

Characterization of the Aniline Dyes in the Colored Papers of José Posada's Prints Using Time-of-Flight Secondary Ion Mass Spectrometry to Aid in Developing a Treatment Protocol for the Removal of Pressure-sensitive Tapes

INTRODUCTION

José Guadalupe Posada (1852–1913) was a Mexican Artist active during the turn of the 20th century. He has been dubbed by many scholars as the father of modern Mexican printmaking, producing thousands of illustrations during his lifetime. Posada's work was of paramount importance to the development of modern Mexican art. In the 20th century, Mexican muralists including Diego Rivera and José Clemente Orozco drew inspiration from Posada and acknowledged his influence on their work. His *Calaveras* were his most iconic images, skeleton caricatures that he popularized, produced for *Día de Muertos* (Day of the Dead) celebrations.

The Amon Carter Museum has approximately 400 prints attributed to Posada. The collection is in remarkable condition. With many of the prints retaining their bright colors. A recent survey of the works on paper collection highlighted a group of the Posada prints as "high-priority" treatment items. These prints contain oxidized pressure-sensitive tape (PST) residue, which is penetrating and weakening the short-fibered papers. The works affected in the collection are some of Posada's broadsides (figs. 1a-e), produced when he worked with publisher Antonio Vanegas Arroyo. Broadsides are penny pamphlets—ephemeral publications covering a wide range of topics. These broadsides were produced quickly and inexpensively, and they were circulated around much of Mexico.

The dyes that give these broadsides their vivid colors are synthetic organic dyes (also known as aniline dyes), which are extremely soluble in many solvents. Unfortunately, common PST removal techniques in paper conservation involve the use of solvents. This challenge led to the following research project, which was to characterize the aniline dyes in Posada's

prints to develop a treatment protocol that would keep these highly soluble dyes intact during treatment.

CHARACTERIZING THE ANILINE DYES

ANALYSIS OF DYES

When it comes to analyzing works of art, nondestructive in situ analysis is preferred. If samples are taken, they should be so inconsequential that the integrity and the appearance of the object are unaltered. This limitation of sample size, coupled with the fact that aniline dyes have high tinting strengths (resulting in extremely low dye content within a sample), make organic dyes particularly challenging to analyze.

Analyses of organic dyes in paper are usually done using chromatographic or vibrational spectrometry techniques (Kirby and White 1996). Chromatographic techniques often require large samples and lengthy sample preparation involving dye extraction (Kirby and White 1996). Noninvasive spectroscopic methods such as infrared spectroscopy and reflectance UV/Vis spectroscopy have also been used for the analysis of dyes (Low and Baer 1977; Gillard et al. 1994; Kirby and White 1996; Casadio et al. 2010). However, these techniques are made complicated when applied to paper dye analysis due to the additional spectra from the paper substrate itself, as well as changes in the paper over time.

Raman spectroscopy has been used with some success for the nondestructive analysis of dyes (Guineau 1989; Massonnet et al. 2005). Unfortunately, the Raman signal is often swamped by the fluorescence from the colorants and other organic material present (Kirby and White 1996). Surface-enhanced Raman scattering (SERS) and Fourier transform (FT)-Raman are techniques that have been used to improve the Raman signal and reduce fluorescence in the analysis of dyestuffs. However, SERS requires the preparation and use of a SERS-active substrate, which introduces an additional step in the sample preparation process that is not always ideal (Mukhopadhyay 2010). Although FT-Raman is a suitable method for the in situ

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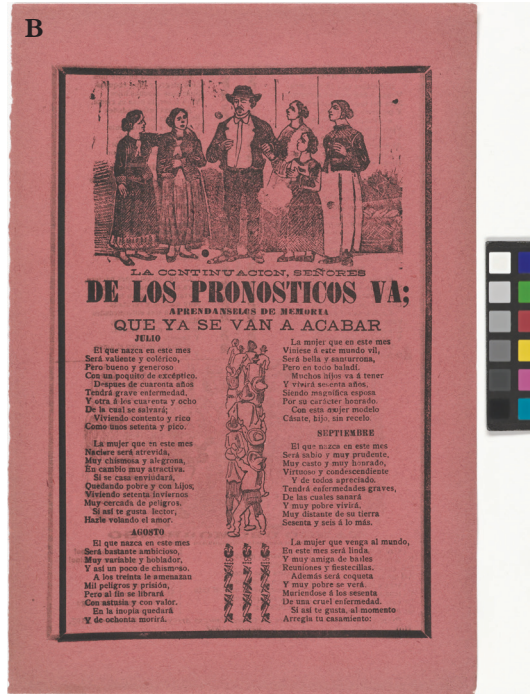


Fig. 1a. Posada, José Guadalupe (1852–1913), *Guadalupe Bejarano en las bartolinas de Belen. Careo entre la mujer verdugo y su hijo*, ca. 1890–1913, intaglio print (39.9 x 29.9 cm). Amon Carter Museum of American Art, Fort Worth, Texas, 1985.20.

Fig. 1b. Posada, José Guadalupe (1852–1913), *La continuación, señores de los pronósticos va; apréndanlos de memoria que ya se van a acabar*, 1904, intaglio print (30.3 x 20.3 cm). Amon Carter Museum of American Art, Fort Worth, Texas. Gift of Dr. and Mrs. W. W. Moorman as a memorial to their son, Robert Maxey Moorman, 1981.47.



Fig. 1c. Posada, José Guadalupe (1852–1913), *Corrido dedicado al 16 septiembre de 1897*, after 1897, intaglio print (20.3 x 29.9 cm). Amon Carter Museum of American Art, Fort Worth, Texas, 1978.84.



Fig. 1d. Posada, José Guadalupe (1852–1913), *Ya llegó calavera de la penitenciaría, no se arruguen cueros viejos oue [sic] aquí está Rafael Buendía*, ca. 1890–1913, intaglio print (40.3 x 30 cm). Amon Carter Museum of American Art, Fort Worth, Texas, 1978.182.



Fig. 1e. Posada, José Guadalupe (1852–1913), *El Mosquito Americano*, ca. 1890–1913, intaglio print (29.9 x 19.8 cm). Amon Carter Museum of American Art, Fort Worth, Texas, 1978.119.

analysis of dyes on works on paper, it is limited in its capacity to identify yellow dyes or differentiate between different blue dyestuffs (Casadio et al. 2010).

A study by Casadio et al. (2010) used FT-Raman with success to identify some of the dyes used in Posada's prints. Unfortunately, FT-Raman was not able to characterize all of the dyes, particularly the dyes in the yellow Posada prints. Raman techniques interrogate the vibrations of bonds within a molecule, and some dyes (especially yellows) do not produce unique vibrational frequencies to identify them from a list of possibilities. In this study, a mass spectrometry method was chosen to complement the results obtained from the Casadio et al. (2010) FT-Raman study of Posada's prints.

TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a surface analytical technique capable of collecting chemical information from inorganic and organic materials. It requires extremely small samples and little to no sample preparation. TOF-SIMS has been used in the cultural heritage field in a variety of applications, including the study of polymers (Abel

and Coppiters 2008), investigating surface changes on textiles (Carr, Mitchell, and Howell 2004), organic pigment analysis (Van Ham et al. 2005), and the identification of dyes on textiles (Lee et al. 2008). In TOF-SIMS, the surface of the sample is bombarded by high-energy ions, leading to the ejection of both neutral and charged (+/-) species from the surface of the sample (fig. 2). These ejected molecules are accelerated to a specific energy at a fixed distance and detected with an analyzer, producing spectra. TOF-SIMS is a type of mass analyzer that can provide substantially higher sensitivity and mass resolution, and a much greater mass range (Walker 2013).

SAMPLES

The appropriate experimental parameters for TOF-SIMS analysis were set up by first testing the technique on dye samples taken from a dye manual contemporary to Posada's prints (fig. 3a). This dye manual, *Dyeing of Paper Pulp* by Julius Erfurt (1901) contains 157 swatches made from 34 different synthetic dyes and their mixtures. Encased in a book, the swatches remained protected from light, keeping their colors intense. Spectra were obtained from samples cut from this book. These reference samples were instrumental in setting the appropriate experimental parameters for TOF-SIMS

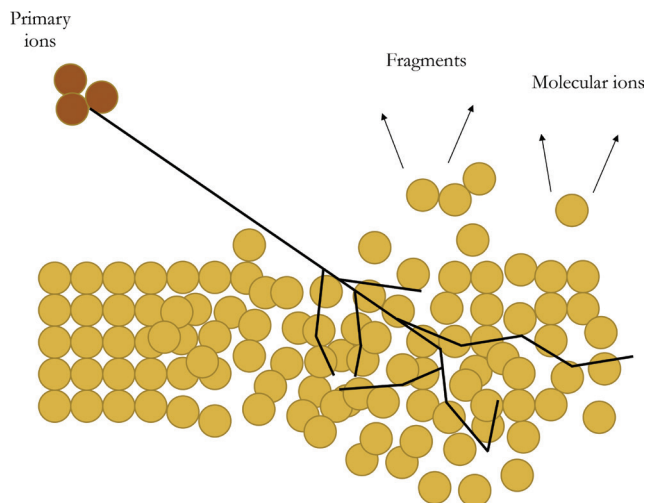


Fig. 2. Diagram showing secondary ion production during TOF-SIMS analysis. Adapted from Mazel and Richardin (2009).

analysis and also proved useful in gauging the feasibility of using TOF-SIMS with aniline dyes on paper (fig. 3b).

Five posada prints from the Amon Carter Museum's collection were selected for analysis based on color and dye intensity. They are listed here by color and accession number: Magenta (1978.84), Scarlet (1981.47), Orange (1986.20), Green (1978.182), and Yellow (1978.119). Each print was sampled by gentle scraping a tungsten needle over an existing loss and gathering the fibers onto double-sided copper tape.

INSTRUMENTATION

TOF-SIMS spectra were acquired using an ION TOF IV spectrometer (ION TOF Inc., Chestnut Hill, NY) equipped with a Bi liquid metal ion gun. The instrument consists of a load lock for sample introduction, preparation, and analysis chambers each separated by a gate valve. The pressure of the preparation and analysis chambers were maintained at less than 8×10^{-9} mbar. The primary Bi⁺ ions had a kinetic energy of 25 keV and were contained in an approximately 100-nm-diameter probe beam, which was rastered over either (500 × 500) μm^2 or (100 × 100) μm^2 areas during spectra acquisition. All spectra were acquired using a total ion dose less than 10^{11} ions/cm², which is within the static SIMS regime, and charge compensation was employed. The secondary ions were extracted into a time-of-flight mass spectrometer using a potential of 2000 V and were reaccelerated to 10 keV before reaching the detector. At least six positive and negative ion spectra were acquired for each sample. The peak intensities were reproducible to within $\pm 15\%$ from scan to scan.

RESULTS

SIMS provides both elemental and molecular information on a submicron scale. Each peak in the spectra is a data point

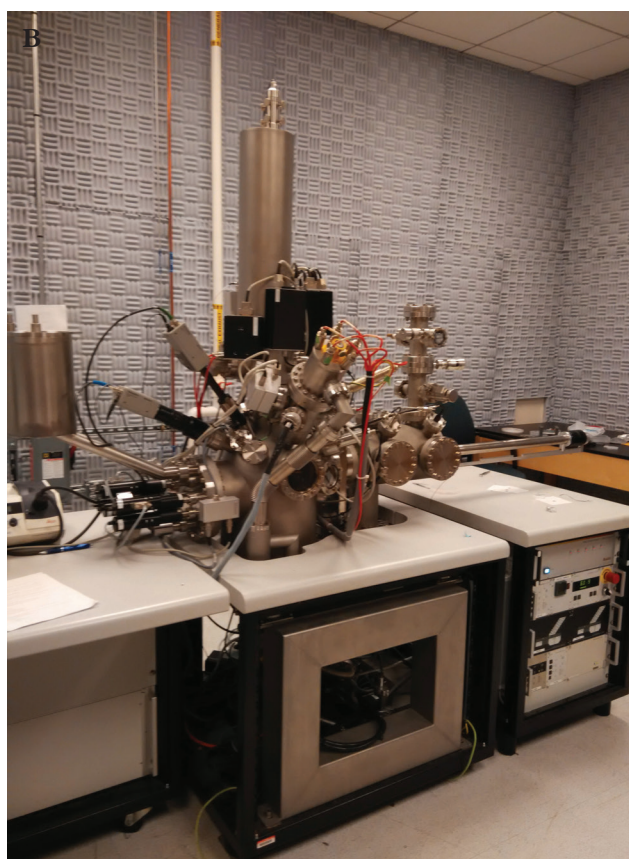
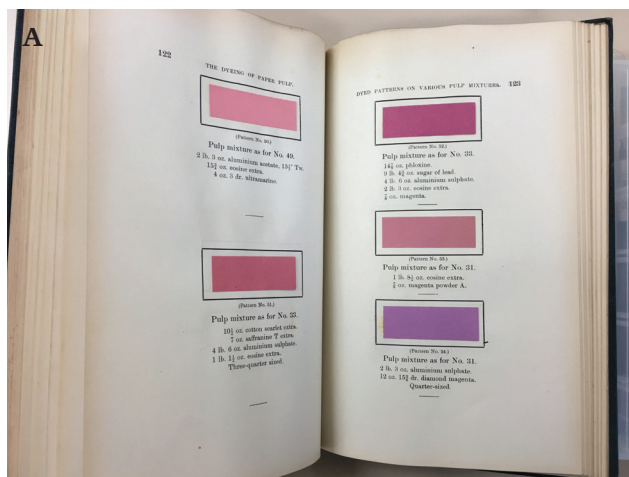


Fig. 3. (a) Dye swatches from the dye manual *Dyeing of Paper Pulp* by Erfurt (1901). (b) TOF-SIMS instrument at University of Texas, Dallas.

(mass-to-charge ratio or m/z) that relates to a particular structural/chemical fragment. To identify the components in a sample, the ions in the spectra must first be identified. These ions indicate how the molecule breaks apart. Working backward, it is then possible to establish the molecular structure from which these ions came.

Aided by the Casadio et al. (2010) FT-Raman study, which includes a table of 20 widely used dyes in the 19th century

paper industry, together with historical papers and books listing commonly used aniline dyes (Schweppe 1987), the dyes in the Posada samples were successfully characterized through a process of deductive reasoning.

The samples in this study have two components: the paper and the dye. It is necessary to first determine the common ions associated with the paper, after which the remaining ions are then used to ascertain which organic dyes are present in the sample. The fibers of the five Posada prints have common *m/z* peaks, indicating that these peaks come from the paper, and the papers are most likely the same/similar (probably wood pulp). The remaining peaks are the unique mass-to-charge peaks for each fiber that come from the dye (table 1).

Table 2 shows TOF-SIMS analysis for all five Posada prints, for which the accession number, paper color, TOF-SIMS result, and unique *m/z* peaks associated with the dyes are given for each print. The known vulnerabilities of each identified dye are also listed. Orange II, Cotton Scarlet, Phloxine BBN, Malachite Green, and Metanil Yellow were detected. The successful identification of Metanil Yellow in the yellow

Posada print is significant, as yellow colorants are notoriously difficult to characterize. These findings correspond to the results obtained from the Casadio et al. (2010) FT-Raman study of the dyes in Posada's prints, further validating the methodology used in this project. These results also confirm that TOF-SIMS is a suitable method for the identification of dyes in works of art on paper. This information provided a better understanding of the known sensitivities of these dyes with regard to treatment.

DEVELOPING A TREATMENT PROTOCOL FOR THE REMOVAL OF OXIDIZED PSTS AND ADHESIVES

EXPERIMENTAL SETUP

Surrogate Samples

A group of surrogate samples were made using ephemera from the turn of the 20th century that contained aniline dyes (a similar time frame to Posada's prints). A group of colored and noncolored papers were chosen. The samples were divided to allow the testing of a variety of tapes/adhesives, as well as a variety of removal methods (fig. 4).

Orange Fiber (+)	Orange Fiber (-)	Scarlet Fiber (+)	Scarlet Fiber (-)	Magenta Fiber (+)	Magenta Fiber (-)	Green Fiber (+)	Green Fiber (-)	Yellow Fiber (+)	Yellow Fiber (-)
57	62	69	63	69	35	69	71	69	71
69	70	71	66	71	37	71	80	71	80
71	78	73	70	95	79	95	96	73	265
95	86	95	78	147	81	97	127	95	281
133	109	147	85	178	127	109	137	109	311
147	127	191	110	207	175	147	183	147	325
207	140	207	140	221	265	207	203	165	339
221	155	221	142	281	269	221	223	207	473
281	188	265	188	343	357	281	253	221	
341	214	267	190	358	473	283	257	265	
359	222	281	224			301	265	279	
368	237	305	250			329	281	281	
	245	359	300			343	293		
	258	523				358	309		
	260	551				372	311		
	271					385	325		
	273						353		
	281						357		
	283								
	297								
	392								

Table 1. Unique Data Points (*m/z* Peaks) for the Five Posada Prints Analyzed with TOF-SIMS

Accession Number	Color	<i>m/z</i> Peaks (Positive)	<i>m/z</i> Peaks (Negative)	TOF-SIMS Analysis Results	Vulnerabilities
1985.20 	Orange	57, 133, 341, 359, 368	62, 70, 78, 86, 109, 127, 140, 155, 188, 214, 222, 237, 245, 258, 260, 271, 273, 281, 283, 297, 392	Orange II (Acid Orange 7)	Soluble in water, ethanol, glycol ethers; sensitive to pH changes
1981.47 	Scarlet	73, 191, 265, 267, 305, 359, 523, 551	63, 66, 70, 78, 85, 110, 140, 142, 188, 190, 224, 250, 300	Cotton Scarlet (Acid Red 73)	Soluble in water and alcohol
1978.84 	Magenta	178, 343, 358	35, 37, 79, 81, 127, 175, 265, 269, 357, 473	Phloxine BBN (Acid Red 92)	Soluble in water
1978.182 	Green	97, 109, 283, 301, 329, 343, 358, 372, 385	71, 80, 96, 127, 137, 183, 203, 223, 253, 257, 265, 281, 293, 309, 311, 325, 353, 357	Malachite Green (Basic Green 4)	Soluble in water, ethanol, glycol ethers
1978.119 	Yellow	73, 109, 165, 265, 279	71, 80, 265, 281, 311, 325, 339, 473	Metanil Yellow (Acid Yellow 36)	Soluble in water, alcohol, benzene, ether, acetone

Table 2. List of Posada prints analyzed with TOF-SIMS

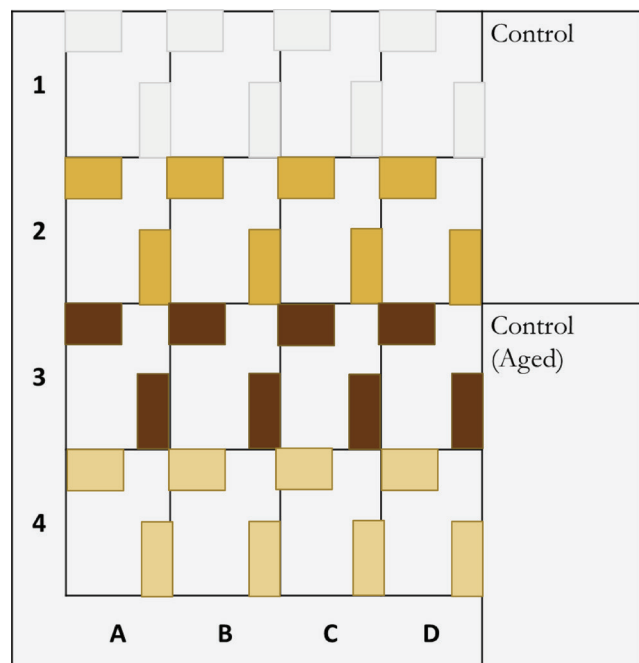


Fig. 4. Samples were divided according to this diagram, allowing the testing of the removal of a variety of tapes/adhesives, as well as a variety of methods. (1) Scotch magic tape: acetate backing; acrylic adhesive; (2) 3M 2214 paper tape: crepe paper backing; rubber adhesive; (3) gummed brown paper tape: Kraft paper backing; starch adhesive; (4) Slime rubber cement: rubber-based adhesive; (A) local application of solvent and suction table; (B) solvent and Gellan gel; (C) Gore-Tex with solvent; (D) extras.

Artificial Aging

After the tape/adhesives were placed, the samples underwent thermal aging at 80°C for 35 days until the tape deterioration mimicked the deterioration seen on the Posada prints (Stage II: oxidation stage). At the oxidation stage, the tape adhesive has begun to degrade, causing it to darken, turn sticky and oily, and seep into the paper—causing translucency.

SELECTION OF SOLVENT

Solvents Tested

Using the Teas chart, a variety of solvents were tested ranging in polarities, including xylene, toluene, methylene chloride, chloroform, acetone, and methyl ethyl ketone. As adhesive ages, it becomes more polar, requiring more polar solvents to remove. The higher the polarity of the solvent, the more likely the dyes in the paper will solubilize. The challenge in this study was finding a solvent that would solubilize the adhesive while keeping the dyes intact.

Absorbency and Dye Stability Tests

The first priority was to identify the solvents that would work well with the paper and not solubilize the dyes. Absorbency tests were conducted on the controls: the samples were

placed over Whatman filter paper, and a drop of solvent was deposited on the surface. The time taken for the solvent to be absorbed in the paper was measured. The formation of tide lines and dye bleed was also noted to keep track of dye solubility (figs. 5a-c).

Preliminary Adhesive Reduction Tests

To identify the solvents capable of solubilizing the various adhesives, preliminary adhesive reduction tests were conducted. The samples were flooded with solvent and the adhesive scraped off with a spatula. Effectiveness in removing the adhesive and dye bleed were considered. A handheld UV torch was used to keep track of dye bleeding and adhesive residue in the paper.

Solvents Selected for Each Color/Adhesive Combination

Following these tests, the selected solvents for each color/adhesive combination were predominately xylene, methylene chloride, toluene, and chloroform, which were among the least polar of the solvents originally tested (table 3).

PRIOR TO TREATMENT

Before treatment, tape carriers were removed mechanically with heat where possible. Gellan gel samples were humidified using a Gore-Tex sandwich. These steps were taken to simulate real treatment scenarios.

LOCAL APPLICATION OF SOLVENT AND SUCTION

Technique

While on the suction table, the selected solvent was locally applied using a dropper or swab. Suction would then pull the solvent and solubilized adhesive through the paper onto a blotter.

Observations

This method was very effective in removing the solubilized adhesive residue from the samples. It showed good results on samples with and without carriers still attached (fig. 6a). Tide lines formed during treatment but were mostly controllable; some bleeding of the pink and yellow dyes occurred (fig. 6b). This method is not suitable for fragile samples, as it can cause additional physical stress and damage.

SOLVENT AND GELLAN GEL

Technique

Gellan gel was tested due to its availability in the Amon Carter Museum's conservation lab. A 3% Gellan gel was made to ensure high absorption and minimize the release of moisture from the gel. Figure 7 shows the treatment setup. Solvent was applied to the underside of the gel and placed on the samples in 15-minute applications.¹



Fig. 5a. Conducting absorbency and dye stability tests on a control sample.

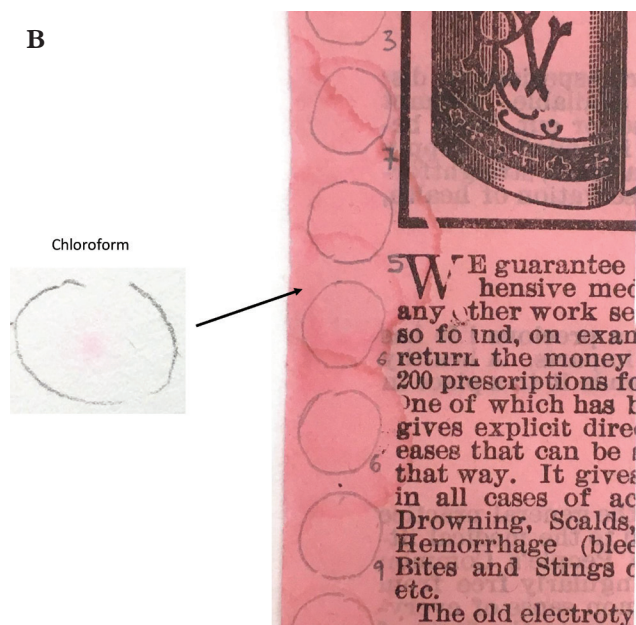


Fig. 5b. Dye bleeding of the pink sample during chloroform testing; solubilized dye captured on Whatman filter paper.

Observations

Using solvent with Gellan gel did not produce good results. The solvent, when brushed on, did not penetrate the gel, resulting in its immediate release once the loaded gel was

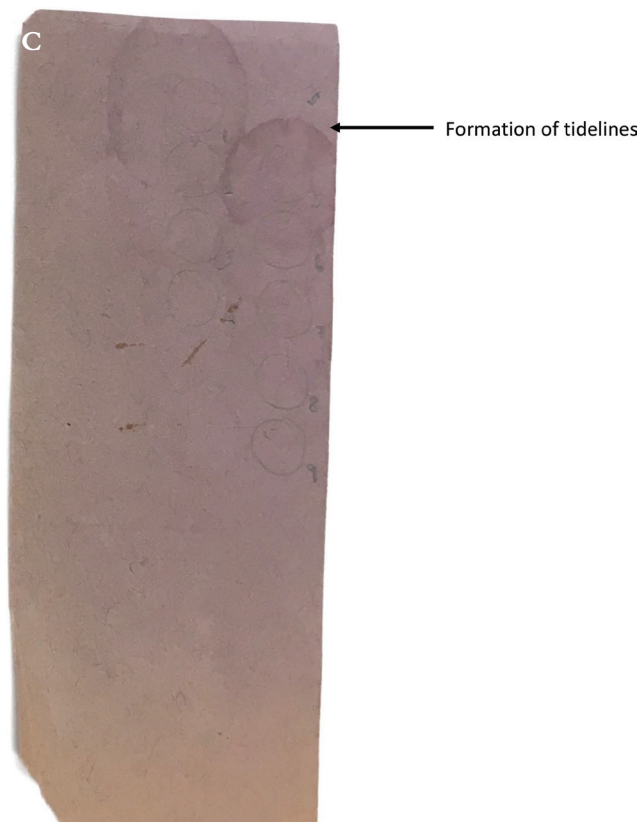


Fig. 5c. An example of tide lines on the purple sample during absorbency and dye stability tests.

applied to the surface of the sample. There was no controlled release of the solvent. As such, this treatment was not very effective, especially for samples with carriers still attached. Severe tide lines were noted in many samples (due to the pooling of the solvent), and solubilization of the dyes occurred, causing the dyes to be absorbed into the gel matrix (figs. 8a-b). Some samples showed a visible change in color in treated areas, which was unacceptable.

This experiment showed that solvents not miscible in water could not be incorporated into the Gellan gel matrix, preventing the formation of a functional solvent gel. Other possible variations to this method could be the use of an intermediate solvent that can also bond to the water in the gel or trying different gels such as agarose or xanthan. However, Gellan gel is extremely effective for the removal of brown paper tape, requiring no manipulation of the samples, as the carrier and adhesive lift off with the gel as a single unit.

	Pink	Purple	Yellow	Plain	Green
Clear tape	Xylene	Methylene chloride	Methylene chloride	Chloroform	Toluene
Masking tape	Xylene	Xylene	Xylene	Methylene chloride	Toluene
Rubber cement	Xylene	Xylene	Xylene	Methylene chloride	Toluene

Table 3. Selected Solvents for Each Color/Adhesive Combination

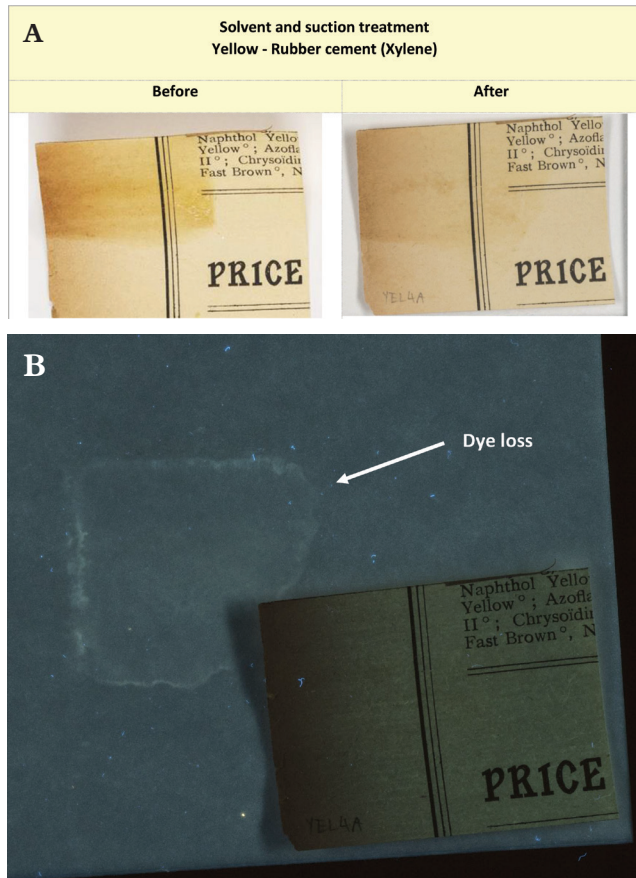


Fig. 6. (a) Before and after solvent and suction treatment images of the yellow rubber cement sample. (b) Although solvent and suction was effective, dye loss was observed and can be seen clearly under UV light.

GORE-TEX WITH SOLVENT

Technique

The Gore-Tex membrane has a pore size of 0.2 μm , allowing ultrafine particles to permeate through the membrane (Purinton and Filter 1992). Theoretically, this would allow the controlled release of solvent.² Initial testing confirmed that the tested solvents would not affect the Gore-Tex or the polyester to which it is bonded.

Figure 9a shows the setup for the Gore-Tex sandwich that was placed on the samples in 12-minute intervals.³ An interleaving



Fig. 7. Diagram showing solvent gel setup.

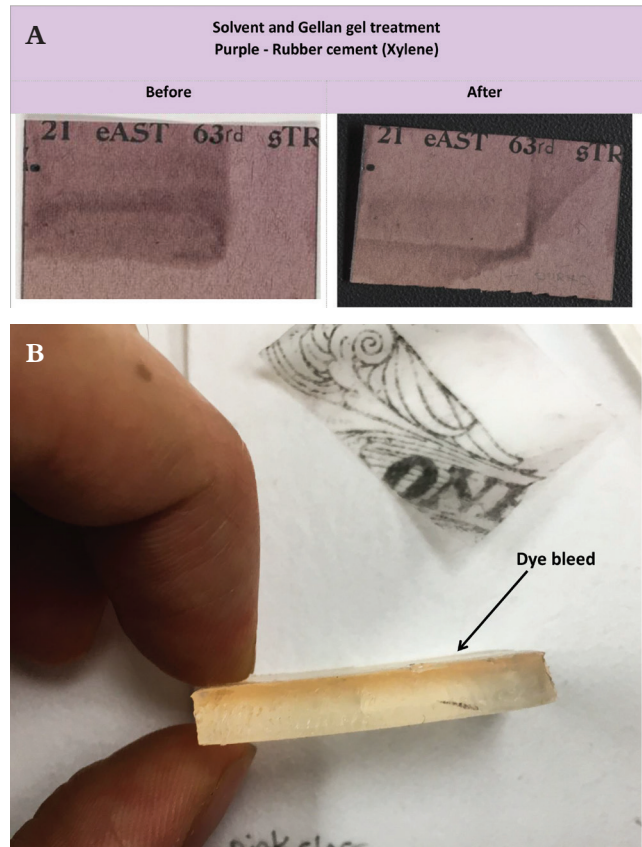


Fig. 8. (a) Before and after solvent and Gellan gel treatment images of the purple rubber cement sample. (b) Dye transfer observed in Gellan gel after treatment.

layer of Japanese paper was applied over the adhesive to absorb the swelled adhesive. As the adhesive swelled, the paper was removed and any remaining surface adhesive was scraped off using a spatula (fig. 9b). The Japanese interleaving and Gore-Tex were changed as needed. Excess weight should not be used in this process, as too much pressure will force the solvent through the membrane. Solvent-saturated blotter (not overly wet or dripping) was used to introduce solvent to the object.

Observations

The use of Gore-Tex and solvent was an effective method for the reduction of adhesives (figs. 10a-b). Staining was reduced, and no dye bleeding and minimal tide lines (controllable) occurred. The method was effective on samples with and without carriers. Treatment times were approximately 10 to 15 applications of 12 minutes each and could go longer with a greater improvement in results.

SUMMARY OF TECHNIQUES

Figure 11 shows a summary of the three methods tested. It is important to emphasize that the goal of this research is to

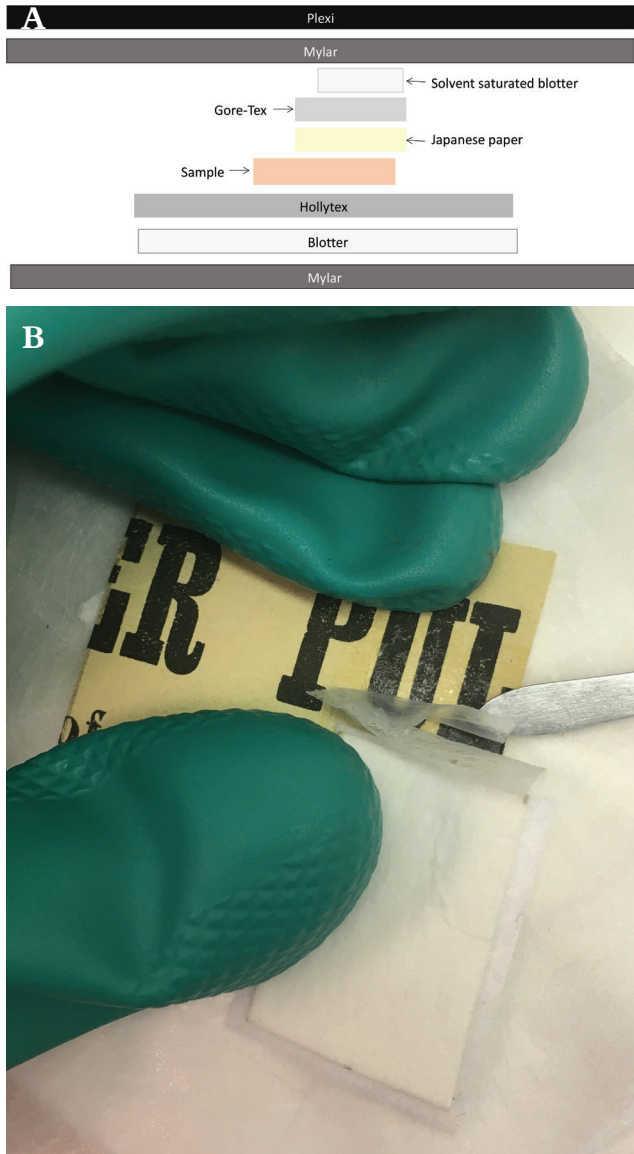


Fig. 9. (a) Diagram showing Gore-Tex setup. (b) Removing the carrier while keeping the Gore-Tex sandwich in place.

reduce the adhesive on the prints, not to reduce staining; that achievement would be considered a bonus. Due to the gentle and effective treatment provided by the Gore-Tex option, as well as the lack of dye bleeding, the methodology was adjusted to see if better results could be achieved.

PERFECTING THE GORE-TEX TECHNIQUE

Techniques

A second set of samples (green) were made following the same parameters. This time, two methods were tested: the single Gore-Tex sandwich applied as described before and a double Gore-Tex sandwich applied to the recto and the verso



Fig. 10. (a) Visible reduction of surface adhesive on yellow masking tape after four 12-minute applications of Gore-Tex sandwich (xylene). (b) Before and after Gore-Tex and solvent treatment images of the purple rubber cement sample.

<p><u>Solvent and suction</u></p> <ul style="list-style-type: none"> • Effective adhesive removal • Effective stain reduction • Bleeding of dye • Tidelines 	<p><u>Gellan gel and solvent</u></p> <ul style="list-style-type: none"> • Moderate adhesive removal • Moderate stain reduction • Bleeding of dye • Severe tidelines • Good for brown paper
<p><u>Gore-Tex with solvent</u></p> <ul style="list-style-type: none"> • Effective adhesive removal • Moderate stain reduction • No dye bleed • Minimal tidelines 	

Fig. 11. Summary of the techniques tested.

of the samples. Interleaving paper was applied only to the recto. Application times remained at 12-minute intervals. After absorbency, dye stability tests, and adhesive removal tests, Toluene was selected as the appropriate solvent for clear tape, masking tape, and rubber cement removal on the green samples.

Single Gore-Tex Sandwich Results

The single Gore-Tex sandwich results were again extremely promising. Table 4 shows the before and after treatment images of the samples. Results were obtained after 16 to 20 (12- minute) applications. There was a marked reduction of adhesive and staining of all three adhesives. Although tide lines did form, they can be attributed to the Gore-Tex sandwiches being cut to the exact size of the treated area. As the adhesive solubilized, it spread laterally in the support. This can be avoided by cutting the Gore-Tex larger (all round) than the treated area.

Double Gore-Tex Sandwich Results

The double Gore-Tex sandwich results showed extremely effective reduction of adhesive residue and staining in the samples (table 5). Results were also achieved at a much faster rate: 8 to 16 (12-minute) applications. Once again, tide lines formed due to the size of the Gore-Tex applied, which can be reduced as mentioned earlier. Table 5 shows the before- and after-treatment images of the samples. The spectrophotometer readings of the control area and the taped area after treatment are also listed, showing the

similarity in L*, a*, and b* values. Most of the readings have less than a 1.0 difference, indicating that the after-treatment areas are visibly and numerically identical to the controls.

CONCLUSION

TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY

TOF-SIMS was found to be an effective method for the analysis of dyes on paper. By characterizing the dyes, there was a better understanding of the sensitivities of the aniline dyes in Posada's prints—directing solvent choices for safe treatment.

CHOOSING THE SOLVENT

Less polar solvents, such as toluene, xylene, methylene chloride, and chloroform, were the solvents of choice for most dye and adhesive combinations. Table 6 shows the effectiveness of various solvents on the three tapes/adhesives from nonpolar options to more polar, without considering the dyes in the paper. The threshold limit values in parts per million are also listed to aid in making an informed solvent choice. Using this table, together with the understanding of the dye sensitivities in the paper, it is possible to get a solid starting point for choosing solvents. It is important to use appropriate personal protective equipment and ventilation when working with solvents. During this study, toluene was found to be the most effective solvent and may serve as a good starting point.

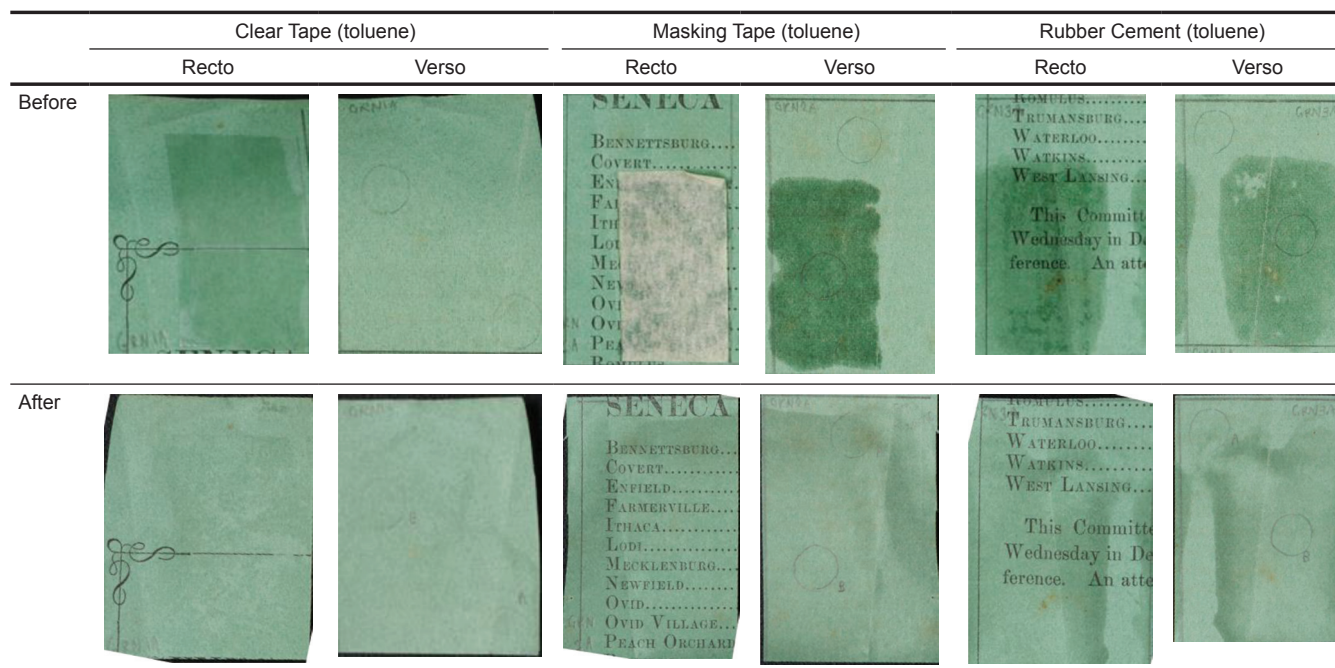


Table 4. Before- and After-treatment Images of the Samples Using the Single Gore-Tex Sandwich Method

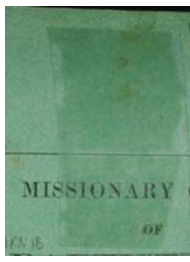

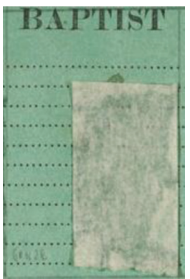



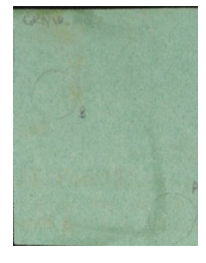
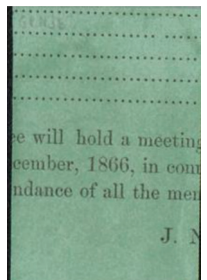

	Clear Tape (toluene)			Masking Tape (toluene)			Rubber Cement (toluene)			
	Recto	Verso		Recto	Verso		Recto	Verso		
Before										
After										
	L*	a*	b*	L*	a*	b*	L*	a*	b*	
Control	66.63	-13.63	9.94	66.99	-13.93	9.62	66.99	-14.29	9.73	
Tape (AT)	66.48	-13.55	10.22	64.56	-14.21	10.23	65.53	-14.38	10.08	

Table 5. Before- and After-treatment Images of the Samples Using the Double Gore-Tex Sandwich Method

However, it is important to remember that absorbency and dye stability tests are paramount.

TREATMENT METHODS

Gore-Tex with solvent treatment was extremely effective. Using a double Gore-Tex sandwich achieved excellent results while decreasing treatment times. Lateral movement of the adhesive will occur, and it is recommended to cut Gore-Tex larger (all round) than the treated area. With Gore-Tex

treatment, no bleeding of the dyes occurred. This leads to the idea that more polar solvents can be considered for use. Please do appropriate testing before treatment.

Unfortunately, Gore-Tex is no longer manufactured, but a comparable option is now available through Conservation-by-Design, called *Hydra Air PTFE*. It is made using the same materials but has a pore size of $2 \mu\text{m}$. It would be worth testing with a less saturated blotter to reduce the rate of solvent transfer. Finally, this is the methodology that is being used on the Amon Carter Museum's Posada collection (fig. 12).

	Clear Tape	Masking Tape	Rubber Cement	Threshold Limit Value (ppm)
Toluene	Very effective	Very effective	Very effective	100 (N,S)
Xylene	Very effective	Very effective	Moderately effective	100 (S)
Methylene chloride	Very effective; dissolves carrier	Very effective	Moderately effective	100 (N)
Chloroform	Very effective	Very effective	Moderately effective	10 (N,C)
Acetone	Very effective; dissolves carrier	Ineffective	Moderately effective	750 (N)
Methyl ethyl ketone	Very effective; dissolves carrier	Ineffective	Moderately effective	200 (N)

Effective Ineffective

N = Narcotic
C = Chronic
S = Skin

Table 6. Effectiveness of the Solvents on the Three Adhesives Tested

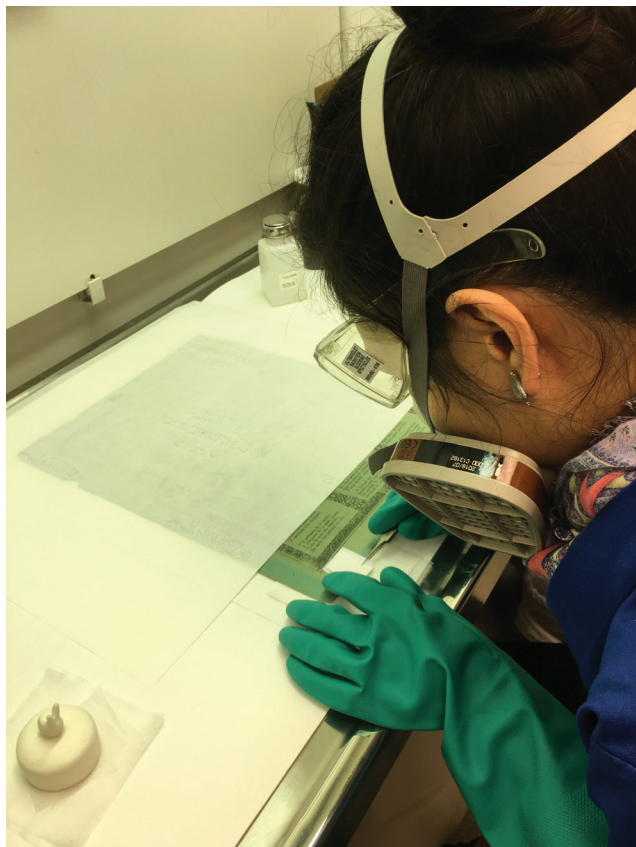


Fig. 12. Treating a Posada print in the Amon Carter Museum of American Art's collection using Gore-Tex and solvent.

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NOTES

1. Solvent gel treatment methodology was developed from research done by Vallieres (2013).
2. A study was conducted by the authors exploring the use of solvent vapor to remove masking tape adhesive from dyed paper. Two samples were placed in solvent vapor chambers (one in acetone vapor and one in ethanol vapor) and observed over time (approximately 655 hours). Using a digital microscope and TOF-SIMS analysis, it was determined that ethanol or acetone fuming successfully removed masking tape adhesive (3M 2214) from the surface of the samples (dissolved by solvent vapor) and that few other changes in the samples occurred. Ions indicative of dye remained present in all treated samples. $C_xH_y^+$

decreased after treatment, showing that dirt is also removed from the samples. This experiment gave rise to the idea of using Gore-Tex as a more practical treatment option: introducing solvent in vapor form while reducing treatment time.

3. Gore-Tex treatment methodology was developed from various techniques used by Ash (1993).

REFERENCES

- Abel, M. L., and C. Coppiters. 2008. Conservation of polymers: A view to the future. *Surface Interface Analysis* 40 (3-4): 445-449.
- Ash, N. 1993. The use of Gore-Tex to transmit solvent vapors in the treatment of drawings by Henry Ossawa Tanner. *AIC Book and Paper Group Annual* 12: 1-4. <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v12/bp12-01.html>.
- Carr, C. M., R. Mitchell, and D. Howell. 2004. Surface chemical investigation into the cleaning procedures of ancient tapestry materials. Part 1. *Journal of Material Science* 39 (24): 7317-7325.
- Casadio, F., K. Mauck, M. Chefitz, and R. Freeman. 2010. Direct identification of early synthetic dyes: FT-Raman study of the illustrated broadside prints of José Guadalupe Posada (1852-1913). *Applied Physics A* 100 (3): 885-899.
- Erfurt, J. 1901. *The dyeing of paper pulp*. Translated by J. Hübner. London, England: Scott, Greenwood & Co.
- Gillard, R. D., S. M. Hardman, R. G. Thomas, and D. E. Watkinson. 1994. The detection of dyes by FTIR microscopy. *Studies in Conservation* 39 (3): 187-192.
- Guineau, B. 1989. Non-destructive analysis of organic pigments and dyes using Raman microprobe, microfluorometer or absorption microspectrophotometer. *Studies in Conservation* 34 (1): 38-44.
- Kirby, J., and R. White. 1996. The identification of red lake pigment dyestuffs and a discussion of their use. *National Gallery Technical Bulletin* 17: 56-80.
- Lee, Y., J. Lee, Y. Kim, S. Choi, S. W. Ham, and K. J. Kim. 2008. Investigation of natural dyes and ancient textiles from Korea using TOF-SIMS. *Applied Surface Science* 255 (4): 1033-1036.
- Low, M. J. D., and N. S. Baer. 1977. Application of infrared Fourier transform spectroscopy to problems in conservation. *Studies in Conservation*, 22 (3): 116-128.
- Massonnet, G., P. Buzzini, G. Jochem, M. Stauber, T. Coyle, C. Roux, J. Thomas, H. Leijenhorst, Z. Van Zanten, K. Wiggins, C. Russel, S. Chabli, and A. Rosengarten. 2005. Evaluation of Raman spectroscopy for the analysis of colored fibers: A collaborative study. *Journal of Forensic Sciences* 50 (5): 1028-1038.
- Mazel, V., and P. Richardin. 2009. ToF-SIMS Study of Organic Materials in Cultural Heritage: Identification and Chemical Imaging. In *Organic Mass Spectrometry in Art*

and *Archeology*, eds. M. Perla Colombini and F. Modugno. Chichester, West Sussex, UK: John Wiley & Sons. 433-457.

Mukhopadhyay, R. 2010. The art of Raman. *Chemistry World* 7: 44-47.

Purinton, N., and S. Filter. 1992. Gore-Tex: An introduction to the material and treatments. *AIC Book and Paper Group Annual* 11: 141-155.

Schwepe, H. 1987. *Practical information for the identification of early synthetic dyes: Practical hints on dyeing with early synthetic dyes*. Washington, DC: Smithsonian Institution.

Van Ham, R., L. Van Vaeck, F. Adams, and A. Adriaens. 2005. Feasibility of analyzing molecular pigments in paint layers using TOF S-SIMS. *Analytical and Bioanalytical Chemistry* 383: 991-997.

Vallieres, J. 2013. Gellan gum: Investigating applications as a solvent gel. Research project submitted to the Department of Art in conformity with the requirements for the degree of Master of Art Conservation, Queen's University, Kingston, Ontario, Canada.

Walker A. V. 2013. Secondary ion mass spectrometry. In *Elsevier reference module in chemistry, molecular sciences and chemical engineering*, ed. J. Reedijk. Waltham, MA: Elsevier.

FURTHER READING

Chen, K., M. Leona, and T. Vo-Dinh. 2007. Surface-enhanced Raman scattering for identification of organic pigments and dyes in works of art and cultural heritage material. *Sensor Review* 27 (2): 109-120.

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