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Cellulose Acetate Lamination at the National Archives
Part 2: Analysis of Laminated Documents
Using Solid-Phase Microextraction

ABSTRACT

To evaluate the condition of a laminated document it is helpful to identify the plasticizers present in the cellulose acetate lamination film. Plasticizers degrade more readily than the polymer, and some are less stable than others. Solid-phase microextraction (SPME) in combination with gas chromotography/mass spectroscopy (GC/MS) analysis is a simple, nondestructive, and sensitive technique for studying plasticizers and other additives in laminated documents. In this project five types of SPME fibers were used to study experimental films that contained various combinations of plasticizers. Laminated documents related to the Louisiana Purchase were also studied. Plasticizers were easily identified as well as the possible degradation products phthalic anhydride and phenol.

INTRODUCTION

As Susan Page discussed above in the first part of this presentation, the National Archives and Records Administration (NARA) laminated documents from the 1930s to the 1980s. During this time the laminating procedure evolved, including changes in the use of tissue reinforcement and deacidification (Stiber 1988). The formulation of the cellulose acetate (CA) lamination film also varied. At least three different brands of films were used (Gear 1958), and the composition of these may have changed over time depending on the manufacturer's formulation and quality control (Clements 1972).

The main difference between these films and others available was in the type and amount of plasticizers added to lower the softening temperature of CA. Without these additives the heat and pressure needed to melt the film for

lamination would damage the paper. CA lamination film typically contains 20 to 30% plasticizers by weight.

The National Bureau of Standards (NBS, now the National Institute of Standards Technology) conducted several research projects focusing on document lamination beginning in 1933 and culminating in 1959 with specifications for archival lamination films (Wilson and Forshee 1955; Wilson and Forshee 1959a; Wilson and Forshee 1959b). Research by NBS and others showed that some plasticizers are more stable than others. In fact, the plasticizer is typically more susceptible to degradation than the CA polymer (DeCroes and Tamblyn 1952; Shinagawa 1992). Therefore, to evaluate the condition of a laminated document it is helpful to identify the plasticizers present. This information may provide insight into the long-term stability of the document and may affect treatment decisions. For NARA, identifying the plasticizers can also suggest when a document was laminated since the time periods during which different films were used is known.

Fourier transform infrared (FTIR) spectroscopy is a commonly used method for identifying plasticizers (Ballany et al. 1998). Because CA has strong peaks in its FTIR spectrum that can overlap and obscure peaks from the plasticizers, it is often necessary to extract the plasticizers from the document. In addition, many of the commonly used plasticizers have similar spectra, so it can be difficult to positively identify a specific compound. The sample may also contain a mixture of plasticizers and other additives, further complicating the spectral interpretation.

Solid-phase microextraction (SPME) in combination with analysis by gas chromatography/mass spectroscopy (GC/MS) is a convenient alternative method for identifying plasticizers. Invented in the early 1990s, SPME is a simple, sensitive, and economical technique that has become popular in a wide range of applications (Pawliszyn 1998; Pawliszyn 1999; Supelco 2002). In the conservation field it has been used to study pollutant gases and volatile degradation products as well as to screen materials to be used in exhibit and storage construction (Ryhl-Svendsen

Extraction Procedure

Pierce septum on sample container.

Expose SPME fiber/extract analytes.

Retract fiber/withdraw needle.

Desorption Procedure

Pierce septum in GC inlet (or introduce needle into SPME/HPLC interface).

Expose fiber/desorb analytes.
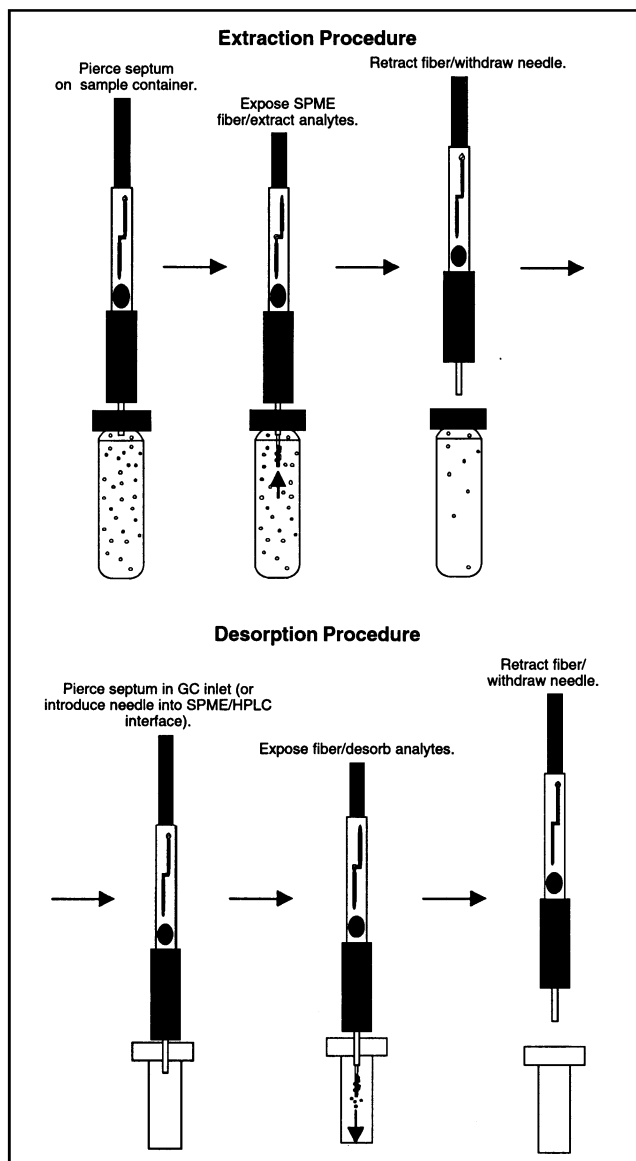
Retract fiber/withdraw needle.

Fig. 1. The plunger of a SPME fiber is pressed to expose the polymer-coated tip to a sample. After a suitable exposure time the fiber is retracted into the protective hollow needle. The fiber is then inserted into the heated injector port of a gas chromatograph (GC). The heat drives off the sample from the fiber into the GC column for analysis. The fiber is then ready to be reused. Figure used with permission of Supelco, Bellefonte, PA.

and Glastrup 2002; Ryhl-Svendsen 2003; Maines 2002). SPME is well suited for conservation uses because samples can often be collected simply and nondestructively.

This paper describes the use of SPME-GC/MS for identifying plasticizers in CA lamination films. Various sampling methods were explored to refine the procedure. Laboratory samples prepared by NBS as part of its earlier research were studied as well as other materials in the collection of the NARA's Research and Testing Laboratory. These techniques were applied to documents from the
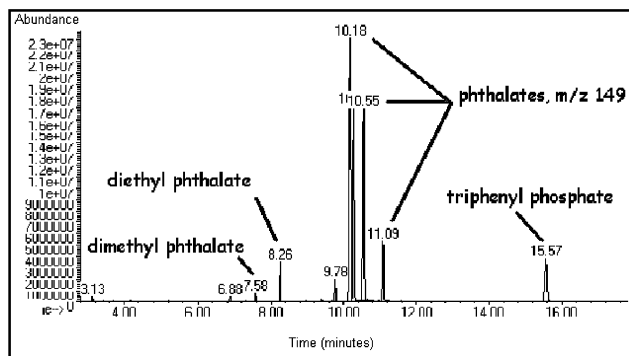

Fig. 2a. The GC separates a mixture of compounds into its components. In this total ion chromatogram (TIC) the peaks correspond to different compounds that emerge over time from the end of the GC column. These peaks are then identified using the mass spectrometer.
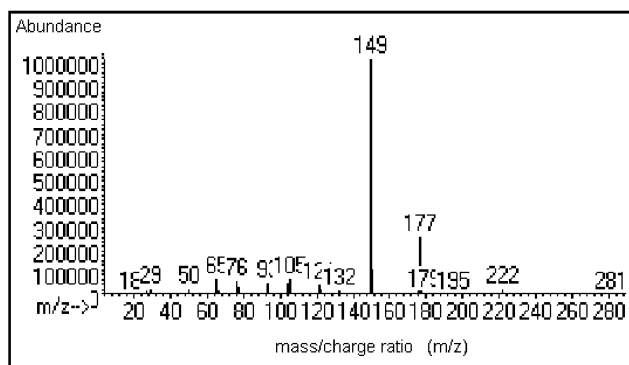

Fig. 2b. The mass spectrum of diethyl phthalate is shown. Peaks in figure 2a can be identified by comparing their mass spectra with a database of reference standards. Diethyl phthalate has strong peaks at m/z 149 and 177 in its mass spectrum. Many phthalates have only a strong peak at 149, so it is difficult to identify them based only on their mass spectra.

Louisiana Purchase that were delaminated as discussed in Part 1.

BACKGROUND

The basic steps of the SPME procedure are illustrated in figures 1 and 2. A SPME sampling device is similar to a syringe with a quartz fiber tip attached to a stainless steel plunger. The tip is coated with a polymer and is shielded inside a hollow needle. When the plunger is depressed the fiber extends, the polymer is exposed, and the sample is adsorbed onto it. After a suitable exposure time (a few seconds to a few hours, depending on the application), the fiber is retracted. To analyze the sample, the fiber is inserted into a GC (high performance liquid chromatography (HPLC) analysis is also possible). The heated injector port drives off the adsorbed compounds, which then flow into the GC column for qualitative or quantitative analysis. The total ion chromatogram (TIC) in figure 2a shows the peaks

Fig. 3. This newspaper was laminated in 1936 during the first run of the presses at the National Archives. The volatile plasticizers in the lamination film were sampled by placing a beaker upside-down on the document and slipping a SPME fiber underneath the lip of the beaker. The PDMS/DVB fiber was exposed for 40 minutes.

Fig. 4. The TIC from the laminated 1936 newspaper is shown. Several phthalate plasticizers are present as well as phenol. The other peaks are background from the beaker, the fiber, and contaminants.

from the various compounds that have been separated by the GC column. For this project individual peaks were identified by using the MS to compare their mass spectra (fig. 2b) to a database of standards. Since the fiber has been "cleaned" by heating in the injector, it is ready to be reused.

The SPME fiber can be exposed directly to a liquid, or it can extract volatiles from the headspace above the sample. Both methods were used in this study of plasticizers. Figure 3 shows a simple setup for headspace analysis. A small glass beaker was placed upside down on top of a laminated document. The sample shown is a newspaper laminated in 1936 during the first run of the lamination presses at NARA. The tip of a SPME fiber was inserted under the lip of the beaker, and the fiber was exposed for 40 minutes. The chromatogram obtained from this sample is shown in figure 4.

Phthalates (fig. 5) are commonly used as CA plasticizers (Stannett 1950). Since they are semi-volatile, they are easily detected using the headspace technique. Triphenyl phosphate (TPP), another common plasticizer, is less volatile. To detect it, a drop of ethanol was placed on the laminated document, and the tip of the fiber was inserted into the drop for a few seconds. A drop of water may be used to extract some plasticizers, but
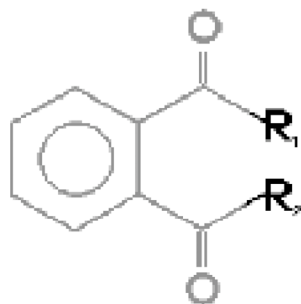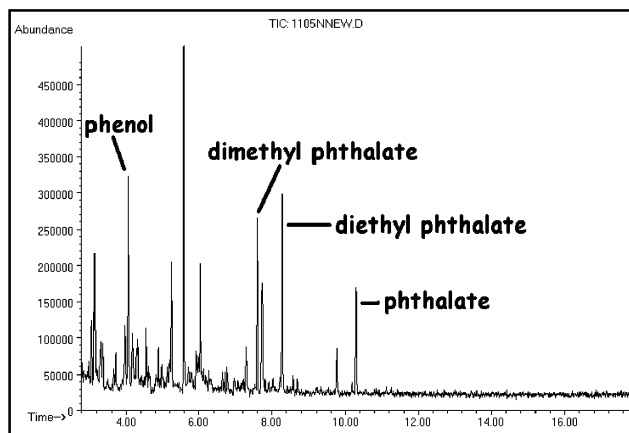

Fig. 5. The general structure of the phthalate family is shown. Phthalates are common plasticizers for CA as well as other plastics.

ethanol was necessary for TPP since it is not water-soluble.

A variety of plasticizers can be found in CA, and several types of SPME fibers are available. To determine which fibers were most effective for extracting the plasticizers a set of lamination films was studied systematically. These samples were prepared by NBS as part of their research programs in the 1950s and are now in the files of the Research and Testing Laboratory.

PROCEDURE

Five types of SPME fibers with different polymer coatings were purchased from Supelco (Bellefonte, Pennsylvania). Some fibers are better suited for certain molecular weight ranges, for polar compounds, etc. For this study the fiber types used were: polyacrylate (PA), Carbowax/divinylbenzene (CW/DVB), polydimethylsiloxane/divinylbenzene (PDMS/DVB), polydimethylsiloxane (PDMS), and Carboxen/polydimethylsiloxane (CX/PDMS).

Analysis was performed on a Hewlett-Packard (now Agilent) HP5890/5971 GC/MS with a 30-meter HP5-MS (5%-phenyl)-methylpolysiloxane column. A narrow-bore inlet liner optimized for SPME (Supelco) was installed in the injection port. This was the only modification required to use SPME on the GC/MS system. All the necessary SPME supplies, including three reusable fibers, were purchased for less than $800.

A splitless injection was made with the injector port at 250˚C and the detector at 280˚C. The oven was held at 80˚C for the first 2.5 minutes, heated at 30˚C/min to 240˚C, and held at the final temperature for 10 minutes. These program settings were based on various references, including Environmental Protection Agency methods for

the analysis of semivolatiles. Further work will help refine these setting to reduce the time needed for each sample.

As part of its research projects in the 1950s, NBS prepared experimental CA films made with various combinations of plasticizers and other additives. Samples of these films were taken by cutting a small piece approximately 1 square centimeter and placing it in a 10-ml glass vial capped with a PTFE/silicone septum (Supelco). A SPME fiber was inserted through the septum, exposed to the headspace for 10 minutes, removed, and immediately analyzed. This procedure was repeated for five SPME fiber types and various experimental films. To compare the sensitivity of the fibers the area of the plasticizer peaks was calculated using the HP ChemStation analysis program.

These semi-quantitative tests indicated that the PA, CW/DVB, and PDMS/DVB fibers were suitable for headspace detection of the plasticizers dimethyl phthalate, diethyl phthalate, and triacetin as well as phenol, discussed below. These results agree with a study of fiber types used for detecting phthalates in water (Penalver et al. 2000). The PDMS fiber was much less sensitive to phenol. For all four compounds the CX/PDMS fiber had much lower sensitivity. It is excellent, however, for studying the acetic acid that is produced by degrading CA (Rhyl-Svendsen and Glastrup 2002).

As noted above, TPP is difficult to detect by headspace sampling because of its low volatility. It was easily detected along with the phthalates by placing a drop of ethanol on the film and inserting the fiber into the drop for a few seconds.

The procedure was modified for documents and objects from which a sample could not be cut and placed in a vial. When possible, a drop of ethanol was placed on the document. For headspace sampling, a small beaker or petri dish top was placed on the document, and the fiber was slipped under the edge of the cover.

RESULTS

Figure 4 shows the results of headspace sampling from the newspaper laminated in the first run of NARA's presses in 1936. A peak for phenol is present along with the phthalates. The phenol is probably from the hydrolytic breakdown of TPP (Shinagawa et al. 1992; Glastrup 1995). This reaction occurs more readily in an alkaline environment (Muir 1984).

Figure 6 shows the TICs from two lamination films that were sampled with a PDMS/DVB fiber and an ethanol drop. The upper graph is from a sample of DuPont 88CA48 film that NARA used from the 1940s to 1956. The largest peak could not be identified. Its mass spectrum has a strong signal for m/z 149, which is common for phthalates (George and Prest 2002). Based on the film's type and date, the peak is probably bis(2-methoxyethyl) phthalate
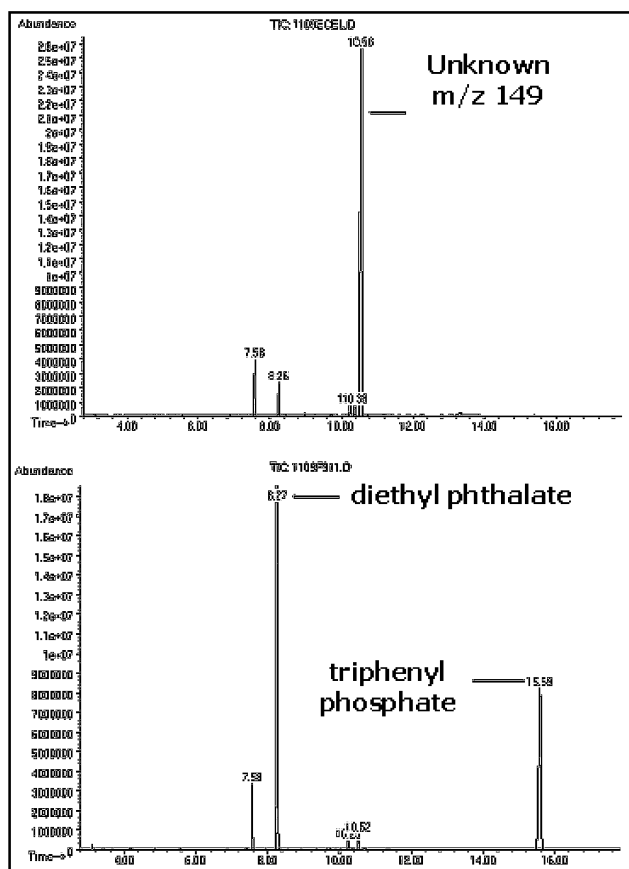

Fig. 6. The upper graph is the total ion chromatogram (TIC) of DuPont 88CA48 film with a large peak that could not be positively identified but which is probably bis(2-methoxyethyl) phthalate. The lower TIC is Celanese P911 film used by NARA after 1956. Both films were sampled with a PDMS/DVB fiber and an ethanol drop.

(Blair 1956; Stiber 1988; Conley 1998). NBS research in the 1950s showed that this plasticizer is vulnerable to degradation. As a result of these studies, NARA switched to P911 film from Celanese Corporation of America in 1956 and continued using this film into the 1980s (Gear 1958). The lower graph in figure 6 shows a TIC from P911 film. The three largest peaks were identified from their mass spectra as dimethyl phthalate, diethyl phthalate, and triphenyl phosphate.

The Louisiana Purchase documents had been delaminated and returned to storage at least one year before being analyzed with SPME. Scraps of CA were retained from the treatment and were sampled using a drop of ethanol. As shown in figure 7, dimethyl and diethyl phthalate were found as well as a number of compounds that could not be positively identified but which probably are phthalates based on the m/z 149 peak in their mass spectra. A small peak from phthalic anhydride was also found in several CA scraps. It is used to synthesize many phthalates (Wilson 1995), and its presence may indicate that a plasticizer is
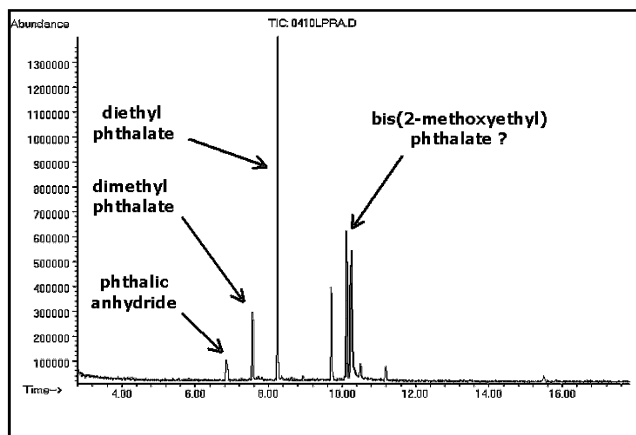
Fig. 7. Scraps of CA removed from some of the Louisiana Purchase documents during delamination were retained for analysis. Dimethyl and diethyl phthalate were present as well as a number of other compounds that are probably phthalates. Phthalic anhydride was also found. Used to synthesize phthalates plasticizers, its presence may indicate that a plasticizer is degrading. The sample was collected using a drop of ethanol and a CW/DVB fiber.

degrading (Shashoua 2001). In this project phthalic anhydride has only been detected in early CA films from the 1930s or in films that exhibited signs of deterioration.

One of the Louisiana Purchase documents was also sampled after delamination. As shown in figure 8, a PA fiber was placed on the document and covered with a top of a petri dish. The fiber was exposed for 75 minutes. The TIC in figure 9 shows that diethyl phthalate and other compounds (probably phthalates) were detected more than one year after the document had been delaminated.

CONCLUSIONS AND FUTURE WORK

This project demonstrates that SPME-GC/MS is a very useful technique for studying plasticizers in CA laminated documents. The method is simple and sensitive, and data can be collected with minimal risk to the objects. These features make SPME an attractive option for many conservation applications.

Several common plasticizers were easily identified using this approach. Further work is needed to positively identify some phthalates. NARA has recently acquired a new GC/MS system that features positive chemical ionization and retention time locking, techniques that are useful for discriminating among the many phthalates (George and Prest 2002).

The presence of phthalic anhydride or phenol may indicate that certain plasticizers are degrading. This information may be useful in assessing the condition of a laminated document before conservation treatment. Plasticizers were also detected in one document that had already been delaminated. To better understand these
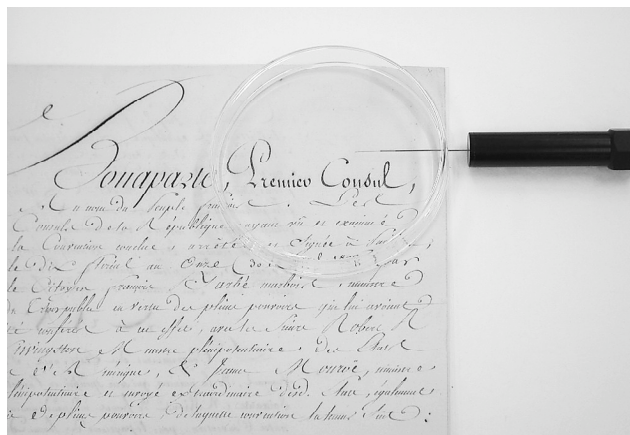

Fig. 8. This document from the Louisiana Purchase collection was analyzed more than one year after delamination. A PA fiber was placed on the document and covered with a glass petri dish. The fiber was exposed for 75 minutes before analysis.
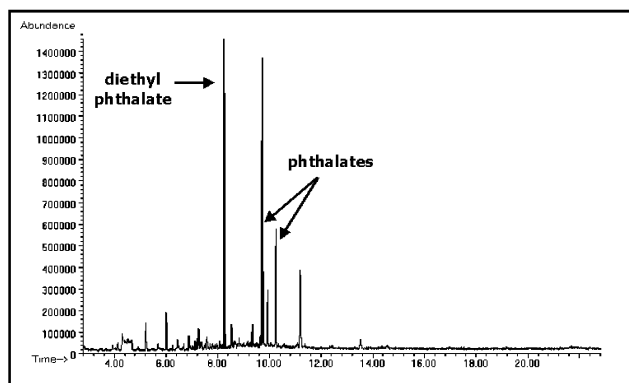

Fig. 9. Phthalate plasticizers were detected in the document shown in figure 8 more than one year after the CA was removed.

results it will be helpful to develop quantitative methods.

The practice of deacidifying documents before lamination did not become a standard procedure until the NBS studies of the 1950s. It would be interesting to explore the relationship between the hydrolysis of TPP and the pH of the document since TPP breaks down more readily in an alkaline environment.

These techniques for studying plasticizers in laminated documents can easily be adapted to many other types of objects and compounds. Thus far, the majority of work with SPME in conservation has focused on gaseous pollutants, but there are many other potential applications for this simple yet versatile technique.

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