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# Non-destructive mass spectrometry of historical poly(vinyl chloride) object surfaces with swab analysis

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Tjaša Rijavec<sup>1,2</sup> , Leah Bright<sup>3</sup>, Jessica Walthew<sup>4</sup>, Irena Kralj Cigić<sup>1</sup>, Matija Strlič<sup>1</sup> & G. Asher Newsome<sup>2</sup>

A non-destructive dry swabbing sampling method was developed and validated to characterize surface exudates on heritage poly(vinyl chloride) (PVC) objects that show evidence of degradation. Coupled with non-proximate desorption photoionization high-resolution mass spectrometry (NPDPI-MS), this approach enabled direct untargeted analysis of swabs. The methodology was applied at the Smithsonian American Art Museum (Washington DC, USA) and the Cooper Hewitt, Smithsonian Design Museum (New York, USA), identifying organic compounds such as plasticizers, fire retardants, and lubricants. NPDPI-MS distinguished chemical variations within an art series and revealed differences influenced by age and handling. The efficiency of direct swab analysis was compared to direct object analysis, and the correlation between surface and bulk plasticizer content was investigated. Designed for museum accessibility, this method requires no advanced equipment for sampling while providing comprehensive chemical insights into surface exudates.

Plasticized poly(vinyl chloride) (PVC) is found in heritage collections in the form of unique artwork (sculptures and installations) and as design objects (furniture, clothes, inflatables, toys, etc.). Such versatility is achieved because the material's properties can be engineered by incorporating additives, such as plasticizers, lubricants, heat stabilizers, antioxidants, fillers, fire retardants, etc. In flexible PVC objects, plasticizers constitute major parts of the material (up to 50% by mass). Unfortunately, PVC has been recognized as one of the materials prone to degradation, evident as yellowing due to chemical degradation<sup>1</sup> or as surface exudation due to additive migration or phase separation. Surface exudates may present as liquid deposits as 'sweating'/'bleeding', or as solid deposits as 'crystalline blooming', 'powdery' deposits, or 'efflorescence'<sup>2–4</sup>. The presence of visible surface exudates has been connected with phase-separation due to low solubility, in contrast to diffusion-evaporation controlled plasticizer migration, not leading to visible surface accumulation<sup>5–7</sup>. Exudation of additives can cause 'sticky' and 'tacky' surfaces that may trap dust and other pollutants, posing an advanced conservation challenge. Surface exudates on heritage PVC objects have not been systematically studied, only reported as case-studies<sup>8,9</sup>. Phthalate plasticizers are known to have been used<sup>10–12</sup>, such as di(2-ethylhexyl phthalate) (DEHP), dibutyl phthalate (DBP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), but non-phthalate plasticizers such as dioctyl terephthalate (DOTP) and diisononyl 1,2-

cyclohexane dicarboxylate (DINCH) can also be found in historical objects. Some objects contain mixtures of plasticizers, making characterization complex.

There are currently no standard methods for the chemical characterization of surface exudates on plastic materials. Optical microscopy can provide non-specific visual information about surface soiling but lacks chemical specificity<sup>3</sup>. Techniques such as Raman microscopy and FTIR can detect phthalates on the surface<sup>13</sup>, however, they are limited in their ability to unambiguously identify compounds, especially in complex compositions. Similarly, scanning-electron microscopy (SEM) and atomic force microscopy (AFM) can provide morphological data at the microscale<sup>14</sup> but do not offer molecular identification of unknown exudates.

The use of swabs is common among analytical methodologies. Polyester swabs moistened with water were used for quantitative analysis of ions on the surface of unstable historic glass<sup>15</sup>. Moistened cotton swabs were used for identifying cellulose nitrate objects prone to degradation based on the presence of organic acids<sup>16</sup>. Dry swabs and swabs wetted with hexane have also been used as support to detect pesticides in heritage collections<sup>17,18</sup>. Swabbing analysis is frequently used in the pharmaceutical industry<sup>19</sup>, forensic<sup>20–23</sup>, and food safety<sup>24–26</sup> for screening. Advances have been made with real-time ambient sampling and ionization mass spectrometry techniques, such as DART<sup>27–29</sup>, DESI<sup>30</sup>, and ion-mobility spectrometry<sup>31,32</sup>, that enable improved detection capabilities on direct swab analysis. In contrast,

<sup>1</sup>Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia. <sup>2</sup>Museum Conservation Institute, Smithsonian Institution, Suitland, MD, USA. <sup>3</sup>Smithsonian American Art Museum, Washington, DC, USA. <sup>4</sup>Cooper Hewitt, Smithsonian Design Museum, New York, NY, USA.

e-mail: [tjasa.rjavec@fkk.uni-lj.si](mailto:tjasa.rjavec@fkk.uni-lj.si)

Newsome and Martin have presented non-proximate desorption photoionization mass spectrometry (NPDPI-MS), a novel system for studying intact objects that alleviates the dimensional constraints of other direct analysis techniques<sup>33</sup>. The benefits of NPDPI-MS in combination with dry swabbing have not yet been exploited in the heritage science field.

The present study develops a non-destructive method for characterizing unknown exudates on heritage PVC with non-proximate desorption photoionization (NPDPI) with high resolution mass spectrometry (MS) for untargeted analysis and implements the method in a pilot study at the Smithsonian American Art Museum (SAAM) and the Cooper Hewitt, Smithsonian Design Museum (CHSDM). The results have been validated against direct object analysis by NPDPI-MS. Secondly, we investigate the correlation of bulk plasticizer content with the surface concentration sampled with dry swabbing and determined with targeted GC-MS analysis after liquid extraction<sup>7</sup>. The swabbing method was designed for working directly with cultural heritage objects, prioritizing a non-destructive, low-tech, and accessible approach by sampling directly with dry swabs<sup>7</sup>.

## Methods

No prior preparation of the investigated objects was required before sampling by swabbing. The swabbing was performed in each museum's storage. The objects analysed at the Smithsonian American Art Museum (SAAM) and the Cooper Hewitt, Smithsonian Design Museum (CHSDM) are presented in Table 1.

### Swabbing

The swabbing methodology has been published previously<sup>7</sup>. Briefly, Texwipe swabs (TX714A) made of knitted lint-free polyester (poly(ethylene terephthalate), PET) with a low total organic content residue and no adhesives were selected for sampling by swabbing. A stencil the size of 5 × 5-cm, made from acid-free paper, was used to define the swabbing surface of an object. A dry swab was used to wipe across the surface from left to right and back four times on one side of the swab while moving downwards, before flipping the swab and using it to wipe the same surface again perpendicular to the first direction (Supplementary Fig. S1). Each object was swabbed in four replicates, each time on a new surface. One replicate was used for NPDPI with an Orbitrap for untargeted analysis and identification of surface compounds, and three replicates were used for targeted quantitative analysis with GC-MS. The swabs intended for NPDPI-MS were stored in a 50 mL centrifuge tube, suspended with cardboard holders. The swabs for targeted quantitative analysis with GC-MS were stored by clipping the head into a glass scintillation vial. It was shown that the swabs remain stable for at least one week between sampling and analysis<sup>7</sup>.

### NPDPI-MS for untargeted analysis

25.7 × 12.7 mm swab heads were analysed by NPDPI-MS<sup>33</sup> to take advantage of the wide access non-proximate to the mass spectrometer inlet for convenient sample mounting. The swab was positioned less than 1 mm below a stationary gas jet probe. The swab head was exposed for 2.0 s to nitrogen at 200 °C flowing 1.0 L/min. Analytes desorbed into the gas phase were pulled into a 2 m long, 195 °C transfer tube along with room air at 4.8 L/min, mixed with gas-phase anisole from an in-line permeation tube<sup>34</sup>, and ionized with a krypton vacuum ultraviolet source (Syagen Technology, Tustin, CA). Analyte ions were analyzed with an Orbitrap Elite (Thermo Scientific, Waltham, MA, USA) scanning  $m/z$  120–600 at 30k resolving power. For MS<sup>n</sup> experiments different collision voltages were used for collision induced dissociation (CID) to obtain information from fragmentation.

### GC-MS analysis of swabs

GC-MS analyses were performed on an Agilent 7890B gas chromatograph with a 5977B mass spectrometer with electron ionization. A constant flow of helium at 1 mL/min was used. The inlet and the transfer line were held at 300 °C. The ion source temperature was set at 250 °C and the quadrupoles at

150 °C. Chromatographic separations were performed on an Agilent capillary column HP-5MS (30 m, 0.25 mm i.d., 0.25 μm film thickness). The temperature gradient was: 50 °C for 2 min, 50 °C/min until 260 °C and 8 °C/min until 300 °C and maintaining the final temperature for 2 min. The solvent delay was 3 min. Selected ion monitoring (SIM) of qualitative and quantitative ions characteristic for DEHP and DOTP ( $m/z$  149, 167, 261, 279) were monitored with a dwell time of 50 ms for each ion<sup>7</sup>.

The analytes were extracted for GC-MS analysis by clipping the head of a swab into a 20 mL glass scintillation vial and adding 6 mL of hexane. The vial was capped and shaken for 25 min. The extract was filtered through a 0.45-μm nylon filter before analysis<sup>7</sup>.

Calibration for determining the surface plasticizer content was performed on glass panels as an inert non-absorbent surface. A known amount of DEHP and DOTP was evenly applied to a defined 5 × 5 cm<sup>2</sup> glass surface using a pipette. A calibration curve was carried out in a low-concentration zone from 0.2 mg/m<sup>2</sup> to 4 mg/m<sup>2</sup> and in a high-concentration zone from 4 mg/m<sup>2</sup> to 40 mg/m<sup>2</sup>, each level in four replicates. The average was used for quantitation<sup>7</sup>.

### Direct object analysis by NPDPI-MS

The methodology was as described in the 'NPDPI-MS for untargeted analysis' with a change that the museum objects were positioned ~1 mm below a stationary gas jet probe and exposed to 2.0 s of nitrogen heated to 140 °C.

## Results

### Chemical composition of surface exudates at SAAM and CHSDM

The chemical composition of surface exudates on historical PVC objects was determined from untargeted analysis with NPDPI-MS<sup>33,35</sup>. The method was first validated by analysing a collection of well-characterised reference samples with no historical value<sup>12</sup> (Table 2). Then it was deployed to determine the surface composition of heritage PVC objects at the Smithsonian American Art Museum and the Cooper Hewitt, Smithsonian Design Museum (Fig. 1, Tables 3 and 4).

The surfaces of 27 reference PVC objects were swabbed in a 25 cm<sup>2</sup> area. 24/27 objects had no visible surface exudates, while the surface of three objects exhibited sweating in an even layer (PVCT) or as droplets (PVCV and PVCV). The analytes were thermally desorbed from the swab by heated nitrogen, pulled into the inlet tube (Fig. 1, right), mixed with anisole as a dopant and ionized with a UV source before being analyzed with a high-resolution mass spectrometer.

NPDPI-MS produced signal from protonated molecules  $[M + H]^+$  along with some fragment ions. The analysis of blank swabs showed the presence of ions characteristic for poly(ethylene glycol) (PEG), recognized as a pattern with a mass difference of 44 mass units<sup>36</sup>. In addition, ions  $m/z$  394.352,  $m/z$  149.023,  $m/z$  279.159,  $m/z$  391.284 were detected from the blank swab (Supplementary Fig. S2). The swab heads are made of poly(ethylene terephthalate) (PET), but no ions characteristic for it (apart from the non-specific  $m/z$  149) were detected<sup>37</sup>. Ion  $m/z$  394.352 was characteristic for the swab, while  $m/z$  149.023,  $m/z$  279.159,  $m/z$  391.284 are characteristic ions for di(2-ethylhexyl) phthalate (DEHP) and dioctyl terephthalate (DOTP). The criteria for confirming the presence of DEHP and DOTP was thus a more than tenfold increase from the blank levels. Eighteen of the objects' mass spectra were simple in composition, consisting of an intense  $m/z$  391.281,  $m/z$  279.159, and  $m/z$  149.023 characteristic for DEHP or DOTP plasticizers. These three ions were detected on all the investigated reference objects' surfaces. DOTP is a structural isomer of DEHP, making it challenging to differentiate between the two compounds without chromatography. Additionally, diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) and diisononyl cyclohexane-1,2-dicarboxylate (DINCH) were detected on the surfaces of certain reference samples, which can be used as a main plasticizing compound or as part of a plasticizing mixture<sup>12</sup>. The identification of compounds in Tables 3 and 4 was supported by MS<sup>n</sup> experiments and the fragmentation structures are presented in Supplementary Fig. S3.

**Table 1 | The information about the analysed objects at the SAAM and CHSDM collections**

Museum ID, Museum	Artist, Title	Date	Description	Swabbing location
1992.61, SAAM	Glen Kaufman, <i>The Knights</i>	1976	vinyl and Plexiglas, Smithsonian American Art Museum, Gift of the artist	The bottom strands of (i) a yellow and (ii) a black piece were swabbed.
1976.48.8, SAAM	Clarence Schmidt, <i>Untitled</i>	1966–1971	One of a Group of Distorted Dolls, molded and painted plastic, 22 1/4 x 10 3/4 x 5 in. (56.5 x 27.3 x 12.6 cm), Smithsonian American Art Museum, Gift of William C. Lipke	Cheeks of the doll were swabbed.
2020.44.1, SAAM	Alejandro Diaz, <i>I (Heart) Cuba</i>	2003	plastic beach ball, overall: 6 3/4 in. x 14 1/2 in. x 1 in. [uninflated] (17.1 x 36.8 x 2.5 cm), Smithsonian American Art Museum, Museum purchase through the Patricia Tobacco Forrester Endowment. © 2003, Alejandro Diaz.	The red part of the ball was swabbed.
1985.82.2, SAAM	William King, <i>Any Questions?</i>	1985	vinyl sewn over metal armature, 91 3/8 x 52 1/2 x 21 1/8 in. (232.2 x 133.4 x 53.6 cm.), Smithsonian American Art Museum, Gift of the Sara Roby Foundation	The back white part of the sculpture was swabbed.
1971.82.5A, SAAM	Duane Iselin, <i>Ottoman</i>	1971	vinyl and polyurethane foam, 13 3/4 x 18 1/2 x 23 1/2 in. (34.9 x 47.0 x 59.7 cm), Smithsonian American Art Museum, Gift of Mobi Corporation	The top of the ottoman was swabbed.
1971.82.6, SAAM	Duane Iselin, <i>Bench</i>	1971	vinyl and polyurethane foam, 15 x 47 1/2 x 21 1/2 in. (38.1 x 120.6 x 54.6 cm.), Smithsonian American Art Museum, Gift of Mobi Corporation	The side of the bench was swabbed.
2012.36, SAAM	Margarita Cabrera, <i>Black and Grey Toaster</i>	2011	vinyl, copper wire and thread, 7 1/4 x 10 1/2 x 7 1/8 in. (18.4 x 26.7 x 18.1 cm), Smithsonian American Art Museum, Museum purchase through the Frank K. Ribelin Endowment, © 2011, Margarita Cabrera	The side of the black toaster was swabbed.
2012.35.1, SAAM	Margarita Cabrera, <i>Brown Blender</i>	2011	vinyl, copper wire and thread, 14 1/4 x 6 1/2 x 9 3/8 in. (36.3 x 16.5 x 23.9 cm), Smithsonian American Art Museum, Museum purchase through the Luisita L. and Franz H. Denghaussen Endowment	The side of the pitcher was swabbed.
(i) 1971-23-1-B, CHSDM and (ii) 2019-29-20, CHSDM	Co-Designer: Carla Scolari, Donato D'Urbino, Paolo Lomazzi, Jonathan de Pas, "Blow" Armchair	(i) 1971 and (ii) 1980-2010	Double-seamed pvc plastic. Manufactured by Zanotta S.p.A. (Italy)	(i) 1971-23-1-B: the cushion was swabbed. (ii) 2019-29-20: the cushion was swabbed
1969-165-1021, CHSDM	Designed by Alexander Hayden Girard, <i>Textile Sample, HM Naugahyde</i>	1957-1960	Produced by Herman Miller Furniture Company (United States); vinyl-coated cotton "naugahyde"; Warp: 12 in. Weft: 12 in.; Gift of Alexander H. Girard	Page n. 10 (white) was analysed.
(i) 2001-8-1-A, CHSDM and (ii) 2001-8-1-D, CHSDM	Designed by Gary Shigeru Natsume, <i>Bound Packet Computing Computer Prototype</i>	1997	foam, acrylic, plastic (abs), steel, aluminum, vinyl, automotive paint. Cranbrook Academy of Art, USA	Parts 'A' (strap of the computer casing) and 'D' (inner folder) were analysed.
1991-47-2, CHSDM	Designed by William Katavolos, Ross Littell, Douglas Kelley, <i>T Chair Side Chair</i>	1952	Manufactured by Laverne (United States); USA; steel, plastic; Overall: 80 x 54.3 x 61 cm (31 1/2 x 21 3/8 x 24 in.); Museum purchase from Decorative Arts Association Acquisition Fund	Back part of the backrest was swabbed.
1995-152, CHSDM	<i>Sample Book, Blue River Handprints Vol. 1</i>	1971	Manufactured by Blue River Handprints; USA; screen-printed vinyl, mylar; 46 x 36 x 4.5 cm (18 1/8 x 14 3/16 x 1 3/4 in.); Transfer from the Renwick Gallery, Washington D.C.	Page n. 7 ('New shoes', white area) was swabbed.
1998-75-180, CHSDM	Designed by John Rombola, <i>Sidewall, Alice in Wonderland</i>	1968	Manufactured by Piazza Prints Inc. (United States); USA; screen-printed vinyl; H x W x D: 77.8 x 74.5 cm (30 5/8 x 29 5/16 in.); Gift of The Museum at The Fashion Institute of Technology	White area was swabbed.
1971-15-1, CHSDM	Designed by Tadao Inouye, <i>Kantan Armchair</i>	1956 (ca.)	Manufactured by Brown Jordan Company; USA; aluminum, vinyl, paint; 63 x 66 x 69 cm (24 13/16 x 26 x 27 3/16 in.)	The plastic wrapping on the left side was swabbed.
2017-51-15-A, CHSDM	GK 100 Jelly Fish Watch	1985	Manufactured by Swatch (Switzerland); molded plastic, metal; L x W x D: 22.3 x 3.4 x 0.5 cm (8 3/4 x 1 5/16 x 3/16 in.); Gift of Robert M. Greenberg	The watch armband was swabbed

**Table 2 | The results of NPDPI-MS analysis of swabbed reference PVC samples**

Object ID	<i>m/z</i>	Neutral Formula	Compound/Info
P119, P405, P412, P414, P415, P417, P422, P4B, P4C, P4D, P4E, P50, P54, PVC1, PVC2, PVC3, PVC5, PVCT	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
P177A	425.361	C <sub>26</sub> H <sub>48</sub> O <sub>4</sub>	DINCH
	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
P183	447.347	C <sub>28</sub> H <sub>46</sub> O <sub>4</sub>	DIDP
	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
	461.362	C <sub>29</sub> H <sub>48</sub> O <sub>4</sub>	decyl undecyl phthalate
P185	447.347	C <sub>28</sub> H <sub>46</sub> O <sub>4</sub>	DIDP
	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
P406	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
	234.104	C <sub>17</sub> H <sub>13</sub> O	
	447.347	C <sub>28</sub> H <sub>46</sub> O <sub>4</sub>	DIDP
P413	279.159	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	fragment from <i>m/z</i> 391
	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
P4F, PVC4	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
	447.347	C <sub>28</sub> H <sub>46</sub> O <sub>4</sub>	DIDP; trace amounts
PVC M	299.258	C <sub>18</sub> H <sub>34</sub> O <sub>3</sub>	ricinoleic acid
	313.274	C <sub>19</sub> H <sub>36</sub> O <sub>3</sub>	methyl ricinoleate
	425.362	C <sub>26</sub> H <sub>48</sub> O <sub>4</sub>	DINCH
	573.414	C <sub>35</sub> H <sub>56</sub> O <sub>6</sub>	
	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
	281.247	C <sub>18</sub> H <sub>33</sub> O <sub>2</sub>	loss of H <sub>2</sub> O from C <sub>18</sub> H <sub>34</sub> O <sub>3</sub>
PVC V	327.289	C <sub>20</sub> H <sub>38</sub> O <sub>3</sub>	
	313.273	C <sub>19</sub> H <sub>36</sub> O <sub>3</sub>	methyl ricinoleate
	311.258	C <sub>19</sub> H <sub>34</sub> O <sub>3</sub>	
	295.263	C <sub>19</sub> H <sub>34</sub> O <sub>2</sub>	loss of H <sub>2</sub> O from C <sub>19</sub> H <sub>36</sub> O <sub>3</sub>
	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP
	573.414	C <sub>35</sub> H <sub>56</sub> O <sub>6</sub>	

The ions detected for each PVC sample are listed in order of decreasing intensity detected according to the methods described. All mass spectra also included *m/z* 149.023 and *m/z* 279.159, fragments of DEHP, which were excluded from the table.

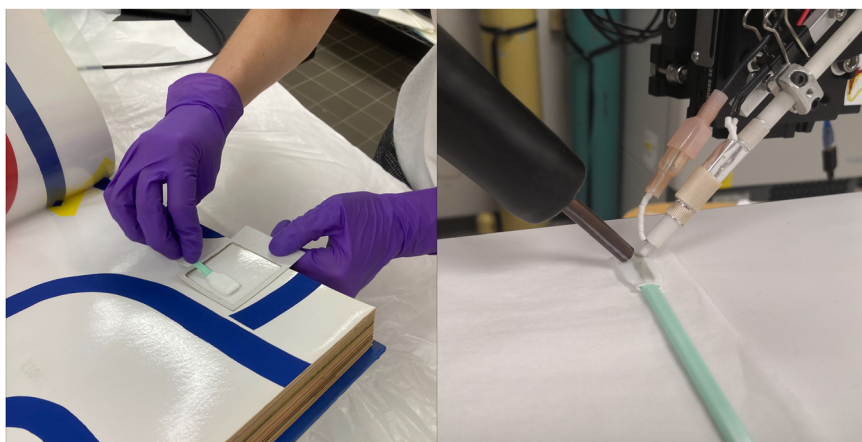
Nineteen objects from the Smithsonian American Art Museum (SAAM) and the Cooper Hewitt, Smithsonian Design Museum (CHSDM) were swabbed once according to the protocol. Phthalates (DEHP, DOTP, diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), diheptyl phthalate, benzyl butyl phthalate, nonyl octyl phthalate and heptyl octyl phthalate) represented a significant part of the compounds present on the surfaces of museum objects. In general, the swab analysis of museum objects with no visible exudates (NVE) showed a simple composition, that was a single primary phthalate plasticizer. Analysis of objects with visible surface exudates detected additional unique compounds. A viscous sticky exudate was evident on both variants (black and yellow pieces) of *The Knights* artwork by Glen Kaufman (1992.61, SAAM), with a noticeable gradient forming toward the lower portion of the artwork, attributed to gravity because the artwork was stored hung. The most abundant signal was identified as dioctyl azelate (neutral formula C<sub>25</sub>H<sub>48</sub>O<sub>4</sub>), but larger ions such as *m/z* 524.255 and *m/z* 465.380 ([M + H]<sup>+</sup> C<sub>25</sub>H<sub>52</sub>O<sub>7</sub>) were also detected. Dioctyl azelate is a non-phthalate plasticizer, that can be used as a main plasticizer or a coplasticizer.

In 2011, Margarita Cabrera created a collection of vinyl sculptures resembling household appliances, two of which were analysed during this study (2012.35.1 and 2012.36, SAAM). The surface chemistry of these sculptures notably differed: only DINP was identified on the surface of the *Blender* (2012.35.1), whereas plasticizers DEHP and dioctyl adipate were detected on the surface of the *Toaster* (2012.36, Supplementary Fig. S4). The surfaces of two Duane Iselin artworks (*Chair*, 1971.82.5A and *Bench*, 1971.82.6, SAAM) exhibited a sticky viscous exudate with a neutral molecular formula C<sub>20</sub>H<sub>40</sub>O<sub>3</sub> which was identified as 17-hydroxyicosanoic acid, the origin and purpose of which remains unknown. Compound C<sub>18</sub>H<sub>34</sub>O<sub>3</sub>, identified as hydroxyoctadecenoic acid was present on the surface of the *'Blow' Armchair* (CHSDM, 1971-23-1-B) designed by Carla Scolari, Donato D'Urbino, Paolo Lomazzi and Jonathan de Pas and manufactured by Zanotta S.p.A, in addition to plasticizers DEHP and dioctyl azelate. The oldest investigated object was the *T Chair* from 1952 (1991-47-2, CHSDM) designed by William Katavolos, Ross Littell, and Douglas Kelley and manufactured by Laverne. Remarkably, triphenyl phosphate (C<sub>18</sub>H<sub>15</sub>O<sub>4</sub>P) and drometrizole (C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O) were detected on its surface. Triphenyl phosphate is a phosphate plasticizer that imparts non-flammability to plastic materials, which is less common in PVC, because it is considered flame resistant<sup>38</sup>. Drometrizole is a UV-absorber that belongs in the group of light stabilizers, the use of which is common in PVC intended for outdoor use<sup>39</sup>. Although light stabilizers and thermal stabilizers are ubiquitous in PVC materials, this was the only case of detection, indicating that it is present in higher concentrations.

In contrast to the typical sticky exudates or sweating, the sculpture *Any Questions?* by William King (1985.82.2, SAAM) had visible crystalline blooming that was sampled with an additional swab. The mass spectrum of the analysed crystals was complex, but octadecylamine, a white solid

**Fig. 1 | Sampling by dry swabbing and analysis of the swab by NPDPI-MS enables non-destructive mass spectrometry analysis of heritage objects.**

Sampling by dry swabbing of the CHSDM object 1969-165-1021 (page n. 10), Textile Sample, HM Naugahyde; Designed by Alexander Hayden Girard (American, 1907–1993); Produced by Herman Miller Furniture Company (United States); vinyl-coated cotton “naugahyde”; Warp: 12 in. Weft: 12 in.; Gift of Alexander H. Girard; 1969-165-1021 (left). Non-proximate desorption of the analytes from the swab and transfer to the MS (right). The white probe on the right supplies heated nitrogen gas causing thermal desorption of the analytes from the swab, which are pulled into a transfer tube, photo-ionized and analysed by a mass spectrometer.



**Table 3 | Surface composition of swabbed heritage PVC objects from SAAM based on NPDPI-MS and description of observed surface exudates**

Object ID	Date	<i>m/z</i>	Neutral Formula	Compound	MS <sup>n</sup> product ions	Comments
1971.82.5A, Sticky exudate, dust, dirt	1971	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		329.305	C <sub>20</sub> H <sub>40</sub> O <sub>3</sub>	17-hydroxyicosanoic acid	329.30 → 311.29, 257.25, 257.25 → 201.19, 103.08 (MS <sup>3</sup> )	
		311.294	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	eicosenoic acid	257.25, 239.24	water loss from C <sub>20</sub> H <sub>40</sub> O <sub>3</sub>
		529.408	C <sub>30</sub> H <sub>56</sub> O <sub>7</sub>		529.41 → 511.40 ([C <sub>30</sub> H <sub>55</sub> O <sub>6</sub> ] <sup>+</sup> ), 311.29, 273.17	formula associated with plasticizers
1971.82.6, Sticky exudate, dust, dirt	1971	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		329.305	C <sub>20</sub> H <sub>40</sub> O <sub>3</sub>	17-hydroxyicosanoic acid		
		311.294	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	eicosenoic acid		water loss from C <sub>20</sub> H <sub>40</sub> O <sub>3</sub>
		529.408	C <sub>30</sub> H <sub>56</sub> O <sub>7</sub>		529.41 → 511.40 ([C <sub>30</sub> H <sub>55</sub> O <sub>6</sub> ] <sup>+</sup> ), 311.29, 273.17	formula associated with plasticizers
1976.48.8, Yellowing, discolouration (black)	1966-1971	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>		DEHP/DOTP	
		313.143	C <sub>19</sub> H <sub>20</sub> O <sub>4</sub>	benzyl butyl phthalate	313.14 → 149.02 (loss of C <sub>11</sub> H <sub>15</sub> O)	
		405.300	C <sub>25</sub> H <sub>40</sub> O <sub>4</sub>	octyl nonyl phthalate	405.30 → 279.16, 149.02	plasticizer
		377.326	C <sub>21</sub> H <sub>44</sub> O <sub>5</sub>		377.33 → 195.12 (loss of C <sub>13</sub> H <sub>26</sub> )	surfactant <sup>43</sup>
		377.270	C <sub>23</sub> H <sub>36</sub> O <sub>4</sub>	octyl heptyl phthalate		plasticizer
		521.493	C <sub>34</sub> H <sub>64</sub> O <sub>3</sub>		521.49 → 279.23 (loss of C <sub>16</sub> H <sub>34</sub> O)	
1985.82.2, Part of surface with NVE	1985	447.347	C <sub>28</sub> H <sub>46</sub> O <sub>4</sub>	DIDP	447.35 → 307.19 (loss of C <sub>10</sub> H <sub>22</sub> )	trace amounts
		391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		363.253	C <sub>22</sub> H <sub>34</sub> O <sub>4</sub>	diheptyl phthalate		
		419.316	C <sub>26</sub> H <sub>42</sub> O <sub>4</sub>	DINP		
		475.378				
1985.82.2, Part of surface with crystalline blooming, craquelure	1985	152.143	C <sub>10</sub> H <sub>17</sub> N		152.14 → 96, 135, 84	
		542.420	C <sub>34</sub> H <sub>55</sub> O <sub>4</sub> N		542.42 → 285.28 (loss of C <sub>16</sub> H <sub>19</sub> O <sub>2</sub> N), 152.14 (loss of C <sub>24</sub> H <sub>38</sub> O <sub>4</sub> )	
		270.315	C <sub>18</sub> H <sub>39</sub> N	octadecylamine <sup>a</sup>		white solid emulsifier and lubricant
		391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>		DEHP/DOTP	
		363.253	C <sub>22</sub> H <sub>34</sub> O <sub>4</sub>	diheptyl phthalate	363.25 → 247.13 (loss of C <sub>7</sub> H <sub>16</sub> O), 149.02 (loss of C <sub>14</sub> H <sub>30</sub> )	
		371.316	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	dioctyl adipate	371.32 → 259.19, 129.05	
1992.61, (black knight) Sticky exudate	1976	413.363	C <sub>25</sub> H <sub>48</sub> O <sub>4</sub>	dioctyl azelate	413.36 → 301.24, 171.10	
		441.393	C <sub>27</sub> H <sub>52</sub> O <sub>4</sub>	dioctyl undecanedioate	441.39 → 329.27, 199.13	
		524.255			524.24 → 411.17, 411.17 → 289, 383 (MS <sup>3</sup> )	
		391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		465.38	C <sub>25</sub> H <sub>52</sub> O <sub>7</sub>		465.38 → 283.17, 423.17	
1992.61, (yellow knight) Sticky exudate	1976	413.363	C <sub>25</sub> H <sub>48</sub> O <sub>4</sub>	dioctyl azelate		
		441.393	C <sub>27</sub> H <sub>52</sub> O <sub>4</sub>	dioctyl undecanedioate		
		524.255			524.24 → 411.17, 411.17 → 289, 383 (MS <sup>3</sup> )	
		391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		465.380	C <sub>25</sub> H <sub>52</sub> O <sub>7</sub>			
2012.35.1, NVE	2011	419.316	C <sub>26</sub> H <sub>42</sub> O <sub>4</sub>	DINP		
2012.36, NVE	2011	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		371.316	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	dioctyl adipate		
2020.44.1, NVE	2003	419.316	C <sub>26</sub> H <sub>42</sub> O <sub>4</sub>	DINP		

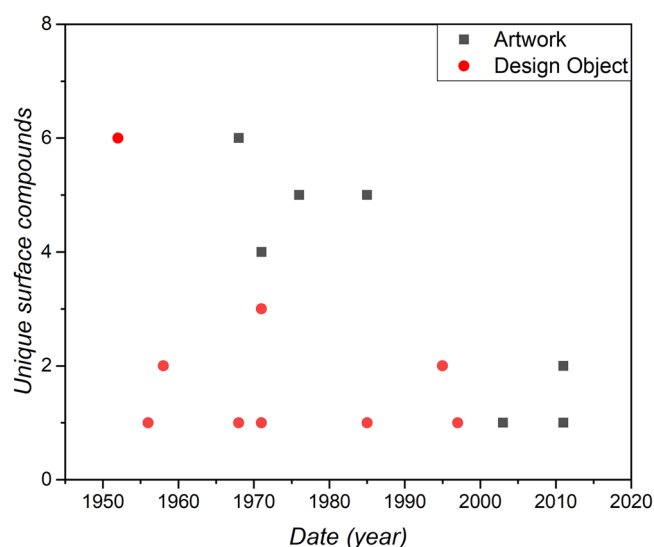
<sup>a</sup>Tentatively identified.

All mass spectra also included *m/z* 149.023 and *m/z* 279.159, fragments of DEHP/DOTP, which were excluded from the table. All MS<sup>n</sup> experiments were performed at 30V collision energy, except for ion 329.305, which was performed at 35V. Presence of visible exudates or other damage was noted. NVE indicates no visible exudates.

**Table 4 | Surface composition of swabbed heritage PVC objects from CHSDM based on NPDPI-MS and description of observed surface exudates**

Object ID	Date	<i>m/z</i>	Neutral Formula	Compound	MS <sup>n</sup> product ions	Comments
1971-23-1-B, Sweating, yellowing, adhesive tape	1971	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		413.363	C <sub>25</sub> H <sub>48</sub> O <sub>4</sub>	dioctyl azelate		
		299.258	C <sub>18</sub> H <sub>34</sub> O <sub>3</sub>	hydroxyoctadecenoic acid		
2019-29-20, NVE	1980-2010	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		377.326	C <sub>21</sub> H <sub>44</sub> O <sub>5</sub>			
1991-47-2, Sweating, yellowing, dust	1952	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		225.090	C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O	drometrizole	225.09 → 196.08, 120.06, 154.06	Stabiliser and UV absorber. Ion present as [M <sup>+</sup> ], product ions matching NIST GC-MS library reference.
		413.363	C <sub>25</sub> H <sub>48</sub> O <sub>4</sub>	dioctyl azelate		
		327.078	C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P	triphenyl phosphate	327.08 → 233.04 (C <sub>12</sub> H <sub>10</sub> O <sub>3</sub> P), 215.03 (C <sub>12</sub> H <sub>8</sub> O <sub>2</sub> P)	fire retardant
		464.374			464.37 → 391.28 (loss of C <sub>4</sub> H <sub>11</sub> N), 391.28 → 149.02, 279.16, 167.03 (MS <sup>3</sup> )	391.28 product ions match DEHP
		464.299				
2001-8-1-A, NVE	1997	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
2001-8-1-D, slight yellowing, NVE	1997	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
1969-165-1021, NVE	1957-1960	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
		408.311	C <sub>24</sub> H <sub>41</sub> NO <sub>4</sub>			
1995-152, NVE	1971	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
1998-75-180, NVE	1968	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
1971-15-1, NVE	1956 (ca.)	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		
2017-51-15-A, Sweating, dust	1985	391.284	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	DEHP/DOTP		

All mass spectra also included *m/z* 149.023 and *m/z* 279.159, fragments of DEHP/DOTP, which were excluded from the table. All MS<sup>n</sup> experiments were performed at 30V collision energy. Presence of visible exudates or other damage was noted. NVE indicates no visible exudates.



**Fig. 2 | Number of unique organic compounds detected from swabbing the SAAM and CHSDM collection objects plotted by their date of origin.** Objects from SAAM, categorised as *artworks*, are depicted in black, while objects from CHSDM are categorised as *design objects* and are depicted in red. *Artworks* were found to have a larger number of detected compounds compared to *design objects*. For objects where the exact year is unknown, the date was calculated as an average of the documented range.

emulsifier and lubricant could be tentatively identified. Overall, while certain ions detected from the swab, particularly those with higher mass, could not be unambiguously identified, at least one compound was successfully identified in all cases, contributing to a better understanding of the complex surface chemistry of heritage plastic objects. This can progress the field's ability to preserve plasticized PVC objects and alleviate the health risk assessment from handling such objects<sup>40</sup>.

Correlation of the number of unique organic compounds (plasticizers, lubricants, surfactants, stabilizers) detected from swabbing collection items and their date of origin is illustrated in Fig. 2. The objects were categorised into groups of *Artworks* (SAAM collection) or *Design Objects* (CHSDM collection). In general, as objects age, the number of unique organic compounds increased, suggesting that the surfaces of older objects are more complex in composition. This trend is more pronounced within the *Artwork* group. With the *Design objects*, fewer compounds were typically detected, with the *T Chair* (1991-47-2, CHSDM) as a notable outlier. This is the oldest object investigated in the group, and the observed surface complexity might result from it being manufactured by calendaring, which typically requires a more complex formulation including multiple plasticizers and external lubricants than extrusion<sup>41</sup>. However, the manufacturing process is not documented for most objects. Instead, we consider that the complexity of surface exudates increases with age also because of a more intricate composition of the bulk material in older objects or the influence of their previous history. Factors such as storage conditions, exhibition history, and cleaning practices can impact the current surface composition. *Artworks*, which are more likely to change owners and undergo handling, exhibit a more varied history of storage, contributing to the complexity of results.

Overall, the increase in detected compounds with object age should be understood as a result of both material, manufacturing, storage and handling factors, rather than any single cause.

While swabbing areas with visible exudates (dusty, soiled or sticky areas) may result in a slightly cleaner square that could be visually distinguishable, such objects would not typically be displayed without prior conservation treatment. Therefore, this effect aligns with standard conservation practices, where surface cleaning is commonly performed before exhibition.

### Direct analysis of SAAM objects by NPDPI-MS

NPDPI-MS was designed to avoid using solvent exposure or leaving any visible marks by exposing the object surface to a timed thermal desorption<sup>33,34</sup>. The setup was first tested on reference PVC films, which would be most sensitive to any surface changes due to their minimal thickness (ca. 0.2 mm). The temperature of the gas jet and the distance from the object affected the visible changes to the surface. Low temperature (140 °C) or increased distances left no visible marks or deformation to the PVC film, while high temperatures (200 °C) or closer sampling led to slight melting or produced an indentation while increasing the plasticizer signal. Taking care to prevent any damage to museum objects, the desorption was performed at 140 °C at ~1 mm distance minimum. Direct analysis of plastic museum objects by NPDPI-MS was used to expand its capabilities and take advantage of its non-destructive nature and low detection levels. Direct object analysis was also used to validate the results obtained by thermal desorption off swabs.

Four museum objects from the SAAM collection were transported to the laboratory with NPDPI-MS instrumentation. An adjustable-height table or a Genie platform load lifter was used to position the objects underneath the gas probe. The largest museum object was the *Bench* by Duane Iselin (SAAM, 1971.82.6), measuring 38.1 × 120.6 × 54.6 cm. There were no visible marks or deformation on any of the museum objects caused by the NPDPI. The ion signal from the object closely matched that obtained from the swab NPDPI-MS analysis (Supplementary Table S1). All the main plasticizer molecular ions were detected and matched the swab analysis. There was some inconsistency at detecting low-abundance compounds with a larger molecular weight, which can be explained by the difference in the desorption temperature. In consideration of object integrity, direct analysis can be performed at a lower temperature (140 °C) than the analysis of swabs (200 °C).

One of the limitations of direct MS techniques is the difficulty in distinguishing positional isomers. DEHP is a phthalate with regulated use in the EU due to its endocrine-disrupting properties<sup>42</sup>. Differentiating it from its positional isomer DOTP is therefore of particular importance. We propose a method to distinguish between the two based on the relative intensities of the parent and fragment ions in NPDPI-MS. This approach enables identification in simple mixtures but is limited when interfering compounds (e.g., other phthalates) are present. Complete identification in complex matrices requires further studies. Full methodology and results are provided in Supplementary Section 1.

**Effect of handling history and storage on surface composition.** One of the motivations for developing quantitative surface swabbing for plasticizers<sup>7</sup> was to investigate if the surface concentration can be related to the bulk content or if it is mainly affected by handling and storage conditions. For this purpose, 12 reference L-shape PVC folders with DEHP, DOTP or no plasticizer<sup>10,12</sup>, and no visible exudates were swabbed on their inner- and outer-facing sides. These L-shape folders are usually stored in a stack so contact on the outer-facing sides of the folders can occur. The results in Supplementary Fig. S5 show that there is no relationship between the surface concentration and the bulk content of DEHP or DOTP. Additionally, it was observed that the determined surface concentrations of the inner-facing (folded) and outer-facing surfaces of 12 reference PVC objects significantly differed. Some of the objects were unplasticized, which matched the results of swabbing their

**Table 5 | Results of quantitative swabbing of heritage PVC in SAAM and CHSDM collections**

Museum	Object ID	Surface concentration of DEHP (mg/m <sup>2</sup> )	Surface concentration of DOTP (mg/m <sup>2</sup> )
SAAM	1971.82.5A	5.2	0.4
SAAM	1971.85.6	12	0.3
SAAM	1976.48.8	0.2	<LOQ
SAAM	1985.82.2	1.9	0.2
SAAM	1992.61 (YL)	0.3	<LOQ
SAAM	1992.61 (BK)	2.0	<LOQ
SAAM	2012.35.1	<LOQ	<LOQ
SAAM	2012.36	2.2	<LOQ
SAAM	2020.44.1	<LOQ	0.3
CHSDM	1971-23-1-B	5.8	<LOQ
CHSDM	2019-29-20	1.2	<LOQ
CHSDM	1991-47-2	102	<LOQ
CHSDM	2001-8-1-A	0.8	<LOQ
CHSDM	2001-8-1-D	0.5	<LOQ
CHSDM	1969-165-1021	0.6	0.2
CHSDM	1995-152	1.0	<LOQ
CHSDM	1998-75-180	0.3	<LOQ
CHSDM	1971-15-1	1.5	<LOQ
CHSDM	2017-51-15-A	25	0.2

inner surface, whilst DEHP could be detected on the outer surface of the object due to transfer by physical contact. Sample inhomogeneity and swabbing uncertainty also contributed to the observed differences. The quantity of the surface exudates was therefore not determined by the initial plasticizer concentration, but likely by more complex stability of the mixture, storage conditions and handling history.

### Quantitative results of swabbing the SAAM and CHSDM collections.

Surface concentrations of DEHP and DOTP on PVC objects at the SAAM and CHSDM collections ranged from 0.2 mg/m<sup>2</sup> to 102 mg/m<sup>2</sup>, while DOTP was detected up to 0.4 mg/m<sup>2</sup> (Table 5). Either compound was detected in all the investigated objects, which corroborates the NPDPI-MS results off swabs. The highest surface concentration of DEHP was measured on the *T Chair* manufactured by Laverne (1991-47-2, CHSDM), where its characteristic signal was detected in the highest abundance along with additional unique compounds. High concentrations of DEHP were measured also on the 2017-51-15-A (CHSDM), 1971-23-1-B (CHSDM), 1971.82.5A (SAAM) and 1971.82.6 (SAAM), where visible surface exudates were noted. Objects 1992.61 (YL) and 1992.61 (BK) had visible surface exudates, which were not caused by DEHP or DOTP, but by dioctyl azelate identified with NPDPI-MS analysis. A concentration of 4 mg/m<sup>2</sup> DEHP or DOTP was previously identified as a threshold visibility level<sup>7</sup>. Implementing periodic monitoring of the surface concentration of select objects can support conservation planning and cleaning.

### Discussion

Thermal desorption of the analytes from swab heads with an innovative non-proximate desorption photoionization with high resolution mass spectrometry was able to successfully detect and identify compounds on the surface of heritage PVC objects. The method was validated on a reference collection of PVC objects and used to characterize the surfaces of 19 PVC objects from the Smithsonian American Art Museum and the Cooper Hewitt, Smithsonian Design Museum. The NPDPI-MS analysis proved to

be sensitive and capable of identifying organic compounds on the surfaces of museum PVC objects. The mass spectra of the analysed swabs of museum objects without visible exudates were generally simple in composition, i.e., traditional PVC plasticizers (DEHP, DOTP, DINP, DIDP, and other phthalates). Objects with visible exudates exhibited additional compounds, such as dioctyl azelate in Glen Kaufman's *Any Questions?* and triphenyl phosphate and drometrizole detected in the *T Chair* from 1952. The study also revealed that this simple non-destructive sampling method can show interesting differences in the composition of art pieces from the same series, e.g., Margarita Cabrera's sculptures. A trend was observed that older artworks had a larger number of unique organic compounds on their surfaces compared to design objects, suggesting the complexity of their surface chemistry is influenced by age and handling history.

Additionally, the NPDPI-MS was used for a direct object analysis of four museum objects from the SAAM collection. The temperature of the gas jet and the distance of the probe from the object were successfully optimised to prevent any damage to the museum objects while obtaining characteristic surface signals. The method is expected to also detect analytes from the bulk near the surface due to thermal desorption, which was also considered as the final validation of the results obtained from swabbing.

In conclusion, the presented method for characterizing surface exudates based on dry swabbing was developed to be sensitive, non-destructive, low-tech and versatile. The methodology was designed to be accessible to all museums, require no advanced equipment for sampling, and provide comprehensive information on the chemical composition of surface exudates. The sampling technique can be especially useful for offsite analysis of museum objects regardless of their geographical proximity to the laboratory or for analysing objects too delicate or otherwise impractical to transport. The information obtained from these analyses is important for conservators, as it enhances their understanding of the composition of plastic objects, identifies the primary plasticizers and potential degradation products or compounds with increased health-risk. Differences in surface composition between objects or over time can reflect material ageing, migration of additives, or handling history, thus supporting conservation planning and monitoring.

### Data availability

All data generated or analysed during this study are included in this published article and its supplementary information file.

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## Author contributions

T.R.: conceptualization, writing—original draft preparation, methodology, investigation (chromatographic analysis, mass spectrometry, validation), data curation, funding acquisition; L.B.: investigation (object handling, condition assessment), writing—review & editing; J.W.: investigation (object handling, condition assessment), writing—review & editing; I.K.C.: conceptualization, methodology, writing—review & editing; M.S.: conceptualization, methodology, writing—review & editing; G.A.N.: conceptualization, writing—review & editing, methodology, investigation (mass spectrometry), data curation, supervision. All authors read and approved the final manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

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**Correspondence** and requests for materials should be addressed to Tjaša Rijavec.

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