# The Effect of Various Aqueous Bathing Solutions on the Calcium Content of Paper

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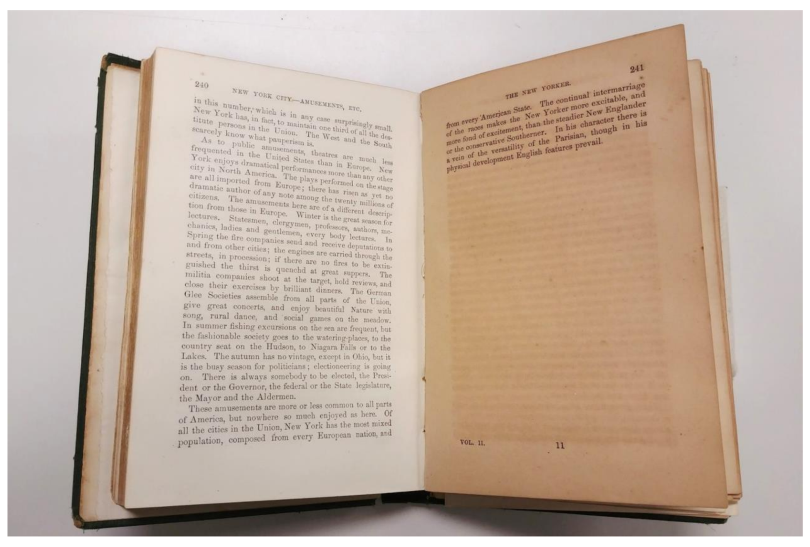
## INTRODUCTION



Careful tailoring of aqueous solutions for paper bathing has long been part of paper conservation. Previous research (Bogaard and Whitmore 2001; Hanson 1939; and more) has suggested that calcium content within paper promotes better aging qualities (e.g. retention of strength and reduced yellowing with age), thus calcium has been used to enrich bathing solutions.

However, the comparison of different bathing solutions and their quantifiable effect on the calcium content of paper has rarely been discussed. Therefore, answers were sought to the following questions: In aqueous paper bathing procedures, how much is the inherent calcium content of the paper affected? Does the use of chelators remove calcium from the paper? When paper is bathed with calcium-enriched water, is calcium successfully incorporated into the paper substrate? In an attempt to answer these questions, a series of baths was designed to emulate common bathing, cleaning, and rinsing solutions. Atomic absorption spectroscopy (AAS) was used to quantify the calcium content of historical paper in ppm throughout the bathing process.

(Left) This book from 1853 was investigated by John Krill and analyzed by Matt Cushman and Janice Carlson using energy dispersive XRF spectroscopy. The comparison of the spectra showed that the only significant compositional difference between the light and dark pages was a large difference in the presence of calcium. The left page with its light color and good condition had high calcium content, while the page on the right with its dark color and worse condition had low calcium content.

## EXPERIMENTAL DETAILS

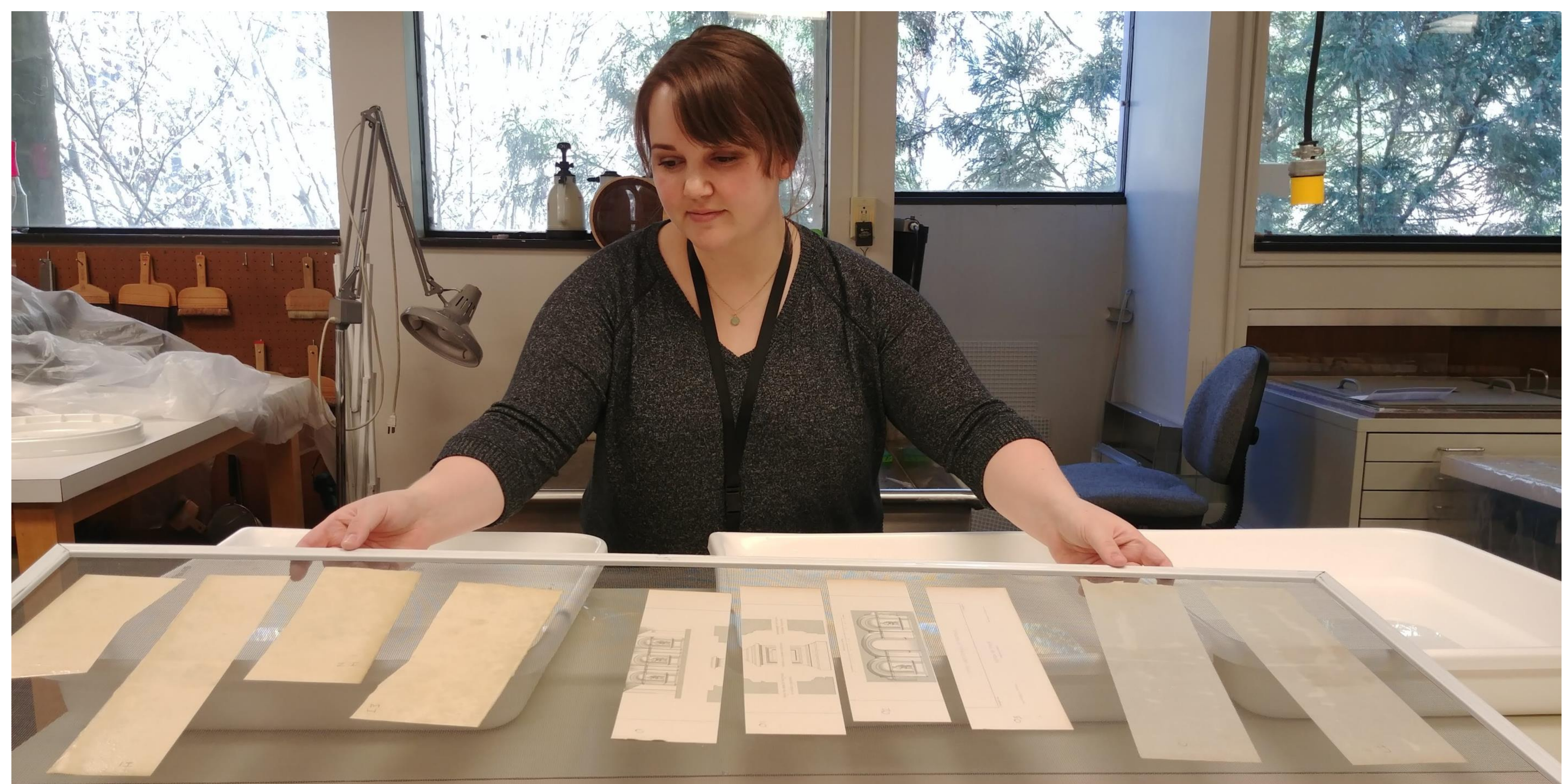
| Historical Paper Sources – Fragmentary Study Collection Books | Fiber Content | Average ppm Ca |
|---|---|---|
| Interleaving Pages, *Engravings of the Marquis of Stafford's Gallery of Pictures (Vol. II)*, William Ottley and Peltro Tomkins, 1818 | Bast/Cotton | 494 |
| Text Pages (Only blank margins were used), *Engravings of the Marquis of Stafford's Gallery of Pictures (Vol. II)*, William Ottley and Peltro Tomkins, 1818 (Watermark: Whatman 1808) | Bast/Cotton | 1963 |
| Image Plate Pages, *Palais Chateaux Hotels et Maisons de France*, Claude Sauvageot, 1867 | Bast/Cotton | 3542 |

| Bath #1 Solutions | pH [1] | µS/cm | Rationale |
|---|---|---|---|
| DI Water | 5.5 [2] | 2.7 | Very hypotonic in nature. Not often used without adjustment because of its often-termed "aggressive" pull of ions out of the paper. |
| Calcium Hydroxide | 7.5 | 5.3 | Often added to DI water to adjust the pH to neutral or slightly basic with additional possibilities of imparting calcium. |
| Ammonium Acetate (Isotonic)[3] | 7.0<br>5.2 | 161.3<br>586.7 | Can be adjusted for pH and conductivity to match individual papers (2 variations made), and should theoretically volatilize, leaving no additions in the paper. |
| Ammonium Citrate (1%) | 5.0 | 6670.0 | Made at 1% is often used for stain reduction, functioning as a chelator while being hypertonic, potentially causing the paper fibers to swell and open up to a greater degree. |
| Sodium Citrate (Isotonic)[3] | 7.1 | 104.0 | Can be adjusted for pH and conductivity to match individual papers, while also adjusting pH high enough to have the molecule function most efficiently as a chelator (above pH 6.4). |
| Ammonium Citrate (Isotonic)[3] | 7.1 | 105.7 | Can be adjusted for pH and conductivity to match individual papers (contrasting the 1%), while also adjusting pH high enough to have the molecule function most efficiently as a chelator (above pH 6.4). |
| **Bath #2 Solutions** | **pH [1]** | **µS/cm** | **Rationale** |
| Calcium Hydroxide | 7.6 | 6.0 | Often used as a final bath after other bathing procedures to "rinse" paper, adding to DI water to the desired pH with the possibility of imparting calcium. |
| Calcium Bicarbonate | 6.5 | 1990.0 | Historically used to impart an "alkaline reserve" in paper in previously termed "deacidification." |
| Calcium Acetate | 7.1 | 102.0 | Experimentally used to replenish calcium in paper or impart an alkaline reserve, theoretically leaving calcium in the paper when the other components volatilize. |

(1) Measurements for pH and conductivity of the solutions were taken three times and averaged using a Horiba LAQUA Twin pH and a Horiba Twin Conductivity B-173 meter.
(2) Winterthur's Deionized Water has been reported within a range of pH 5.5-6.5.
(3) Conductivity and pH were measured for each of the paper sources using 5% agarose gel plugs and the same meters, with three locations tested and averaged. These measurements were used to create the solutions labeled "isotonic," making the solution's pH and conductivity close to that of the paper.

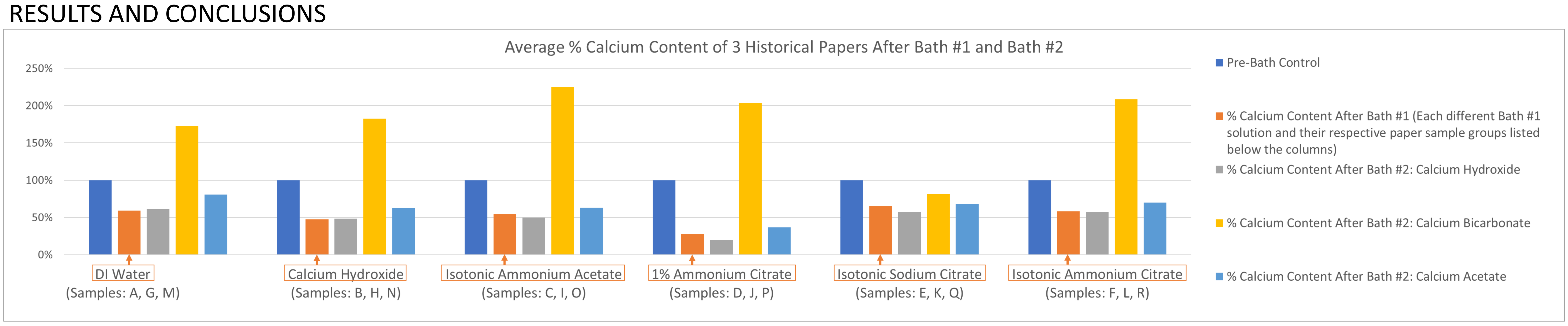
### Steps for Each Sheet of Paper:

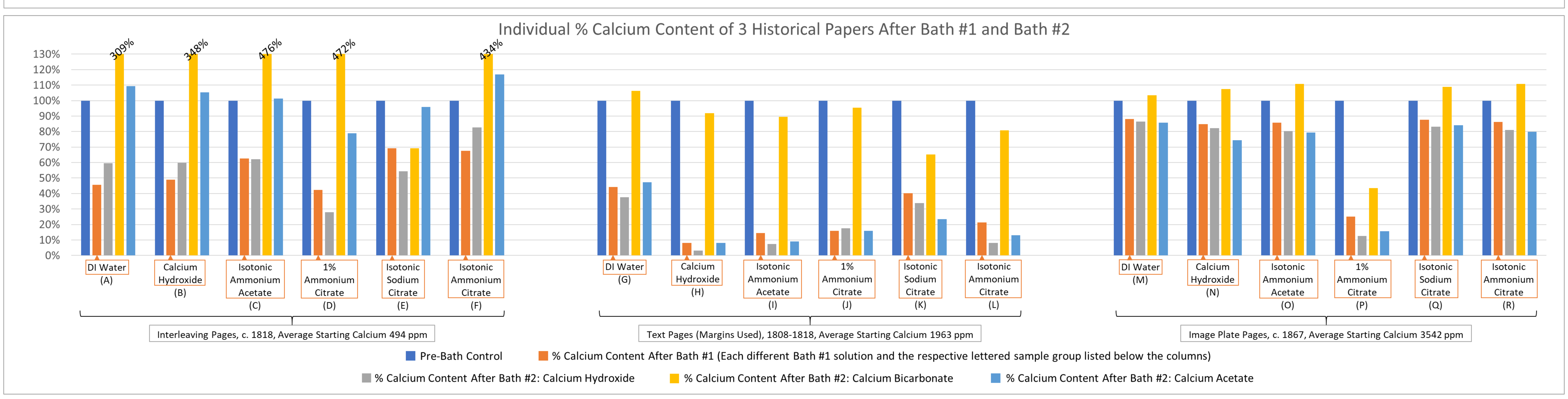
1. Take sample of sheet as a control
2. Bathe in chosen Bath #1 (30 min)
3. Take post-Bath #1 sample
4. Divide remainder of sheet into 3
5. Bathe 3 pieces each in 1 of 3 Bath #2 Solutions (30 min)



(Above Right) Solutions were made in large quantities and divided into individual trays to ensure solution parameters remained the same for each paper group. (Above) After being placed on screens, the bathed samples were allowed to fully air dry.

## RESULTS AND CONCLUSIONS




### Key Observations

**Bath #1**

- All Bath #1 solutions removed calcium content by at least 12%, up to 92%.
- On average, 1% ammonium citrate removed the most calcium, with 28% remaining, likely due to the pH and its hypertonic nature causing greater swell to the paper.
- On average, the calcium hydroxide solution (the only calcium-enriched solution from Bath #1) removed the second largest amount of calcium, with 47% remaining.
- Contrasting the 1% Ammonium Citrate (hypertonic to the paper), the isotonic citrates removed similar amounts of calcium as the other non-chelating solutions.
- Image Plate Page samples saw the smallest decrease in inherent calcium content, possibly due to starting with much higher levels than the other two paper sources.

**Bath #2**

- Calcium bicarbonate is the only Bath #2 solution that consistently returned the calcium near to its original levels and/or imparted a reserve for all three paper sources.
- 78% of the time (14/18 sample groups), rinsing in a calcium hydroxide solution reduced the calcium content further.
- Calcium bicarbonate imparted a very large addition of calcium to the interleaving pages compared to the other two sources, indicating other components or lack thereof within the paper may have influenced the effect of the solution.
- Calcium acetate performed well for the interleaving pages, returning the calcium values to nearly their original content, but not as well for the other two papers.

*Don't throw the calcium out with the bath water…* If retaining calcium in paper during treatment remains a goal, paper conservators must continue to reexamine our bathing solutions, such as the use of calcium-enriched deionized water, which performs very similarly to unaltered deionized water. Further study may incorporate the investigation of how the presence of additional components in paper, such as fillers and sizing, may influence the effect different solutions have on the calcium content. Additionally, alternate methods of re-introducing calcium to paper as well as methods of adjusting and manipulating conductivity of solutions and chelators to spare calcium content could be investigated. Ultimately, further study on a larger scale is necessary to fully understand the effect bathing solutions have on the calcium content of paper.

## ACKNOWLEDGEMENTS

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