Improved Interpretation of A-D strips with Colorimetry & Visible Light Spectrophotometry

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Abstract

Detection of off-gassing acids using A-D strips is a proven method of evaluating degradation of cellulose acetate films. However, the visual interpretation of each strip's color change is inherently subjective and prone to variability depending on factors such as lighting and individual inspector interpretation. Recently, at The Mariners' Museum and Park, we have been conducting a survey of motion picture film to assess condition and are incorporating the use of A-D strips to detect off-gassing acids. We use both individual assessment and colorimetry as well as visible light spectrophotometry to evaluate the resulting color changes to the test strips with the goal of standardizing a colorimetric/spectrophotometric method that reduces interpretative error. The results of these assessments and tests show that the addition of colorimetry and visible light spectrophotometry enhances interpretation through quantification and characterization of the color change.

Introduction

The Mariners' Museum and Park houses a collection of over 800 films dating across the 20th century. The collection contains important and unique films documenting aspects of maritime history including the shipbuilding industry, Arctic exploration, and recreational boating. The collection is stored in vented polypropylene cans in a climate-controlled room averaging 66°F.

Previous testing with ATR-FTIR* showed that approximately 97 % of the films have a cellulose acetate base, a material which has been shown to deteriorate rapidly at room temperature.

The deterioration mechanism causes severe shrinkage and distortion (as seen at right) and produces acetic acid vapors which induce degradation of nearby materials, a phenomenon known as 'vinegar syndrome.'

Concern over a strong vinegar odor in the storage space prompted a survey of the collection in 2018 using A-D strips to assess the condition of individual films.

2018 results indicated that roughly 75 % of the collection was actively deteriorating.

A follow-up survey was completed in 2022 with the goal of understanding the rate of degradation and providing data to support construction of a low-temperature storage unit for the collection.

A-D Strips: The Subjectivity Problem

In both surveys, each film tested with A-D strips was given a score to indicate their relative condition using the 0-3 scale recommended by the *User's Guide for A-D Strips.** Traditionally, this requires the individual(s) to visually assess the color change of each strip across the entire spectrum from blue to yellow. This process is inherently subjective, as interpretation and scoring may be affected by personal judgement, lighting conditions or, if assessed from images, color rendering and calibration of screens.

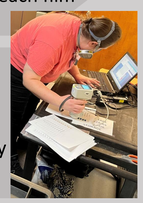
Below are two examples of A-D strips from the 2022 survey, along with the varying scores given by each assessor.

Given the scale provided with the strips, what score would you give each of these?

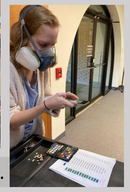
To achieve a more quantitative assessment and a reduction of subjectivity, the use of a colorimeter/spectrophotometer was introduced to the process for the 2022 survey.

Survey Methods

An A-D strip was enclosed in each film container for 24 hours.



After removal strips were adhered to copy paper with double sided tape, evaluated by colorimetry /spectrophotometry…



…and photographed for later interpretation and scoring.

Technical Information*
- *Colorimeter/Spectrophotometer*: Konica Minolta Spectrophotometer CM700, SAV head, 3mm aperture
- *Test Strips*: A-D Strips, Image Permanence Institute
- *Photography*: iPhone 13 mini Model MLA33LL/A or iPhone SE Model MXCT2LL/A
- *Color Card*: Colorchecker Passport Photo 2 by Calibrite© LLC, 2021
- *Tape*: 3M™ 415 double-sided tape

Safety The survey was undertaken multiple days a week for approximately 3 hours at a time. Each surveyor wore a half-face respirator with a 3M™ Multi Gas/Vapor Cartridge 6006 after respiratory irritation caused concerns about breathing in the acetic acid present in the space.

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Standardization & Quantification Experiments

Visual Scoring Standardization and Reevaluation

Given that interpretation of A-D strips is subjective, during the evaluation process a concern evolved that even within an individual's scoring there would be variation from strip to strip, especially without having a reference scale that includes half-step scores. In an effort to remedy this, representative examples of each possible score were intuitively chosen from the range of A-D strip colors seen during the collection survey and made into a color scale bar. This scale bar was then used as a reference to verify and/or adjust previous scoring.

Even using this reference scale, 33 % of scores varied between assessors in the 2022 survey.

Experimental Standards for Colorimetry/Spectrophotometry

In order to convert colorimetry data to A-D strip scores, a scale relating ΔE*ab values to known concentrations of acetic acid was required. To achieve this, three strips were exposed to acetic acid at each of these concentrations: 0, 0.5, 1.5, 4, 7, 19 and 25 ppm. These concentrations correspond to The A-D strip scores 0-3 as listed in the *User's Guide for A-D Strips.** After 24 hours the strips were measured with colorimetry/spectrophotometry and photographed.

Strips were held at the top of screw-top Pyrex™ jars using 3D printed nylon coupon holders.

Viton™ O-Rings and INTLLAB polypropylene screw caps closed the containers.*

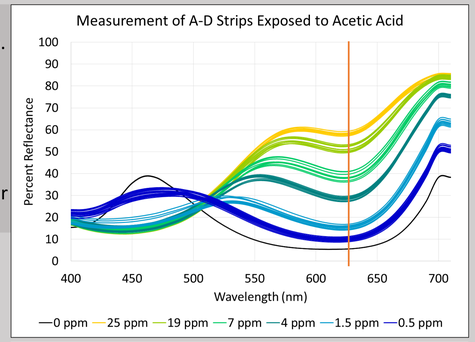
A New and Improved Scale

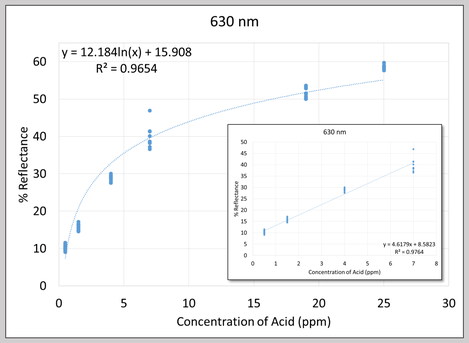
25ppm	19ppm	7ppm	4ppm	1.5ppm	0.5ppm	0ppm
3	2.5	2	1.5	1	0.5	0
ΔE*ab >85.1	77.5-85	67.9-77.4	55.1-67.8	35.1-55	10-35	0-9.9

The experimentally standardized scale above shows the strips after exposure to set acid concentrations, the range of associated color change (ΔE*ab) and the correlating A-D strip scores. Further work is needed to account for humidity and other environmental factors to improve accuracy.

Reflectance Spectrophotometry

Grouping of spectra shows that results are reproducible for each tested concentration. Thus, the potential for quantitative measurement of acid concentration at differing wavelengths was explored. It was found that the best correlation occurs at 630 nm (designated by the orange line at right), with best linear fit below 7 ppm.





Bouguer-Beer-Lambert Law vs Kubelka-Munk or Allen-Goldfinger models

Reflectance spectrophotometry can be used to model the concentration of acid in air via reaction with the A-D test strips in a manner similar to the Bouguer-Beer-Lambert Law, though this is used for transmitted light. At this juncture the most appropriate formula relating the reflectance to concentration is under review.*

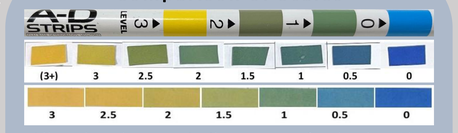
Results & Discussion

A Tale of Two (Three?) Scales

When compared side-by-side, the intuitive scale separated out the varieties of green seen while surveying much more than the experimental standard scale. As a result, the scores assigned using the experimental standard scale tended to be lower than the scores assigned using the intuitive scale, especially in the mid-upper acid levels. Therefore, the average condition of the individual films was likely better (less acidic) than originally perceived.

To confirm that this discrepancy was caused by the difference in reference scales rather than in human vs. instrumental interpretation, a random selection of 50 survey strip images was reassessed visually using the standard scale. This exercise determined that human interpretation and colorimetric interpretation had only negligible differences when using the same reference scale – the scale that you use for interpretation matters!

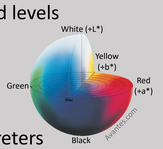
Comparison of Scales



All scales show a similar range of color but the intuitive scale gave more importance to the mid-range acid levels, while the standard scale is more nuanced at higher levels. The official scale is similar to the intuitive scale, but lacks half-step scores, making it harder to interpret the wide range of strip colors seen in practice.

Advantages of Colorimetry

- The scale created using the standardized acid concentrations more accurately reflects the color variation caused by different acid levels
- Ambient lighting does not play a role in assessment
- Colorimetric readings can be taken quickly
- Acid content/strip scoring can be extrapolated from the data automatically and scores can be decisively determined
- Achieves objectivity of results without the need for multiple interpreters



Color Reversion of A-D Strips

Reversal of the strips after exposure was noticeable as a function of time. It was hypothesized that attaching the strips to copy paper containing calcium carbonate was causing the color reversion. To understand the cause and the rate of color reversal, six strips were exposed to ~7 ppm acetic acid for 24 hours. These strips were then removed and placed on: copy paper, Mylar, or tape on Mylar. They were then photographed and analyzed with the colorimeter in intervals of 15 minutes.

All A-D strips showed enough color reversion to result in a reduction of score within 30 minutes.

Substrate	0 min	15 min	30 min	45 min
Copy Paper	Score: 2	1.5	1.5	1
Tape	2	2	1.5	1.5
Mylar	2	2	1.5	1.5

Conclusions

- Colorimetric assessment allows for quick, objective determination and calibration (or recalibration) of A-D strip scores.
- To ensure the highest level of accuracy in interpretation, color change must be assessed immediately after removal from the object enclosure.
- Colorimetric data is as, or more, accurate than the human eye in recognizing color change.
- In the absence of a colorimeter, having an accurate, experimentally standardized scale increases accuracy of individual visual interpretation.
- The colorimetry determined that the collection was not off-gassing as much acid as was previously determined using the intuitive collection-based scale.

THE BRONZE DOOR SOCIETY of The Mariners' Museum and Park

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** See digital version on CulturalHeritage.org for bibliography and additional technical specifications*

Improved Interpretation of A-D strips with Colorimetry & Visible Light Spectrophotometry

Supplemental Information

Technical Specifications

Colorimeter and Spectrophotometer
The Konica Minolta Spectrophotometer CM700 was used with a 3mm aperture SAV head attachment and CM-S100w 3.20.0002 on the Standard Setting from SpectraMagic NX 12. This instrument collects CIEL*a*b*(D65) data and spectra from 400-700 nm with 10 nm resolution.

Photography
All photos were taken with primarily an iPhone 13 mini Model MLA33LL/A, but when unavailable, an iPhone SE Model MXCT2LL/A. A color reference card, Colorchecker Passport Photo 2 by Calibrite© LLC, copyright 2021, was included in all photos and was used to white balance using ImageJ with a macro written by Yves Vander Haeghen version 1.1. published Jan 3, 2009.

Test Strips
A-D Strips - Film Base Deterioration Monitors were purchased from the Image Permanence Institute (IPI) address: RIT/IPI, Gannet, Bldg. 7B, Room 2000, 70 Lomb Memorial Drive, Rochester, NY 14623 USA. Color Change Reversal Experiments. Each strip was cut in half for use during survey.

Acetic Acid Test Chambers
Strips were held at the top of the screw-top Pyrex™ jars using 3D printed nylon coupon holders. The O-rings were Viton™ and the lids were INTLLAB polypropylene screw caps, the same materials recommended for use by The Metropolitan Museum of Art's Oddy test (Stephens 2018).

Bibliography

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