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Monitoring air pollutants in showcases by proton-transfer-reaction mass spectrometry and passive samples tubes

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ABSTRACT

Air pollutants which originate from volatile organic compounds like organic acids and solvents are a threat to objects of various materials displayed in a showcase. Proton-transfer-reaction mass spectrometry (PTR-MS) is a new approach which offers the possibly to carry out real-time monitoring measurements for air pollutants directly from air at atmospheric pressure. The showcase does not need to be opened entirely as the air is sampled by a capillary which can enter the interior of the showcase via a small interstice. In this way a large number of showcases can be analyzed within a short time. The feasibility and usefulness of such measurements in a museum is shown. The results of the PTR-MS measurements for acetic acid are compared to results of passive sampling methods.

INTRODUCTION

Volatile organic compounds (VOCs) like organic acids and solvents are considered air pollutants because they are a threat to cultural heritage objects of every kind of material (Nicholls 1934, Schmidt 1992, Tennent et al. 1993, Dupont and Tétreault 2000, Tétreault 2003, Linnow et al. 2007). The Neues Museum on the Museum Island in Berlin was restored and reopened in 2009. Its new architecture is characterized by the combination of new and historical elements. This style is also reflected in the interior and the exhibition areas where both historical and newly constructed showcases are in use.

All construction materials connected to the area where the showcases are displayed have to pass the Oddy test before being approved for use. However, it would seem advisable to monitor the air pollutant levels in the showcases as part of quality-control measures. A common analytical practice utilizes passive samplers to determine the levels of pollutants (Gibson et al. 1997, Stranger et al. 2008). This approach has the advantage of being low cost and easy to realize as no power supply is needed for sampling. On the other hand, placing and recovering the samplers is time consuming. The samplers have to remain in the showcase for a relatively long period, which may sometimes be perceived as intrusive by the museum's audience. Proton-transfer-reaction mass spectrometry (PTR-MS) offers the possibility to carry out monitoring measurements for air pollutants directly from air under atmospheric pressure. The measurement of a showcase can be accomplished within several minutes. Both analytical approaches have been used in this study. The PTR-MS measurements were carried out about a year after the museum reopened. The passive sampler measurements were carried out before (including some measurements of empty cases) and after this period in selected showcases.

The showcases varied in size and design. The materials on display ranged from organic, such as wood, paper and textiles, to inorganic, such as stone, metal and ceramics, or a mixture of both. For the data evaluation, the showcases were divided into groups depending on their construction materials. The historical showcases were made from massive wood (lacquered). The cases for permanent display were made from metal with an acrylic polymer interior. This polymer, with alumina trihydrate as filler, is sold as Corian.[1] These opaque acrylic polymer boards (APB)

Figure 1
Real-time PTR-MS measurement in a gallery carried out by J. Kames. The capillary is entering the showcase via an interstice at the doors gasket

are solid-coloured. Other showcases designed for sculptures were made from metal and contained a concrete pedestal. Showcases for temporary display were used in a separate exhibition area. These were made from wood-based medium-density fiberboard (MDF). All showcases had panes made from inorganic glass.

The evaluation of the data was used for an assessment of the showcases and to compare the air pollutants inside differently made cases, as well as to compare the PTR-MS results with results from passive sampler measurements.

EXPERIMENTAL

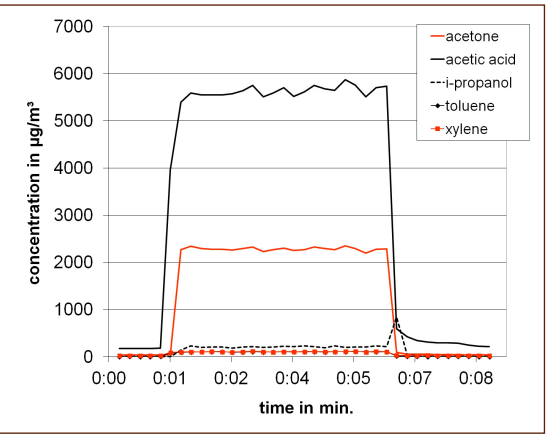
The PTR-MS analytical method is a particular type of mass spectroscopy adapted for the analysis of trace compounds in air.[2] Suitable for trace compound analysis by MS are soft ionization mechanisms which convert a high portion of the analyte molecules into separately detectable ions without their unwanted fragmentation.

Chemical ionization methods – such as proton transfer reactions (PTR) – are soft methods of this sort. PTR makes use of an ion source that produces H_3O^+ ions from water vapour. These primary ions transfer protons to proton-accepting atoms of molecules, specifically oxygen, nitrogen or sulfur atoms within target molecules, but also aromatic systems. Therefore, molecules containing functional groups with the mentioned atoms can easily be ionized, whereas other compounds such as aliphatic hydrocarbons (alkanes, alkenes), molecular nitrogen and oxygen cannot.

This leads to a desirable simplification of the mass spectrum and promotes low detection limits for the detected ions. Most of the compounds regarded as potential or hazardous contaminants in museums and archives have functional groups such as these and can be ionized by PTR: e.g., organic acids, aldehydes, ketons, esters and siloxanes. Hence, the method is specifically suitable for detection of air pollutants in the museum environment.

A prototype of the AMC-Monitor C-1000 was used in this study (Figure 1). The analyte ions were separated in a tunable quadrupole and registered with a channeltron. The instrument is able to detect concentrations down to the 1–2 µg/m³ level within 5 s of measurement. The instrument was placed on a trolley and thus made mobile with the application of an uninterrupted power supply (UPS) which maintained the power while the power cable was relocated from one socket to another. Air flow taken from the showcases was set to 500 ml/min of which 5 ml/min were injected continuously into the ionization chamber. The mass spectrometer had been calibrated prior to the measurement for a number of compounds: ethanoic acid (acetic acid), propanone (acetone), 2-propanol (*i*-propanol), benzene, methylbenzene (toluene) and dimethylbenzene (xylene). For the calibration, it was necessary to have some information about the analyte matrix. This was obtained by measurements with radial passive samplers in a few selected showcases before the PTR-MS campaign.

To sample the air inside a showcase, a capillary (i.e., sampling tube with an external diameter of 4 mm) had to enter the volume of the display area. Depending on the design of the showcase, this was possible via interstices



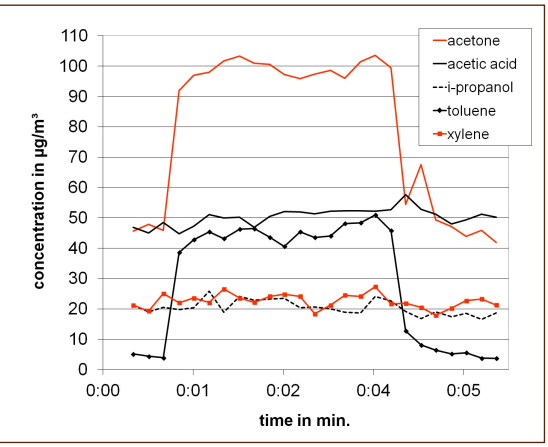


Figure 2
Real-time PTR-MS measurement of a showcase (made from MDF)

Figure 3
Real-time PTR-MS measurement of a showcase (made from metal/APB)

at the gaskets for doors or the interconnection between maintenance compartments and display space.

Passive sampler measurements with two kinds of samplers, radial and axial, were carried out. Radial diffusion tubes from Radiello were used. Four chemically different types of samplers were used, optimized for various acids and acid-forming species (e.g., acetic acid, methanoic (formic) acid, SO_2, NO_2), NH_3, H_2S, and finally VOCs. The samplers were exposed to the atmosphere in the showcases for 11 days. The samplers were analyzed by photometry, ion chromatography and thermodesorption-GC/MS. The analysis of the acetic acid is based on a protocol similar to the one previously published (Stranger 2008).

Additional passive sampler measurements were carried out with axial diffusion tubes for formic and acetic acid. The diffusion tubes were prepared with KOH as described by Gibson et al. (1997). The samplers were exposed for 28 days. The chemical analysis of the sampled compounds in the laboratory was carried out by ion chromatography using a Metrohm 690 with a P-X300 ion exclusion column. The measurements were carried out repeatedly; the average deviation of a signal measurement from the mean value was 10%.

In a clean room environment where the air is circulated permanently, the PTR-MS results were in accordance, with an accuracy of ± 30% rel. with radial passive samplers for acetic acid levels in the range of 1.3 µg/m³ to 1250 µg/m³.

RESULTS AND DISCUSSION

Over 40 showcases and air pollutant levels in the corresponding galleries were measured by PTR-MS in a two-day campaign. Figures 2 and 3 show two measurements taken. On the x-axis, time (an arbitrary moment was defined as zero) is plotted against the concentration of the calibrated compounds. At zero time, the capillary was still outside the showcase and was sampling the air from the gallery. At about the one-minute mark, the capillary entered the area where the showcase was displayed, which was noticeable by the sudden rise in concentrations of most of the measured compounds. The concentration values in the inside air were taken once the readings had been stabilized. The values moved back toward the corresponding concentration level in the gallery after the capillary was removed from the showcase. They dropped more slowly than they had risen because it takes a little time to purge the spectrometer of the pollutants.

In general, the concentration readings from the inside air formed a stable plateau. The values for a showcase were calculated by averaging the plateau values. In more than 80% of the cases, the relative standard deviation average for the plateau was less than 10%. In 70% of all measurements, the standard deviation for acetic acid was less than 5%. The plateau also indicates that the pollutant concentrations inside were usually not influenced by air exchange caused by the intrusion of the capillary. In a few cases, a dilution effect was observed, with decreasing pollutant concentration during the measuring. In these cases, the highest initial values were taken as an indication of the pollutant levels.

Comparison of showcase types

The results of the PTR-MS measurement are summarized in Table 1. The values are arranged according to the four types of showcase mentioned above. Each group of showcases is characterized by a different "fingerprint" of concentrations relating to the construction materials. However, it should be kept in mind that these values do include contributions released from the dressing of the case and by the displayed objects.

The lowest air pollutant levels were found in showcases made from concrete and metal followed by the APB/metal cases. The particularly low levels of acetic acid in the concrete/metal cases were caused by the concrete, which may act as an acid sink because of its calcium hydroxide content. Higher levels of acetic acid were found in the historical wooden cases and in the cases made from MDF. The highest levels for all measured compounds were found in the temporary showcases made from MDF. One of these cases had moderate values indicated by the minimum values in Table 1. The historical cases had lower acetone, *i*-propanol and toluene levels than the MDF cases. The concentrations of these solvents were at lower levels or equal to those in the metal/concrete or APB cases. The high maximum value of *i*-propanol for the metal/APB cases was due to one single case which contains a 3-D reproduction of an architectural feature made of a modern polymer material which is probably off-gassing this solvent.

Table 1
Air pollutant levels in µg/m^3 measured by PTR-MS and grouped by showcase construction types. N is the number of showcases measured

showcase construction type	N		acetone	acetic acid	i-propanol	toluene	xylene
metal / APB	27	average	**193**	**381**	**93**	**56**	**35**
		max	859	1108	**1255**	120	105
		min	40	51	21	16	16
metal / concrete	7	average	**194**	**50**	**84**	**15**	**35**
		max	330	176	111	24	67
		min	82	16	60	5	16
MDF	4	average	**3409**	**2342**	**218**	**60**	**192**
		max	10150	5620	536	106	507
		min	201	424	20	18	34
historic case wooden	2	average	**100**	**1987**	**34**	**12**	**176**
		max	115	2390	42	15	256
		min	85	1584	26	9	96

Comparison of methods

For the acetic acid, the PTR-MS values were compared with the results from the passive samplers. An overview of the values from the various measurement campaigns is given in Table 2. It should be noted that the measurements were not carried out in parallel but successively. The values for campaign 1 are from empty showcases; for campaigns 2 to 5, the showcases had objects on display.

The results for the three methods show some differences. The two passive sampling methods using axial and radial diffusion tubes (campaigns 2, 4 and 5) gave similar results, with a tendency to give lower values for the radial diffusion tube measurements. In general, the PTR-MS measurements

gave higher values than the passive sampler measurements. Only a slight disagreement between the axial passive sampler results from the metal/concrete or APB showcases was found, with the exception of one case (showcase 5), where the difference was a factor of 3. A more pronounced difference was encountered in the cases containing wood or wood-based construction materials. The PTR-MS values were higher by a factor of 2 to 7 as compared to radial diffusion tubes. Several reasons could account for this. First, the measurements were not carried out at the same time. Campaign 2 was performed roughly six months earlier and campaign 4 approximately one month after the PTR-MS measurements. It has been reported that pollutant levels in showcases can change with time and may follow seasonal changes in RH and T (Hahn et al. 2007, Grøntoft 2012). Inside an air-conditioned museum, this factor should be marginal. Some of the showcases maintained a microclimate that was different from the surrounding gallery, but the actual RH and T values at the times the measurements were taken are not available. The difference might also be due to a systematic error. Studies (Schieweck and Salthammer 2011) have shown that passive measurements tend to give lower results than active sampling. The static conditions inside a case can lead to a "starvation effect," causing an underestimation of the level by passive sampling.

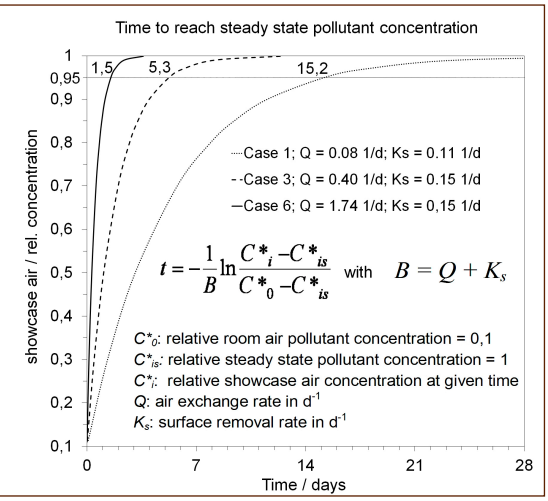
Table 2
Acetic acid levels in side showcases measured by different methods in different campaigns

Showcase number and construction type	material objects	radial diffusion tube (empty case)	axial diffusion tube	radial diffusion tube	PTR-MS
Campaign No.		1	5	2, 4	3
1 metal / APB	mixed		247	172	285
2 metal / APB	mixed		254	190	215
3 metal / APB	mixed	<20		315	276
4 metal / APB	mixed		239	175	339
5 metal / APB	mixed		151	175	458
6 metal / concrete	wood			<20	32
7 metal / concrete	metal	<20		<20	16
8 MDF	bone			302	2083
9 MDF	amber			936	5602
10 historic wooden	ceramic	1024	2013	1199	2390

Steady-state concentration

Another cause could be the disturbance of the steady-state concentration inside the case. Pollutant concentration will reach a steady state when the mass flows causing a rise and fall in the air-pollutant concentration are at equilibrium. Air exchange, emission sources inside the display case and the deposition of pollutants on material surfaces are the causes for the mass flows. Opening the showcase to place passive samplers allows a much larger air exchange which generally causes a temporary drop in pollutant levels. Steady-state concentration is only reached again after some time. According to the equations of Grøntoft (2010) and Thickett (2012), this time depends on the surface removal rates *Ks* of the pollutant gas and the air exchange rate of the showcase. (*Ks* is the product of deposition velocity to a surface multiplied by surface area, divided by the volume of the showcase.) Since the data for calculation was not available for the

MONITORING AIR POLLUTANTS IN SHOWCASES BY PROTON-TRANSFER-REACTION MASS SPECTROMETRY AND PASSIVE SAMPLES TUBES



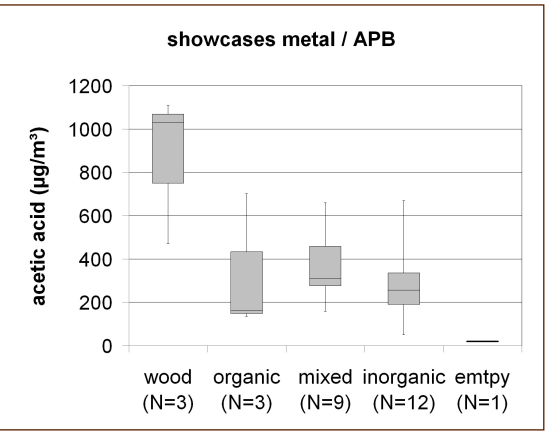


Figure 4
The time taken to reach 95% of the steady-state concentration, calculated according to Grøntoft (2010), example for acetic acid with surface removal rate *Ks* and air exchange rate *Q* values from Thickett (2012, 242)

Figure 5
Box plot of acetic acid concentration in metal/APB showcases with various materials on display measured with PTR-MS

showcases from the Neues Museum, data for acetic acid from Thickett (2012, 242) was used for a representative calculation. The time taken to reach 95% of the steady-state equilibrium concentration for metal cases with sealed MDF in room air at 10% of the equilibrium concentration can be several days or even weeks (1.5 d, 5.3 d and 15.2 d in Figure 4). As passive samplers give an average level over the exposure time, this may result in levels lower than the steady-state concentration, especially for passive samplers which are exposed for a short period of time. This might account for the radial passive sampler, which gave lower values compared to the axial sampler, because the radial samplers were only exposed for 11 days as opposed to 28 days for the axial samplers. These showcases, which gave similar results for the three analytical methods, might reach their steady state faster than the others.

Assessment of acetic acid levels

In most cases, the acetic acid value was below the one-year preservation target level of 1000 µg/m³ but above the 10-year preservation target level of 100 µg/m³ (Tétreault 2003). The high values of the wooden and MDF cases were no surprise. But it was unexpected that the gallery air with exclusively MDF or wood showcases would reach values over 100 µg/m³ (Table 3).

The reason for high acetic acid values in metal/APB cases is still unclear. Some dressing materials have attracted attention because some double-sided adhesive tape, photographic paper and laminate film failed in the Oddy test but were used nevertheless because of a lack of alternatives. However, the use of this material does not correlate with the acetic acid levels. In Figure 5, the acetic acid concentrations are shown for groups of displayed material and for an empty case. Wooden objects have a significant influence on acetic acid concentration. Showcases with other materials on display have lower acetic acid concentrations largely irrespective of these materials. During the first measurement campaign, only a few empty showcases were measured because of timing problems during the installation (nos. 3, 7 and 10 in Table 2). These measurements show lower acetic acid levels compared to later measurements when they were on display. This might suggest that the objects have an influence on the acetic acid concentrations. Inorganic materials themselves are unlikely sources of the acetic acid, therefore the adhesives used on the objects, such as cellulose acetate or polyvinyl acetate, might have to be considered. The outcome of this study will be used to plan further actions to determine the sources of the acetic acid and to reduce its concentration.

Table 3
Air pollutant levels in gallery air in µg/m³

Air measured outside (gallery)	Showcases in that gallery	acetone	acetic acid	i-propanol	toluene	xylene
metal / APB	1, 2	20	74	26	7	26
metal / APB	3	23	56	47	5	24
metal / APB	4, 5	22	43	41	4	26
metal / concrete	6, 7	13	51	36	3	23
temp MDF	8	18	145	34	8	29
temp MDF	9	17	163	32	7	28
historic wooden	10	21	144	27	8	32

CONCLUSIONS

PTR-MS was used successfully to sample the air inside showcases without the need to open them completely. During a four-minute measurement, the PTR-MS had a gross air intake of 2 l. This volume was much lower than the volume of the display space. Also the exchange between the inner atmosphere and the environment through the small interstice needed for the capillary to enter the case was insignificant. Therefore, the PTR-MS truly "samples" the air of the case and does not significantly disturb the steady-state equilibrium concentration if the showcase can be opened in an appropriate way.

The measurements confirmed the already known problem of acetic-acid emission from wood and wood-based materials, but showed that the room air may also reach problematic levels. The acetic acid levels of the metal/APB showcase were higher than expected, but the source of the pollutant was not directly traceable, leaving the objects, which included the materials used on the objects as well as the dressing or construction materials, as the likely sources.

NOTES

[1] Poly(methyl 2-methylpropenoate) or poly(methyl methacrylate) (PMMA) is also used for Perspex.

[2] The PTR-MS technology used was from Ionicon Analytik GmbH, Innsbruck, and Artemis Control AG, Uster, to provide an easy to apply online monitoring for trace contamination, e.g., in semiconductor clean rooms or in cultural heritage institutions. For further information see www.amc-monitor.com.

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