Measurement of Volatile Organic Compounds Emissions from Cellulose Acetate by Thin-Film Solid-Phase Microextraction Coupled with Gas Chromatography–Mass Spectrometry

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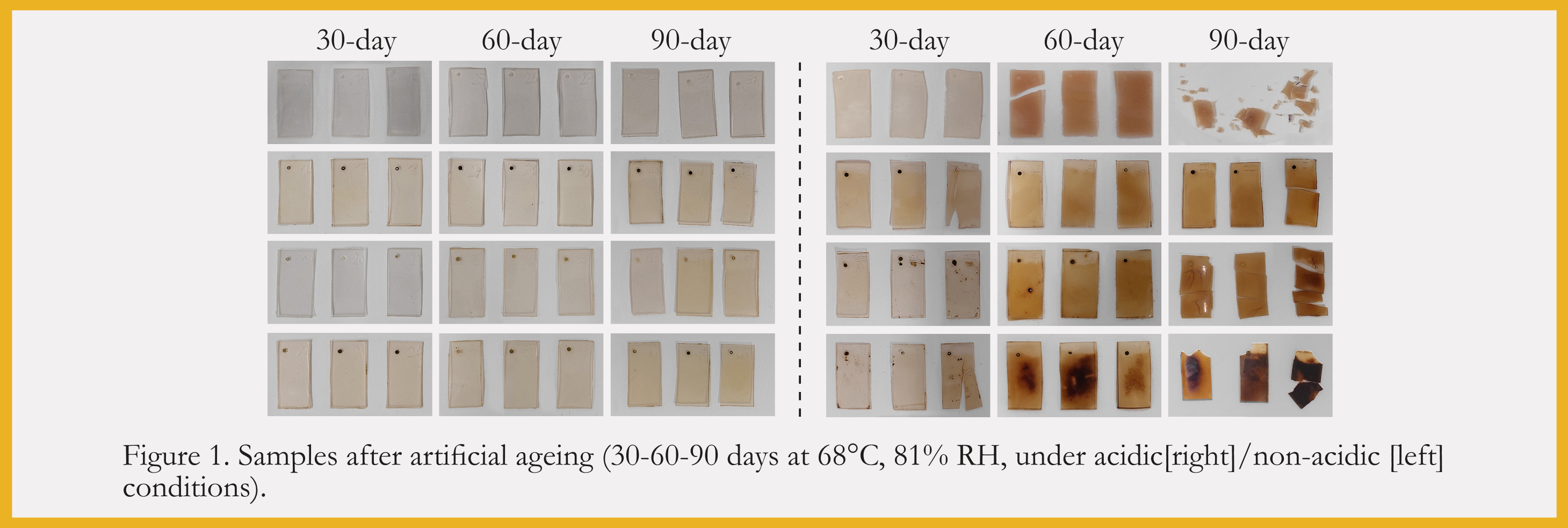[3]WMG, University of Warwick, Coventry, CV4 7AL, UK

INTRODUCTION

Plastics found in heritage collections—especially those made from cellulose acetate (CA)— are highly vulnerable to environmental degradation, such as **moisture, heat, light, and pollutants**[1].

Common degradation processes include:
• Deacetylation (loss of acetyl groups)
• Plasticiser migration (loss of flexibility)
• Polymer chain scission (breakdown of molecular structure)
This degradation is **autocatalytic**, meaning it accelerates itself over time, leading to **irreversible chemical changes**. These changes threaten both the **physical integrity** and **historical value** of the CA objects and those nearby.

Current methods for analysing volatile organic compounds (VOCs) emitted by degrading CA materials can suffer from **poor sensitivity**, **limited repeatability**, and their ability to accomodate **objects of varying sizes**. Heritage professionals need improved **non-distructive and non-invasive methods** capable of detecting **early-stage deterioration** across collections.

Figure 1. Samples after artificial ageing (30-60-90 days at 68°C, 81% RH, under acidic[right]/non-acidic [left] conditions).

OBJECTIVES

This study investigates the use of **Thin Film Solid Phase Micro-Extraction** (TF-SPME) with **Gas Chromatography Mass Spectrometry** as a promising and under-explore **alternative of regular SPME**[2].

Key advantages include: • **High sensitivity** due to increased surface area (190 mm²) and phase volume (9 uL) • **Rapid VOCs extraction** • **Cost-effective reusability** (up to 100 extractions) • Non-destructive **headspace sampling**.

The **Hydrophilic Lipophilic Balanced/ Polydimethylsiloxane** (PDMS-HLB) coating enables detection of polar and non-polar compounds, including unknown VOCs and semi-VOCs (Table 1).

Application: TF-SPME technique was applied to artificially aged CA samples, with varying surface compositions[1], to quantify **acetic acid (AcOH)** most recurrent key indicator of CA degradation, and **assess sensitivity** for non-destructive, early-stage CA degradation monitoring.

METHODOLOGY

Sampling Method

Sample set: Four plasticized CA types (CA-1 through CA-4) with three replicates each (Figure 1).

Aging conditions: 68°C, 81% RH, with acidic/non-acidic vapours to accelerate degradation for 30-60-90 days.

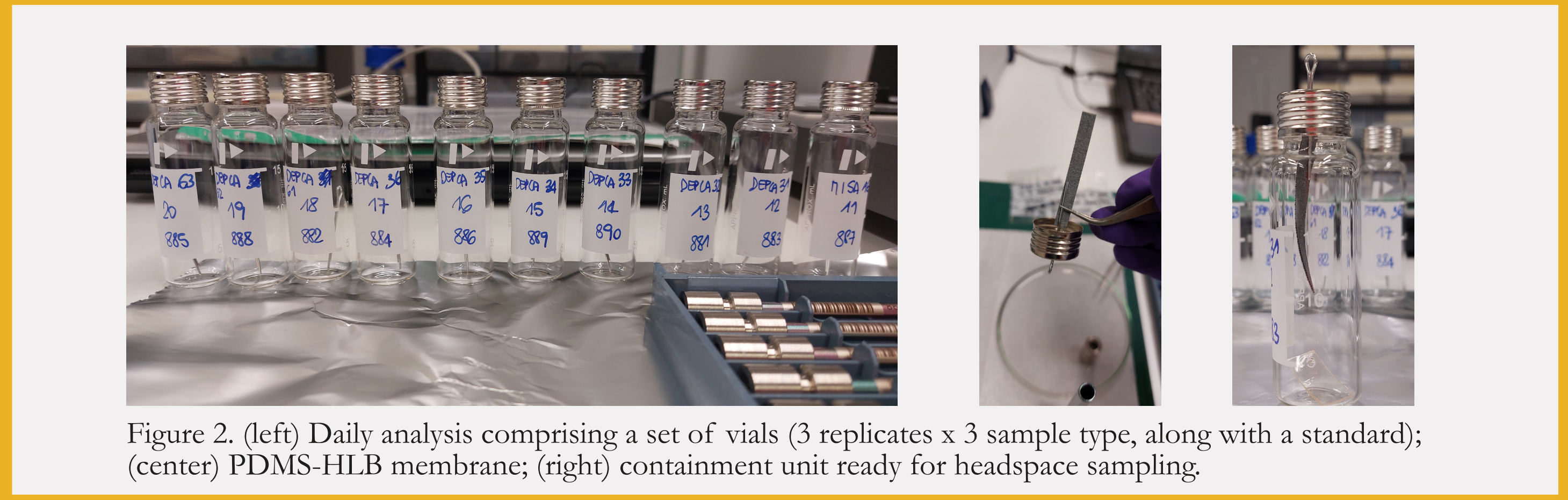Sample size: 107 ± 25 mg

Sampling time: **60 min at 60 °C**[2]

Vial: 20 mL headspace vial with headspace cup (N9306242, Perkin Elmer)

Extraction:
• TF-SPME PDMS-HLB membranes (C-TF-PHLB, Markes International)
• Suspended using stainless-steel split pin (no contact with sample) (Figure 2)
• Transferred to sorbent tubes (C3-CAXX-5304, Markes International)

Data Normalisation & Quantification

Peak areas were normalized to an **external standard** (MISA 48133, Merck), performed on the day of analysis, to ensure consistent acetic acid quantification and account for analytical variability[2].

Figure 2. (left) Daily analysis comprising a set of vials (3 replicates x 3 sample type, along with a standard); (center) PDMS-HLB membrane; (right) containment unit ready for headspace sampling.

RESULTS

1. Detection capability: Method reliably detects AcOH off-gassing from tested CA samples with strong statistical discrimination ($R^2 > 92\%$, $p < 0.0001$) [One-way ANOVA] (Figure 3).

2. Comparative analysis: Perfect inverse correlation ($r \approx -1.0$) between datasets (e.g., timepoints) **confirms detection of identical chemical phenomena** [post-hoc Tukey analysis].

3. Method precision: Equivalent analytical quality between acidic (mean RSD= 24% ± 13%) and non-acidic data set (RSD= 37% ± 35%), meeting only partially **acceptable** precision standards [t-test, p= 0.17] (Figure 4). Wide precision variability reflects matrix-dependent chromatographic challenges potentially associated with the acetic acid peak shape.

4. Strength of analytical validation: MISA standard shows **excellent retention time stability** (0.08% RSD) and **acceptable peak area precision** (20% RSD) across inter- and intra-day measurements[2] [Descriptive statistic].

Entry	Retention time (min)	Main m/z value	Assignment
1	6.41	81	Photodieldrin
2	11.25	58	Acetone
3	12.04	79	Methanesulfonyl Chloride
4	13.07	75	Sinalol-trimethyl
5	16.70	60	Acetic acid
6	18.77	75	Acetic acid, TMS derivative
7	24.2	207	Cyclotrisiloxane, hexamethyl-
8	29.45	133	Ethylbenzoic acid
9	30.46	95	Furfural
10	31.24	281	Cyclotretrasiloxane, octamethyl-
11	36.78	267	2,4-Dihydroxylbenzaldehyde, 2TMS derivative
12	42.84	149	Diethyl phthalate
13	44.62	95	Camphor
14	49.31	135	Phenol
15	59.91	163	3,4-Dimethylbenzoic acid, TBDMS derivative

Table 1. Chemical compound assignment to numbered peaks, retention times and main m/z values.

Figure 3. Mean acetic acid peak area (n=3 replicates) with standard deviation error bars across a 90-day aging period under different environmental conditions (68°C, 81% RH, acidic [below] and non-acidic [above] conditions).

Figure 4. Precision performance matrix showing RSD% for peak area ratio measurements across AcOH and non-AcOH conditions over 90 days (values arbitrary adjusted according to ASTM D6196/ EPA 8260 guidelines).

CONCLUSION

The results suggest that **TF-SPME-GC/MS provides accurate early detection of acetic acid off-gassing**. These emissions, whether originating from the object itself or its immediate environment, can serve as early indicators of chemical instability within collections.

Building on this approach, future work could explore the use of TF-SPME in Tedlar® **bags**[2] or **contact sampling**[3] methods for broader applicability to heritage objects, particularly in scenarios where objects accomodation is limited.

REFERENCES

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