e-PS, 2010, **7**, 59-70
ISSN: 1581-9280 web edition
ISSN: 1854-3928 print edition

www.Morana-rtd.com

e-PRESERVATIONScience

published by MORANA RTD d.o.o.

SCIENTIFIC PAPER

MEASUREMENT OF ORGANIC AND INORGANIC POLLUTANTS IN MICROCLIMATE FRAMES FOR PAINTINGS

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Recent studies have shown that indoor environment in museums can pose a risk to cultural heritage objects due to adverse effects. Current practice is moving towards protection of artworks such as paintings by placing them into microclimate frames (mc-frames). However, little is known about the effects of enclosing paintings in such a way. Pollutants can enter mc-frames from outside the frame (e.g. NOx) or they can be originated from materials within the frame (e.g. volatile organic compounds). In this study, pollutant concentrations of organic (VOCs, acetic and formic acid, formaldehyde) and inorganic compounds (NO2, SO2 and O3) were measured for the first time both inside and outside 15 mc-frames. The results showed that the concentration of inorganic gases is lower inside the mc-frames than outside. In contrast, higher concentrations of potentially aggressive organic compounds, such as acetic and formic acid, toluene, α-pinene, p- and m-xylenes, limonene and 3-carene, were measured inside than outside the frames.

1 Introduction

Over the last decades, indoor air pollution from building materials has received an increased interest in the scientific community. Many studies focused on the so called sick building syndrome, indoor organic compounds and / or the associated effects on health.[1-4] In conservation science, the interest moved towards the effect of indoor air quality on art objects.[5-8] Light, temperature, and relative humidity effects on the artworks were of main concern for conservation scientists. In the last two decades interest has extended from the climate control in museum, archives and libraries to include control of indoor air pollution.

Indoor air pollutants can be divided according to their sources in two main groups, those generated outdoors which infiltrate into the indoor environment, and those generated indoors. Nitrogen oxides (NO_x),

received: 16.02.2010
accepted: 02.05.2010

key words:
Mc-frame, VOCs, inorganic gases, museum, painting

ozone (O_3), sulphur dioxide (SO_2) and particulate matter are among the most common and important outdoor pollutants which enter the museum environment and their effects on cultural heritage objects have been studied.[5,7-9] The pollutants emitted indoors are mainly organic (e.g. volatile organic compounds, VOCs) and are usually emitted from building materials. Some documented effects of organic compounds, such as carboxylic acids and aldehydes, on artworks are corrosion of metals, efflorescence on calcareous materials and depolymerisation of cellulose.[7-8] As the interest in VOCs has increased, research has been performed to determine the indoor sources of VOCs[10-11] and the effects of specific organic compounds such as acetic acid on pigments.[12] However, in contrast to the available knowledge about adverse effects of exposure to the inorganic compounds NO_2 and O_3, knowledge about effects of VOCs on cultural heritage objects and the establishment of threshold levels for specific compounds still needs to be addressed.

The use of microclimate frames (mc-frames) as protective microenvironments is the current practice in many museums. These consist of a glass front, and an impermeable back board, enclosed in an airtight frame. The aim is to protect paintings physically, against externally generated pollutants, and to provide climate buffering by diminishing internal relative humidity variations as compare to external variations.[13] The use of mc-frames is associated in some situations with sustainability issues, due to the possibility of reducing environmental control and related energy costs in the gallery as a result of enclosing paintings in mc-frames. The positive effects are assumed to outweigh the negative ones of added weight, difficulty of handling, risk of breakage, cost, possible "green house" effects, microbiological and insect colonization, and trapping of internally generated pollutants such as volatile organic compounds.

VOCs are organic chemical compounds emitted from certain materials under room temperature and atmospheric pressure. Although they may occur from traffic sources, our main concern is the emissions from materials especially from mc-frames. The known sources of primary and secondary VOCs include a wide variety of materials and their degradation processes.[3-4,14] The major factors that determine concentrations of VOCs in mc-frames are their emission strength, and the resulting steady-state concentration will depend on desorption and adsorption characteristics and possible heterogeneous reactions, the surface to volume ratio, the air exchange rate of the mc-frame and possible chemical gas phase reactions. The surface to volume ratio of mc-frames is usually large and the air exchange rate low (typically <1 per day), and even relatively low internal emission rates can build up high concentrations of compounds that may be harmful to the paintings. In the case of less airtight mc-frames, the concentration of organic compounds will be lowered by ventilation at the cost of increased risk of penetration of externally generated pollutants.

Several studies have been performed about characteristics of showcases in relation to the general principles for conservation of artworks.[13,15-16] Risk assessment studies have evaluated the protective effect of showcases against climate variations, air pollution, bio-agents and light.[13,17-19] However, as mentioned previously no actual study has evaluated pollutant concentrations inside and outside a range of mc-frames and this is the main focus of this paper. This study presents the results of measurements performed for the first time of organic (VOCs, acetic and formic acid and formaldehyde) and inorganic (NO_2, SO_2 and O_3) pollutant gases in 15 mc-frames and 12 corresponding room locations as part of the work carried out in the EU project PROPAINT (FP6 SSPI no 044254). The interpretation of results is based on the characteristics of the mc-frames and the rooms, and on comparisons between the concentration levels observed inside and outside the mc-frames. Based on the available literature about threshold levels for pollutants an evaluation of the protective effects of mc-frames for paintings is performed.

2 Methodology

2.1 Microclimate frames

Sampling was performed at selected museum sites, inside 14 mc-frames and one built-in glass enclosure, and in the rooms where they were exhibited (Table 1). Measurements were performed in mc-frames both with and without paintings installed. The frames were classified in different groups based on the design and constituent materials. Six were "modern", newly built mc-frames, eight were mc-frames adapted to classic existing frames in the museums and one was a glass enclosure for painting. The modern mc-frames were made partially from synthetic materials (e.g. neoprene, methacrylic) and wood, and designed and manufactured by the SIT-Artyd Company in Madrid (Spain). Four modern mc-frames were produced specifically for this study and located in the SIT-Artyd workshop. Frame no. 4 was a special "worst case" model with an oak wood panel freshly prepared with natural varnish and old white carpenter's glue on one side (i.e.

	F	R	V (m^3)	AER (day^{-1})	Age	Painting installed	Materials inside F
1. SIT-Artyd (Madrid, Spain)	M (4)	W	0.077	0.19	2007	No	acrylic paint, silicon tape, methacrylic (plexi), aluminium tape, polycarbonate board, art-sorb, stainless steel, neoprene, glass
2. National Museum of Art, Architecture and Design, National Gallery (NG, Oslo, Norway)	C	G	0.013	0.67	1970	Yes (canvas)	wood, polycarbonate board, aluminium tape, glass
3. English Heritage (EH, London, UK)							
3.1. Kenwood (EH K)	C	G	0.041	1.39	2007	Yes (panel painting)	wood, oil tempered hardboard, silicone sealaluminium foil, PVC coated, cable, art-sorb, brass screws, glass
3.2. Apsley House	C	G	n/a	0.17	1980s	Yes (panel painting	wood, silicone seal, aluminium foil, oil tempered hardboard,brass screws, glass
4. Tate (London, UK)							
4.1. Tate Store (Tate S.)	C	S	0.027	6.69	1990	No	softwood, oil tempered hardboard, brass screws, PE film, gesso/gold leaf, paper clips, steel screws, glass
4.2. Tate Britain (Tate B.)	C	ST	0.010	8.59	1910	No	softwood, oil tempered hardboard, brass screws, gummed paper, PE film, gesso/gold leaf, steel screws, glass
5. Staten Museum for Kunst (SMK, Copenhagen, Denmark)	C	G	0.024	0.39	2007	No	balsa wood, acrylic paint, felt, screws, cork, aluminium tape, polycarbonate board, glass
6. Fine Art Museum (MBV, Valencia, Spain)	M	G	0.028	0.15	2005	Yes (panel painting	methacrylic (plexi), silicon tape, polycarbonate board, art-sorb, neoprene, aluminium tape, stainless steel, aluminium tape, glass
7. National Museum of Art (MNA, Mexico City, Mexico)	M	G	n/a	n/a	2007	Yes (panel painting)	n/a
8. Germanic National Museum (GNM, Nürnberg, Germany)	C	G	0.046	n/a	2003	Yes (canvas)	rubber, aluminium profiles, tape, glass
9. National Museum in Krakow (NMK, Krakow, Poland)							
9.1. Leonardo's frame (NMK1)	Sh	G	0.28	14.9	2004	Yes (panel painting	fiber board, tapestry, velcro, glass
9.2. New mc-frame (NMK2)	C	G	0.06	0.42	2007	Yes (panel painting	polycarbonate board, aluminium profiles, aluminium tape, glass

Table 1. Sampling sites, classification of the mc-frame (F) and room (R) locations and main characteristics of the frames. V: volume of air inside the mc-frame. AER = air exchange rate. Mc-frame types: M = "modern" mc-frame, C = adapted to classic frames existing in the museums, Sh = glass enclosure for painting. Room types: W: workshop, G: gallery, S: store, ST: staircase. n/a = not available.

Artyd 4; Table 2). Two modern mc-frames were located in exhibitions in different museum galleries (Table 1).

The mc-frames adapted to classic frames were constructed from wood with protective glass on the front and panel at the back with sealing tape (Table 1). Some amounts of modern synthetic supporting materials (e.g. polycarbonate) were used in a number of the frames. The mc-frames adapted to classic frames were on exhibition in museums, located in storerooms or in other unconditioned areas during the sampling period. At one location, the National Museum in Krakow (Poland), the sampling enclosure was a purpose built glass enclosure for the painting, with glass (front and sides) fitted to the wall. The volume of air inside the glass enclosure was 0.32 m^3 while the air volume inside the other mc-frames varied between 0.01 and 0.08 m^3 (Table 1).

Different types of construction materials are found in the mc-frames (Table 1). The most common material is the cover glass, which is held in place by a strainer of wood from the original frame, or by a purpose built strainer of methacrylic (plexi) or aluminium profiles. Aluminium tape or sheets and polyethylene (PE) film have been used to seals the wooden strainers. The backing of the mc-frames was commonly polycarbonate sheets, and a few frames have aluminium sheets and oil temperate hardboards. The materials are held together by aluminium tape, brass and / or steel screws. Only the SIT frames and the mc-frame in Kenwood (English Heritage) have humidity buffer material enclosed in the frame (Art-Sorb).

2.2 Pollutant sampling and air exchange rate (AER)

Passive diffusion samplers for VOCs were exposed inside and outside of the mc-frames for one week, except in the Artyd workshop, where the exposures lasted 24 hours. The passive samplers used were Thermal Desorption VOC sampling tubes with Tenax TA sorbent. The absorption tubes are sealed with brass nuts in both sides and stored in the refrigerator before and after exposure until the analysis is performed. One of the brass nuts is substitute for the diffusion cap just before exposure and, once the sampling has finalized, the diffusion cap is removed and the tube is sealed

with the brass nut, ensuring no contamination during transport.

For monitoring of the individual gases, NO_2, SO_2, acetic and formic acid, passive diffusion samplers[20] from the Norwegian Institute for Air Research (NILU) were used. For O_3, passive diffusion samplers[20] from the Swedish Environmental Institute (IVL) were used. Measurements of formaldehyde were performed by UME*100 passive sampler designed for one-time use. The passive diffusion samplers for NO_2, SO_2, acetic and formic acids, O_3 and formaldehyde were exposed during one month. Inside the mc-frames duplicate samplers were used to collect acetic acid plus formic acid, whereas the other gases were collected on one passive sampler to reduce the risk of interference on the result by the sampling inside the frames. Outside the mc-frames duplicate sampling was used for all the gases.

The air exchange rate was measured in nearly all mc-frames by the tracer gas concentration decay technique.[21-22]

2.3 Analytical Procedure

The VOC samplers with Tenax TA sorbent were analyzed by thermal desorption gas chromatography-mass spectrometry (GC-MS). From the total ion chromatogram the 30 peaks with the largest area in retention time window from 2 to 46 min (i.e. corresponding to C5 to C20 compounds) were selected for further identification routines. An automated mass spectra library check was used for the first preliminary identification. Each of the suggestions for component identification was then cross checked against a database of the Norwegian Institute for Air Research (NILU) for indoor air pollutants which contains approximately 1000 components. This database contains retention time indexes of compounds that were identified in indoor air samples at NILU by the same analytical system over the last 20 years. Most of the compounds within this database have been verified by direct injection of pure standard solutions or mixed standard solutions. The criteria for identification were over 80% confidence match from the mass spectra library, the retention time database and manual check of the retrieved mass spectrogram against the library mass spectrogram. A peak that does not meet these criteria is named as “unidentified compound”. The 30 compounds with the highest concentrations are identified, named and, their concentrations as toluene-equivalents and concentration-sum (i.e. TVOCid) reported. In addition the concentration-sum of all compounds within each sample with a concentration above a baseline-threshold of 0.1 ppb (usually between 180 and 250 compounds) is reported (i.e. TVOC). The calibration is based on toluene equivalents. Ten samples are run together with two standard injections before and after each series. A solution of benzene, toluene, ethylbenzene and xylenes in methanol is introduced to the same type of adsorption tubes via an injector and a syringe and blown onto the adsorbent with a flow of 20 ml/min within 5 min.

Passive gas samplers for SO_2, acetic and formic acid were analyzed by ion chromatography, those for NO_2 by photometry and those for formaldehyde by liquid chromatography (HPLC). The filter of the SO_2-passive sampler is impregnated in an alkali, which is dissolved in an aqueous solution after exposures and the extracted sulphate (SO_4^{2-}) is determined by ion chromatography. The mean concentration during the exposure time is estimated based on the quantity of extracted sulphate and a constant, which contains the diffusion constant for SO_2 and a factor based on the dimensions of the passive sampler. A similar filter impregnated with an alkali solution and similar procedure is used for the determination of acetic and formic acid. For NO_2, the filter of the passive sampler is impregnated in iodide (I^-) and the formed nitrite (NO_2^-) is determined by photometry. The NO_2 average concentration for the exposure time is estimated in the same way as for SO2. The ozone passive samplers are provided and analyzed by the Swedish Environmental Institute (IVL). The detection limit for NO_2 after one month of exposure is approximately 0.03 µg m^{-3}, the detection limit after the same exposure time for SO_2 is 0.1 µg m^{-3}, for acetic acid and formic acid is 0.5 µg m^{-3}, for O_3 is reported as 1 µg m^{-3} and for formaldehyde is 0.05 µg m^{-3}.

3 Results

3.1 Measurements in mc-frames

The highest concentration of total volatile organic compounds (TVOC; 28300 µg m^{-3}) and of most of the individual compounds, such as hexanoic acid, p- and m- xylene, hexanal and octanal (Table 2) were measured in the “worst case” mc-frame (frame no. 4; Table 2). These results indicate high emission of VOCs from the freshly prepared varnish and adhesives in the very tight enclosure. This was an exposure especially set up to provide the highest level of VOCs in the mc-frame and it will not be referred to in the further discussion.

The concentration of TVOC detected inside the other 13 mc-frames and one glass enclosure in

Location	Artyd 1	Artyd 2	Artyd 3	Artyd 4	NG	EH K.	EH A.H.	Tate S.	Tate B.	SMK	MBV	MNA	GNM	NMK 1	NMK 2
TVOC	3372	5274	3650	28242	1113	1612	163	707	3995	4347	4692	5217	477	107	1156
TVOC id.	2340	4284	3146	24210	959	1357	122	648	3745	3836	3844	4553	363	79	830
Type	M	M	M	M	C	C	C	C	C	C	M	M	C	Sh	C
Compound	Concentration (µg m^{-3})														
chloroform	652	195	1560	6413							451	1309			
toluene	113	1103	506	4923	26	19	10	7		56	124	137		5	100
alfa pinene	76	232	106	500	391	91	2	190	2263	45	807	83		3	79
2-methyl-2-propenoic acid methylester	119	43	1297								117	485			
undecane	166	137		715		24	2	3	28	38	55	236	11	8	34
2-butoxyethanol				1275					20			106	47		
2-ethyl-1-hexanol	34				54					1136					
acetic acid*			21		5	228	2	240	20	582			40		
decane	138	263	73	310			2			24	100	143		5	
hexanoic acid				687	18	15		17	43		208		12		
3-carene	41	114	47		136			35			536				16
p- and m- xylene	54	275	65	496			3	3					7	4	12
2-propanone (acetone)	82	56	451		10			18		74	110		34	1	27
hexanal		54		441	6	93	2	7		97	82		14		11
limonene	60	206	32		10	18		13	110	23	177	97	4	2	14
1-ethyl-4-methylbenzene	45	136	40	425							36			1	11
1,3,5-trimethylbenzene		74		560						27					
1,2,4-trimethylbenzene	49		28	423							54			1	
3-methylnonane				511			1								
4-methyl-2-pentanone										488					
2,2,4,6,6-pentamethyl heptane				345							108				26
acetic acid butylester		328	141										5		
octanal	51	39	17	253	7			4		37	32		6	2	
2-methylpropylbenzene				441											
propyl cyclohexane				429											
3-methyldecane	44			382										1	
1-ethyl-2-methylbenzene	40	99		285										1	
nonane		53	22	343			1							3	
2,6-dimethyloctane				380											
1-ethyl-3,5-dimethylbenzene		67		310											

Table 2: VOC inside mc-frames sampled by tubes with Tenax TA sorbent. Compounds with highest total added concentration for the entire study inside mc-frames. TVOC: total concentration of volatile organic compounds. TVOC id.: total concentration of identified volatile organic compounds. Mc-frame types: M = modern mc-frame, C= mc-frame adapted to classic frames existing in the museums, Sh = glass enclosure for painting. * = compound is not fully absorbed by Tenax TA sorbent. For the abbreviation of the locations see Table 1.

either exhibition or storage, varied between 107 µg m^{-3} and 5274 µg m^{-3} (Table 2). The highest concentration inside the mc-frames was detected for the empty SIT-Artyd (frame no. 2; 5274 µg m^{-3}; Table 2). In contrast, the lowest TVOC concentration was observed in the glass enclosure at the National Museum in Krakow (NMK1; 107 µg m^{-3}), followed by the mc-frame in Apsley House (163 µg m^{-3}; Table 2; Figure 1).

α-pinene and limonene were observed in 13 out of 14 mc-frames (Table 2) with the highest concentration measured in the empty mc-frame in Tate Britain (2263 µg m^{-3}) and in the empty mc-frame no. 2 of SIT-Artyd (206 µg m^{-3}), respectively. Toluene was also widely measured in nearly all mc-frames (12 out of 14 mc-frames), with concentrations varying from 5 µg m^{-3} to 1103 µg m^{-3} (frame no. 2, SIT-Artyd). Chloroform, 2-methyl-2-propenoic acid methylester, 2-ethyl-1-hexanol and 3-carene were measured at high concentrations (>500 µg m^{-3}) in some of the mc-frames.

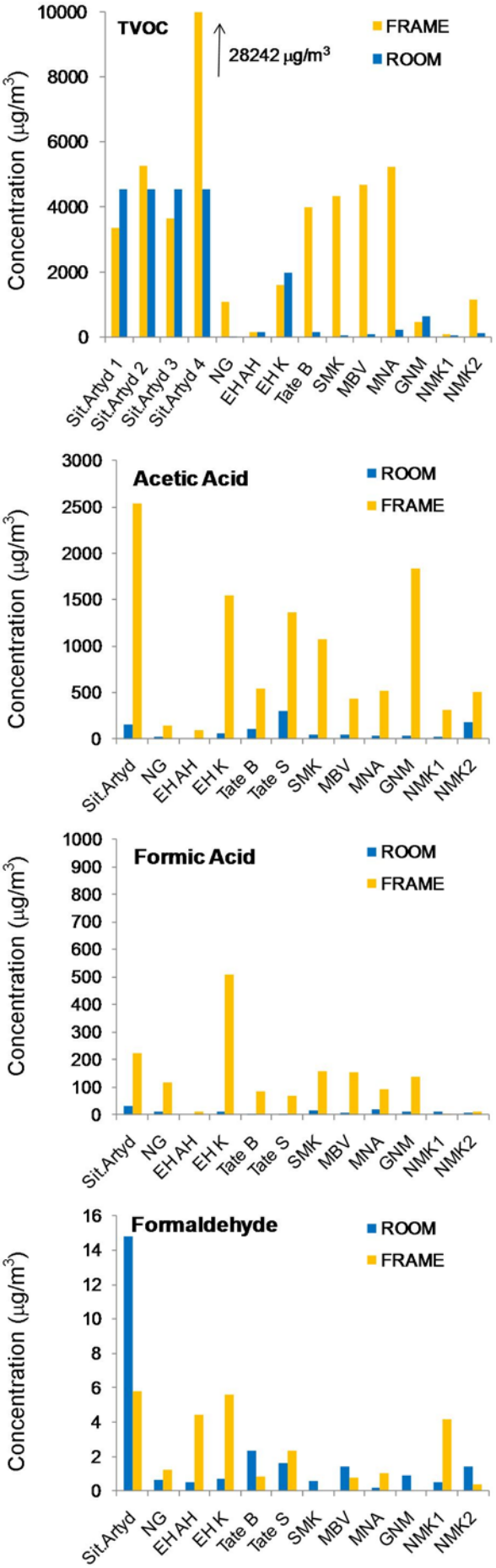

Figure 1. Total concentration of volatile organic compounds (TVOC), acetic acid, formic acid and formaldehyde measured inside and outside mc-frames. TVOC measured by tubes with Tenax sorbent. Acetic acid, formic acid and formaldehyde were measured by passive diffusion samplers. For location abbreviations see Table 1. Sit.Artyd corresponds to the analysis inside the mc-frame no. 4 in Tables 2 and 3.

Light organic compounds, such as formic and acetic acid, are not fully absorbed by the Tenax used for the VOC sampling. Thus, the concentration of the organic acids (acetic and formic) was measured by individual passive diffusion samplers[20]. Concentrations of acetic acid were measured inside nearly all the mc-frames varying from 100 to levels higher than 2000 µg m^{-3} (Figure 1). Formic acid follows a similar pattern to acetic acid with concentrations varying from <10 to 510 µg m^{-3} (Figure 1). The highest concentration of formaldehyde was observed in the mc-frame at Kenwood (6 µg m^{-3}; Figure 1), which may well originate from urea formaldehyde resin used in the small plywood inner frame to hold the Artsorb sheet.

The concentrations of the inorganic gases (NO_2, O_3 and SO_2) measured inside the mc-frames were significantly lower than those of the organic compounds, as expected. NO_2 and O_3 varied between 1 and 5 µg m^{-3}, and 1 and 7 µg m^{-3}, respectively (Figure 2). Low concentrations of SO_2 were measured inside the mc-frames (<0.5 µg m^{-3}).

3.2 Measurements in rooms

The results from the VOC measurements in room locations are shown in Table 3. The concentration of TVOCs was the lowest in the National Museum of Art, Architecture and Design, National Gallery in Oslo (39 µg m^{-3}), and highest in the SIT-Artyd workshop (4545 µg m^{-3}). The room in English Heritage, Kenwood (2008 µg m^{-3}) showed the highest concentration of the 10 other museums and storage locations (Table 3; Figure 1).

Toluene was detected in all 11 rooms with concentrations varying from 2 µg m^{-3} in the Statens Museum for Kunst (Copenhagen) to 111 µg m^{-3} in Kenwood (English Heritage) and 546 µg m^{-3} in the workshop of SIT-Artyd. The benzene derivatives p- and m-xylene, decane and 2-propanone (acetone) were detected in eight of the 11 locations (Table 3). The concentrations of p- and m-xylene varied from 1 µg m^{-3} in the National Gallery in Oslo to 13 µg m^{-3} in the National Museum of Art in Mexico City, and 217 µg m^{-3} measured in the SIT-Artyd workshop. The highest concentration of decane was observed in one of the locations of English Heritage (Kenwood; 33 µg m^{-3}) and in the workshop of SIT-Artyd (123 µg m^{-3}). Other VOCs

observed at relatively high concentration (more than 60 μg m^{-3}) are acetic acid ethylester, 2-propanol, undecane, three different benzene compounds (English Heritage, Kenwood) and 2-furancarboxaldehyde and benzoic acid (Germanic National Museum; Table 3).

The acetic and formic acid concentrations measured in rooms by the separate passive gas samplers were significantly lower than those measured inside the mc-frames, with the highest values of 300 and 160 μg m^{-3}, respectively. The relation between the concentrations of formaldehyde inside and outside of mc-frames is not systematic; in some locations, the concentration of formaldehyde was higher inside the mc-frame, while in other locations the outside concentration was higher (Figure 1). In contrast, high concentrations of inorganic gases, mainly generated outdoors, were detected in the room locations (Figure 2). In almost every room location (except Tate S.) NO_2 concentration was higher than 10 μg m^{-3}, and for two locations, Apsley House (English Heritage, London) and National Museum of Art (Mexico City) concentrations of approximately 40 μg m^{-3} were measured.

Location	Artyd	NG	EH K.	EH A.H.	Tate S.	Tate B.	SMK	MBV	MNA	GNM	NMK 1	NMK 2
TVOC	4545	39	2008	177	*	180	76	107	223	655	61	118
TVOC id.	3491	31	1507	138	*	126	58	90	172	495	44	87
Type	W	G	G	G	S	ST	G	G	G	G	G	G
Compound	Concentration (μg m^{-3})											
toluene	546	3	111	9		5	2	37	53	6	3	10
benzoic acid	446	3					3	1	10	63		
1-ethenyl-4-ethyl benzene	381											
p-and m- xylene	217	1		3			2	12	13	8	2	
acetic acid ethylester (ethylacetate)			205						5			
alfa pinene	160					3		7		5	2	16
1-ethenyl-3-ethyl benzene	189											
5-(hydroxymethyl)-2-furancarboxaldehyde										182		
decane	123	1	33	1		2		2	3		1	
acetic acid*	133					2	1			6		2
1,2,4-trimethylbenzene			132					1	4		1	
2-propanol (isopropylalkohol)		1	129				1	1			1	5
2-propanone (acetone)	73	1	46				2	3	4		1	3
undecane			116					1	3	7	2	1
2,3-dihydro-4-methyl-1H-inden	122											
ethylbenzene	90					2		4	3			2
styrene (ethenylbenzene)	100								2			
1-ethyl-4-methylbenzene	48		40					1	3			
benzaldehyde	59	1		3		8	5			7	1	
ethylbenzaldehyde	81											
cyclohexane	46			35								
2-furancarboxaldehyde										80		
2,3-dihydro-2-methyl-1H-inden	77											
benzene	65	1		2			1	1	3		1	1
formic acid*	69											
1-methyl-3-propylbenzene			66									
1,2,3,5-tetramethylbenzene			63									
butylbenzene	60											
1-butanol			51	6						3		
nonane	40	1		2		3	2	1	2		1	

Table 3. VOC outside the mc-frame in the room locations sampled by tubes with Tenax TA sorbent. Compounds with highest total added concentration in the rooms for the entire study. TVOC: total concentration of volatile organic compounds. TVOC id.: total concentration of identified volatile organic compounds. Room types: W: workshop, G: gallery, S: store, ST: staircase. * = compound is not fully absorbed by Tenax TA sorbent. For the abbreviation of the locations see Table 1.

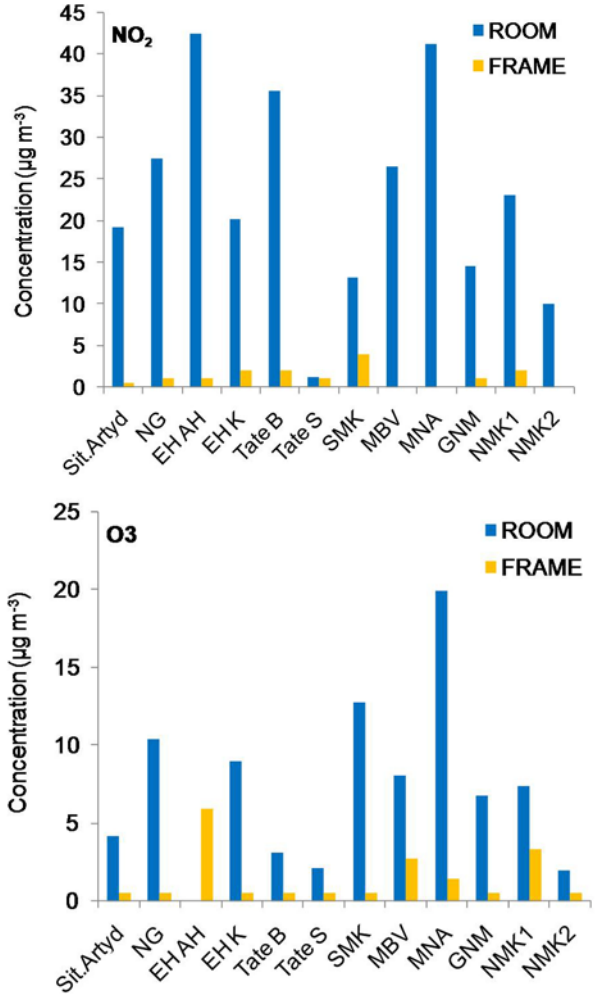

Figure 2: Concentration of NO2 and O3 inside and outside mc-frames. For location abbreviations see Table 1. Sit.Artyd corresponds to the analysis inside the mc-frame no. 4 in Table 2 and 3.

3.3 Air Exchange Rate

The mc-enclosure constructions were found to vary from almost airtight to highly ventilated. Seven out of 10 measured mc-frames showed air exchange rates between 0.15 and 1.4 day^{-1}. Measurements performed in the mc-frames located in Tate Store and Tate Britain gave an air exchange rate of 6.7 and 8.6 day^{-1}, respectively, and the glass enclosure located in the National Museum in Krakow showed the highest air exchange rate in this study, 15 day^{-1} (Table 1).

4 Discussion

4.1 Pollutants inside mc-frames

The mc-frames in this study were produced from different materials with different designs in order to satisfy the particular requirements of the paintings. The particular design of each mc-frame

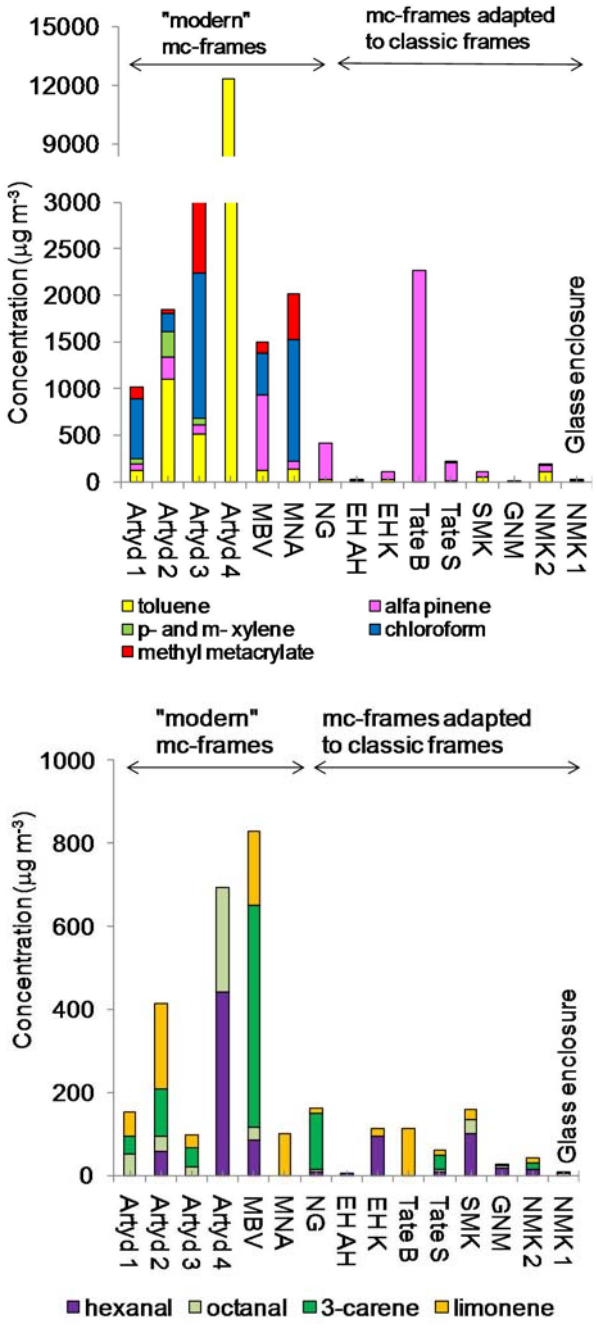

Figure 3. Concentration of specific VOC inside modern mc-frames and mc-frames adapted to classic frames including the glass enclosure.

makes it unique and the discussion about pollutant concentrations and the risk assessment becomes complex. The mc-frames newly made by SIT and classified as “modern” (Table 1) showed higher concentrations of TVOCs than the mc-frames adapted to classic frames (Figure 1). This may be explained by an expected reduction of emissions with time[17] as modern frame are generally younger than classic frames (Table 1). Exceptions to this are the “classic” frames located in the Statens Museum for Kunst (Copenhagen) and in Tate Britain (London), where TVOC at the same level as

for the “modern” frames were measured (SMK, 4347 µg m^{-3}; Tate B., 3995 µg m^{-3}; Table 2, Figure 1). The mc-frame in Statens Museum for Kunst was constructed in 2007; however, the mc-frame in Tate Britain is the oldest of the studied mc-frames.

Some organic compounds were mainly or exclusively detected in one of the three groups of mc-frames. Chloroform (195 - 6413 µg m^{-3}) and 2-methyl-2-propenoic acid methylester (methyl methacrylate; 43 - 1297 µg m^{-3}) were only, along with some aromatic hydrocarbons, detected in the “modern” mc-frames (Table 1 and Figure 3). Chloroform solvent was used as an additive of the adhesive, necessary to join the frame structure (personal communication, 2008), which explains its presence inside the mc-frames. The effects of chloroform and methyl methacrylate on health have been reported.[23-24] However, no information is available about their possible effects on materials. Chloroform vapour trapped inside tight enclosure could probably have an adverse effect on varnishes of paintings. In order to avoid internal emissions of chloroform, the design of the “modern” mc-frames by SIT-Artyd was modified based on these results and chloroform is no longer used in the adhesive.

Some VOCs, such as toluene, were detected in almost all the mc-frames and rooms. Toluene showed the most widespread presence and highest concentrations, apart from chloroform, in this study (Figure 3). It was measured in every “modern” frame, in about 80% of the “classic” frames and in every room location, except Tate Store. The presence of benzene derivatives p- and m-xylene was detected in nine mc-frames (four modern and five classic) and in eight room locations (Tables 2 and 3). Toluene can be emitted from solvents used in the manufacturing processes of mc-frames or from paints or lacquers[17]. p-and m-xylene are used in cleaning agents, in varnishes, as thinner in paints and they are widespread substitutes for toluene in slower drying lacquers. The source determination is complicated by the diversity of possible sources and its presence both inside and outside the mc-frames. The use of paints and lacquers inside mc-frames is common practice and may explain the extensive presence of toluene (e.g. MNA = 1309 µg m^{-3}) and p- and m-xylene (e.g. mc-frame no 2 SIT-Artyd = 275 µg m^{-3}), and their high concentrations inside some mc-frames. However, the risk posed to paintings in mc-frames is difficult to assess as established dose - effect relationships do not exist.

The presence of terpenes was also detected and high values were measured inside mc-frames (e.g. α-pinene, Tate B. = 2263 µg m^{-3}; Table 2). Terpenes, such as α-pinene, β-pinene, limonene and 3-carene, are all typical volatile ingredients of wood and wood based products and are known to be highly reactive together with oxidizing agents and in particular with ozone. The low value of α-pinene, limonene and 3-carene in the rooms, but higher levels measured inside almost all the mc-frames suggests a source inside the mc-frame (Figure 3). Terpenes are potentially important for the evaluation of the protective effects of mc-frames. Alfa-pinene and limonene are oxidized by ozone, nitrogen dioxide and hydroxy radicals[4] forming acetic acid, formic acid and particles as products of the reaction[25-27]. Thus, the infiltration of strong oxidizing agents such as NO_2 and O_3 into mc-frames with high air exchange rate could pose a risk for the paintings by increasing the concentration levels of oxidizing agents in the frames and subsequently the concentration level of secondary pollutants, such as acetic acid.

Acetic acid is known to corrode metals; in particular lead[28] and calcareous materials[29], while wood products, adhesives, sealants and the degradation process of various polymer materials constitute the main sources.[7-8] Concentration higher than 500 µg m^{-3} of acetic acid was measured inside most of the mc-frames (Figure 1). Realistic assessment of the risk posed by acetic acid is therefore required to evaluate the protective effects of mc-frames. No information exists about possible damage effects for acetic acid on varnishes or paintings. The available information is mainly related to effects on metals.[8] In the same reference, the concentration of acetic acid at which adverse effects on lead are observed is established at 400 µg m^{-3}. However, this value is not applicable to sensitive materials such as colorants or varnishes. Thus, for the evaluation of the protective effect of mc-frames for paintings information about dose–damage relationships and suitable threshold levels for effects of organic pollutants such as acetic acid on paintings is urgently needed. In the frame of the PROPAINT project, effects of acetic acid on natural and artificial varnishes are being studied and will be published elsewhere.

The presence of aldehydes was also detected inside mc-frames. Aldehydes such as hexanal may be formed by degradation of linoleic acid. Those in the range from heptanal to decanal may be formed by degradation of oleic acid[30]. Hexanal and octanal were widely present inside the mc-frames (Figure 3) and were measured at relatively high concentrations in 10 frames, reaching the high values of 97 µg m^{-3} (Staten Museum for Kunst, SMK)

and 51 μg m^{-3} (Artyd frame no. 1), respectively (Table 2). Aldehydes can be oxidized to carboxylic acids, such as hexanoic acid, under high relative humidity conditions or in the presence of strong oxidants. Hexanoic acid was detected in six mc-frames (concentrations between 12 μg m^{-3} and 208 μg m^{-3}). Hexanoic acid is a fatty acid naturally present in oils. The general effects of fatty acids, for instance hexanoic acid, on materials are the corrosion of bronze and lead, the existence of ghost images on glass, and yellowing of paper and photographic documents.[8]

4.2 Pollutants in the room locations

Of special concern are the levels of oxidizing agents in the room locations. The known adverse effects of exposure to NO_2 are fading of pigments[7,8,31] or losses of strength of textiles and papers[7,8,32]. NO_2 concentrations higher than the recommended value for museums for the suitable preservation of most objects [NO_2 = 10 μg m^{-3}; [5,8,33]] were measured in almost every room location (except Tate Store). The three highest levels were measured in the room locations in Apsley House (English Heritage, London), Tate Britain (London) and the National Museum of Art (Mexico City). In some cases ozone exceeded acceptable levels. The highest ozone concentrations, over the acceptable value for preservation [O_3 = 10 μg m^{-3}; [5,8,33]], were measured in the room at National Museum of Art, Architecture and Design, National Gallery (Oslo), Staten Museum for Kunst (Copenhagen) and National Museum of Art (Mexico City). The low concentration of these inorganic gases measured inside the mc-frames shows that the frames effectively protect paintings against the ingress of externally generated pollutants.

In general, the measured concentrations of organic compounds in the room locations were very low. However, TVOC concentrations higher than 500 μg m^{-3} were measured in two locations, SIT-Artyd workshop (4500 μg m^{-3}; Table 3) and Kenwood (2000 μg m^{-3}; Table 3). As the total VOC exposure recommended for indoor air quality by the Commission of the European Communities[34] is 300 μg m^{-3}, this concentration of TVOC constitutes a possible health risk for the personnel in Kenwood House and in the SIT-Artyd workshop.

4.3 Air Exchange Rate

Mc-frames offer good protection against externally generated inorganic air pollutants. For mc-frames designed with low air exchange rate, the infiltration of externally generated oxidizing and / or acidic air pollutants is very low. The “modern” mc-frame in the Fine Art Museum (Valencia) was designed to have a very low air exchange rate (AER = 0.15 day^{-1}) which gives a low concentration level of O_3 (2.7 μg m^{-3}) and no detectable level of NO_2. The glass enclosure in the National Museum in Krakow, however, shows very high air exchange rate (AER ≈ 15 day^{-1}) allowing a high rate of infiltration of oxidizing agents from the museum environment. The relationship between air exchange rate and the ratio of the concentration of pollutants inside to outside the frames was studied but no systematic relationship was observed.

5 Conclusions

The study has reported for the first time a wide range of specific compounds inside microclimate frames for paintings and especially the range of VOCs measured. The study has demonstrated the protective effects of mc-frames for paintings against externally generated pollutants. Generally, oxidizing compounds were detected in low concentrations inside mc-frames while high concentrations were measured in the rooms. In contrast, high levels of VOCs such as acetic and formic acid, toluene, p- and m-xylenes, α-pinene, limonene and 3-carene were detected inside mc-frames. The high concentration of some of these VOCs inside mc-frames may be harmful for enclosed paintings. α-pinene and limonene may react with infiltrating oxidizing agents and will result in secondary emissions of VOCs such as formic and acetic acid, aldehydes and fatty acids. Some VOCs, such as chloroform and 2-methyl-2-propenoic acid methylester (methyl metacrylate) were detected exclusively in modern mc-frames. The use of new synthetic materials in mc-frames will open a new line of research concerning emissions from new and modern materials, the reactivity of the emitted compounds and their effects on materials, and especially on cultural heritage objects such as paintings.

The balance between acceptable levels for oxidizing agents and acceptable levels for organic compounds may constitute the criteria for the design of mc-frames. However, threshold levels for specific organic compounds and their effects on paintings need to be defined. The air exchange rate is an important parameter in the design of such mc-frames; airtight mc-frames offer the best technology against the infiltration of oxidizing pollutants and possible reactions with organic compounds. The present common recommendation is to make mc-frames as air tight as possible for the optimum

protection of the paintings. However, this may lead to the accumulation of a variety of internally generated organic compounds. Due to the lack of information about degradation effects on paintings, varnishes or pigments of exposure to organic compounds, and the related lack of specific thresholds levels, the present best recommendation is to avoid the use of construction materials in the mc-frames with high emission of organic compounds, and to observe a longer period of time between construction of the mc-frame and installation of the painting.

6 Acknowledgements

It was only possible to perform this study due to the financing of the PROPAINT (SSPI-044254) project supported by the European Commission under FP6. The authors gratefully acknowledge the partners and end user museums participating in the PROPAINT project allowing the study to be performed and conservators in the museums who did the practical work with the sampling.

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