Tea: An Alternative Adsorbent for the Preservation of Cellulose Triacetate Film

Julianne Bell[1], Mick Newnham[2] and Petronella Nel[1]

1. The Grimwade Centre for Cultural Materials Conservation, School of Historical and Philosophical Studies, The University of Melbourne
2. National Sound and Film Archive (until 2017)

Abstract

Cellulose triacetate film, the main film base of the 20th century, is inherently unstable, affected by autocatalytic deterioration through hydrolysis. The release of, and subsequent exposure to acetic acid, known as ‘vinegar syndrome’ accelerates deterioration, placing all cellulose acetate materials at risk, or actively deteriorating. Preservation techniques rely on cold storage to slow deterioration, or microenvironments with adsorbent materials to remove corrosives and/or pollutants. However, commercially available adsorbents can be expensive and difficult to access. This research investigated the potential for tea and tea waste to act as an alternative, low cost, accessible adsorbent for the preservation of cellulose triacetate film. Adsorption capabilities of various tea varieties and treatments were compared with activated charcoal, silica gel and molecular sieves. Testing established tea as an effective adsorbent of water and acetic acid vapour, with an aversion to adsorption of the plasticiser dibutyl-phthalate. Use of tea waste also involves additional cost, sustainability and accessibility benefits along with lessened corrosive potential. These findings support tea as a potentially viable alternative adsorbent for the preservation of cellulose triacetate film, requiring further research into optimum application systems.

Keywords: Film preservation; Cellulose triacetate; Adsorbents; Tea leaves; Acetic acid and DBP adsorption

Background

Cellulose acetate (CA), widely considered a 20th century ‘wonder product’, was developed and valued for its flexibility, strength and transparency (Richardson et al. 2014, p.231). Replacing the highly flammable cellulose nitrate (CN), CA was considered a stable, long-term support, ‘being comparable to permanent-record paper’ (Hill & Weber 1936, p.677). By the 1940s CA was the preferred medium for film and was the chief manufactured film base until the introduction of polyester supports in the late 1980s. The significance of CA objects cannot be overstated with the National Library of Australia (NLA), Canberra conservatively estimating a body of <10 million objects nationally (NLA 2000, p.16). Information stored within this medium hold a valuable cultural record of the last half of the 20th century. When considered internationally, the potential loss of cultural heritage is significant.

Over time, the composition of CA film materials underwent a number of developmental variations to improve stability, solubility and resistance to heat and moisture. Cellulose tri-acetate (CTA), the fully esterified form with a higher acetate content imparting a higher resistance to heat and moisture, emerged as the dominant film stock in use (Waentig 2008, p.218). Addition of plasticisers to CA film made thermoplastic processing possible, improved flow properties, and facilitated the removal of solvents during manufacture (Ballany et al. 2001, p.146). Other functional additives such as thermal, weathering, UV and infrared stabilisers increase the strength and durability of the material (Waentig 2008, p.218).

As instances of CA instability in high humidity locations began to be reported in the 1950s, research into the perceived permanence of the material revealed an unforeseen problem; the autocatalytic nature of CA degradation (Wilson & Forshee 1959, p.155). Further research focused on establishing the physical and chemical degradation characteristics of CTA film, identifying an acid catalysed hydrolysis, in which the acetate ions react with moisture to form acetic acid (Edge et al. 1989, p.347). Release of acetic acid's characteristic scent led to the deterioration process being labelled 'vinegar syndrome' (Reilly 1993, p.2). Rapid breakdown is initiated if the off gassed acetic acid remains in contact with the degrading polymer, and as the acetate film decays, it shrinks, loses flexibility, curls and warps rendering the carrier unplayable and the content lost (Shashoua 2008, p.182). Thus, the previously understood long-term stability of CA was drastically reduced to 40 years, rendering it chemically unusable within the timeframe of historical significance (Tumosa et al. 2001, p.136).

Researchers at the Image Permanence Institute (IPI) found that un-degraded CTA film readily absorbs acetic acid from adjacent degraded film with physical contact unnecessary (Adelstein et al. 1995, p.446). Alternatively, some films up to 55 years old were found to still be in excellent condition, demonstrating the impact storage environment may have on the deterioration process. Research into preservation techniques for CTA film, have therefore focused on identifying ideal storage conditions to delay and prevent deterioration, maximising the time available for content digitisation or duplication. Two main storage techniques emerged, which remain the international standard for CA film preservation today. One technique incorporates macro-environment cold, dark and dry controlled storage to delay deterioration by lowering the rate at which chemical reactions take place (NFSA 2015, p.181). The other technique utilises microenvironments with ventilation or adsorbent materials to slow deterioration by adsorbing pollutants that initiate or accelerate the degradation process. However, macro-environments require extensive set up and equipment, which are costly to maintain and involve high energy use. Whereas microenvironment techniques require staff knowledge and time to implement, along with ongoing funding for adsorbent materials. As a result, both techniques hold limited accessibility due to cost and expertise, which are out of reach for small, remote, under-funded or community run archives.

In the context of microenvironment preservation, the mechanisms of adsorption and absorption require differentiation. Adsorption refers to the collection of one substance onto the surface of another substance as a thin film, as in the adsorption of acetic acid vapour onto the surface network of adsorbent materials such as molecular sieves. Whereas absorption refers to the penetration of one substance into another, as in the absorption of acetic acid into the CTA film base (Zumdahl & Zumdahl 2010, p.584).

Shashoua (2014) conducted a study to evaluate the effectiveness of adsorbents at inhibiting the degradation of CA film. A range of commercially available adsorbent materials were tested, aged with stable and degraded CA film and analysed with gas chromatography-mass spectrometry (GC-MS). Results showed that the plasticiser diethyl-phthalate is adsorbed preferentially to acetic acid, effectively accelerating plasticiser loss, resulting in physical deterioration of CA film (Shashoua, Schilling & Mazurek 2014, pp.6-7). However, experimentation utilised cellulose di-acetate (CDA) film, rather than the more common CTA film. It is the third acetate group in CTA film which is more readily released from the material resulting in acid-catalysed deterioration (Willet, Newnham & Nel 2015, p.98). Thus, the present study focused on CTA film to assess the efficacy of adsorbent materials for storage environment control.

A national questionnaire conducted by the NLA, revealed widespread deterioration is already occurring, with institutions reporting a severe lack of expertise and funding to tackle an ever-increasing problem (NLA 2000, p.36). However, current industry recommended techniques for the preservation of CTA film are both expensive and require specialist materials and knowledge. This study intends to position tea as a potential alternative, low cost, easily accessible adsorbent material for preserving CTA film. Mick Newnham of the National Film and Sound Archive, Canberra (NFSA) initially proposed this research based on anecdotal evidence that the storage of tea adjacent to CA films resulted in an unexpectedly low rate of deterioration (Willet 2012, p.8).

Tea, prized for its flavour, stimulating effects and health benefits, is an extremely versatile material with its applications far exceeding that of a popular beverage. Catechins, the distinguishing characteristic of tea, are the source of the many health claims, specifically antioxidants, which block oxidative reactions by scavenging, neutralising and preventing the formation of free radicals (Harbowy et al. 1997, p.463). As tea catechins can maintain a high level of antioxidant activity in a wide range of pHs, the potential applications of tea, and tea waste, as an adsorbent and pollution scavenger are extremely varied (Nanjo et al. 1996, p.901). Manufacture of tea for consumption produces 2-4% tea waste for total production, an enormous amount of waste globally (Chowdhury et al. 2016, p.5). 'Tea waste' includes discarded leaves, buds and stems of tea plants which, if not recycled or disposed of properly, can have significant environmental impact (Zuorro & Lavecchia 2010, p.158). Recent innovative applications of tea waste include the removal of heavy metals contaminants from industrial wastewater (Zuorro & Lavecchia 2010), the removal of harmful dyes from textile industry wastewater (Khosla, Kaur & Dave, 2013), indoor air purification from formaldehyde based wood resins and adhesives (Hojo, Fukai & Nanjo 2000), and even the adsorbance of overdosed pharmaceutical drugs in the body (Seedher & Sidhu 2007). Willet conducted preliminary testing of tea as an adsorbent for water vapour in 2012 and found the material worthy of undergoing further testing (Willet, Newnham & Nel 2015, p.97). Based on these findings, this study further investigated the adsorption capabilities of tea and tea waste, and its application as an alternative, low cost, easily accessible and sustainable adsorbent material for the preservation of CTA film materials.

Materials

Three different types of tea were chosen for experimentation with an effort made to ensure all products were as unaltered as possible to ensure additives did not interfere with experimental results: green tea (Nerada Organics Green Tea), black tea (Nerada Black Tea) and red tea (Just Rooibos African Red Tea). All of the chosen teas are organically grown, with no pesticides, fungicides or chemical fertilizers used in cultivation, no artificial flavours, colours or preservatives added, and using only oxygen whitened teabag filter paper (Ethical Consumer Group 2016). Unlike previous experiments conducted by Willet (2012, pp.22-24) in which tea was purchased from a specialty store, all teas were purchased from local supermarkets in Australia to ensure accessibility.

In addition, three different methods of processing tea were tested: (1) unaltered tea straight from the packet; (2) oven dried tea as a form of regeneration to ensure all adsorption sites were available; and (3) tea brewed as per the manufacturer's instructions and oven dried to represent a recycled waste product.

For comparison purposes, the commercially available adsorbents silica gel, activated charcoal, and molecular sieves were chosen due to their common use in conservation and citation in the literature (Grzywacs 2006; Shashoua, Schilling & Mazurek 2014; Willet, Newnham & Nel 2015). Two sizes of molecular sieves, 3Å (1.5-2.5mm) and 4Å (2.5-5.0mm), were tested to ensure vapour molecules of different sizes were accommodated (Sigma-Aldrich® 1999). Molecular sieves were tested both unaltered straight from a new packet, and regenerated thermally according to the manufacturer's instructions to ensure optimal performance. For a full list of tested materials and treatments see Table 1.

Table 1: Summary of Tested Materials and Treatments

Material	Title	Colour
Unaltered Green Tea *	1. Green Tea	🟩
Oven Dried Green Tea *	2. Dried Green Tea	🟩
Brewed and Oven Dried Green Tea *	3. Brewed Green Tea	🟩
Unaltered Red Tea **	4. Red Tea	🟥
Oven Dried Red Tea **	5. Dried Red Tea	🟥
Brewed and Oven Dried Red Tea **	6. Brewed Red Tea	🟥
Unaltered Black Tea ***	7. Black Tea	⬛
Oven Dried Black Tea ***	8. Dried Black Tea	⬜
Brewed and Oven Dried Black Tea ***	9. Brewed Black Tea	⬛
Molecular Sieve Type 3Å Unaltered	10. MS 3Å	🟦
Molecular Sieve Type 3Å Regenerated	11. MS 3Å Regen	🟦

Molecular Sieve Type 4Å Unaltered	12. MS 4Å	🟪
Molecular Sieve Type 4Å Regenerated	13. MS 4Å Regen	🟪
Silica Gel	14. Silica	🟧
Activated Charcoal	15. A. Charcoal	🟨

* Nerada Organics Green Tea
** Just Rooibos African Red Tea
*** Nerada Black Tea

Method

Water Vapour Adsorption

Gravimetric analysis of water vapour adsorption in a microclimate was performed to confirm tea leaves as effective adsorbents of moisture, as CA degradation is accelerated by high relative humidity (Allen et al. 1987, p.386). The method described by Willet (2012, pp.22-24), was conducted twice to establish the efficacy of the technique. Slight alterations in method included different glass vials for the distilled water to avoid spill issues, and only 1g of each adsorbent material being tested, as repeating the experiment with 5g, 10g, 15g, 20g and 30g was unnecessary. After two rounds of testing with distilled water, the method was established as accurate and reproducible with results replicating those of Willet (2012, pp. 27-38).

Acetone was then introduced as the testing solvent to model for acetic acid, which has a similar molecular size with fewer safety issues (Zumdahl & Zumdahl 2010, p.508). However, permeability of the polypropylene containers to acetone vapour, produced inconsistent results (SciLabware® 2012). To address this issue, the method was refined, by replacing the plastic containers with glass tubes (24x150mm) and silicone stoppers as utilised in the British Museum's '3 in 1' modified Oddy testing methodology (Thickett & Lee 2004). This allowed for the safe and reliable testing of acetic acid, and the common plasticiser dibutyl-phthalate (DBP).

Acetic Acid and DBP Adsorption

50ml Pyrex™ glass rimmed tubes (24x150mm) and 3ml glass vials with screw on lids were soaked, cleaned, rinsed and dried in an oven. Each material to be tested was prepared with the various treatments. For oven dried tea, green, black and red tea samples were removed from their bags, spread onto lined trays and dried in an oven for 30 minutes at 80°C (Geleby 2015). For brewed and oven dried tea, infusions of each tea were prepared to manufacturer's instructions. The wet tea leaves were removed from bags, spread onto lined trays and dried in an oven for 1 hour at 80°C (Geleby 2015). Molecular sieves, 3Å and 4Å, were regenerated in a 200°C oven for 24 hours with a slow heat up and enclosed cooling period as per manufacturer's instructions (Sigma-Aldrich® 2016).

1g of each prepared adsorbent material was weighed and added to the tubes. Inert conical silicone stoppers were inserted, the tubes labelled, and total weight recorded in triplicate on an analytical balance to 4 decimal places. Nylon filament was tied around the neck of the glass vials and 1ml of solvent (glacial acetic acid or DBP) measured with a disposable pipette was added to each. The vials were lowered into the glass tubes using the nylon filament to rest approximately 1cm above the adsorbent material in the bottom of the tube. Tubes were closed with the silicone stoppers, with additional nylon filament protruding from the closed tubes to facilitate removal of the vials (Figure 1). After a set period of time, the tubes were opened, the solvent vial removed, and the tubes re-weighed with changes in weight recorded indicating the adsorbance of vapour.

As an experimental control, identical glass tubes with each adsorbent material, but no solvent, were prepared and weighed simultaneously. Control results demonstrated 2.31% variability with the glass tube method.

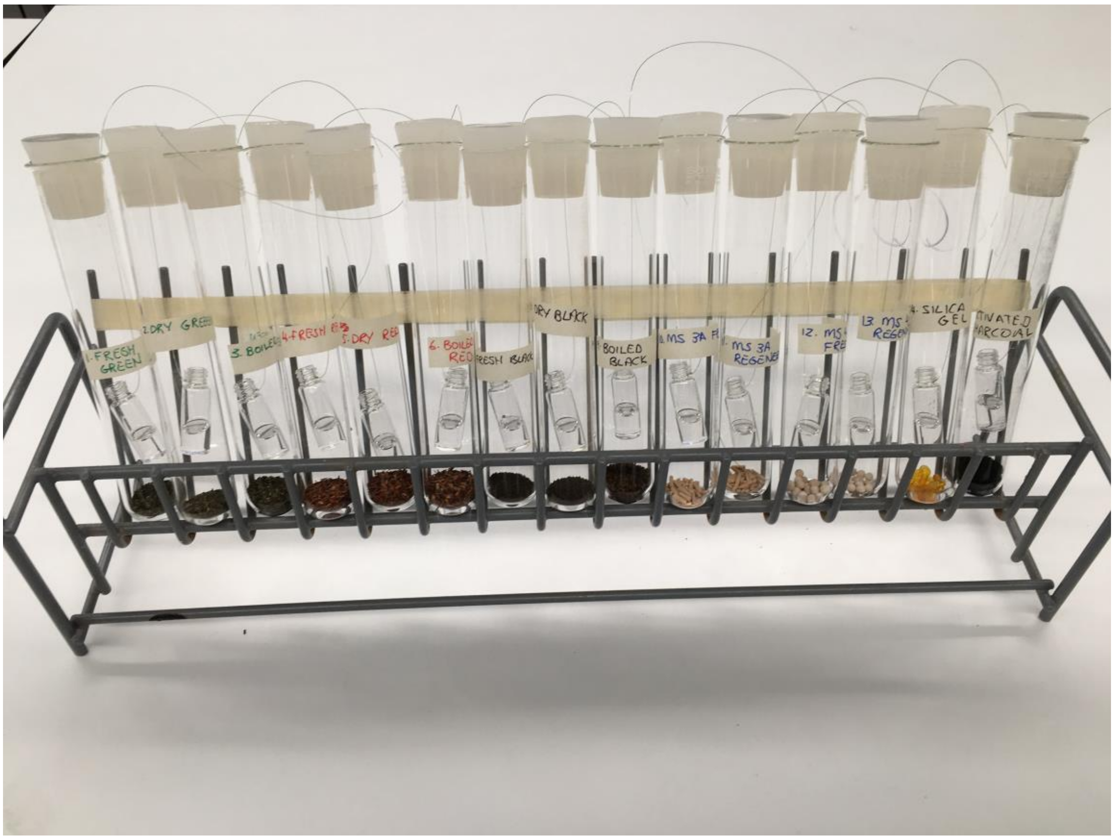

Figure 1: Experiment set up for vapour adsorption testing with glass tube methodology

In order to facilitate more meaningful data comparisons, the total number of mols adsorbed by each material were calculated from the molar mass of acetic acid (CH_3COOH, 60.05 g/mol) and DBP ($C_{16}H_{22}O_4$, 278.34 g/mol). As outlined in Equation 1, the total number of mols (n) of solvent adsorbed by each adsorbent material is the mass (or the maximum change in mass (Δ m) per 1g of material) (m) divided by the molar mass (M) of the solvent adsorbed:

Equation 1: (n) = (m) / (MW)

For example, Δ m (g) of unaltered green tea for the acetic acid vapour adsorption experiment was 0.3819. Therefore, n = 0.3819 g / 60.05 $g.mol^{-1}$ = 0.0064 mol.

Oddy Testing

Accelerated corrosion testing was performed on brewed and oven dried, and unaltered green, black and red tea in order to test for the adverse impact of volatiles from tea on metal coupons. This tested the suitability of tea leaves for permanent use in close proximity to cultural heritage objects such as silver in film or metal canister materials (Thickett & Lee 2004, p.12). Comparative research was carried out on all available Oddy test protocols (Banik 2013; Green & Thickett 1995; Robinet & Thickett 2003; Shiro 2015; Thickett & Lee 2004). The British Museum's '3 in 1' modified procedure was chosen to ensure accurate results while streamlining the testing method (Thickett & Lee 2004). The experiment was conducted twice to ensure consistent and accurate results. In addition to the standard copper, lead and silver coupons, aluminium and mild steel coupons were also sourced for testing due to their common use in film storage canisters (NFSA 2015, p.75). Although these materials are not traditionally included in Oddy testing, previous studies have found that the technique can be used to effectively evaluate the corrosive effects of materials on aluminium (Green & Thickett 1991, p.267), as well as iron and mild steel (Green & Bradley 1997, p.307).

Results

Water Vapour Adsorption

All tested material exhibited an initial high rate of adsorption, which slows and plateaus over time. As the adsorption sites are initially open and empty, the vapour molecules interact easily, hence the initially higher rate of adsorption observed (Amarasinghe & Williams 2007, p.304). All tea varieties demonstrated high levels of water vapour adsorption with the oven dried treatment performing best, suggesting the 'regeneration' maximised the availability of adsorption sites.

Mould activity proved to be an issue with all tea varieties for the initial water vapour adsorption experiment as the sealed container with water created a high humidity environment ideal for mould growth (Bertalan, Wood-Lee, & Olcott-Price 1994, pp.2-3). In general, the development of mould inhibited further vapour adsorption, halting weight gain, with subsequent loss of weight. Initial mould activity was detected on all black and green tea samples within the first 8-17 days, however, red tea showed significantly less biological activity, and at a later point in the experiment (24-32 days). This result appears to be related to the inherent antifungal and antimicrobial properties of red tea (Hubsch, Van Vuuren & Van Zyl 2014, p.149).

An encouraging result was the lack of mould development on any tea samples in the acetic acid and DBP adsorption experiments, as well as all control tests without solvent. This suggests in a lower humidity microenvironment, tea will not spontaneously develop mould. In addition, research has found acetic acid is effective at inhibiting the growth of certain mould strains (Stratford et al. 2009, p.41). CTA film does not readily sustain biological growth, particularly when deteriorating and releasing acetic acid (Morgan 1991, p.24). Storage recommendations of low temperature and RH also inhibit the development of biological activity (Bertalan, Wood-Lee, & Olcott-Price 1994, pp.2-3). Thus, the tea samples development of mould during the water vapour adsorption experiments may be mitigated by a low humidity microenvironment, the presence and adsorption of acetic acid, as well as the use of red tea based adsorbents.

Acetic Acid Vapour Adsorption

Acetic acid vapour adsorption tests, carried out over 50 days, measured the amount of acetic acid vapour adsorbed by the test materials (±2SD). All materials demonstrated an initial period of high adsorption as the empty pores interacted readily with the vapour molecules. Adsorption rates then slowed to an equilibrium plateau, followed by a drop in weight adsorbed. Maximum adsorption levels for each material (Figure 2) are vital as once the material becomes saturated, it loses some of its protective potential and releases some of the adsorbed vapour (Brokerhof 1998).

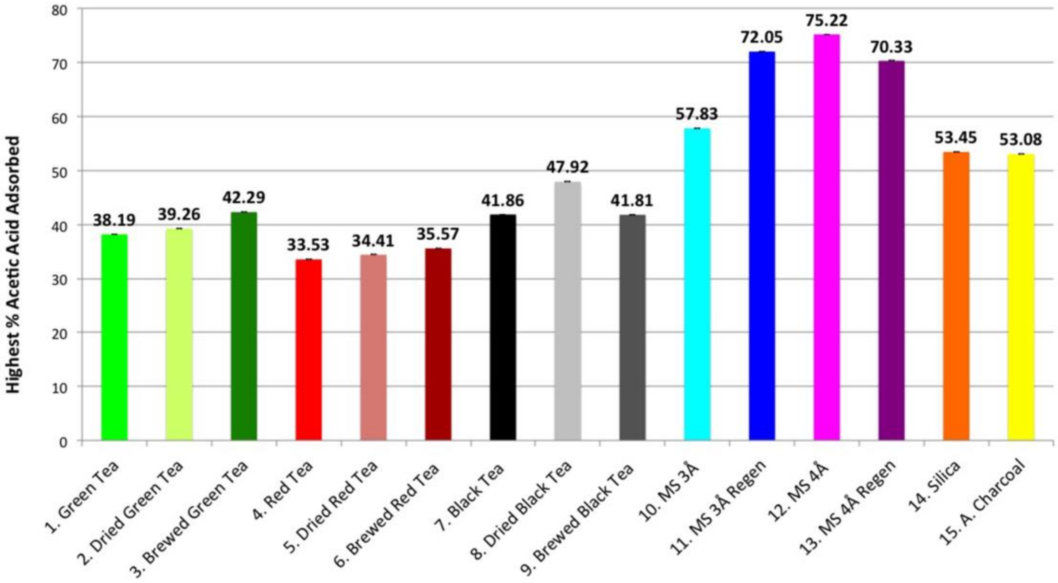

Figure 2: Highest % of Acetic Acid Vapour Adsorbed per 1g of Adsorbent Material for Experiment Conducted Over 50 Days (±2SD)

As illustrated in Figure 2, all commercial adsorbents outperformed all tea varieties with maximum adsorption levels averaging ~39% for teas vs. ~69% for the molecular sieves. This is a significant difference in maximum performance in favour of the specifically designed molecular sieves, however, support for the use of tea as an alternative adsorbent resides in other additional considerations.

Of the three tea varieties tested, black tea performed the best overall. As adsorption takes place on the surface of the material, the total surface area is more important than the total amount of material used (Brokerhof 1998). Black tea undergoes more processing steps than green or red tea, resulting in a smaller particle size and larger overall surface area (Wan, Li & Zhang 2009, pp.2-3). Of the tested tea varieties, the green tea leaf size was approximately 2x2mm, the red tea leaf size approximately 1x4mm, and the black tea approximately 1x1mm. Therefore, the higher adsorption capabilities of black tea could be due to the increased relative surface area of the black tea.

Across all experiments, tea treatments had limited impact on adsorption levels. Dried tea, and brewed and dried tea performed slightly better than untreated tea (~1.8%) suggesting the oven drying process is effective at removing additional moisture, as in the regeneration process (Geleby 2015; Grzywacz 2006, p.23). While tea treatment appears to have limited effect on adsorption potential, utilising brewed and dried tea, or tea waste has other implications for use.

DBP Vapour Adsorption

The DBP vapour adsorption experiment, carried out over 50 days, tested the ability of the materials to adsorb the vapour of a common plasticiser (±2SD). Adsorption rates for DBP were found to be ~10 fold lower than for the other tested solvents, with no material adsorbing more than 5.4% of their weight. Silica gel and all molecular sieves adsorbed more DBP (>4.4%) than all tea varieties and activated charcoal (<1.7%).

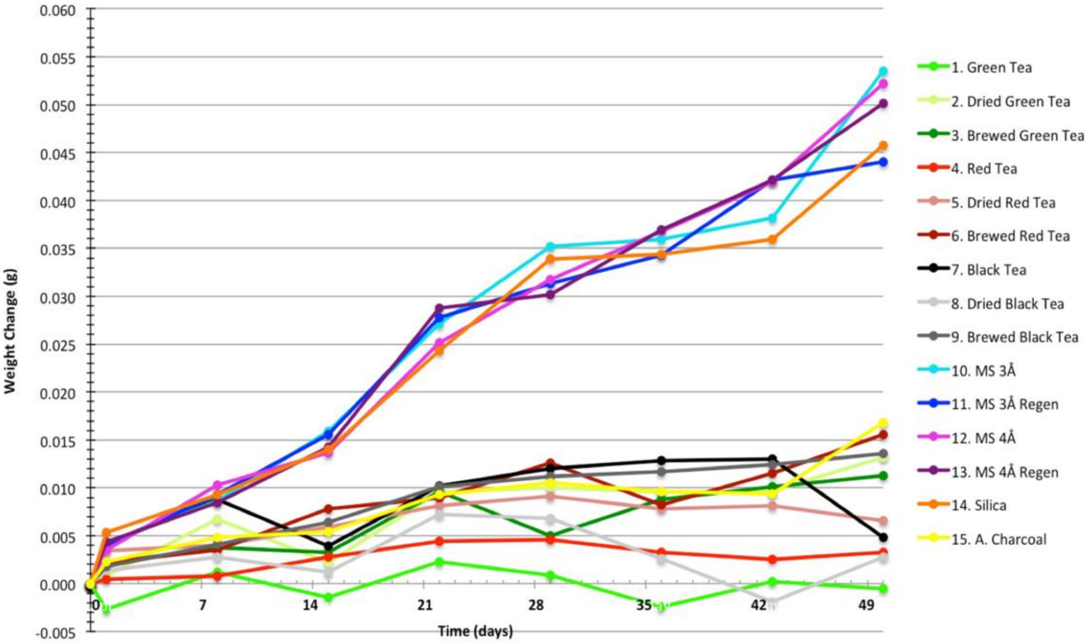

Figure 3: DBP Vapour Adsorption per 1g of Adsorbent Material Over 50 Days (±2SD).

As illustrated in Figure 3, the molecular sieves demonstrated a steady adsorption rate, with ongoing upward trajectories when the experimentation was concluded, suggesting peak adsorption had not yet been reached. Whereas the tea varieties did not demonstrate increasing adsorption trajectories, rather adsorbing and desorbing over time, indicating equilibrium had already been achieved. Pre-treatment and variety of tea appeared to have little effect on DBP vapour adsorption potential, with brewed varieties performing only slightly better. The glass tube control test data exhibited a variable adsorption rate ranging from -0.0118 to 0.0113, or 2.31%. When considered in relation to the tea samples adsorption of DBP, the variability rate negates the adsorption measurements of the DBP experiment. This indicates all tea varieties demonstrate an aversion to the adsorption of the plasticiser DBP.

Combined Acetic Acid and DBP Vapour Adsorption

Calculations facilitated a more meaningful comparison between total number of mols adsorbed of acetic acid and DBP. Values were then converted to percentages of a whole to demonstrate preferential adsorption potential between acetic acid and DBP (Table 2). This revealed the tea varieties exhibit an overall lower percentage of plasticiser adsorption (all <1%) in comparison to the commercially available adsorbents (all >1.3%). This suggests tea will adsorb off-gassed acetic acid, with a lower risk of preferential plasticiser adsorption.

Table 2: Total mols of Solvent Adsorbed by 1g of Material

Adsorbent Material	Acetic Acid (mol) x 10^{-4}	DBP (mol) x 10^{-4}	Acetic Acid %	DBP %
1. Green Tea	63.60	0.08	99.87%	**0.13%**
2. Dried Green Tea	65.38	0.47	99.29%	**0.71%**
3. Brewed Green Tea	70.42	0.41	99.42%	**0.58%**
4. Red Tea	55.84	0.17	99.70%	**0.30%**
5. Dried Red Tea	57.30	0.33	99.43%	**0.57%**
6. Brewed Red Tea	56.23	0.56	99.01%	**0.99%**
7. Black Tea	69.71	0.46	99.34%	**0.66%**
8. Dried Black Tea	79.80	0.26	99.86%	**0.32%**
9. Brewed Black Tea	69.63	0.49	99.30%	**0.70%**
10. MS 3Å	96.30	1.92	98.05%	**1.95%**
11. MS 3Å Regen	119.98	1.58	98.70%	**1.30%**
12. MS 4Å	125.26	1.88	98.52%	**1.48%**
13. MS 4Å Regen	117.12	1.80	98.49%	**1.51%**
14. Silica	89.01	1.65	98.18%	**1.82%**
15. A. Charcoal	88.39	0.60	99.33%	**0.67%**

Oddy Testing

Results from the Oddy test are summarised in Table 3. Of the six tested tea variants, four (brewed green, black and red tea and untreated red tea) exhibited no change on the silver coupons indicating they are safe for long-term use with cultural heritage materials. However, untreated black and green tea exhibited silver tarnish on the lower edge of the coupons suggesting the release of sulphides (Grzywacz 2006, p.33). All the lead coupons, apart from the unaltered black tea, failed by developing a complete layer of white, powdery corrosion product on all or most of the coupon. The development of basic lead carbonate is an indication of active lead corrosion, induced by vapours of weak organic acids naturally contained in tea (Harbowy et al. 1997, pp.426-7; Logan 2007, p.2).

Table 3: Combined Oddy Test Results

Material	Silver	Lead	Copper	Mild Steel	Aluminium
1. Unaltered Green Tea	✗ Fail	✗ Fail	Unclear	✗ Fail	✓Pass
2. Brewed Green Tea	✓Pass	✗ Fail	Unclear	✗ Fail	✓Pass
3. Unaltered Red Tea	✓Pass	✗ Fail	Temporary	✗ Fail	✓Pass

4. Brewed Red Tea	✓ Pass	✗ Fail	Temporary	✗ Fail	✓ Pass
5. Unaltered Black Tea	✗ Fail	✓ Pass	✗ Fail	✗ Fail	✓ Pass
6. Brewed Black Tea	✓ Pass	✗ Fail	Unclear	✗ Fail	✓ Pass

The tests on film canister materials, mild steel and aluminium, were consistent and fairly expected across the board. All mild steel coupons developed a full covering of black corrosion product resulting in a fail. All aluminium coupons, including the control, developed a protective oxide layer, confirming all materials passed for aluminium (Green & Thickett 1991, p.262).

Accurately interpreting the copper results proved problematic. Development of a solid black corrosion product on the control coupons in both experiments suggests contamination of materials (Thickett & Lee 2004, p.16). Untreated and brewed green tea samples developed slight discolouration but no corrosion product in the first round, but failed in round 2. Untreated and brewed red tea samples each exhibited slight black discolouration, with no spots of corrosion in both rounds, suggesting they are acceptable for temporary use (Thickett & Lee, 2004, p.16). The untreated black tea failed in both rounds, while the brewed black tea failed in round 1 but exhibited no changes in round 2. Difficulty with interpretation is often an issue with Oddy testing as subjective observations are often impossible to avoid and clear determination of corrosive effect is difficult (Banik 2013). Due to the very inconsistent and problematic results from the copper coupons, the related data is determined to be inaccurate and unreliable.

Discussion

Systematic testing of a range of tea varieties, treatments and solvents demonstrate that tea leaves are an effective adsorbent of moisture and acetic acid vapour in a microclimate, while exhibiting an aversion to adsorption of the plasticiser DBP. Molecular sieves did show higher adsorption potential for acetic acid vapour, however, this correlates with an increased potential for adsorption of plasticiser, a contributor to physical deterioration of CTA film (Shashoua, Schilling & Mazurek 2014, p.6).

The potential of tea to emit harmful volatiles and its suitability for use in close proximity to cultural heritage objects was also investigated. Of particular interest were the results from the silver coupon as CTA film contains silver halides in the image forming material (NFSA 2015, p.23), and silver coupons were not included in previous adapted Oddy testing of tea (Willet 2012, p.25). Results suggest red tea does not emit any sulphide based VOCs and the brewing process removed such compounds from green and black tea (Thickett & Lee 2004, p.4). These results support the application of tea, particularly waste tea, as an adsorbent material for CTA films. Corrosion of the mild steel coupons indicate use of tea as an adsorbent material for CTA film would be appropriate for aluminium or plastic canisters, but not with steel canisters. The following additional implications of utilising tea or tea waste as an alternative adsorbent material, further support its application.

A major advantage for establishing an alternative adsorbent material for the preservation of CTA film is the associated cost benefit. This is best demonstrated in a direct application cost comparison between the current industry recommended molecular sieves, and the equivalent of unaltered black tea, and tea waste.

Kodak recommends 6 x 12.5g (total 75g) molecular sieve packets per 35mm film roll, replaced every 2 years if stored at ambient temperature (Kodak 2016). If a small audiovisual archive holds 1000 CTA materials with no cold storage, 6000 x 12.5g packets of molecular sieve, or 75kg is required every 2 years. If purchased in large quantities from a chemical supplier at $250 for 200 x 25g bags, with 3 bags per film roll (75g), the cost of 3000 molecular sieve packets is $3750 (SilicaGel Direct 2012).

Black tea is available in 10g bags at $1.50 for 100 bags from local supermarkets (Coles™). 8 x 10g bags (total 80g) are required per film roll, equivalent to Kodak's recommendations. Thus, 8000 tea bags are required every 2 years. If purchased in normal quantities from a local supermarket, the cost of 8000 tea bags is $1200. Thus, equivalent application of tea for a small archive with 1000 CTA materials is $2550 cheaper over 2 years (Table 4).

Table 4: Direct cost comparison between industry recommended molecular sieves, unaltered black tea and spent tea for 1000 CTA object collection over 2 years

	Molecular Sieves	Unaltered Black Tea	Tea Waste
Material per film roll (Kodak 2016)	6 x 12.5g packets per roll	8 x 10g bags per roll	80g tea waste per roll
Material Cost	$250 for 200 x 25g bags	$1.50 for 100 x 10g bags	-
Total Material Required	3000 x 25g packets = 75kg	8000 x 10g tea bags = 80kg	80kg tea waste
Total Material Cost	**$3750**	**$1200**	**$0**

Alternatively, by utilising tea waste, produced in most homes and offices as spent tea bags, or produced on a massive scale in the tea manufacturing industry, material costs are negated. Lack of funding was the highest reported issue in relation to national museums' ability to effectively preserve CTA collections (NLA 2000, p.36). For small, remote, community run archives, the financial burden is exponentially higher. Whether the CTA film collection resides in a large institution, a small archive or a private collection, reduction of ongoing costs associated with preservation needs is of vital importance.

In conjunction with the clear cost advantages of utilising tea as an alternative adsorbent for CTA materials, accessibility to the material is greatly improved. Particularly for small, remote or community run archives, access to specialised materials and information may be restricted. Purchasing molecular sieves first requires an Internet connection to order from online distributors, which may not be affordable or available in remote areas of Australia (Edwards 2016). In addition, the purchasing process is often complicated, with many chemical suppliers restricting purchases to large institutions or accredited professionals, requiring large minimum orders, or having limited postal reach (Sigma-Aldrich® 2016, SilicaGel Direct 2012). Tea, as the second most consumed beverage after water, is available in any local supermarket, convenience store, petrol station etc. (Ho & Zhu 2000, p.316). Even the most remote and isolated community archive would realistically have some access to tea, even if through the local collection of used tea bags. Therefore, introduction of tea as an adsorbent material for the preservation of CTA film materials would vastly improve accessibility to preservation techniques for remote collections around Australia.

In addition to the financial and accessibility advantages of tea as an alternative adsorbent for CTA film collections, environmental benefits exist on multiple levels. On a local level, following the adsorbent and microenvironment storage strategy for CTA materials removes the high-energy needs of maintaining macro-environment cold storage (Bigourdan 2000, p.5). Minimising energy usage for the storage and display of cultural heritage objects is a key goal for sustainable conservation practices (AICCM 2002, art.6). In addition, utilising tea waste removes the need for purchasing specialised materials reducing overall material usage, while also recycling a waste product, both key sustainability practices inline with the 'reduce, reuse, recycle' mantra (AIC 2015, art.2.1). On a global level, substantial tea waste from processing and manufacturing is produced in nearly all parts of the world and, although of no commercial value, disposal is costly and not devoid of environmental impact (Zuorro & Lavecchia 2010, p.158). Utilisation of tea waste from the tea manufacturing industry therefore, represents an attractive strategy for the effective reduction and reuse of this abundant waste product.

Conclusion

Solvent vapour adsorption testing of three tea varieties: green, red and black, and three methods of tea pre-processing: unaltered, oven dried, and brewed and oven dried, were conducted to test the adsorption capabilities of tea and its potential application as an alternative adsorbent material for the preservation of cellulose acetate (CA) film. Tea demonstrated a solid ability to adsorb moisture and acetic acid vapour in a microclimate, along with an aversion to adsorb the common plasticiser dibutyl-phthalate. Brewed tea, or tea waste, demonstrated equivalent adsorption capabilities, lessened corrosive potential, cost advantages, and environmental benefits. In comparison to the commonly used, commercially available adsorbent materials tested, tea generally adsorbed more moisture and less acetic acid and DBP.

These results suggest tea may not be as effective at adsorbing off-gassed acetic acid as the industry recommended commercial adsorbent, molecular sieves. However, other considerations support further research into the application of tea as an alternative adsorbent. Tea demonstrated lower preferential adsorption of dibutyl-phthalate over acetic acid than the molecular sieves, an advantageous characteristic as loss of plasticiser advances the physical deterioration of CA. In addition, the use of brewed tea, which demonstrated no corrosive effect on silver, offers the additional sustainability benefits of repurposing a waste product, reducing material usage and eliminating material costs. Finally, the use of tea would increase accessibility for small, remote, underfunded or community run archives to preserve materials in their CA collections.

Through investigating the viability of tea as an alternative, low cost, accessible and sustainable adsorbent material, this research contributes to the time sensitive task of preserving CA film. The vast amount of our recorded cultural heritage at risk from CA deterioration positions this research as innovative, valuable, and worthy of further investigation.

References

Adelstein, PZ, Reilly, JM, Nishimura, DW, Erbland, CJ and Bigourdan, JL 1995, 'Stability of Cellulose Ester Base Photographic Film: Part V – Recent Findings', *Society of Motion Picture and Television Engineering,* vol. 104, no. 7, pp. 439-447.

Allen, NS, Edge, M, Appleyard, JH and Jewitt, TS 1987, 'Degradation of Historic Cellulose Triacetate Cinematographic Film: The Vinegar Syndrome', *Polymer Degradation and Stability,* vol. 19, pp. 379-387.

Amarasinghe, BMWPK and Williams, RA 2007, 'Tea Waste as a Low Cost Adsorbent for the Removal of Cu and Pb from Wastewater', *Chemical Engineering Journal,* vol. 132, pp. 299-309.

American Institute for Conservation of Historic and Artistic Works 2015, *Sustainable Practices,* viewed 19 June 2016, <http://www.conservation-wiki.com/wiki/Sustainable_Practices>

Australian Institute for Conservation of Cultural Material 2002, *Code of Ethics and Code of Practice,* viewed 20 January 2016, <https://aiccm.org.au/sites/default/files/docs/AICCMBusinessDocs/CODE%20OF%20ETHICS%20AND%20CODE%20OF%20PRACTICE%20Australian%20Institute%20for%20Conservation%20of%20Cultural%20Material.pdf>

Ballany, J, Littlejohn, D, Pethrick, RA and Quye, A 2001, 'Probing the Factors that Control Degradation in Museum Collections of Cellulose Acetate Artefacts', in JM Cardamone and MT Baker (eds.), *Historic Textiles, Papers and Polymers in Museums,* American Chemical Society, Washington DC, pp. 145-165.

Banik, G 2013, *The Oddy Test: What Works and What Doesn't,* Klug Conservation, viewed 9 Feb 2016, <http://www.klug-conservation.com/Current-News/2013/The-Oddy-Test-What-Works-and-What-Doesn-t>

Bertalan, S, Wood-Lee, M and Olcott-Price, L 1994, 'Mold/Fungi', *Paper Conservation Cataloguer,* American Institute for Conservation, Washington.

Brokerhof, A 1998, 'Application of Sorbents to Protect Calcareous Materials Against Acetic Acid Vapours', *Indoor Air Pollution: Detection and Mitigation of Carbonyls, Presentation Abstracts and Additional Notes,* The Netherlands Institute for Cultural Heritage, viewed 20 Feb 2015, <http://iaq.dk/iap/iap1998/1998_10.htm>

Bigourdan, JL 2000, 'Vinegar Syndrome: An Action Plan', in *The Vinegar Syndrome: A Handbook, Prevention, Remedies and the Use of New Technologies,* The GAMMA Group, Bologna, pp. 45-59.

Chowdhury, A, Sarkar, S, Chowdhury, A, Bardhan, S, Mandal, P and Chowdhury, M 2016, 'Tea Waste Management: A Case Study from West Bengal, India', *Indian Journal of Science and Technology,* vol. 9, no. 42, pp. 1-6.

Edge, M, Allen, NS, Jewitt, TS and Horie, CV 1989, 'Fundamental Aspects of the Degradation of Cellulose Triacetate Base Cinematograph Film', *Polymer Degradation and Stability,* vol. 25, pp. 345-362.

Edwards, M 2016, 'World Economic Forum Scores Australia Lowest for Internet Access Affordability', *ABC News,* 20 April, viewed 2 August 2016, <http://www.abc.net.au/news/2016-04-20/millions-of-australians-living-without-internet/7340434>

Ethical Consumer Group 2016, *Shop Ethical: Tea,* viewed 19 January 2016, <http://guide.ethical.org.au/guide/browse/guide/?type=11>

Geleby, T 2015 *Drying in Tea Processing,* World of Tea, viewed 19 January 2016, <http://www.worldoftea.org/drying-in-tea-processing/>

Green, LR and Bradley, SM 1997, 'An Investigation of Strategies for the Long-Term Storage of Archaeological Iron', in ID MacLeod, SL Pennec and L Robbiola (eds.), *Metal 95: Proceedings of the International Conference on Metals Conservation,* Maney Publishing, London, UK, pp. 305-309.

Green, LR and Thickett, D 1991, 'Modern Metals in Museum Collections', in DW Grattan (ed.), *Saving the Twentieth Century: The Conservation of Modern Materials: Proceedings of Symposium 91,* Canadian Conservation Institute, Ottawa, pp. 261-269.

Green, LR and Thickett, D 1995, 'Testing Materials for Use in the Storage and Display of Antiquities: A Revised Methodology', *Studies in Conservation,* vol. 40, no. 3, pp. 145-152.

Grzywacz, CM 2006, *Monitoring for Gaseous Pollutants in Museum Environments,* The Getty Conservation Institute, Los Angeles, CA.

Harbowy, ME, Balentine, DA, Davies, AP and Cai, Y 1997, 'Tea Chemistry', *Critical Reviews in Plant Sciences,* vol. 16, no. 5, pp. 415-480.

Hill, JR and Weber, CG 1936, 'Stability of Motion Picture Films as Determined by Accelerated Aging', *Journal of the Society of Motion Picture Engineering,* vol. 27, no. 6, pp. 677-690.

Ho, C and Zhu, N 2000, 'The Chemistry of Tea', in TH Parliament, C Ho and P Schieberle (eds.), *Caffeinated Beverages: Health Benefits, Physiological Effects, and Chemistry,* American Chemical Society, Washington, DC, pp. 316-326.

Hojo, H, Fukai, K and Nanjo, F 2000, 'Application of Green Tea Catechins as Formaldehyde Scavengers' Journal of the Japan Wood Research Society, vol. 46, no. 3, pp. 231-237.

Hubsch, Z, Van Vuuren, SF and Van Zyl, RL 2014, 'Can Rooibos (*Aspalathus linearis)* Tea have an Effect on Conventional Antimicrobial Therapies?', *South African Journal of Botany,* vol. 93, pp. 148-156.

Khosla, E, Kaur, S and Dave, PN 2013, ‘Tea Waste as Adsorbent for Ionic Dyes’, *Desalination and Water Treatment,* vol. 51, no. 34-36, pp. 6552-6561.

Kodak 2016, *Molecular Sieve Acid Scavenger,* viewed 21 July 2016, <http://motion.kodak.com/AU/en/motion/Support/Technical_Information/Storage/Acid_Scavenger/default.htm>

Morgan, J 1991, *Conservation of Plastics: An Introduction to Their History, Manufacture, Deterioration, Identification and Care,* The Conservation Unit of the Museums & Galleries Commission and the Plastics Historical Society, London.

Nanjo, F, Goto, K, Seto, R, Suzuki, M, Sakai, M and Hara, Y 1996, ‘Scavenging Effects of Tea Catechins and their Derivatives on 1,1-Diphenyl-2-picrylhydrazyl Radical’, in *Free Radical Biology & Medicine,* vol. 21, no. 6, pp.895-902.

National Film and Sound Archive of Australia (NFSA) 2015, *The Film Preservation Handbook,* National Film and Sound Archive of Australia, Canberra.

National Library of Australia (NLA) 2000, *Cellulose Acetate Project: Stage One,* National Library of Australia, Canberra.

Reilly, JM 1993, *IPI Storage Guide for Acetate Film,* Image Permanence Institute, Rochester.

Richardson, E, Giachet, MT, Schilling, M and Learner, T 2014, ‘Assessing the physical stability of archival cellulose acetate films by monitoring plasticizer loss’, *Polymer Degradation and Stability,* vol. 107, pp.231-236.

Robinet, L and Thickett, D 2003, ‘A New Methodology for Accelerated Corrosion Testing’, *Studies in Conservation,* vol. 48, no. 4, pp. 263-268.

SciLabware® 2012, *Physical Properties and Chemical Resistance of Plastics,* viewed 15 January 2016, <http://www.scilabware.com/uploads/PDFs/2010/Technical_information_Plastics.pdf>

Seedher, N and Sidhu, K 2007, ‘Studies on the use of tea leaves as pharmaceutical adsorbent’, *International Journal of Biological Chemistry,* vol. 1, no. 3, pp. 162-167.

Shashoua, Y 2008, *Conservation of Plastics: Materials Science, Degradation and Preservation,* Butterworth-Heinmann, Oxford.

Shashoua, Y, Schilling, M and Mazurek, J 2014, ‘The Effectiveness of Conservation Adsorbents at Inhibiting Degradation of Cellulose Acetate’, in J Bridgland (ed.), *ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15-19 September 2014,* ICOM Committee for Conservation, Paris.

Shiro, M 2015, *Getty Conservation Institute Protocol,* American Institute of Conservation, viewed 9 Feb 2016, http://www.conservation-wiki.com/wiki/Oddy_Test_Protocols

Sigma® 1999, ‘Molecular Sieves’, *Technical Information Bulletin,* no. AL-143, viewed 21 January 2016, <http://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/technical-bulletins/al-1430/molecular-sieves.html>

SilicaGel Direct 2012, *Zeolites,* viewed 2 August 2016, <http://www.silicageldirect.com.au/zeolites-1/>

Stratford, M, Plumridge, A, Nebe-von-Caron, G and Archer, DB 2009, 'Inhibition of Spoilage Mould *conidia* by Acetic Acid and Sorbic Acid Involves Different Modes of Action, Requiring Modification of the Classical Weak-Acid Theory', *International Journal of Food Microbiology,* vol. 136, no. 1, pp. 37-43.

Thickett, D and Lee, LR 2004, 'Selection of Materials for the Storage or Display of Museum Objects', *The British Museum Occasional Papers,* no. 111.

Tumosa, CS, Mechlenburg, MF and McCormick-Goodhart, MH 2001, 'The Physical Properties of Photographic Film Polymers Subjected to Cold Storage Environments', in JM Cardamone and MT Baker (eds.), *Historic Textiles, Papers and Polymers in Museums,* American Chemical Society, Washington DC, pp. 136-144.

Waentig, F 2008, *Plastics in Art: A Study from the Conservation Point of View,* trans., M Scuffil, Michael Imhof Verlag GmbH & Co., Petersberg, Germany.

Wan, X, Li, D and Zhang, Z 2009, 'Green Tea and Black Tea', in C Ho, J Lin and F Shahidi (eds.), *Tea and Tea Products: Chemistry and Health-Promoting Properties,* Taylor & Francis Group, Boca Raton, FL.

Willet, L 2012, *The use of tea leaves as an adsorbent material in the conservation of motion picture film,* University of Melbourne, Masters by Coursework minor thesis in Cultural Materials Conservation.

Willet, L, Newnham, M and Nel, P 2015, 'Preliminary Testing of Tea Leaves as Alternative 5ents for Preserving Early Cellulosic Motion Picture Film', *Bulletin of the Australian Institute for the Conservation of Cultural Material,* vol. 36, no. 2, pp. 97-104.

Wilson, WK and Forshee, BW 1959 'Degradation of Cellulose Acetate Films', *Society for Plastics Engineers Journal,* vol. 15, no. 2, pp. 146-156.

Zumdahl, SS and Zumdahl SA 2010, *Chemistry,* ninth edition, Brooks Cole, Belmont, California.

Zuorro, A and Lavecchia, R 2010, 'Adsorption of Pb(II) on Spent Leaves of Green and Black Tea', *American Journal of Applied Sciences,* vol. 7, no. 2, pp. 153-159.

Materials List

Nerada Organics Green Tea and **Nerada Black Tea:** Nerada Tea, PO Box 1420, Sunnybank Hills, QLD, 4109, Australia. Tel: 61 (07) 3272 0444, 61 (07) 3272 0243

Just Rooibos African Red Tea: 14 Tulbagh Ave, Kenridge, Durbanville, Western Cape, 7550, South Africa. Tel: +27-21-976 5514, +27-86-611 4963, info@just-rooibos.com

Activated Charcoal (untreated, granular 4-8 mesh) and **Dibutyl-Phthalate**: Sigma-Aldrich, PO Box 970, Castle Hill, NSW, 1765, Australia. Tel: 1800 800 097, anzcs@sial.com

Silica Gel (self-indicating orange 205mm beads) and **Molecular Sieves** (type 3Å 1.5-2.5mm and type 4Å 2.5-5.0mm): LabChem Inc, Jackson's Pointe Commerce Park –

Building 1000, 1010 Jackson's Pointe Court, Zelienople, PA, 16063, USA. Tel: +1 412-826-5203, +1 724-473-0647, info@labchem.com

Glacial Acetic Acid: Asia Pacific Specialty Chemicals Ltd, 9 Short St, Auburn, NSW, 2144, Australia. Tel: 61 (02) 9735 8000

Klip It™ 400ml polypropylene containers: Sistema Plastics Limited, PO Box 201202, Auckland Airport, Auckland, 2151, New Zealand. Tel: 64 9 579 7903, info@sistemaplastics.com

50ml Pyrex™ glass tubes (24x150mm): Corning Incorporated, One Riverfront Plaza, Corning, NY 14831, USA. Tel: +1 607-974-9000, inquiries@corning.com

Inert conical silicone stoppers (item no. 3808, 19mm base, 26mm top x 28mm): Kartell® Labware, kartelllabware.com.au Tel: (02) 9352 0600, labware@kartell.it

Silver Coupons: John Lazos & Associates Precious Metal Dealer, Suite 302, 125 Swanston Street, Melbourne, VIC, 3000, Australia. Tel: (03) 9654 0307.

Copper and Lead Coupons: Thermo Fisher Scientific Australia Pty Ltd, 5 Caribbean Drive, Scoresby, VIC, 3179, Australia. Tel: 1300 735 292, AUinfo@thermofisher.com

Mild Steel and Aluminium Coupons: Williamstown Metal Merchants Pty Ltd, 44 Tennyson Street, Williamstown North, VIC, 3016, Australia. Tel: (03) 9397 8385, info@metalstore.com.au

Author Biographies

Julianne Bell has completed a Master of Cultural Material Conservation (2016) specialising in objects conservation, and a Bachelor of Arts (Honours, 2013) majoring in Classics and Archaeology with a History minor, both obtained at the University of Melbourne. In 2017 Julianne commenced a PhD at the University of Melbourne funded by an ARC Linkage Project, supervised by Dr Petronella Nel and Prof Robyn Sloggett. Julianne's PhD research aims to focus on developing analytical techniques for characterising and identifying the condition and preservation requirements of three-dimensional objects composed of early cellulose ester plastics.

Until his retirement in 2017 Mick Newnham was the Manager, Conservation Services at the National Film & Sound Archive of Australia. He is the Immediate Past President of the South East Asia Pacific Audio Visual Archive Association (SEAPAVAA) and has contributed to the work of the International Federation of Film Archives (FIAF) Technical Commission, the Association of Moving Image Archivists (AMIA) Preservation Committee and the International Organization for Standardization's TC WG – the working group responsible for ISO standards and recommended practices pertaining to the care of audio visual materials.

Dr Petronella Nel is a lecturer at the Grimwade Centre. She has a BSc (Honours, 1990) in Chemistry and a PhD in Chemistry (2000) and MA in Cultural Materials Conservation (2006), from the University of Melbourne. She is currently leading an ARC Linkage Project 'A National Framework for managing malignant plastics in

Museum Collections’ in partnership with Museum Victoria, Queensland Museum, Museum of Applied Arts and Sciences - Powerhouse Museum, South Australian Museum, Art Gallery of NSW, University of Technology Sydney and Flinders University.

Acknowledgements: The authors would like to thank the National Film and Sound Archive, Canberra for identifying and proposing this innovative research topic, and the Grimwade Centre, The University of Melbourne for facilitating this research.