RESEARCH ARTICLE

Validation of passive samplers for monitoring of acetic and formic acid in museum environments

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Abstract

Acetic acid and formic acid are volatile pollutants leading to degradation of some heritage materials. They are usually determined in museum environments with various types of passive samplers. In this work, SKC UMEx 200 passive samplers, originally intended for sampling of NO_2 and SO_2, have been validated for sampling of these organic acids. The sampling rates, extraction efficiency, loss through reverse diffusion or during storage, capacity, and detection limits were determined for both acids. For laboratory exposure, a known concentration of both acids was prepared in a flow-through reactor system at controlled temperature and humidity, the samplers were extracted, followed by analysis using ion chromatography. The sampling rates were determined to be 16.7 ml/min for acetic and 17.7 ml/min for formic acid and the detection limits for 7-day exposure were determined to be 2.1 μg/m^3 for acetic and 1.9 μg/m^3 for formic acid. The validated method was finally used for sampling of air in two case studies at the National Museum of Slovenia, where the concentrations in the range of 2–54 μg/m^3 were determined.

Keywords: Passive sampling, Organic acids, Air quality, Indoor air quality, Heritage science, Preventive conservation

Introduction

Formic acid (HCOOH) and acetic acid (CH$_3$COOH, AcOH) are volatile pollutants in museum environments, representing well-known risks to artefacts. Corrosion of non-noble metals (particularly lead) [1–3], efflorescence of carbonates (limestone and shells) [3], corrosion of glass [4], oxidation and cross-linking of natural resin varnishes [5] and discolouration of pigments [6, 7] have been attributed to these carboxylic acids at elevated concentrations.

In most museum environments, furnishing is the main source and emits these pollutants as products of wood degradation or formaldehyde oxidation in glues, especially in high humidity and in the presence of oxidants [8, 9]. Particleboard and MDF (medium density fibreboard)

[10], as well as some polymeric materials are also known sources of AcOH, as a consequence of hydrolysis of acetyl esters, epoxy resins, cellulose-nitrate, polyurethane and polyacrylate [8]. Conservation products, and artefacts themselves can also represent significant sources, and infiltration from the outdoors, while normally insignificant, cannot be discarded either [9, 10].

AcOH is often the most abundant indoor-generated pollutant, with HCOOH concentrations usually being lower [11]. Higher concentrations are usually observed in confined spaces, such as display cases or storage enclosures, due to low air-exchange rates and large surface-to-volume ratios [9, 12], and due to more airtight construction, contemporary display cases may exhibit high values [8]. Pollutant concentrations also fluctuate seasonally, with 3–6 times higher values observed during summer compared to winter [13–15] which could be a consequence of increased emissions from materials due to higher T and RH [3, 14]. Higher concentrations were

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also determined at floor level than at ceiling level in the same storage room [16].

AcOH concentrations ranging $42–481 \mu g/m^3$ and HCOOH concentrations up to $100 \mu g/m^3$ were determined in museum exhibition spaces and libraries [4, 13, 15, 17, 18]. In display cases and microclimate frames $20–6000 \mu g/m^3$ AcOH and $10–2100 \mu g/m^3$ HCOOH were determined [4, 9, 12, 18, 19], with extreme values of up to $11384 \mu g/m^3$ AcOH being found in wooden display cabinets [11, 19]. In museum and archive storage areas, $< 5–614 \mu g/m^3$ AcOH and $< 5–220 \mu g/m^3$ HCOOH were observed, while in storage cases and enclosures the concentrations were in the range of $121–1193 \mu g/m^3$ and $42–366 \mu g/m^3$ for AcOH and HCOOH, respectively [4, 14, 17, 20].

For general collections, concentration limits of $100–700 \mu g/m^3$ for AcOH and $10–40 \mu g/m^3$ for HCOOH [21], or $2500 \mu g/m^3$ of AcOH and $950 \mu g/m^3$ of HCOOH [22, 23] are suggested. For lead collections less than $100 \mu g/m^3$ [1, 2] or $250 \mu g/m^3$ [22, 23] of AcOH have been recommended. For sensitive collections, limits of $12.5 \mu g/m^3$ AcOH and $9.5 \mu g/m^3$ HCOOH have been suggested by Grzywacz [21]. These limits are rarely determined experimentally and may be much higher for some materials (e.g. acetic acid has been shown to not affect paper lifetime significantly at values below $250 \mu g/m^3$ (100 ppb) [24]). The effects of formic acid at low concentrations on materials are even less investigated [21], although materials such as copper, iron, leather and varnishes have been shown to be susceptible to degradation at higher concentrations [25]. As evident from the range of concentrations, determined in collections (see above), the values in collections often surpass the suggested limits, therefore various methods for reduction

of organic acid concentrations in air have been recommended: sealing of highly emitting surfaces, increasing ventilation of spaces, introducing air filtration [14, 26] or the use of different absorbers, such as silica gel, zeolites or (alkaline impregnated) activated charcoal [27–29]. From the range of recommended limits, it is evident that the effects of organic acids on museum materials are still widely debated. Nevertheless, these compounds are of high interest to the institutions that house heritage collections, which is another reason why an accessible and validated method of determination would be useful.

Gaseous pollutants can be sampled either actively or passively, with passive sampling being less expensive, easier to deploy and with no requirements for power, however, it does need longer sampling times than active sampling [10, 30].

For active sampling, liquid absorbers/impingers [8, 17], silica gel tubes [9, 14], activated charcoal tubes [31–33] and Tenax [6] have been used.

Passive sampling was initially carried out with Palmes diffusion tubes, where the analytes diffuse through static air inside a tube onto a filter at the opposite end, impregnated with a suitable reagent, e.g. $20 \mu l$ 1 M KOH and glycerine on paper filters [3, 4, 11, 20]. PA SPME fibres derivatised with 1-pyrenyldiazomethane were also used, with the fibre pulled inside the casing, forming a small diffusion chamber [31]. These methods have relatively high LODs and are strongly affected by air velocity.

More recently, passive samplers with different geometries have come into use (Table 1). Radial diffusive samplers (Radiello®) have higher sampling rates than diffusion tubes and are less influenced by air velocities. They consist of microporous polyethylene cylinders, impregnated with wet triethanolamine (TEA), placed

Table 1 Comparison of passive samplers of various configurations in regards to the geometry, sampling reagent, sampling rate and LOD (for the recommended sampling period)

Name	Geometry	Reagent	Sampling rate (ml/min)	LOD ($\mu g/m^3$)	Refs.
Palmes diffusion tube	Tube, $l = 7.1$ cm, $d = 1.1$ cm	1 M KOH, 10% v/v glycerine		AcOH: 44, HCOOH: 13	[11]
SPME				AcOH: 5.3, HCOOH: 28.9	[35]
SKC diffusive sampler		Coconut charcoal	AcOH: 19.6	AcOH: 10	[9]
Diffusive sampler	Badge, $h = 7$ mm, $d = 55$ mm	10% TEA, 5% glycerine		AcOH: 3.7, HCOOH: 3.2	[36]
Radiello	radial diff. sampler, $h = 6$ cm, $d = 5.8$ mm	Wet TEA	AcOH: 97±3, HCOOH: 91±4 – 112±3	AcOH: 0.4, HCOOH: 0.2	[10]
NILU passive sampler	Badge	Alkaline solution impregnated filter		Both 0.5	[12]
IVL passive sampler	Badge, $h = 13$ mm, $d = 25$ mm	Impregnated membrane		AcOH: 4, HCOOH: 1.5	[14, 16]

$l =$ length, $d =$ diameter, $h =$ height

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inside tubular PP diffusive bodies [10, 13, 34]. AcOH and HCOOH are retained on TEA in the form of the corresponding adducts $(HOCH_2CH_2)_3NH^+RCOO^-$ [10].

Axial diffusive samplers are also often used for air quality monitoring. Their compact bodies provide shorter diffusion paths than the tubes and the analytes are collected on alkaline impregnated filters [12, 14–16] or silica fibre filters, impregnated with 10% TEA and glycerine [36]. In the case of both NILU and IVL samplers (Table 1), the experimental sampling rates and repeatability are not published openly by the manufacturers, although research performed with duplicates of NILU samplers resulted in average repeatability of 21% for AcOH and 19% for HCOOH (as relative standard deviation, %RSD) [28, 37, 38]. Coconut charcoal passive samplers have also been used, but the authors reported low recoveries for AcOH and no retention for HCOOH [9].

After desorption, AcOH and HCOOH are most often determined with IC [11] (with carbonate buffer [10] or with NaOH [20] mobile phase), less often with HPLC-UV (C_{18} column, detection at 210 nm, isocratic elution with a KH_2PO_4/H_3PO_4 buffer [9]). If sampled with SPME, GC-MS was used for determination [31], although these analytes are considered less suitable for gas-chromatographic determination [39].
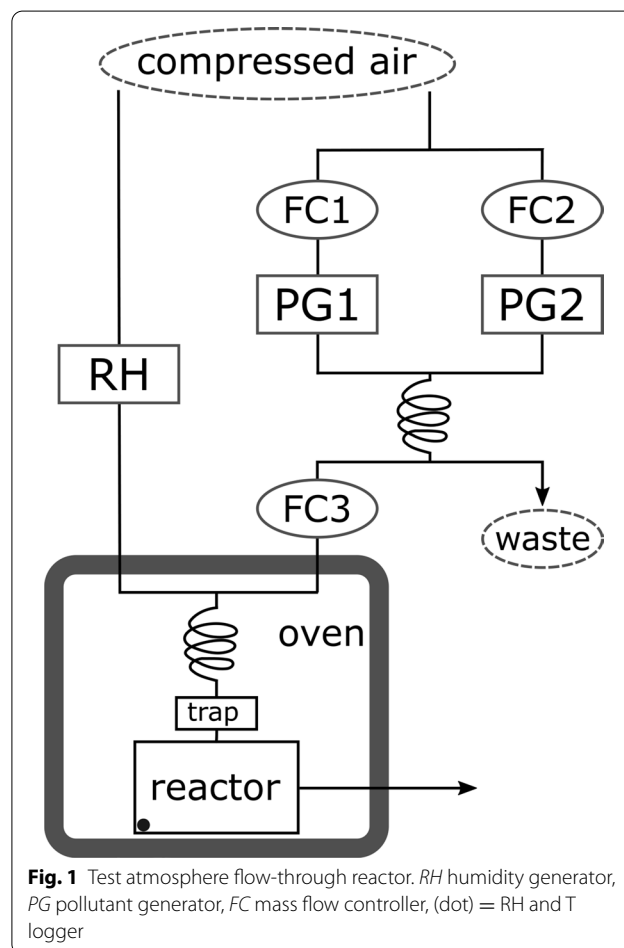
SKC UMEx 200 Passive samplers were originally intended for environmental monitoring of NO_2 and SO_2 in workplace atmosphere [40]. They consist of a polypropylene casing (i.e. a tag) covering two 2 cm × 2 cm reactive strips (or tapes), treated with TEA. The sample strip is covered by a perforated diffusion barrier and the field blank is covered with a full PP cover. The samplers are low cost and easy to use, and only require for the cover to be slid open before sampling begins. In comparison with some of the samplers discussed above, the absorption chemistry is the same, and it was assumed that the SKC UMEx samplers could be used for the determination of HCOOH and AcOH simultaneously with NO_2 and SO_2, following appropriate validation (determination of sampling rates for at least two concentration levels [10, 41] and the possible loss of analytes through reverse diffusion and storage of tags after exposure [42]). For most of the samplers, e.g. the widely used IVL samplers, separate samplers have to be purchased for the sampling of NO_2, SO_2 and organic acids (IVL samplers also sample HCl and HF, the latter is usually not a contaminant in museum environment), while the UMEx samplers are simultaneously sensitive to the exact set of compounds, that are of interest in the museum environment. In contrast to all of the samplers discussed above, UMEx samplers also include a blank strip in every sampler as a control against contamination, which reduces the cost of each sampling as no additional samplers need to be purchased as separate blanks.

Experimental

Test atmosphere

The samplers (SKC UMEx 200, SKC, UK) were exposed to test atmospheres in a flow-through reactor setup (Fig. 1) adapted from [43]. A line of compressed air (200 ml/min), used as the carrier gas, was humidified in a humidity generator (V-Gen Model 1, InstruQuest, USA). The second line was led through two pollutant generators (Dynacalibrator 150, Vici, USA; AcOH and HCOOH permeation devices with emission rates of 1000 ng/min at 60 °C, Vici AG International, Switzerland), with a combined outflow of 200 ml/min. The humidified and polluted streams of air were combined in a glass reactor positioned within a laboratory oven (ED 115, Binder, Germany). The air flows were set with three mass flow controllers (GFC17A, Aalborg, USA), while the tubing was from PTFE (Cole-Parmer, USA), with stainless steel connectors and adapters (Swagelok, USA). The temperature and humidity within the reactor were monitored via a HOBO MX2301 logger (Onset, USA).

Fig. 1 Test atmosphere flow-through reactor. *RH* humidity generator, *PG* pollutant generator, *FC* mass flow controller, (dot) = RH and T logger

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Pollutant concentration was confirmed by active sampling of 48 L of polluted air on SKC Anasorb CSC sorption tubes (229-09, SKC, UK) using OSHA ID-186SG and PV2119 methods [32, 33].

Sample analysis

After exposure, the sampling strip was removed to a glass vial and ultrasonicated in 2 ml of ultrapure water (MQ; Millipore, USA) for 20 min. The extracts were filtered through 0.45 μm filters (Chrom4, Germany) before injection into an ion chromatograph, Dionex ICS-5000 (Thermo, USA), consisting of a gradient pump, an electrochemical suppressor (Dionex AERS 500 4 mm, set to 56 mA) and a conductivity detector. A Dionex IonPac AS11-HC 4 mm analytical column (Thermo, USA) was used, with the mobile phase composed of MQ and 100 mM NaOH in MQ, 1.5 ml/min flow, 25 μl sample injection volume. Each sample was injected in duplicate.

The gradient of mobile phase composition is listed in Table 2, where A is MQ water and B is 100 mM NaOH in MQ. Before each analysis, the system was conditioned for 5 min.

The analytical method validation results are reported in Table 3. Calibration was carried out in standard water solutions (prepared from solid standards), and the linear range was estimated between ILOQ and 10 mg/L for both analytes. The instrumental limits of detection (ILOD) and quantification (ILOQ) have been calculated from calibration curves as $ILOD = 3.3 \times S/k$ and $ILOQ = 10 \times S/k$ (where S is the standard deviation of the intercept and k the calibration curve slope [44]). Resolution between the peaks was 3.6. These validation parameters show that this instrumental method is appropriate for the analysis of AcOH and HCOOH from water solutions with low concentrations, that are expected in the extracts of sampling strips after sampling in a low polluted indoor environment.

Sampling validation

The extraction efficiency was tested at three levels (5, 50 and 100 μg of each acid), with 3 repetitions each. 5 μl of methanolic solutions were pipetted directly onto the sampling strip and exposed to the laboratory atmosphere for 5 min to promote solvent evaporation. The strips were then enclosed in plastic vials for 24 h and finally moved into new vials for extraction.

Table 2 Gradient composition of the mobile phase

Time (min)	6	13	16	17	19	21
% B	5	10	40	40	5	5

B = 100 mM NaOH

Table 3 IC method validation parameters

Analyte	Retention time (min)	ILOD (μg/l)	ILOQ (μg/l)
Acetate (AcO⁻)	3.6	10	30
Formate (HCOO⁻)	4.5	37	111

The sampling rates were determined with the sampling apparatus shown in Fig. 1, set up to produce a test atmosphere at 30 °C, 50% RH and either low (0.2 ppb, corresponding to 491 μg/m³ of AcOH and 376 μg/m³ of HCOOH) or high (1 ppm, corresponding to 2457 μg/m³ of AcOH and 1883 μg/m³ of HCOOH) concentration of each pollutant. The samplers were exposed for 1, 3, 5, 7 or 10 days, with 3 samplers exposed simultaneously. The sampling rates in ml/min were calculated as the sampled mass with the blank subtracted, divided by the product of sampling time and the sampled concentration, averaged over all experiments.

The possibility of loss of analytes through reverse diffusion was investigated in two experiments. After the samplers were exposed for 24 h to the test atmosphere with low pollutant concentration, they were exposed to a clean atmosphere, continuously purged with N_2 (99,999%, Messer, Germany) for 24 h, two samplers at 0% RH and two at 100%.

The effects of storage after exposure were examined by exposing three pairs of samplers to the test atmosphere with low pollutant concentration. One pair was analysed immediately, while two were kept at room temperature (22–24 °C) and two at 4 °C for 7 days before analyses.

The capacity of the samplers for AcOH and HCOOH was determined by exposing the samplers to the test atmosphere with the high concentration of pollutants for 4 weeks.

Limits of detection and quantification after 7 days of sampling were determined by analysing 5 unopened samplers (i.e. with unexposed strip), stored in aluminized pouches at 4 °C, as $LOD = 3.3 \times s$ and $LOQ = 10 \times s$, where s is the standard deviation of the measured signals for AcOH or HCOOH. These LODs and LOQs include the combined sampling and analytical method.

Field testing in a museum environment

The developed sampling method was tested at the National Museum of Slovenia. Pairs of samplers were exposed in four locations: in a display case with a silk cloak (DC, Fig. 2, left), in a storage enclosure (SE, metal drawer with objects from mixed materials, Fig. 2, right), and in the two respective spaces (display room DR, storage room SR) for 7 days. The DC (volume 0.714 m³)

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is constructed from metal, glass and PMMA and is not airtight, the materials inside the case include silk and silver thread. The DR (volume 95 m³) additionally includes various textile and wood objects, along with metal, wax, glass and paint material. The SE is a metal drawer (volume 0.0644 m³), which is a part of a larger metal cabinet, therefore it is not airtight. The materials in the drawer are mostly various plastic materials, but also include some wood, paper, textile and metal. The SR (volume 186 m³) is a mixed material storage room, which contains various plastics, textile, wood, glass and metal. Additionally, one sampler was stored unopened in a room (a field blank FB) and one was placed unopened in a freezer (a batch blank BB). The samplers were placed either horizontally with the perforated cover facing upwards, or vertically, hung on the provided clips. After sampling, the tags were enclosed into metal foil pouches and transported to the laboratory for analysis.

The analytes were identified through comparison of retention times of peaks with those in standard solutions. Each sample and blank was injected twice and the peak areas for each analyte averaged. Using calibration curves the concentrations and the masses of analytes were calculated and corrected by the gravimetric factor (molar mass ratio between the determined anion and parental compound). The value of the blank strip was subtracted from the value of the sample strip. Based on the so obtained mass m, known sampling rates v and sampling times t, the concentration of analytes in the sampled air in mass per air volume unit was calculated with Eq. (1).

$$\text{Air concentration} = \frac{m}{v \times t}. \tag{1}$$

Results and discussion

Test atmosphere pollutant concentrations validation

The concentrations of AcOH and HCOOH, as generated by the setup in Fig. 1, were checked using active sampling. At two sampling points (at combined PG output and at combined output of the two PG and the RH generator) the average concentrations corresponding to low (0.2 ppb) reactor concentrations were determined as 496 ± 66 µg/m³ of AcOH and 400 ± 95 µg/m³ of HCOOH. The deviation from the expected concentrations was < 1% and < 7% for AcOH and HCOOH respectively, which was considered acceptable.

Fig. 2 Sampling in the National Museum of Slovenia. Left: display case with a silk cloak (DC); right: storage enclosure with objects from mixed materials (SE)

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Sampling validation

Extraction efficiency

The average recovery in all the experiments was 108% for AcOH and 87% for HCOOH with no significant difference between the tested concentrations (Table 4), confirming that the extraction procedure is effective (> 85% of analytes desorb from the sorbent). In addition, the effect of filtering was also investigated, as extraction can result in particles being found in the extracts, which is undesirable for IC analysis. Based on the comparison of filtered and unfiltered solutions, filtration through a 0.45 μm Nylon filter immediately after extraction had no significant effect on analyte concentrations. The AcOH recovery values above 100% indicate that some AcOH is present in the sampling strips themselves, which could be due to its formation from TEA or due to impurities in the strip reagents. The latter seems more probable, since organic acid sampling is not the intended use of these samplers and the production is more likely to be focussed on decreasing NO_2 and SO_2 backgrounds. This result was not considered critical, since the analysis of the blank strip from the same batch (included in each tag), would compensate for this error. The parameter of extraction efficiency was not explicitly used in further calculations, as it is incorporated into the parameter of sampling rate.

Sampling rates

The masses of analytes, collected after different periods of sampling in the test atmosphere are presented in Table 5 and an example chromatogram is presented in Fig. 3. The values show that the uptake is proportional to sampling time, therefore the samplers operate in the linear uptake region [30] and their sampling rates can be assumed to

be constant. The sampling rates, based on all the experiments presented in Table 5, were therefore determined to be 16.7 ml/min for AcOH and 17.7 ml/min for HCOOH, with %RSD at 21 and 19%. These values are similar to the sampling rates for NO_2 and SO_2 reported by the manufacturer (17.3 and 15.2 ml/min respectively), which is as expected, since the same sampler geometry and reagent are used. It is also similar to the value, reported by Dremetsika et al. [9] for SKC diffusive samplers with coconut charcoal adsorbent. On the other hand, the sampling rates are much higher with radial diffusive samplers due to their geometry (see Table 1).

The sampling rates have been determined only at one temperature and relative humidity, as the same samplers have been shown to be not sensitive to T and RH changes in the range of 22–40 °C and 20–80% RH for NO_2 determination [42]. This is a possible source of error.

Loss through reverse diffusion

Reverse diffusion of passive samplers refers to the loss of analyte due to weak interactions between sorbent and analyte or due to its displacement through competitive adsorption (of water vapour or other volatiles) [45]. The term covers various physical and chemical processes, including desorption, association and diffusion. In the case of UMEx 200 samplers, exposure to either humid or dry pollutant-free atmosphere after sampling caused no significant loss of analytes from the samplers. The losses were on average 2.6% for AcOH and 3.5% for HCOOH, with no observable effect of the humidity. These results show that TEA effectively traps the investigated acids, as these do not evaporate from the sampling strip at least for 24 h.

Loss during storage

The effects of storage prior to analysis were tested by keeping exposed samplers at room temperature (22–24 °C) or at 4 °C for 7 days. At room temperature, the mass change of adsorbed HCOOH was 13% and 4.3% of AcOH. At 4 °C the mass change was only 0.4–2.9% for both analytes, indicating that the exposed samplers

Table 4 Extraction recoveries in %; in parentheses %RSD

Analyte	5 μg	50 μg	100 μg	Average
AcOH	104 (3.5)	112 (5.2)	109 (3.5)	108 (5)
HCOOH	82 (7.5)	91 (2.3)	89 (3.3)	87 (5)

Table 5 Analytes (in μg; SD in parentheses, for three replicates) collected after various periods of exposure, at two different concentrations in the test atmosphere (low = 491 μg/m³ of AcOH and 376 μg/m³ of HCOOH, high = 2457 μg/m³ of AcOH and 1883 μg/m³ of HCOOH)

Analyte	Conc. level	1 day	3 days	5 days	7 days	10 days
AcOH	Low	13 (2)	39 (6)	74 (2)	102 (13)	140 (11)
	High	48 (5)	155 (5)	267 (31)	319 (33)	458 (18)
HCOOH	Low	8 (1)	28 (5)	58 (1)	74 (5)	128 (12)
	High	38 (5)	132 (5)	239 (31)	316 (46)	465 (19)

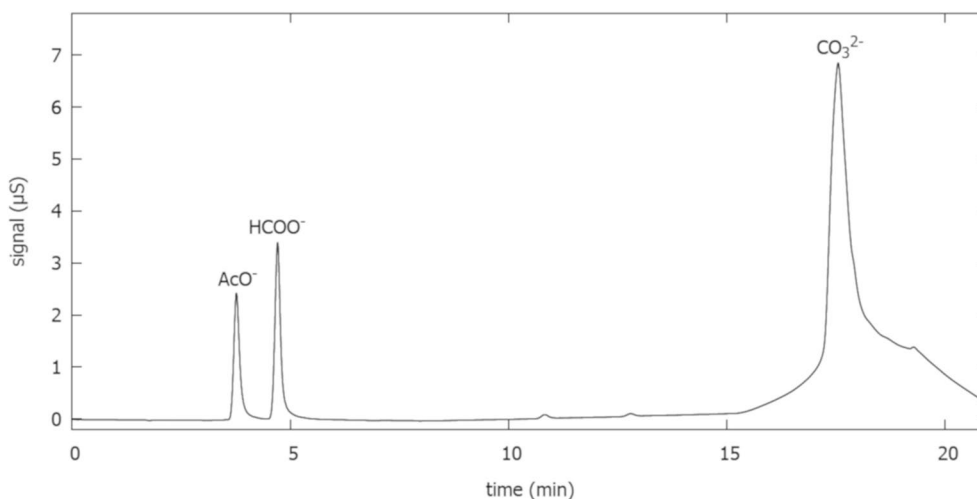Kraševec *et al. Herit Sci*   (2021) 9:19

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Fig. 3 Ion chromatogram of an extract after 7 days of sampling in the test atmosphere with low pollutant concentration (diluted 10×; CO_3^{2-} originates from mobile phase)

should be refrigerated during transport and before analysis, which is, according to the manufacturer, not necessary in the case of NO_2 and SO_2 analysis.

Capacity

The capacity of the samplers for these organic acids, defined as the amount of analyte at the upper end of the linear response region, was estimated to be 500 µg of AcOH and 800 µg of HCOOH, since after 4 weeks of exposure to the high test concentration (2457 µg/m^3 of AcOH and 1883 µg/m^3 of HCOOH) the response was no longer within the linear uptake region. For a 7 days sampling period, this corresponds to air concentrations of 3 mg/m^3 of AcOH and 4.5 mg/m^3 of HCOOH. Therefore, at higher air concentrations, shorter sampling times would have to be used to obtain exact concentration values.

Limits of detection and quantification

LOD and LOQ for AcOH in indoor air after 7 days of exposure were determined experimentally as 2.1 and 6.2 µg/m^3. For HCOOH, these values were 1.9 and 5.6 µg/m^3, respectively. In addition, LODs and LOQ for both acids were also calculated from the ILODs and ILOQs and sampling rates for each compound. For

AcOH, 0.1 and 0.4 µg/m^3 were calculated as LOD and LOQ, respectively, while for HCOOH, these values were 0.4 and 1.2 µg/m^3. The calculated values were 4.6 to 21 times lower than those, obtained experimentally, and are not achievable practically. This underlines the importance of determining crucial parameters experimentally, not only theoretically.

The experimentally determined LODs are lower than for Palmes tubes and SPME, lower or comparable to those of other diffusive samplers, but expectedly higher than those, obtained with Radiello (see Tables 1, 6). LODs of both investigated acids, achieved with UMEx 200 samplers, are low enough to enable air quality monitoring of museum environments, as they are below even the lowest of the suggested concentration limits for AcOH and HCOOH (12.5 and 9.5 µg/m^3, respectively [21]). The measurements at about the suggested limits are therefore possible.

Field testing in a museum environment

In the museum environment, acetic and formic acid were determined in all the collected samples (Table 7) and in all cases acetic acid was observed in higher concentrations than formic acid. In comparison to the literature [4, 13, 14, 17], these values are at the low end for all locations and in no case exceed the recommended limit values.

Table 6 UMEx 200 sampler properties (geometry, sampling reagent, sampling rate and LOD for 7-days exposure)

Name	Geometry	Reagent	Sampling rate (ml/min)	LOD (µg/m^3)
UMEx 200 passive sampler	Tag, $l = 8.6$ cm, $w = 2.8$ cm, $h = 0.9$ cm	TEA	AcOH: 16.7, HCOOH: 17.7	AcOH: 2.1, HCOOH: 1.9

$l = $ length, $h = $ height, $w = $ width

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This was expected, as the measurements were performed in a new museum building, purpose-built less than 15 years ago, with climate control and filtered air conditioning in both display and storage areas. In addition to acetic and formic acid, NO_2 and SO_2 were analysed using the same samplers (Fig. 4) and were determined in the ranges of 5.8–29 and 2.3–6.3 μg/m^3, respectively, which is less than their average outdoor concentrations at the time of sampling.

In the case of DC and DR concentrations, it appears that most of the acids observed in the display case originate from the exhibition space environment. Possible sources could be the wood flooring material or other objects displayed in this space. The display case thus offers some protection to the silk object, given that the organic acid concentrations are lower than in the room.

Emission from materials within the drawer (SE) is likely the cause for the increased observed concentrations of both acids in comparison to SR. The enclosure has a small volume and therefore the pollutants inside could be more concentrated. The small volume could also lead to the samplers influencing the concentration of pollutants, which is one of the main problems for passive samplers

in general. In cases where the enclosure air exchange rate or the pollutant emission rates are much lower than the sampler uptake rates, the determined concentrations can underestimate the actual concentrations. While the air exchange rates for both enclosures were not known, neither was designed to be airtight and this effect was estimated to be small. Also, air velocity was measured in the drawer and at the location of the samplers in the flow-through system (used for validation) and was found to be comparable in both locations (< 0.03 m/s), further confirming that the sampler validation is applicable also in the case of this enclosure.

Uncertainty estimation

In the controlled test atmosphere, sampling was carried out in triplicate and the uncertainty (expressed as %RSD) of the collected analytes ranged from 2.1–16% (average 9%) for AcOH and 2.5–17% (average 10%) for HCOOH. This is acceptable as it is < 25%, a requirement for diffusion samplers in [15] and comparable to the values, reported for NO_2 sampling with these samplers [42].

In the museum atmosphere, the sampling was performed in duplicate and the %RSD ranged 7.7–40% (average 23%) for AcOH and 1.5–50% (average 16%) for HCOOH. These values are higher than for sampling in the test atmosphere, which could be due to the variations of air velocity, temperature or humidity in the real museum environment (these conditions were all fixed in the test atmosphere), but are on average still satisfying the < 25% requirement. The highest observed deviations in the case of samplers in the museum could also be a consequence of their horizontal orientation during sampling, which could lead to deposition of particulate
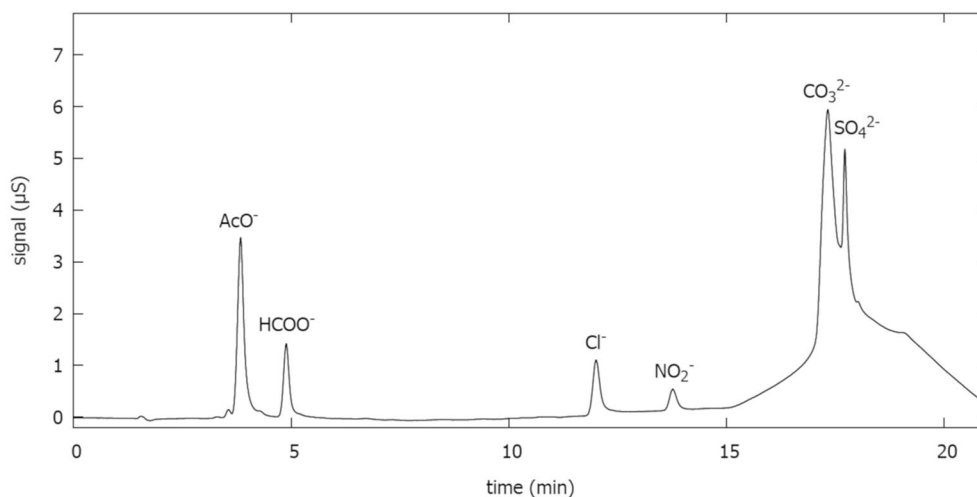
Table 7 Concentrations of organic acids and NO₂ in the indoor environments of the National Museum of Slovenia (in μg/m^3; in parentheses: SD of two replicates)

Acid	DR	DC	SR	SE
AcOH	39 (3.0)	27 (2.9)	28 (9)	54 (21)
HCOOH	9.0 (0.13)	6.1 (0.46)	2 (1.2)	8.5 (0.3)
NO₂	22.3 (0.5)	13 (6.4)	29 (2.4)	5.81 (0.02)

DR display room, *DC* display case, *SR* storage room, *SE* storage enclosure

Fig. 4 A sample ion chromatogram (SE) obtained after sampling the indoor air at the National Museum of Slovenia. The SO_4^{2-} signal, observable in this chromatogram, was quantified using a different chromatographic method, as it was not separated from the CO_3^{2-} signal in this case

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matter with a high content of the investigated analyte or to changes in diffusion rates due to deposition of particulate matter on the diffusion barrier. The %RSD values obtained in our experiments are also comparable to the values obtained by similar means (duplicate measurements in object enclosure) with NILU samplers by Grøntoft et al. (21% for AcOH, 19% for HCOOH) [28, 37, 38].

Conclusions

SKC UMEx 200 passive samplers were partially validated for sampling of acetic and formic acids in indoor environment and can be proposed for air quality monitoring in the heritage sector. Sampling can be can be carried out by non-technical personnel in these institutions, however, ion chromatography is needed for subsequent analysis. In addition, NO_2 and SO_2 can be sampled at the same time, thereby reducing the total costs of pollution monitoring.

The presented sampling method is comparable to other methods in current use with respect to the sampling rates and LODs. For UMEx 200 samplers, the sampling rates for acetic and formic acids have been determined as 16.7 ml/min and 17.7 ml/min, respectively. This is comparable to the rates published for sampling of NO_2 and SO_2 with these samplers.

The detection limits were determined as $2.1\,\mu g/m^3$ for AcOH and $1.9\,\mu g/m^3$, which is suitable for monitoring of less polluted indoor environments. This was demonstrated in a case study at the National Museum of Slovenia, where low concentrations (2–$54\,\mu g/m^3$) of both compounds were determined in a display case, a storage drawer and the museum spaces with these environments.

The methods are currently being used in a survey of pollutants in environments in a number of heritage institutions, which we plan to report on in the future.

Abbreviations

AcOH: Acetic acid; CH_3COOH: Acetic acid; DC: Display case; DR: Display room; GC-MS: Gas chromatography coupled with mass spectrometry; HCOOH: Formic acid; HPLC-MS: High-performance liquid chromatography coupled with mass spectrometry; IC: Ion chromatography; ILOD: Instrumental limit of detection; ILOQ: Instrumental limit of quantification; LOD: Limit of detection; LOQ: Limit of quantification; MDF: Medium density fibreboard; MQ: Ultrapure water; PA: Polyacrylate; PG: Pollutant generator; PMMA: Poly(methyl methacrylate); PP: Polypropylene; RH: Relative humidity; %RSD: Relative standard deviation; SD: Standard deviation; SE: Storage enclosure; SPME: Solid-phase microextraction; SR: Storage room; T: Temperature; TEA: Triethanolamine.

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Author's contributions

IK designed the analysis, processed experimental data and drafted the manuscript. EM carried out the sampling at the museum and contributed to the interpretation of data. MS contributed to the interpretation of data and manuscript writing. IKC conceived the investigation, supervised the work and provided critical revision of the manuscript. All authors read and approved the final manuscript.

Availability of data and materials

The data generated during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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