Characterization of Aniline Dyes in the Modern Colored Papers and the Prints of José Posada: A Collaboration with Conservators at the Amon Carter Museum of American Art

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Amon Carter Museum of American Art

1. Introduction - José Guadelupe Posada (1852-1913)

- Mexican Artist active during the turn of the 20th century.
- Dubbed by many scholars as the "Father of Modern Mexican Printmaking".
- Posada producted thousands of illustrations (est. 2000 – 20,000).
- Posada's work extremely influential and paramount to the development of modern Mexican art, influencing many artists including Diego Riviera and Jose Clemente Orozco.
- Most iconic imagery is *Calavaras* - skeleton caricatures. They appear everywhere, particularly during Day of the Dead celebrations.

La Calavera Catrina

1. Introduction – Posada and the Amon Carter Museum

- Approximately 400 prints attributed to Posada and 25 printing blocks.
- Collection is in reasonable condition with many broadsides retaining their vivid colors.
- However, multiple items flagged as "High priority treatment" items.
  - Unstable due to the presence of oxidised pressure-sensitive tape residue.
- Prints contain highly soluble aniline dyes.

Problem common pressure-sensitive tape removal techniques involve the use of solvents.

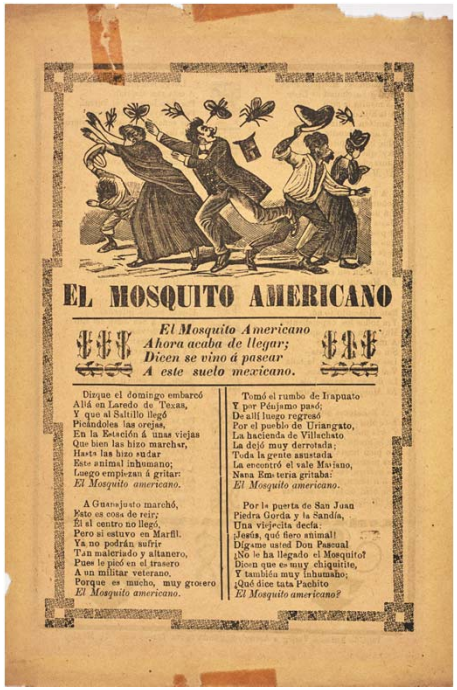
La calavera Moreliana, (n.d.)

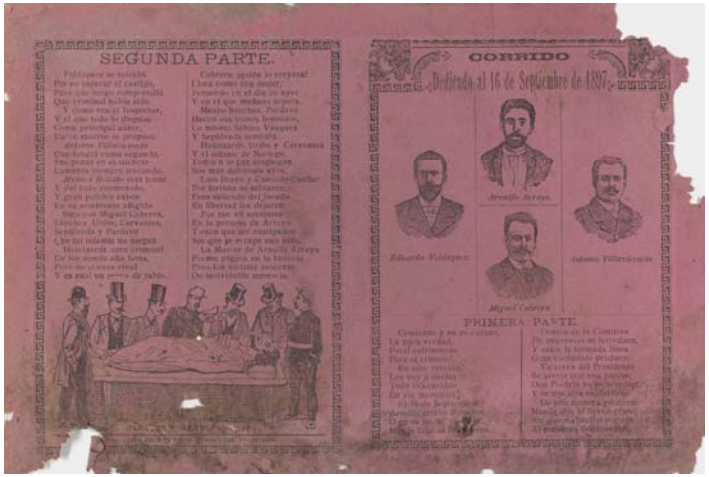
El Mosquito Americano, ca. 1890-1913

Ya llegó calavera de la penitenciaria… (n.d.)

La calavera clerical, 1902

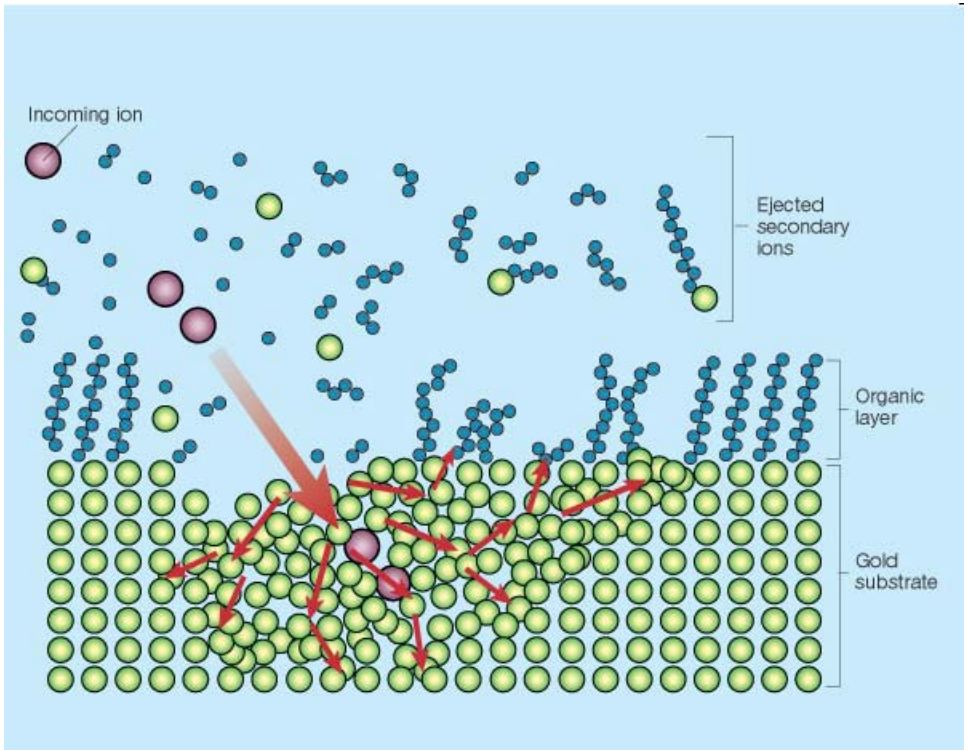
2. Samples





Yellow: 1978.119 *El Mosquito Americano*, (n.d.)
Magenta: 1978.84 *Corrido dedicado al 16 septiembre de 1897*, (n.d.)
Scarlet: 1981.47 *La continuación, señores de los pronósticos va; apréndanlos de memoria que ya se van a acabar*, 1904
Orange: 1986.20 *Guadalupe Bejarano en las bartolinas de Belen. Careo entre la mujer verdugo y su hijo,* (n.d.)
Green: 1978.182 *Ya llegó calavera de la penitenciaria, no se arruguen cueros viejos oue [sic] aquí está Rafael Buendía,* (n.d.)

3. Time-of-Flight Mass Spectrometry (TOF SIMS)

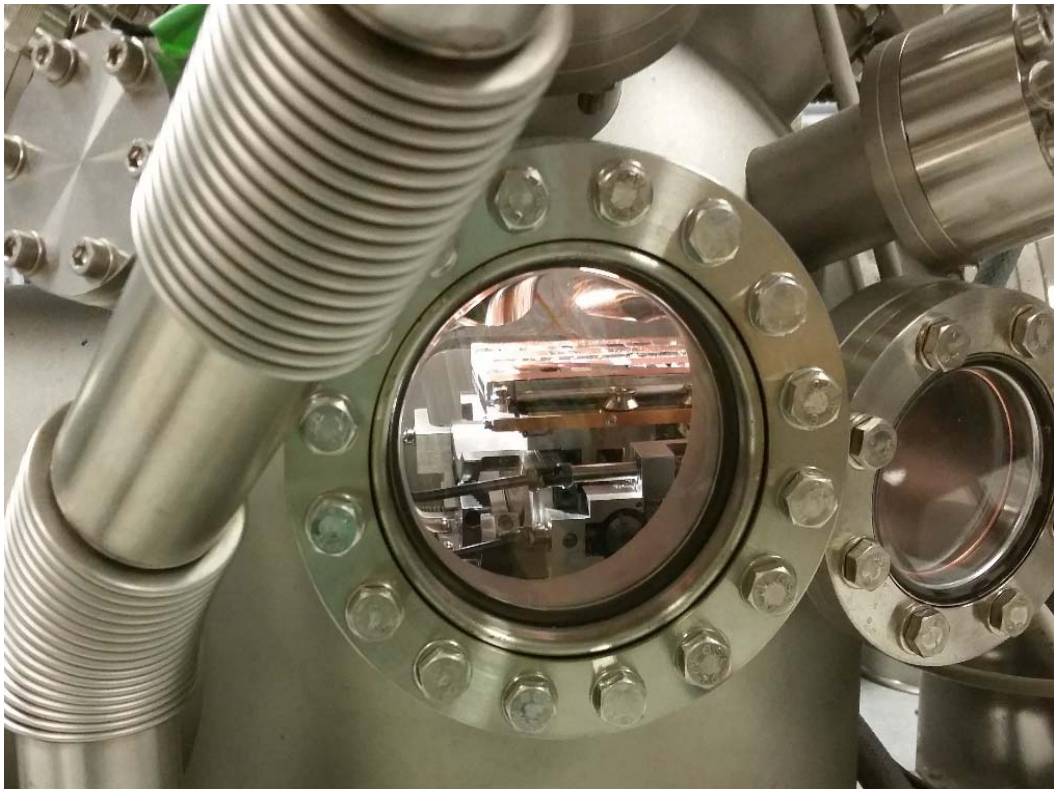


High energy beam of ions is incident upon surface. Energy is transferred to the atoms in the sample – causing a “collision cascade”
leading to the ejection of **secondary species.**
The ejected secondary ions are detected (weighed) using a mass spectrometer.

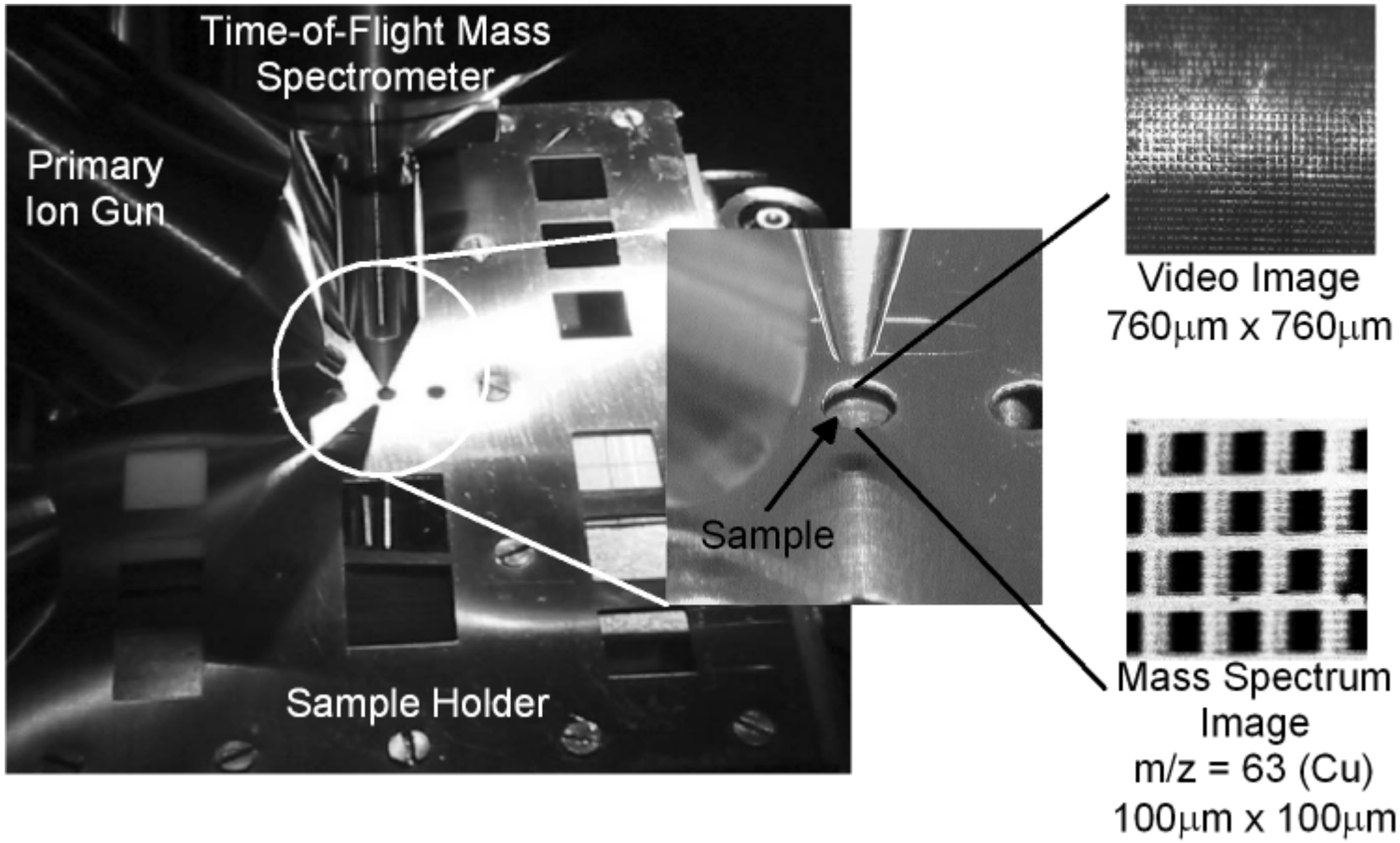
Advantages: Very sensitive ⇒ can use small sample sizes
Can detect inorganic and organic materials
Little or no sample preparation needed

D.G. Castner, Nature 422, 129-130(13 March 2003)

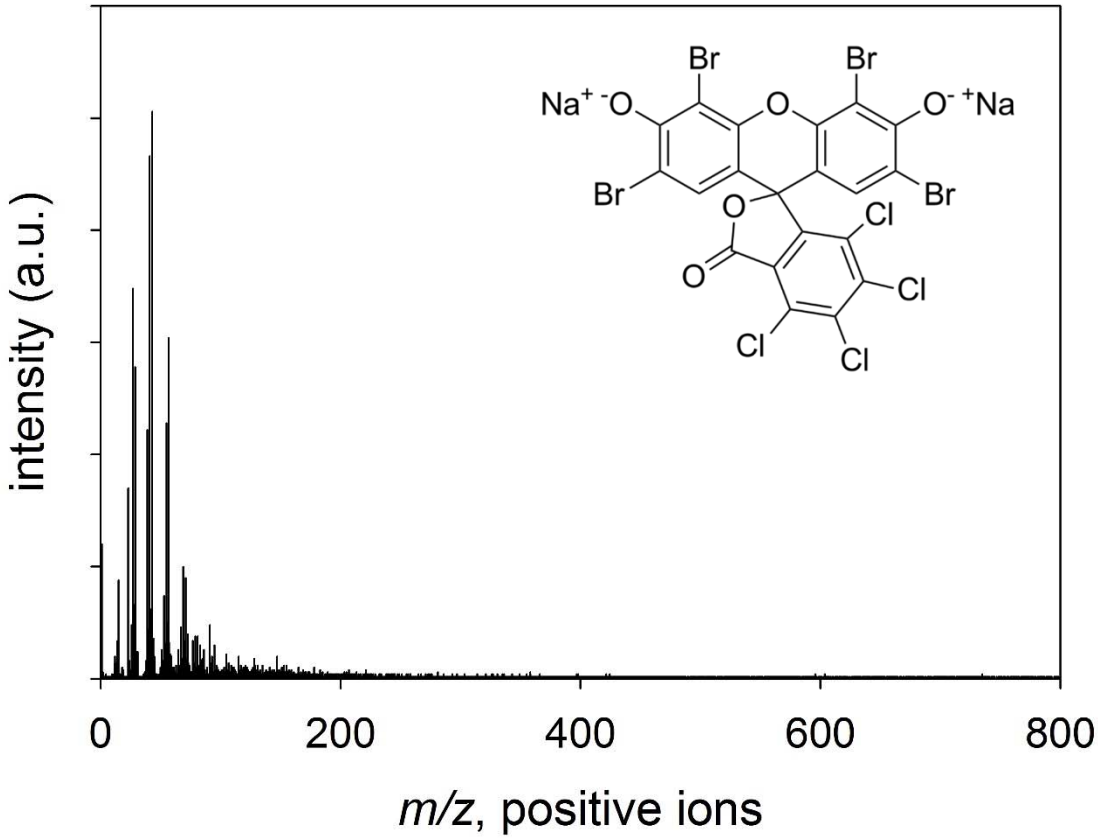
3. Time-of-Flight Mass Spectrometry (TOF SIMS)
The Instrument



3. Time-of-Flight Secondary Ion Mass Spectrometry: The Instrument

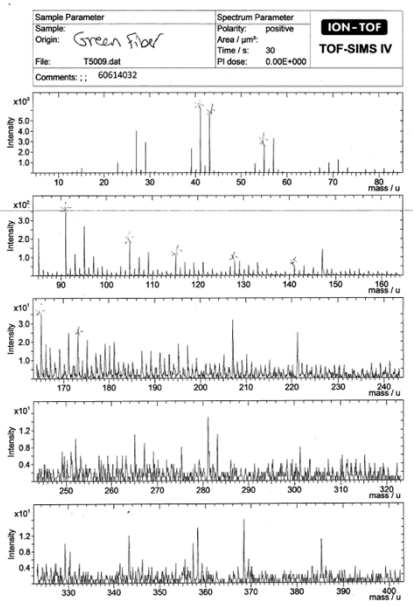


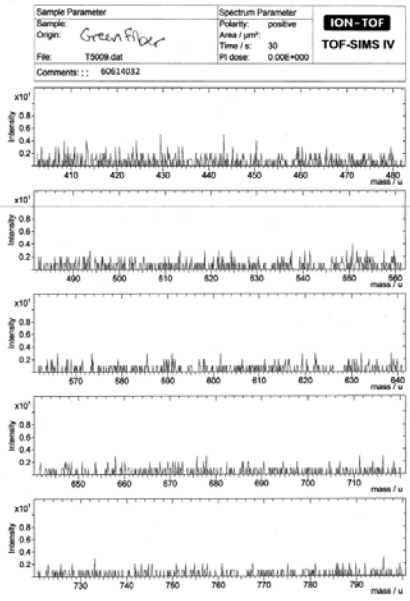
3. Time-of-Flight Mass Spectrometry (TOF SIMS)

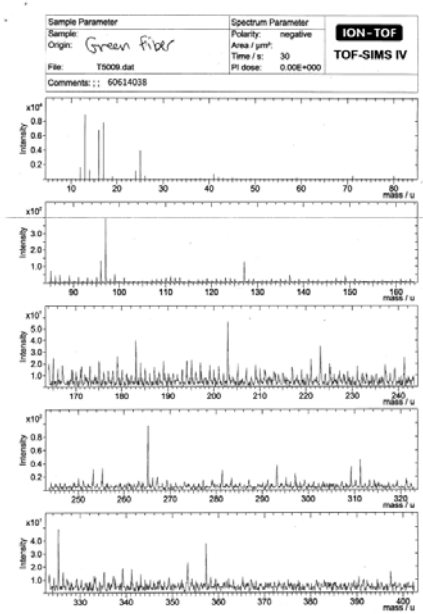


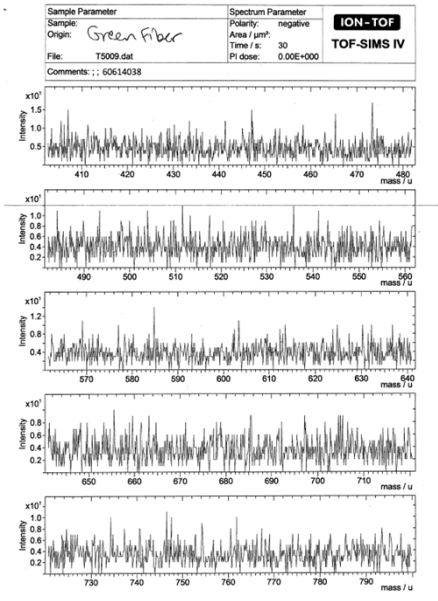
S.M. Kelly, J. Utter, A.V. Walker, A.A. Ellsworth, J.K. Hedlund, *The Book and Paper Group Annual*, **36** (2017) 87-100.

3. Time-of-Flight Mass Spectrometry (TOF SIMS)
The Data



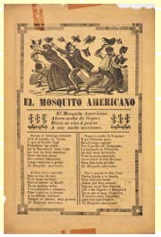






3. Time-of-Flight Mass Spectrometry (TOF SIMS)
The Data

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								



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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		
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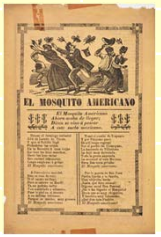

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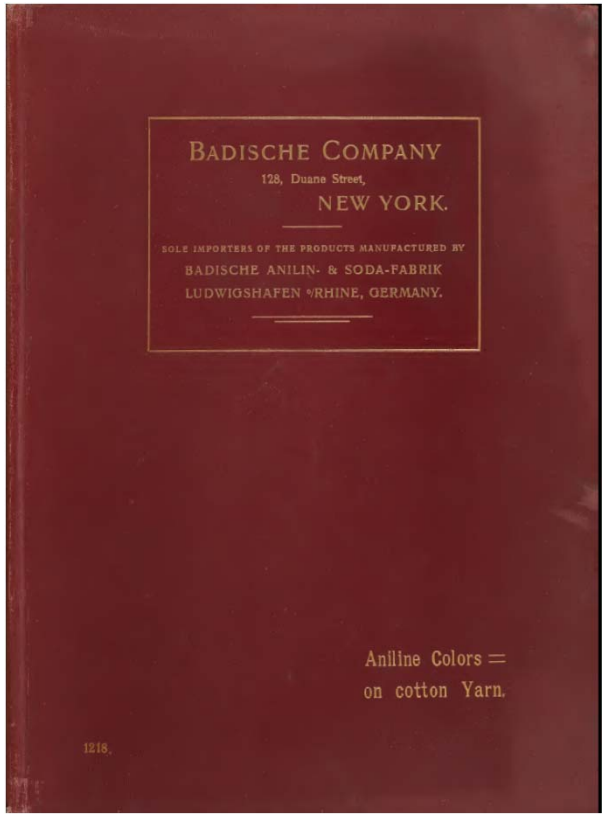
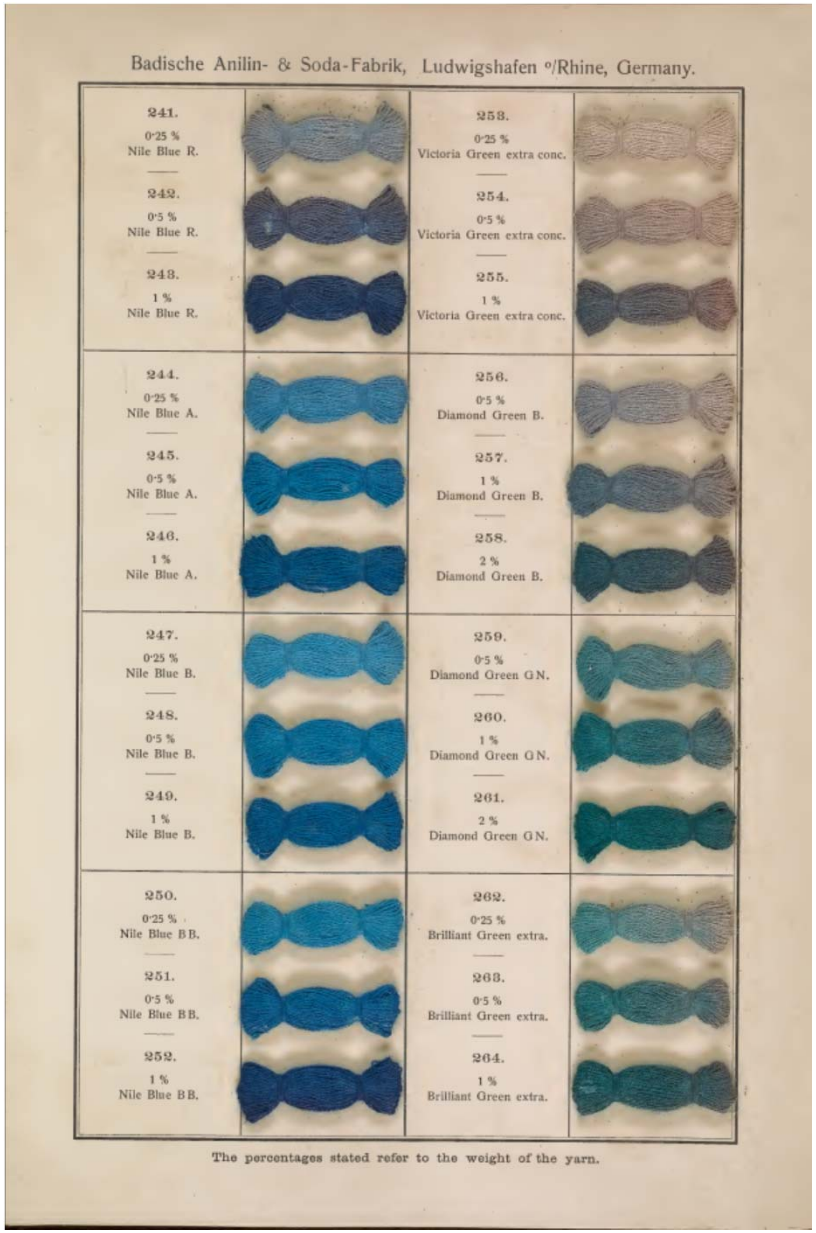
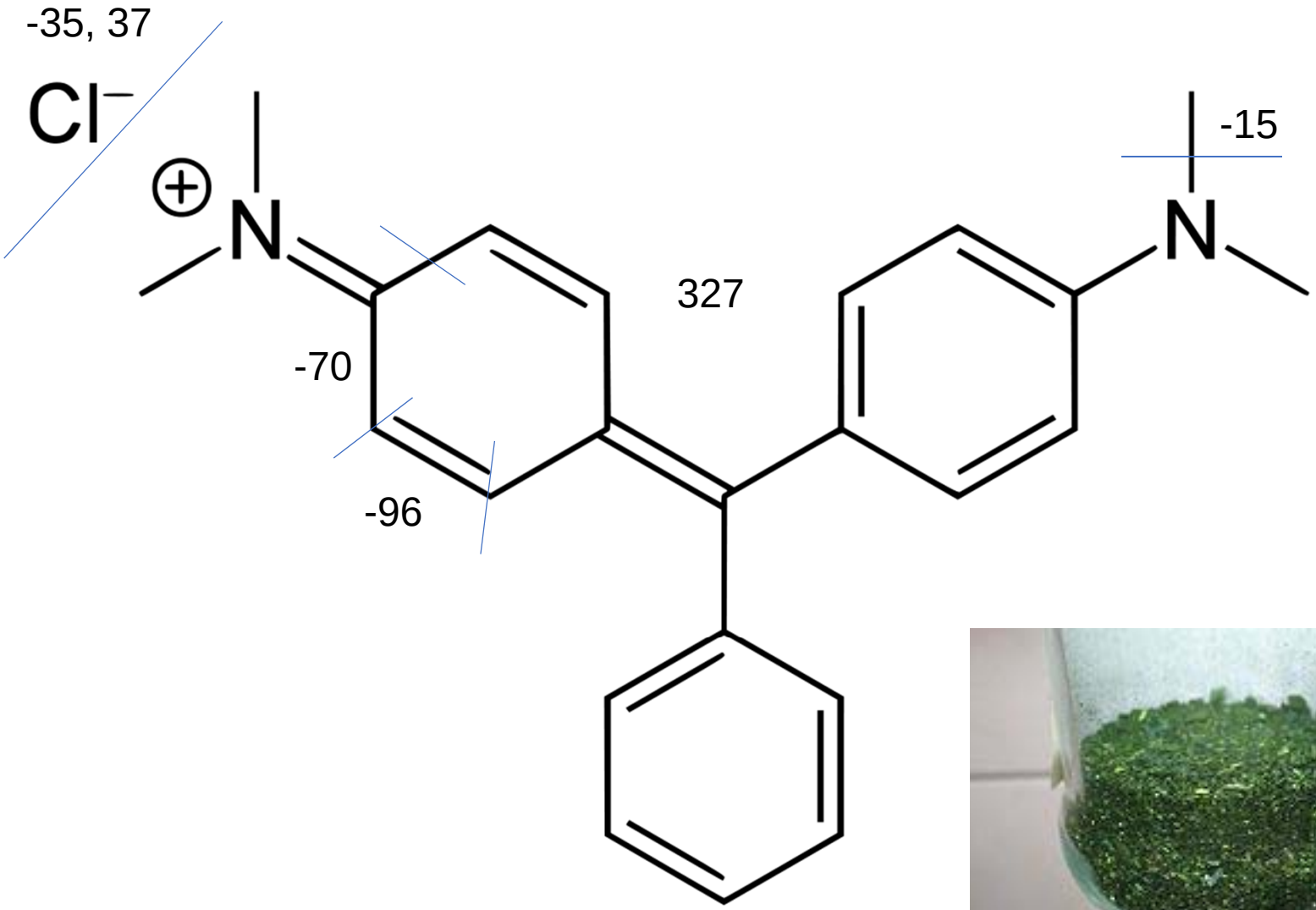
3. Time-of-Flight Mass Spectrometry (TOF SIMS) Identifying the Dye



There are many aniline dyes…..

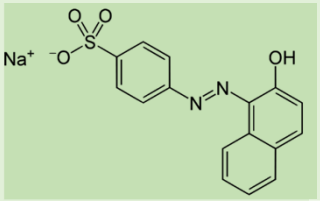
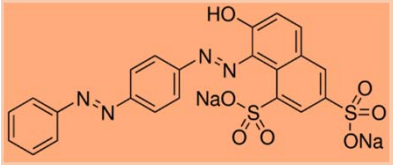
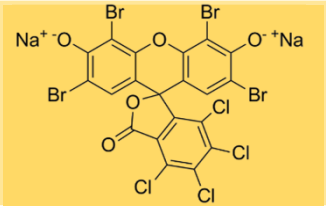
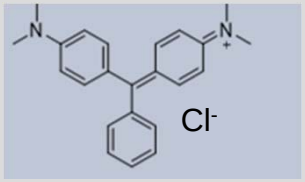
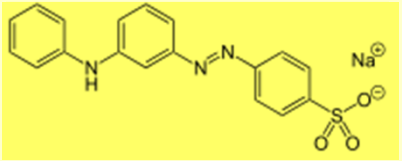


3. Time-of-Flight Mass Spectrometry (TOF SIMS)
Identifying the Dye



Malachite Green
(Basic Green 4)

3. Time-of-Flight Mass Spectrometry (TOF SIMS) Identifying the Dye

Accession number	Color	Significant *m/z* peaks, positive ion	Significant *m/z* peaks, negative ion	Dye	
1978.51 	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)	
1985.18 	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)	
1978.84 	Magenta	178, 343, 358	35, 37, 79, 81, 127, 175, 265, 269, 357, 473	Phloxine BBN (Acid Red 92)	
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)	
1978.119 	Yellow	73, 109, 165, 265, 279	71, 80, 265, 281, 311, 325, 339, 473	Metanil Yellow (Acid Yellow 36)	

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What’s next?

Gore-Tex with solvent

- Gore-Tex sandwich applied to recto of sample
- Adhesive was scraped/swabbed off once swelled
- Series of 12 minute applications
- Interleaving layer of Japanese paper applied to absorb adhesive
- Japanese paper and Gore-Tex were changed as needed

Purple sample undergoing Gore-Tex treatment

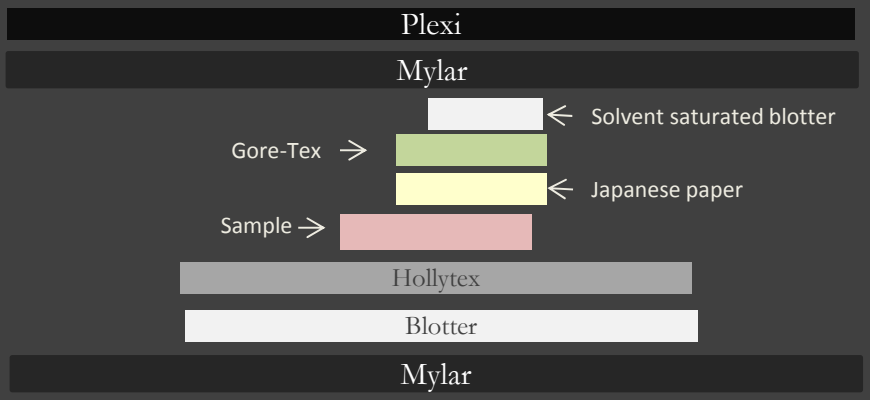
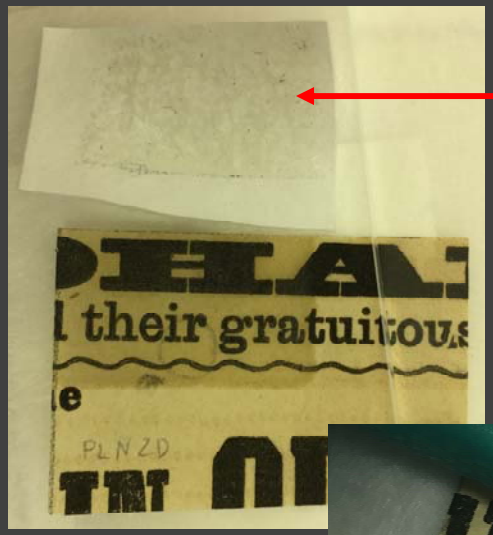


Diagram showing Gore-Tex set up

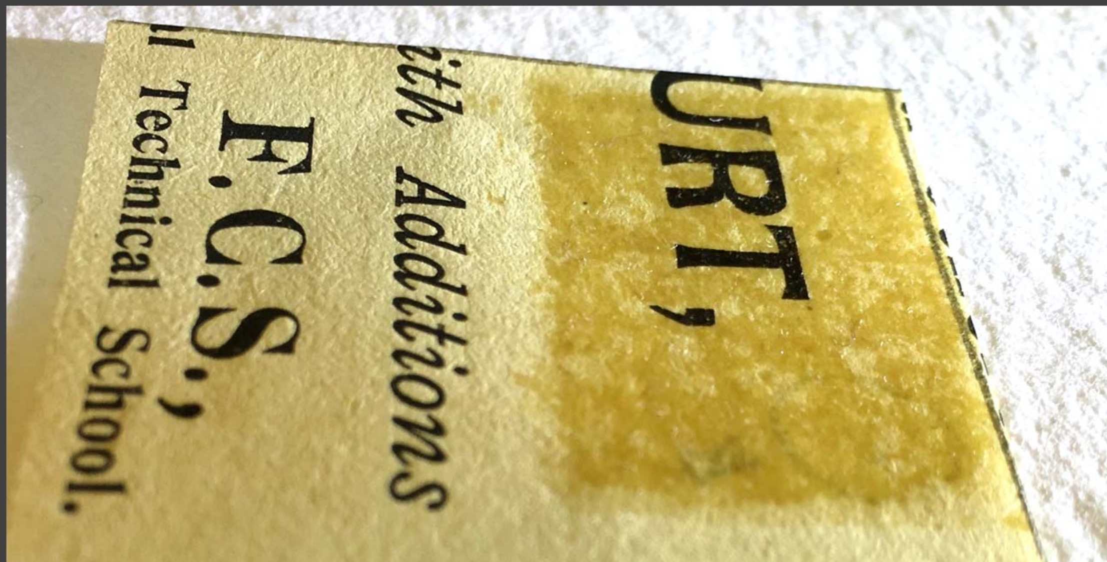
Gore-Tex with solvent results

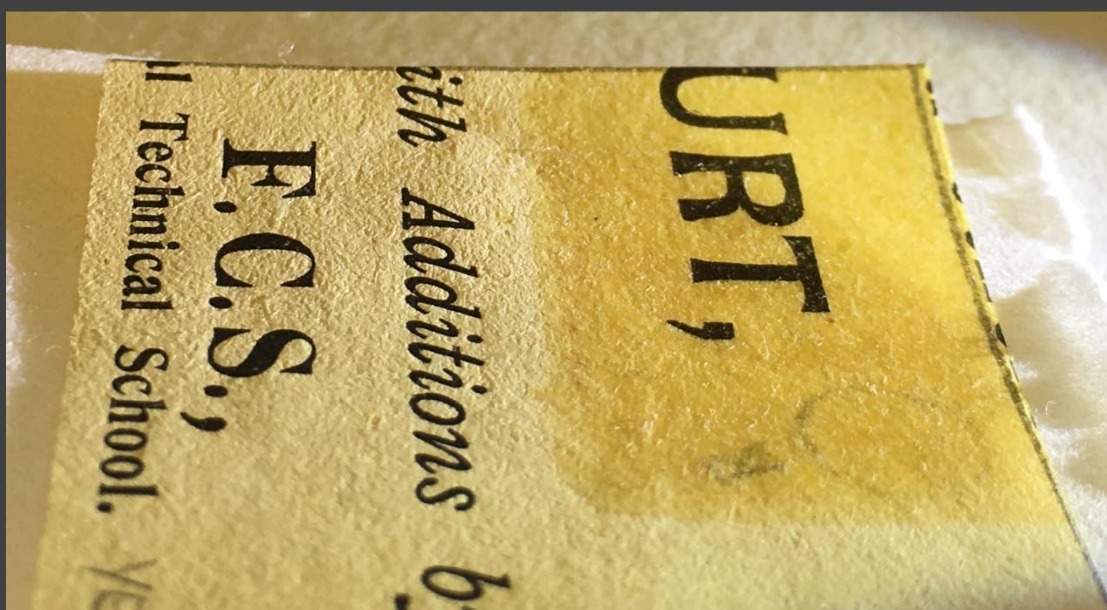
- Effective with samples with carriers
- Reduced residue but stains remained
- Minimal tidelines – controllable
- No bleeding of dye occurred
- Tacky samples picked up Gore-Tex fibers – further treatment will reduce this
- Longer treatment times ~ 10 – 15 applications (12 minute)



Adhesive deposited onto Gore-Tex

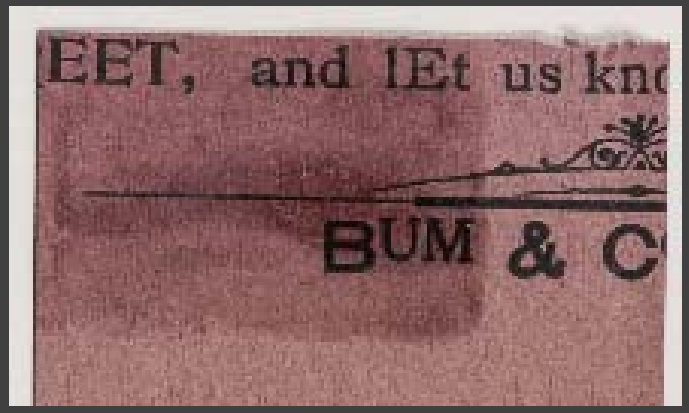
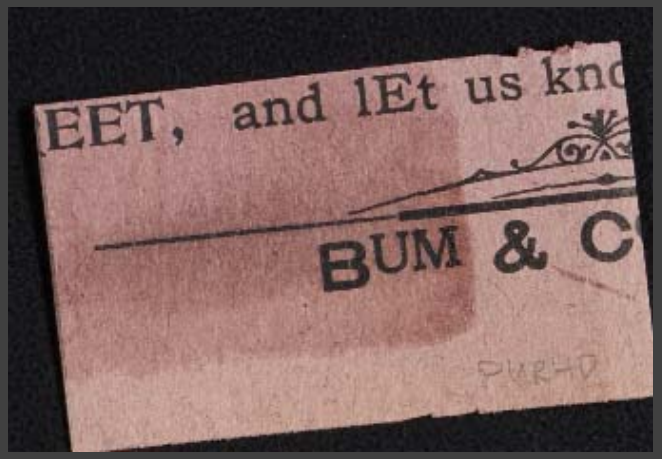
Carrier removed while keeping the Gore-Tex sandwich in place





Visible reduction of surface adhesive – samples no longer tacky – yellow masking tape after 4x 12 min applications

Gore-Tex with solvent results (Rubber cement)

Purple - Rubber cement (Xylene)	
Before	After
	

5. Maximum *a posteriori* (MAP) reconstruction

The probability that sample parameters $\boldsymbol{\theta}$ are correct given data $\boldsymbol{E}$ is found from Bayes' Theorem (1763):

$$\boldsymbol{P(\theta|E)} = \frac{P(\boldsymbol{E}|\boldsymbol{\theta}) \cdot P(\boldsymbol{\theta})}{P(\boldsymbol{E})} \propto P(\boldsymbol{E}|\boldsymbol{\theta})$$

…if no prior information $P(\boldsymbol{\theta})$ is available.

$\boldsymbol{P(\theta|E)}$ = probability of true image given the data we got

Can we use MAP analysis to help us identify the dyes and ultimately obtain information about the paper used?

R. C. Puetter, T. R. Gosnell, A. Yahil, *Ann. Rev. Astron. Astr.* **43** 2005, 139
Lee, D. D., Seung, H. S., *Advances in neural information processing systems 13,* **2001**, 556-562.

7. Discussion and Conclusions

1. Working together is very rewarding!
2. Communication is key.
3. We have identified the dyes used in Posada's broadsides using SIMS. Raman spectroscopy, which is commonly employed, has had limited success especially in identifying blue and yellow pigments.
4. Stacy Kelly and Jodie Utter were able to develop new methods to remove pressure sensitive tape from the broadsides.
5. Using MAP analysis we are able to obtain both the mass spectra of the acidic and basic aniline dyes, and also the paper stock.

8. Acknowledgements

William Mandt, UT Dallas undergraduate researcher
Funding: National Science Foundation