV-4	MA/MMA/HEMA	HMPP	-	+
UV-5	MMA/HEMA	HMPP	-	+

Abbreviations Table 5.1-6

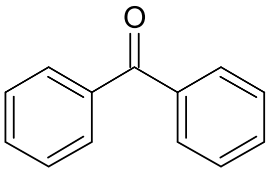
MA	methacrylate
MMA	methyl methacrylate
BMA	butyl methacrylate
HEMA	2-hydroxyethyl methacrylate
IBOA	isobornyl acrylate
POEA	2-phenoxyethyl acrylate
HDDA	1,6-hexanediol diacrylate
HCPK	1-hydroxycyclohexyl phenyl ketone
HMPP	2-hydroxy-2-methyl-1-phenyl-propane-1-one
DMPA	2,2-dimethoxy-2-phenyl-acetophenone
BP	benzophenone
-	unknown



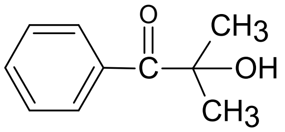
HCPK



DMPA



BP



HMPP

Figure 5.1-3. Molecular structures of photoinitiators applied in investigated UV-curing systems.

5.1.1.4 Wood-based materials

Subject of investigation were different core-boards, chipboards, un-/coated or dyed medium density fibreboard (MDF), laminated/veneered plywood and plywood with anti-slip covering. From a total of 17 wood-based products, a selection of 11 materials (see Table 5.1-7) will be described in the following and will also be discussed in the results chapter.

Table 5.1-7. Wood-based materials selected for emission analysis via thermal extraction (screening) and/or emission test chambers.

Sample no.	Material	Labelling/ Certification	Thermal extraction	Chamber test
PB-1	Coated particle board	E1, Blue Angel	-	+
PB-2	Coated particle board	E1, Blue Angel	-	+
PB-2a	Coated particle board, laminated cut surfaces	E1, Blue Angel	-	+
MDF-1	Medium density fibreboard	ZF	-	+
MDF-2	Medium density fibreboard	E1, ZF	-	+
MDF-3	Dyed medium density fibreboard	-	+	-
MDF-4	Medium density fibreboard, untreated	E1	+	-
MDF-4a	Medium density fibreboard, lacquered (2P-PUR)	E1	+	-
MDF-5	Medium density fibreboard, untreated	F0, ZF	+	-
MDF-5a	Medium density fibreboard, lacquered (2P-PUR)	F0, ZF	+	-
P-1	Plywood with anti-slip covering	-	-	+

2P-PUR two-pack polyurethane lacquer

Samples PB-2 and PB-2a corresponded to each other, whereas sample PB-2a had laminated cut surfaces. Also samples MDF-4/MDF-4a and MDF-5/MDF-5a were the same each with and without lacquered surfaces. PB-1, PB-2 and PB-2a were particle boards with a decorative plastic foil on both sides on the basis of melamine resin.

The majority of tested wood-based products were labelled as low formaldehyde emissive. According to the European Directive DIN EN 13986 (2005), wood-based products are classified in dependence of the formaldehyde equilibrium concentration that is reached in an emission test chamber. Formaldehyde equilibrium concentration ≤ 0.1 ppm (120 µg/m³) complies with an "E1" labelling. "F0"-particle boards are formaldehyde free as no binding media on the basis of formaldehyde resins is applied. There exist also certification regulations for the environmental label Blue Angel (Blauer Engel) RAL UZ 76 (2008). This certification limits formaldehyde emissions from (non-)laquered wood-based products for the use in the indoor environment to an equilibrium concentration in chamber air of 0.05 ppm (~60 µg/m³).

Samples MDF-1, MDF-2 as well as MDF-5 and MDF-5a were bought from a supplier in the UK and were declared as "ZF" (zero added formaldehyde). It could not be clarified if this is a licensed labelling.

5.1.1.5 Construction and other materials

In search of alternatives to wood-based materials, inert substances, such as aluminium composite boards, plastic plates and ceramic plates are increasingly selected for showcase equipment. For exhibition design, adhesive foils are used on showcase glasses to achieve a special effect.

Table 5.1-8. Construction and other materials selected for emission analysis via thermal extraction (screening) and/or emission test chambers.

Sample no.	Material	Thermal extraction	Chamber test
AL-P	Aluminium composite plate	+	-
PP-P	Propylene plastic plate	+	-
AC-P	Acrylic plastic plate	+	-
CP	Ceramic plate	+	-
GF	Adhesive glass foil	+	-

5.1.1.6 Cover fabrics

Cover fabrics are used as background or underground in exhibition showcases. Coloured textiles may be an alternative to coated or dyed wood, glass and metal, but were not investigated during this study. Selected fabrics were untreated cotton, book linen with/without adhesive, un-/boiled half-linen and polyester (100%).

Table 5.1-9. Cover fabrics selected for emission analysis via thermal extraction (screening) and/or emission test chambers.

Sample no.	Material	Thermal extraction	Chamber test
T-1	Cotton	+	-
T-2	Book linen	+	-
T-2a	Book linen with adhesive	+	-
T-3	Half-linen, unboiled	+	-
T-3a	Half-linen, boiled	+	-
T-4	Polyester (100%)	+	-

5.1.2 Conservation and restoration materials

Among materials for conservation and restoration of cultural assets, a selection of organic materials as well as of synthetic products was made. In total, 14 products were investigated and are compiled in Table 5.1-10.

5.1.2.1 Natural products

Among commonly used natural products, animal glues as consolidation materials of paint layers were selected (hide glue, fish glue) as well as the natural resin dammar. Animal glues may originate from the animals' bone or hide. Hide glues are obtained by the collagenous materials from the connective tissues or hide pieces. It has to be noted that the glue may contain contaminants from skin preservatives and tanning agents (Horie, 1987). From the chemical point of view the glue consists of proteins. Hide glues have a broad application area as they are the most versatile of animal glues. Before usage, hide glue, which is available in pulverized, flake or pearl form, has to swell in water to form a gel (Horie, 1987). The solidified glue must be again gentle heated (30-50°C) before application. Fish glue is produced under utilization of hide, bones and cartilage. This cold glue is ready to use and needs no additional preparation.

Natural resins are obtained as exudates from trees and are therefore based on the terpene skeleton. Dammar is composed of a mixture of dammarenediol-molecules, whose proportions differ in each sample material (Horie, 1987). The resin is commonly used for picture varnishes as well as additive for oil paints in order to delay drying time. Several forms of dammar resin were chosen in order to investigate differences in the emission profiles. Sample D-1 was the solid raw material, samples D-2 and D-3 were dissolved forms. In sample D-2 dammar was dissolved in double rectified turpentine (1:2), whereas sample D-3 was a turpentine-free dammar varnish dissolved in a mixture of (C_9-C_{12}) iso-alkanes and solvent naphtha (petroleum). Both sample D-2 and D-3 were finished products and ready to use.

Sample C-1 was low viscous hydroxypropyl cellulose and may be used in conservation as vehicle for watercolour and gouache paints. Moreover, it can be applied for pigment consolidation where non-aqueous treatment is required (Horie, 1987). In order to protect the glue from mould growth, formaldehyde may be added.

5.1.2.2 Synthetic products

The liquid samples R-1 and R-2 are also used as picture varnishes. According to the material safety data sheet, sample R-1 consisted of a thermoplastic molecular hydrocarbon resin (10%). Further constituents were a styrene-ethylene/butylene-styrene copolymere (0.2%) as well as a light stabilizer (bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacat/methyl(1,2,2,6,6-pentamethyl-4-piper-idyl)sebacat; 0.2%). These two additives ensure elastic and durable varnish layers. According to the technical data sheet, the resin and the copolymers were dissolved in aliphatic hydrocarbon (79.7%) and xylene (10%).

R-2 was a methyl methacrylate (MMA)/ethyl acrylate (EA) copolymer forming clear, coherent films and is therefore applied as coating or varnish. It is commonly applied dissolved in aromatic hydrocarbons. In order to prevent fungal growth, the addition of 1 ppm formaldehyde is reported (Heyn, 2002).

AD-1 was a thermoplastic, water-soluble acrylic dispersion consisting of methyl methacrylate (MMA), 2-ethylhexyl acrylate and phthalate. It is used as liquid adhesive, binding and/or consolidation medium. AD-2 was a thermoplastic copolymer from polyvinyl acetate (PVAC) and maleic acid. Dibutyl maleate is added as plasticizer (Horie, 1987). This PVAC is applied as adhesive or binder. AD-3 was also an acrylic copolymerisate and is used as medium for consolidation for loose and pulverized paint layers as well as for gildings and thin glue-bound paintings.

Also artist colours were investigated. P-1 was a pastose ready-for use white paint on vinyl basis. Polyvinyl resins are a comprehensive class of binding agents, even though they are not as important as e.g. alkyd resins. Polyvinyl resins are formed by polymerisation of monomers with a terminal vinyl group, among others polyvinyl esters, polyvinyl alcohol, polyvinyl ethers and polyvinyl styrene. Polyvinyl paints are evaporation curing. As no technical data sheet or other supplier information was available, no evidence can be given regarding the specific polymeric matrix and additives in sample P-1. However, it was labelled as conform to ASTM D 4236 (ASTM *Standard Practice for Labelling Art Materials for Chronic Health Hazards*). This standard is published by the ASTM International (former: American Society for Testing and Materials). The labelling does not mean that the product is non-toxic, it rather means that the product has been evaluated by a toxicologist for acute and chronic toxicity and that hazardous ingredients are named on the label and that safe use instructions are enclosed. Sample P-2 was an acrylic paint with titanium dioxide (TiO_2)-coated mica pigments. Similarly to sample P-1 any labelling or supplier information was lacking.

Table 5.1-10. Materials for conservation and restoration purposes selected for emission analysis via thermal extraction (screening) and/or emission test chambers.

Sample no.	Material	Solid/Liquid	Purpose of use	Thermal extraction	Chamber test
Natural products					
G-1	Hide Glue	Solid (pearls), dissolved in distilled water (10%)	Adhesive; consolidation medium for (polychrome) wooden surfaces; for gildings, violin varnish	+	-
G-2	Fish Glue	Liquid (in water, phenol)	Adhesive for high-strength bonding; consolidation medium	+	-
C-1	Hydroxypropyl cellulose	Solid, dissolved in distilled water (15%)	Consolidation medium for paint layers; vehicle for watercolour and gouache paints	+	-
D-1	Dammar resin	Solid raw material	Picture varnish	+	-
D-2	Dammar varnish glossy	Liquid (1:2 in double rectified turpentine)	Picture varnish	+	-
D-3	Dammar varnish	Liquid [mixture of (C_9-C_{12}) iso-alkanes and solvent naphtha (petroleum), UV-stabilized]	Picture varnish	+	-
Synthetic products					
R-1	Hydrogenated hydrocarbon resin	Liquid	Picture varnish	+	-
R-2	Ethyl methacrylate (PEMA)/methylacrylate (MA) (70:30)	Solid, dissolved in toluene (15%)	Picture varnish, consolidation for wood	+	-
AA-1	Homopolymer acrylic acid (Carboxypolymethylene)	Solid, dissolved in distilled water (1%)	Conservation material for cleaning	+	-
AD-1	Acrylic dispersion (methyl methacrylate, 2-ethylhexyl acrylate)	Liquid	Binder	+	-
AD-2	Polyvinylacetate (PVAC) dispersion (53%); dibutyl maleate (35%)	Liquid	Binder, adhesive	+	-
AD-3	Acrylic copolymer (methacrylate)	Liquid (aqueous dispersion)	Consolidation medium	+	-
P-1	Vinyl paint	Pastose	Artist colour	+	-
P-2	Acrylic paint	Pastose	Artist colour	+	-

5.2 Sample preparation and investigation parameters

All showcase construction samples were prepared by the manufacturers to ensure a common fabrication. In order to avoid substrate effects on VOC emissions (Chang et al., 1997) and to obtain clear information about emission behaviour of test specimens, samples were prepared on an aluminium substrate as this is a non-porous and non-absorbent material. After curing according to the recommended curing time of each material, the samples were tightly wrapped in aluminium and polyethylene foil and send to the laboratory. All samples were analysed immediately after receipt from the manufacturers. If this was not possible due to temporal reasons, the packed samples were stored in a 40 m³ climate room at 23°C and 45% relative humidity. Conservation and restoration products were prepared in the laboratory. Emission tests started immediately after curing and hardening, respectively.

5.2.1 Screening emission analysis

All two dimensional materials were provided in samples of 100x100 mm. Adhesives and sealants were prepared as rolls. For screening emission testing, pieces of 10x45 mm (two-dimensional samples) and 10x70 mm (adhesives/ sealants), respectively, were cut off from all samples. Concerning UV-curing adhesives, this kind of preparation is not comparable with real life conditions as they are used to glue the mitre joints of glass panels. This results in a very thin film that complicates emission testing. However, this set-up was helpful in order to obtain information about emitted substances. Materials for conservation and restoration purposes were accordingly applied on small aluminium plates (10x45 mm). If necessary, solid raw materials were first dissolved and then applied to the substrate.

As indicated in Table 4.1, test specimens were subjected to thermal extraction for screening emission analyses on (S)VOCs. Active air sampling was performed on Tenax TA® (further information is given in section 5.2.3). Investigation parameters were chosen according to the emission potential of the examined material classes. All materials were tested at room temperature (*t*: 25°C) with exception of lacquers and coatings. In order to detect all generated compounds a higher test temperature for the whole material class was necessary (*t*: 65°C). The sampling volume (*V*) varied between 1 l and 9 l. Products with high emissions were sampled with 0.5 l and 1 l, respectively, to prevent contaminations during analysis. Concerning low emissive materials, a sampling volume of 6–9 l was necessary to achieve good results. Air sampling was performed with a flow rate of 100 ml/min and 150 ml/min, respectively, so that sampling time (t) 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 (n) was 233 h^{-1}. Table 5.2-1 compiles the chosen investigation parameters during thermal extraction.

Table 5.2-1. Investigation parameters during screening emission analyses by thermal extraction.

Material category	**T [°C]**	**V [l]**	**t [min]**	**n [h^{-1}]**
Construction/decoration materials				
Lacquers/Coatings	65	6	40	233
Adhesive/Sealants	25	1	10	
UV-curing adhesives	25	1	10	
Printer's inks	25	6	40	
Wood-based products	25	6	40	
Construction and other materials	25	9	60	
Cover fabrics	25	6	40	
Conservation/restoration products				
Animal glues	25	6	40	233
Dammar varnishes	25	0.5	5	
Acrylic dispersions	25	6	40	
Paints	25	2	20	

5.2.2 Chamber emission tests

Experiments were carried out in self-constructed 1m³ glass chambers and 250 l stainless steel chambers under the following conditions: 23±2°C temperature, 50±5% relative humidity. Chamber emission tests were performed according to DIN EN ISO 16000 Part 9 (2008) and Part 11 (2006).

According to the specific conditions inside of museum enclosures, the air exchange rate was reduced to a minimum as technical possible ($n=0.18\ h^{-1}$) and the loading factor was appropriate adopted. Following the surface to volume ratio of coating materials and sealants in showcases, representative total surface areas of 0.5 m² and 0.03 m², respectively, were chosen. This corresponds to a loading factor of 0.5 m²/m³ regarding coating materials and 0.03 m²/m³ regarding sealants. This adoption is necessary for emission testing to relate the rates in order to be relevant to this specific type of enclosure (Gunnarsen, 1997). Consequently, coating materials were applied on aluminium plates of 707x707 mm. Samples of adhesives and sealants were prepared according to DIN EN ISO 16000 Part 11 (2006) by injecting into U-shaped aluminium profiles, 10 mm width and 3 mm depth. The total length of an aluminium profile was 3 m, thus three U-shaped profiles each of 1 m length were put in a 1 m³-glass emission test chamber. The profiles were weight before and after filling with adhesives and sealants, respectively.

Temperature and relative humidity were continuously recorded during chamber emission tests with a time resolution of 1 min. using data loggers (HygroLog D, rotronic AG). To avoid temperature gradients, the chambers were covered with insulating boards. Before each test and to avoid memory effects, the chambers were heated to 65°C for 15 h.

All samples were placed at the bottom of the test chamber. Test start (time = 0) was established when the chamber was closed. Air sampling was conducted after 5 h, 24 h, 48 h, 72 h and (120 h) 144 h for analysing (S)VOCs, formaldehyde and organic acids. Further information is given in section 5.2.3. Air sampling after 5 h was just conducted for detection of (S)VOCs. Each determination was performed in duplicate for analytical reliability. Testing parameters are given in Table 5.2-2.

Table 5.2-2. Investigation parameters for chamber emission tests.

Parameter	Lacquers/coatings	Adhesives/sealants	Wood-based products
Chamber volume [m³]	1	1	0.25
Temperature [°C]	23 ± 2	23 ± 3	23 ± 2
Relative humidity [%]	50 ± 5	50 ± 5	50 ± 5
Air exchange rate n [h^{-1}]	0.18	0.18	0.18
Loading factor [m²/m³]	0.5	0.03	1
Air flow rate q [m³/(m²*h)]	0.36	6	0.18
Sampling intervals [h]	5, 24, 48, 72, (120)144	5, 24, 48, 72, (120)144	5, 24, 48, 72

Testing UV-curing adhesives

UV-curing adhesives are used to glue the mitre joints of glass panels by getting them in the mitre just by capillary forces, which results in a very thin film. In order to identify and quantify VOCs released during application, 0.5 g of adhesives were spread over 22.5 cm² on cleaned glass plates and were immediately set into a 23.5 l glass emission test chamber. As UV-curing adhesives photochemical crosslink when subjected to UV-radiation and/or visible light, two experimental set-ups were accomplished. In the first experiment, a 280–400 nm UV-radiator with 300 W/230 V was placed directly over the lid of the chamber. After closing the chamber, the UV-radiator was switched on for 8 h each day and the thin adhesive film was allowed to dry. In a second series the same experimental set-up was repeated, but without UV-radiation.

Facing the purpose of use, as mentioned above, chamber emission tests of UV-curing adhesives corresponded rather to a *"worst case scenario"* than to reality. However, the experimental set-up delivers insights into primary emissions and secondary processes. Air sampling on (S)VOCs was accomplished in each case after 0.5 h, 1 h, 2 h, 4 h, 24 h, 48 h and 72 h. Climatic conditions were the same as during the 1 m³ glass emission test chamber investigations (see Table 5.2-2) and were also recorded each minute.

5.2.3 Air sampling and analysis

Discontinuously active air sampling was performed during material emission tests. Target compounds were enriched on an appropriate sorbent material and subsequently transferred to the analytical device.

5.2.3.1 Volatile organic compounds (VOCs)

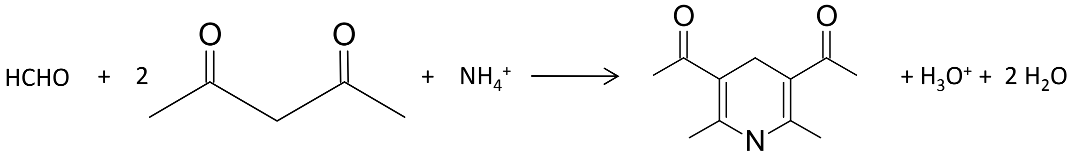
Active air sampling of volatile and semi-volatile organic compounds (VOCs/SVOCs) was performed according to DIN ISO 16000 Part 6 (2004). Air was pumped with a flow of 150 ml/min (40 min) through stainless steel desorption tubes (Perkin Elmer) filled with Tenax TA® (60/80 mesh, Chrompack). In order to identify and quantify emissions from wood-based products (especially terpenes), multibed sorbent tubes packed with Tenax TA® and CarboTrap® (20/40 mesh, Chrompack) were utilized (Uhde, 2003).

After exposure, the tubes were thermally desorbed (320°C, 10 min; Perkin Elmer ATD 400) into a GC/MS system (Agilent 6890/5972). The compounds were separated on a HP-5 MS column (60 m x 0.25 mm, 0.25 µm). Qualifying was based on a PBM library search (McLafferty and Turecek, 1993). Moreover, mass spectra and retention data were compared with those of reference compounds. All identified compounds were quantified using their own response factors. The areas of unidentified peaks were converted to concentrations using the toluene response factor. For calibration the linear regression model was used (Massold et al., 2005). Limit of quantitation (LOQ) was < 1 µg/m³.

5.2.3.2 Formaldehyde

The determination of formaldehyde emissions regarding chamber emission tests was performed according to the acetylacetone method (DIN EN 717 Part 1, 2005).

Air sampling was carried out by passing 80 l of air with a flow of 2 l/min through distilled water as liquid absorber. Formaldehyde *(1)* was subsequently derivatized with 2,4-pentandione (acetylacetone) *(2)* and ammonium acetate *(3)* to form dihydropyridine-3,5-diacetyl-1,4-dihydrolutidine (DDL) *(4)*, the so called Hantzsch complex (see Equation 5-1). DDL was measured photometrically at a wavelength of λ = 412 nm. Limit of quantitation (LOQ) was 2 µg/m³.



(5-1)

(1) *(2)* *(3)* *(4)*

5.2.3.3 Organic acids (formic acid, acetic acid)

Formic acid (HCOOH) and acetic acid (CH_3COOH) were absorbed in 0.1 n NaOH (120 l of air with a flow of 2 l/min). High Performance Ion Chromatography Exclusion (HPICE) was applied for analysis (Metrosep Organic Acids, 250 mm, Methrom) (Kellner et al., 2004). As the stationary phase displays negatively charged functional groups (polystyrene-divinylbenzene-copolymer with sulphonic acids), positively charged cations and undissociated molecules, such as weak acids, are retained. Anions cannot interact with the stationary phase. For calibration the linear regression model was used (Einax et al., 2007). Limit of detection (LODs) for formic acid was 12 µg/m³, limit of quantitation (LOQ) was 35 µg/m³. Limit of detection (LODs) for acetic acid was 35 µg/m³, limit of quantitation (LOQ) was 134 µg/m³ (Markewitz, 2006).

5.3 Results and discussion

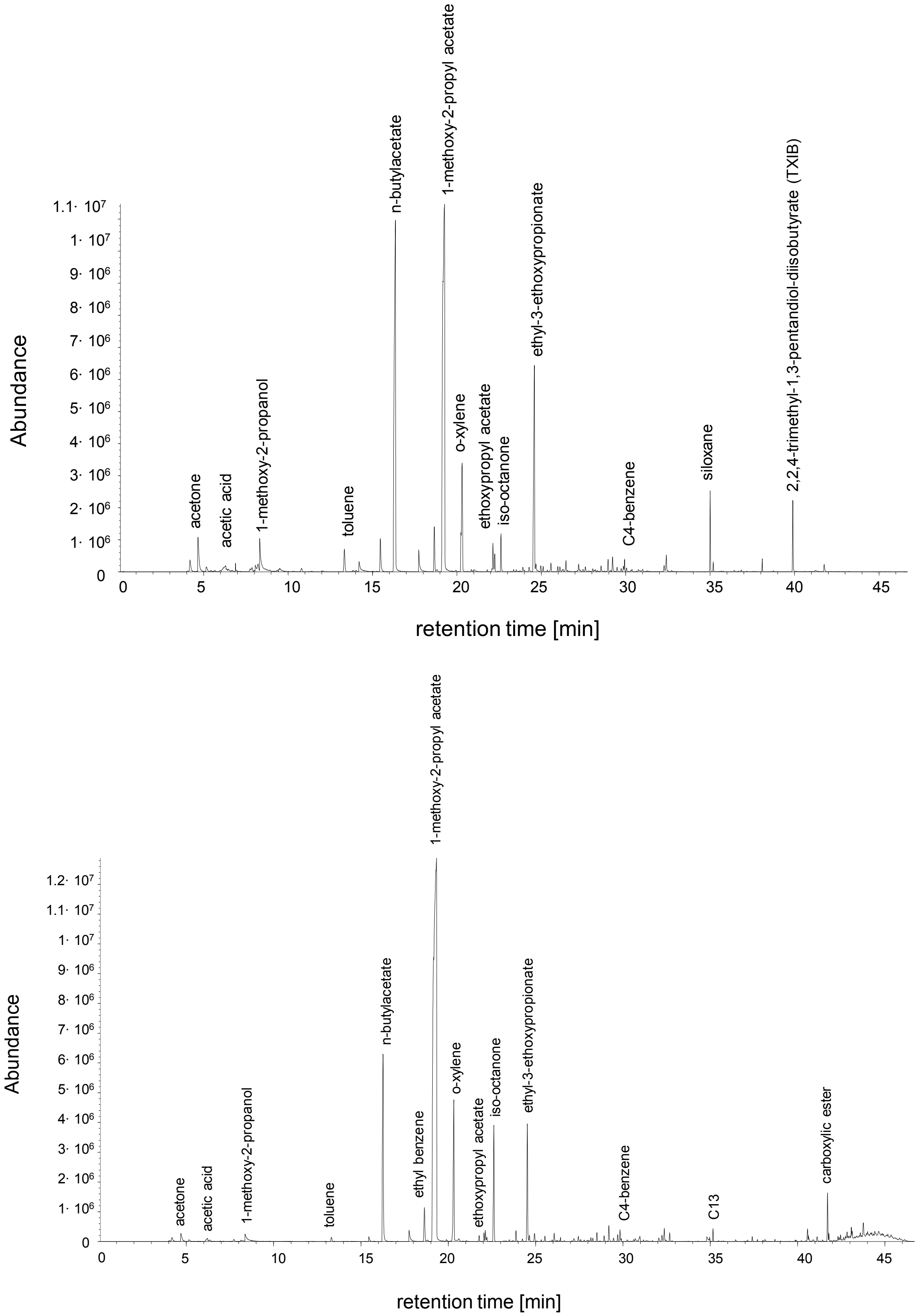
In total 80 products for construction and decoration of showcases were analysed via thermal extraction. 28 materials were selected for further investigations in emission test chambers, namely 8 lacquers/coatings, 7 adhesives/sealants, 2 printer's inks, 5 UV-curing adhesives and 6 wood-based materials. Other construction materials and textiles were low-emissive so that further tests were not carried out. Moreover, screening emission analyses of 14 products for conservation and restoration purposes were accomplished.

All given values from material emission tests are mean values from duplicate measurements. Results of chamber emission tests are given in chamber concentrations c (µg/m^3) or sum values of volatile organic compounds [Σ(VOC)], which is the sum of the concentrations of all identified and unidentified volatile organic compounds between and inclusively n-hexane and n-hexadecane (C_6-C_{16}).

Results of emission analyses were moreover statistically evaluated by giving the following values:

the minimum (MIN)	smallest element of data
the maximum (MAX)	largest element of data
the median (MED)	cuts data set in half (≈ 50th percentile)
25th percentile (25-P)	cuts off lowest 25% of data
75th percentile (95-P)	cuts off highest 25% of data

The comparison of the results obtained from thermal extraction and emission test chamber measurements revealed a good correlation of the identified lead substance peaks and the ratio of integrated areas as shown in Figures 5.3-1a and 5.3-1b. Hence, results obtained by thermal extraction can be regarded as representative concerning most abundant substances and their proportions to each other.



Figures 5.3-1a and b. Total ion chromatograms (GC/MS) obtained (a) from thermal extraction and (b) from chamber emission tests revealed high correlations regarding main characteristic compounds. Exemplary illustrated on sample L-5 (epoxy resin coating).

5.3.1 Emissions from construction and decoration materials

The diagram in Figure 5.3-2 gives an overview of the emission ranges from lacquers and coatings, gasket materials and wood-based products during chamber emission tests. ∑(VOC)-values of lacquers and coatings varied between 745 µg m^{-3} and 14029 µg m^{-3} after 24 h and between 537 µg m^{-3} and 7117 µg m^{-3} after 144 h. Emissions of gasket materials caused concentrations of 582-18507 µg m^{-3} after 24 h and 400-6131 µg m^{-3} after 120/144 h. ∑(VOC)-values of wood-based materials ranged from 125 µg m^{-3} to 41314 µg m^{-3} after 24 h and from 131 µg m^{-3} to 3492 µg m^{-3} after 72 h.

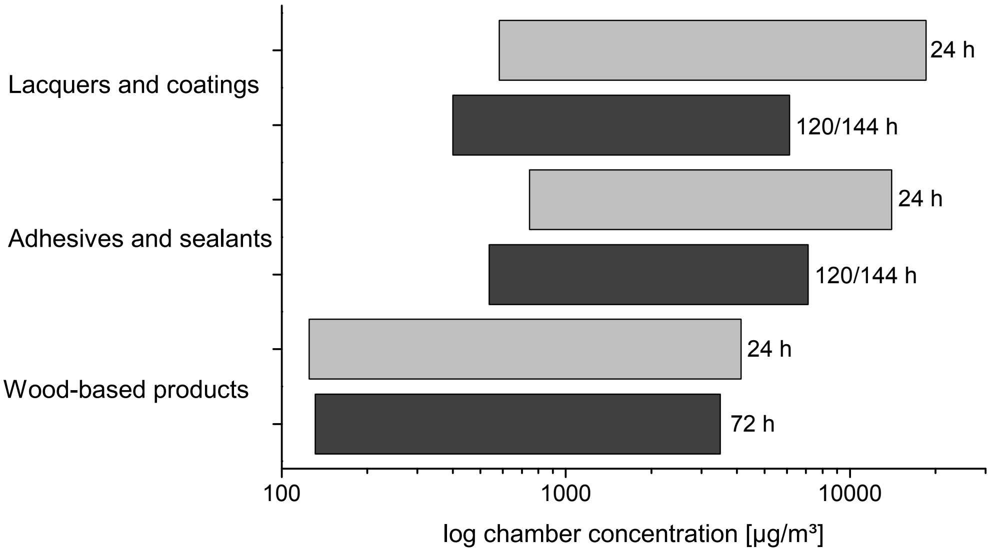


Figure 5.3-2. Σ(VOC) values of lacquers and coatings (n = 8), adhesives and sealants (n = 7) and wood-based materials (n = 5) in emission test chambers after 24 h and 72 and 120/144 h, respectively.

According to the results obtained by thermal extraction, emissions from other construction materials and textiles were lower than those of wood-based materials. Especially emissions of untreated textiles (neither dyes nor laminations) were negligible. Concentrations caused by UV-curing adhesives are not comparable as the experimental set-up for thermal extraction related rather to a kind of worst-case scenario. However, it must be stressed that under almost static conditions as they are claimed by conservators with air exchange rates of n ≅ 0.004 h^{-1}, concentrations caused by material emissions will be several factors higher.

From this illustration it is clearly shown that lacquers and coatings as well as adhesives and sealants showed an increased emission potential. This observation agreed with results yielded from emission test chamber investigations. Concentration *versus* time profiles showed declining emission curves for the majority of all test specimens and are exemplarily visualized in Figure 5.3-3 for Σ(VOC)-values of coating materials. Hence, volatile substances are emitted fastly reaching the maximum values after around 24 h and subsequently pass into a constant emission strength, which suggests diffusion controlled mechanisms. Samples L-3, L-8 and L-9 were the only exceptions with slightly increasing concentrations assuming a primarily diffusion controlled emission mechanism from the beginning, but also passing into nearly constant emission strength.

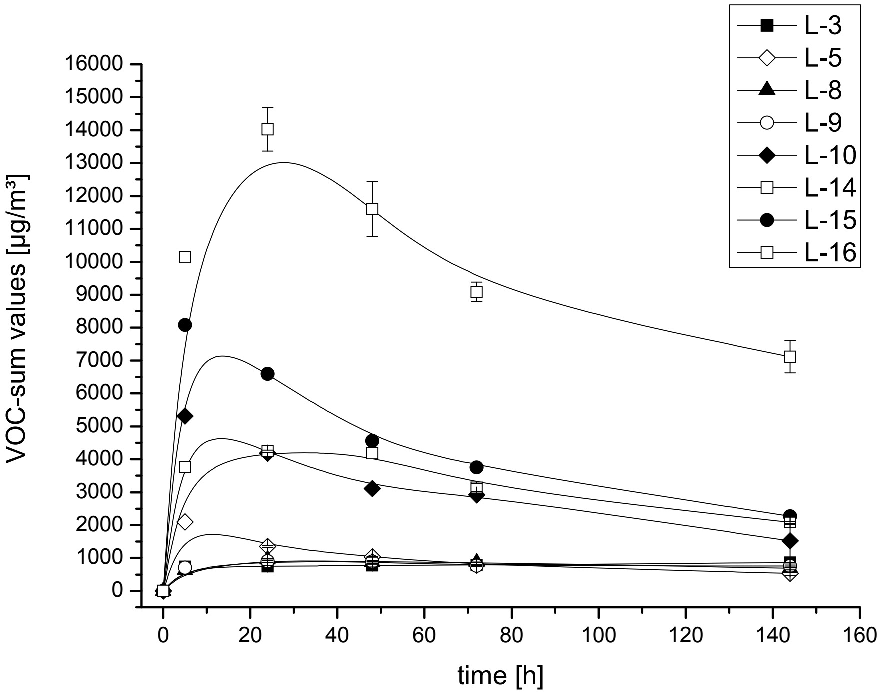
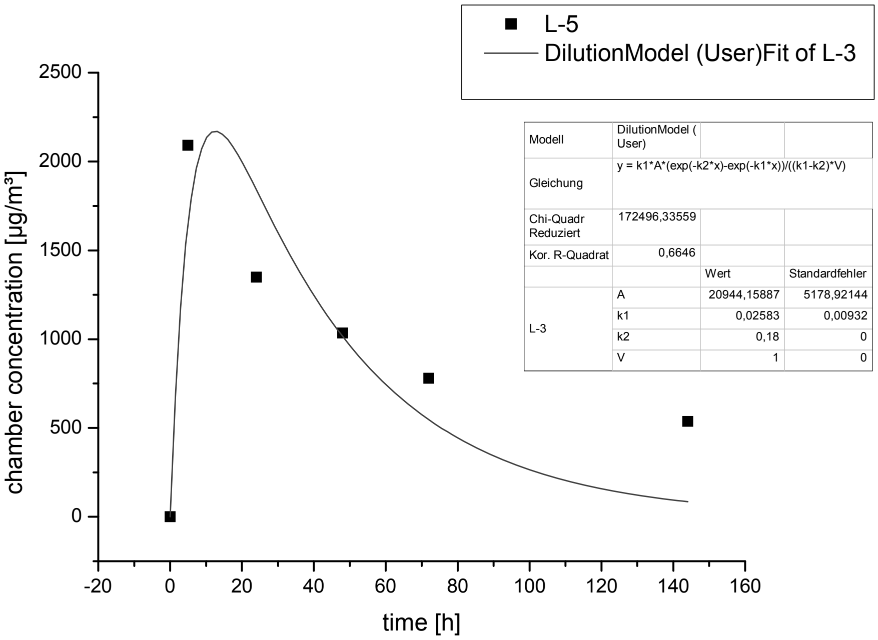


Figure 5.3-3. Concentration *versus* time profiles for Σ(VOC)-values of lacquers. The graph was obtained by compensating spline interpretation. For abbreviations, see Table 5.1-3.

For a better comparability of the individual data sets obtained from chamber emission tests, an attempt was made to calculate specific emission rates (SER) according to the dilution model for decreasing emission rates published by Dunn and Tichenor (1988), see also section 3.1.4. Facing the six data points obtained for each test specimen during emission test chamber investigations, it becomes clear that the more complicated dilution model for decreasing emission sources [see Equation (3-5), section 3.1.4] is over parameterized. Figure 5.3-4 visualizes exemplarily the obtained fit curve for sample L-5 (epoxy resin).



Modell	DilutionModel (User)		
Gleichung	y = k1*A*(exp(-k2*x)-exp(-k1*x))/((k1-k2)*V)		
Chi-Quadr Reduziert	172496,33559		
Kor. R-Quadrat	0,6646		
		Wert	Standardfehler
L-3	A	20944,15887	5178,92144
	k1	0,02583	0,00932
	k2	0,18	0
	V	1	0

Figure 5.3-4. Measured (■) and modelled (-) concentration *versus* time profile after the dilution model by Dunn and Tichenor (1988) assuming no sink effects.

It is obvious, that the model does not fit the data sets *C (t)* in an appropriate way. The decay rate of the model is faster than the real data as it assumes a higher air exchange rate. Nevertheless, this model illustrates well the fact that immediately after chamber loading and, thus, during the first 144 h the emission is primarily evaporation controlled. After this testing time emissions pass into a constant emission strength, which suggests diffusion controlled emission mechanisms. For this reason, calculation of specific emission rates (SER) for decaying emission rates were solved numerically according to Equation (3-3) (see section 3.1.4).

Statistical parameters and decreasing emission rates obtained from chamber emission tests are summarized in Table 5.3-1 by listing the number of basic data set (N) and the numbers of identified substances (No. of ident. VOCs) of each material class, the specific minimum (MIN) and maximum (MAX) value, the median (MED) as well as the 25th percentile (25-P) and the 75th percentile (75-P). Moreover, surface area specific emission rates (SER_A) and mass specific emission rates (SER_m), respectively, are indicated for comparison with Σ(VOC)-values. UV-curing formulations, namely printer’s inks and UV-curing adhesives are not listed here as the experimental set-up related to a worst-case scenario.

Table 5.3-1. Statistical evaluation of emission test chamber results.

	Lacquers/ coatings	Adhesives/ sealants	Wood-based materials	Lacquers/ coatings	Adhesives/ sealants	Wood-based materials
Chamber concentration [µg/m³] after	**24 h**			**120 h/144 h**	**120 h/144 h**	**72 h**
No.	8	7	5	8	7	5
No. of ident. VOCs*	100	63	86	93	37	75
MIN Σ(VOC)	745	582	125	537	400	131
MAX Σ(VOC)	14690	18507	4134	7117	6097	3492
MED Σ(VOC)	2767	3785	2169	1188	3476	1510
25-P	927	1470	1343	719	1109	1012
75-P	5421	15539	3196	2175	4820	2589
MIN SER_A [µg/m²*h)]	302	3446	22	247	2400	24
MAX SER_A [µg/m²*h)]	5154	95573	744	2562	36783	272
MIN SER_m [µg/(g*h)]	-	1	-	-	1	-
MAX SER_m [µg/(g*h)]	-	29	-	-	15	-

*without unidentified substances

An overview of characteristic main compounds of each material category is given in Table 5.3-2. Moreover, it is quoted, whether their origin is believed to be primary or secondary emission. In accordance to these definitions, material emissions will be presented and discussed in the following chapter.

Table 5.3-2. Characteristic main compounds of each material class identified during emission test chamber analyses. P: Primary emission. S: Secondary emission.

Material category	Characteristic main compounds	Primary (P) Secondary (S)	Remarks
Lacquers/Coatings	Diacetone	P	Solvent
	Acetone	S	*retro*-aldol addition
	Acetic acid	S	Ester hydrolysis
	n-Butylacetate	P	Solvent
	2-Ethylhexylacetate	P	Solvent
	Dimethyladipate/dimethylglutarate/ dimethylsuccinate	P	Filming agents; substitutes for chlorinated substances
	Toluene	P	Solvent
	Ethylbenzenes*	P	Solvent
	Xylene-isomers	P	Solvent
	C3-/C4-benzenes**	P	Solvent
	1-Methoxy-2-propylacetate	P	Solvent; defoamer, wetting and leveling agent
	Ethoxypropylacetate	P	Solvent
	Ethyl-3-ethoxypropionate	P	Solvent
	Butylglycolacetate	P	Solvent
	Iso-alkanes, alcohol, aldehydes	P	Solvents
Printer's inks	Isobornylacrylate (IBOA)	P	Acrylic monomer
	1-Hydroxycyclohexyl phenyl ketone (HCPK)	P	Photoinitiator
	2-Hydroxy-2-methyl-1-phenyl-propane-1-one (HMPP)	P	Photoinitiator
	Benzophenone (BP)	P	Photoinitiator
	2-Phenoxyethyl acrylate (POEA)	P	Acrylic monomer
	1,6-Hexandiol diacrylate (HDDA)	P	Acrylic monomer
	Cyclohexanone, benzaldehyde	S	Fragments of HCPK via Norrish-I reaction (α-cleavage)
	2-Phenoxyethanol	S	Decomposition product of POEA via hydrolysis
	2,4,6-Trimethylbenzaldehyde	P	Fragmentation product
Adhesives/Sealants	Alcohol, iso-alkanes	P	Solvents
	3-Cyclohexene-1-carboxaldehyde	S	Diels-Alder product
	Methylcyclohexene-carboxaldehyde	S	Diels-Alder product
	n-Butylacetate	P	Solvent
	4-Vinylcyclohexene	S	Diels-Alder product
	Toluene	P	Solvent
	Xylene-isomers	P	Solvent
	C3-/C4-benzenes**	P	Solvent
	Acetone oxime	S	Crosslinking agent
	2-Butanone oxime (MEKO)	S	Crosslinking agent
	2-Propanone oxime	S	Crosslinking agent
	4-Methyl-2-pentanone oxime	S	Crosslinking agent

* isomers not listed ** identification of the exact isomer was not possible

Material category	Characteristic main compounds	Primary (P) Secondary (S)	Remarks
	Cyclic siloxanes	P	Polymer matrix
	o-Phenetidine	P	Solvent
	2,5-Dimethyl-1,4-dioxane	P	-
	2,6-Di-tert.butyl-4-methylphenol (BHT)	P	Antioxidant
UV-curing adhesives	Methyl methacrylate (MMA)	P	Acrylic monomer
	2-Hydroxyethyl methacrylate (HEMA)	P	Acrylic monomer
	Isobornyl acrylate (IBOA)	P	Acrylic monomer
	2,2-Dimethoxy-2-phenyl-acetophenone (DMPA)	P	Photoinitiator
	1-Hydroxycyclohexyl phenyl ketone (HCPK)	P	Photoinitiator
	2-Hydroxy-2-methyl-1-phenyl-propane-1-one (HMPP)	P	Photoinitiator
	Cyclohexanone, benzaldehyde	S	Fragments of HCPK via Norrish-I reaction (α-cleavage)
	Nitrogen-containing compounds	-	Non-identifiable
Wood-based materials	α-, β-Pinene	P	Bicyclic terpene
	3-Carene, limonene	P	Bicyclic terpene
	Aldehydes	S	Degradation products
	Acetic acid, hexanoic acid	S	Degradation products
Construction and other materials	Iso-alkanes, cyclic alkanes, iso-alkenes	P	-
	Phenol	P	-
	2-Ethyl-1-hexanol	S	Degradation product of DEHP
Cover fabrics	Maleine acid di-butyl ester	P	Precursor of an adhesive
	iso-Alkanes	P	-
	Toluene	P	Solvent

* isomers not listed ** identification of the exact isomer was not possible - unknown

5.3.1.1 Lacquers and coatings

As summarized in Table 5.3-1, Σ(VOC)-values of all coating systems investigated in emission test chambers ranged from a maximum of 14690 µg/m³ after 24 h to a minimum of 537 µg/m³ after 144 h. This is equal to surface area specific emission rates (SER_A) varying from 5154 µg/(m²*h) to 247 µg/(m²*h). Figure 5.3-5 illustrates chamber concentrations *versus* time (*t*).

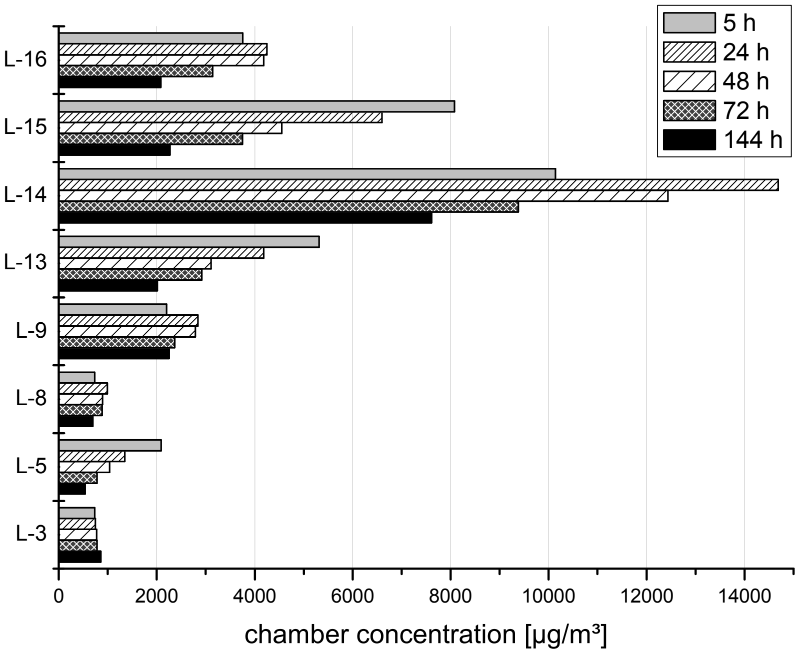


Figure 5.3-5. Chamber concentration [Σ(VOC)] *versus* time (*t*) for coating materials during chamber emission tests, identified by GC/MS.

Highest chamber concentrations showed a two-pack polyurethane/polyacrylate coating (L-14) used as filler with 14690 µg/m³ after 24 h and a cellulose nitrate coating applied as a refining top coat (sample L-15) with 6595 µg/m³ after 24 h. The lowest Σ(VOC)-value after 24 h was documented for sample L-3, a combined two-pack polyacrylate/polyester resin (745 µg/m³), although with a slight, but constant increasing emission rate over 144 h (857 µg/m³).

Solvent borne coatings were characterized by each emitting 15-41 several compounds during emission test chamber investigations. In total, up to 100 individual VOCs could be identified. The pigment components of a lacquer normally do not contribute to VOC emissions. The majority of released organic volatiles originate mainly from the solvent components. Thus, relevant primary emissions were identified as a broad range of different solvents and additives, namely glycols and glycol ethers, aliphatic and aromatic hydrocarbons, (di)carboxylic esters, alcohol and aldehydes. Table 5.3-3 lists lead compounds of primary emissions which are characteristic for solvent borne coating materials and indicates the purpose of use.

Table 5.3-3. Characteristic lead compounds emitted from solvent borne coating materials identified in chamber air by GC/MS.

Substance	CAS-No.	Remarks
Ketones		
Acetone	67-64-1	Solvent
Aromatic hydrocarbons		
Toluene	108-88-3	Solvent
Ethylbenzene	100-41-4	Solvent
m,p-Xylene	1330-20-7	Solvent
o-Xylene	95-47-6	Solvent
Ethyltoluenes*	-	Solvent
Trimethylbenzenes*	-	Solvent
(Di)carboxylic esters		
n-Butylacetate	123-86-4	Solvents for synthetic resins
Dimethylglutarate	1119-40-0	Filming agents; substitutes for chlorinated and required labelling substances
Dimethylsuccinate	106-65-0	
Dimethyladipate	627-93-0	
Glycol esters		
1-Methoxy-2-propylacetate	108-65-6	Solvent; defoamer, wetting and levelling agent
Ethoxypropylacetate	98516-30-4	Solvent for synthetic resins
Ethyl-3-ethoxypropionate	763-69-9	Solvent
TXIB®	6846-50-0	Solvent, film former

* isomers not indicated

Aromatic hydrocarbons were main emitters with 17 identified substances. Ethylbenzene, xylene isomers and a broad range of different C3-/C4-benzenes (ethyltoluene isomers, trimethylbenzene isomers) constituted 30% to 65% of the specific Σ(VOC)-values. Such chemicals are used as solvents for a wide variety of lacquer systems. (Di)carboxylic esters and glycol ethers/glycol esters constituted up to 28% of all emitted compounds with 29 identified substances in total. n-Butylacetate and ethoxypropylacetate are widely used solvents for synthetic resins, e.g. polyurethane, acrylic and epoxy resins. 1-Methoxy-2-propylacetate is not only a common solvent for two-pack polyurethane coatings, but has also an additive function, e.g. as a defoamer, wetting and levelling agent. Moreover, dimethylglutarate, dimethylsuccinate and dimethyladipate were identified as conspicuous compounds. These dicarboxylic esters are used as composite both as filming agent and as chemical substitute for chlorinated and required labelling substances. Acetone as a widely-used low boiling solvent was detected among emissions from all lacquers/coatings. Figure 5.3-6 shows chamber concentrations of characteristic lead compounds after 144 h.

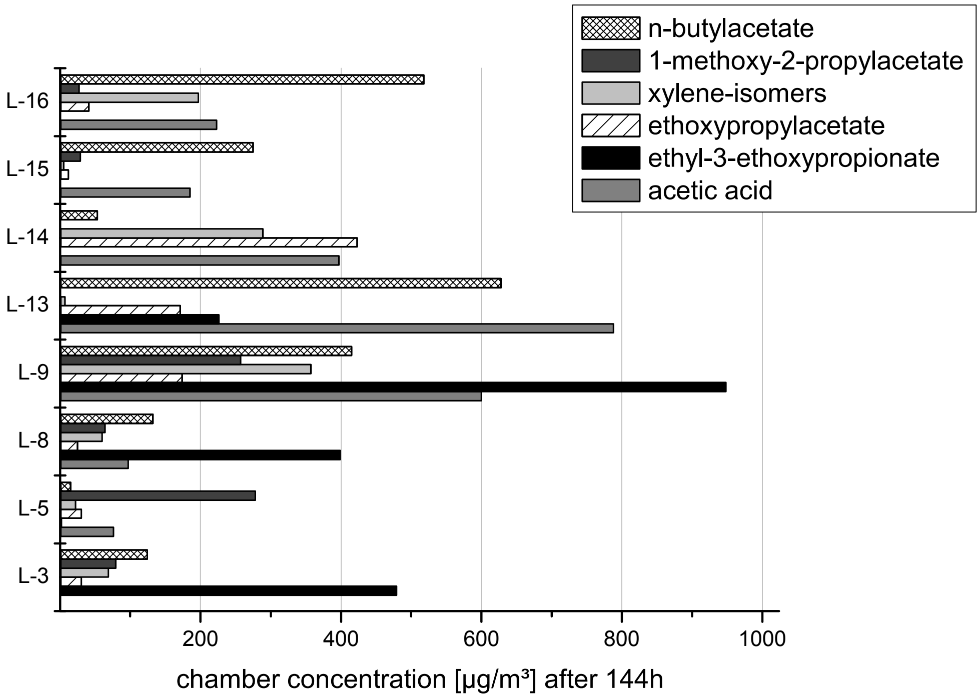


Figure 5.3-6. Chamber concentrations of characteristic lead compounds after 144 h, identified by GC/MS.

Also two isomers of the glycol ester 2,2,4-trimethyl-1,3-pentanediol-monoisobutyrate (TMPD-MIB) were identified in chamber air during testing of samples L-5 and L-3. The isomers are often referred to as Texanol® ester alcohol and TXIB®, respectively, and are used as solvents, film formers and plasticizers. Even though it is not an irritating agent to human health, several studies reported correlations between TXIB®-emissions and eye and nose irritation (Villberg et al., 2000). Furthermore, it is assumed that a kind of dose-response between irritation symptoms and TXIB®-concentration in indoor air exist (Metiäninen et al., 2002).

Aliphatic polyisocyanates, which are used as hardeners for two-pack polyurethane coatings or acrylic lacquers and which are contained in nearly all product formulations according to the material safety data sheets (see section 5.1.1.1), could not be detected during emission analyses due to their high reactivity and low concentration levels in indoor air, which are in the magnitude of ng/m³ (Schulz and Salthammer, 1998).

The results show that emissions of coating systems are attributed to solvents and additives in the formulation, which is illustrated by comparing the total ion chromatograms of a solvent borne coating (sample L-3, two-pack polyacrylate/polyester resin) and a powder coating (sample L-6), see Figures 5.3-7 and 5.3-8. The powder coating showed the lowest emission potential among all tested coating materials.

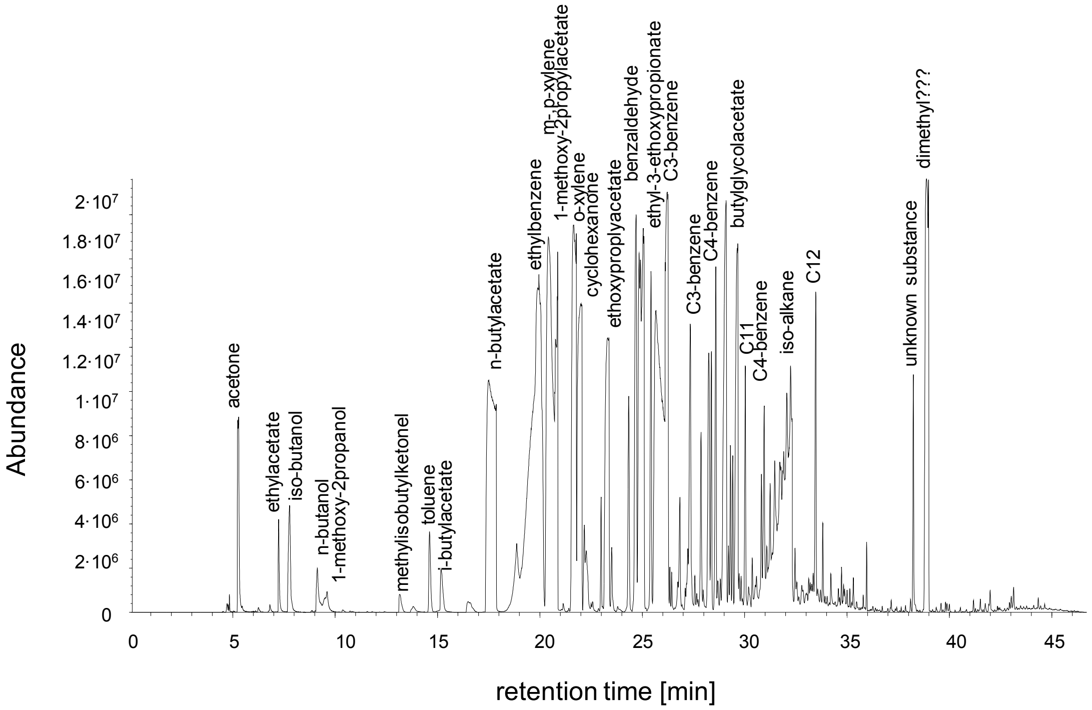


Figure 5.3-7. Total ion chromatogram (GC/MS) of sample L-3 (two-pack polyacrylate/polyester resin) obtained by thermal extraction.

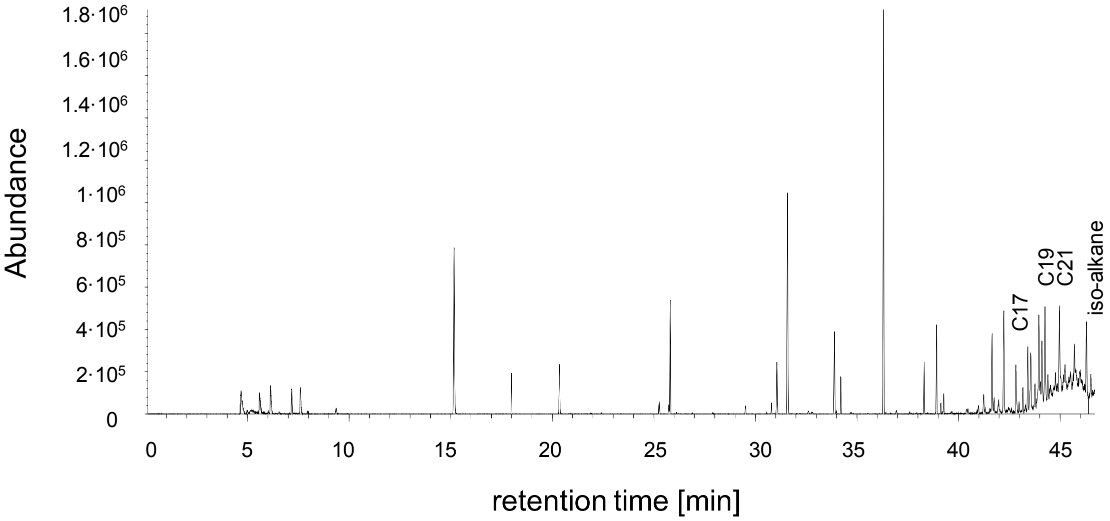
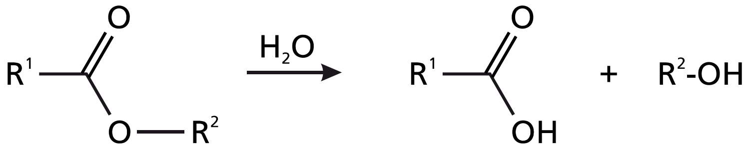


Figure 5.3-8. Total ion chromatogram (GC/MS) of sample L-6 (powder coating on polyester basis) obtained by thermal extraction.

Ester hydrolysis

Even though currently applied lacquers and coatings neither contain acetic acids in their formulations nor passing hardening processes under separation of acetic acid, it was detected during all chamber experiments with the exception of L-3 (epoxy resin). Concentrations in chamber air ranged from 1491 µg/m³ at maximum after 24 h to 76 µg/m³ at minimum after 144 h. As mentioned above, organic esters, namely carboxylic esters and glycol esters, were identified in elevated concentrations as characteristic primary emissions. Organic esters tend to hydrolyze to carboxylic acids and alcohol over time in dependence of the specific climatic parameters (temperature, relative humidity, pH value of the material) and the type of ester (Uhde and Salthammer, 2007). Hence, the detection of acetic acid in chamber air can be clearly attributed to acetyl ester hydrolysis as a result of material decomposition (Equation 5-2).



(5-2)

Several substance pairs occurred in chamber air, amongst others 1-methoxy-2-propylacetate/1-methoxy-2-propanol and n-butylacetate and n-/iso-butanol. This process of ester hydrolysis in the gas phase caused a delayed release of acetic acid as illustrated in Figure 5.3-9.

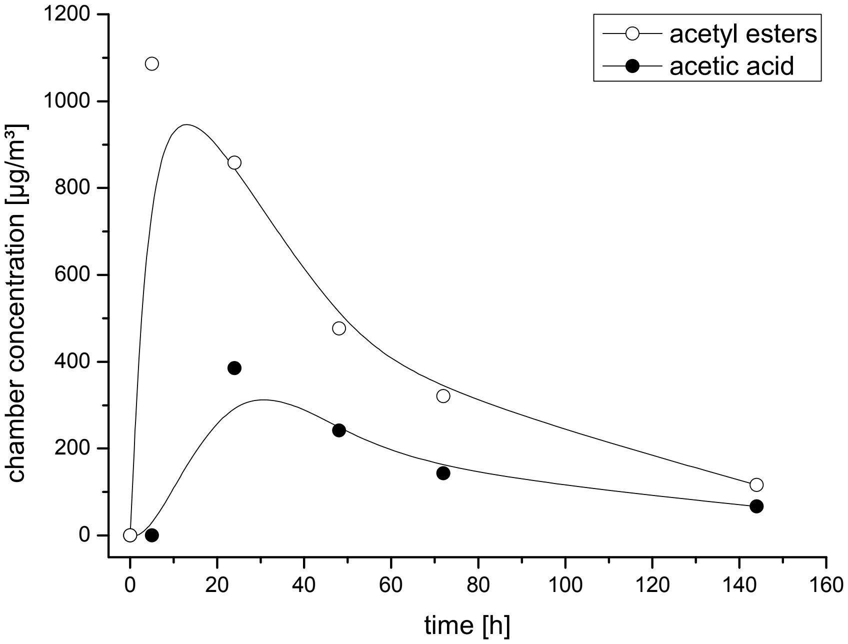
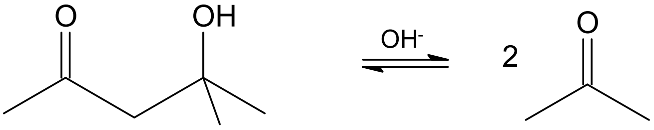


Figure 5.3-9. Delayed release of acetic acid in chamber air of sample L-15 (cellulose nitrate coating) due to hydrolytic cleavage of acetyl esters. The graph was obtained by compensating spline interpretation.

Retro-aldol addition

During chamber emission tests of sample L-14 (polyurethane/polyacrylate coating) diacetone alcohol as a primary emission product underwent alkaline *retro*-aldol addition forming acetone (Equation 5-3). Under alkaline conditions, propanone (*acetone*) forms 4-hydroxy-4-methyl-2-pentanone (*diacetone alcohol*), known as aldol addition. As the chemical equilibrium is almost on the side of the raw material, the reverse reaction proceeds fast (*retro-aldol addition*) (Sykes, 1988). Thus, diacetone alcohol decomposes under alkaline conditions into acetone. Figure 5.3-10 illustrates the complementary curve progression of these two substances.



(5-3)

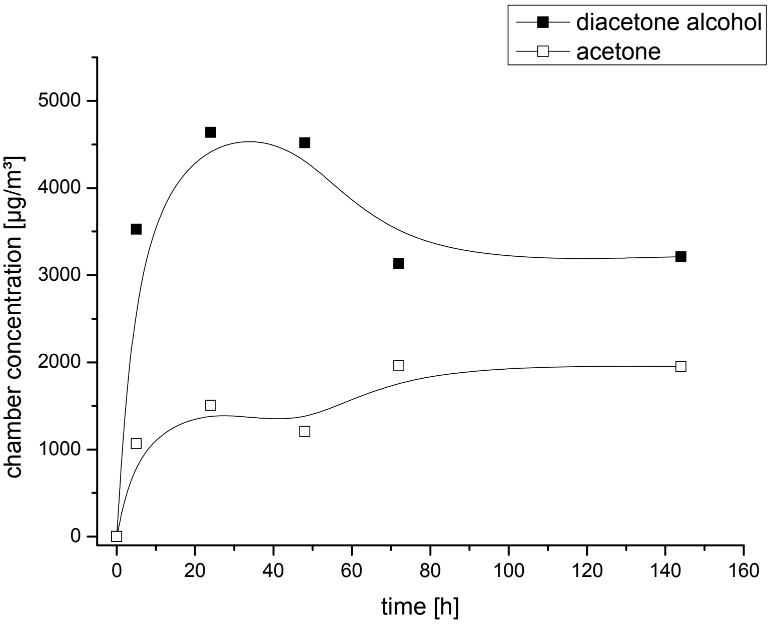


Figure 5.3-10. Concentration *versus* time curves for diacetone alcohol and acetone in chamber air of sample L-14 (polyurethane/polyacrylate coating), identified by GC/MS. The graph was obtained by compensating spline interpretation.

5.3.1.2 Adhesives and sealants

Mass specific emission rates (SER$_m$-values) of sealants declined over the tested time interval due to decreasing lead compounds. Emission rates varied between 29 µg/(g*h) at maximum after 24 h and 1 µg/(g*h) at minimum after 120 h/144 h, which corresponds to Σ(VOC)-values between 18507 µg/m³ and 400 µg/m³. Low emission rates were analysed for a polybutadiene rubber (sample S-3), whereas highest emissions were detected for a one-pack polyurethane sealant (sample S-10). It has to be noted that this specimen showed slightly increasing emission rates over testing time of 120 h with 15 µg/(g*h) [Σ(VOC)-value: 6000 µg/m³] after 24 h and 15 µg/(g*h) [Σ(VOC)-value: 6131 µg/m³] after 120 h.

The rapid increase of emissions during the first h, especially regarding samples S-5 and S-6 indicate an evaporation controlled mechanism passing to diffusion limited emissions after several days. Figure 5.3-11 illustrates chamber concentrations *versus* time (*t*).

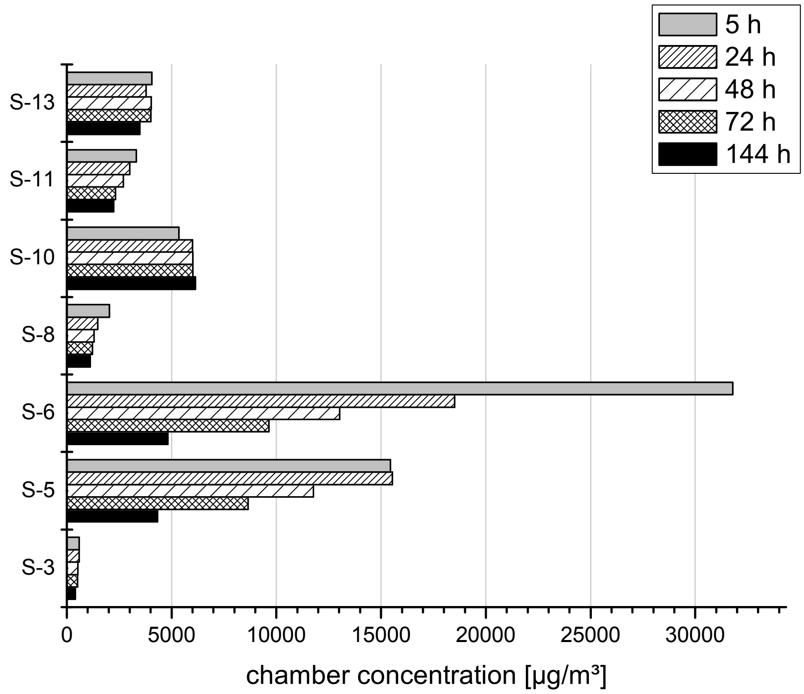


Figure 5.3-11. Chamber concentration *versus* time (*t*) for adhesives and sealants during chamber emission tests, identified by GC/MS.

Sealants were characterized by emitting each between 15 and 28 several compounds during emission test chamber investigations. In total, up to 60 individual VOCs could be identified.

Neutral curing silicone rubbers are currently the most applied gasket materials. Remarkable substances were therefore different cyclic siloxanes, which are separated by the polymer matrix and can reach very high concentrations in the test chamber. They constituted up to 72% of the Σ(VOC)-value from silicone rubbers and can therefore be outlined as significant emission sources. Alkoxy curing silicones release alcohol during the curing process. Methanol is a common fragmentation product, but could not be analysed due to its high volatility. In contrast, ketoxime curing silicone sealants released elevated ketoxime concentrations during curing. 2-Butanone oxime (MEKO: methylethylketone oxime), 2-propanone oxime and 4-methyl-2-pentanone oxime were identified as characteristic substances. MEKO can reach high initial chamber concentrations (~18000 µg/m³) in emission test chambers, although it was stated by Kempter et al. (1999) that MEKO is just released in small amounts from sealants. MEKO is a harmful compound with limited evidence of a carcinogenic effect (GefStoffV, 2005). Further characteristic primary emissions were a broad variety of typical solvents contained in sealant and adhesive formulations independent of the polymeric matrix. They can reach up to 50% of the Σ(VOC)-value of specific compositions. Table 5.3-5 lists dominant substances/substance groups and indicates the purpose of use.

Table 5.3-5. Characteristic lead compounds emitted from adhesives and sealants, identified in chamber air by GC/MS.

Substance	CAS-No.	Remarks
Cyclic siloxanes	-	Polymeric matrix
Ketoximes		
2-Butanone oxime (MEKO)	96-29-7	Crosslinking agent, fragmentation product
2-Propanone oxime	127-06-6	Crosslinking agent, fragmentation product
4-Methyl-2-pentanone oxime	105-44-2	Crosslinking agent, fragmentation product
Aromatic hydrocarbons		
Toluene	108-88-3	Solvent
Ethylbenzene	100-41-4	Solvent
m,p-Xylene	1330-20-7	Solvent
o-Xylene	95-47-6	Solvent
Alcohol	-	Solvents
Terpenes		
α-Pinene	80-56-8	Solvent
β-Pinene	18172-67-3	Solvent
3-Carene	498-15-7	Solvent
Limonene	5989-27-5	Solvent
Glycol esters		
Texanol®	25265-77-4	Solvent, film former
TXIB®	6846-50-0	Solvent, film former

Figure 5.3-12 shows a total ion chromatogram of a ketoxime curing silicone sealant.

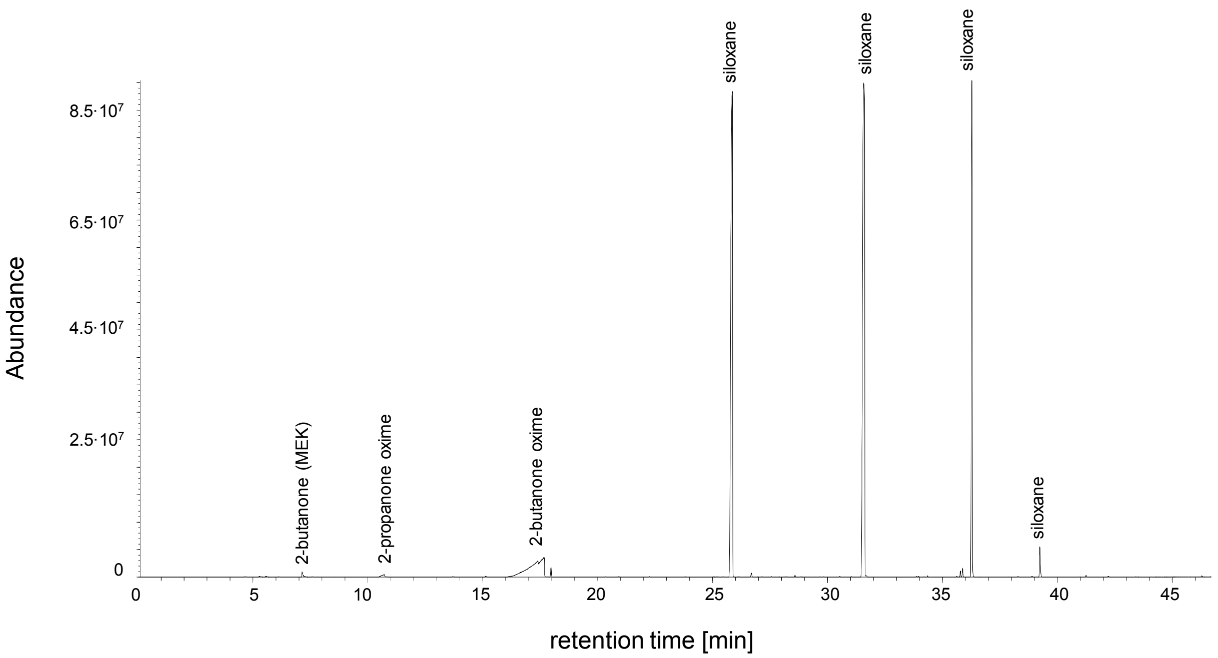


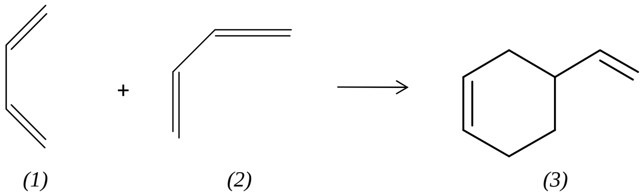
Figure 5.3-12. Total ion chromatogram (GC/MS) obtained by thermal extraction from a ketoxime curing silicone rubber (sample S-7).

It has to be pointed out that further toxic substances were identified during material emission tests. The polyurethane rubber (sample S-10) released o-phenetidine, a toxic hydroxylamine, in significant chamber concentrations of 100 µg/m³ after 24 h increasing to 116 µg/m³ after 120 h. A polybutadiene rubber (sample S-3) generated benzene, a known toxic compound, with chamber concentrations of 18 µg/m³ after 24 h, decreasing to 3 µg/m³ after 144 h.

The emissions from the polybutadiene rubber (sample S-3) differed in generally from the other sealant materials. Instead of a broad range of primary emissions, such as solvents, secondary products occurred during chamber tests.

Diels-Alder cyclic addition

Reaction products of Diels-Alder cyclic addition are well-known substances, which can be formed during the production of styrene-butadiene-copolymers (SBR) in the material itself. Common applications of SBR are e.g. foam backings for carpets (Sollinger et al., 2003). A conspicuous substance is 4-vinylcyclohexene (4-VCH) *(3)* as reaction product from the residual monomers *cis*- *(1)* and *trans*-butadiene *(2)* (Equation 5-4). As such secondary products are generated in the depth of the material, long-term emissions within museum showcases are suspected. Moreover, the substances 3-cyclohexene-1-carboxaldehyde and methyl-cyclohexene-carboxaldehyde (the specific isomer could not be identified) were analysed in chamber air. However, it remained unanswered if these compounds were also formed as secondary emissions by a similar reaction process as no feasible reactants were detected.



(5-4)

Alternatives to these customary sealant formulations proved to be very low emissive. Book linen adhesive emitted mainly maleine acid dibutyl ester. Polyurethane cold glue showed negligible emissions of butylhydroxytoluene (BHT), phenol and squalene.

It has to be highlighted that for all investigated adhesives and sealants, no acetic acid emissions were identified. However, similar to lacquers and coatings, secondary reactions proceeded.

Furthermore, deviations in the emission spectrum even in one sample became obvious during this test series, which shows that the process of material preparation varies significantly and can be attributed to the manual application of coating materials and the mixing of two-pack products.

5.3.1.3 UV-curing systems

Printer's inks

Emissions from printer's inks increased fast immediately after loading reaching chamber concentrations of 1422 µg/m³ (sample PI-4) and 1653 µg/m³ (sample PI-2) after 5 h. This increase resulted from high solvent portions of very volatile compounds, especially of the low-boiling acetone (*bp* = 56°C). Due to a fast evaporation, emissions declined rapidly over the testing time at factors of 4 to 9 to 133 µg/m³ (sample PI-2) and 381 µg/m³ (sample PI-4), respectively. Salthammer (1997) pointed out that the tight wrapping of test specimens with plastic foil immediately after production to inhibit the undesired release of volatiles during transportation to the laboratory might be a problem. Emitted VOCs may be readsorbed on the sample surface again and are then explosively released when the specimen is unwrapped yielding elevated initial values. This fact may also be applied here.

The same curve progress applied for UV-curing adhesives. However, as the conditions were rather a *"worst case scenario"* than real environmental conditions, neither Σ(VOC)-values nor SER_m-values are listed here.

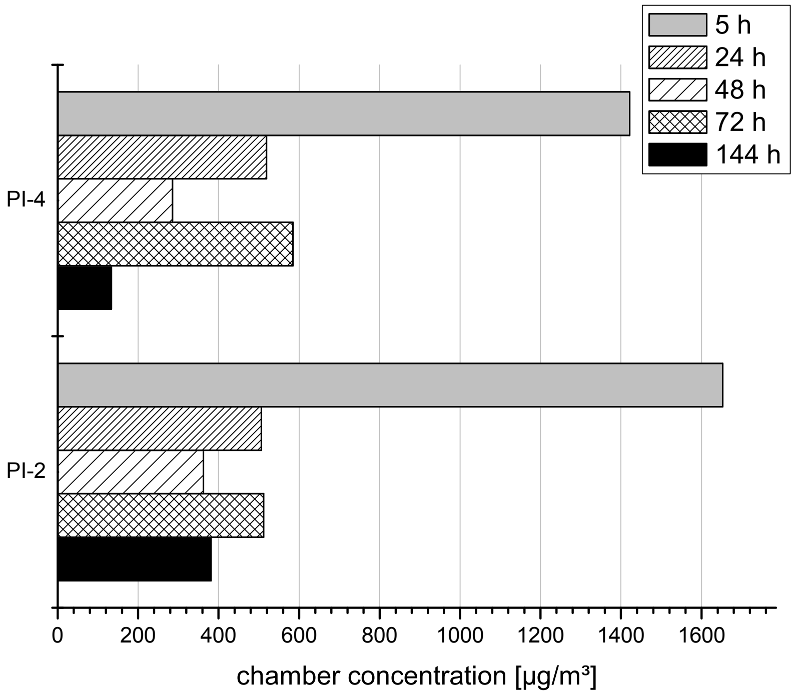


Figure 5.3-13. Chamber concentrations *versus* time (*t*) for printer's inks during chamber emission tests, identified by GC/MS.

All investigated UV-curing systems emitted unreacted acrylate monomers and those photoinitiators which were contained in their formulations as these are usually added in non-stoichiometric amounts for technical reasons (Salthammer et al., 2002).

In order to form radical species which initiate polymerisation reactions, photoinitiators undergo fragmentation processes. In general, two basic groups of photoinitiators are distinguished: The so called Type I photoinitiators undergo α-cleavage (Norrish I reaction) upon irradiation to form radical species which finally initiate the photopolymerisation process. Type II photoinitiators undergo complex formation in the excited state. The reaction efficiency is enhanced by tertiary amines as reaction partners (Hageman, 1989; Allen et al., 1999; Davidson, 1999).

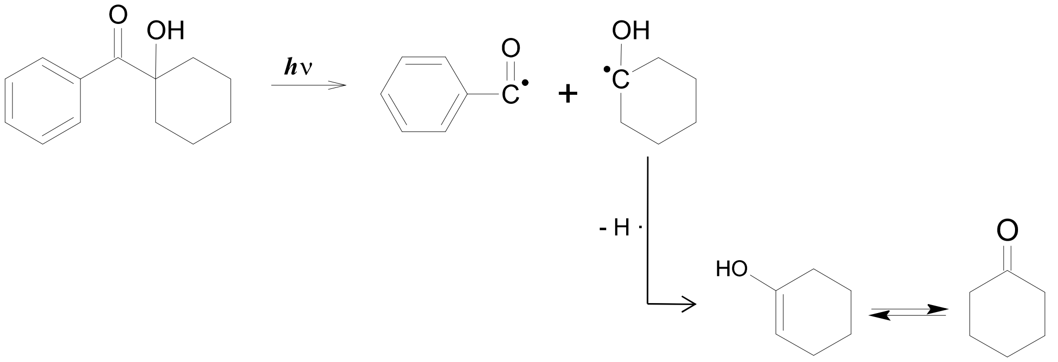
The photoinitiators HCPK, HMPP and DMPA applied in investigated systems undergo α-cleavage (Norrish-I reaction) under formation of benzoyl radicals that initiate the polymerisation process (Chang et al., 1992). Benzophenone (BP) is a Type II photoinitiator with an tertiary amine as reaction partner forming both a ketyl radical and an aminoalkyl radical (Arsu et al., 1995; Fouassier, 1995; Allen, 1996). Due to this fragmentation processes, secondary substances were identified during chamber tests and are listed in Table 5.3-5.

Table 5.3-5. Applied photoinitiators and photofragments identified by GC/MS in the chamber air.

Source	Detected fragments	Sample no.
HCPK	Benzaldehyde, cyclohexanone	PI-1, PI-2, PI-3, UV-1, UV-2
DMPA	Benzaldehyde	UV-1
HMPP	Benzaldehyde	PI-2, PI-4, UV-1, UV-2, UV-4, UV-5
-	2,4,6-Trimethylbenzaldehyde	PI-1, PI-2, PI-3
BP	-	-
POEA	2-Phenoxyethanol	PI-1, PI-2, PI-3, PI-4
POEA	2-Phenoxyethyl acetate	PI-2

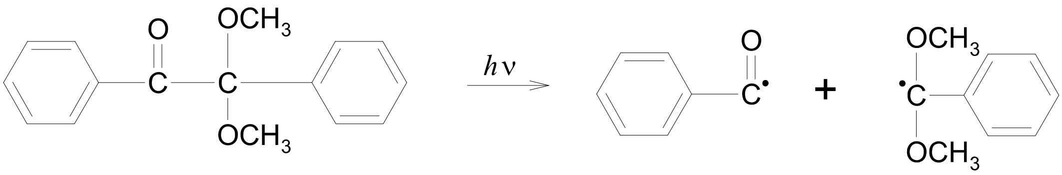
- unknown

Cyclohexanone and benzaldehyde were detected as photofragments of HCPK. In most cases, emitted concentrations of cyclohexanone were a factor of 3 higher than values of benzaldehyde. These findings can be explained by photochemistry of HCPK (Phan, 1986). According to this, α-cleavage of HCPK results in the formation of a benzoyl radical and a hydroxy-cyclohexyl radical, followed by hydrogen abstraction and keto-enol-tautomerization (Equation 5-5, according to: Salthammer, 2000).



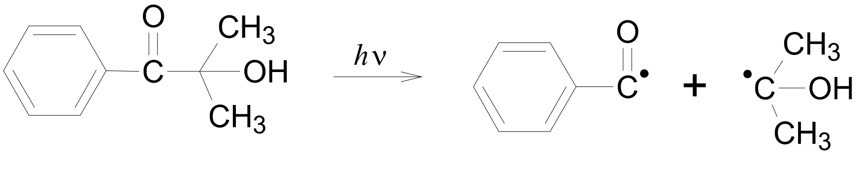
(5-5)

A benzoyl radical can also be produced by photochemical α-cleavage (Norrish I) of DMPA (Phan, 1986) as shown in Equation (5-6, according to: Hageman, 1989).



(5-6)

The same applies for the the fragmentation of HMPP (Equation 5-7, according to: Kirchmayr et al., 1982; Dietliker, 1998).



(5-7)

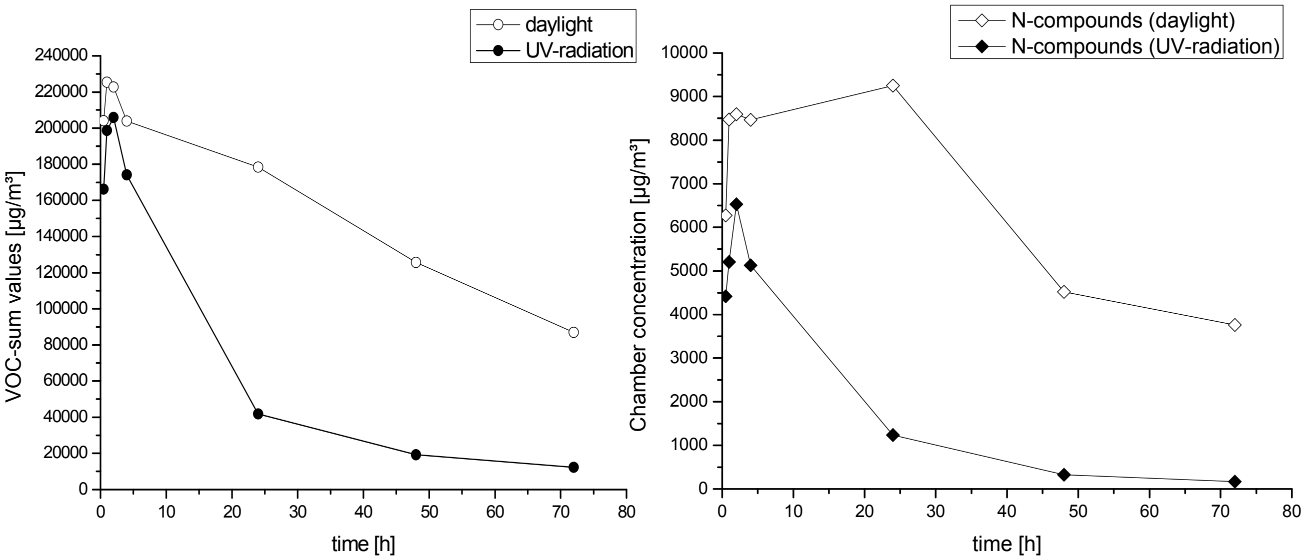
As reported in the literature, the same generation process applies also for 2,4,6-trimethyl-benzaldehyde after α-cleavage of 2,4,6-trimethyl-benzoyl-diphenyl-phosphine-oxide (TBDPO) and di-(2,4,6-trimethyl-benzoyl)-phenyl-phosphine-oxide (DTBPPO) (Salthammer et al., 2002). Even though 2,4,6-trimethylbenzaldehyde were detected during emission analyses of all printer's inks with the exception of sample PI-4 (see Table 5.3-5), none of the photoinitiators mentioned above were identified. It cannot be excluded that one or both of them are applied in the respective formulations, but no evidence could be proved as liquid material samples were not available. 2-Phenoxyethanol and 2-phenoxyethyl acetate were analysed as typical decomposition products formed by hydrolysis of the acrylate monomer POEA.

Odorous problems by application of UV-curing products result from those low-molecular weight by-products, which do not enter into an initial or radical reaction and are, thus, released from the material surface during or after curing (Köhler, 1997).

Comparable to other coating systems, printer's inks emitted also typical solvents, such as acetone, 1-methoxy-2-propylacetate and n-butylacetate as well as the additive 2,6-di-tert. butyl-4-methylphenol (BHT).

UV-curing adhesives

A conspicuous observation regarding UV-curing adhesives was the emission of several nitrogen-containing compounds, which were detected in the chamber air by GC/MS. As mentioned earlier, this kind of experimental set-up was rather a *"worst-case"* situation than comparable with a real indoor scenario, but helpful in order to obtain information about possible photofragments and further volatile organics escaping into chamber air. As described in section 5.2.2, two different chamber emission tests were carried out for samples UV-4 and UV-5: (i) drying under normal daylight and (ii) drying under UV-radiation. As the photoinduced polymeric reactions in the material proceed slow without subjection to UV-radiation, Σ(VOC)-values remained on a high level during testing time of 72 h. The concentration *versus* time curve of Σ(VOC)-values under UV-radiation decreased relatively fast. Whereas 0.5 h after loading there was just a difference of about 1.3 between Σ(VOC) (daylight) and Σ(VOC) (UV-lamp), the Σ(VOC)-value (daylight) was seven-fold higher than Σ(VOC) (UV-lamp) after the testing time of 72 h, as visualized for sample UV-5 in Figure 5.3-14a. This results of the decelerated hardening process of the adhesive without a strong UV-source. The product remains longer in the liquid state; photochemical reactions are on a very low level resulting in high emissions, which continue over a long time period.



Figures 5.3-14a and b. Concentration *versus* time profiles for Σ(VOC)-values (5.3-14a) and for N-containing compounds (5.3-14b) of sample UV-5 under daylight and under UV-radiation, identified by GC/MS.

In addition, N-containing compounds with retention times between 25 min. and 37 min. were detected in chamber air of UV-curing adhesives under daylight. Figure 5.3-14b shows chamber concentration *versus* time for N-containing compounds under daylight and under UV-radiation. N-containing substances occurred in chamber air of each sample at the retention time gaps 25-30 min. and 35–40 min. Main fragment ions were characterized at m/z 123 and m/z 81 (N-substance 1) as well as at m/z 108/109, m/z 55 and m/z 95, respectively (N-substance 2) and m/z 80, m/z 55 and m/z 95, respectively (N-substances 3 and 4). Even if they could not be identified, the accordance of the findings gives strong evidence that the compounds are residues or fragmentation products of constituents within the formulations.

It can just be assumed that those N-containing compounds may be part of the photochemical substances contained in the liquid product ready to initiate a photoinduced polymerisation process. This would rationalize the difference in substance concentrations detected in chamber air under daylight and under UV-radiation as they are used up during reaction processes. In the other way around by assuming that those compounds are fragmentation products, chamber concentrations would have been higher under UV-radiation. Figure 5.3-15a shows a total ion chromatogram of sample UV-4 after 1 h. N-containing compounds are highlighted in the spectrum. A mass spectra of an N-containing compound detected during chamber emission tests of sample UV-4 is given in Figure 5.3-15b.

Additionally, new substances occurred regarding sample UV-5 under UV-radiation, namely camphor, benzaldehyde, atrolactin acid as well as a cyclohexanol derivate. Another conspicuous observation is the fact that samples UV-4 and UV-5 released acetic acid under daylight, but not under UV-radiation. Chamber concentrations of acetic acid were 1011 µg/m³ (sample UV-4) and 445 µg/m³ (sample UV-5) after 0.5 h and decreased rapidly under the limit of detection (LOD: 1 µg/m³) after 72 h.

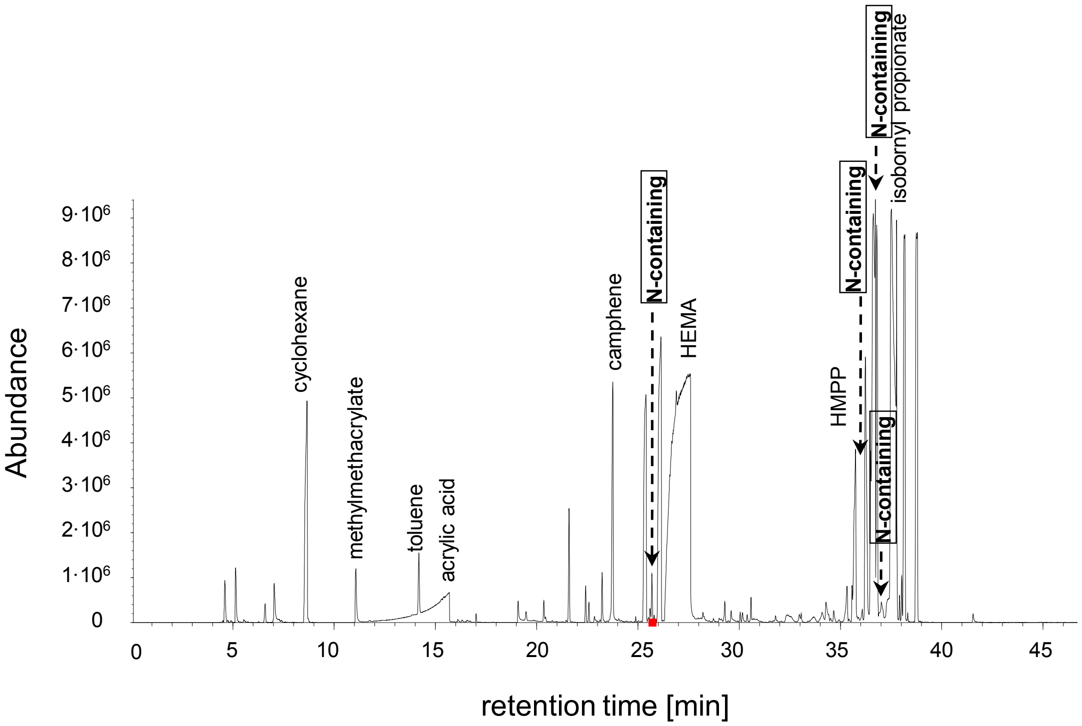


Figure 5.3-15a. Total ion chromatogram (GC/MS) of sample UV-4 under daylight after 0.5 h with marked N-containing substances.

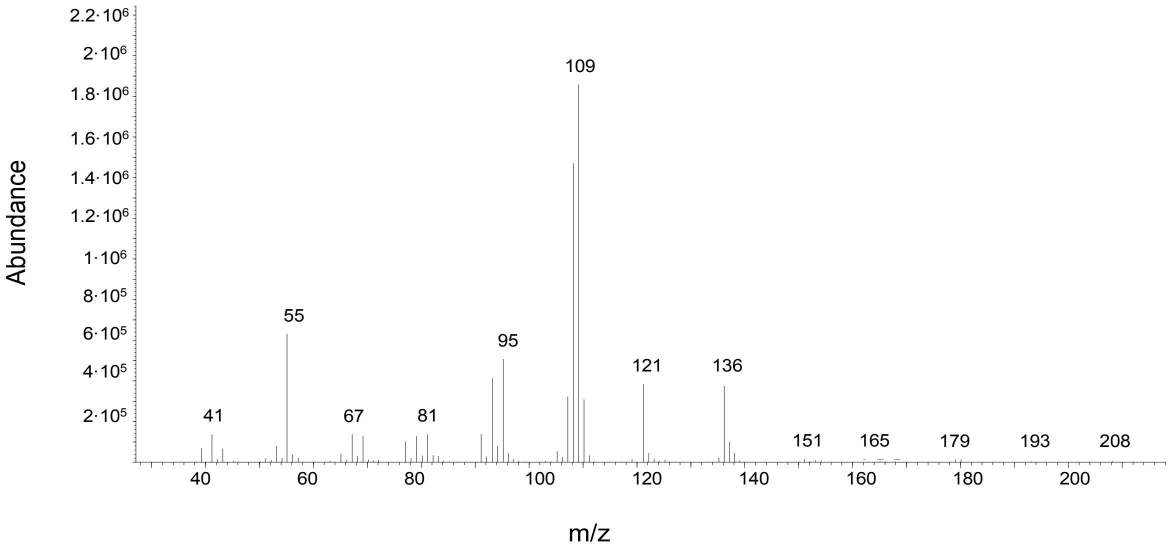


Figure 5.3-15b. Mass spectra of N-containing substance detected in chamber air of sample UV-4 at retention time 36.8 min. with the main fragment ions at m/z 108/109, m/z 55 and m/z 95.

5.3.1.4 Wood-based products

Surface area specific emission rates (SER_A-values) of wood-based products varied between 744 µg/(m^{2*}h) at maximum after 24 h and 24 µg/(m^{2*}h) at minimum after 72 h, which corresponds to Σ(VOC)-values between 4134 µg/m³ and 131 µg/m³. Figure 5.3-16 illustrates chamber concentrations *versus* time (*t*).

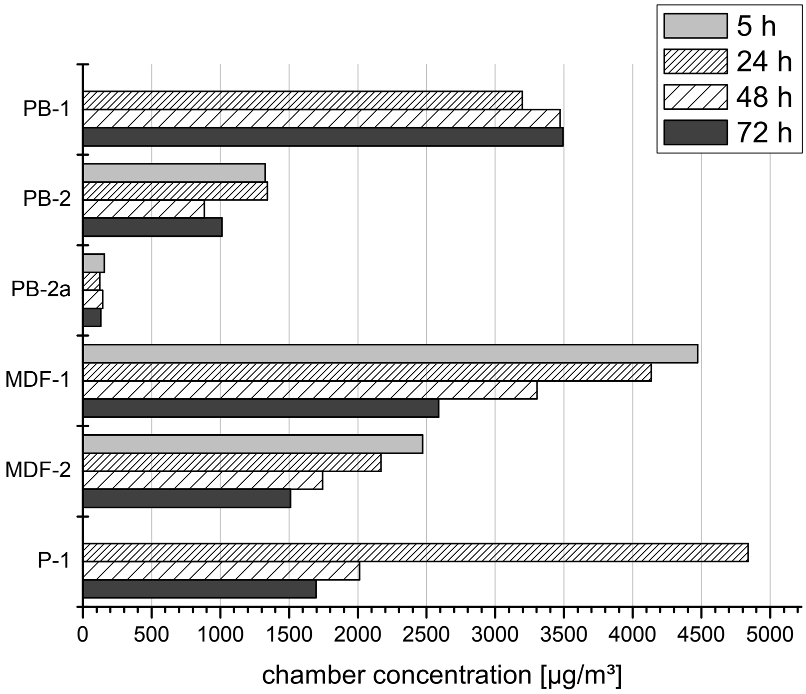


Figure 5.3-16. Chamber concentration *versus* time (*t*) for wood-based products during chamber emission tests.

As can be seen, chamber concentrations of medium density fibreboards as well as of the plywood with anti-slip covering showed highly elevated initial concentrations, which declined fastly so that it can be assumed that emissions can be further lowered by extending the ventilation time before installing the construction material in the showcase.

It was furthermore found that emissions can be markedly reduced by covering cut surfaces. Σ(VOC)-values from a particle board (sample PB-2) ranged between 1343 µg/m³ (24 h) and 1012 µg/m³ (72 h). In contrast, emissions of the same raw material just with laminated cut surfaces (sample PB-2a) were lowered at factors between 10 and 8 due to a markedly reduction of main characteristic compounds, which are summarized in Table 5.3-6.

Table 5.3-6. Sum values of characteristic lead compounds of wood-based products in chamber air after 5h and 72h analysed by GC/MS.

	PB-1	**PB-2**	**PB-2a**	**MDF-1**	**MDF-2**	**P-1**
Lead compounds	**Chamber concentrations in µg/m³ after 24 h/72 h**					
Formaldehyde	176/242[1)]	103/106	87/83	40/40	44/46	9/7
Formic acid	325/337	140/136	< LOD	300/258	350/338	69/58
Acetic acid	829/809	566/470	< LOD	1078/869	742/699	4634/1619
Terpenes	373/320	94/55	3/3	290/193	50/8	n.d.
Σ(VOC)	**3196/3492**	**1343/1012**	**125/131**	**4134/1094**	**2169/1510**	**2013/1695***

LOD limit of detection
[1)] no reliable result due to analytical artefacts
* 48 h-value
n.d. not detected

All tested products emitted the VVOCs formaldehyde, formic acid and acetic acid which are known for their corrosive potential on artwork materials. However, the majority of tested wood-based products were labelled as low formaldehyde emissive and formaldehyde free, respectively. Regarding samples PB-1 and PB-2 it has to be pointed out that equilibrium formaldehyde concentrations are the determining factor for labelling "E1" classification and "Blue Angel" labelling (RAL-UZ 76, 2003), respectively. Investigation time in this study (72 h) was too short to reach equilibrium. During chamber emission tests requested for labelling, test specimens remain at least 10 days in the chamber. If equilibrium is not reached after 28 days, emission tests are broken off.

Samples MDF-1 and MDF-2, labelled as "E1" and "ZF" (*zero added formaldehyde*) released between 40 µg/m³ und 45 µg/m³ formaldehyde into chamber air. As the manufacturer declares that no additional formaldehyde was added, it can be assumed that formaldehyde emissions result from the wood itself. Meyer and Boehme (1997) stated that natural wood emit formaldehyde as secondary emission due to the decomposition of lignin under the influence of light. The main primary emission sources in the past were formaldehyde adhesive agents (urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde resins) (Andersen et al., 1975; Zeppenfeld und Grunwald, 2005). The known potential of these resins to emit formaldehyde is caused either by hydrolysis of the cured resin or by the emission of residual formaldehyde due to incomplete polymerisation during the production process.

Organic acid emissions result from the natural acid content of wood, which is generated by the degradation of saccharides and starch. Thus, acid exists either free or chemically bound within the wooden structure and is emitted during the ageing process. Acid emissions are hence resulting from hydrolysis of acetyl groups of hemicelluloses and of side chains of lignin, respectively (Fengel and Wegener, 1989). Acetic acid may also be emitted as secondary reaction product due to thermal stress during the production process of some wood-based materials and cork from degradation of polyoses (hemicelluloses). For this reason, acetic acid is in most cases emitted paired with the heterocyclic aldehyde furfural (Horn et al., 1998) as detected for samples MDF-1 and MDF-2. Uhde and Salthammer (2007) assumed that the acid-catalyzed degradation process of hemicelluloses is nearly an auto-catalyzed process due to the high amounts of acetic acid formed during thermal production process steps.

Emissions of samples PB-1 and MDF-1 showed the occurrence of some aldehydes and their corresponding carboxylic acids, e.g. n-hexanal/hexanoic acid, n-heptanal/heptanoic acid, octanal/octanoic acid. Carboxylic acids were factors of 2 to 13 lower than values of aldehyde emissions. It can be assumed that these substances are further secondary emission products resulting from thermal and oxidative degradation processes of fatty acids in the wood chips due to drying and pressing processes during manufacturing (Salthammer and Fuhrmann, 2000). Saturated and unsaturated aldehydes from C_5 to C_{11} belong to the most problematic and undesired compound classes in indoor air due to their high odour (Devos et al., 1990). Moreover, aldehydes are strong irritiants, especially formaldehyde.

Terpenes belong to the isoprenoides and are natural components of wood and wood-based products, respectively, especially of coniferous wood due to its higher resin content. Particularly the monoterpenes α-pinene, β-pinene, 3-carene and limonene are typical volatile ingredients of wood and wood-based products and are therefore always released as characteristic primary emissions. Lacquered products, e.g. samples MDF-3a and MDF-4a, released also substances that are typical primary emissions from lacquers and coatings: aromatic hydrocarbons (toluene, xylene-isomers, C3-/C4-benzenes), carboxylic esters and glycol esters (n-butylacetate, 1-

methoxy-2-propylacetate) as well as alcohol (diacetone alcohol). With 11 out of 18 identified substances, lacquer emissions represented 61% of the Σ(VOC)-values.

Another interesting observation was noted for sample P-1, plywood with anti-slip covering, which emitted just five substances (acetone, methylacetate, acetic acid, n-pentanol, n-hexanal) with decreasing emission rates over the testing time. However, this material is to be evaluated as a strong emission source due to highly elevated acetic acid concentrations, which constitute 96% of the Σ(VOC)-value ranging from 4840 µg/m³ after 5 h to 1695 µg/m³ after 24 h.

5.3.1.5 Construction and other materials

Among construction and other materials just nine substances were detected in total. Released compounds were identified just as several aliphatic hydrocarbons constituting nearly 90% of all released substances. Residual emissions are non-identified substances. Only the aluminium composite board showed slightly heightened emissions during thermal extraction in comparison to ceramics and plastic plates due to solvents resulting from the lacquered cover plates. Emissions of the ceramic and the plastic plates were negligible. The main emission source of glass adhesive foil was identified as phenol.

5.3.1.6 Cover fabrics

Cover fabrics proved also to be very low emissive. Raw textiles without any surface treatment, such as linen materials, were nearly emission free. Within this material category, enhanced emissions during thermal extraction were detected concerning book linen with adhesive (sample T-2a) as the adhesive layer releases the common key precursor maleine acid dibutyl ester. Also sample T-4 (100% polyester) as a synthetic material can be evaluated as higher emissive than untreated natural fibres. Ten various substances were detected during emission analysis. Beneath aromatic hydrocarbons, alkanes and aldehydes as low emitters, 2,6-diisopropylnaphthalene (DIPN) was the most abundant substance. DIPN is utilized as hydrophobic modifier of plastic materials.

5.3.1.7 Summary of the results

Results of material emission tests demonstrate that products currently used for construction and decoration of showcases release a broad variety of volatile organics. The emission strength of materials increases in the following order: cover fabrics < construction and other materials < wood-based products < UV-curing systems < adhesives and sealants < lacquers and coatings.

This sequence reveals that solid raw materials without any additional finishing, such as textiles and ceramic plates, can be evaluated as low emissive. The higher the solvent proportion in the formulation, the higher is the emission strength. For this reason, the majority of primary emissions were identified as solvent and additive residues. Solvents and additives are organic liquids which are added to dissolve the resin and to improve the processing properties. No correlation was found between the emission potential and the resin (binder). Furthermore, material compounds undergo chemical reactions resulting in the release of secondary products. Three processes are of main importance regarding the product application in the museum environment: (i) hydrolytic cleavage of acetyl esters, which are contained in high concentrations especially in coating materials, yielding to elevated acetic acid concentrations, (ii) separation of ketoximes by neutral curing silicone sealants during curing and (iii) the release of unreacted photoinitiators and photofragmentation products, such as radical species, by UV-curing systems. Beneath 2-butanone oxime (MEKO), further harmful substances were detected as primary emissions from sealants, namely the toxic hydroxylamine o-phenetidine and the carcinogenic substance benzene.

Regarding the broad range of emissions which are primarily attributed to coating materials, sealants and UV-curing systems, emissions from wood-based products, which are known to be the main emission source in traditional showcase types, become secondary. Even though wooden products, which are even labelled as low emissive and formaldehyde free, respectively, still release formaldehyde, formic acid and acetic acid, the amounts are markedly lower than those of solvent emissions. Information on material safety data sheets does not show any correlation with identified emissions.

The majority of identified most abundant substances correspond with those reported in earlier material emission studies (Mølhave, 1982; Girman et al., 1986; Yu and Crump, 1998; Salthammer et al., 1999; Salthammer, 2004; Wilke et al., 2004). In principle, this finding is not remarkable as there are no products available on the market, which are especially designed for museum purposes.

As also the objects on display may act themselves as potential emission sources, a selection of materials for conservation and restoration purposes was examined in the following step.

5.3.2 Emissions from conservation and restoration materials

In general, natural products proved to be very low emissive. Highly elevated emissions of natural resins as well as of some synthetic resins resulted from solvent addition. Solvents caused huge peaks in the chromatograms, perhaps overlaying VOCs released by the resin or polymer itself. Comparison measurements as done regarding dammar resin (samples D-1 to D-3) showed that those emissions are negligible as peaks are very near the background value. Highly increased emissions caused by the solvent proportion yielded the broad range of synthetic resin emissions and increased natural resin emissions as illustrated in Figure 5.3-17. The data base on the absolute release of each test specimen and are thus quantified in [µg/m³].

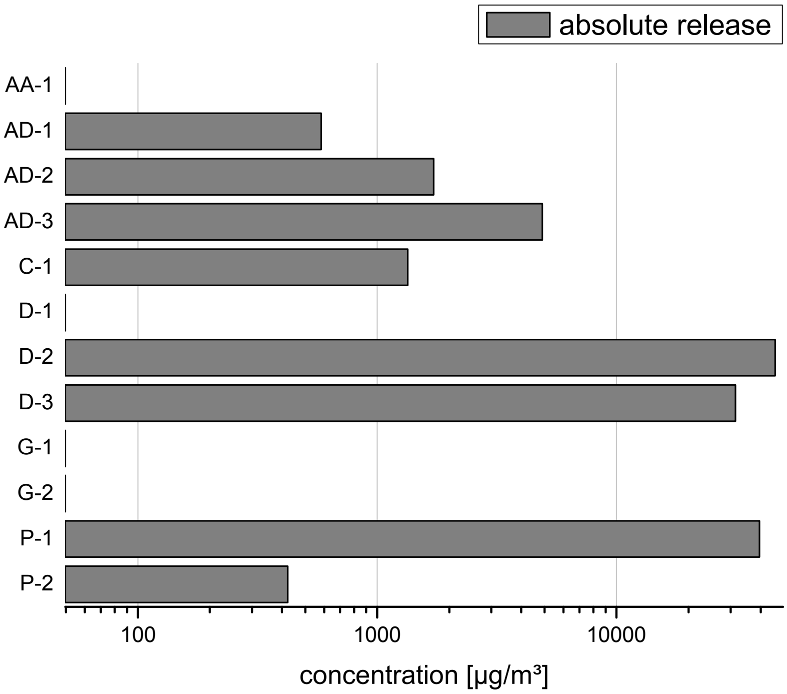


Figure 5.3-17. Absolute release of volatile organic compounds (VOCs) from conservation and restoration material samples during screening emission analysis via thermal extraction (for abbreviations, see Table 5.1-10, page 50).

Table 5.3-7 compiles the number of identified substances (No. of ident. VOCs) as well as the main characteristic compounds inclusive CAS registry number of each test specimen. Moreover, an evaluation based on these findings obtained by thermal extraction is given whether the product is low, moderate or high emissive.

Table 5.3-7. Remarkable substances of conservation and restoration materials during thermal extraction identified by GC/MS. Evaluation of the emission strength on the basis of thermal extraction results.

Sample no.	Material	No. of ident. VOCs	Main characteristic compounds	CAS.-No.	Evaluation
G-1	**Hide glue**	9	Acetic acid	64-19-7	Low emissive
			Butanoic acid	107-92-6	
			n-Decanal	112-31-2	
			n-Nonanal	124-19-6	
G-2	**Fish glue**	4	Acetic acid	64-19-7	Low emissive
			n-Decanal	112-31-2	
			n-Nonanal	124-19-6	
			Phenol	108-95-2	
C-1	**Hydroxypropyl cellulose**	6	Long-chained iso-alkanes (C_{11}-C_{15})	-	Moderate emissive
D-1	**Dammar resin**	1	Sesquiterpenes*	-	Low emissive
D-2	**Dammar varnish glossy**	18	α-Pinene	80-56-8	High emissive
			β-Pinene	18172-67-3	
			3-Carene	498-15-7	
			Limonene	5989-27-5	
			Camphene	79-92-5	
			m-Cymene	535-77-3	
			Terpinolene	586-62-9498-15-7	
			Terpene alcohol*	-	
D-3	**Dammar varnish**	12	1,2,4-Trimethylbenzene	95-63-6	High emissive
			2,2,4,4,4-Pentamethylheptane	13475-82-6	
			Ethyltoluenes**		
			n-Propylbenzene	103-65-1	
			α-Pinene	80-56-8	
			Indane	496-11-7	
R-1	**Hydrogenated hydrocarbon resin**	11	Long-chained iso-alkanes/n-alkanes*	-	High emissive
			Xylene-isomers**	-	
			Methyl decaline*	-	
			Dimethyl decaline*	-	

* isomers not listed ** identification of the exact isomer was not possible

Sample no.	Material	No. of ident. VOCs	Main characteristic compounds	CAS.-No.	Evaluation
R-2	**Acrylate resin**	5	Long-chained iso-alkanes/n-alkanes*	-	Low emissive
			Acetone	67-64-1	
			Toluene	108-88-3	
AA-1	**Homopolymer acrylic acid**	12	Long-chained iso-alkanes**	-	Low emissive
			Cyclic siloxanes**	-	
AD-1	**Acrylic dispersion**	12	Acrylic acid	79-10-7	Moderate emissive
			Acetic acid	64-19-7	
			Butyl acrylate	141-32-2	
			Dibutylether	142-96-1	
			1,2-Propandiol	57-55-6	
			Propione acid dibutylether	590-01-2	
			n-Butylacetate	123-86-4	
AD-2	**Polyvinylacetate (PVAc)/ dibutyl maleate dispersion**	13	Acetic acid	64-19-7	Moderate emissive
			n-Butanol	71-36-3	
			Vinyl acetate	108-05-4	
			Acetamide	60-35-5	
AD-3	**Acrylic dispersion**	20	1,2-Propandiol	57-55-6	High emissive
			2-(2-Butoxyethoxy)ethanol	112-34-5	
			1-Methoxy-2-propanol	107-98-2	
			DPGMME	34590-94-8	
			Acetic acid	64-19-7	
P-1	**Vinyl paint**	13	Dicarboxylic esters**	-	High emissive
			1,2-Propandiol	57-55-6	
P-2	**Acrylic paint**	14	2-(2-Butoxyethoxy)ethylacetate	124-17-4	Low emissive
			2-(2-Butoxyethoxy)ethanol	112-34-5	
			TXIB®	6846-50-0	

* isomers not listed ** identification of the exact isomer was not possible

5.3.2.1 Natural products

Animal glues

Animal glues proved to be low emissive by releasing nine (sample G-1) and four (sample G-2) substances, respectively. Even if sample G-1 (hide glue) emitted twice as much as sample G-2 (fish glue), individual peaks of emitted compounds were just slightly above the baseline values in both cases (see Figure 5.3-18). Regarding fish glue (sample G-2), phenol as well as the aldehydes n-nonanal and n-decanal were identified. Beneath these substances, hide glue (sample G-1) emitted additionally butanoic acid, pentanoic acid and neryl acetone. The ketone neryl acetone is detectable as essential oil in plants. Moreover, it is reported to occur as flavour in animal scents, e.g. in pheromones. Butanoic acid as short-chain fatty acid is generated by decomposition of proteins and fats and is therefore a natural ingredient. As further emitted volatile, acetic acid was detected by thermal extraction of both test specimens. Hide glue contains several amino acids, among others 27% glycin (aminoethanoic acid), and is fabricated under utilization of hide and leather waste. It may be supposed that acetic acid results of the recycling of leather waste as this is used for tanning dermals. Another explanation would be the decomposition of glycin either due to animal metabolism or during the treatment of animal waste. However, as hide glue and fish glue are quite heterogeneous materials, the specific origin and ways of treatment from raw materials cannot be traced.

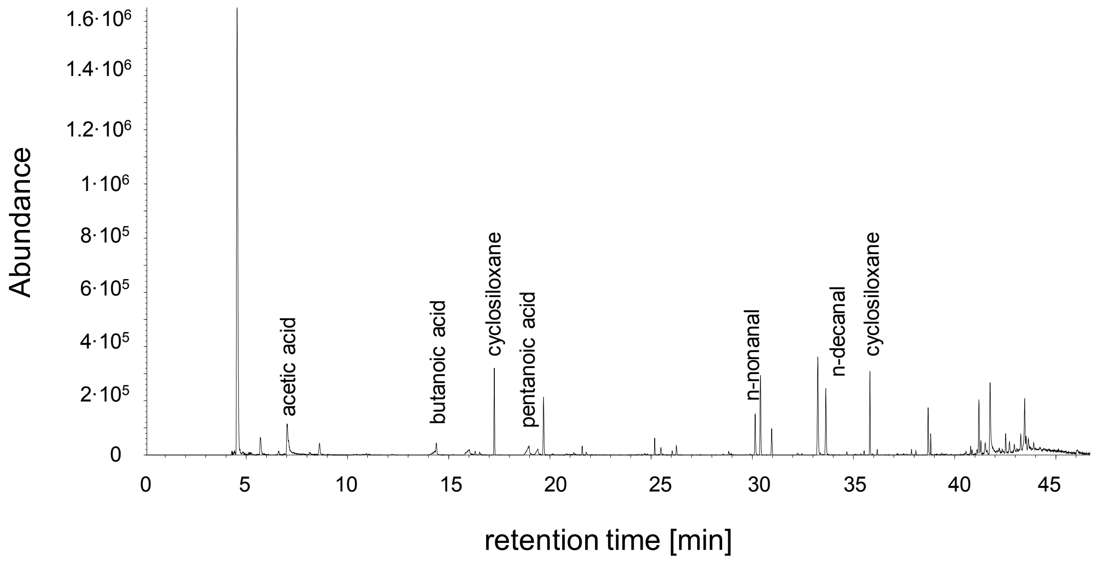


Figure 5.3-18. Total ion chromatogram (GC/MS) obtained by thermal extraction from sample G-1 (hide glue).

Sample C-1, a hydroxypropyl cellulose applied as consolidation medium for paint layers, was moderate emissive by generating several long-chained iso-alkanes and acetone. Moreover, Heyn (2002) analysed 3 ppm formaldehyde within this material.

Natural resins

The pure dammar resin itself (sample D-1) is nearly emission free. Due to its composition, just some sesquiterpenes could be detected in a negligible amount. It becomes a high emissive product when it is dissolved in organic solvents as a processible varnish. Sample D-2, dammar varnish glossy, is dissolved in double rectified turpentine (1:2). Due to the turpentine most abundant substances were the bicyclic terpenes α-pinene, champhene, β-pinene, myrcene and 3-carene as well as monocyclic terpenes, such as limonene, terpinolene and cymene. Also different sesquiterpenes have been analysed. Emissions from sample D-3 as *turpentine free* marked dammar resin are highly elevated. Instead of monocyclic and bicyclic terpenes, main characteristic compounds were identified as a mixture of aromatic hydrocarbons, e.g. ethyl toluenes and trimethyl benzenes.

5.3.2.2 Synthetic products

Synthetic resins

According to the technical data sheet, sample R-1 is a synthetic hydrogenated hydrocarbon resin, which is used as picture varnish and is, therefore, dissolved in a broad variety of organic solvents. The composition explains the emission spectra (see Figure 5.3-19) consisting of long-chained n-alkanes and iso-alkanes and aromatic hydrocarbons (xylene isomers, decalin). Decalin (decahydronaphthalene) is a bicyclic organic compound and widely-used as an industrial solvent. Facing also the other emittents it becomes clear that the resin is dissolved in a typical industrial benzene mixture. In comparison to the high emissive liquid dammar varnishes D-2 and D-3, emissions of sample R-1 are again a factor of 10 higher and can be evaluated as high emissive due to the high solvent portions. Emissions from the resin itself could not be analysed.

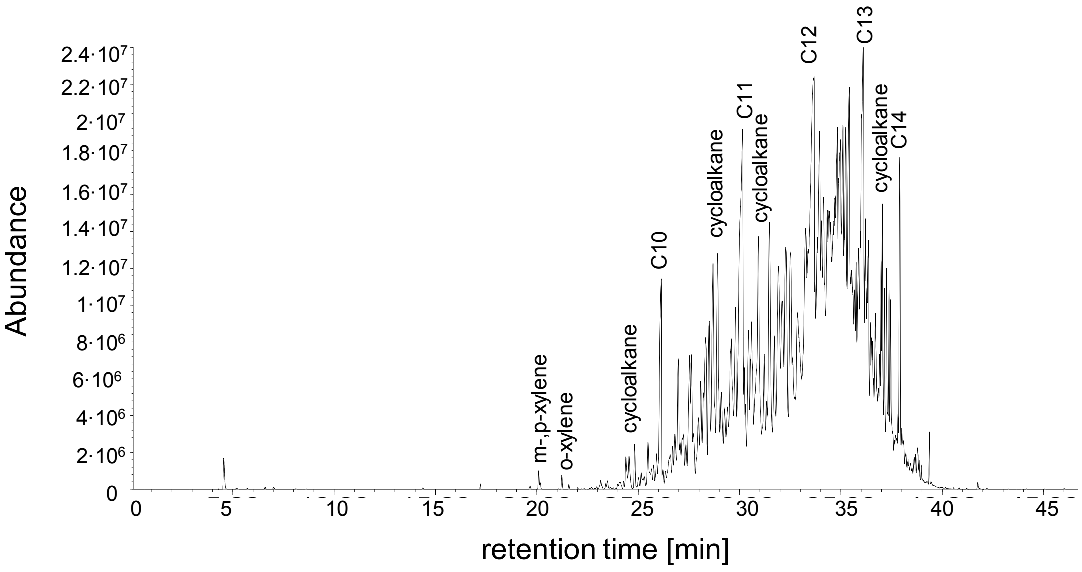


Figure 5.3-19. Total ion chromatogram (GC/MS) obtained by thermal extraction from sample R-1, a synthetic picture varnish.

Another synthetic resin is sample R-2, which may also be used as varnish or as consolidation medium. According to sample R-1, emissions of the resin itself could not be analysed. As it was dissolved in toluene (15%), the solvent was the most abundant substance. Acetone as well as some iso-alkanes were released in negligible amounts. In contrast to samples D-2, D-3 and R-1, this product was low emissive with just five released VOCs.

Acrylic dispersions

Samples AD-1, AD-2 and AD-3 are acrylic dispersions (AD-1, AD-3) and polyvinyl acetate dispersions (AD-2), respectively, which are applied as binding media for paints and/or for consolidation work. The materials released between 12 and 20 individual VOCs during screening emission analysis via thermal extraction. Main emitters were acrylic monomers and various solvents. Sample AD-1 emitted due to its formulation acrylic acid and butyl acrylate as acrylate monomers as well as n-butylacetate, dibutyl ether, 1,2-propandiol and dipropylene glycol as solvents. Ingredients listed in the material safety data sheet (ammonia solution, octylphenoxy polyethoxy ethanol) could not be detected.

According to the material safety data sheet, sample AD-2 is an aqueous polyvinyl acetate/ dibutyl maleate dispersion free of plasticizers. However, diisobutyl phthalate (DIBP) was identified as plasticizer. The amounts were clearly above the baseline value. Further main characteristic compounds were vinylacetate and maleine acid derivates as monomers and n-butanol and acetamide as solvents. Acetamide is a harmful chemical (Xn) and classified as carcinogenic. Similarly to sample AD-1, also sample AD-3 as acrylic dispersion released the monomers methacrylic acid and butyl acrylate. Furthermore, a broad range of various solvents was identified including 1-methoxy-2-propylacetate, 1,2-propandiol, dibutylether and butyl diglycol as well as dipropylene glycol monomethyl ether (DPGMME). Another dominant substance was 2,4,7,9-tetramethyl-5-decin-4,7-diol, which is utilized in water-borne coatings as surfactant. Silicone oils and silicone emulsions are acting as antifoam agents so that silicone compounds were identified in the chromatogram. Although most abundant substances from samples AD-1 and AD-3 were coincide, AD-3 is the highest emissive material among the three tested synthetic consolidation media with the most released individual VOCs in higher amounts than samples AD-1 and AD-2 (see Figure 5.3-20).

However, all three materials emitted acetic acid which suggests that the dispersions contain ethyl acrylates as polymers, even though no supplier information about the specific compositions is available. Acetic acid is formed by ester hydrolysis. It can be assumed that this reaction proceeds already in the material as emission analysis by means of thermal extraction does not allow long diffusion and evaporation processes to the boundary layer between the material and the environmental air and, thus, the progress of secondary reactions within the gas phase.

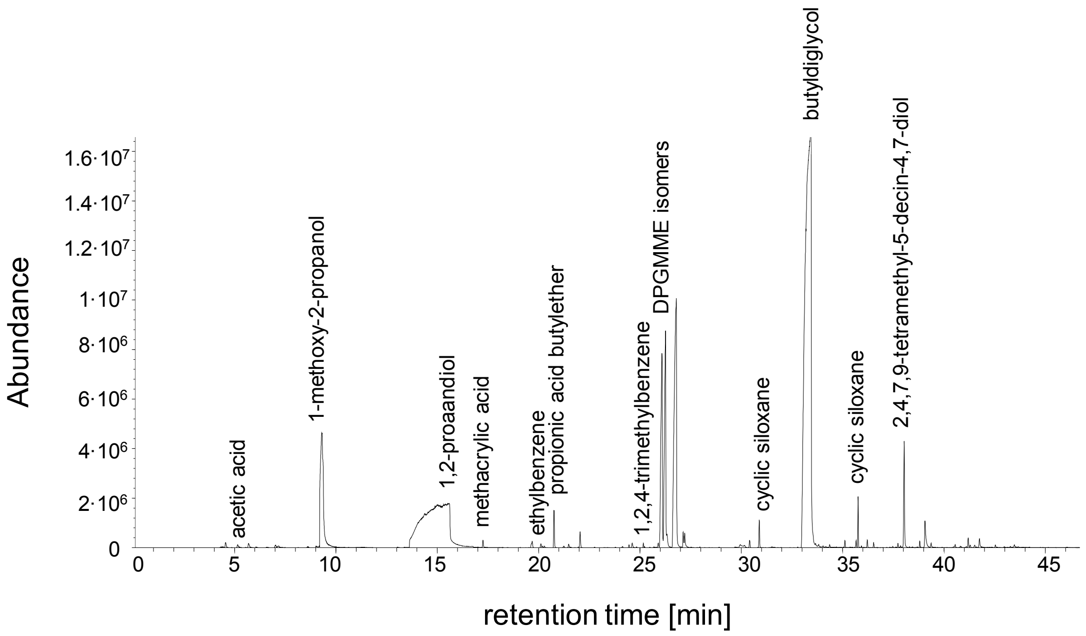


Figure 5.3-20. Total ion chromatogram (GC/MS) obtained by thermal extraction from sample AD-3, an aqueous acrylic dispersion developed for consolidation purposes in conservation.

Paints

Sample P-1 emitted in total 13 individual VOCs. Due to high peak areas of most abundant substances, it is evaluated as high emissive (see Figure 5.3-21). The lead compound was identified as 1,2-propandiol (propylene glycol), which is applied as solvent and plasticizer in paints. Moreover, various non-identifiable dicarboxylic esters and diisobutyl adipate were detected. Adipates are applied as low-temperature plasticizers for vinyl resins and offer in this regard better properties than phthalates (Stoye, 1993). Beneath some long-chained alkanes 2-amino-2-methylpropanol, an alkanolamine, which is often contained in lacquers and paints as additives, has been identified. Emissions of TXIB® were expected as it is a known emission from vinyl products (Yu and Crump, 1998) but could not be detected. According to adhesive testing results it is probable to detect TXIB® within emission chamber tests. In contrast to this, the acrylic paint (sample P-2) was low-emissive by releasing 14 individual VOCs of minor peak areas, as shown in Figure 5.3-22. Most abundant substances were organic esters, such as 2-(2-Butoxyethoxy)ethylacetate and TXIB® as film forming additive. Further identified compounds were long-chained alkanes, acetone as solvent and the plasticizer diisobutyl phthalate (DIBP).

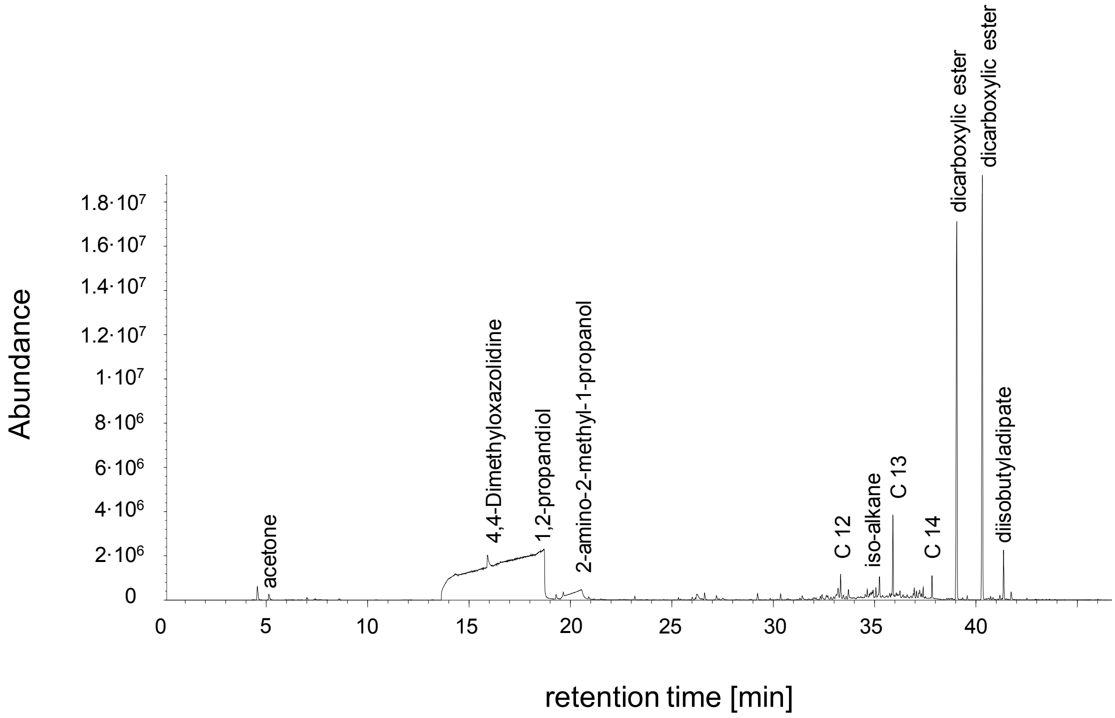


Figure 5.3-21. Total ion chromatogram (GC/MS) obtained by thermal extraction from sample P-1, a vinyl paint (artist colour).

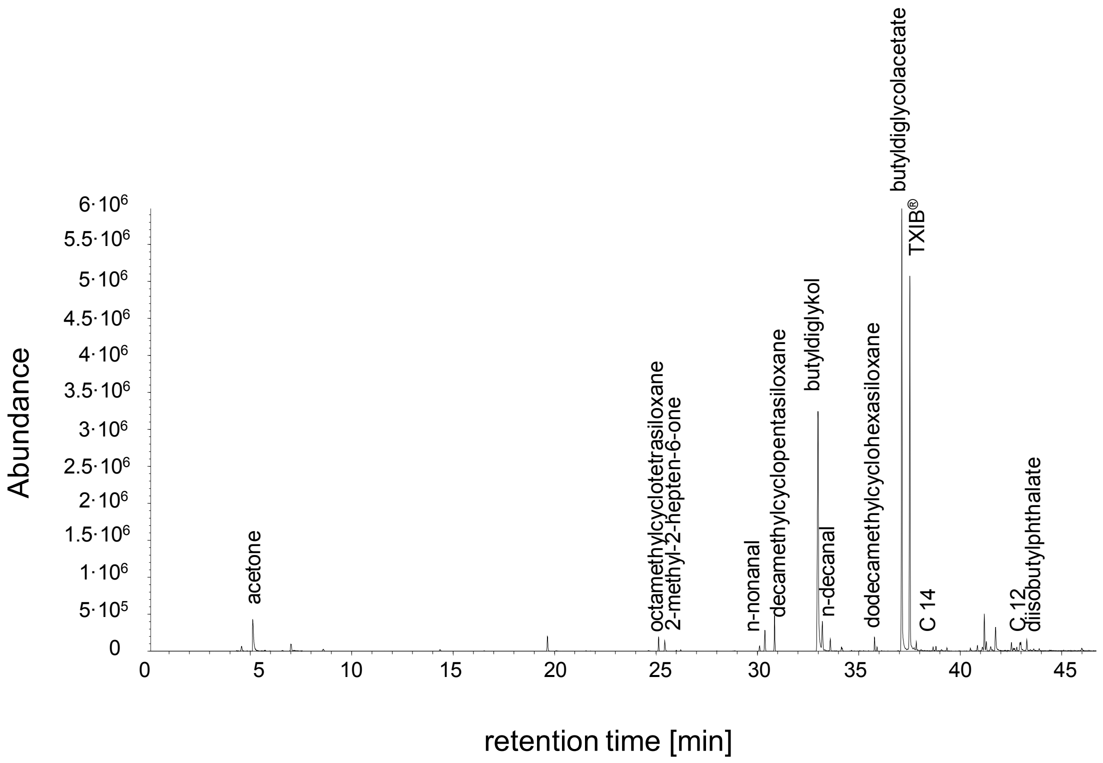


Figure 5.3-22. Total ion chromatogram (GC/MS) obtained by thermal extraction from sample P-2, an acrylic paint (artist colour).

5.3.2.3 Summary of the results

Emissions from conservation and restoration materials are in general comparable to those from construction and decoration materials discussed above. High emissions are always attributed to solvents, which are needed to dissolve synthetic and natural resins. Resins as raw materials, irrespective if natural or synthetic resin, do not contribute markedly to the emission profile. Especially natural products proved to be low emissive, even if natural glues emitted negligible amounts of acetic acid. Moreover, acrylic dispersions might generate increased concentrations of acetic acid due to the polymeric matrix. Similar to coating materials it is also assumed that it is formed by ester hydrolysis. Again there was no correlation between substance lists provided by material safety data sheets and emission results. Among the emissions from an acrylic dispersion, the carcinogenic acetamide was identified. It has to be stated that most of the products released acetic acid, even though all peak values were relatively low. Provided that the materials are not applied on large surface areas, the contribution to indoor air quality should be negligible.

Both emissions from construction and from conservation/restoration materials seem to be evaporation controlled in the initial phase resulting in a decreasing emission rate under test chamber conditions. However, comprehensive analyses of indoor air in museum showcases are necessitated as air exchange rates are to be assumed several factors lower than during material emission tests.

6 Experimental series II

Indoor air quality within museum showcases

In order to pursue the question of correlations and differences between (i) material emission spectra and pollution levels under test conditions and (ii) within a completed showcase, investigations of indoor air quality within museum showcases were performed in the subsequent step. It was furthermore of special interest if secondary products will be detected inside of showcases and if it is possible to conclude from indoor air composition to the specific emission sources.

In a first test series, objects of investigation were seven modern-type showcases directly after construction. Indoor air analyses within thirteen modern-type showcases, which were in museum use for few months up to several years at the time of measurement, were performed in a second test series in order to clarify the question of long-term emissions. The third test series focussed on fourteen showcases of the so called old-type, which have been in museum use for nearly ten to twenty years at the time of measurement.

In the following section investigation parameters, methods of air sampling and utilized analytical devices are explained, before construction types and equipments of investigated showcases are presented. Afterwards, the results of each test series are explained and discussed.

6.1 Parameters of investigation

Emphasize during this investigation step was again on concentrations of volatile and semi-volatile organic compounds (VOCs/SVOCs), formaldehyde and organic acids (formic acid, acetic acid). Attention was also directed to air exchange rates regarding highly sealed *versus* open construction types.

Showcases were closed at least one week before start of the experiments in order to reach equilibrium of material emissions and indoor concentration. If necessary they were additionally sealed to avoid an air exchange with the outer air insofar it was not intended by the manufacturer, e.g. by an open construction with gaps. During sampling it was not allowed to open the enclosure. For this reason, air was sucked through small tubes, which were brought in from outside, where they were coupled with the sampling devices. Parallel to showcase analyses, air sampling was also performed in the environmental room in order to reveal feasible diffusion processes between the environment and the showcase and, thus, for clear identification of emission sources.

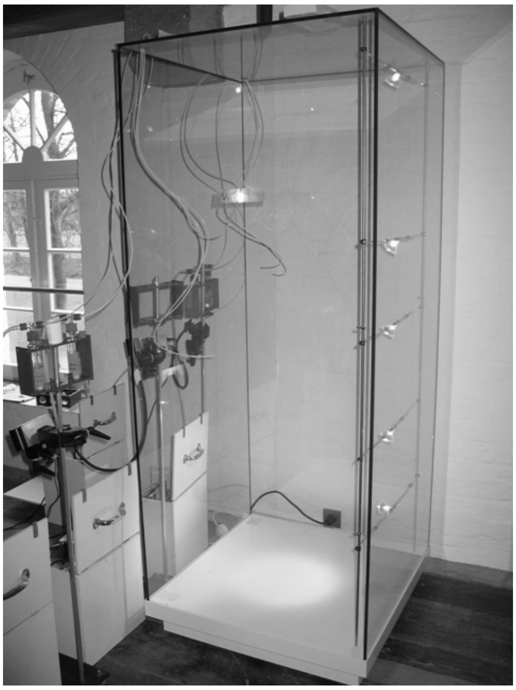


Figure 6.1-1.
Indoor air analyses in modern-type showcases in museum use.

6.1.1 Air sampling and analysis

Air sampling and analysis of VOCs/SVOCs and organic acids were accomplished in the same way as during chamber emission tests. It is therefore referred to section 5.2.3. As air sampling was conducted in ambient air, sampling of formaldehyde was carried out according to VDI 3484 (2001).

Also passive air sampling on Tenax TA® was performed in cases of too small showcase volumes, e.g. regarding table display cases, or if no outer access was available. Tenax TA®-tubes were hung with one closed end and one end equipped with a diffusion cap in the showcase for fourteen days. Analysis was the same as described for active air sampling on Tenax TA®. All given results in this chapter are mean values from duplicate measurements.

Furthermore, analysis of condensable semi-volatile organic compounds (SVOCs) was carried out. This phenomenon of SVOCs which tend toward condensation on glossy surfaces is also denoted as *"fogging"*. Hazy surface films on showcase glasses were washed off with acetone soaked paper towels. Before sampling the paper towels were prepared by extraction with toluene over 20 h and subsequently drying in a nitrogen flow (2 l/min) over night. After sampling the towels were extracted again with acetone and the extract was analysed via GC/MS.

6.1.2 Air exchange rate measurements

Air exchange rate measurements can be performed by three different methods utilizing tracer gas: (i) the concentration-decay method, (ii) the constant-emission method and (iii) the constant-concentration method. For measuring air-exchange rates within showcases, the concentration-decay method was utilized according to VDI 4300-7 (2001) to obtain discrete rates even over short time periods. The measuring device and a fan were mounted inside the showcase. After closing, the showcase was doped with tracer gas (~ 200 ppm N_2O) through a tiny hole in the cover plate. The fan inside ensured a homogenously mixing of the tracer gas into the air. Provided that no tracer gas diffuses from outside into the showcase and that the airflow inside is constant, the tracer gas concentration will decay in an exponentially curve over time. The decreasing tracer gas concentration was plotted against time with a N_2O-analyser (Leybold-Heraeus BINOS) and was also recorded with a voltmeter (Metex M-3610D).

For ideal mixing of tracer gas with the room air, the decay in tracer gas concentration is given by Equation (6-1):

$$\sigma_t = \sigma_{t=t_0} \cdot e^{-nt} \tag{6-1}$$

The obtained gradient between two measured values gives the air exchange rate using Equation (6-2):

$$n = \frac{60}{t_2 - t_1} \cdot \ln \frac{\sigma_{t=t_1}}{\sigma_{t=t_2}} \qquad [h^{-1}] \qquad (6\text{-}2)$$

With n = air exchange rate, h^{-1}, t = time of sampling the tracer gas, min, $\sigma_{t=t0}$ = initial tracer gas content at time t=t_0 (start of injection), cm³/m³, $\sigma_{t=t1}$ = tracer gas content at time t=t_1, cm³/m³, $\sigma_{t=t2}$ = tracer gas content at time t=t_2, cm³/m³ [according to VDI 4300-7 (2001)].

Due to the expected low air exchange rates, measurements were accomplished over 15 h.

6.2 Showcases directly after production

Indoor air analyses were conducted in seven showcases immediately after production at the manufacturer's site. All showcases were of a highly sealed freestanding type and consisted in general of a class cube with glass cover plates and lacquered fibreboard base plates. At measurement dates, no special equipment, such as light systems, buffer or adsorption materials, was installed inside the cases.

Table 6.2-1 gives an overview of main results by summarizing the showcases age, the volume, the climatic parameters (T, RH) as well as sum values of detected VOCs [Σ(VOC)], formaldehyde (HCHO), formic acid (HCOOH) and acetic acid (CH_3COOH). Moreover, results of air exchange rate measurements (n) are compiled. Comparison measurements which were conducted in the environmental rooms are given below the related showcases. Showcase analyses were accomplished while the enclosures were positioned in production halls of the specific manufacturer. Climatic conditions in the halls were comparable with those inside museum exhibition rooms (T: ~23°C, RH: ~50%).

Table 6.2-1. Overview over main results obtained from active air sampling in newly (N) constructed showcases. Results of environmental room analyses are given below. Air exchange rate measurements were not performed in the environmental rooms.

Manufacturer	Location	Age	Volume	T	RH	Σ(VOC)	HCHO	HCOOH	CH_3COOH	n
		[days]	[m³]	[°C]	[%]	[µg/m³]				[h^{-1}]
1	Showcase N1.1	1	0.68	-	-	7071	33	33	2294	0.02
	Showcase N1.2	1	0.68	-	-	5125	27	30	2209	-
	Production hall	-	-	23	49	1579	15	38	1414	-
2	Showcase N2.1	7	0.76	-	-	9328	68	80	2352	-
	Production hall	-	-	-	-	4014	20	< LOD	405	-
	Showcase N2.2	28	0.68	-	-	25213	-	-	-	-
	Showcase N2.3	-	-	-	-	4378	70	< LOD	< LOD	0.05
	Production hall	-	-	20	48	-	-	-	-	-
3	Showcase N3.1	7	0.83	-	-	6487	30	< LOD	456	0.01
	Showcase N3.2	7	0.83	-	-	3819	35	< LOD	397	-
	Production hall	-	-	23	55	1882	24	< LOD	289	-

LOD (HCOOH): 12 µg/m³ LOD (CH_3COOH): 42 µg/m³ - not determined

6.2.1 Volatile organic compounds (VOCs)

Sum values of volatile organic compounds [Σ(VOC)] varied from 3819 µg/m³ up to 25213 µg/m³ at total showcase volumes between 0.68 m³ and 0.83 m³. Even though also background values in the production halls can be regarded as heightened with Σ(VOC)-values of 1500 µg/m³ up to ~4400 µg/m³, concentrations within showcases were up to four-fold higher. In production halls with several windows and big doors, which were open all the time and, thus, allowed an unhindered exchange with the outer air, air exchange rates can be assumed to be > 1 h^{-1}. In contrast, air exchange rates within showcases varied between 0.01 h^{-1} and 0.05 h^{-1} and were a twenty-fold up to a fifty-fold lower than within an open hall. Under these almost static conditions, between 26 and 45 individual substances were identified inside the enclosures and could be clearly attributed to specific emission sources and their contribution to pollution levels. Organic volatiles detected in the environmental production halls were in general the same, but in lower concentrations. Even though the indoor air quality in production halls inevitably influences concentrations within showcases, as these are produced and closed in the halls before transportation to the clients, it is obviously from these results that organic volatiles accumulate under nearly static conditions. This explains that some VOCs with low boiling points, as e.g. alcohol, were just analysed within showcases, but not in the production hall air as they were already escaped to outer air. A list of all identified substances within showcases directly after production is given in the appendix (see Table 11.1-1) as well as a statistical evaluation of the detected substance groups (Table 11.1-2).

Figure 6.2-1 compares concentrations of substance groups and individual main VOCs detected within showcase N1.1 and the environmental production hall R.

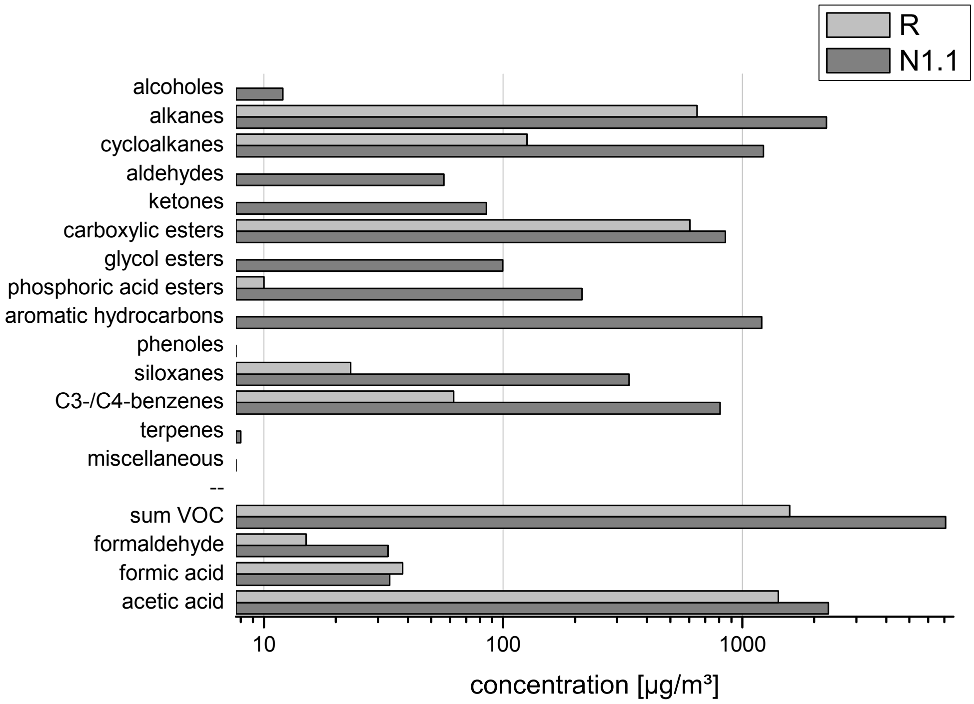


Figure 6.2-1. Comparison of concentrations of substance groups and individual VOCs detected within showcase N1.1 and the environmental production hall R.

Aromatic hydrocarbons, carboxylic esters and glycol esters as well as *n-/iso*-alkanes and ketones were identified within all enclosures. These solvents and additives were released as primary emissions mainly from solvent borne coating systems, which contributed until 30-50% to Σ(VOC)-values. The second main emission source was identified as silicone rubber sealants releasing also solvents, but particularly emitting increased concentrations of cyclic siloxanes with a maximum value (MAX) of 3353 µg/m³ and a median (MED) of 935 µg/m³. Thus, emissions from sealants contributed with 25% to Σ(VOC)-values. In two enclosures (N1.2 and N2.1), siloxane values were > 3000 µg/m³. Ketoximes as fragmentation products from neutral curing silicones were analysed with markedly heightened concentrations in N2.2 (17709 µg/m³). Further dominant substance groups were alcohol and cycloalkanes. In comparison to material emission analyses it can be concluded that these substances were evaporated as solvent residues from lacquer systems and sealants.

Table 6.2-2 lists most abundant substances, their CAS registry number and the emission source to which they are attributed.

Table 6.2-2. Characteristic lead compounds identified in modern-type showcases immediately after production.

Substance	CAS-No.	Emission sources
Alcohol	**-**	
Ethanol	64-17-5	Common solvent in coatings, sealants
Aromatic hydrocarbons		
Toluene	108-88-3	Coating materials, sealants
Ethyltoluenes*	-	Coating materials, sealants
m,p-Xylene	1330-20-7	Coating materials, sealants
o-Xylene	95-47-6	Coating materials, sealants
Ethylbenzenes*	-	Coating materials, sealants
Carboxylic esters		
Acetic acid	64-19-7	Coating materials, wood-based products
Carboxylic esters		
Ethylacetate	141-78-6	Coating materials, sealants
n-Butylacetate	123-86-4	Coating materials, sealants
Glycol ether		
2-Butoxyethanol	111-76-2	Coating materials
1-Butoxy-2-propanol	5131-66-8	Coating materials
Cyclic siloxanes	**-**	Silicone rubber sealants
Ketoximes		
2-Butanone oxime (MEKO)	96-29-7	Neutral curing silicone rubber sealants
Methylisobutylketoxime (≈ 4-Methyl-2-pentanone oxime)	105-44-2	Neutral curing silicone rubber sealants
Glycol esters		
Ethoxypropylacetate	98516-30-4	Coating materials
1-Methoxy-2-propylacetate	108-65-6	Coating materials

* isomers not listed

The contribution of solvents to high Σ(VOC)-values is illustrated in Figure 6.2-2.

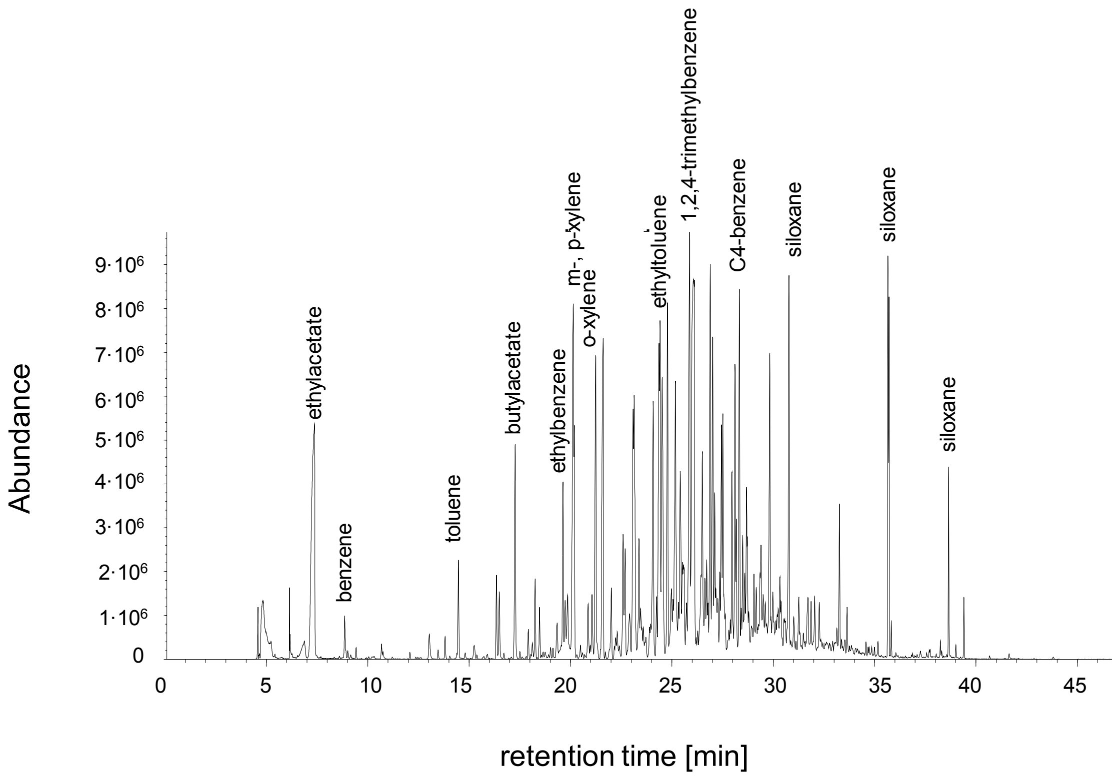


Figure 6.2-2. Total ion chromatogram (GC/MS) obtained by active air sampling in showcase (N1.1).

As can be seen, benzene as known toxic agent was identified. Concentrations were around 12 µg/m³ and can be clearly attributed to a polybutadiene rubber (sample S-3) based on the results obtained by material emission tests. The rubber is applied in the showcase for sealing the base plate edges. Another harmful substance was the chlorinated hydrocarbon trichloroethene, which is categorized as carcinogenic category 2 and mutagen category 3 (GefStoffV, 2005). It was analysed in the air of showcases N3.1 and N3.2 as well as in the surrounding production hall so that it is likely that it is released during the manufacturing process, even though no emission source could be specified.

6.2.2 Formaldehyde, organic acids (formic acid, acetic acid)

In contrast to heightened VOC-concentrations, emissions of formaldehyde and formic acid could be evaluated as low. Both substances were analysed in minor values (30-70 µg/m³) within all showcases and were released as characteristic primary emissions from wood-based products, which have been installed as base plates. Acetic acid values were increased in all showcases with a median (MED) of 2209 µg/m³. Just in one showcase (N2.3) concentrations were below the limit of detection (LOD). In three of seven showcases increased acetic acid values ranged between 2200 µg/m³ and nearly 2400 µg/m³. Acetic acid is a characteristic emission product from wood-based materials. Comparing the detected levels with results of chamber emission tests, analysed acetic acid values cannot be exclusively result from wooden emissions. Moreover, facing the heightened concentrations of organic esters analysed in the showcases [MED (carboxylic esters): 765 µg/m³, MED (glycol esters): 100 µg/m³], it can be concluded that acetic acid has been generated by hydrolytic cleavage of acetyl esters as demonstrated in section 5.3.1.1.

6.2.3 Comparison of chamber test results and pollution levels inside of showcases

It has to be pointed out that also heightened emission values were detected within showcases which have been built by use of relatively low-emissive construction materials. Σ(VOC)-values of showcases N1.1 and N1.2 were 7072 µg/m³ and 5125 µg/m³, respectively. Main emission sources were the lacquered base plate (sample PB-1, lacquered with L-3) as well as the sealant material (sample S-3). Sample L-3 showed slightly increasing emissions over time under test chamber conditions (745 µg/m³ after 24 h to 857 µg/m³ after 144 h), whereas the sealant proved to be relatively low emissive with 582 µg/m³ after 24 h and 400 µg/m³ after 144 h in comparison to other sealant test specimens. Surprisingly, concentrations of most abundant substances identified in chamber air were several factors (factor 2–10) higher than within the showcase. Moreover, in the showcase various cycloalkanes, iso-alkanes and C3-/C4-benzenes were detected which were not analysed or just in minor concentrations in chamber air. Additionally, also secondary reaction products analysed in chamber air during emission testing, especially with regard to sample S-3, could not be identified within the showcase.

On the one hand, it can be presumed that this distinction results of the differing air exchange rates, which were lower inside the enclosures than during chamber emission tests (0.02 h^{-1} *versus* 0.18 h^{-1}), and also from the fact that showcases were positioned in the production halls with elevated background values. However, on the other hand it cannot be excluded that these deviations are due to manual showcase production. As already stated, the manual application of coating layers as well as the manual mixing of two-pack lacquers and sealant formulations, respectively, produces inevitably irregularities in the composition and yields to different emission spectra.

6.3 Showcases in museum use

Most of the investigated showcases were in museum use during measurements, which means that artefacts were on display. In this case, air exchange rate measurements were not possible for security reasons as the measurement device had to be positioned inside the showcase, which demands a potential risk for museum artworks. As mentioned before, passive air sampling instead of active air sampling was performed due to low showcase volumes or if it was not possible to insert a tube from outside without opening or damaging the enclosure.

Objects of investigations were a variety of showcases with differing volumes, various years of construction and, thus, different kinds of materials used for construction and decoration.

6.3.1 Modern-type showcases

Results of indoor air analyses in thirteen modern-type showcases in museums are presented and discussed in this section. All showcases were in museum use during the test series with exception of showcases M7.1-M7.3. As it was not allowed on the part of the manufacturer to perform indoor air analyses in museums, three showcases were provided, which have been stored in the manufacturer exhibition since production between two to four years ago. At measuring time showcases M7.2 and M7.3 were located in the production halls, in which showcases are constructed and finished. As in showcases in museum use exhibits were positioned inside, neither air exchange rate measurements nor recording of climatic parameters was possible. In the majority active air sampling could be realized (ten showcases). Just in one showcase passive sampling was performed due to a missing outer access.

Investigated showcases were comparable with those analysed immediately after production as they were mainly from the same manufacturers and therefore built from the same kind of materials. All showcases were freestanding with the exception of the wall display case M8.1 and consisted of glass cubes with lacquered wooden base plates. Cover plates were made of glass or of lacquered metal and fibreboard, respectively. Some of the enclosures were equipped with light systems integrated into the cover plates. However, measurements were taken out without showcase lighting. Showcase M8.3 was equipped with a buffer material for constant relative humidity values.

All showcases were highly sealed to minimize outdoor influences with the exception of three showcases of open construction types. Gaps between the vertical glass edges of ca. 3 mm width ensured a continuously exchange with outdoor air regarding showcases M6.1. Showcase M7.1 exhibited sealed glass edges, but were not sealed in the pedestal zone and therefore open to air movement, whereas the wall showcase M8.1 had wide gaps in the base plate and in the cover plate.

Table 6.3-1 compiles the showcases age, the volume, the climatic parameters, the kind of air sampling performed and sum values of main pollution categories as well as air exchange rates (n). Results of comparison measurements in the specific environmental rooms are given below the specific showcase.

Table 6.3-1. Overview of main results obtained from indoor air analyses in *modern-type* (M) showcases. Results of environmental room analyses are given below. Air exchange rate measurements were not performed in the environmental rooms.

Museum	Location	Age	Volume [m³]	T [°C]	RH [%]	Active/ passive sampling	ΣVOC [µg/m³]	HCHO [µg/m³]	HCOOH [µg/m³]	CH_3COOH [µg/m³]	n $[h^{-1}]$
1	Showcase M1.1	~ 5 y	-	-	-	*passive*	2192	-	-	-	-
	Exhibition room	-	-	20	55	active	469	16	45	339	-
4	Showcase M4.1[1,2]	~ 3 m	-	-	-	active	3055	29	348	262	-
	Exhibition room	-	-	19	42	active	240	12	261	316	-
5	Showcase M5.1	~ 4 m	0.68	-	-	active	1907	52	89	831	-
	Showcase M5.2	~ 4 m	0.68	22	45	active	1203	41	95	876	0.04
	Exhibition room	-	-	21	42	active	290	20	42	212	-
6	Showcase M6.1[2,*]	~ 1-2 y	-	-	-	active	682	17	< LOD	133	-
	Exhibition room	-	-	18	50	active	528	22	< LOD	< LOD	4
7	Showcase M7.1[3,*]	~ 2 y	1.45	-	-	active	868	24	< LOD	108	-
	Exhibition room	-	-	18	46	active	887	17	< LOD	249	-
	Showcase M7.2[3]	~ 4 y	0.68	-	-	active	26516	28	< LOD	461	0.01
	Showcase M7.3[3]	~ 4 y	0.71	23	54	active	16830	46	< LOD	508	-
	Production hall	-	-	20	57	active	7349	39	< LOD	354	-
8	Showcase M8.1[2,*]	~ 9 y	0.58	-	-	active	102	< LOD	< LOD	< LOD	-
	Exhibition room (vault)	-	-	19	48	active	67	< LOD	< LOD	< LOD	-
	Showcase M8.2[2]	~ 3 y	0.97	-	-	active	1358	158	350	4935	-
	Exhibition room	-	-	23	29	active	83	14	46	111	-
	Showcase M8.3[2]	~ 6 y	1.1	-	-	active	16098	147	348	5698	-
	Special exhibition room	-	-	22	45	active	200	54	95	436	-

[1] not averaged [2] with exhibits inside (loaded) [3] at the manufacturer [*] open construction type

- not determined LOD (HCOOH): 12 µg/m³ LOD (CH_3COOH): 42 µg/m³

Facing the main results above it becomes obvious that pollution levels are mainly influenced by the construction type (highly sealed *versus* open).

6.3.1.1 Volatile organic compounds (VOCs)

Σ(VOC)-values for highly sealed showcases ranged between 1203 µg/m³ and 26516 µg/m³. Between 13 and 47 individual VOCs were identified, whereas Σ(VOC)-values of open constructed showcases varied from 102 µg/m³ to 868 µg/m³. As today a specific range of building and decoration materials is used for showcase production, remarkable substances detected in modern-type showcases in museum use corresponded inevitably to those analysed in showcases directly after production (see section 6.2). Table 6.3-2 summarizes most abundant compounds, their CAS registry number and the emission source to which they are attributed. A list of all identified substances as well as a statistical evaluation of substance groups is summarized in the appendix (see Table 11.2-1 and Table 11.2-2).

Table 6.3-2. Characteristic lead compounds identified in modern-type showcases in museum use.

Substance	CAS-No.	Emission sources
Ketones		
Acetone	67-64-1	Common solvent in coatings, sealants
Aromatic hydrocarbons		
m,p-Xylene	1330-20-7	Coating materials, sealants
o-Xylene	95-47-6	Coating materials, sealants
Ethylbenzenes*	-	Coating materials, sealants
Carboxylic acids		
Acetic acid	64-19-7	Coating materials, wood-based products
Carboxylic esters		
n-Butylacetate	123-86-4	Coating materials, sealants
Glycol ether		
1-Butoxy-2-propanol	5131-66-8	Coating materials
Cyclic siloxanes	**-**	Silicone rubber sealants
Ketoximes		
Methylisobutylketoxime (≈ 4-Methyl-2-pentanone oxime)	105-44-2	Neutral curing silicone rubber sealants
Glycol esters		
Ethyl-3-ethoxypropionate	763-69-9	Coating materials
1-Methoxy-2-propylacetate	108-65-6	Coating materials

* isomers not listed

In most showcases (five out of seven) between 45 and 47 individual substances were detected compared with 10 up to 37 individual compounds in open construction types. The difference is illustrated in Figures 6.3-1 and 6.3-2.

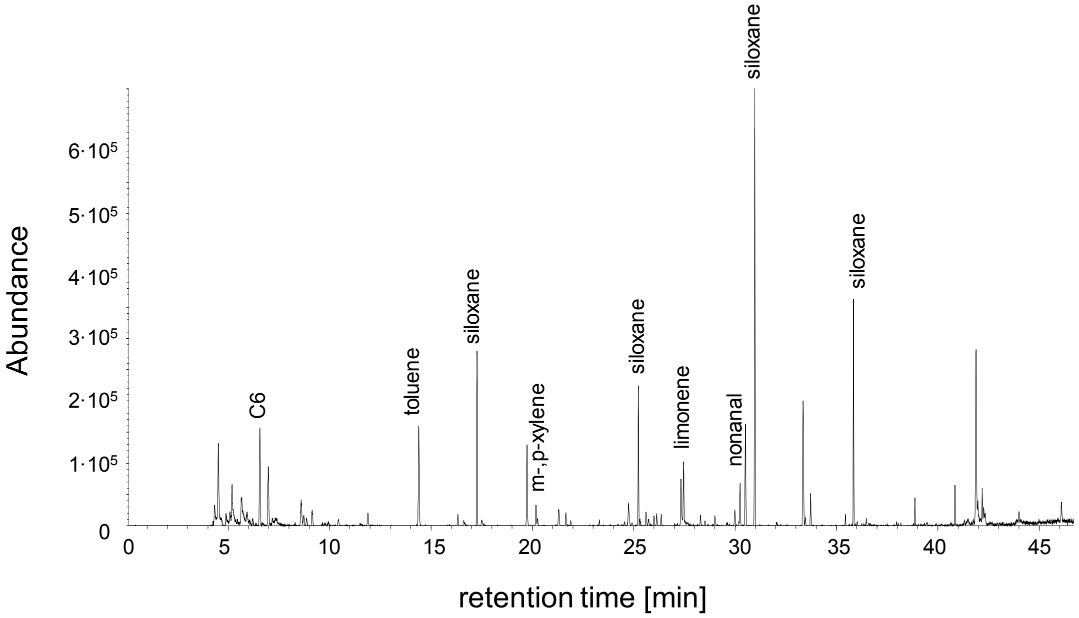


Figure 6.3-1. Total ion chromatogram (GC/MS) obtained by active air sampling in showcase M8.1.

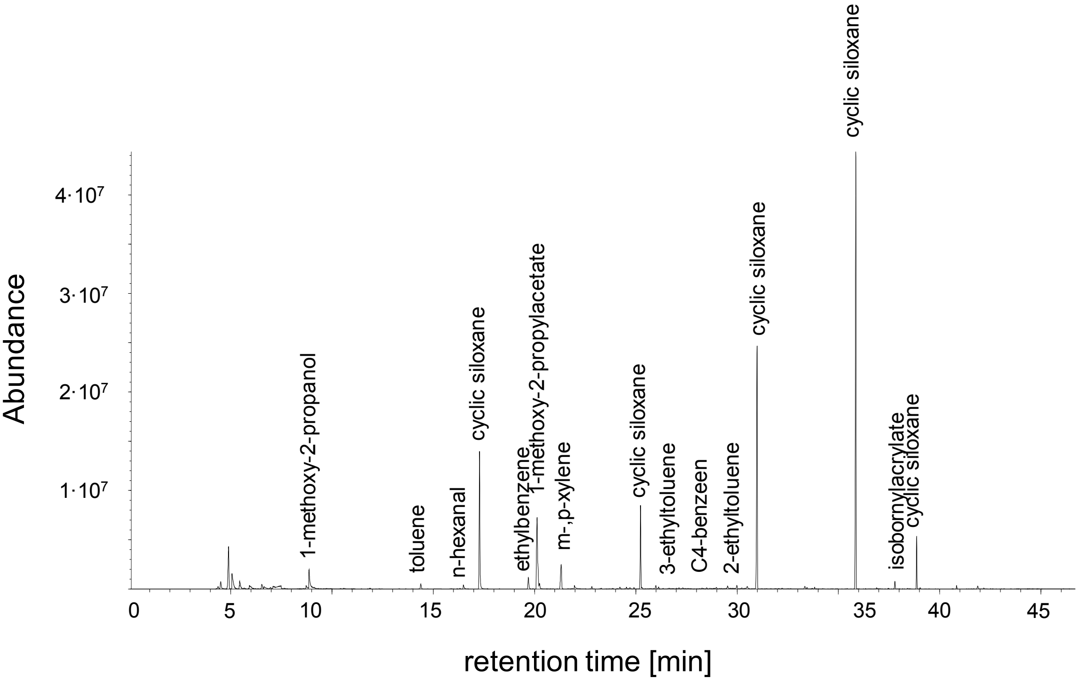


Figure 6.3-2. Total ion chromatogram (GC/MS) obtained by active air sampling in showcase M8.3.

Elevated Σ(VOC)-values were analysed in showcases M7.2 and M7.3 at the manufacturers site. The fact that these were located in a production hall during measurements explains the heightened background Σ(VOC)-value with 7349 µg/m³. As already discussed regarding indoor air quality in showcases directly after production, this circumstance may inevitably contribute to some extend to increased VOC concentrations because showcases might be opened. However, all substances were detected several factors higher than in the production hall so that accumulation of indoor generated emissions can be again suspected.

Highest indoor air pollution levels for a modern-type showcase in museum use were documented regarding showcase M8.3 with a Σ(VOC)-value of 16098 µg/m³. Particularly cyclic siloxanes contributed with nearly 70% to the high pollution level. During measurements, two Egyptian mummies (loans) were exhibited inside the enclosure on the occasion of a special exhibition. It was not possible to trace conservation and/or restoration measures. However, minor emissions of the mummies themselves can in principle not be excluded. Facing remarkable substances, coating materials and silicone sealants were the main emission sources. Due to the high concentrations, it is presumable that artwork emissions would be overlain. In addition it cannot be excluded that the showcase was redecorated over the years on the part of the museum staff itself. This would be a reason for the high air pollution although the showcase was constructed already six years ago.

Due to the allowed air exchange of open constructed enclosures with the environmental air, nearly the same volatile organics in almost the same concentrations could be detected within the specific enclosure and in the environmental room. Particularly low pollution levels regarding showcase M8.1 with 102 µg/m³ resulted also from the exhibition room, a vault with a minor background value itself (see Table 6.3-1). Also the exhibition room in museum 6, in which showcase M6.1 was located, proved to have a very low background value [Σ(VOC): 528 µg/m³] due to the setting of the HVAC (*heating ventilation air conditioning*) system which ensures an air exchange rate of $n > 4\ h^{-1}$.

6.3.1.2 Formaldehyde and organic acids (formic acid and acetic acid)

In general, formaldehyde and formic acid were in a lower range within new-type enclosures, especially those of an open constructed type. Formic acid and acetic acid were slightly elevated in showcase M4.1 as in this enclosure wooden base plates have been installed causing a high surface to volume-ratio. Exceptions were showcases M8.2 and M8.3 in museum 8. Showcase M8.2 exhibits an archeological wooden object, which is quite sensitive against fluctuations in relative humidity. For this reason, the showcase is equipped with a pump for active air circulation and with a buffer material in order to ensure a constant and homogeneous relative humidity (~50-55% RH). Specific emission sources causing increased concentrations of formaldehyde (158 µg/m³) as well as of formic acid (350 µg/m³) and organic acid (4935 µg/m³) could not be clarified as there is no information about applied construction products on hand. Facing the fact that the showcase is in museum use for three years, especially such elevated acetic acid concentrations were not expected. However, facing the level of relative humidity it is supposed that either acetic acid is formed as secondary emission due to ester hydrolysis or due to applied acid curing silicone rubbers. In addition it cannot be excluded that the wooden artwork itself may act as emission source.

Also in showcase M8.3 highly increased levels of formaldehyde (147 µg/m³), formic acid (348 µg/m³) and acetic acid (5698 µg/m³) were analysed. Facing the mummies displayed inside it is very likely that emissions result from construction and decoration materials, e.g. caused by various renovations as mentioned above.

Comparing substance group levels within modern-type showcases directly after production and those in museum use (see Figure 6.3.3), it becomes clear that concentrations of typical solvents (i.a. alkanes, aldehydes, glycols, aromatic hydrocarbons) are lowered in modern-type showcases in museum use.

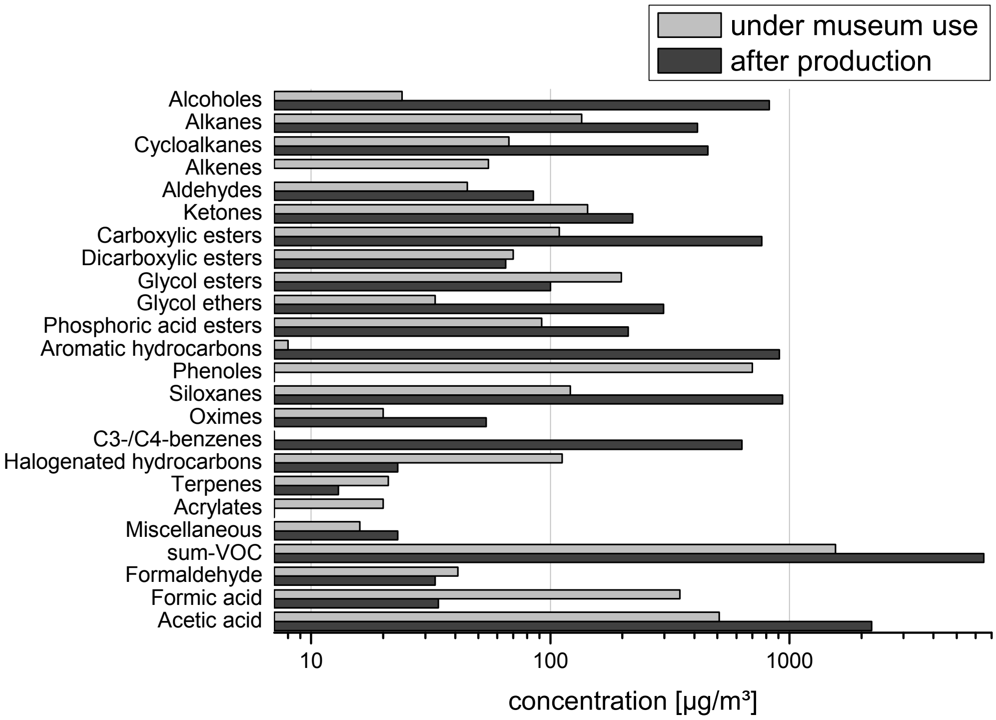


Figure 6.3-3. Comparison of concentrations of substance groups and individual VOCs detected in showcases directly after production and in new-type showcases in museum use.

It has to be noted that these findings are not representative as they are markedly depending on the type of showcase, technical and climatic parameters, the materials installed, the exhibit inside and the kind of use. Also renovations carried out by the museum staff itself cannot be excluded and will have a strong impact on air pollution levels.

6.3.2 Old-type showcases

Indoor air analyses were performed in fourteen old-type showcases, which were in museum for nearly ten to twenty years. As items were on display during analyses, no air exchange rate measurements could be realized.

All showcases were of traditional construction types. The freestanding or wall case types consisted of a low wooden pedestal zone; base plates and back boards were made of wood-based materials, which were covered with felt or coated with lacquers. Lighting systems were installed in a hood above the glass cover plate to separate the light elements from the interior. Regarding various showcases it was not possible to insert tubes for indoor air sampling from the outside into the interior so that passive sampling was necessitated.

Table 6.3-3 compiles the location, the showcases age, the volume, the climatic parameters, the kind of air sampling performed and sum values of main pollution categories. Results of comparison measurements in the specific environmental rooms are given below the specific showcase.

Table 6.3-3. Overview of main results obtained from indoor air analyses in *old-type* (O) showcases. Results of environmental room analyses are given below. Air exchange rate measurements could not be performed as items were on display.

Museum	Location	Age	Volume [m^3]	T [°C]	RH [%]	Active/ passive sampling	Σ(VOC) [µg/m^3]	HCHO [µg/m^3]	HCOOH [µg/m^3]	CH$_3$COOH [µg/m^3]
1	Diorama O1.1		12	22	45	active	758	69	106	452
	Exhibition room	-	-	23	41	active	745	45	87	298
	Diorama O1.2		12	22	45	active	745	-	-	-
	Exhibition room	-	-	22	41	active	712	-	-	-
	Diorama O1.3		12	-	-	*passive*	362	-	-	-
	Showcase O1.4		-	-	-	*passive*	215	-	-	-
	Showcase O1.5		-	-	-	*passive*	522	-	-	-
	Exhibition room	-	-	21	46	active	319	18	111	306
	Showcase O1.6		0.5	-	-	*passive*	133	-	-	-
	Exhibition room	-	-	20	47	active	347	18	102	393
	Showcase O1.7		2	-	-	*passive*	2800	-	-	-
	Exhibition room	-	-	20	55	active	469	16	45	339
	Showcase O1.8	~ 20 y	4.8	23	58	active	2101	757	656	3282
						passive	1057	-	-	-
	Showcase O1.9		0.68	-	-	active	1859	435	405	1157
	Exhibition room	-	-	22	34	active	520	47	170	526
2	Showcase O2.1*	~ 20 y	-	25	46	active	87	91	218	527
	Exhibition room	-	-	24	50	active	86	46	105	345
	Storage case O2.2	~ 20 y	-	-	-	active	659	322	364	1490[1]
	Exhibition room	-	-	24	49	active	79	56	112	332
3	Showcase O3.1	~ 20 y	-	-	-	active	239	326	710	2598
	Exhibition room	-	-	26	43	active	135*	17	58	416
	Showcase O3.2	~ 20 y	0.5	-	-	active	102	310	782	2101
	Exhibition room	-	-	25	41	active	193	21	64	450

[1] not averaged *open construction type - not determined LOD (HCOOH): 12 µg/m^3 LOD (CH$_3$COOH): 42 µg/m^3

6.3.2.1 Volatile organic compounds (VOCs)

Σ(VOC)-values in old-type showcases ranged from 102 µg/m³ to 2101 µg/m³. Between 4 and 35 individual substances were identified. The least organic volatiles were detected in showcase O3.2, namely hexanal as aldehyde and α-pinene, 3-carene and campher as bicyclic monoterpenes. All these compounds are remarkable emissions from wood and wood-based products, respectively, and are therefore clearly attributed to the main construction material. Bicyclic monoterpenes were identified in all showcases. Their occurrence is a significant evidence of the application of resinous softwood used for construction and furnishing showcases, such as pine and spruce (Fengel and Wegener, 1989).

Highest concentrations in showcase O1.8 (museum 1) are primarily caused by carboxylic esters, especially acetic acid, constituting 67% of the Σ(VOC)-value. Showcase O2.1 and storage case O2.2 formed together one showcase compartment. The showcase part was constructed with gaps (~ 4 mm) which explains the fact that nearly the same concentration inside the case and in the environmental room were detected. In contrast, Σ(VOC)-values of the storage case were a factor of eight higher than in the environmental indoor room as it was highly sealed and consisted in contrast to the showcase not mainly of glass but of lacquered fibreboard. Thus, beneath characteristic emissions from wooden products also typical solvent residues and additives were identified and attributed to the lacquer, such as n-butanol, 1,2-ethandiol, toluene, 2-butoxyethanol. The same applies for the identification of glycols and aromatic hydrocarbons inside of the diorama as these are large enclosures illustrating landscapes by utilizing a variety of products, i.a. adhesives and lacquers.

Table 6.3-4 gives an overview of most abundant volatile organics, their CAS registry number and the emission source to which they are attributed. A compilation of all identified organic volatiles and a statistical evaluation of substance groups and individual compounds are contained in the appendix, see Tables 11.3-1 and 11.3-2.

Table 6.3-4 Characteristic lead compounds identified in old-type showcases in museum use.

Substance	CAS-No.	Emission sources
Aldehydes		
Hexanal	66-25-1	Wood-based materials, degradation product
Nonanal	124-19-6	Wood-based materials, degradation product
Furfural	98-01-1	Wood-based materials, degradation product
Bicyclic monoterpenes		
α-Pinene	80-56-8	Wood-based materials
β-Pinene	127-91-3	Wood-based materials
Limonene	138-86-3	Wood-based materials
3-Carene	13466-78-9	Wood-based materials
Carboxylic acids		
Acetic acid	64-19-7	Wood-based products, degradation product
Aromatic hydrocarbons		
Toluene	108-88-3	Coating materials, sealants
m,p-Xylene	1330-20-7	Coating materials, sealants
o-Xylene	95-47-6	Coating materials, sealants
Glycol ether		
2-Butoxyethanol	111-76-2	Coating materials
Cyclic siloxanes	-	Silicone rubber sealants

* isomers not listed

Figure 6.3-4 shows a typical total ion chromatogram (GC/MS) obtained by active air sampling in showcase O3.1.

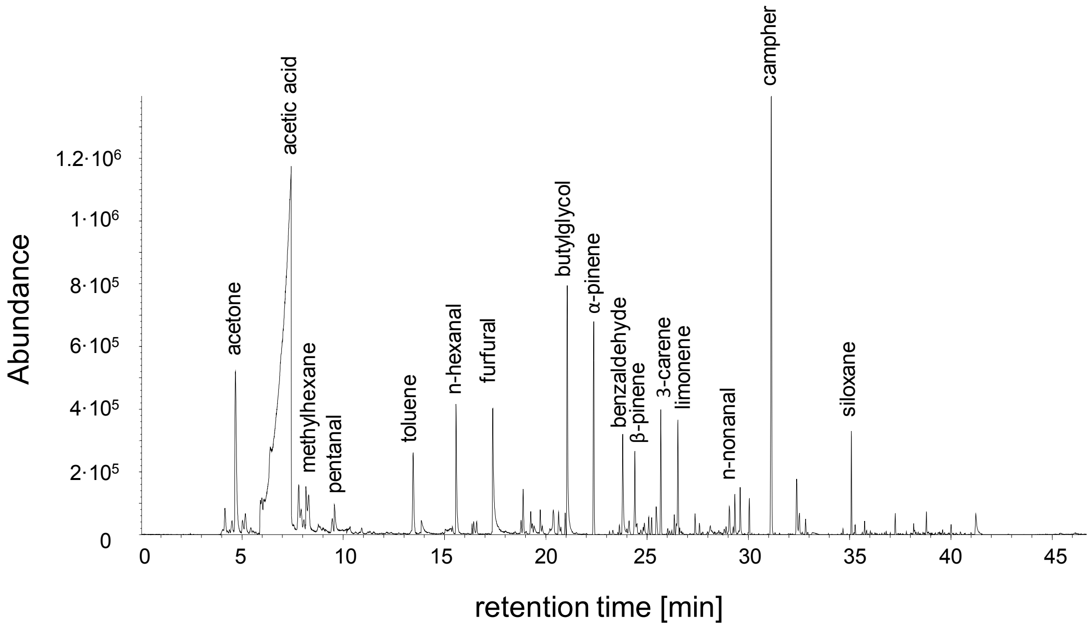


Figure 6.3-4. Total ion chromatogram (GC/MS) obtained by active air sampling in showcase O3.1.

6.3.2.2 Formaldehyde and organic acids (formic acid and acetic acid)

Formaldehyde and formic acid levels were increased with both ranging between ~100 µg/m³ and ~ 800 µg/m³. Concentrations of acetic acid reached up to 3600 µg/m³ and can therefore be evaluated as highly increased. It is remarkable that just four individual VOCs were detected in showcase O3.2 but the highest acetic acid level. Another maximum acetic acid value was analysed in showcase O1.8 with 3283 µg/m³. These findings result clearly from the construction type with wood-based products (backside, cover and base plate, tableaus). Also the application of acid curing silicone rubber as it was common in previous times cannot be excluded. Showcase O1.8 exhibits the coat of a bog body. In order to protect this light sensible object, the showcase has just a front glazing; the other side walls and the back board are light-tight and consist of wood-based products covered with felt which results in elevated levels of formaldehyde, formic acid and acetic acid.

Damages on artwork materials are already observed on glass objects which were stored inside storage case O2.2 and had become brittle and opaque over the years. This damage is obviously caused by exposure to acetic acid. Even though the glass itself was not examined, it is presumably that natrium formate and natrium acetate, respectively, have been formed (Bradley and Thickett, 1999; Müller et al., 2000; Torge et al., 2000). Efflorescence's cause volume extension and increasingly cracking. In showcases O3.1 and O3.2 sensible metal instruments are exhibited. Wide efflorescence's on lead bars from an antique thermometer were identified as lead acetate. This was the starting point for indoor air analyses which yielded heightened concentrations for formaldehyde (300-330 µg/m³), formic acid (710-780 µg/m³) and acetic acid (~2600-3600 µg/m³).

In general, elevated formic acid values were detected within all old-type showcases. Formic acid may be released from a primary emission source or may be formed by oxidation of formaldehyde. In this case, formaldehyde would be the precursor, but not the corrosive agent (Raychaudhuri and Brimblecombe, 2000). Thus, not the concentration of formaldehyde in the indoor atmosphere would be of importance, but the probability of oxidation to formic acid. Consequently, formaldehyde would be just of hazardous potential for artwork materials at very high relative humidity and at the unusual presence of oxidants. Facing typical relative humidity levels in the museum environment (50-55%) the impact of formaldehyde on artwork materials due to oxidation seems low. For a first evaluation of the potential of formaldehyde to be oxidized, measurements of oxidizing agents are necessitated (Raychaudhuri and Brimblecombe, 2000).

Passive air sampling

Passive air sampling on Tenax TA® was performed in six showcases. 11-35% of the identified substances could not be quantified properly as no uptake rates are listed so far (Anonymus, 2001) and were, therefore, estimated on the basis of molecular weights and structures. Hence, results are not exact and uncertain. In direct comparison of active and passive air sampling, as it was accomplished for showcase O1.8 (see Figure 6.3-5), it becomes obvious that some volatiles have not been trapped on the adsorbent during diffusive passive sampling, but were detectable by using active air sampling. This applies for phthalic acid esters, such as dibutylphthalate (DBP) due to its high boiling point (*bp* = 340°C), as well as to low boiling substances such as e.g. acetone (*bp* = 56°C), ethanol (*bp* = 78°C), and 2-butanone (*bp* = 80°C). This fact makes it difficult to sample those volatiles by dint of a pure diffusion based method.

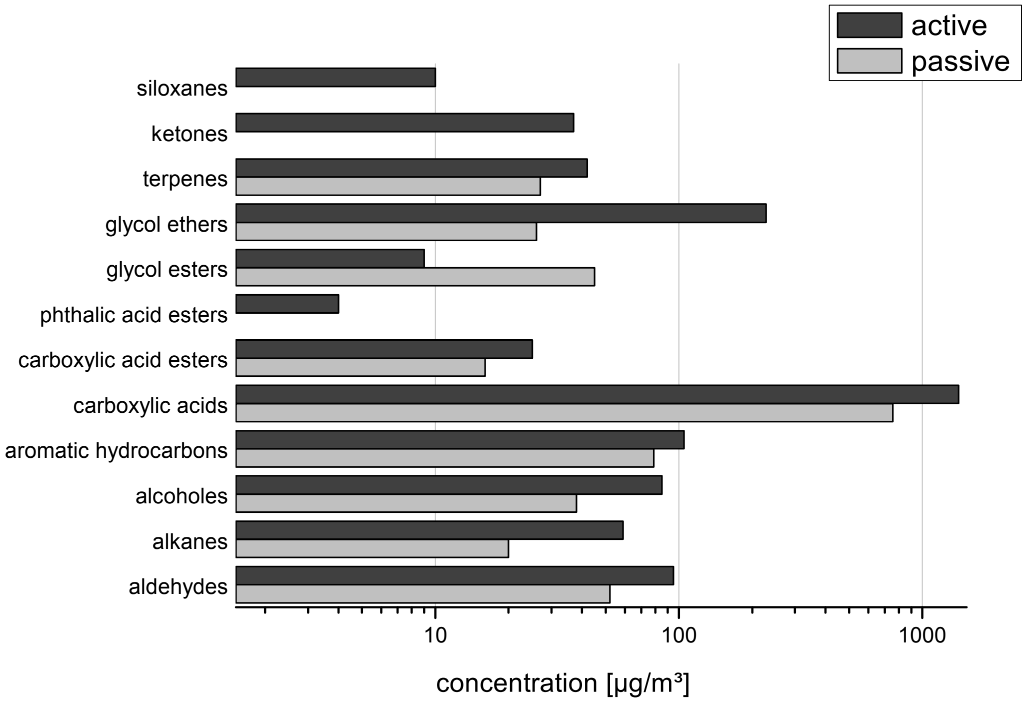


Figure 6.3-5. Comparison of substance group levels obtained by active and passive air sampling on Tenax TA® within showcase O1.8.

It becomes clear from Figure 6.3-5 that proportions among individual substances classes were inconsistent. Regarding showcase O1.8, diffusive passive sampling results of substance classes were in average 37% lower than active sampling results (N=11). For this reason, lead substance classes and dominating emissions, respectively, would be evaluated in a different way.

6.4 Artworks as emission sources

During indoor air analyses in showcases in museum use, it became obvious that also the artworks themselves act as emission sources and contribute to indoor air pollution.

6.4.1 Biocide treatments

Conspicuous concentrations of chlorinated and non-chlorinated aromatic compounds like 1,4-dichlorobenzene (1,4-DCB), mono- (MCN) and dichlorinated naphthalenes (DCN) and naphthalene were detected in the adjacency of diorama and display cases. In showcase M1.1 indoor air sampling was performed by passive sampling on Tenax TA®. The total ion chromatogram (GC/MS) is shown in Figure 6.4-1 and represents the composition of organic air pollutants in the gas phase of the showcase.

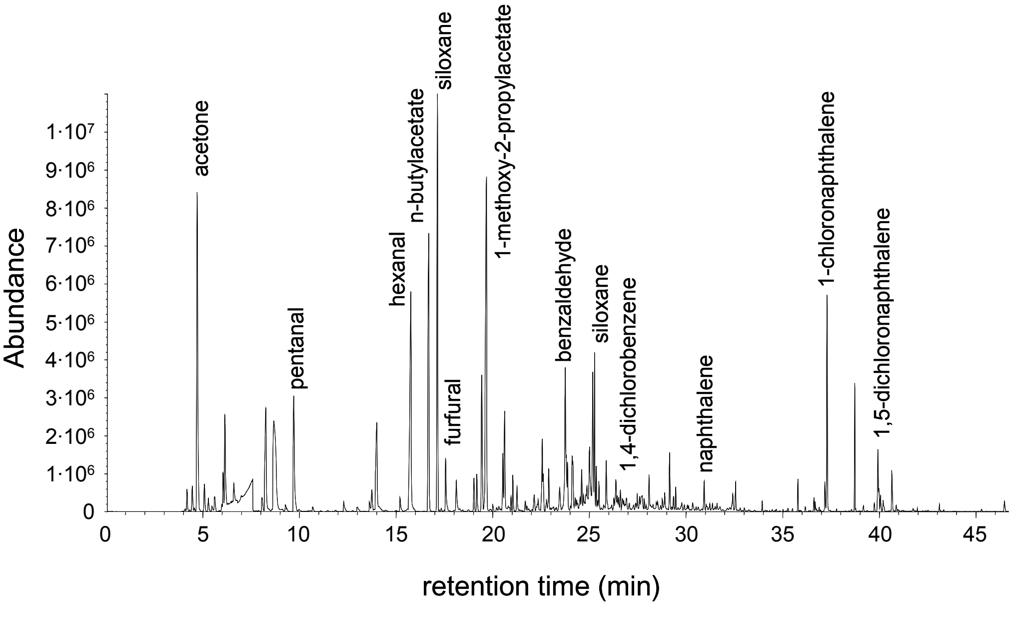


Figure 6.4-1. Total ion chromatogram (GC/MS) obtained by passive sampling on Tenax TA® in showcase M1.1.

The detected VOCs result from building products and applied biocides. Whereas n-butylacetate and 1-methoxy-2-propylacetate can be attributed to the applied lacquer, an epoxy resin (sample L-5), the occurrence of 1,4-dichlorobenzene (1,4-DCB), naphthalene, 1-chloronaphthalene and 1,5-dichloronaphthalene indicates that the wooden sculpture that is exhibited inside the showcase has been treated with biocides, which are now released in the gas phase.

Most of the detected VOCs in the retention time gap 5–25 min are released from building products (Salthammer, 2004). The peaks of 1,4-DCB, naphthalene and the chlorinated naphthalenes appear at retention times > 25 min. Moreover, also indoor air analysis in the dioramas in museum 1 yielded dichlorobenzene and chlorinated naphthalenes. Therefore, the air concentrations of the above mentioned compounds were measured inside these facilities. In Table 6.4-1 the results of air analyses are summarized for the three diorama in the department of zoology and for showcase M1.1 in the art gallery of museum 1 (Schieweck et al., 2007).

Table 6.4-1. Air concentrations of biocides in three diorama, an exhibition room and one showcase in museum 1 [reprinted from Schieweck et al., 2007 with permission from Elsevier].

Compound	Diorama O1.1	Diorama O1.2	Diorama O1.3	Exhibition room	Showcase M1.1
	Concentration in [µg/m³]				
1,4-DCB	17	19	24	7	4
Naphthalene	3	3	3	3	3
MCN	3	3	27	2	32
DCN	<1	<1	30	<1	23

1,4-DCB: 1,4-dichlorobenzene
MCN: monochlorinated naphthalenes
DCN: dichlorinated naphthalenes

Inside the diorama the air concentrations of 1,4-DCB were in the range of 17–24 µg/m³ and significantly increased in comparison to the exhibition room. Moreover, the concentrations of 23-32 µg/m³ indicate that both diorama O1.3 and the wooden sculpture in the display case have been treated with MCN and DCN. The 1,4-DCB concentration of 7 µg/m³ in the exhibition rooms probably results of diffusion effects. Additionally, soil samples were taken in diorama O1.1-O1.3 and analysed for certain biocides.

Material analyses

At suspicion of biocide contamination of showcase materials due to emissions of displayed items, continuative analyses were performed. 1- and 2-monochloronaphthalene (MCN), 1,4- and 1,5-dichloronaphthalene (DCN), methoxychlor (1,1,1-trichloro-2,2-bis(4-methoxyphenyl)-

ethane), DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)-ethane) and DDT isomers/derivatives were extracted from solid samples (paper towels, dust or material) in acetone/hexane (50:50) using Soxhlet or ultrasonication and analysed by GC/MS or GC/ECD. The DDT values represent the sum of isomers and derivatives (o,p-DDD, p,p-DDD, o,p-DDE, p,p-DDE, o,p-DDT, p,p-DDT). Pentachlorophenol and lindane (γ-cyclohexane) were extracted and analysed according to a method described by Buhr et al. (2000). The limits of detection (LOD) and limits of quantitation (LOQ) were calculated from calibration curves as recommended by DIN 32645 (Einax et al., 1997). In all cases LOQ was > 1 mg/kg and 1 mg/m², respectively. The presented results were obtained from dual analysis of the extracts and are compiled in Table 6.4-2. They show that the soil is contaminated with many of the compounds being applied in German museums since 1950 for the protection of artifacts (Unger et al., 2001).

Table 6.4-2. Biocide concentrations in diorama O1.1-O1.3 in museum 1 [reprinted from Schieweck et al., 2007 with permission from Elsevier].

Compound	**Soil O1.1**	**Soil O1.2**	**Soil O1.3**	**Wipe sample O1.3 (window inside)**
	[mg/kg]			**[µg/m²]**
MCN	n.d.	n.d.	42	n.d.
DCN	n.d.	n.d.	38	n.d.
Lindane	< 1	2	10	n.d.
PCP	< 1	< 1	4	n.d.
Methoxychlor	4	< 1	9	n.d.
DDT	5	17	82	17

n.d. not detected

In diorama O1.3 the high values of MCN (42 mg/kg) and DCN (38 mg/kg) were in accordance with the results of air analysis. The increased concentration of 82 mg/kg DDT in diorama O1.3 was surprising because this compound was banned in former West Germany in 1972 and mainly applied in the former German Democratic Republic. In the German Democratic Republic DDT was used in combination with lindane under the trade name Hylotox® until the reunion in 1990. Mono- (MCN) and dichlorinated (DCN) naphthalenes were utilized as main components for the protection of wood and wood-based materials from 1923 up to the sixties under the trade name Xylamon® in Germany. Later, the chlorinated naphthalenes were abandoned because of their toxicity and their unpleasant smell and substituted by a combination of pentachlorophenol (PCP) and lindane, which was frequently used from the fifties to the seventies (Unger et al., 2001). In Germany PCP was banned by law in 1989. Possible periods of time for the use of certain biocides are shown in Figure 6.4-2.

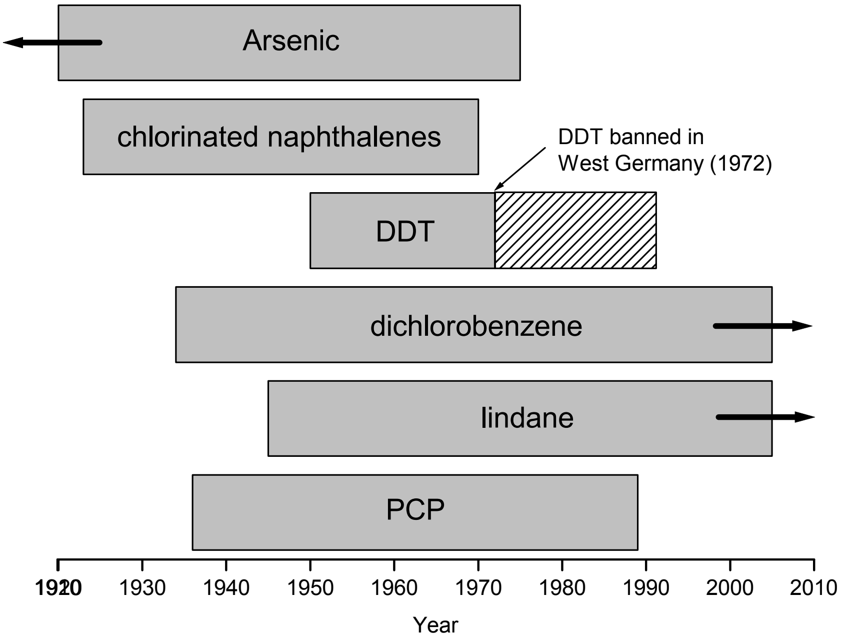


Figure 6.4-2. Time periods of possible application of biocides in museums (MCN: monochloronaphthalene; DCN: dichloronaphthalene; PCP: pentachlorophenol; DDT: 1,1,1-trichloro-2,2-bis(4-chlorophenyl)-ethane; 1,4-DCB: 1,4-dichlorobenzene) [reprinted from Schieweck et al., 2007 with permission from Elsevier].

DDT could also be identified in a wipe sample taken from the inside of the display window of diorama O1.3 with a surface value of 17 µg/m². Methoxychlor was detected in the soil of diorama O1.1 (4 mg/kg) and diorama O1.3 (9 mg/kg). For this compound only little information can be found in the literature. Butte and Heinzow (2002) mention a 95-P value of 27 mg/kg for sieved house dust. This means that the measured concentrations in diorama O1.1 and diorama O1.3 can be regarded as low under statistical aspects. In the exhibition rooms outside the diorama and showcases the concentrations of the mentioned biocides were marginal or below the detection limit. This assumes that migration of these compounds is slow and a low health risk for visitors can be estimated. It is interesting to note that Glastrup (1987) has found *p*-dichlorobenzene, naphthalene, lindane, aldrin, dieldrin, DDT and methoxychlor when analysing 118 samples taken in the store of the Danish National Museum's ethnographic collection.

6.4.2 Semi-volatile organic compounds (SVOCs) - "*Fogging effect*"

Gaseous volatiles with high boiling points tend to condensate on glazy surfaces which are cooler than the environmental air. The so called "*fogging effect*" in the museum area is observable by clouded and hazy glass panels either from showcases and storage cases, respectively. This phenomenon may also appear on the inside surface of a protective glass covering from a painting forming a negative of the painted subject. Analysis of hazy films from four protective glass panels of oil paintings (museum 1) yielded deposits of saturated fatty acids, such as nonanoic acid, octanoic acid and tetradecanoic acid as well as hexadecanoic acid (see Figure 6.4-3).

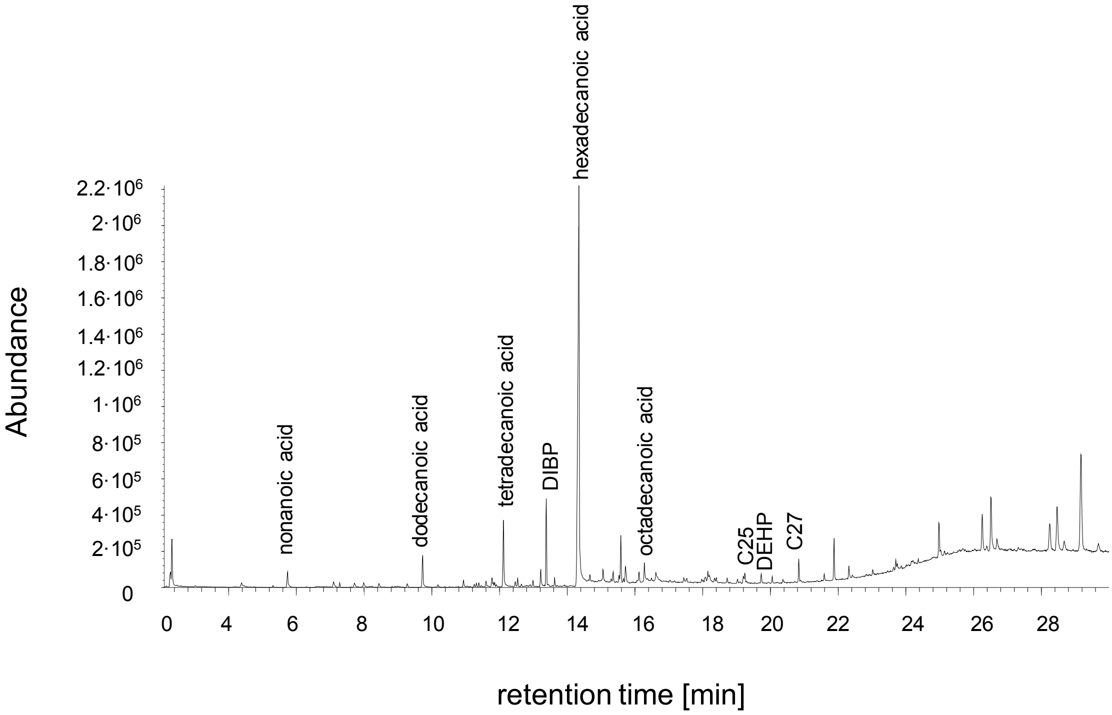


Figure 6.4-3. Total ion chromatogram (GC/MS) of a hazy film from a protective glazing of an oil painting [source: Schieweck und Salthammer, 2006].

The formation of so called "*ghost images*" is explained by two coupled mechanisms: (1) induced migration by hygric (cluster) permeation and (2) thermodynamic migration by heterogenic density fluctuation (Zumbühl et al., 2004). Such migration mechanisms are interpreted on the basis of an extended model of the "*free volume theory*". Migration processes caused by hygric permeation lead to efflorescence on the painting surface. In case of a minor water affinity of the migrating compounds, a special dominance of efflorescence is to be observed. Fatty acids blooming on the surface form a kind of thin films, which are readily observable due to the efficient light scattering as consequence of their large surface area. Subsequently, the more volatile fatty acids sublimate on the protective glazing forming so called "*ghost images*". This migration process depends on temperature. Fatty acids melt and form both agglomerates and laminar deposits. The quantitative extend of these deposits is not inevitably influenced by the specific painting area (pigment-binder ratio) (Zumbühl et al., 2004). However, Shilling et al. (1998) found that the evaporation rate of palmitic acid is four times as rapidly as either fatty acids at room temperature. Moreover, a relationship between the kind of influence (heating and/or light exposure) and the kind of fatty acids evaporated seemed to be detected. Hence, images formed by heating tended to consist largely of saturated fatty acids (Shilling et al., 1998). This would support the thesis that ghost images formed on the four protective glazings investigated result from high temperatures in the exhibition gallery during summer months. According to an oral communication with the chief restorer temperatures during the summer months exceed normal room temperatures and can reach up to 35°C. Furthermore, during analysis of wiping samples sulphurous compounds were detected. The origin is unknown so far, it can be assumed that it is released by the gasket (vulcanized rubber).

Similar SVOCs were detected by analysing fogging deposits in showcase M6.1, a new showcase constructed with gaps (~5 mm) to avoid high indoor air pollution concentrations inside. As detected SVOCs are not characteristic emissions from modern showcase materials, it is suspected that the objects themselves act as emission sources (Figure 6.4-4).

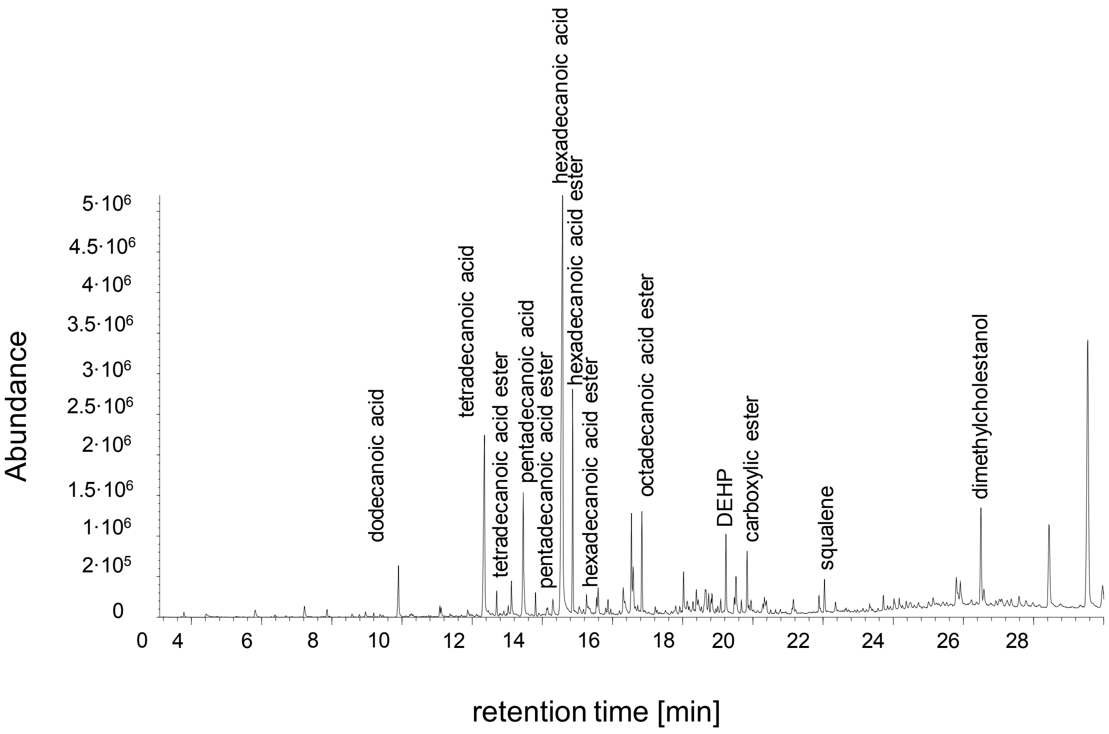
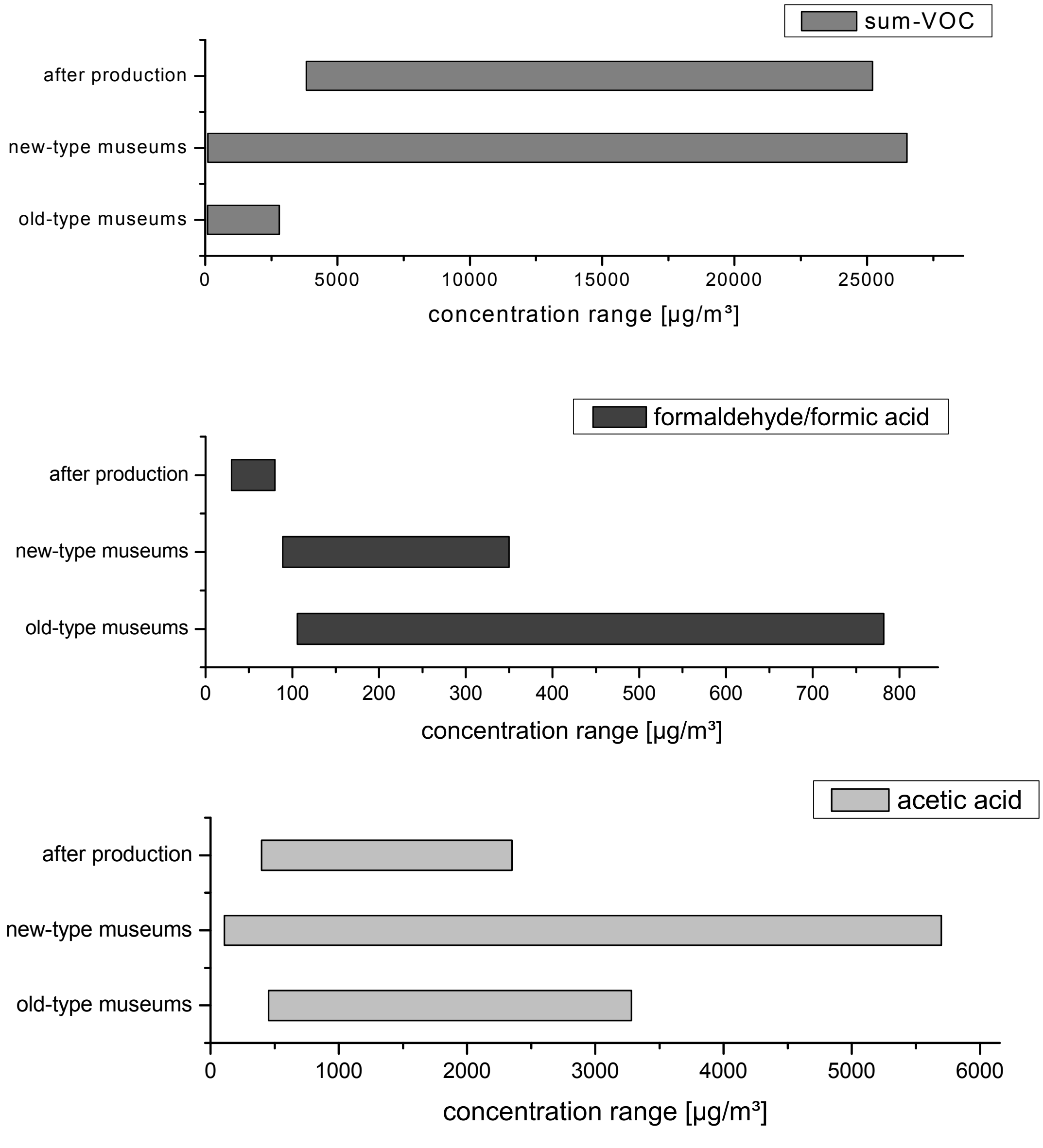


Figure 6.4-4. Total ion chromatogram (GC/MS) of a hazy film from a glass shelf in showcase M6.1.

For the sake of completeness it should be mentioned that formaldehyde and formic acid are still applied in the conservation and preparation of zoological exhibits. Formic acid is used for tanning the dermis of animals. Zoological preparations and anatomical specimens are often conserved in formalin, an aqueous formaldehyde solution (30-40%) possibly yielding to elevated indoor air concentrations of formaldehyde. In the Niedersächsisches Landesmuseum Hannover indoor air analysis in front of a metal cupboard was performed in which animal specimens are stored in formalin solutions causing an intense smell. In normal conditions of use when the cabinet doors were kept closed, the formaldehyde concentration was 28 µg/m³, whereas the concentration increased to 90 µg/m³ when the doors were opened (Schieweck et al., 2005a). Even if impact on human health is secondary regarding optimum storage conditions for museum artworks, it shall be pointed out that formaldehyde is known to cause adverse health effects like irritation of the mucous membrane.

6.5 Summary of the results

Based on the knowledge about applied construction materials and their emission potential, which was obtained during the first experimental series, it was possible to correlate identified substances with emission sources as there were no substantial differences. In modern-type museum showcases directly after production between 26 and 45 individual VOCs were identified, in modern-type showcases in museum use between 10 and 46 and in old-type enclosures in museum use detected individual VOCs ranged between 4 and 35. Comparable to material emission tests, the majority of analysed compounds were again attributed to solvent evaporations. Static conditions inside the enclosures ($n = 0.01\ h^{-1}$) lead to the accumulation of generated emissions inside. This fact is mirrored by Figure 6.4-5a comparing the range of Σ(VOC)-levels of the three investigated showcase types. The consequences from the material shift in showcase production, which was undergone during the last decades, becomes clear when comparing Σ(VOC)-levels from modern-type and old-type showcases. Pollution levels inside modern showcases are highly increased, especially directly after production. Levels can remain high in museum use in dependence of the construction type and kind of use. Detected pollution levels were in the same order of magnitude. In contrast, concentrations of VOCs are several factors lower in old-type showcases. The reasons can be assumed to be (i) different materials applied for construction and decoration and (ii) not constructed as sealed as modern showcases. The circumstance that old-type showcases are in museum use for a longer term which contributs to an offgassing of volatiles does not seem to play such a main role facing the heightenend acetic acid concentrations. However, also these levels are again higher in modern cases due to ester hydrolysis (Figure 6.4-5b). Thus, acetic acid is still one of the main problems which is not solved so far.



Figures 6.4-5a-c Concentration ranges of main pollutants/substance groups in different showcase types.

In contrast to old-type showcases, levels of formaldehyde and formic acid can be evaluated as low because nowadays wood-based products of improved quality are installed, even though both substances are still released.

In general, low pollution levels are always attributed to open construction types allowing an unhindered air exchange rate with the environment provided that also a good air quality in the surrounding room, whereas a markedly accumulation of gaseous emissions inside of highly sealed showcases was revealed.

Emissions released by the exhibit itself are hardly to distinguish as it was shown in experimental series I, section 5.3.2 that emissions are mostly attributed to the solvent content and are therefore nearly the same as those released from construction materials. Exceptions are traced active agents of biocides and pesticides, which were widely applied in the museum sector in previous times. Also so called fogging substances on showcase glasses can be suspected to result from the artworks themselves. Whereas the former can be a risk for human health, the latter is primarily an aesthetical problem.

As investigations in modern-type showcases described and discussed so far were taken out without artificial lighting in the case itself, the question about possible influences of the light on indoor air quality was pursued in the next step.

7 Experimental series III

Influences of artificial lighting

As exhibits are illuminated either by the room lighting or by light sources integrated in the showcase itself, a third test series was carried out in order to clarify possible influences of integrated light sources on indoor air quality within showcases.

7.1 Experimental set-up and investigation parameters

One modern-type showcase directly after production and five modern-type showcases in museum use were selected for investigations. It was not possible to realize this experiment in old-type showcases as these were all in exhibition and, as mentioned before, a convenient access into the interior for air sampling was often missing.

Indoor air analyses were accomplished in each case before and after illumination (duration: 8–20 h). Showcases were not opened between both test series if procurable. Focus was again on analysing (S)VOCs, formaldehyde and organic acids (formic acid, acetic acid). For analytical details it is referred to sections 5.3.3 and 6.1.1. Measurement of air exchange rates was carried out during the lighting cycling in one showcase. Investigation parameters and main results are summarized in Table 7.1-1. Abbreviations of showcases are in accordance with Tables 6.2.1 and 6.3.1. The lamps were equipped with UV-filters and therefore adapted for installation without glass guard.

Table 7.1-1. Overview over main results obtained from indoor air analyses in modern-type showcases without and with artificial lighting. Results of environmental room analyses are given below. No air exchange rate measurements were taken out in the environmental rooms.

Showcase no./ Location	**Age [d/m/y]**	**Volume [m^3]**	**T [°C]**	**RH [%]**	**Lighting**	**Lighting source**	**Lighting duration [h]**	**Σ(VOC) [µg/m^3]**	**HCHO [µg/m^3]**	**HCOOH [µg/m^3]**	**CH_3COOH [µg/m^3]**	**n [h^{-1}]**
Showcase N2.2	7 d	0.83	21	58	□			6487	30	< LOD	456	0.01
			22.6	55	■	4 HL	20	34866	-	-	-	-
Production hall	-	-	23	55	**-**	-	-	1882	24	< LOD	289	-
Showcase M5.1	4 m	0.68	-	-	□			1907	52	89	831	-
					■	5 HL	8	2111	49	48	439	-
Exhibition room	-	-	21	42	**-**	-	-	290	20	42	212	-
Showcase M7.2	~ 4 y	0.68	-	-	□			26516	28	< LOD	461	0.01
					■	FL	15	50401	35	< LOD	962	0.03
Showcase M7.3	~ 4 y	0.71	-	-	□			16830	46	< LOD	508	-
			23	54	■	FL	15	16260	38	< LOD	411	0.03
Production hall	-	-	20	57	**-**	-	-	7349	39	< LOD	354	-
Showcase M8.1	~ 9 y	0.58	-	-	□			102	< LOD	< LOD	< LOD	-
					■	HL	13	44	< LOD	< LOD	< LOD	-
Exhibition room (vault)	-	-	23	49	**-**	-	-	67	< LOD	< LOD	< LOD	-

Abbreviations:	-	unknown	HL	halogen lamp
	□	without artificial lighting	FL	fluorescent lamp
	■	with artificial lighting	LOD	limit of detection

7.2 Results

Just in two showcases (N2.2 and M7.2) an effect of artificial lighting on indoor air pollution levels could be observed. In N2.2 the Σ(VOC)-value increased from 6609 µg/m³ to 34870 µg/m³, although no fluctuations in temperature and relative humidity were recorded. Temperature increased slightly from 21°C to 22.6°C (averaged values), whereas relative humidity decreased from 58% to 55% (averaged values). 53 substances were identified in total without lighting, whereas 65 substances were detected under illumination. All 53 individual substances could be clearly identified as primary emissions. No secondary emissions were detected. The majority of all emitted substances rose by a factor of > 3 under artificial lighting. Most of the compounds with *bp* < 100°C increased at a factor of two or three, whereas compounds with *bp* > 100°C rose at a factor > 5. However, no detailed correlation between substance classes, molecular structure and boiling point of identified VOCs and the degree of emission increase could be observed. Increasing factors varied primarily between 3 and > 10. Molecules with functional groups, such as ketones, carboxylic esters and glycol esters, rose at a factor of 3 or 4, also halogenated compounds and siloxanes. Glycol ethers and molecules of less complex structures, like alkanes, cycloalkanes and alcohol increased at a factor of 6. Aromatic hydrocarbons and aldehydes were an exception with a great increase of 8 and 16, respectively. Figure 7.2-1 compares values of each substance class detected in showcase N2.2 without and with light.

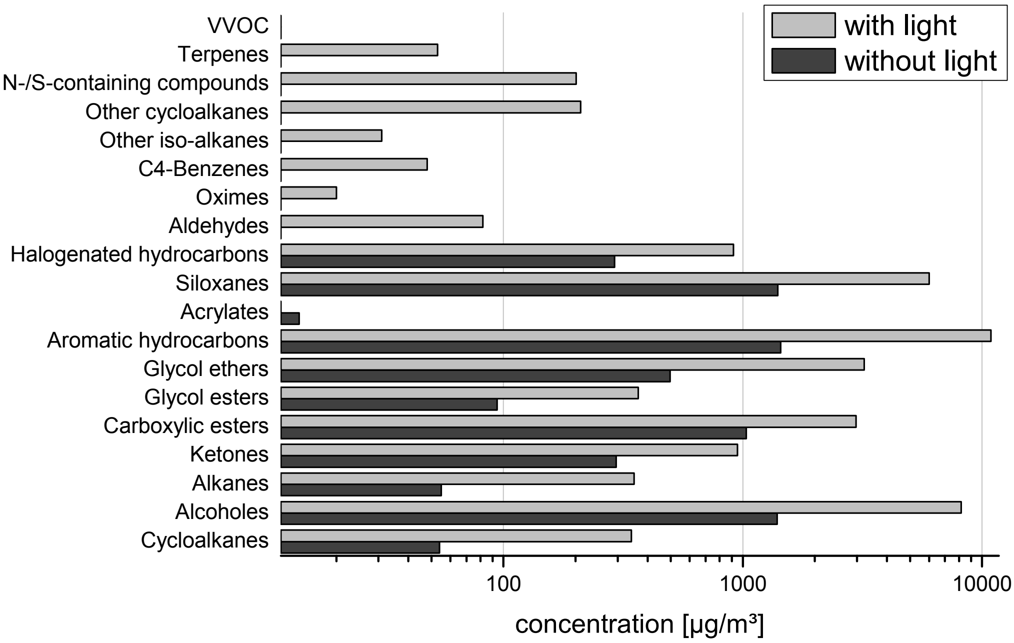


Figure 7.2-1. Concentrations of substance classes detected in showcase N2.2 without and with artificial lighting, identified by GC/MS.

The occurrence of new compounds let assume that not only thermal induced processes, but also photochemical reactions proceed. Some remarkable substances, which were just detected under light were non-identifiable compounds containing nitrogen and/or sulphur (73 µg/m³) in the retention time gap 20–23 min. Comparisons with nitrogen containing substances which were analysed in chamber air of UV-curing adhesives (see section 5.3.1.3) showed no accordance.

Another interesting observation was the fact that few substances with boiling points *bp* > 150°C just occurred without additional lighting. 1-Methoxy-2-propylacetate, 2-ethyl toluene and undecane (C_{11}) were analysed in concentrations of 19 µg/m³ and 7 µg/m³, respectively, but surprisingly could not be detected during the light experiment. The same applies for some non-identifiable VVOCs (10 µg/m³) and isobornyl acrylate (14 µg/m³). Concerning the latter compound as an acrylate monomer, it may be regarded as a monomer excess in UV-curing adhesive formulations, which reacted totally under additional lighting. The halogen spotlights were proved as emitting no UV-radiation (Hönle UV-Meter High End). Impact of UV-radiation, which might influence photochemical reactions and thus contribute to an increase in emissions, can be excluded.

Changes in VOC concentrations were also observed regarding showcase M7.3. Without and with artificial lighting 49 individual substances were in total identified. New substances could not be detected. Whereas it was found that iso-alkanes increased under illumination, most substances based on butane decreased. Other compounds, such as e.g. glycols, aromatic hydrocarbons and siloxanes, remained nearly constant. It was not possible to place a hygrologger inside the showcase so that no information about possible climatic changes could be obtained.

In the other showcases, no markedly effect on pollution levels under illumination was detected. The air exchange rate in showcase M7.3 was lower ($n = 0.01\ h^{-1}$) than with artificial lighting ($n = 0.03\ h^{-1}$). This fact indicates that thermal circulation is caused even by the fluorescent lamps.

Regarding showcase M8.1, a lower Σ(VOC)-value was documented under artificial lighting in contrast to results without light. As already mentioned in section 6.3.1, this showcase is constructed with huge gaps allowing an unhindered air exchange with the environment. It can be assumed that switching on the light causes heating and thermal circulations, which will enhance exchange with the environmental air.

7.3 Discussion

The findings of showcase N2.2 and showcase M7.3 show influences of artificial lighting on indoor air quality despite negligible changes in climatic conditions (temperature, relative humidity). This is contradictory to previous studies. Bake-out studies reported consistently that there is no observable effect on volatile primary emissions at temperature increases of 10°C. One explanation is given by the gas phase diffusion theory, according to which the increase of VOC diffusion coefficients would be less than 10% at a temperature increase from 23°C to 35°C for primary sources. A large increase may be observed due to residual solvents, which are depleted at a rapid rate (Girman et al., 1989). Regarding secondary sources caused by desorption or decom-position products, a much larger effect would be anticipated (Wolkoff, 1998). Large effects have been observed at temperature differences of nearly 30°C from 25°C to 60°C (Van der Wal et al., 1997; Wolkoff, 1998). This is attributed to desorption effects. Moreover, dependencies of VOC-types on relative humidity and temperature are reported: Concerning low relative humidity, influences are attributed to a kind of dry-out processes and hindered transport mechanisms from polar substances by water vapour causing changes in film structures (Wolkoff, 1988). Also a dependency of VOC concentrations and air velocity are reported. Wolkoff (1998) stated that evaporation controlled emission processes as well as secondary reactions are influenced by increased air velocities.

As showcases are mostly closed and transported immediately after production to the customer, evaporation and diffusion controlled processes may overlap and in addition evaporation mechanisms may last longer. However, facing the almost static conditions within showcases, negligible air velocities are presumed. Instead of this, it can be supposed that the low air exchange rate and the heat transfer inside the showcase are of importance as they are influencing the accumulation of emitted VOCs and the emissions from materials.

To clarify the findings in comparison to the results of previous studies, investigations of air flows and temperature distribution within showcases were accomplished.

7.4 Air flows and temperature distribution within showcases

As it is reported from previous studies that air velocity, temperature and relative humidity might influence material emissions, changes of these parameters without and with artificial lighting were focussed. Investigations were performed in the laboratory by passive thermography.

7.4.1 Passive thermography

Temperature gradients and air flows within the test showcase were conducted by means of passive thermography (Ircam, Velox 327k M; spectral range: 3.4-5.0 µm; image format: 640 x 512 pixel, temperature resolution: <20 mK). Long-term sequences of temperature gradients within the showcase were recorded with a picture rate of 1 picture/s and with a 15 mm wide angel objective. Short-term sequences were recorded with a picture rate of 20 pictures/s and a 8 mm wide angel objective.

7.4.2 Test procedure

In a first step, different light sources commonly installed in museum showcases were examined for infrared radiation: halogen spotlights, fluorescent lamps, fibre optics and light emitting diodes (LED). Parameters are given in Table 7.4-1

Table 7.4-1. Light sources examined for infrared radiation.

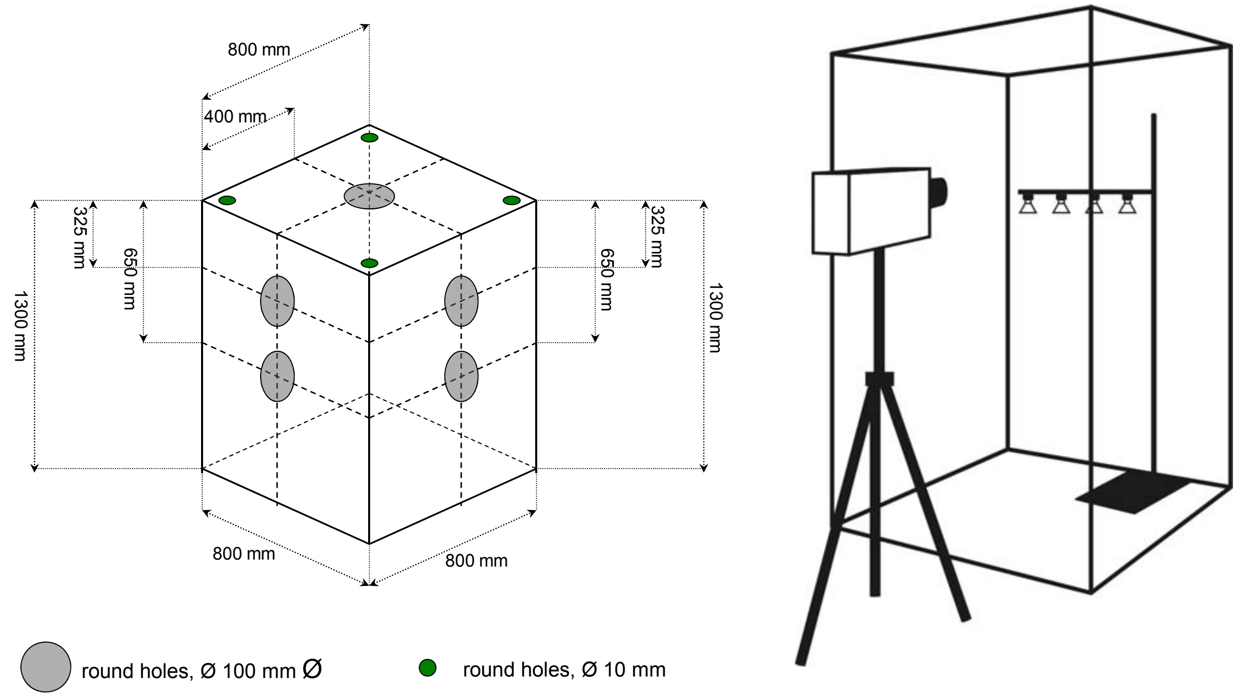
Lighting system	Output [W]	Voltage [V]
Double fluorescent lamp	21	-
Fluorescent lamp	18	20
Halogen lamps	20	12
Fibre optics	100	-
Light-emitting diode (LED)	-	-

- unknown

Subsequently, airflows and temperature distribution within a showcase with and without artificial lighting (four halogen spotlights) were investigated. Object on investigation was a newly constructed showcase provided by the manufacturer of showcase N2.2. As markedly influences of indoor air quality were just observed regarding this enclosure, it was important that the type of construction as well as the dimensions were as comparable as possible. One exception was the sealing material. Instead of UV-curing adhesive for sealing the glass edges acid curing silicone rubber was applied. The material was proved by an intense acid smell inside the enclosure. Additionally, this material choice made it impossible to repeat the N2.2-light experiment due to differing building products and also due to the highly increased emissions inside [Σ(VOC)-value: ~10000 µg/m^3, HCHO: ~200 µg/m^3, HCOOH: 150 µg/m^3; CH_3COOH: ~2800 µg/m^3], which would have overlain light induced effects of smaller-scale.

In order to allow the record of temperature gradients and air flows inside the showcase by thermography, it was necessary to cut out round glass plates from two adjoined glass sides and from the glass cover plate to place the camera objective into a hole for an unhindered view inside. The dimensions of the showcase and of the cut-outs are illustrated in Figure 7.4-1a.

Four halogen spotlights of the same power as those in N2.2 were placed inside the showcase. Air flows and temperature gradients were recorded by passive thermography without light and after switching on the spotlights in long-term sequences (each ca. 8 h). The experimental set-up is shown in Figure 7.4.-1b.



Figures 7.4-1a and b. (a) Scheme of the test showcase with holes, which are necessary for the thermographic camera; (b) experimental set-up for recording air flows and temperature gradients inside the showcase by passive thermography.

7.4.3 Results

As can be seen from Figure series 7.4-2a-c, LED and fluorescent lamps emit small fractions of infrared radiation. Due to the construction of halogen spotlights; up to 60% of thermal radiation is led off backwards through the mirror (Figure series 7.4-2c).

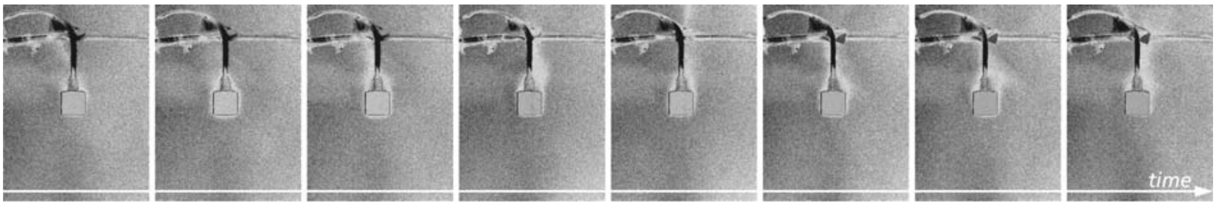


Figure series 7.4-2a. Marginal heat flow around a LED lamp. Thermographic images.

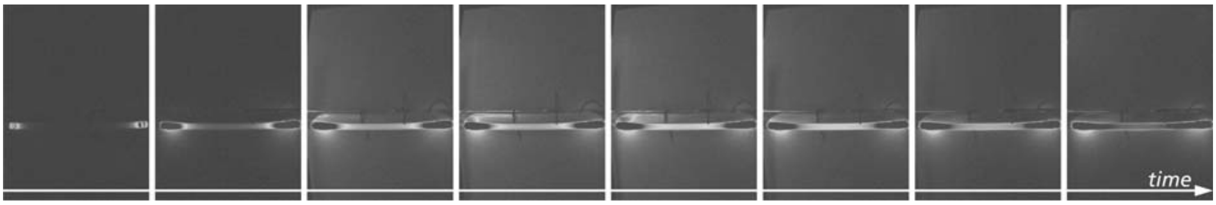


Figure series 7.4-2b. Temperature distribution inside a fluorescent lamp. Thermographic images.

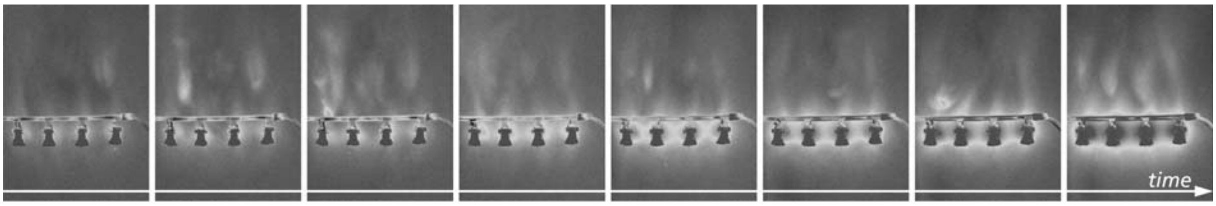
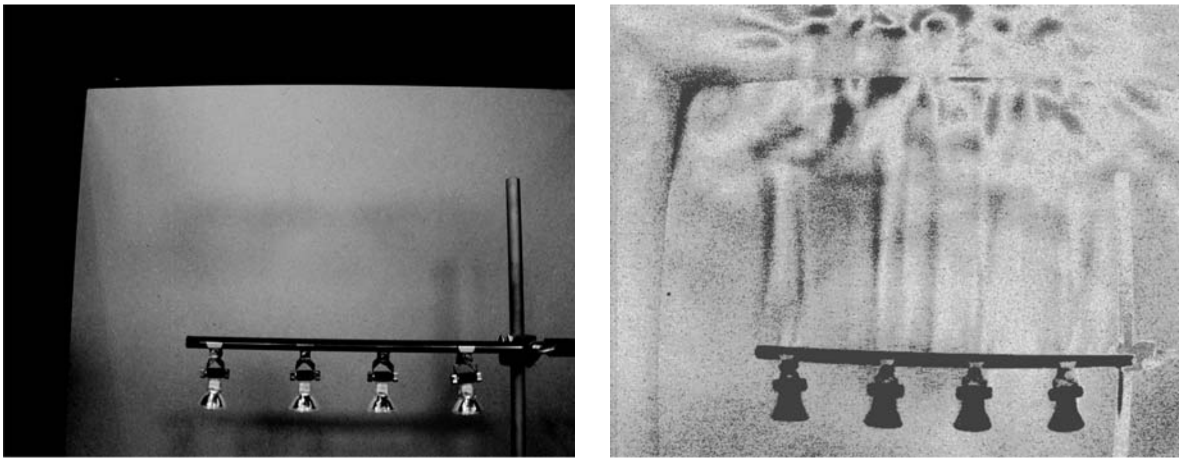


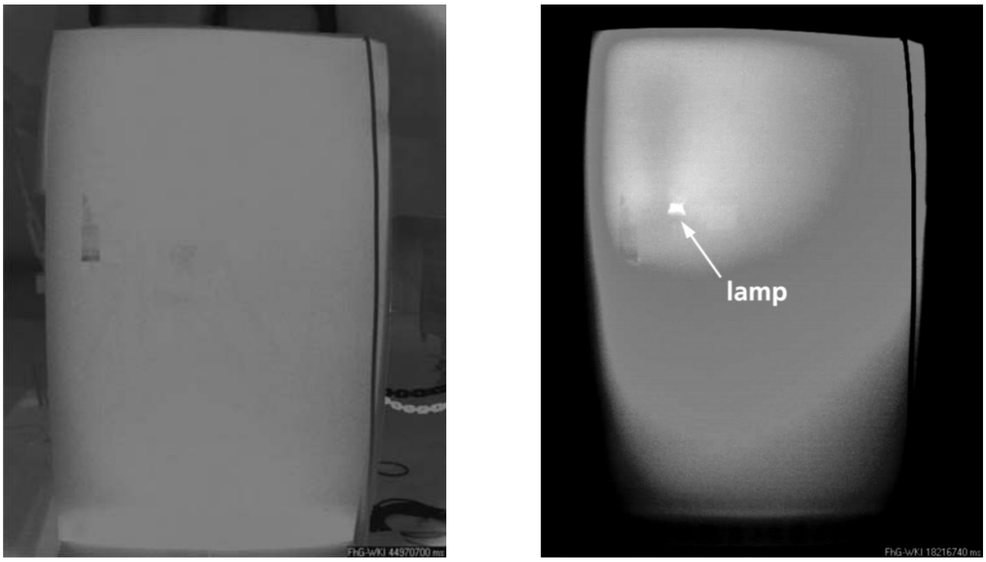
Figure series 7.4-2c. Heat radiation of halogen spotlights. Thermographic images.

The generation of heat from halogen spotlights causes turbulent air motion by heat convection. Heated air rises to the cover plates, cools down and slowly falls down along the glass side panels. Figures 7.4-3a and 7.4-3b illustrate that this convective heat transfer is just limited to the area above the heat source (halogen spotlights).



Figures 7.4-3a and b. (a) Left corner above the four halogen spotlights, close-up view inside the showcase; (b) turbulent air flows induced by halogen spotlights inside a showcase. Thermographic images.

On examination of the whole showcase from outside (see Figures 7.4-4a and b) it becomes clear that despite of these local air flows do not extend over the whole showcase volume. Even though air circulation is induced locally by switching on the light, it can be seen, that a negative temperature gradient occurs from the top to the bottom of the whole showcase originating from the light source. This means that during lighting cycles common for museum use (mostly 8 h a day), equilibrium is reached fastly within a showcase after switching on the light. Despite of local air flows aroung the light source, no perceptible air motion within the whole showcase volume will occur.



Figures 7.4-4a and b. (a) Temperature equilibrium inside a showcase without artificial lighting and (b) temperature layering under illumination. View from outside the showcase. Thermographic images.

An increase of emissions as reported due to higher air velocities [from 1 cm/s up to 9 cm/s, see Wolkoff (1998)] can be excluded as changes of air velocity are closely limited to a small defined space in the direct surrounding of the lamps.

During this experiment, temperature was additionaly recorded in different heights inside the showcase by dataloggers (Datataker DT 600). The first measuring sensor was placed with a small distance under the glass cover plate. The next sensors were located each 20 cm down to the base plate. The obtained temperature versus time plot for different heights during a lighting cycle demonstrates this gradient in Figure 7.4-5.

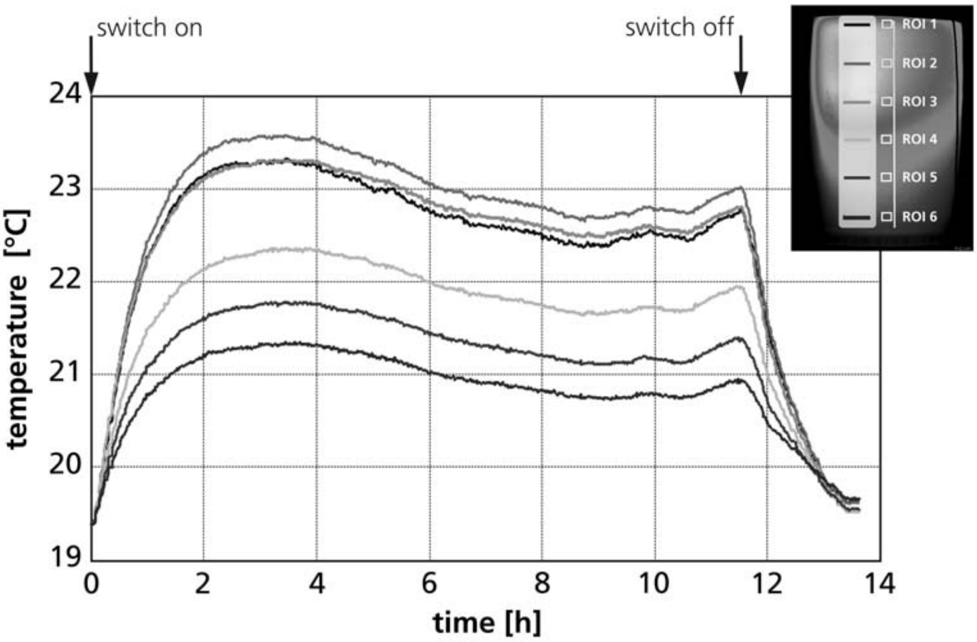


Figure 7.4-5. Gradient profiles of temperature distribution *versus* time under illumination.

The temperature profile clarifies that there is temperature equilibrium within the showcase without artificial lighting. After switching on the light, temperature curves expand in dependence of the distance from the lighting source. In the direct surrounding of the lamps, temperature increases at a maximum of 4°C. At the farthest measuring point, just a temperature increase of 1.7°C was recorded. The findings let conclude that without artificial lighting and/or a surrounding temperature gradient, temperature equilibrium is formed until it is influenced by illumination or heating sources causing temperature gradients (“air layering”). This means that although no temperature recording was possible during light experiments, it is assumed that temperature within the cases was in accordance with temperature in the environmental room.

Furthermore, regarding Figure 7.4-4b it becomes obvious that corners remain cooler than the air inside. The assumption that emissions from UV-curing adhesives will increase due to a higher heating up in comparison to other parts can be excluded. The same applies for the lacquered wooden base-plate, which will not be heated markedly as shown in Figure 7.4-5. Temperature increase cannot be the reason for observations made under artificial lighting in showcase N2.2. The lacquered wooden base-plate was installed after curing, whereas the showcase was closed immediately after sealing the gaps. Thus, emissions from the wooden plate will be diffusion dominated in contrast to the silicone rubber which is dominantly evaporation controlled. Even though it is reported that evaporation controlled emission rates are more affected by higher air velocities than diffusion controlled processes (Wolkoff, 1998), it was shown by Figure 7.4-4b that air velocity will not change over the entire showcase.

7.5 Summary of the results

From the experimental series some influence of artificial lighting directly inside the showcase can be suspected. High increase of VOC-concentrations was observed for one showcase (N2.2) but could not be confirmed by other investigations. The fact that climatic conditions inside the showcase remain nearly constant is contradictory to previous findings, but was proved by a second experimental step. By use of passive thermography it was shown that equilibrium is inside a showcase without artificial lighting until it is influenced by a heating source. This might be a source in the environmental room (e.g. lighting, heating) or in the case itself. After switching on lamps installed directly in the case air circulation can just be observed locally around the light source. Regarding the whole showcase volume, no overall circulation will occur but air layering in minor temperature gradients. As observations neither can be explained by findings of previous studies nor could be confirmed so far, the results of this test series remain unexplained.

All thermographic images are also contained in false colours in the appendix (section 11.4)

8 Evaluating potential damage to artwork materials – a theoretical approach

The fact that gaseous substances are involved in deterioration processes and ageing mechanisms of cultural assets or that they are even the initialising factors, is rarely to realize in the museum everyday life until macroscopic observable damages occur. Damages result from chemical and physical interactions. Those processes may proceed slowly and unnoticed in the beginning until they are physically visible. Furthermore, they depend on various parameters, especially on environmental climatic factors, such as temperature, relative humidity, solar radiation and the presence of oxidizing agents, which may enhance degradation processes.

It has been found that not only high pollution levels of short-term, but also low pollution levels lasting for a long-term period are of importance as they correspond in damaging strength. Thus, the dose of concentration (*concentration x time*) plays a major role (Tétreault, 2003). Further important parameters are i.e. object-inherent materials and their diverse symptoms of age as well as the history of conservation-restoration treatments as during these new materials are added.

Pollutant induced damages on artworks depend markedly on possible sorption interactions between an airborne pollutant and an indoor material surface, which means that the material surface acts as a sink. Very low air exchange rates seem to be necessary for the progress of sorption interactions (Ryhl-Svendsen, 2007), which is a clearly meet condition in museum showcases. Most artworks have rough surfaces of large areas, e.g. textiles, papers, leather, (polychrome) wooden objects. Substrates of porous structure are of higher pollutant removal rates than materials with smooth surfaces. They are also permeable to more volatile and/or apolar compounds. Important parameters regarding potential gaseous-surface reactions are the physical-chemical properties of both the material and the gaseous volatile. Regarding the preservation of artworks it is of particular importance that also base materials which are not in direct contact with indoor air, but which are covered by permeable materials may actively play a role as sink as stated by Meininghaus et al. (1999).

According to Weschler and Shields (1997) polar surfaces attract polar VOCs and water; nonpolar surfaces attract nonpolar VOCs and repel water. The fact that material surface water catalyzes corrosive reactions is known for the surface tarnish process of hydrogen sulphide (H_2S) on metals. Although the exact mechanism(s) is not fully understood so far, for silver, the first stage seems to be an adsorption into the surface water layer, followed by an electrochemical dissolution process (Graedel et al., 1981; Graedel 1992). Schematically, the systems may be represented as (according to Schieweck et al.):

$$H_2S + H_2O \rightarrow HS^- + H_3O^+$$

$$2Ag + HS^- \rightarrow Ag_2S + \frac{1}{2}H_2 + e^- \qquad (8\text{-}1)$$

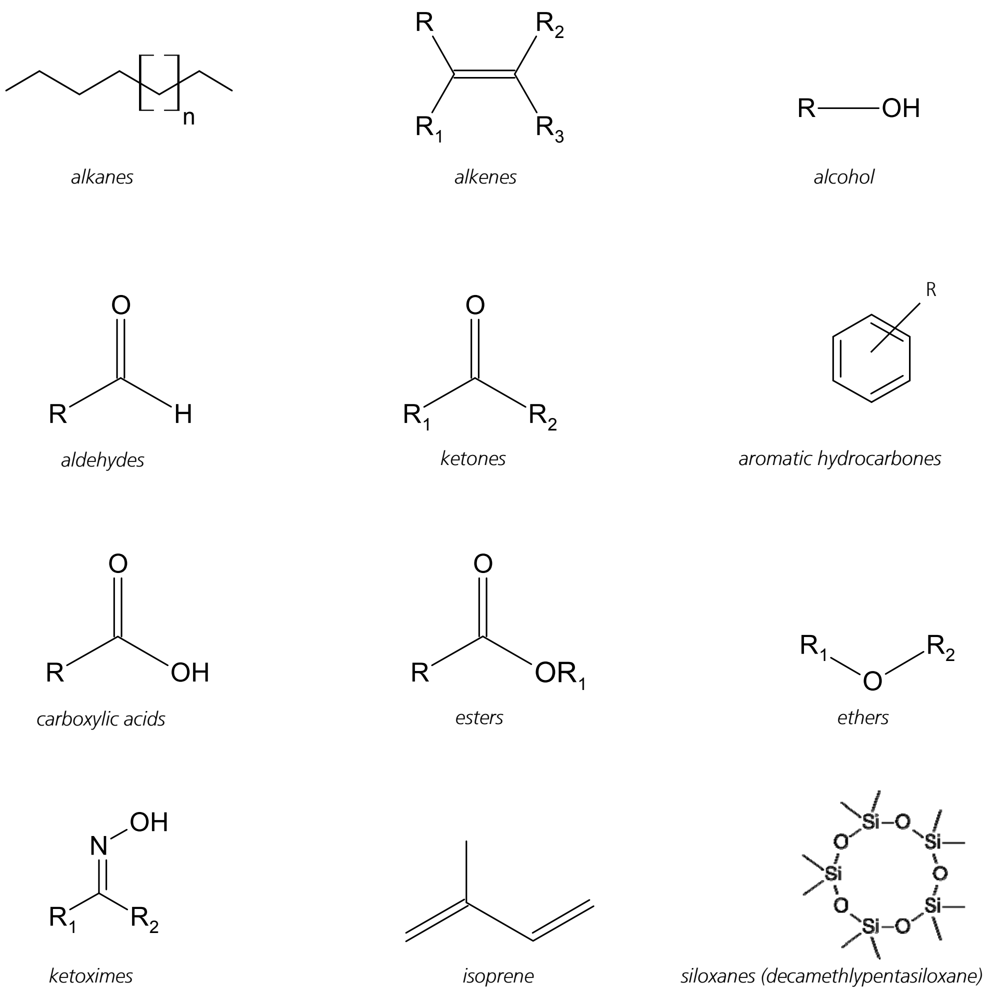
Where carbonyl sulfide is the tarnish agent, for either metal it has been shown that the first stage is the adsorption of the corrodent into the surface water layer (Graedel et al., 1981, Graedel, 1992), analogous to the tarnish of silver with hydrogen sulphide (H_2S) (Schieweck et al.). Further important factors for adsorption/desorption phenomena and reactions catalyzed by a surface are impurities, defects or polychristallinity, which is also met by most historical artworks (Katsanos et al., 1999) and the reactivity of the artefact itself (Ankersmit et al., 2005).

It can be summarized that reactions between airborne pollutants and surfaces of artwork materials are probable at all. Previous studies are restricted to obviously damages, such as impact of inorganic compounds and corrosion due to organic acid exposure (formic acid, acetic acid). Hence, an attempt is made for evaluating potential interactions between volatile organics detected during this study and artwork materials.

Interactions between airborne pollutants and artwork materials

During experiments taken out in this study a broad range of organic volatiles was detected contributing to highly increased air pollution levels in museum showcases. The demand for highly sealed showcases within preventive conservation strategies causes almost static conditions inside the enclosures and enhances the accumulation of indoor air pollutants.

Figure 8-1 gives an overview of detected material classes and their chemical structures.



alkanes *alkenes* *alcohol*

aldehydes *ketones* *aromatic hydrocarbones*

carboxylic acids *esters* *ethers*

ketoximes *isoprene* *siloxanes (decamethlypentasiloxane)*

Figure 8-1. Overview of detected substance groups and their chemical structures.

Simple structured compounds without C=C double bonds and without a functional group, such as alkanes, will not undergo chemical interactions under indoor environment conditions and can be evaluated as non-reactive according to Salthammer (2000). It is suspected that other substance groups have a certain reaction potential with the material surface.

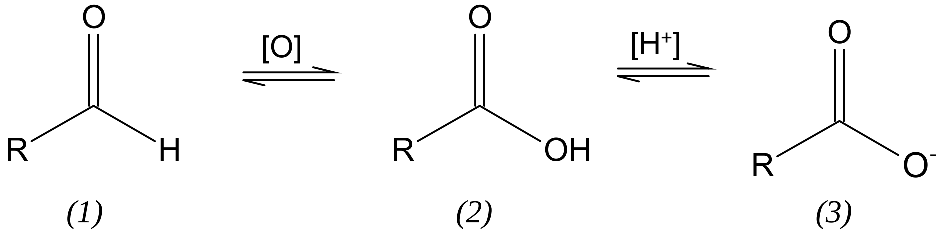
Temperature and relative humidity are main parameters in the preservation of artworks as these are highly sensitive to climatic fluctuations. Tétreault (2003) defines water vapour even as one of his seven key airborne pollutants (see section 2.2.2.1). Contrary to this definition, water vapour is regarded in the present context as one main reactant, which benefits some organic reactions.

Organic esters

Organic esters (carboxylic esters, glycol esters and acrylates) were the most dominant substance groups emitted by modern construction products and were therefore analysed in increased concentrations within modern museum showcases. As already discussed, the most important reaction process in presence of water vapour is ester hydrolysis causing increased acetic acid concentrations in the gaseous phase. This reaction process elucidates the fact of still highly increased acetic acid values inside of new modern museum showcases, although neither acetic acid containing nor acetic acid separation product formulations have been utilized. However, this reaction may also proceed in the surface water layer of an object. Donovan and Moynehan (1965) found that acidic emissions of paints – either as primary or secondary emissions – are able to corrode bare metals in the presence of moisture. Furthermore it was reported that esters can interact with other chemical compounds to form acidic reactants and can additionally solubilise coatings of paint media, varnishes and resinous materials found associated with works of art (Cawthorne et al., 1966).

Aldehydes and organic acids

Facing the current state-of-the-art, acidic pollutants are hazardeous compounds regarding cultural assets as a broad range of artwork materials is acid-sensitive. Formaldehyde, formic acid and acetic acid are known emissions from wooden products. Also it was shown during this study that acetic acid is emitted by solvent borne coating materials due to ester hydrolysis. The process depends on the moisture content of the product and of the relative humidity in ambient air, respectively. According to Grzywacz (2006), a three-step process is suspected (see Equation 8-2) which leads to the oxidation of aldehydes (1) forming at first organic acids (2) and subsequently the corresponding salt due to acidic attack of a material surface. It is supposed that during the interaction of an organic acid and a museum object, the acid is dissociated in a proton and its anion, which finally is identified in the corrosion product.



(8-2)

However, it is not clarified so far if this aldehyde oxidation takes place in the material or in the gasphase as it is not known if strong oxidants will be present in museum atmospheres. Also the relation between levels of aldehydes and the corresponding acids still remained unexplained. A first approach was undertaken by Raychaudhuri and Brimblecombe (2000) and revealed a first correlation between formaldehyde, formic acid and surface corrosion.

It was shown in Equation 8-1 that absorption of a volatile pollutant into the material surface water layer can be the first step of a chemical reaction and might be therefore of major importance. Besides formic acid and acetic acid, propanoic acid, heptanoic acid and octanoic acid were identified as emissions from wood-based materials. According to their acid dissociation constant (pK_a), the acidic strength decreases in the following order: formic acid (pK_a: 3.75) > acetic acid (pK_a: 4.75) > propanoic acid (pK_a: 4.88) > heptanoic acid (pK_a: 4.89) > octanoic acid (pK_a: 4.85). Formic acid is according to the pK_a-values the strongest acid among the detected organic acids. It can be presumed that documented organic acids would dissociate in such surface water layers. However, this process is more likely for formic acid than for the other acids as these are evaluated as weak acids ($pK_a > 4$).

Ketoximes

Ketoximes are released as crosslinking agents during the hardening process of neutral curing silicone rubbers in elevated concentrations. Ketoximes are evaluated as reactive compounds due to the polar hydroxylgroup. Theoretically, oximes can undergo Beckmann rearrangement, an acid-catalyzed process forming amides. Anyhow, Beckmann rearrangement has not been observed during the present study. If this process will take place, aliphatic and aromatic amines can be evolved, of which some substances are of strong odour and others are classified as carcinogenic.

Phenols

Phenol (C_6H_5OH) has been detected as emission from fish glue (sample G-2). Even if phenol has a limited solubility in water, the hydroxyl group may dissociate resulting in a highly water-soluble phenoxide anion ($C_6H_5O^-$). As it was already mentioned, it is assumed that the dissociation of acidic pollutants in a material surface water layer seemed to be an important initiation step for a chemical reaction.

Aromatic hydrocarbons

Previous studies indicate that aromatic hydrocarbons such as benzene and toluene cause adverse effects on inorganic pigments. Kalantzopoulos et al. (1998) have investigated influences of benzene and toluene on metal oxide pigments with and without presence of nitrogen dioxide (NO_2). The starting point of this study was historical buildings and monuments which are decorated with mural paintings and exposed to outdoor pollutants. However, results can be restricted transferred to airborne pollutants inside of buildings and especially inside of showcases as the occurrence of inorganic pollutants cannot be totally excluded.

UV-curable systems / Photoinitiators

As photoinitiators are commonly added in non-stoichiometric amounts (Salthammer et al., 2002), they are partially released unreacted into indoor air together with a broad range of reactive photofragments. As discussed in section 5.3.1.3 several unreacted photoinitiators as well as photofragments have been detected during chamber emission tests and might be released into the showcase. Photoinitiators undergo fragmentation processes in order to form radical species which are of high reactivity. It is assumed that these substances initiate reaction mechanisms with artwork materials under museum conditions.

Biocides and pesticides

Biocides and pesticides in the museum environment are connected with different damages on artworks. Hatchfield (2002) gives a review of relevant studies (Jedrzejewska, 1971; Tilbrooke, 1975; Fenn, 1995).[1] After Tilbrooke (1975),[1] naphthalene is suspected of softening natural resins and accelerating the corrosion of some metals. 1,4-dichlorobenzene can cause fading of ink and yellowing of paper as reported by Jedrzejewska (1971).[1] Furthermore, it can damage leather or feathers (Dawson, 1984). Polyvinyl chloride, which was assumed to be stable at exposure to individual biocides, was found to be damaged by exposure to a mixture of biocides (Fenn, 1995).[1] Exhibition and storage materials as well as furnishing products can absorb volatile biocides. Cellulose nitrate and polyvinyl acetate soften, shrink and gain weight by absorbing 1,4-dichlorobenzene. The same case applies to hide glue which can therefore be a high risk for wooden objects (Dawson, 1984). Some polymeric materials such as methyl methacrylate, polycarbonate and acrylic sheeting can act as secondary emission sources of substances such as

---

[1] Original sources not available. Data adopted from Hatchfield, 2002.

acetic acid and biocides as stated by Fenn (1995). A popular example of damaged objects is the white bloom of DDT (dichlorodiphenyltrichlorethane) attached to surfaces of wooden objects due to the excessive application of oily wood preservatives. After evaporation of the solvent, surface efflorescence is formed (Unger, 1998; Unger et al., 2001).

Fogging effects

It was furthermore found that semi-volatile organic compounds (SVOCs) which tend to condense on glassy surfaces form hazy films on showcases and glazings. Regarding the presented examples (see section 6.4.2) this phenomenon could be attributed to the artefact itself. However, it is known that fogging might also result from building product emissions. Especially phthalic esters, common plastizisers and flame retardants, migrate from the polymer matrix and condense on smooth surfaces (Uhde et al., 2001; Wensing et al., 2005). Ester hydrolysis of phthalates under environmental conditions and its dependence of the moisture content in the material and from relative humidity was reported (Sjöber, 1997; Fang et al., 1999; Salthammer, 2000). A typical example is the hydrolysis of diethylhexyl phthalate (DEHP) to 2-ethyl-1-hexanol and the corrosive compound acetic acid. DEHP is a common applied plasticizer in flooring products. (Sjöberg, 2000). Formed aldehydes might impact the perceived air quality due to their low odour thresholds (Devos et al., 1990). Especially saturated and unsaturated aldehydes (C_5-C_{11}) belong to undesired substances in indoor air (Salthammer, 1999).

Miscellaneous

Moreover, from industrial use corrosion processes resulting from polymeric materials are known. Zinc can corrode by components of styrene-based polyester resins, presumably due to the degradation of peroxide catalysts or by an interaction of the peroxide catalyst with the resin. Moreover, polyester resin releases formic acid during cold-curing and also polystyrene polymerized by peroxides is observed to be corrosive. This process does not appear to be corrosive when non–oxidizing polymerisation is carried out (Cawthorne et al., 1966; Hatchfield, 2002 and citations therein).

9 Conclusions

The majority of our cultural heritage located in museums is nowadays stored and exhibited inside of showcases in order to ensure appropriate preservation conditions. For this reason, installed products for construction and decoration purposes are of high importance, in particular facing known damages due to corrosive emissions from unsuitable materials. For this reason, material emissions and indoor air quality of museum showcases were the focus of this work.

It was clearly shown that the material choice determines the composition of indoor air quality and consequently the levels of airborne pollutants. Whereas so called old-type showcases constructed from traditional materials are characterized by a rather low range of volatile organic compounds (VOCs), but heightened levels of formaldehyde, formic acid and acetic acid, a broad variety of VOCs and still highly increased acetic acid concentrations were found in modern showcases.

The differences in the span of individual VOCs result from the fact that today product formulations with a wide spectrum of solvents and additives are utilized. These characteristic substances are therefore attributed to the currently main emission sources in showcases, namely coating materials and rubber sealants. Raw materials without any additional surface treatment can be evaluated as low emissive. Remarkable substances identified for the investigated material categories correspond with those emissions known from building products for normal indoor use. This finding is not surprising as there are no products available on the market, which have been especially designed for museum purposes.

Also in accordance with findings from environmental chemistry it was demonstrated that under nearly static conditions inside of museum enclosures secondary reactions proceed. The main important mechanism is ester hydrolysis. Carboxylic esters, which constitute the main part among solvents and additives, are splitted under release of acetic acid and the corresponding alcohol. This reaction explains the still elevated acid concentrations inside modern museum showcases, even though no acidic formulations were applied. Comparing these results it becomes clear that main emission sources have shifted from wood-based products and acid curing silicone rubber to solvent borne materials without solving the problem of high acetic acid concentration which is a well-known corrosive agent in the museum environment.

It was also found that air pollution levels inside of showcases constructed with modern materials are markedly higher than those which were detected in old-type showcases. The accumulation of emissions generated inside the enclosure is attributed to the low air exchange rates. Due to the requirements concerning prevention conservation standards, which were introductory formulated, highly sealed showcases are nowadays the most preferred construction types. Air exchange rates proved to range around 0.01 h^{-1}. The almost static conditions hinder the escape of generated emissions inside and enhance high pollution levels. These vary between 100 µg/m³ and 17000 µg/m³ in modern type showcases and are therefore a factor of around eight higher than within old-type enclosures. Minor pollutant concentrations are attributed to an open construction type with gaps which allow an unhindered air exchange with the outer environment. However, this construction type is not as much favoured due to the concern that dust and outdoor air pollutants are infiltrated and security is lowered.

Facing high pollution levels inside and secondary reactions obtained during this study it becomes clear that findings from indoor environments under residential or office use do not allow wholesale transfer to the museum field. The statement that generally low-emitting materials will give low emitting structures (Wilke et al., 2004) seems not to be valid on the museum sector. It was found in this study that pollution levels within showcases that are built from low emissive materials are not lowered as under almost static conditions saturation vapour pressure will be reached.

Moreover, it is suspected that light sources directly installed inside the showcase might have an impact on pollution levels. However, neither any correlation between the findings of several experiments nor any explanatory model could be obtained. No increase in temperature or enhancement of air flows inside the showcase was detected. It was rather demonstrated that without integrated lighting temperature equilibrium is formed through the whole showcase passing to a kind of air layering of minor temperature gradients after switching on the light. The data could not be clarified so that further investigations are necessitated in order to reach a decision how to illuminate museum exhibits.

In addition to building and construction materials also the stored artworks themselves act as emission sources. By investigating emissions from products for conservation and restoration purposes it was obvious that high emission levels result again from solvent systems, in which raw materials have to be dissolved before handling or which are already contained in product formulations. Thus, it is hardly possible to distinguish artwork material emissions from those of construction and decoration materials as remarkable substances off-gasing from solvents and additives are nearly the same. Exceptions are traced active agents of biocides and pesticides, which can be clearly attributed to former preventive treatments. It was discussed that also these compounds may impact artwork materials. Furthermore, they cause adverse effects on human health.

Substances harmful for human health could also be identified among emissions from construction products. As these are classified as toxic (o-phenetidine, trichloroethene) or even as carcinogenic and/or mutagen (2-butanone oxime, benzene), it is clearly stated that formulations emitting hazardous substances should be used cautiously and just in exceptional cases, even though the priority in museum collections is given to the preservation of artworks. The same applies for coating materials which still contain heavy metal pigments as a variety of alternatives is available. Material safety data sheets do not provide adequate help for selecting appropriate materials as there is no correlation between indicated ingredients and analysed substances, which are released into the gas phase.

It can be concluded, that the use of low-emissive products could not be realized so far just by substituting some well-known high-emissive materials. Moreover, the aim to minimize emissions of formaldehyde and acetic acid was also not achieved until now due to ester hydrolysis of carboxylic esters and glycol esters and the continual application of wood-based products. Furthermore, broad variations during the sample preparation on the part of the manufacturers were obvious. They result primarily from differences during the production processes, especially by awarding production steps to third parties and by carrying out some steps manually, which are therefore more fault-prone than automatically processes. Thus it becomes obvious, that testing results are not long-lasting. To achieve an effective quality assurance for museum purposes, periodical emission analyses are indispensable and are therefore highly recommended. To ensure a quality assurance, manufacturers should try to provide homogeneity and reproducibility during production processes to guarantee a constant quality towards the museum costumers.

Adverse effects on artworks

Corrosive potentials on artwork materials both of formic acid and acetic acid are well-known and have been fundamentally investigated in the past. Hence, it is presumable that damages which are usually connected with old-type showcases, such as white efflorescence on susceptible materials as metals, will also occur in modern type showcases with low ventilation levels. In addition, due to high solvent emissions a large range of substances with unsaturated hydrocarbon bonds or functional groups was detected. It can generally be assumed that those substances undergo chemical reactions. An important role in damage mechanisms may be attributed to water layers on material surfaces, which enhance absorption of airborne volatiles and their ionization. Of further importance is the application of UV-curing systems either as adhesives or as alternative coatings. Due to the high amount of photoinitiators contained in the formulations, unreacted photoinitiators and highly reactive photofragments are released into the interior of a showcase. Photoinitiators are forming radical species under irradiation and will undergo chemical interactions with other materials. Reactions with artwork materials are probable. Regarding adverse effects on cultural assets, the application of materials releasing reactive species under museum conditions should be avoided.

Interactions among pollutants

Furthermore, interactions between inorganic air pollutants and typical indoor room emissions are an actual topic in environmental chemistry. One main focus is on ozone/terpene reactions contributing to increased particle formation indoors (Weschler and Shields, 1997; Finlayson-Pitts and Pitts, 2000; Toftum et al., 2008) which will deposit on indoor surfaces. Further topics are the decomposition of VOCs yielding secondary products and reactive species (Atkinson et al., 1995; Weschler and Shields, 1997; Carslaw, 2007).

Some effects on artwork materials due to inorganic pollutants are already known. Ozone attacks organic materials, particularly at unsaturated double bonds. Many pigments and dyes are highly susceptible against an ozone exposure. Most of the pigments in artistic watercolours fade rapidly at ozone levels characteristic for urban environments. Anthrachinone lacquers (including alizarine), indigo pigments, dragon’s blood, curcuma, safran, auripigment and realgar are of increased sensibility. Also natural organic pigments and pigments on paper (Shaver et al., 1983) as well as dyed textiles and synthetic lacquers react with atmospheric ozone. Pigments of western art of the twentieth century and traditional Japanese and Chinese dyes may also be damaged by ozone (Whitmore and Cass, 1988; Williams et al., 1992). The fading of natural pigments and dyes due to an ozone exposure results of a deterioration of the chromophore. As the resulting reaction products are colourless, the pigment fades at constant hue. Auripiment as anorganic compound passes into its more stable oxide (As_2O_3). This reaction proceeds under normal environmental conditions, but is enhanced by increased ozone levels (Ye et al., 2000).

Future research tasks

It is quite difficult to assess which role outdoor inorganic compounds may play in chemical reactions with material emissions inside of museum showcases. Facing the fact that ozone (O_3) decays very fast indoors due to its high reactivity, it seems more likely that ozone will absorb on indoor material surfaces than undergo a chemical reaction in the atmosphere. In addition, museum showcases are highly sealed and surface-to-volume ratios are mostly very high so that the probability of outdoor pollutants present inside seems to be improbable. However, a first approach to reveal interactions of indoor generated volatiles and outdoor pollutants was made by Raychaudhuri and Brimblecombe (2000). Therefore, the discussion of reactions between VOCs detected during this study and outdoor pollutants concerning the preservation of cultural heritage is regarded as necessary and should be investigated in a further step.

Standards for pollutants in the museum environment?

Recommendations or guidelines for indoor air quality in terms of cultural heritage do not yet exist. The indoor environment in specific museum institutions and the parameters affecting museum exhibits are too manifold and the sensitivity of artefacts – depending on the object materials and on previous preservation and restoration treatments, respectively – is too different to establish general recommendations. However, in the last few years Tétreault (2003) has tried to develop an evaluation scheme by transferring a toxicological concept to the conservation field to estimate exposure-effect relationships for artefacts. For a number of compounds the author has published NOAEL, LOAEL and LOAED-values. The NOAEL (*No Observed Adverse Effect Level*) and LOAEL (*Lowest Observed Adverse Effect Level*) concept has been originally developed to estimate the threshold of the effect and the exposure of mammals. Tétreault also defined LOAED (*Lowest Observed Adverse Effect Dose*)-values (*concentration x length of time*). The threshold values were obtained by extrapolating results of various international studies and from experimental approaches. Due to varying conditions and methods during these tests, the obtained values are just limited comparable. Tétreault (2003) himself assessed his concept as experimental data just refer to a specific experimental set-up and, thus, cannot be transferred to divergent experiments and to real indoor situations. Also the model is limited to individual compounds or simple substance mixtures. However, the listed values deliver a first comprehensive approach. By application of the LOAED-values an acceptable grade of damage has to be suffered. From the conservation point of view it is questionable to calculate with predictable impacts on artwork materials.

A debate on principles of this evaluation scheme has not been carried out until now. It will be a major future task to attempt a further approach for setting up requirements and threshold values for showcases and the preservation of assets of artistic and cultural value.

It should be also noted that within the European Committee for Standardization (CEN – Comité Européen de Normalisation) a technical committee (CEN/TC 346) is working at present on standards for the preservation of cultural heritage, including on standards for the indoor environment.

Outlook

In spite of the knowledge of some fundamental processes causing deterioration of cultural assets, detailed mechanisms are not clarified so far.

The variety of parameters contributing to damage mechanisms and the fact that reactions may proceed unknown for long-term until they become visible demonstrates that the investigation of such interactions is a broad subject itself.

This study presents comprehensive data about material emissions and indoor air quality in museum showcases under different boundary conditions and might be a first valuable basis for the establishment of future guidelines or further labelling systems concerning the preservation of artefacts.

10 References

Allen, N.S., 1996. Photoinitiators for UV and visible curing of coatings: mechanisms and properties. Journal of Photochemistry and Photobiology A: Chemistry 100, 101-107.

Allen, N.S., Marin, M.C., Edge, M., Davies, D.W., Garrett, J., Jones, F., Navaratnam, S. and Parsons, B.J., 1999. Photochemistry and photoinduced chemical crosslinking activity of type I & II co-reactive photoinitiators in acrylated prepolymers. Journal of Photochemistry and Photobiology A: Chemistry 126, 135-149.

Andersen, I., Lundqvist, G.R. and Mølhave, L., 1975. Indoor air pollution due to chipboard used as a construction material. Atmospheric Environment 9, 1121-1127.

Ankersmit, H.A., Tennent, N.H. and Watts, S.F., 2005. Hydrogen sulfide and carbony sulfide in the museum environment - part 1. Atmospheric Environment 39, 695-707.

Anonymus, 2001. Diffusive uptake rates on PerkinElmer sorbent tubes. In: Health and Safety Executive CAR Committee (Committee on Analytical Requirements), Working Group 5 (Eds.), The Diffusive Monitor 12. Available online at http://www.hsl.gov.uk/publications/diffusive-monitor.html.

Arsu, N., Davidson, R.S. and Holman, R., 1995. Factors affectin the photoyellowing which occurs during the photoinitiated polymerization of acrylates. Journal of Photochemistry and Photobiology A: Chemistry 87, 169-175.

ASTM D 4236–94, 2005. Standard Practice for Labeling Art Materials for Chronic Health Hazards. ASTM International.

Atkinson, R., Tuazon, E.C. and Aschmann, S.M., 1995. Products of the gas-phase reactions of O3 with alkenes. Environmental Science & Technology 29, 1860-1866.

Baumann, W. und Muth, A., 1997. Farben und Lacke – Daten und Fakten zum Umweltschutz, Springer-Verlag, Berlin Heidelberg.

Bears, N.S. and Banks, P.N., 1985. Indoor air pollution: effects on cultural and historical materials. The International Journal of Museum Management and Curatorship 4, 9-20.

Bencs, L., Spolnik, Z., Limpsen-Neilen, D., Schellen H.L., Jütte, B.A.H.G. and Van Grieken, R., 2007. Comparison of hot-air and low-radiant pew heating systems on the distribution and transport of gaseous air pollutants in the mountain church of Rocca Pietore from artwork conservation points of view. Journal of Cultural Heritage 8, 264-271.

Blades, N., Oreszczyn, T., Bordass, B. and Cassar, M., 2000. Guidelines on pollution control in museum buildings. London, Museum Practice.

Bradley, S. and Thickett, D., 1999. The pollution problem in perspective. In: Bridgeland, J. (ed.), Proceedings of the 12th Triennial Meeting of the ICOM Committee for Conservation, Lyon/France, Vol. 2, 8-14.

Brimblecombe, P., 1990. The composition of museum atmospheres. Atmospheric Environment 24B (1), 1-8.

Brimblecombe, P., Blades, N., Camuffo, D., Sturaro, G., Valentino, A., Gysels, K., van Grieken, R., Busse, H.-J., Kim, O., Ulrych, U. and Wiesner, M., 1999. The Indoor Environment of a Modern Museum Building, The Sainsbury Centre for Visual Arts, Norwich, UK. Indoor Air 9, 146-164.

Brokerhof, A. and van Bommel, M., 1996. Deterioration of calcareous materials by acetic acid vapour: a model study. In: Bridgeland, J. (ed.), Proceedings of the 11th Triennial Meeting of the ICOM Committee for Conservation, Edinburgh/UK, Vol. 2, 769-775.

Buhr, A., Genning, C. and Salthammer, T., 2000. Trace analysis of pentachlorophenol (PCP) in wood and wood based products - comparison of sample preparation procedures. Fresenius J. Analytical Chemistry 367, 73-78.

Butte, W. and Heinzow, B., 2002. Pollutants in house dust as indicators of indoor contamination. Reviews of Environmental Contamination and Toxicology 175, 1-46.

Byne, L. Sgt., 1899. The corrosion of shells in cabinets. Journal of Conchology 9, 172-178; 253-254.

Camuffo, D., 1998. Microclimate for cultural heritage. Elsevier, Amsterdam.

Camuffo, D., Brimblecombe, P., van Grieken, R., Busse, H.-J., Sturaro, G., Valentino, A., Bernardi, A., Blades, N., Shooter, D., De Bock, L., Gysels, K., Wieser, M. and Kim, O., 1999. Indoor air quality at the Correr Museum, Venice, Italy. The Science of the Total Environment 236, 135-152.

Camuffo, D., Sturaro, G.,Valentino, A., 2000. Showcases: a really effective mean for protecting artworks? Thermochimica Acta 365, 65-77.

Carslaw, N., 2007. A new detailed chemical model for indoor air pollution. Atmospheric Environment 41, 1164-1179.

Chang, C.-H., Mar, A., Tiefenthaler, A. and Wostratzky, D., 1992. Photoinitiators: Mechanisms and applications. Calbo, L.J. (ed.), Handbook of Coatings Additives. New York, Marcel Dekker, 2.

Chang, J.C.S., Tichenor, B.A., Guo, Z. and Krebs, K.A., 1997. Substrate effects on VOC emissions from a latex paint. Indoor Air 7, 241-247.

Cawthorne, R., Flavell, W. and Ross, N.C., 1966. The corrosion of zinc by vapours from polyester resins. Journal of Applied Chemistry 16, 284.

Charta of Vantaa, 2000. Recommendations for a European approach in Preventive Conservation. Passed on the Vantaa-meeting, September 21-22.

Clausen, P.A., 1993. Emission of volatile and semivolatile organic compounds from waterborne paints – the effect of the film thickness. Indoor Air 3, 269-275.

Clausen, P.A., Wolkoff, P., Holst, E. and Nielsen, P.A., 1991. Long term emission of volatile organic compounds from waterborne paints – methods of comparison. Indoor Air 4, 562-576.

Clausen, P.A. and Wolkoff, P., 1997. Degradation products of Tenax TA formed during sampling and thermal desorption analysis: indicators of reactive species indoors. Atmospheric Environment 31, 715-725.

Colombo, A., De Bortoli, M., Knöppel, H., Pecchio, E. and Vissers, H., 1993. Adsorption of selected volatile organic compounds on a carpet, a wall coating, and a gypsum board in a test chamber. Indoor Air 3, 276-282.

Crump, D., 1999. Application of diffusive samplers. In: Salthammer, T. (ed.), Organic Indoor Air Pollutants. Occurrence, Measurement, Evaluation. Chapter 1.5, WILEY-VCH, Weinheim, 57-71.

Dawson, J.E., 1984. Effects of pesticides on museum materials: a preliminary report. Biodeterioration IV. Papers presented at the 6th International Biodeterioration Symposium. Washington, DC, 350-354.

Davidson, R.S., 1999. Exploring the sience, technology and applications of U.V. and E.B. curing. SITA Technology Limited, London.

De Bortoli, M., Knöppel, H., Pecchio, E., Schauenburg, H. and Vissers, H., 1992. Comparison of Tenax and Carbotrap for VOC sampling in indoor air. Indoor Air 2, 216-224.

De Bortoli, M., Knöppel, H., Colombo, A. and Kephalopoulos, S., 1996. Attempting to characterize the sink effect in a small stainless steel test chamber. In: Tichenor, B.A. (ed.), Characterizing sources of indoor air pollution and related sink effects. ASTM STP 1287, Pittsburgh, PA, 305-318.

Destaillats, H., Lunden, M.M., Singer, B.C., Coleman, B.K., Hodgson, A.T., Weschler, C.J. and Nazaroff, W.W., 2006. Indoor secondary pollutants from household product emissions in the presence of ozone: a bench-scale chamber study. Environmental Science Technology 40, 4421-4428.

Devos, M., Patte, F., Rouault, J., Laffort, P. and van Gemert, L.J., 1990. Standardized human olfactory thresholds. Oxford University Press, New York.

Dietliker, K., 1998. Free radical polymerisation. In: Crivello, J.V. and Dietliker, K., Photoinitiators for free radical cationic & anionic photopolymerisation, Bradley, G. (ed.), 2nd ed., John Wiley and Sons, New York, Sita Technology Ltd, London, Volume 3, chapter 2.

DIN EN 13986, 2005. Wood-based panels for use in construction – characteristics, evaluation of conformity and marking. Beuth Verlag, Berlin.

DIN EN ISO 16000 Part 6, 2004. Indoor air - Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and gas chromatography using MS/FID. Beuth Verlag, Berlin.

DIN EN 717 Part 1, 2005. Wood-based panels- Determination of formaldehyde release- Part 1: Formaldehyde emission by the chamber method. Beuth Verlag, Berlin.

DIN EN ISO 16000 Part 9, 2008. Indoor air – Part 9: Determination of the emission of volatile organic compounds from building products and furnishing – Emission test chamber method. Beuth Verlag, Berlin.

DIN EN ISO 16000 Part 10, 2006. Indoor air – Part 10: Determination of the emission of volatile organic compounds from building products and furnishing – Emission test cell method. Beuth Verlag, Berlin.

DIN EN ISO 16000 Part 11, 2006. Indoor air – Part 11: Determination of the emission of volatile organic compounds from building products and furnishing – Sampling, storage of samples and preparation of test specimens. Beuth Verlag, Berlin.

Donovan, P.D. and Moynehan, T.M., 1965. The corrosion of metals by vapours from air-drying paints. Corrosion Science 5, 803-814.

Druzik, J.R., Adams, M.S., Tiller, C. and Cass, G.R., 1990. The measurement and model prediction of indoor ozone concentrations in museums. Atmospheric Environment. Part A. 24, 1813-1823.

Dunn, J.E., 1987. Models and statistical methods for gaseous emission testing of finite sources in well-mixed chambers. Atmospheric Environment 21, 425-430.

Dunn, J.E. and Tichenor, B.A., 1988. Compensating for sink effects in emission test chambers by mathematical modeling. Atmospheric Environment 22, 885-894.

Dupont, A.-L. and Tétreault, J., 2000. Cellulose degradation in an acetic acid environment. Studies in Conservation 45, 210-210.

EC-European Commission, 1989. Formaldehyde emission from wood based materials: guideline for the determination of steady state concentrations in test chambers. Indoor Air Quality and its Impact on Man. Report No. 2, Luxembourg.

EC-European Commission, 1997. Totale volatile organic compounds (TVOC) in indoor air quality investigations. Indoor Air Quality and its Impact on Man. Report No. 19, Luxembourg.

Einax J.W., Zwanziger, H.W. and Geiß, S., 1997. Chemometrics in environmental analysis. WILEY-VCH, Weinheim.

Ekberg, L.E., 1999. Real-time monitoring of organic compounds. In: Salthammer, T. (ed.), Organic indoor air pollutants. Occurence, measurement, evaluation. Weinheim, WILEY-VCH, 73-83.

Eremin, K. and Wilthew, P., 1996. The Effectiveness of Barrier Materials in Reducing Emissions of Organic Gases from Fibreboard: Results of Preliminary Tests. In: Bridgeland, J. (ed.), Proceedings of the 11th Triennial Meeting of the ICOM Committee for Conservation, Edinburgh/UK, Vol. 1, 27-35.

Fang, L. Clausen, G. and Fanger, P.O., 1999. Impact of temperature and humidity on chemical and sensory emissions from building materials. Indoor Air 9, 193-201.

Feldman, L.H., 1981. Discoloration of black-and-white photographic prints. Journal of Applied Photographic Engineering 7, 1-9.

Fengel, D. and Wegener, G., 1989. Wood. Berlin, Walter De Gruyter.

Fenn J., 1995. Secret sabotage: reassessing museum plastics in display and storage. In: Wright M.M. and Townsend J.H. (ed.), Resins – Ancient and Modern. Preprints of the SSCR's 2nd Resins Conference, University of Aberdeen, 38-41.

Ferm, M., Karlsson, A. and Galle, B., 2002. A multi-component diffusive sampler for acidic gases. In: Health and Safety Executive CAR Committee (Committee on Analytical Requirements), Working Group 5 (Eds.), The Diffusive Monitor 13. Available online at http://www.hsl.gov.uk/publications/diffusive-monitor.html.

Finlayson-Pitts, B.J. and Pitts, J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego.

Fouassier, J.-P., 1995. Photoinitiation, Photopolymerization, and Photocuring. Munich Vienna New York, Carl Hanser Verlag.

Franey, J.P., Kammlott, G.W. and Graedel, T.E., 1985. The corrosion of silver by atmospheric sulfurous gases. Corrosion Science 25, 133-143.

Girman, J.R., Hodgson, A.T. and Newton, A.S., 1986. Emissions of volatile organic compounds from adhesives with indoor applications. Environment International 12, 317-321.

Girman, J.R., Alevantis, L.E., Kulasingham, G.C., Petreas, M.X. and Webber, L.M., 1989. The bake-out of an office building: a case study. Environment International 15, 449-453.

Glastrup, J., 1987. Insecticide analysis by gas chromatography in the stores of the Danish National Museum's Ethnographic collection. Studies in Conservation 32, 59–64.

Graedel, T.E., 1992. Corrosion mechanisms for silver exposed to the atmosphere. Journal of The Electrochemical Society 139, 1963-1970.

Graedel T.E., Kammlott G.W. and Franey J.P., 1981. OCS a potential agent of atmospheric sulfur corrosion. Science 212, 663-665.

Grosjean, D., Whitmore, P.M., Cass, G.R. and Druzik, J.R., 1988. Ozone fading of natural organic colorants: mechanisms and products of the reaction of ozone with indigos. Environmental Science Technology 22, 292-298.

Grzywacz, C.M., 2006. Monitoring for gaseous pollutants in museum environments. Tools for Conservation, Getty Publications, Los Angeles, California.

Grzywacs, C.M. and Tennent, N.H., 1994. Pollution monitoring in storage and display cabinets: carbonyl pollutant levels in relation to artifact deterioration. IIC, Preprints of the Contributions to the Ottawa Congress, Preventive Conservation - Practice, Theory and Research, Ottawa, 164-170.

Gunnarsen, L., 1997. The influence of area-specific ventilation rate on the emissions from construction products. Indoor Air 7, 116-120.

Gunnarsen, L., Nielsen, P.A. and Wolkoff, P., 1994. Design and characterization of the CLIMPAQ, chamber for laboratory investigations of materials, pollution and air quality. Indoor Air 4, 56-62.

Gustafsson, H., 1999. The field and laboratory emission cell - FLEC. Salthammer, T. (ed.), Organic indoor air pollutants. Occurence, measurement, evaluation. Weinheim, WILEY-VCH, 143-152.

Gysels, K., Deutsch, F. and Van Grieken, R., 2002. Characterisation of particulate matter in the Royal Museum of Fine Arts, Antwerp, Belgium. Atmospheric Environment 36, 4103-4113.

Habenicht, G., 1997. Kleben – Grundlagen, Technologie, Anwendungen. Springer-Verlag Berlin Heidelberg.

Hackney, S., 1984. The distribution of gaseous air pollution within museums. Studies in Conservation 29, 105-116.

Hafkenscheid, T., 2006. Effect of temperature on long-term diffusive sampling - how to properly evaluate effective diffusive uptake rates. In: Health and Safety Executive CAR Committee (Committee on Analytical Requirements), Working Group 5 (Eds.), The Diffusive Monitor 15. Available online at http://www.hsl.gov.uk/publications/diffusive-monitor.html.

Hageman, H.J., 1989. Photoinitiators and photoinitiation mechanisms of free-radical polymerisation processes. Allen, N.S. (ed.), Photopolymerisation and photoimaging science and technology. London New York, Elsevier Science Publishers Ltd, Chapter 1, 1-53.

Hahn, O., Wilke, O. and Jann, O., 2007. Indoor air quality in show cases – an attempt to standardise emission measurements. Zeitschrift für Kunsttechnologie und Konservierung 2, 275-279.

Hatchfield, P.B., 2002. Pollutants in the museum environment. Archetype Publications Ltd., London.

Heyn, C., 2002. Mikrobieller Angriff auf synthetische Polymere: Untersuchungen im Rahmen der Denkmalpflege. Dissertation, Carl von Ossietzky Universität Oldenburg.

Horie, C.V., 1987. Materials for Conservation., Butterworth Heinemann.

Horn, W., Ullrich, D. and Seifert, B., 1998. VOC emissions from cork products for indoor use. Indoor Air 8, 39-46.

ICOM International Council of Museums (ed.), ICOM Code of Ethics for museums, 2006.

Jaffe, L.S., 1967. The effects on photochemical oxidants on materials. Journal of the Air Pollution Control Association 17, 375-378.

Jørgensen, R.B., Bjørseth, O. and Malvik, B., 1999. Chamber testing of adsorption of volatile organic compounds (VOCs) on material surfaces. Indoor Air 9, 2-9.

Kalantzopoulos, A., Birbatakoy, S. and Roubani-Kalantzopoulou, F., 1998. Benzene and toluene influence with or without nitrogen dioxide on inorganic pigments of works of art. Atmospheric Environment 32, 1811-1816.

Katsanos, N.A., De Santis, F., Cordoba, A., Roubani-Kalantozopoulou, F. and Pasella, D., 1999. Corrosive effects from the deposition of gaseous pollutants on surfaces of cultural and artistic value inside museums. Journal of Hazardous Materials 64, 21-36.

Kellner, R., Mermet, J.-M., Otto, M., Valcárcel, M. and Widmer, H.M., 2004. Analytical Chemistry, WILEY-VCH, Weinheim.

Kirchmayr, R., Berner, G., Hüsler, R. and Rist, G., 1982. Vergilbungsfreie Photoinitiatoren. Farbe und Lack 88, 910-916.

Knudsen, H.N., Kjaer, U.D., Nielsen, P.A. and Wolkoff, P., 1999. Sensory and chemical characterization of VOC emissions from building products: impact on concentration and air velocity. Atmospheric Environment 33, 1217-1230.

Köhler, M., 1997. A versatile alpha-hydroxyketone photoinitiator. European Coatings Journal 12, 1118-1120.

Krooß, J. and Stolz, P., 1993. Innenraumbelastung von Museumsmagazinen durch biozide Wirkstoffe. Staub – Reinhaltung der Luft 53, 301-305.

Li, F., Niu, J. and Zhang, L., 2006. A physically-based model for prediction of VOCs emissions from paint applied to an absorptive substrate. Building and Environment 41, 1317-1325.

Lithgow, K. and Brimblecombe, P., 2003. Dust, the visitors' point of view. National Trust Views 39, 47-49.

Lloyd, H., Lithgow, K., Brimblecombe, P., Yoon, Y.H., Frame, K. and Knight, B., 2002. Dust in historic collections, The Conservator 26, 72-84.

Markewitz, D., 2007. Optimierung einer ionenchromatographischen Nachweismethode für Ameisen- und Essigsäure. Diplomarbeit, Fachhochschule Braunschweig/Wolfenbüttel, Studiengang Umwelt- und Hygienetechnik.

Massold, E., Bähr, C., Salthammer, T. and Brown, S.K., 2005. Determination of VOC and TVOC using thermal desorption GC-MS - practical implications for test chamber experiments. Chromatographia 62, 75-85.

McLafferty, F.W. and Turecek F., 1993. Interpretation of mass spectra. University Science Books, Mill Valley, CA.

Meininghaus, R., Salthammer, T. and Knöppel, H., 1999. Interaction of volatile organic compounds with indoor materials – a small-scale screening method. Atmospheric Environment 33, 2395-2401.

Meininghaus, R., Knöppel, H. and Kephalopoulos, S., 2000. Molecular parameters for characterizing the sink effect. Proceedings of Healthy Buildings 2000, Espoo/Finland, Vol. 4, 157-162.

Metiäinen, P., Mussalo-Rauhamaa, H. and Viinikka, M., 2002. TXIB-emissions from floor structure as a marker of increased risk for some specific symptoms. Proceedings of Indoor Air 2002, Monterey/California, Vol. 4, 108-113.

Meyer, B. and Boehme, C. (1997). Formaldehyde emission from solid wood. Forest products journal 47 (5), 45-48.

Michalski, S., 1993. Relative Humidity: A Discussion of Correct/Incorrect Values. Preprints of the 10th Triennial Meeting of the ICOM Committee for Conservation, Washington D.C., USA, 2, 624-629.

Miles, C.E., 1986. Wood coatings for display and storage cases. Studies in Conservation 31, 114-124.

Mills, J.S. and White, R., 1994. Organic Chemistry of Museum Objects. Oxford, Butterworth-Heinemann.

Mølhave, L., 1982. Indoor air pollution due to organic gases and vapours of solvents in building materials. Environment International 8, 117-127.

Moriske, H.-J., 2000. Innenraumlufthygiene III-4.1 Allgemeine Aspekte. Moriske, H.-J.,Turowski, E. (ed.), Handbuch für Bioklima und Lufthygiene. Landsberg am Lech, ecomed verlagsgesellschaft, mit 11. Ergänzungslieferung.

Müller, W., Adam, K., Kruschke, D., Neelmeijer, C. and Mäder, M., 2000. Welche Ursachen haben Schäden an Emailkunstwerken? Restauro 106, 414-418.

National Trust, 2005. The National Trust Manual of housekeeping. The care of collections in historic housed open to the public. Butterworth-Heinemann.

Nazaroff, W.W. and Cass, G.R., 1991. Protecting museum collections from soiling due to the deposition of airborne particles. Atmospheric Environment 25A, 841-852.

Nazaroff, W.W., Ligocki, M.P., Salmon, L.G., Cass, G.R., Fall, T., Jones, M.C., Liu, H.I.H. and Ma, T., 1993. Airborne particles in museums. Research in Conservation, The Getty Conservation Institute.

Niklasson, A., Johannson, L.-G. and Svensson, J.E., 2005. Influence of Acetic Acid Vapor on the Atmospheric Corrosion of Lead. Journal of The Electrochemical Society 152, B519-B525.

Odegaard, N. and Sadongei, A. (ed.)., 2005. Old poisons, new problems. A museum resource for managing contaminated cultural materials. AltaMira Press, Walnut Creek/USA.

Padfield, T., 1966. The control of relative humidity and air pollution in showcases and picture frames. Studies in Conservation 11, 8-30.

Phan, X.T., 1986. Photochemical alpha-cleavage of 2,2-dimethoxy-2-phenylacetophenone and 1-hydroxycyclohexyl phenyl ketone photoinitiators. Effect of molecular oxygen on free radical reaction in solution. Journal of Radiation Curing 13, 11-17.

Pietsch, A., 1994. Vitrinenwerkstoffe und ihre Gefahren für Museumsobjekte. In: Biermann, A.W. (ed.), Der Ausstellungsraum im Ausstellungsraum – Moderne Vitrinentechnik für Museen. Landschaftsverband Rheinland, Rheinisches Museumsamt/Bildungsstätte für Museumspersonal, Schriftenreihe des Rheinischen Museumsamtes Nr. 59, Rheinland-Verlag GmbH Köln.

RAL UZ 76, 2008. Vergabegrundlage für Umweltzeichen – Emissionsarme Holzwerkstoffplatten. RAL Deutsches Institut für Gütesicherung und Kennzeichnung, Sankt Augustin.

Raychaudhuri, M.R. and Brimblecombe, P., 2000. Formaldehyde oxidation and lead corrosion. Studies in Conservation 45, 226-232.

Ryhl-Svendsen, M., 1999. Pollution in the photographic archive – a practical approach to the problem. Preprints of the 9th IADA Congress, The Royal Academy of Fine Arts, Copenhagen/Denmark, 211-215.

Ryhl-Svendsen, M., 2001. Luftschadstoffe in Museen – Eine Einführung in Wirkungsweise, Monitoring und Kontrolle. Restauro 107, 613-619.

Ryhl-Svendsen, M., 2007. Air quality in museum storage buildings. PhD Thesis. The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen.

Salmon, L.G. and Cass, G.R., 1993. The fading of artists' colorants by exposure to atmospheric nitric acid. Studies in Conservation 38, 73-91.

Salthammer, T., 2000. Verunreinigung der Innenraumluft durch reaktive Substanzen – Nachweis und Bedeutung von Sekundärprodukten. In: Moriske, H.-J. und Turowski, E. (ed)., Handbuch für Bioklima und Lufthygiene. Ecomed Verlag, Landsberg, III-6.4.2.

Salthammer, T., 2004. Emissions of volatile organic compounds from products and materials in indoor environments. Pluschke, P. (ed.), Indoor Air Pollution. The Handbook of Environmental Chemistry. Berlin, Springer, 4F, 37-71.

Salthammer, T. und Wensing, M., 1999. Emissionsprüfkammern und –zellen zur Charakterisierung der Freisetzung flüchtiger organischer Verbindungen aus Produkten für den Innenraum. In: Moriske, H.-J. and Turowski, E. (ed.), Handbuch für Bioklima und Lufthygiene. Ecomed Verlag, Landsberg, III-6.4.1.

Salthammer, T., Schwarz, A. and Fuhrmann, F., 1999. Emission of reactive compounds and secondary products from wood-based furniture coatings. Atmospheric Environment 33, 75-84.

Salthammer, T. and Kephalopoulos, S., 2000. Assessment of material emissions on IAQ. In: Proceedings of Healthy Buildings 2000 – Workshop Summaries, Helsinki, 141-146.

Salthammer, T., Bednarek, M., Fuhrmann, F., Funaki, R. And Tanabe, S.-I., 2002. Formation of organic indoor air pollutants by UV-curing chemistry. Journal of Photochemistry and Photobiology A: Chemistry 152, 1-9.

Samek, L., De Maeyer-Worobiec, A., Spolnik, Z., Bencs, L., Kontozova, V., Bratasz, L., Kozlowski, R. And Van Grieken, R., 2007. The impact of electric overhead radiant heating on the indoor environment of historic churches. Journal of Cultural Heritage 8, 361-369.

Saunders, D., 2000. Pollution and the National Gallery. National Gallery technical bulletin, Vol. 21, 77-94.

Saunders, D. and Kirby, J., 1996. Light-Induced Damage: Investigating the Reciprocity Principle. Proceedings of the 11th Triennial Meeting of the ICOM Committee for Conservation, Edinburgh, 1, 87-90.

Scherer, C., Schmohl, A. and Breuer, K., 2006a. Thermal Extraction – a useful supplement to the emission test chamber. Healthy Buildings, Lisboa, 4-8 June, Vol. 4, 29-33.

Scherer, C., Schmohl, A., Breuer, K., Sedlbauer, K., Salthammer, T., Schripp, T., Uhde, E. and Wensing, M., 2006b. Praktische Erfahrungen mit Thermoextraktion als Schnelltestmethode für die Emissionsuntersuchung von Bauprodukten und Kunststoffmaterialien. Gefahrstoffe - Reinhaltung der Luft 66, 87-93.

Schieweck, A., Lohrengel, B., Siwinski, N., Genning, C.,Salthammer, T., 2005a. Organic and inorganic pollutants in storage rooms of the Lower Saxony State Museum Hanover, Germany. Atmospheric Environment 39, 6098-6108.

Schieweck, A., Hoffmann, J., Genning, C. und Salthammer, T., 2005b. Organische und anorganische Schadstoffe – Untersuchungen in Magazinen des Niedersächsischen Landesmuseums Hannover. RESTAURO 111, 354-361.

Schieweck, A. und Salthammer, T., 2006. Luftschadstoffe in Museen, Bibliotheken und Archiven. Fraunhofer Wilhelm-Klauditz-Institut, Braunschweig.

Schieweck, A., Delius, W., Siwinski, N., Vogtenrath, W., Genning, C. and Salthammer, T., 2007. Occurrence of organic and inorganic biocides in the museum environment. Atmospheric Environment 41, 3266-3275.

Schieweck, A., Salthammer, T. and Watts, S.F. Indoor pollutants in the museum environment. In: Salthammer, T. and Uhde, E. (ed.), Organic indoor air pollutants. WILEY-VCH, in press.

Schripp, T., 2005. Schnellanalytische Methoden zur Bestimmung der VOC- und SVOC-Emissionen aus Bauprodukten mittels Thermodesorption und GC/MS. Masterarbeit, Technische Universität Carolo-Wilhelmina Braunschweig.

Schulz, M. and Salthammer, T., 1998. Determination of diisocanate-emissions from building products: 4,4'-dimethylene-diisocyanate (MDI). Fres. J. Anal. Chem. 362, 289-293.

Seifert, B. und Salthammer, T., 2003. Innenraäume. In: Wichmann, H.E., Schlipköter, H.-W. and Fülgraff, G., (ed.), Handbuch Umweltmedizin. Ecomed Verlag, Landsberg, IV-1.

Shashoua, Y., 1999. Ageless oxygen absorber: From theory to practice. In: Bridgeland, J. (ed.), Proceedings of the 11th Triennial Meeting of the ICOM Committee for Conservation, Edinburgh/UK, Vol. 2, 881-887.

Shaver, C.L., Cass, G.R. and Druzik, J.R., 1983. Ozone and the deterioration of works of art. Environmental Science Technology 17, 748-752.

Shilling, M.R., Carson, D.M. and Khanjian, H.P., 1998. Evaporation of fatty acids and the formation of ghost images by framed oil paintings. WAAC Newsletter 21 (1).

Sjöber, A., 1997. Ongoing research. Floor systems, moisture and alkaline. Proceedings of Healthy Buildings 1997, Washington D.C./USA, Vol., 3, 567-572.

Sollinger, S., Levsen, K. and Seidel, P., 1992. Eine Prüfkammer zur Bestimmung der Emission leichtflüchtiger organischer Verbindungen (VOCs) aus Innenraummaterialien. Staub-Reinhaltung der Luft 52, 31-34.

Sollinger, S. and Levsen, K., 1993. Parameter zur Charakterisierung von Adsorptions-erscheinungen bei dynamischen Emissionsprüfungen nach der Prüfkammermethode. Staub - Reinhaltung der Luft 53, 153-156.

Sollinger, S., Levsen, K. and Wünsch, G., 1993. Indoor air pollution by organic emissions from textile floor coverings: climate chamber studies under dynamic conditions. Atmospheric Environment 27B, 183-192.

Spolnik, Z., Worobiec, A., Samek, L., Bencs, L., Belikov, K. and Van Grieken, R., 2007. Influence of different types of heating systems on particulate air pollutant deposition: The case of churches situated in a cold climate. Journal of Cultural Heritage 8, 7-12.

Stoye, D. (ed.), 1993. Paints, coatings and solvents. Weinheim, VCH Verlagsgesellschaft mbH.

Sykes, P., 1988. Reaktionsmechanismen der organischen Chemie. VCH Verlagsgesellschaft mbH, Weinheim.

Tello, H., 2006. Investigations on super fluid extraction (SFE) with carbon dioxide on ethnological materials and objects contaminated with pesticides. Diploma thesis, FHTW Berlin.

Tello, H., Unger, A., Gockel, F. and Jelen, E., 2005. Decontamination of ethnological objects with supercritical carbon dioxide. Proceedings of the 14th Triennial Meeting of the ICOM Committee for Conservation, The Hague/The Netherlands, Vol. 1, 110-119.

Tennent, N. H. and Baird, T., 1985. The Deterioration of mollusca collections: identification of shell efflorescence. Studies in Conservation 30, 73-85.

Tétreault, J., 1994. Display materials: the good, the bad, and the ugly. In: Sage, J. (ed.), Proceedings of the Conference of the Scottish Society for Conservation and Restoration: Exhibitions and Conservation, Edinburgh/UK, 79-87.

Tétreault, J., 1999. Oak display cases: conservation problems and solutions. Conservations Information Database. Canadian Conservation Institute, Ottawa (available at: www.cci-icc.gc.ca)

Tétreault, J., 2003. Airborne pollutants in museums, galleries, and archives: risk assessment, control strategies, and preservation management. Ottawa/Canada, Canadian Conservation Institute.

Tétreault, J., Sirois, J. and Stamatopoulou, E., 1998. Studies of lead corrosion in acetic acid environments. Studies in Conservation 43, 17-32.

Thomson, G., 1965. Air pollution – a review for conservation chemists. Studies in Conservation 10, 147-167.

Thomson, G., 1986. The museum environment. Butterworths Series in Conservation and Museology. 2. Edition, Butterworth-Heinemann Ltd., London.

Tichenor, B.A., 1989. Indoor air sources: using small environmental test chambers to characterize organic emissions from indoor materials and products. U.S. Environmental Protection Agency (EPA), Report No. EPA-600/8 – 89-074.

Tichenor, B.A., Guo, Z., Dunn, J.E., Sparks, L.E. and Mason, M.A., 1991. The interaction of vapour phase organic compounds with indoor sinks. Indoor Air 1, 23-35.

Tichenor, B.A., Guo, Z. and Sparks, L.E., 1993. Fundamental mass transfer model for indoor air emissions from surface coatings. Indoor Air 3, 263-268.

Toftum, J., Freund, S., Salthammer, T. and Weschler, C.J. Secondary organic aerosols from ozone-initiated reaction with emissions from wood-based materials and a “green” paint. Atmospheric Environment. In press.

Torge, M., Jann, O. and Pilz, M., 2000. Das Simulieren von Schadstoff- und Klimabelastungen. Restauro 106, 436-441.

Tucker, W.G., 2001. Volatile organic compounds. Spengler, J.D., Samet, J.M.,McCarthy, J.F. (ed.), Indoor Air Quality Handbook. New York, Mc Graw-Hill, Chapter 31.

Uhde, E., 1998. Vergleich von Emissionsprüfkammern: Untersuchungen unter dynamischen Bedingungen. Dissertation, Braunschweig, Technische Universität Carolo-Wilhelmina Braunschweig.

Uhde, E., 1999. Application of solid sorbents for the sampling of volatile organic compounds in indoor air. In: Salthammer, T. (ed.), Organic Indoor Air Pollutants. Occurrence, Measurement, Evaluation. Chapter 1.1, WILEY-VCH, Weinheim, 3-14.

Uhde, E., 2003. Sampling of volatile terpenes in indoor air. Proceedings of the 7th International Conference on Healthy Buildings 2003, Singapore, Vol. 1, 277-282.

Uhde, E., Bednarek, M., Fuhrmann, F. and Salthammer, 2001. Phthalic esters in the indoor environment – test chamber studies on PVC coated wallcoverings. Indoor Air 11, 150-155.

Uhde, E. and Salthammer, T., 2006. Influence of molecular parameters on the sink effect in test chambers. Indoor Air 16, 158-165.

Uhde, E. and Salthammer, T., 2007. Impact of reaction products from building materials and furnishings on indoor air quality – A review of recent advances in indoor chemistry. Atmospheric Environment 41, 3111-3128.

Unger, A., 1998. Umweltschädliche Holzschutzmittel – Möglichkeiten der Dekontaminierung und Maskierung. Restauro 104, 186-191.

Unger, A., Schniewind, A.P. and Unger, W., 2001. Conservation of wood artifacts. In: Hermann, B. and Wagner, G.A. (ed.), Natural science in archaeology. Springer-Verlag, Berlin Heidelberg.

Van der Wal, J.F., Hoogeveen, A.W. and Wouda, P., 1997. The influence of temperature on the emission of volatile organic compounds from PVC flooring, carpet, and paint. Indoor Air 7, 215-221.

Villberg, K., Saarela, K., Lukkarinen, T. and Mussalo-Rauhamaa, H., 2000. Comparison of different chemical groups related to sick building syndrome (SBS). Proceedings of Healthy Buildings 2000, Espoo/Finland, Vol. 1, 419-424.

VDI 3484 Part 2, 2001. Gaseous ambient air measurements - Indoor-air pollution measurements - Measurement of the formaldehyde concentration with the acatylacetone method. Beuth Verlag, Berlin.

VDI 4300-7, 2001. Indoor-air pollution measurement - Measurement of indoor air change rate. Beuth Verlag, Berlin.

Wensing, M., 1999. Environmental test chambers. In: Salthammer, T. (ed.), Organic Indoor Air Pollutants. Occurrence, Measurement, Evaluation. Chapter 2.1, WILEY-VCH, Weinheim, 129-141.

Wensing, M., Uhde, E. and Salthammer, 2005. Plastic additives in the indoor environment: flame retardants and plastizicers. The Science of the Total Environment 339, 19-40.

Weschler, C.J. and Shields, H.C., 1997. Potential reactions among indoor pollutants. Atmospheric Environment 31, 3487-3495.

Whitmore, P.M. and Cass, G.R., 1988. The Ozone Fading of Traditional Japanese Colorants. Studies in Conservation 33, 29-40.

Whitmore, P.M. and Cass, G.R., 1989. The fading of artists' colorants by exposure to atmospheric nitrogen dioxide. Studies in Conservation 34, 85-97.

WHO (World Heritage Organization), 1989. Indoor air quality: organic pollutants. EURO Reports and Studies 111, Copenhagen.

Wilke, O., Jann, O. and Brödner, D., 2004. VOC- and SVOC-emissions from adhesives, floor coverings and complete floor structures. Indoor Air 14, 98-107.

Williams, E.L., Grosjean, E. and Grosjean, D., 1992. Exposure of artists' colorants to airborne formaldehyde. Studies in Conservation 37, 201-210.

Winkler, K., Föckel, A. and Unger, A., 2002. Das Vakuumwaschverfahren – Dekontaminierung belasteter Hölzer im Einbauzustand. Restauro 108, 339-343.

Wolkoff, P., 1995. Volatile organic compounds - sources, measurements, emissions, and the impact on indoor air quality. Indoor Air Suppl. 3, 9-73.

Wolkoff, P., 1996. An emission cell for measurement of volatile organic compounds emitted from building materials for indoor use – the Field and Laboratory Emission Cell (FLEC). Gefahrstoffe – Reinhaltung der Luft 56, 151-157.

Wolkoff, P., 1998. Impact of air velocity, temperature, humidity, and air on long-term VOC emissions from building products. Atmospheric Environment 32, 2659-2668.

Wolkoff, P., Clausen, P.A., Nielsen, P.A., Gustafsson, H., Jonsson, B. and Rasmusen, E., 1991. Field and laboratory emission cell (FLEC). Proceedings of Healthy Buildings 1991, Washington D.C./USA, 160-165.

Wolkoff, P., Clausen, P.A., Nielsen, P.A. and Gunnarsen, L., 1993. Documentation of field and laboratory emission cell (FLEC): Identification of emission processes from carpet, paint and sealant by modeling. Indoor Air 3, 291-297.

Wolkoff, P. and Nielsen, P.A., 1997. How to evaluate VOC emissions from building products? A perspective. Proceedings of Healthy Buildings/IAQ 97, Washington DC/USA, Vol. 3, 491-496.

Wolkoff, P., Clausen, P.A., Jensen, B., Nielsen, G.D. and Wilkins, C.K., 1997. Are we measuring the relevant indoor pollutants? Indoor Air 7, 92-106.

Worobiec, A., Samek, L., Karaszkiewicz, P., Kontozova-Deutsch, V., Stefaniak, E.A., Van Meel, K., Krata, A., Bencs, L. and Van Grieken, R., 2008. A seasonal study of atmospheric conditions influenced by the intensive tourist flow in the Royal Museum of Wawel Castle in Cracow, Poland. Microchemical Journal. In Press.

Ye, Y., Salmon, L.G. and Cass, G.R., 2000. The ozone fading of traditional chinese plant dyes. JAIC Journal oft he American Institute for Conservation 39, 245-257.

Yoon, Y.H. and Brimblecombe, P., 2001. The distribution of soiling by coarse particulate matter in the museum environment, Indoor Air 11, 232-240.

Yu, C. and Crump, D., 1998. A review of the emission of VOCs from polymeric materials used in buildings. Building and Environment 33, 357-374.

Zeppenfeld, G. und Grunwald, D., 2005. Klebstoffe in der Holz- und Möbelindustrie. 2. Auflage, DRW-Verlag Weinbrenner GmbH & Co. KG, Leinfelden-Echterdingen.

Zumbühl, S., Hons, S. und von Stockhausen, J., 2004. Migrationsprozesse freier Fettsäuren in Malmittelfilmen. Zeitschrift für Kunsttechnologie und Konservierung 1, 61-70.

11 Appendix

11.1 Modern-type showcases directly after production - overview of detected substances

Table 11.1-1. Overview of detected substances in modern-type showcases directly after production, identified by GC/MS.

Substance	CAS.-No.	Substance	CAS.-No.
Alcohols		**Alkanes**	
Ethanol	64-17-5	C 5 (Pentane)	109-66-0
iso-Butanol	78-83-1	C 7 (Heptane)	142-82-5
n-Butanol	71-36-3	C 8 (Octane)	111-65-9
tert. Butanol	75-65-0	C 9 (Nonane)	111-84-2
n-Propanol	71-23-8	C 10 (Decane)	124-18-5
2-Ethyl-1-hexanol	104-76-7	C 11 (Undecane)	1120-21-4
Propylheptanol	10042-59-8	C 12 (Dodecane)	112-40-3
		C 13 (Tridecane)	629-50-5
Aldehydes		C 14 (Tetradecane)	629-59-4
n-Pentanal	110-62-3	2-Methylhexane	591-76-4
n-Butanal	123-72-8	3-Methylhexane	589-34-4
n-Hexanal	66-25-1	Iso-alkanes*	-
n-Nonanal	124-19-6		
Benzaldehyde	100-52-7	**Cycloalkanes**	
		Cyclohexane	110-82-7
Ketones		Methylcyclohexane	108-87-2
Acetone	67-64-1	Methylcyclopentane	96-37-7
Diacetone alcohol	123-42-2	Butylcyclohexane	1678-93-9
Cyclohexanone	108-94-1	Pentamethylheptane*	-
2-Butanone (MEK)	78-93-3	Cycloalkanes*	-
Methylisobutylketone (MIBK)	108-10-1		-
Mesityloxide	141-79-7	**Aromatic hydrocarbons**	
2,6-Di-t-butyl-4-methylene-2,5-cyclohexadiene-1-one	2607-52-5	Toluene	108-88-3
		Ethylbenzene	100-41-4
Acetophenone	98-86-2	m,p-Xylene	1330-20-7
		o-Xylene	95-47-6
Carboxylic esters		Styrene	100-42-5
n-Butylacetate	123-86-4	Isopropylbenzene	98-82-8
Ethylacetate	141-78-6	n-Propylbenzene	103-65-1
Isobornylacetat	125-12-2	2-Ethyltoluene	611-14-3
Isopropylacetate	108-21-4	3-Ethyltoluene	620-14-4
Dimethyl succinate	106-65-0	4-Ethyltoluene	622-96-8
		1,2,3-Trimethylbenzene	526-73-8
Glycol ethers		1,2,4-Trimethylbenzene	95-63-6
Butyl glycol	111-76-2	1,3,5-Trimethylbenzene	108-67-8
1-Methoxy-2-propanol	107-98-2	Benzene	71-43-2
1-Butoxy-2-propanol	5131-66-8	C3-benzene*	-
		C4-benzene*	-

* identification of the exact isomer was not possible

Substance	CAS.-No.
Glycol esters	
1-Methoxy-2-propylacetate	108-65-6
Ethoxypropylacetate	98516-30-4
Ethyl-3-ethoxypropionate	763-69-9
2-Butoxyethyl acetate	112-07-2
Ketoximes	
2-Butanone oxime	96-29-7
4-Methyl-2-pentanone oxime	105-44-2
2-Propanone oxime	127-06-0
Cyclohexanone oxime	100-64-1
Carboxylic acids	
Acetic acid	64-19-7
Triacetine	102-76-1
2-Propenoic acid	923-26-2
1,2,3-Propantriol-triacetate	102-76-1
Halogenated hydrocarbons	
Dichloromethane	75-09-2
3-(Chloromethyl)heptane	123-04-6
Trichlorethene	79-01-6
Miscellaneous	
Pentylfurane	3777-69-3
Tetrahydrofurane	109-99-9
Aromatic hydrocarbons	
2,3-Dihydro-1-methyl-1H-indene	767-58-8
Naphthalene	91-20-3
Terpenes	
α-Pinene	80-56-8
Limonene	5989-27-5
Sesquiterpenes*	
Phosphoric esters	
Triethylphosphate	78-40-0
Phenols	
2,6-Di-tert.butyl-4-methylphenol (BHT)	128-37-0
Silanes	
Dimethoxydimethylsilane	1112-39-6
Trimethoxydimethylsilane	1185-55-3
Siloxanes	
Octamethyltrisiloxane	107-51-7
Octamethylcyclotetrasiloxan	556-67-2
Decamethylcyclopentasiloxane	541-02-6
Dodecamethylcyclohexasiloxane	540-97-6
Tetradecamethylcycloheptasiloxane	107-50-6
Cyclic siloxanes*	-

* identification of the exact isomer was not possible

Table 11.1-2. Statistical parameters of concentrations of substance classes and individual compounds identified in modern-type showcases directly after production (N: number of datasets).

Substance class	**N**	**Minimum (MIN)**	**Maximum (MAX)**	**Median (MED)**
			concentration [µg/m³]	
Alcohols	6	7	1878	824
Alkanes	7	35	2251	412
Cycloalkanes	4	89	1228	456
Aldehydes	4	43	1945	85
Ketones	7	85	1767	221
Carboxylic esters	7	213	1686	765
Dicarboxylic esters	1	-	65	-
Glycol esters	7	39	529	100
Glycol ethers	3	138	345	297
Phosphoric acid esters	2	210	214	212
Aromatic hydrocarbons	7	236	1301	907
Phenoles	2	6	7	6
Siloxanes	7	102	3353	935
Oximes	3	9	17709	54
C3-/C4-benzenes*	2	457	807	632
Halogenated hydrocarbons	2	23	23	23
Terpenes	5	6	87	13
Acrylates	2	7	7	7
Miscellaneous	4	7	65	23
Σ(VOC)	**7**	**3819**	**25213**	**6487**
Formaldehyde	5	27	68	33
Formic acid	3	30	80	34
Acetic acid	5	389	2352	2209

11.2 Modern-type showcases in museum use - overview of detected substances

Table 11.2-1. Overview of detected substances in modern-type showcases in museum use, identified by GC/MS.

Substance	CAS.-No.	Substance	CAS.-No.
Alcohols		**Alkanes**	
Ethanol	64-17-5	C 5 (Pentane)	109-66-0
iso-Butanol	78-83-1	C 6 (Hexane)	110-54-3
n-Butanol	71-36-3	C 7 (Heptane)	142-82-5
tert. Butanol	75-65-0	C 8 (Octane)	111-65-9
n-Propanol	71-23-8	C 9 (Nonane)	111-84-2
2-Propanol	67-63-0	C 10 (Decane)	124-18-5
2-Ethyl-1-hexanol	104-76-7	C 11 (Undecane)	1120-21-4
3-Methyl-1-butanol	123-51-3	C 12 (Dodecane)	112-40-3
2-Methyl-1-butanol	1565-80-6	C 13 (Tridecane)	629-50-5
		C 14 (Tetradecane)	629-59-4
Aldehydes		**Alkanes**	
n-Pentanal	110-62-3	C 15 (Pentadecane)	
n-Hexanal	66-25-1	2-Methylpentane	107-83-5
n-Nonanal	124-19-6	3-Methylpentane	96-14-0
Octanal	124-13-0	2-Methylhexane	591-76-4
n-Decanal	112-31-2	3-Methylhexane	589-34-4
2-Methyl-propanal	78-84-2	2,2,4,6,6-Pentamethylheptane	13475-82-6
2-Ethyl-2-hexenal	645-62-5	Iso-alkanes*	-
Benzaldehyde	100-52-7		
		Alkenes	
Ketones		2-Ethyl-2-hexenal	645-62-5
Acetone	67-64-1		
Diacetone alcohol	123-42-2	**Cycloalkanes**	
2-Butanone (MEK)	78-93-3	Cyclohexane	110-82-7
2-Heptanone	110-43-0	Methylcyclohexane	108-87-2
2-Methyl-2-heptene-6-one	110-93-0	trans-Decaline	207-771-4
2,6-Dimethyl-4-heptanone	108-83-8	Methyldecaline	-
Mesityloxide	141-79-7	Cycloalkanes*	-
2,6-Di-t-butyl-4-methylene-2,5-cyclohexadiene-1-one	2607-52-5		
Acetophenone	98-86-2	**Aromatic hydrocarbons**	
		Toluene	108-88-3
Carboxylic esters		Ethylbenzene	100-41-4
Methylacetate	79-20-9	m,p-Xylene	1330-20-7
n-Butylacetate	123-86-4	o-Xylene	95-47-6
Ethylacetate	141-78-6	Styrene	100-42-5
Isopropylacetate	108-21-4	Isopropylbenzene	98-82-8

* identification of the exact isomer was not possible

Substance	CAS.-No.	Substance	CAS.-No.
Glycol ethers		**Aromatic hydrocarbons**	
2-Butoxyethanol	111-76-2	2-Ethyltoluene	611-14-3
2-(2-Butoxyethoxy)ethanol	112-34-5	3-Ethyltoluene	620-14-4
Glycol ethers		1,2,3-Trimethylbenzene	526-73-8
1-Methoxy-2-propanol	107-98-2	1,2,4-Trimethylbenzene	95-63-6
1-Butoxy-2-propanol	5131-66-8	1,3,5-Trimethylbenzene	108-67-8
		m-Cymene	535-77-3
Glycol esters			
1-Methoxy-2-propylacetate	108-65-6	**Terpenes**	
2-Butoxyethyl acetate	112-07-2	α-Pinene	80-56-8
		β-Pinene	18172-67-3
Ketoximes		Limonene	5989-27-5
Acetone oxime	107-26-0	3-Carene	498-15-7
2-Butanone oxime	96-29-7		
4-Methyl-2-pentanone oxime	105-44-2	**Phosphoric esters**	
		Triethylphosphate	78-40-0
Carboxylic acids		**Phthalic esters**	
Acetic acid	64-19-7	Diisobutylphthalate	84-69-5
Hexanoic acid	142-62-1		
Triacetine	102-76-1	**Phenols**	
		Phenol	108-95-2
Halogenated hydrocarbons			
1,2,4-Trichlorobenzene	120-82-1	**Silanes**	
Trichlorethene	79-01-6	Dimethoxydimethylsilane	1112-39-6
1-Chloronapthalene**	90-13-1		
2-Chloronapthalene**	91-58-7	**Siloxanes**	
2,6-Dichloronaphthalene**	2065-70-5	Octamethyltrisiloxane	107-51-7
2,3,6-Trichloronaphthalene**	55720-40-6	Hexamethylcyclotrisiloxan	541-05-9
gamma-Lindane**	58-89-9	Octamethylcyclotetrasiloxane	556-67-2
		Decamethylcyclopentasiloxane	541-02-6
Miscellaneous		Dodecamethylcyclohexasiloxane	540-97-6
Pentylfurane	3777-69-3	Tetradecamethylcycloheptasiloxane	107-50-6
2,6-Di-tert.butyl-4-methylphenol (BHT)	128-37-0	Tetracosamethylcyclododecasiloxane	18919-94-3
		Cyclic siloxanes*	-
Acrylate esters			
Isobornylacrylate	5888-33-5		
Methylmethacrylate	80-62-6		

* identification of the exact isomer was not possible

**active agents of wood preservatives; artworks as emission sources are assumed

Table 11.2-2. Concentrations of substance classes and individual compounds identified in modern-type showcases in museum use. Statistical parameters (N: number of datasets).

Substance class	**N**	**Minimum (MIN)**	**Maximum (MAX)**	**Median (MED)**
		concentration [µg/m³]		
Alcohols	10	3	3844	24
Alkanes	10	12	2941	135
Cycloalkanes	9	3	2159	67
Alkenes	1	-	55	-
Aldehydes	9	2	339	45
Ketones	9	7	4955	143
Carboxylic acids	7	28	591	109
Carboxylic esters	7	20	1236	70
Glycol esters	9	13	894	198
Glycol ethers	6	4	302	33
Aromatic hydrocarbons	9	8	975	92
Phenoles	4	1	13	8
Siloxanes	9	46	11069	699
Ketoximes	3	115	250	121
C3-/C4-benzenes	3	7	62	20
Halogenated hydrocarbons	1	-	3	-
Terpenes	7	3	215	112
Acrylatic esters	2	11	31	21
Phosphoric acid esters	3	6	32	20
Miscellaneous	6	5	92	16
Σ(VOC)	10	102	26516	1555
Formaldehyde	9	17	158	41
Formic acid	5	89	381	348
Acetic acid	9	108	5698	508

11.3 Old-type showcases in museum use - overview of detected substances

Table 11.3-1. Overview of detected substances in old-type showcases in museum use, identified by GC/MS.

Substance	CAS.-No.	Substance	CAS.-No.
Alcohols		**Alkanes**	
Ethanol	64-17-5	C 7 (Heptane)	142-82-5
iso-Butanol	78-83-1	C 9 (Nonane)	111-84-2
n-Butanol	71-36-3	C 10 (Decane)	124-18-5
n-Propanol	71-23-8	C 11 (Undecane)	1120-21-4
2-Ethyl-1-hexanol	104-76-7	C 12 (Dodecane)	112-40-3
Aldehydes		**Aromatic hydrocarbons**	
n-Pentanal	110-62-3	Toluene	108-88-3
n-Hexanal	66-25-1	Ethylbenzene	100-41-4
n-Heptanal	111-71-7	m,p-Xylene	1330-20-7
n-Nonanal	124-19-6	o-Xylene	95-47-6
Octanal	124-13-0	Styrene	100-42-5
n-Decanal	112-31-2	2-Ethyltoluene	611-14-3
Furfural	98-01-1	3-Ethyltoluene	620-14-4
Benzaldehyde	100-52-7	1,2,3-Trimethylbenzene	526-73-8
		1,2,4-Trimethylbenzene	95-63-6
Ketones		1,3,5-Trimethylbenzene	108-67-8
Acetone	67-64-1	Naphthalene**	91-20-3
2-Butanone (MEK)	78-93-3		
2-Butanone (MEK)	78-93-3	**Glycol ethers**	
Methylisobutylketone (MIBK)	108-10-1	2-Butoxyethanol	111-76-2
Carboxylic esters		**Glycol ethers**	
Methylacetate	79-20-9	1-Methoxy-2-propanol	107-98-2
n-Butylacetate	123-86-4	1-Butoxy-2-propanol	5131-66-8
Ethylacetate	141-78-6		
		Terpenes	
Glycol esters		α-Pinene	80-56-8
1-Methoxy-2-propylacetate	108-65-6	β-Pinene	18172-67-3
TXIB®	6846-50-0	Limonene	5989-27-5
Texanol®	25265-77-4	3-Carene	498-15-7
		Campher	76-22-2

* identification of the exact isomer was not possible

**active agents of wood preservatives; artworks as emission sources are assumed

Substance	CAS.-No.	Substance	CAS.-No.
Carboxylic acids		**Phthalic esters**	
Acetic acid	64-19-7	Diisobutylphthalate	84-69-5
Butanoic acid	107-92-6		
Hexanoic acid	142-62-1	**Phenols**	
		Phenol	108-95-2
Halogenated hydrocarbons			
1,4-Dichlorobenzene**	106-46-7	**Siloxanes**	
1-Chloronaphthalene**	90-13-1	Cyclic siloxanes*	-
2-Chloronaphthalene**	91-58-7		

* identification of the exact isomer was not possible

**active agents of wood preservatives; artworks as emission sources are assumed

Table 11.3-2. Concentrations of substance classes and individual compounds identified in old-type showcases in museum use. Statistical parameters (N: number of datasets).

Substance class	N	Minimum (MIN)	Maximum (MAX)	Median (MED)
		concentration [µg/m³]		
Alcohols	7	16	515	123
Alkanes	7	3	143	55
Alkenes	1	-	11	-
Aldehydes	8	19	205	88
Ketones	8	21	87	41
Carboxylic acids	3	170	1405	575
Carboxylic esters	5	16	62	30
Glycol esters	4	2	15	7
Glycol ethers	6	12	228	33
Aromatic hydrocarbons	7	6	67	53
Phenoles	2	1	2	2
Siloxanes	2	10	489	250
C3-/C4-benzenes	4	21	51	41
Halogenated hydrocarbons	2	20	22	21
Terpenes	8	6	101	53
Acrylatic esters	2	5	31	18
Phthalic esters	1	-	4	-
Miscellaneous	2	3	4	4
Σ(VOC)	8	102	2101	702
Formaldehyde	7	69	757	322
Formic acid	7	106	782	405
Acetic acid	7	452	3601	1446

11.4 Thermographic images – false colour

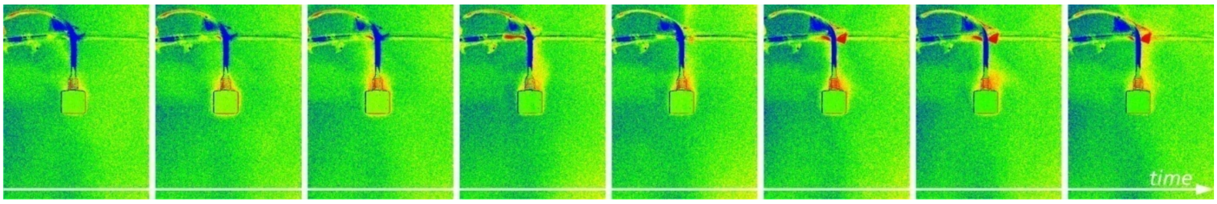


Figure series 11.4-1a. Marginal heat flow around a LED lamp. Thermographic images. False colour.

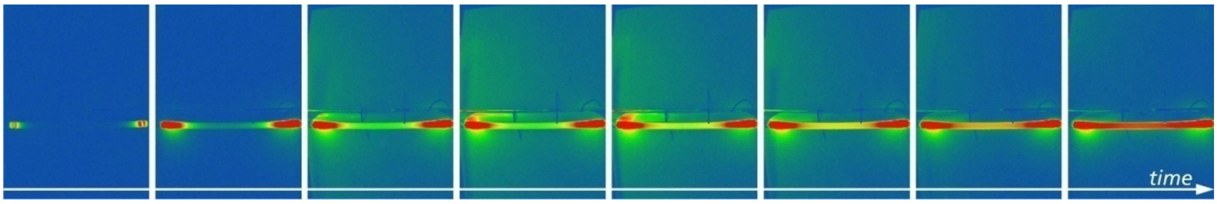


Figure series 11.4-1b. Temperature distribution inside a fluorescent lamp. Thermographic images. False colour.

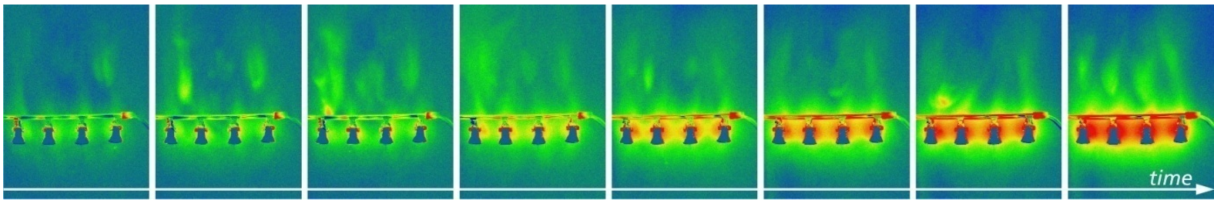
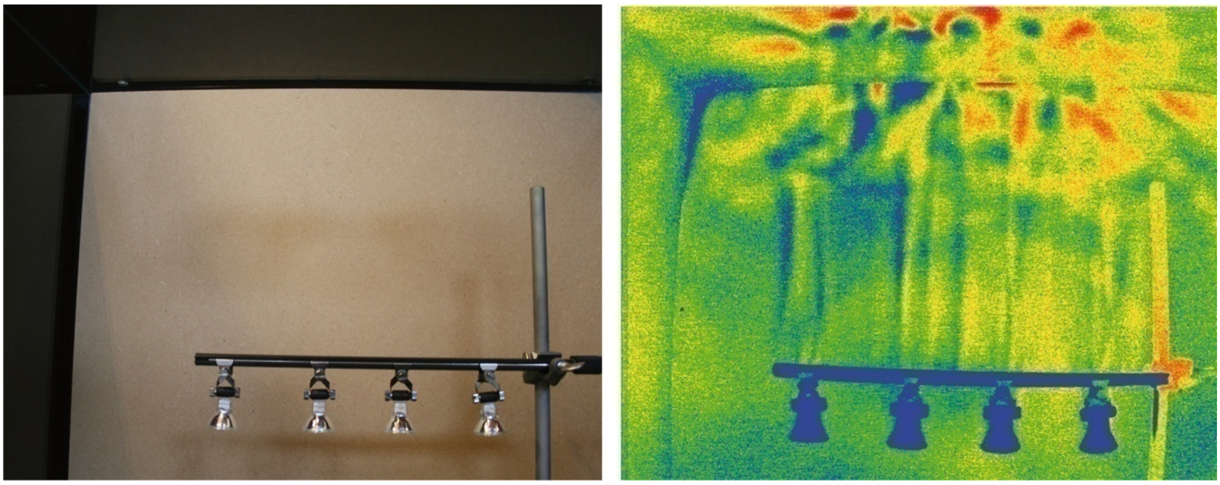
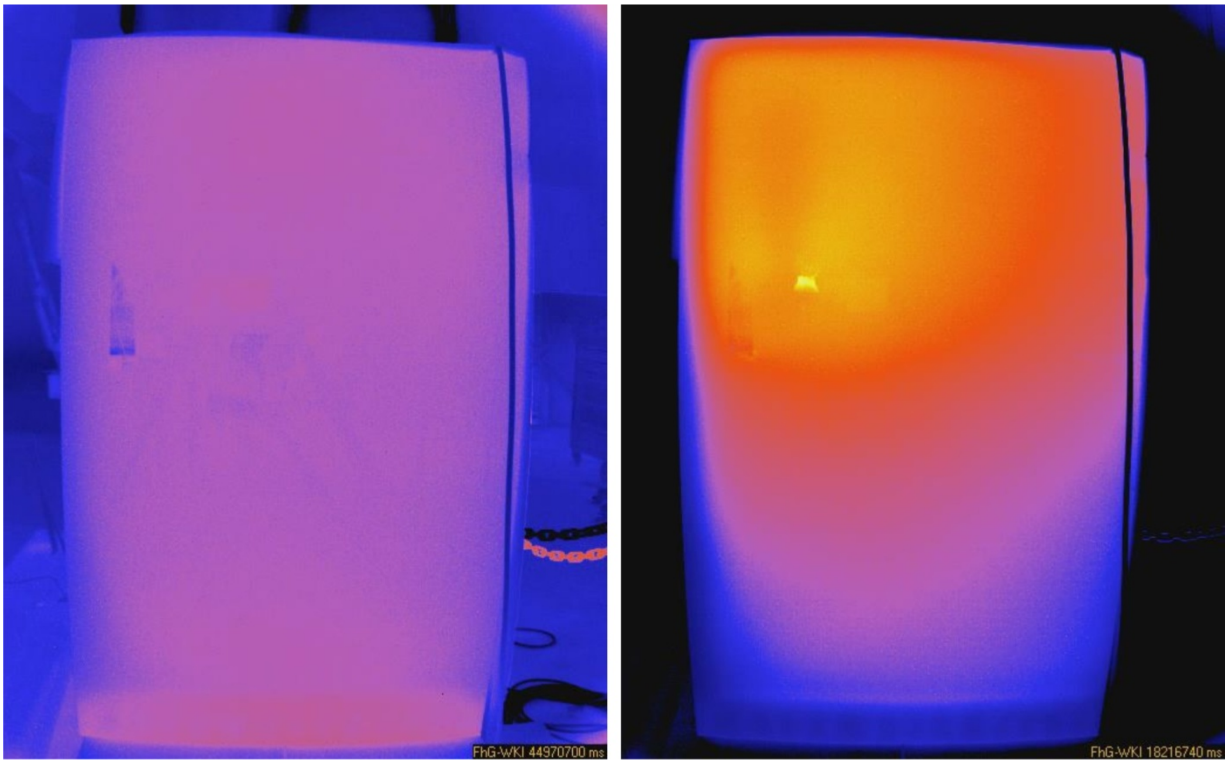


Figure series 11.4-1c. Heat radiation of halogen spotlights. Thermographic images. False colour.



Figures 11.4-2a and b. (a) Left corner above the four halogen spotlights, close-up view inside the showcase; (b) turbulent air flows induced by halogen spotlights inside a showcase. Thermographic images.



Figures 11.4-3a and b. (a) Temperature equilibrium inside a showcase without artificial lighting and (b) temperature layering under illumination. View from outside the showcase. Thermographic images.

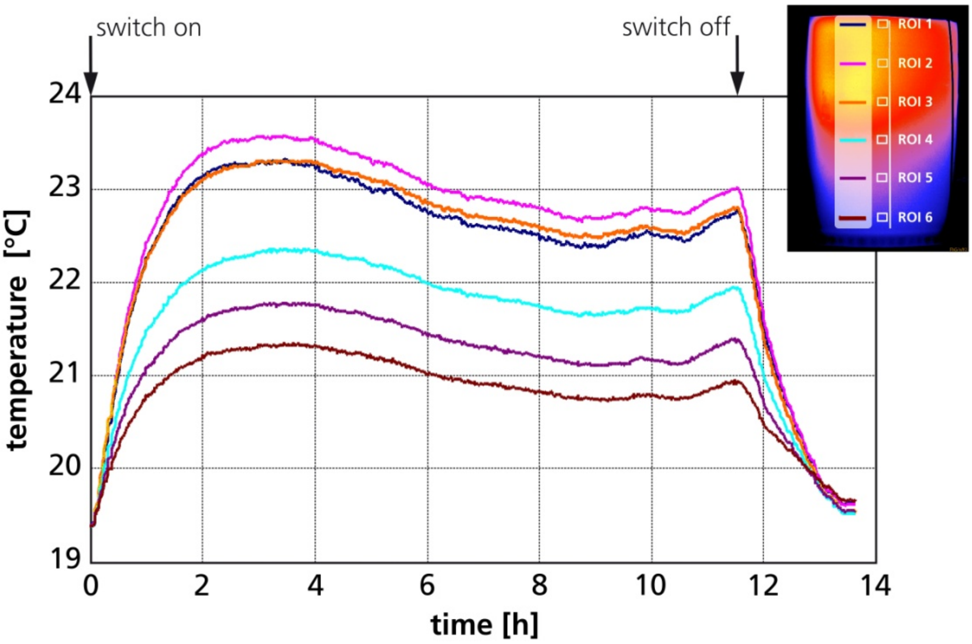


Figure 11.4-5. Gradient profiles of temperature distribution *versus* time under illumination. Thermographic image, false colour.

Die Dissertation wurde in einem kooperativen Promotionsverfahren der Hochschule für Bildende Künste Dresden, Studiengang Kunsttechnologie, Konservierung und Restaurierung von Kunst- und Kulturgut, und der Hochschule für angewandte Wissenschaft und Kunst FH Hildesheim/Holzminden/Göttingen, Fakultät Erhaltung von Kulturgut, in Zusammenarbeit mit dem Fraunhofer Wilhelm-Klauditz-Institut (WKI) Braunschweig, Abteilung Materialanalytik und Innenluftchemie, durchgeführt.

Betreuer der Hochschule für Bildende Künste Dresden

Herr Prof. Dr. rer. nat. Christoph Herm

Betreuer der Hochschule für angewandte Wissenschaft und Kunst
Hildesheim/Holzminden/Göttingen

Herr Prof. Dr. phil. Michael Graf von der Goltz

Betreuer des Fraunhofer Wilhelm-Klauditz-Institutes (WKI) Braunschweig

Herr Prof. Dr. rer. nat. Tunga Salthammer

CURRICULUM VITAE

Name:	Schieweck
First name:	Alexandra
07/1997	University-entrance Qualification
09/1998-01/2004	Study of "conservation and restoration of paintings and polychrome wooden objects" at the University of Applied Sciences and Arts Hildesheim/Holzminden/Göttingen, Germany, faculty of conservation
Since 1998	Member of the German conservator-restorers association Verband der Restauratoren e.V.
01/2004	Degree in conservation and restoration, University of Applied Sciences and Arts Hildesheim/Holzminden/Göttingen, Germany
04/2004-12/2005	Scientific Coworker at the University of Applied Sciences Braunschweig/Wolfenbüttel, Germany
Since 2005	Guest lecturer at the University of Applied Sciences and Arts Hildesheim/Holzminden/Göttingen, Germany, faculty of conservation
10/2005	Member of the Management Committee of the German conservator-restorers association Verband der Restauratoren e.V.; Cofounder and coordinator of the working group "Preventive Conservation"
10/2005-11/2008	Dissertation fellowship, Studienstiftung des Deutschen Volkes (German National Academic Foundation)
01/2006-01/2009	Ph.D. student, Fraunhofer Wilhelm-Klauditz-Institute (WKI), department of Material Analysis and Indoor Chemistry, Braunschweig
10/2006	Member of CEN/TC 346 Conservation of Cultural Property
10/2006	Member of COST D42 "Chemical Interactions between Cultural Artefacts and Indoor Environment [Envi^{Art}]"
10/2007	Research at the University of London, Birkbeck College, School of Biological and Chemical Sciences
01/2008-12/2008	Member of the International Society of Indoor Air Quality and Climate (ISIAQ)
01/2009	Ph.D. in natural sciences, Dresden Academy of Fine Arts, Germany
Since 02/2009	Scientific Coworker (Post Doc), Fraunhofer Wilhelm-Klauditz-Institute (WKI), department of Material Analysis and Indoor Chemistry, Braunschweig