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DISCUSSION GROUP CO-CHAIRS

Art on Paper Discussion Group 2025
Citrates in Paper Conservation

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INTRODUCTION

Paper conservators have long sought effective methods to remove discoloration and staining from works on paper, employing various chemical treatments that have resulted in a mix of successes and failures. As treatments done with oxidative bleaches have not proven to consistently age well, conservators have become more interested in alternatives to chemical bleaching agents, such as chelating agents. Ammonium and sodium citrate solutions have gained traction in paper conservation over the past 10 years, although they have been utilized as cleaning tools by other conservation specialties for several decades. Citrates show particular promise for addressing aesthetic concerns, namely reducing staining and brightening paper while preserving its natural tone. Ideally, these results are achieved while preserving the integrity of the cellulose and other paper components.

Despite growing interest in citrates within the paper conservation community, resources remain scarce in the literature. Few publications have systematically examined the long-term effects of citrate solutions on cellulosic objects, and their chemical mechanisms remain poorly understood. Conservators seeking treatment protocols and case studies find limited information beyond the pioneering work of Antoinette Dwan (Dwan 2015; Dwan and Stavroudis 2020), leaving practitioners navigating largely uncharted territory when considering these treatments.

This panel addressed these knowledge gaps by bringing together recently published analytical research, practical case studies, and theoretical considerations regarding the use of citrate solutions in the treatment of works on paper. Through three focused presentations followed by collaborative discussion, the event served to share emergent treatment approaches while identifying critical areas requiring further investigation. While much remains to be understood about citrate chemistry and application, the dialogue generated compelling research questions and demonstrated the potential use of these compounds as valuable tools for advancing our understanding of treatment applications in paper conservation.

SUMMARY OF PRESENTATIONS

TESTING AMMONIUM CITRATES FOR ENHANCED WASHING OF GELATIN-SIZED RAG PAPER

CRYSTAL MAITLAND
SENIOR CONSERVATOR OF PAPER AT THE WINTERTHUR MUSEUM, GARDEN & LIBRARY AND AFFILIATED PROFESSOR FOR THE WINTERTHUR/UNIVERSITY OF DELAWARE PROGRAM IN ART CONSERVATION (WUDPAC)

THERESA J. SMITH
ASSOCIATE PROFESSOR OF PAPER CONSERVATION IN THE PATRICIA H. AND RICHARD E. GARMAN ART CONSERVATION DEPARTMENT AT SUNY BUFFALO STATE UNIVERSITY

Crystal Maitland and Theresa J. Smith showcased selected aspects of their paper, "Testing Ammonium Citrates for Enhanced Washing of Paper," which was recently published in *Journal of the American Institute for Conservation* online (Venus et al. 2025). The research compared the effects of aqueous treatments on aging and on calcium and iron levels after washing for three different test papers: chromatography filter paper, a 19th century gelatin-sized rag ledger paper, and a 19th century rag unsized printing paper. The presentation at the Art on Paper Discussion Group session focused on the findings from the gelatin-sized rag paper.

Smith began by describing the experimental design. One sample of gelatin-sized rag paper was reserved as an untreated control, and all remaining samples were immersed three times

Summaries of discussion groups at the Book and Paper Group Session, AIC's 53rd Annual Meeting, May 27–31, 2025, Minneapolis, Minnesota

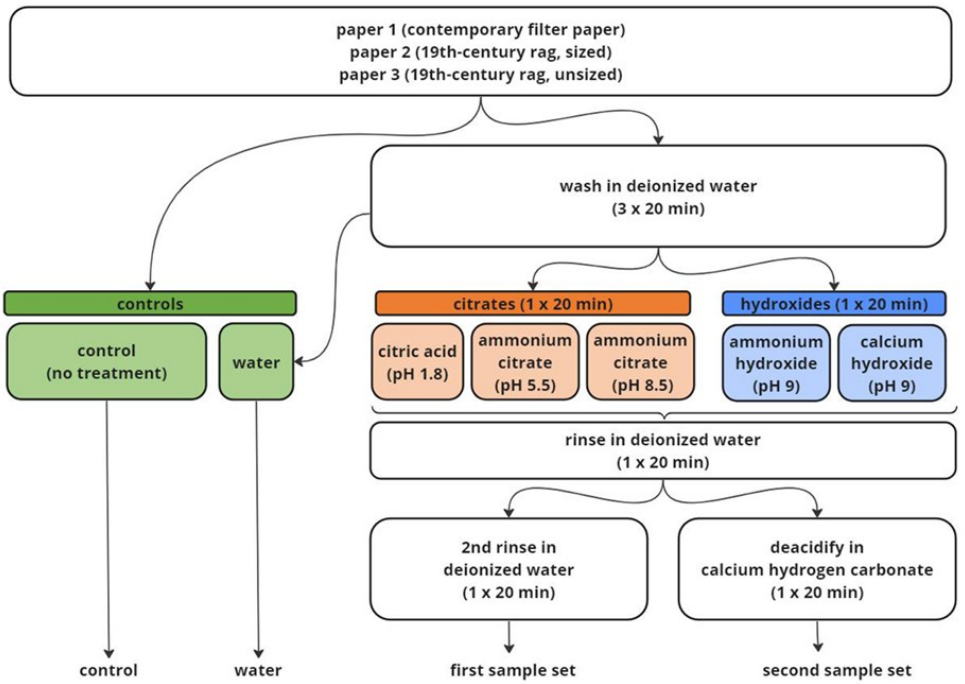


Fig. 1. Overview of the experiment: sample papers (controls, first set, and second set), each with respective treatment durations and pH values. The color coding (green: controls; orange: citrates; blue: hydroxides) is consistent throughout the following figures. Reprinted with permission from the *Journal of the American Institute for Conservation*.

in deionized (DI) water as a pretreatment step to remove soluble degradation products. From the group washed in DI water, a second sample set was reserved. The rest of the samples were immersed in one of the following five solutions: citric acid (pH 1.8), ammonium citrate (pH 5.5 and 8.5), ammonium hydroxide (pH 9), and calcium hydroxide (pH 9). All samples were rinsed in DI and then subdivided into two groups. One group received a second rinse in DI, and the other group was deacidified in a dilute calcium bicarbonate (calcium hydrogen carbonate) bath. Smith noted that the visual differences in color between the treated papers were subtle in both the aged and nonaged groups. However, the samples that received the deacidification treatment step showed that the citrate-treated papers retained the most brightness after aging. Interestingly, the pH of the citrates did not affect the level of brightness as measured by colorimetry (fig. 1). Maitland interpreted the findings regarding calcium and iron levels before and after treatment for the gelatin-sized rag ledger paper. X-ray fluorescence (XRF) spectroscopy was used to scan 1 cm^2 areas of the samples for calcium and iron, and the data were organized into box plots to assess the homogeneity of metal distribution within the samples. Prior to treatment, the XRF scans revealed a heterogeneous spread of calcium. Upon further analysis using scanning electron microscopy/energy dispersive x-ray spectrometry (SEM/EDX), it was discovered that before treatment, much of the calcium was in the form of clustered particles lodged among the paper fibers. X-ray diffraction (XRD) suggested that many of these aggregates might be calcium sulfate. After treatment, XRF scans indicated a homogeneous distribution of calcium implying the removal of the particle clusters.

All aqueous treatments, including the calcium hydroxide treatment, reduced calcium levels. This is an important finding, as even the alkaline calcium hydroxide rinse diminished the total amount of calcium in the paper. The citric acid and two ammonium citrate solutions removed the greatest amount of calcium. Rinsing in DI water followed by dilute calcium bicarbonate deacidification of treated samples was able to reestablish calcium within the papers, although not to pretreatment levels. Maitland suggested that a more concentrated calcium bicarbonate deacidification could further increase the calcium content.

Surprisingly, levels of iron detected by XRF were not affected by any of the aqueous treatments in this study. Before treatment, XRF scans showed low levels of iron homogeneously spread throughout the samples, punctuated by larger iron inclusions. Analysis performed with inductively coupled plasma mass spectroscopy (ICP-MS) indicated that iron and calcium levels in the papers treated by the research team were low relative to similar historical papers. To explain the insolubility of the iron in their study, Maitland referred to another research group that found iron ion removal occurred

in high-iron containing historical papers but not in low iron-containing historical papers (Niehus et al. 2012).

Maitland concluded with the significant finding that the addition of the calcium bicarbonate step proved to be critical to retain the molar mass and brightness of cellulose after any of the aqueous treatments in the study. Maitland, Smith, and their co-authors would like to continue this line of research by studying a wider range of papers, including higher calcium and/or iron-containing papers, different types of staining, localized citrate treatments, and the systematic analysis of the chemical products removed by wash water.

CITRATES IN PAPER CONSERVATION: A RETROSPECTIVE

MADISON BROCKMAN
PAPER CONSERVATOR, LOS ANGELES ART CONSERVATION

Madison Brockman joined the panel via a prerecorded presentation. They began by sharing a treatment experience during their graduate training that became central to their interest in exploring citrate solutions for stain reduction. When treating a Piranesi print during the second year of training at the Winterthur/University of Delaware Program in Art Conservation with classmates Emily Farek, Amber Kehoe, and Victoria Wong, under the supervision of Joan Irving, Winterthur paper conservator and affiliated professor, the group employed a series of baths designed to gradually increase in pH while simultaneously decreasing in concentration to successfully remove significant amounts of staining and discoloration from the paper support. Brockman reasoned that beginning the treatment with a higher ionic content would not aggressively strip the paper of beneficial mineral content immediately, and would allow for effective cleaning across the range of pH levels and citrate concentrations. The series of baths solubilized the tide line stains and engrained surface soiling without overly lightening the color of the support. The treatment was considered a success and did not require any further aesthetic treatments. While at the Los Angeles County Museum of Art (LACMA), Brockman conducted analysis on the aging of papers after treatment with citrates (Brockman 2020). Brockman compared Whatman filter paper and antique western paper after local and overall treatment with 1% sodium citrate at pH 7, and found no adverse effects after aging (Brockman 2020a). More recently, they investigated the effects of 1% sodium citrate at pH 7 on friable media, showing that citrates more readily lift unbound media like charcoal off paper supports during aqueous immersion treatments compared to pure water.

Brockman presented an array of treatment case studies showcasing different ways of working with citrate solutions on a wide variety of paper objects. They noted some benefits of using ammonium and sodium citrate solutions, including affordability, access, and simple preparation. Brockman specified that they prefer to use sodium citrate because it is less hazardous to handle than ammonium citrate and can be safely disposed down the drain in California (note 1). Brockman has found that citrates appear to better preserve the tonality of historical paper, as opposed to their experience with oxidative and reductive bleaches. Brockman added that citrate solutions pair well with gels, sodium borohydride, and light bleaching to remove a wide variety of stains.

Brockman presented several case studies including the treatment of a blue and yellow watercolor with foxing in the margins. The object was bathed on a 2% gellan gum slab while a 1% sodium citrate solution at pH 7 was sprayed through the margins on the front, avoiding the image area. This was followed by a rinse in filtered water. A Marc Chagall print in black ink was immersed in sodium citrate solution before light bleaching to address aesthetic damage from light exposure. This treatment nearly removed the disfiguring rectangle of discoloration, balancing the image area and the unexposed margins. Brockman explained that citrates can successfully combat light-induced discoloration when paired with oxidative or reductive bleaches. They shared a print by Pieter Bruegel in which immersion in citrate solution reduced overall discoloration of the support before a localized stain was further reduced with selective application of hydrogen peroxide. Brockman felt that the support retained a warm, aged look appropriate for a preindustrial paper.

Brockman often uses citrates in combination with gels. Less expensive gellan gum can be used for capillary washing, with a Japanese paper barrier between the gel and the object to prevent gel residues from depositing on the object. Tide lines can be locally treated with thin-cast agarose gels loaded with a citrate solution, cut to the shape of the stain. They shared treatment images of a screen print on thick paper with irregular discoloration around the margins. Immersion and treatment on a suction table were not possible, so citrate-loaded gels were used to gradually even out the staining. To prepare both gellan and agarose gels, the citrate solution is used in place of water.

Citrates may be incompatible with certain colored media. Brockman shared a test treatment of a colored crayon enlargement, the right half of which was fixed with B72 in toluene. The left remained unfixed. The bottom half of the object was treated with citrate solution and the top half was treated with water. The half treated with the citrate solution experienced a remarkable color shift, from an emerald green to a pale blue, despite the right side being fixed (fig. 2). Brockman generally avoids using citrates to treat colored media and friable media. Brockman's final remarks about citrates included tips on how to prepare them with citric acid powder and sodium hydroxide solution versus purchasing the citrate salts. They explained that pH is important to consider because the citrate will not be fully ionized in acidic aqueous solutions below approximately pH 6.4, and therefore the solution may not work as effectively as a chelator. Citric acid is only fully ionized (deprotonated) at pH 7.3 and above (Dwan and



Fig. 2. Test treatment of a crayon enlargement comparing the effect of washing in straight deionized water (top half) with washing in a citrate solution (bottom half). Despite the use of B72 applied as a fixative to the right half of the work, the bottom half that was washed in the citrate solution underwent a dramatic color change.

Stavroudis 2020). Brockman's final treatment tips included surface cleaning that they perform with a cotton swab dampened with a 1% citrate solution to reduce ingrained surface soiling. Another surface treatment Brockman recommends is using an agarose "stain stick," prepared with citrate solution in place of water (Cremonesi 2016; Brockman 2020b). Brockman's presentation illustrated many potential applications of citrates and drew attention to some limitations.

TREATMENT CHALLENGES POSED BY INORGANIC ADDITIVES IN 19TH AND 20TH CENTURY PAPERS

SARAH BERTALAN
CONSERVATOR, WORKS ON PAPER, NEW YORK, NY

In the final talk of the program, Sarah Bertalan presented a compelling argument that inorganic additives in modern papers are chemically unstable and responsible for many of the aesthetic condition problems that conservators encounter among 19th and 20th century works of art on paper. Drawing on research conducted throughout the past 15 years, originally sparked by her collaboration with Antoinette Dwan in the early days of Dwan's development and use of citrate treatments as a washing and stain reduction aid, Bertalan challenged the belief that common paper additives like metal oxides are stable (Bertalan 2015). Unlike traditional approaches to diagnosing paper condition problems that focus primarily on cellulose degradation and acid migration, Bertalan proposed that successful treatment of modern paper requires addressing the reactive inorganic components within the paper.

Bertalan's presentation provided evidence for the instability of metal oxide additives, particularly iron oxides, titanium dioxide, and zinc oxide, which were commonly used in late 19th and early 20th century papermaking. These additives, including iron oxides used for mechanical coloring of pulp (a practice acknowledged by Simon Barcham Green of Hayle Mill), may form salts in humid conditions and may undergo color-changing reactions when exposed to light and varying pH levels. The speaker demonstrated that these additives are not uniformly distributed throughout paper sheets and often concentrate at surfaces during manufacturing, creating "sensitized surfaces" that are particularly vulnerable to environmental conditions. Bertalan illustrated this with examples of prints by Degas, Cassatt, Matisse, Picasso, and Homer, and papers from Arches, Rives, and Van Gelder Zonen (fig. 3). Through visual documentation supported by documentary research and some analysis, the speaker illustrated how metal oxide additives may explain previously puzzling condition problems such as reverse foxing, mat burn, unusual staining patterns, and overall color shifts in paper. The research suggests that many condition issues traditionally attributed to poor-quality housing, humidity fluctuations, and light exposure in reaction with paper fibers or alum-rosin sizing could be attributed to chemical reactions involving unstable inorganic additives, requiring conservators to fundamentally



Fig. 3. Gray-brown staining at the mat window edge, caused by exposure of the modern paper support to unfiltered daylight. Edgar Degas, *Mary Cassatt at the Louvre: The Etruscan Gallery*, 1879–80, intaglio print.

reconsider their treatment approaches for modern paper artworks. While Bertalan's talk was not about the effects of citrate solutions per se, her research has important implications for conservators considering any chemical treatment.

SUMMARY OF DISCUSSION

The presentations inspired an engaging discussion with the attendees across a broad range of topics including the effects of citrates on media, counter ion preference, and the importance of using precise vocabulary when discussing treatment. Many questions were raised that directed the dialogue continuously back to the research potential for citrates as well as philosophical considerations about the inherent character of modern and historical papers.

The conversation began with participants emphasizing the need for specific language when discussing "citrate" treatments, as we have been using this term broadly to encompass various aqueous chelating solutions (sodium citrate, ammonium citrate, diammonium citrate, triammonium citrate), each with different properties and effects that are pH dependent. Future discussions should include the specific solution used for each treatment along with pH and concentration. A question about iron speciation directed toward Maitland and Smith's research highlighted an additional concern around the general broad use of language when discussing analytical findings. Maitland remarked that while XRF is a valuable tool, the elemental data it provides gives an incomplete picture of these inorganic materials. When we speak about calcium or iron, generally, we are not acknowledging the form or oxidation state of the element at the time of papermaking or how it may have chemically changed through aging.

This attention to scientific precision naturally led discussants to question the importance of involving the client or curatorial stakeholder when considering an irreversible treatment using a citrate solution. How can we best advise the nonconservator on the risks of the treatment? Bertalan emphasized the positive outcomes of her own discussions about treatment chemistry with stakeholders, as they have served to set expectations, demonstrate the value of our work, and can even help to build client relationships over time. Brockman sometimes invites clients back to their studio for progress updates and uses the opportunity to talk through the next steps of the treatment.

Central to these conversations was the challenge of balancing treatment benefits against inevitable material changes, particularly the removal of original components that were intentionally incorporated into papers during manufacture. The removal of calcium from paper was a recurring concern among discussants. Maitland and Smith responded to a question about binding constants for calcium and explained that citrate solutions are known to be strong chelators for calcium and relatively weak chelators for iron. In their research, they hoped to show that pH would allow for some degree of "tunability" in these solutions toward targeting the removal of iron over calcium. However, pH did not contribute to preferential removal of iron for the paper types that they studied. It seems that the ability of ammonium citrate solutions to chelate iron varies significantly depending on concentration levels of the iron—while effective at high concentrations, ammonium citrate shows limited success with the low iron concentrations typically found in historical papers. Other concerns highlighted by participants included the effects of citrate solutions on friable media like graphite and charcoal (citrates can act as deflocculants under certain conditions), experiencing unwanted tonal shifts in colored papers after treatment and natural aging, and increase in transparency of some papers.

The question of which counter ion to use—sodium or ammonium—emerged as another key consideration. While acknowledging sodium citrate as deserving study, Maitland, Smith, and co-authors had to limit their study to a single counter ion for the sake of time and resources. The team decided that ammonium was a good choice for the experimental design because it could be compared more easily to ammonium hydroxide solutions that are already well accepted in the field. The ammonium cation is volatile and evaporates from the paper substrate after treatment, leaving the acidic citrate anion behind. The volatility of the ammonium ion can also result in declining pH values over the course of a long treatment. Maitland agreed that sodium citrate should be studied to determine how detrimental it may or may not be from the perspective of fiber swelling and is curious about how we should approach the practice of rinsing objects treated with sodium citrate solutions. One participant shared their comparison of conductivity levels between ammonium and sodium citrate, noting that his sodium citrate solutions are much lower in conductivity than ammonium citrate solutions.

Related to the concern about calcium removal, participants explored the relative merits of different rinsing and deacidification approaches. Maitland and Smith rinsed using calcium hydroxide in their study, and they found that the calcium hydroxide rinse did not prevent paper darkening upon artificial aging, nor were they able to add an appreciable reserve of calcium back into the paper with this method. They showed that the ionic strength (and conductivity) of pH 8–9 calcium hydroxide solution is exceedingly low. The amount of calcium carbonate deposited using a calcium bicarbonate (calcium hydrogen carbonate) solution is still limited but provides a greater calcium reserve than calcium hydroxide. By way of some instructive charts and graphs, Maitland encouraged the audience to revisit the chapter on deacidification in *Paper and Water* (Smith 2018).

Several practitioners shared modified approaches to citrate treatment that they have found successful in their own work. One participant reported success using low concentration 0.25% ammonium citrate solutions, finding them less aggressive while maintaining effectiveness, and noted reduced

color reversion after aging compared to higher concentrations. Another participant described using citrate as a spray treatment between rinsing baths rather than full immersion, allowing for more controlled application while maintaining effectiveness for stain removal. Multiple speakers warned against using metal spray bottles with citrate solutions due to metal leaching, recommending plastic spray bottles instead.

FUTURE RESEARCH DIRECTIONS

Participants noted the difficulty of predicting which papers will react adversely to citrate treatment without extensive analysis, suggesting the need for targeted research on commonly encountered types of paper. To date, aging studies have been limited to only a few types of paper.

The panel and participants identified several other areas needing further investigation: identifying the most appropriate counter ions for citrate solutions, determining best practices for rinsing and restoring lost calcium, analyzing wash waters to better understand what materials are being removed during treatment, studying binding constants for the chelating agents with various metal ions, and systematically examining the effects of citrate solutions on 20th century art papers like the ubiquitous Arches and Rives.

The discussion concluded with recognition that citrate solutions represent powerful tools for stain reduction but their use requires careful consideration of paper type, treatment goals, and long-term effects. The combination of analytical data and extensive practical experience presented at the Art on Paper Discussion Group session offers valuable guidance for conservators considering citrate treatments and highlights the ongoing need for systematic study of these complex chemical interactions.

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NOTE

1. Ammonia and its salts can be harmful for plumbing systems and aquatic life. Please refer to the chemical safety data sheet prior to handling ammonium or sodium citrate, and consult your local waste regulations before disposing of any chemical.

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