Journal of Chromatography A, 1426 (2015) 201–208

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

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

Michael J. Samide [a,*], Gregory D. Smith [b]

[a] Department of Chemistry, Butler University, Indianapolis, IN 46208, USA
[b] Indianapolis Museum of Art, Indianapolis, IN 46208, USA

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form
17 November 2015
Accepted 19 November 2015
Available online 21 November 2015

Keywords:
VOC
Pollution
Off-gassing
Museum construction
Artwork

ABSTRACT

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.

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

* Corresponding author. Tel.: +1 317 940 9973.
E-mail address: msamide@butler.edu (M.J. Samide).

http://dx.doi.org/10.1016/j.chroma.2015.11.066
0021-9673/

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 H_2S, NO_x, SO_x, O_3, 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 adsorption 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. Schiewech and co-workers [26,27] also describe 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 cool 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 onto 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 ($\approx -195\,^{\circ}$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].