Analysis and quantitation of volatile organic compounds emitted from plastics used in museum construction by evolved gas analysis–gas chromatography–mass spectrometry

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A B S T R A C T

Construction materials used in museums for the display, storage, and transportation of artwork must be assessed for their tendency to emit harmful pollution that could potentially damage cultural treasures. Traditionally, a subjective metals corrosion test known as the Oddy test has been widely utilized in museums for this purpose. To augment the Oddy test, an instrumental sampling approach based on evolved gas analysis (EGA) coupled to gas chromatography (GC) with mass spectral (MS) detection has been implemented for the first time to qualitatively identify off-gassed pollutants under specific conditions. This approach is compared to other instrumental methods reported in the literature. This novel application of the EGA sampling technique yields several benefits over traditional testing, including rapidity, high sensitivity, and broad detectability of volatile organic compounds (VOCs). Furthermore, unlike other reported instrumental approaches, the EGA method was used to determine quantitatively the amount of VOCs emitted by acetate resins and polyurethane foams under specific conditions using both an external calibration method as well as surrogate response factors. EGA was successfully employed to rapidly characterize emissions from 12 types of common plastics. This analysis is advocated as a rapid pre-screening method to rule out poorly performing materials prior to investing time and energy in Oddy testing. The approach is also useful for rapid, routine testing of construction materials previously vetted by traditional testing, but which may experience detrimental formulation changes over time. As an example, a case study on batch re-orders of rigid expanded poly(vinyl chloride) board stock is presented.

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1. Introduction

Volatile organic compounds (VOCs) are organic chemicals that have a relatively high vapor pressure at room temperature and are often emitted in their gas phase from construction materials such as wood, coatings, plastics, and adhesives [1]. VOCs can have a deleterious effect on artworks due to chemical reactions causing degradation, surface crazing, tarnishing, softening, or efflorescence [2]. The ability to detect the presence, and in some cases determine the identity and concentration, of these VOCs is important when selecting materials for the storage, display, or transport of works of art. Currently, the suitability of materials for use in a museum environment is evaluated by the so-called “Oddy test” [3]. This eponymous test is named after Dr. Andrew Oddy, former Keeper of Conservation at the British Museum, who sought an inexpensive means of identifying materials that could harm collections of metal antiquities. The test has since been improved and standardized [4–6] and many variations have been introduced [7–11].

In the Oddy test [6], the material for evaluation is placed in a sealed borosilicate glass tube containing a small amount of water and three high purity metal coupons: lead, silver, and copper. The sealed reactor is aged for 28 days at 60 °C, and at the end of this period the coupons are examined for signs of corrosion. On the basis of the level of corrosion on the coupons, a determination is made for the permanent use, temporary use, or unsuitability of the material for museum applications. Although the original test was meant only to vet materials to be used in casework holding metal objects, Oddy test results are now widely applied to the protection of diverse museum objects and to the suitability of construction materials for general museum building projects.

While this method is simple to run, requires minimal equipment, and is able to assess many off-gassed VOCs as well as harmful degradation products from oxidation or hydrolysis of...
the material being vetted, it also exhibits severe shortcomings. The Oddy test has been criticized for its relatively long time to complete, the fact that it only detects pollutants that are corrosive to the three metals, and that its assessment is subjective in nature [12]. While the Oddy test is able to detect corrosion-inducing pollutants such as H2S, NOx, SOx, O3, mineral acids, peroxides, and others, it fails to identify specifically the chemical species that are emitted from the material under investigation. In addition, it may not respond at all to non-corrosive pollutants (e.g., residual solvents, pesticides, unreacted monomers, etc.) that could still damage cultural heritage materials. In order to vet potential construction materials on the timescale typical of a museum construction project, a new approach is needed that is rapid, comprehensive, sensitive, and potentially quantitative. Efforts to find an instrument-based technique to examine VOCs emitted from museum materials are underway in many museum laboratories [13].

Solid-phase microextraction (SPME) sampling of the headspace above an object is one such method currently being investigated for the analysis of the VOCs emitted from various construction materials and from the artworks themselves [12,14–22]. In this sampling strategy, VOCs emitted from a sample are allowed to equilibrate in the headspace of a sealed vial with the material under test. After equilibration, the SPME fiber, which is coated with an adsorbent material, is exposed to the headspace without breaking the seal of the vial. Certain VOCs are pre-concentrated onto the SPME tip as a result of their high affinity for the adsorbent used. After pre-concentration, the needle is removed from the vial and inserted into the heated injector of a gas chromatograph (GC) for desorption and analysis. Work by Tsukada and co-workers [12] involved the use of three different SPME adsorbents to examine the VOCs emitted from polyester polyurethane (PUR) packing foam during Oddy testing. The combined results of their three experiments indicated the presence of various alkylmorpholines from the foam, which also were found as white crystallites on museum objects that had been stored using the polyurethane foam. In addition, a series of studies by Lattuati-Derieux et al. [18–21] describes the SPME analyses of PUR foams, wood pulp from a book, beeswax, and plastic samples of museum interest.

Another approach being explored for the analysis of VOCs in the museum atmosphere is thermal desorption coupled to gas chromatography–mass spectrometry (TD–GC–MS) [23–28]. In this technique, VOCs emitted by a material in an enclosed circulating airstream are trapped and concentrated on an adsorbent material (like Tenax-AR or Carbotrap®) packed in a steel tube. After desorption for a set time, trapped materials are desorbed in an oven or washed free using a solvent. These released VOCs are introduced into a GC–MS for analysis. Mitchell and co-workers [24] used Tenax-AR to trap VOCs emitted from polymeric materials typically found in museum objects or used in the construction of museum casework. Analysis using TD–GC–MS resulted in chromatographic profiles that identified several unique markers for some plastic materials. Schieweck and co-workers [26,27] also described a TD method whereby VOCs given off by construction materials for museum cases were identified.

While VOC analysis by SPME and TD have advantages over traditional Oddy testing, including the detection of a broad range of VOCs and the possibility of quantifying these contaminants, each also comes with its own limitations. Headspace analysis using a SPME accessory allows for pre-concentration of the VOCs prior to analysis, thereby increasing the sensitivity of the technique, but the specific choice of the adsorbent material limits which organic components are detected and may change the perceived distribution of product VOCs during analysis. Thermal desorption trapping on a resin material like Tenax-AR is common, but trapping times are often long (e.g. 8 h), and trapping is not necessarily universally effective as different compounds have different breakthrough volumes.

In this research, the VOCs emitted from several plastic standards and from various commercial construction materials were studied using an evolved-gas analysis (EGA) technique commonly available – but rarely implemented – by museum laboratories that use a furnace or resistive coil pyrolyzer (e.g., Frontier or CDS). In one of the only published examples of EGA analysis in a museum context, Schilling and co-workers [29,30] utilize the sampling technique without chromatographic separation for the identification of plastic samples through their characteristic VOC signatures as detected directly by MS. In addition, they used the furnace to perform a heart-cut GC–MS analysis of plastic materials at various desorption temperature ranges. The goal of the current work is to demonstrate the utility of EGA as a method for rapid pre-screening of construction materials for the presence of harmful VOCs prior to conducting a 28-day Oddy test. In this way, new materials can be quickly rejected if a known pollutant (formaldehyde or acetic acid, for example) is detected at significant quantities, and new batches of previously studied and approved materials can be routinely screened in a way that they rarely are today to help identify if the new batch has undergone a questionable manufacturing or formulation change.

In this EGA approach, samples of plastic construction materials are placed into a helium-purged oven at elevated temperature under isothermal conditions for 30 s to accelerate the emission of VOCs. All of the emitted VOCs are transferred directly into the GC injector port and onto a capillary column for analysis. By using this method, VOCs emitted by the plastic samples can be quickly separated and identified with high sensitivity. Importantly, pre-concentration equilibrium on a selective adsorbent is not an issue like in other approaches—that is to say all analytes that are amenable to GC separation and MS detection are analyzed—and a large volume of evolved gases can be analyzed for improved detection limits. Furthermore, if pollutants of particularly high volatility are suspected, cryo-trapping through the use of a GC column initially cooled to liquid nitrogen temperatures (≈−195°C) can provide complete sample collection and pre-concentration for analysis. The work described herein utilizing this novel approach to study museum pollution focuses on four main topics: (1) the rapid analysis of VOCs emitted from an array of plastic samples commonly used in museum construction or found in museum collections; (2) the detection of the particularly problematic pollutant formaldehyde in specific plastics; (3) a rapid, semi-quantitative analysis of alkylmorpholines previously identified in PUR packing foams [12] and a quantitative analysis of acetic acid emitted by common vinyl acetate based adhesives; and (4) a case study centered on the analysis of several batches of rigid poly(vinyl chloride) foam board used in gallery construction at the Indianapolis Museum of Art (IMA).

2. Experimental

2.1. Polymer samples

Eighteen different plastics were studied in this work, as shown in Table 1. All reference polymer standards were obtained from Scientific Polymer Products, Inc. (Ontario, NY) and used in pellet or powder form as received. All commercial construction materials were obtained from various departments within the IMA. Additional plastic samples for analysis were obtained from the SamCo POPART sample collection [31]. Samples of rigid PVC boards were obtained from Meyer Plastics and Laird Plastics, and all have previously undergone Oddy testing at the IMA and other cultural institutions [32].
### Table 1

<table>
<thead>
<tr>
<th>Name, form, abbreviation, mass analyzed</th>
<th>VOCs detected</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate, pellet, PC, 18 mg</td>
<td>Naphthalene (trace) biphenyl (trace)</td>
<td>A generally accepted plastic for museum use. It is unlikely that minor residual chemicals will cause damage to museum objects based on prior experience with the material [2]</td>
</tr>
<tr>
<td>Polycarbonate, commercial sheet, PC, 27 mg</td>
<td>Chlorobenzene</td>
<td>Chlorobenzene is likely present as a residual solvent from the phosgene-based formation of the polymer and has been detected previously during the extrusion process for PC resin [33,34]</td>
</tr>
<tr>
<td>Polyethylene, HD, pellet, HDPE, 22 mg</td>
<td>Dodecane Tetradecane Hexadecane Octadecene Eicosene</td>
<td>Routinely used in museum settings for shipping, display, and storage in the form of products like Volara®, Ethafoam®, and Tyvek® [2,35,36]</td>
</tr>
<tr>
<td>Polypropylene, isotatic, pellet, PP, 15 mg</td>
<td>Various branched hydrocarbons</td>
<td>Widely deployed in the museum in the form of Coroplast® corrugated board stock used for box construction and to line shelving. These results are similar to findings reported elsewhere [2,24,37]</td>
</tr>
<tr>
<td>Polystyrene, pellet, PS, 25 mg</td>
<td>Styrene Styrene dimer</td>
<td>Polystyrene boards like Fome-Cor® find application in museums as an attractive material for display cases, as a backing board for art objects, and in storage and packing. However, styrene monomer is a known toxin and has been shown to cause crazing and clouding in other plastics [2,38]</td>
</tr>
<tr>
<td>Poly(vinyl chloride), powder, PVC, 5 mg</td>
<td>3-Nonene p-Ethyltoluene α-Methylstyrene 2,3,6,7-Tetramethyloctane 2,6-Dimethyloctane 5-Ethyl-2,2,3-trimethylheptane α,α-Dimethyl-benzyl alcohol</td>
<td>These VOCs are similar to those reported previously [24,37]</td>
</tr>
<tr>
<td>Poly(vinyl chloride), plasticized, POPART, 10 mg</td>
<td>Dimethyl phthalate Diethyl phthalate Isobutyl octyl phthalate</td>
<td>Plasticized PVC is largely discouraged for use in museums due to the migration of plasticizers and their tendency to emit hydrochloric acid during aging [2,39–41] In addition, semi-volatile plasticizers have been detected in PVC samples using HS–SPME sampling and may migrate to and cause softening of neighboring plastics [42]</td>
</tr>
<tr>
<td>Poly(vinyl acetate), pellet, PVAc, 18 mg</td>
<td>Vinyl acetate Acetic acid Nonane Octadecane</td>
<td>Polymers bearing acetate side groups have the tendency to emit acetic acid as they decompose, and yet they are pervasive materials in most museums as (1) a waterborne adhesive like Jade 403®, (2) a solvent varnish or inpainting medium like Union Carbide’s AYAC, or (3) in artworks of the 19th and 20th century. The vinegary off-gassing of these materials exhibits a negative influence on artwork stored or displayed alongside the offending pieces [2,39,43,44] Propylene glycols are commonly used as co-solvents or plasticizers in waterborne coatings and can also pose a problem in that their presence in the atmosphere might contribute to the softening of other plastics nearby [2]</td>
</tr>
<tr>
<td>Cellulose acetate, powder, CA, 4 mg</td>
<td>Acetic acid Diethyl phthalate</td>
<td>These acrylate polymers have not generally been found to be problematic in the museum environment. [2] However electrochemical testing of Plexiglas has shown unexpectedly high levels of lead coupon corrosion [45]</td>
</tr>
<tr>
<td>Jade 403®, PVA, 9 mg</td>
<td>Acetic acid Tripropylene glycols Propylene glycol</td>
<td>Poly(vinyl acetate), popcorn, PMMA, 6 mg</td>
</tr>
<tr>
<td>Elmer’s glue, PVAc, 10 mg</td>
<td>Acetic acid Tripropylene glycols Propylene glycol</td>
<td>Poly(vinyl chloride), plasticized, POPART, 10 mg</td>
</tr>
<tr>
<td>Poly(methyl methacrylate), powder, PMMA, 6 mg</td>
<td>Methyl methacrylate</td>
<td>These acrylate polymers have not generally been found to be problematic in the museum environment. [2] However electrochemical testing of Plexiglas has shown unexpectedly high levels of lead coupon corrosion [45]</td>
</tr>
<tr>
<td>Poly(acrylic acid), powder, PAA, 5 mg</td>
<td>Acrylic acid Butenoic acid</td>
<td>Poly(vinyl acetate), pellet, PVAc, 18 mg</td>
</tr>
<tr>
<td>Poly(oxyethylene), polymer, POM, 18 mg</td>
<td>Formaldehyde Decahydro-indanecenes</td>
<td>Formaldehyde-containing polymers are not recommended for use in museums due to their potential emission of formaldehyde during thermal degradation of the plastic. [2] Although Delrin® has passed an Oddy test, the material failed a basic acidity test when enclosed with an acid detection strip</td>
</tr>
<tr>
<td>Poly(vinyl formal), powder, PVF, 3 mg</td>
<td>Formaldehyde Naphthalene</td>
<td>The presence of formaldehyde as an off-gassed VOC strongly suggests the unsuitability of these formaldehyde-containing polymeric materials for museum construction due to the pollutant’s ability to oxidize in air to form corrosive formic acid</td>
</tr>
<tr>
<td>Melamine-formaldehyde plastic, POPART, 18 mg</td>
<td>Formaldehyde</td>
<td>These have been identified as museum pollutants capable of leaving crystalline residues on artworks [12] Cyclic diesters are formed as by-products during the production of the polyurethane product [48]</td>
</tr>
<tr>
<td>urea-formaldehyde plastic, POPART, 19 mg</td>
<td>2,6-di-t-butyl-4-sec-butylphenol</td>
<td>Alkylmorpholines are used as catalysts in the production of polyurethane foams [47]. These have been identified as museum pollutants capable of leaving crystalline residues on artworks [12] Cyclic diesters are formed as by-products during the production of the polyurethane product [48]</td>
</tr>
</tbody>
</table>

Notes:
- Detection was improved using cryofocusing, due to the highly volatile nature of the VOC.

### 2.2. EGA–GC–MS procedure for analysis of plastic materials

EGA was accomplished using a Frontier double-shot pyrolyzer (PY-2020ID). Between 1.5 and 30 mg of sample was added to a stainless steel Eco-cup sample holder (Frontier) and exposed to the 115 °C pyrolyzer furnace for 30 s. The furnace was interfaced at 215 °C to a GC inlet with a split ratio of 20:1. Emitted VOCs were trapped on the front end of a 40 °C Thermo TG-5ms capillary column (30 m × 0.25 mm × 0.25 μm). When necessary for the analysis of extremely volatile compounds, cryofocusing with liquid nitrogen was employed using a Frontier Lab Micro Jet Cryo-Trap (MJT–1030E). Chromatographic separation was accomplished on a Thermo Trace GC Ultra with a He carrier gas flow rate of 1.5 mL/min−1. The oven temperature program was 40 °C for 3 min;
a 20 °C min⁻¹ ramp to 150 °C; a 10 °C min⁻¹ ramp to 250 °C with an isothermal hold for 6.5 min. Detection of ions was accomplished using a Thermo ISQ mass spectrometer scanning a mass range of 29 to 31 m/z for the first 2.2 min to detect formaldehyde, followed by a mass range of 45 to 450 m/z for the remainder of the analysis. Identification of volatile components was performed using the NIST Mass Spectral Search Program, ver. 2.0f.

2.3. Quantitative analysis

The quantitative analysis of 4-alkylmorpholines and acetic acid pollutants from polymer samples was performed without derivatization using the same instrumentation but using a Restek Stabilwax (15 m × 0.25 mm × 0.25 μm) column. Use of a polar stationary phase resulted in chromatograms with good peak shape that allowed for reproducible peak area determination for the polar compounds under study. The oven temperature program was identical to that described above except the maximum temperature was set at 280 °C.

Quantitative analysis of alkylmorpholines emitted from a PUR packing foam sample was performed by generating response factors for a surrogate analyte, 4-ethylmorpholine (TCI, 99%). To prepare a standard for analysis, 10 μL each of the surrogate and an internal standard of hexadecane (Sigma-Aldrich, 99%) were added to 50 mL of acetone (Sigma-Aldrich, Chromasolv, >99.8%) in a volumetric flask. Replicate analyses of a 2 μL aliquot of this solution were used to generate response factors. Quantification of 4-alkylmorpholines in the PUR foam sample was then accomplished by adding a 2 μL aliquot of hexadecane internal standard solution (5 μL hexadecane in 50 mL of acetone) to the 1.4 mg sample of foam prior to analysis. The percent relative standard deviation of the response factor for 4-ethylmorpholine with respect to hexadecane was 6.6%, indicating that the data can be considered quantitative in nature and useful for comparative studies under these specific EGA conditions.

Quantitation of acetic acid was performed using an external calibration. Known volumes of a 210 ppb standard were added to an Eco-cup pre-loaded with a 4 mm-diameter circle of a glass microfiber filter that prevented rapid evaporation. This sample was immediately analyzed by the EGA-GC-MS technique. A calibration curve was generated using area counts from the selected-ion chromatogram (SIC, m/z = 60 amu). Acetic acid in polymer samples was determined using a known mass (12 mg) of polymer cut into uniform pieces of 1 mm square.

3. Results & discussion

3.1. Analysis of standard polymer samples and their corresponding construction materials

Fig. 1 depicts an example chromatogram obtained for the EGA–GC–MS analysis of 22 mg of high-density polyethylene. Major VOCs include a series of n-alkenes as identified by mass spectrometry that were likely formed during the polymerization of ethylene. In all, nineteen different materials representing 12 polymer substances were analyzed using this technique. Table 1 lists the primary VOCs detected for various plastic standards and samples analyzed using EGA. These samples represent common museum construction materials and common components of museum collection pieces. In some cases, the VOCs emitted are extremely volatile (e.g. formaldehyde, acetic acid, chlorobenzene) and traditional EGA sampling produced chromatograms in which peak shape for these highly volatile compounds was not optimal. These compounds remain in the gas phase upon entering the GC column and are not “trapped” on the front of the cool (i.e. 40 °C) column; therefore they travel through the column as broad bands. To remedy the problem of broad peak shape, cryofocusing was employed to trap these highly volatile compounds near the column inlet during the EGA process and compress the chromatographic band during the GC separation. Discussion of known pollutants is provided in the table when appropriate.

3.2. Analysis of polyurethane foam and quantitation of 4-alkylmorpholines

PUR foam often finds short term applications in the shipping of museum objects and artworks. In an earlier qualitative study, Tsukada and coworkers [12] examined similar foam implicated in damage to a museum object by monitoring the headspace of a sample in an Oddy test jar using 3 separate SPME–GC–MS analyses. Tsukada attributed efflorescence found on museum objects stored with this foam for long periods to the build-up of alkylmorpholines in the storage environment. In the present work, quantitative analysis of the VOCs released from a known mass of PUR foam during the accelerated emission in the 115 °C EGA oven was accomplished. Using the EGA method described above, several pollutant VOCs, 4-decylmorpholine, 4-dodecylmorpholine, and 4-tetradecylmorpholine, were observed to be emitted from polyester-based PUR foam (Fig. 2).

![Fig. 1. An example chromatogram for the EGA of high-density polyethylene. Peaks represent n-alkenes from C₁₂ to C₂₂. Also detected at 11.4 min is the antioxidant 2,6-di-t-butyl-1,4-benzoquinone.](image-url)
Using commercially available 4-ethylmorpholine as a surrogate analyte standard, along with hexadecane as an internal standard, a response factor specific for 4-ethylmorpholine was obtained and applied to the signal produced by the various longer chain 4-alkylmorpholine homologs emitted from the PUR foam during the EGA experiment. Table 2 lists the quantity of each 4-alkylmorpholine detected, along with their associated statistical data. Results show that nanomole quantities of these VOCs can be detected by EGA–GC–MS under the conditions of the EGA emission. Statistical analysis of replicate runs of the surrogate standard showed a 6.6% RSD, however errors as large as 30% in the analysis of the foam are likely due to non-uniformity of the material. Since only a 1.4 mg core sample is cut from the foam and analyzed during each trial, any inconsistencies in foam production will be manifest as a differing concentration of alkylmorpholine. This result suggests that grinding a large sample for quantitative EGA analysis, especially in the case of foams, may improve precision.

### 3.3. Quantitative analysis of acetic acid emitted by plastic samples

Acetic acid is a well-documented, serious pollutant in the museum environment [2]. Its off-gassing from wood products and some polymers has been shown to corrode metal surfaces (in particular lead and copper) and to accelerate the degradation of paper-based artifacts. Quantitative analysis of acetic acid emitted from polymer samples at 115 °C for 30 s was accomplished through external calibration. A known mass of acetic acid was placed into an Eco-cup and analyzed immediately. Peak area from the selected-ion chromatogram (SIC, m/z = 60 amu) was used to generate the calibration curve shown in Fig. 3. The regression coefficient (R²) value was determined to be 0.9996, and the maximum percent relative standard deviation for a calibration point, as shown by the error bars, increased with increasing concentration to 12% (n = 3).

Acetic acid emitted from a polymer sample during the accelerated EGA at 115 °C was analyzed by placing a known mass (12 mg) of sample in the Eco-cup and immediately performing the EGA–GS–MS analysis. Area count values were converted to ng of acetic acid using the calibration regression line and the ng acetic acid/mg of sample was determined (Table 3). The samples analyzed include a range of acetate polymers including four PVAc emulsions used as commercial adhesives. While the determined amount of acetic acid found during the EGA experiment may not represent all of the pollutant VOC present in the material at the time of analysis, the quantitative study does provide comparative data to aid in selecting among various acetate-based adhesives for use in a museum environment.

These results show the serious pollution problems expected of cellulose acetate materials, which had the highest acetic acid level in the current study, and confirm the notion that these materials are considered “malignant” plastics when encountered in museum

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount (nmol/mg)</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Decylmorpholine</td>
<td>0.5 ± 0.2</td>
<td>32</td>
</tr>
<tr>
<td>4-Dodecylmorpholine</td>
<td>2.3 ± 0.4</td>
<td>15</td>
</tr>
<tr>
<td>4-Tetradecylmorpholine</td>
<td>0.6 ± 0.1</td>
<td>14</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount (ng/mg)</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acrate</td>
<td>53 ± 0.2</td>
<td>4.7</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>0.00826 ± 0.0001</td>
<td>0.13</td>
</tr>
<tr>
<td>Jade 403 (TALAS)</td>
<td>0.0462 ± 0.0006</td>
<td>1.2</td>
</tr>
<tr>
<td>Jade 403 (Light Impressions)</td>
<td>0.059 ± 0.002</td>
<td>2.6</td>
</tr>
<tr>
<td>Titebond II, freshly cured</td>
<td>5.0 ± 0.5</td>
<td>9.1</td>
</tr>
<tr>
<td>Elmer’s school glue, aged</td>
<td>0.21 ± 0.01</td>
<td>5.3</td>
</tr>
</tbody>
</table>
collections [49]. Reference PVAc pellets by comparison had much lower acetic acid levels. Of the 4 waterborne adhesives tested, the Jade 403 products, one recent and one formulation over a decade old, showed much lower acetic acid levels than the two household adhesives, Titebond II and Elmer’s glue.

These results verify the literature on short term [43] and long term [44] aging studies of PVAc adhesives and are in line with the years of vetting that have established Jade 403 as a conservation grade adhesive. Household white glues are also shown by this study to have no place in direct contact with artworks as better performing adhesives are available. In this instance, the quantitative analysis by EGA allows an objective and judicious choice to be made between similar materials in a short time period.

When the EGA procedure was carried out on smaller pieces of PVAc as opposed to one large piece, the detected amount of acetic acid increased slightly. This increase could be due to an increased surface area from which the acetic acid could be emitted, and is further evidence that comparative testing should strictly control the sample dimensions being studied. Furthermore, when a sample of PVAc was analyzed repeatedly in successive analyses, the amount of acetic acid decreased per analysis. This data again suggests that the EGA technique is sampling the acetic acid at the surface of the plastic under the conditions of the EGA furnace and is not detecting all acetic acid that could potentially be emitted during the life of the plastic, not to mention that which is generated during the long-term degradation of the material.
3.4. Case study involving the analysis of rigid PVC board used in gallery case construction

Rigid expanded PVC boards (e.g. Celtec, Sintra, and EX-CEL FF) are an inexpensive, easily machined product that could be useful in the fabrication of museum signage and casework. Rigid PVC also appears occasionally in artworks themselves, for instance as a common backing board for mounted photographs. Historically, the use of chloride containing plastics has been discouraged over fears that their degradation can result in the release of hydrochloric acid [2]. However, recent Oddy testing of PVC board at the IMA and elsewhere [32] showed no corrosion of the test coupons and validated the use of the material for museum construction.

While rigid PVC boards are comprised of mainly PVC (70–95%), the material safety data sheets from various manufacturers indicate the use of other organic and inorganic compounds that act as fillers, heat stabilizers, lubricants, processing aids, impact modifiers, and colorants. The presence and relative amounts of these additional organic compounds could influence the suitability of the material for use in a museum setting.

To demonstrate the utility of the EGA–GC–MS technique for the rapid evaluation of museum materials, two different samples of rigid PVC sheets from two manufacturers (Celtec® and EX-CEL FF®) recently acquired in a single order from the same supplier (Meyer Plastics) were analyzed as well as a sample of Celtec® from a different supplier (Laird Plastics) that had previously passed the Oddy test and was accepted for use in gallery construction. Fig. 4 shows a chromatogram for the EGA of a 3/4’’-8’’ Celtec® PVC board (Meyer, Trace A) and 3/4’’ Celtec® board previously used to create gallery casework (Laird, Trace B). The chromatogram for the new material shows identical components, albeit at slightly different relative percentages, to those observed for the material previously purchased and used by the museum. Major VOC components in these two samples include 2-ethyl-1-hexanol, with much smaller amounts of 4-chlorooctane and 2-ethylhexyl thioglycolate. The last component is likely a by-product from an organotin heat stabilizer commonly used in the manufacture of the PVC board [46].

Also shown in Fig. 4 is a chromatogram for a 3/4’’-10’’ EX-CEL FF® PVC board (Meyer, Trace C) received in the same shipment as the other Celtec® board (Trace A). Comparison of this chromatogram to those in plots A and B reveals a VOC profile which is significantly different from the Celtec® samples previously vetted for use in the museum. Major VOC components in this sample include 2-ethyl-1-hexanol as seen previously, but now also include chlorotrimethylstannane, ethylbenzene, styrene, 2,2-dimethyl-1,3,2-dithiasiloxane, and 1,2,5-trithiophene.

The difference in the VOC profile discovered using the EGA protocol quickly revealed a difference in the formulation of the two different sizes of the PVC board provided by the same supplier but manufactured at different production plants. These results show that the two plastics manufacturers, Celtec® and EX-CEL FF®, utilize different formulations for their rigid PVC product. Oddy testing is likely not necessary for the new Celtec® boards because the VOC profile is nearly identical to older material previously tested and accepted for use in the museum. Because of this, the fabrication shop can begin using this material for construction of casework without waiting for additional testing. Because of the significant difference in VOC profile observed for EX-CEL FF® board, however, this material should undergo further Oddy testing to ensure suitability for use in the museum environment.

As a result, the museum must wait 28 days before knowing if the 10-ft boards can be used for construction. By using the 30 min EGA–GC–MS technique, roughly a month of time can be saved and construction of casework for the new exhibit can begin immediately.

4. Conclusion

The EGA analysis technique described in this paper is capable of producing a profile of VOCs off-gassed from a variety of plastic samples common to museums. The technique is simple, requires small amounts of sample (1 to 30 mg), and is relatively rapid (30 s sampling + 25 min GC–MS analysis) compared to existing techniques like SPME and TD. Although the present technique is considerably faster, the results from the EGA of various plastic samples compare well with those previously published in the literature [12,24,29,35,37,43,44].

Instrumental approaches to materials suitability studies have largely dealt with the qualitative identification of a range of pollutants emitted from potential museum construction materials. We have demonstrated that this EGA method can perform semi-quantitative to quantitative determination of VOCs generated during accelerated off-gassing based on the availability of surrogate analytes and suitable standards. Questions still remain as to what exactly is being “quantified” during accelerated testing protocols. For example, the EGA technique is run at an exaggerated temperature, and because it is a microanalytical approach, it utilizes small samples with an abnormally high surface area. These experimental features enhance the sensitivity of the technique to rapidly measure low level emissions from the material, but they also present an “unnatural” situation in terms of the pollution environment generated in the accelerated laboratory test. This condition is not unique to the EGA method described here but is inherent in all of the currently practiced accelerated materials tests. Quantification of the emitted pollutants under these conditions can still be of direct and immediate benefit, for instance selecting between two similar materials analyzed under identical conditions such as demonstrated here for the PVC adhesives—the one with the lower pollution levels should be chosen if all other considerations are equal. But how will a material with a pollution profile that contains low levels of a noxious gas behave under normal conditions of use? Should it be discarded outright, keeping in mind that “the dose makes the poison”? Additional research must tackle issues related to the adverse effect level of a pollutant under ambient conditions of use, and how this concentration relates to that being determined through accelerated testing conditions.

Finally, the new EGA method has proven useful toward the routine screening of new batches of construction materials that have previously passed the Oddy test and been approved for museum use. Potentially negative reformulations of approved materials can be identified and inferior imitation products identified prior to investing time and energy in Oddy testing to determine if the pollution profile could jeopardize museum collections. In summary, this new EGA sampling technique can detect a number of important organic and organometallic pollutants emitted by museum construction materials, but it is important to note that at this time it serves only as a pre-screening method or supplementary method to the Oddy testing, which remains the de facto standard for vetting museum construction materials.

References
