

"

Information archived on the Web

Ù&[||Á[, } Á[Á^^Á@Á[& { ^} dÈ

You can request alternate formats from the [Canadian Conservation Institute](http://www.cci-icc.gc.ca) via the website www.cci-icc.gc.ca.

A Closer Analysis of Old Cellulose Nitrate Repairs Obtained From a Cypriot Pottery Collection

Petronella Nel, Deborah Lau, and Carl Braybrook

(biographies and contact information for authors can be found at the end of this paper)

Abstract

After an infrared (IR) adhesive analysis survey of the Cypriot pottery collection at the University of Melbourne, a more detailed investigation was conducted into the 111 cellulose nitrate (CN) samples. The aim was to identify and understand differentiating factors between the CN samples. Principal component analysis (PCA) of the IR spectra identified two groups – correlating with the two acquisition periods of the collection (1972 and 1987) – and a difference in intensity of the IR peak due to the carbonyl group of the plasticizer. Gas chromatography with mass spectroscopy (GC-MS) analysis of ~100 CN samples from the collection identified the plasticizer to be dibutyl phthalate (DBP) and quantified the DBP levels as follows:

- ~15% (w/w) for the 1972 cluster and the HMG and UHU brands
- ~2% (w/w) for the 1987 cluster and an old formulation of Tarzans Grip

This difference in DBP levels between the two accession periods is most likely due to the use of different CN adhesive formulations. Previous conservation research found that plasticized CN is more stable than pure CN. Therefore, the low DBP levels of the 1987 cluster give it a higher conservation priority than vessels from the earlier 1972 acquisition period.

Titre et Résumé

Le réexamen de vieilles réparations effectuées avec le nitrate de cellulose sur des objets d'une collection de poteries chypriotes

L'analyse par spectroscopie infrarouge (IR) des adhésifs présents sur des objets de la collection de poteries chypriotes de l'Université de Melbourne a entraîné l'exécution d'une étude plus poussée qui ciblait les 111 échantillons de nitrate de cellulose (NC). Elle avait pour objectif d'identifier et de bien comprendre les facteurs qui différencient les échantillons de NC. L'analyse en composantes principales (ACP) des spectres IR a permis d'identifier deux groupes, lesquels correspondent aux deux périodes d'acquisition de la collection (soit 1972 et 1987), et une variation de l'intensité de la bande infrarouge associée au groupement carbonyle du plastifiant. L'analyse par chromatographie en phase gazeuse couplée à la spectrométrie de masse (CG-SM) de quelque 100 échantillons de NC de la collection a permis d'identifier le plastifiant, le phtalate de dibutyle (PDB), et d'en déterminer les concentrations :

- environ 15 % (p/p), dans le cas du groupe de 1972 et des produits de marques HMG et UHU;
- environ 2 % (p/p), dans le cas du groupe de 1987 et d'une ancienne formulation du produit Tarzans Grip.

La différence observée entre les concentrations de PDB des deux périodes d'acquisition est fort probablement due à l'utilisation de formulations différentes pour les adhésifs à base de NC. Les résultats de travaux de restauration antérieurs indiquent que le NC modifié par un plastifiant est plus stable que le NC pur. Par conséquent, la conservation et la restauration des poteries du groupe de 1987, caractérisées par de faibles concentrations de PDB, est une priorité par rapport à celle des récipients appartenant à la période d'acquisition antérieure (1972).

Introduction

Cellulose nitrate (CN) the first semi-synthetic polymer was first discovered in 1833 and developed during the 1840s (Fenichell 1996; Friedel 1983, Mills & White 1994; Mossman 1997; Quye & Williamson 1999; Stuart 2007). The fully tri-nitrated material (Figure 1), with degree of substitution (DS) of 3, 14.4% (wt/wt) nitrogen (N), called guncotton was used as an explosive. The less completely di-nitrated and more stable product containing ~11.11% N (wt/wt) with DS=2 (Roff & Scott 1971), was called pyroxylin, and could be moulded or when its alcohol/ether solution is applied to a surface, dry to a thin transparent film.

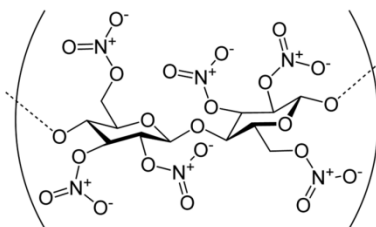


Figure 1. Chemical structure of fully nitrated cellulose nitrate polymer.

To overcome shrinkage and stiffness, plasticizers were employed to soften the polymer. Alexander Parkes plasticised CN with oils and camphor to produce Parkesine (Fenichell 1996; Friedel 1983; Mossman 1997). John Wesley Hyatt mixed CN with camphor (Figure 2a) 30% by weight to produce Celluloid, which was commercially introduced in the 1870s (Fenichell 1996; Friedel 1983; Mossman 1997). Due to its decorative versatility, it could be coloured and easily moulded, and was successfully marketed as an imitation material for ivory, marble, mother-of-pearl, tortoiseshell and ebony (Friedel 1983; Mossman 1997). Celluloid also found a unique technological niche when it was developed by the Eastman Kodak Company to manufacture the first successful roll film system for the Kodak camera and later motion picture film.

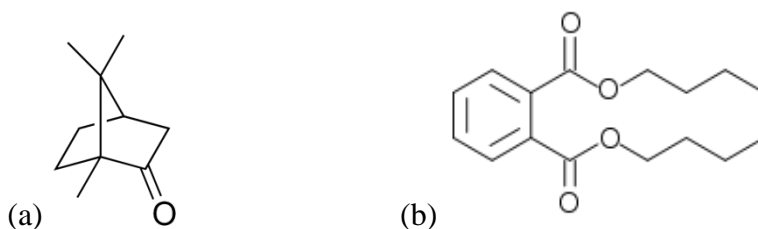


Figure 2. Chemical structures of two commonly used CN plasticizers:
 (a) Camphor, molecular formula $C_{10}H_{16}O$, molar mass $152.23 \text{ g}\cdot\text{mol}^{-1}$ and
 (b) DBP, molecular formula $C_{16}H_{22}O_4$, molar mass $278.34 \text{ g}\cdot\text{mol}^{-1}$.

Plasticised CN has found numerous applications (Paist 1977) and in 1899 it was introduced to conservation (Horie 1987), where it has been used as an adhesive, consolidant and as a coating, retaining its usefulness due to its ability to rapidly release solvents and form a strong dry film. However camphor volatilizes rapidly causing polymer shrinkage, so non-volatile plasticizers such as dibutyl phthalate (DBP) (Figure 2b) are preferred. A typical formulation is composed of 5% DBP, 20% CN and 75% solvent (Horie 1987; Buys & Oakley 1993). Plasticised CN is still popular, especially with conservators of archaeological earthenware (Barov 1988; Elston 1990), due to its ease of use and high glass temperature (T_g) of $\sim 50^\circ\text{C}$, making it suitable for use in hot climates.

Identification

Use of CN can be identified non-destructively by appearance and odour (Morgan 1991). Simple destructive tests are the flame pyrolysis test (Braun 1996; Quye & Williamson 1999) and a spot test employing diphenylamine in concentrated sulphuric acid (Braun 1996; Odegaard et al. 2000). More recently the complementary non-destructive techniques of Fourier Transform Infrared (FTIR) (Mills & White 1994; Keneghan 1998; Derrick et al. 1999; Quye & Williamson 1999; Stuart 2007; Shashoua 2008) and Raman spectroscopy (Quye & Williamson 1999; Paris & Coupry 2005; Stuart 2007) have been used to differentiate materials such as ivory from modern synthetic polymers. The main IR peaks that are characteristic of the nitrate group on CN are observed as asymmetric and symmetric stretches at 1634 and 1278 cm^{-1} respectively (Silverstein & Webster 1998; Socrates 2001). A minor peak due to the carbonyl peak of the plasticizer is usually observed at 1728 cm^{-1} . Additives such as plasticizers can be identified using Gas Chromatography with Mass Spectroscopy (GC-MS) (Quye & Williamson 1999, Shashoua 2008).

Deterioration

Issues regarding the stability of CN are well known (Koob 1986; Selwitz 1988, Williams 2002). It is susceptible to decomposition via acid catalysis, heat and ultraviolet (UV) radiation, producing nitric oxides, which combine with water to form acids, resulting in molecular weight (MW) reduction, causing the polymer to yellow, dry out and become brittle and to initiate the degradation of other organic materials and metals that are in close proximity. However a thermal decomposition study (Shashoua et al. 1992), found that DBP-CN adhesive has a significantly slower rate of decomposition than the pure CN polymer. Furthermore in an open ventilated system the polymer has a significantly slower rate of decomposition than in a closed system.

Case study

Acquisitions (finds and purchases) by the archaeologist Professor James Stewart created a comprehensive archaeological record representative of the ancient Bronze and Iron Ages of Cyprus for study purposes in Australia. These acquisitions were comprised of three excavation seasons he conducted in Cyprus and purchases from Cypriot antiquities dealers and the reserves of the Cyprus Museum in Nicosia. As a consequence numerous universities, museums and institutions in Australia received assemblages of Cypriot artefacts (Garner 1983; Sagona & Zimmer 1988; Salter 2008).

The Cypriot pottery collection at the University of Melbourne was surveyed as a case study. Currently the collection is composed of ~350 pottery vessels, housed in the Ian Potter Museum of Art. Acquisition over two major periods, 1972 and 1987 (Salter 2008; Nel & Jamieson 2008; Nel et al. 2010) has culminated in a collection, which spans 2000 years from the early Bronze Age through to Roman times. Artefacts from the 1972 acquisition are derived from Ayai Paraskevi (1955-1956), Lapatsa (1960-1961) and Palealona (1960-1961). Those acquired in 1987, via a purchase from the Australian Institute of Archaeology (AIA) came predominantly from Vounous (1937-1938) and Stephania (1951) (see Figure 3a & b). However it is also composed of vessels from a scattering of other excavation sites: Sphageion (4), Ayios Iakovo (2), Rizokarpas (1) and Pano Dikomo (1) and some for which the provenance is unknown.



Figure 3: Two vessels from the Cypriot Collection: (a) Red Polished Ware Basin (MU No. 1987.0259) excavated from Vounous and (b) Base Ring Ware Jug (MU No. 1987.0308) excavated from Stephania. Photography by Petronella Nel 2005.

Due to a lack of written records from early restoration and conservation treatments, the circumstances surrounding the adhesive repairs on the vessels are unknown. FTIR-ATR analysis with a portable unit and a set of control samples were used to identify micro samples obtained using solvent swabs (Nel et al. 2010). Out of the 146 adhesive repairs analysed against spectral matches of control samples, 5 adhesive classes were identified: CN (67%), poly(vinyl acetate) (PVAc) (23%), acrylic (3%), protein (1%), polystyrene (PS) (3%), with only 2% failing to be identified. Therefore two thirds of repaired vessels are known to be adhered with CN. Due to concerns about the stability of CN, a large number of vessels are a priority for conservation intervention.

It was thought that analysis of the FTIR spectra would be able to isolate the use of different commercial products or differences in deterioration and hence differences in environmental exposure. So the aim of this study was to pursue two methods of analysis: (1) Principal Components Analysis (PCA) of the IR spectra to identify groupings within the CN family and (2) GC-MS analysis for plasticizer identification and quantification if required.

Methods

Principal component analysis (PCA) of FTIR spectra obtained from survey

IR spectra were collected as previously described (Nel et al. 2010) using a FTIR spectrometer equipped with a diamond ATR window and micro sampling with a cotton wool swab moistened with acetone. PCA is a multivariate statistical data analysis technique for reducing the complexity and interpreting large data sets and was performed as previously described (Nel et al. 2010) using “The Unscrambler” software. PCA represents a complex multi-dimensional data set as a handful of principal components (PC), which indicate variance in decreasing amounts within the data set. Loadings plots calculated for each PC, indicate the degree to which each variable or wavenumber contributes to the variance represented by that particular PC.

Gas chromatography with mass spectroscopy (GC-MS) analysis

Criteria for the selection of vessels to be sampled were as follows: (1) In order to prevent the possibility of sample cross-contamination, vessels previously identified to contain multiple adhesive repairs were ruled out and those containing only a CN repair included; and (2) Ensure that each excavation site was represented in the sample batch in order to capture the presence of plasticizers other than DBP or the use of different formulations associated with specific dig sites.

Polymer film samples were manually removed from vessels and placed in glass vials. In order to quantify plasticizer content, ~2 mg amounts of each sample was weighed to four decimal places (+/- 0.0001) and cut and transferred with the aid of clean scalpel blades and tweezers, into glass vials 32 x 11.6 mm with a combination red rubber seal and polytetrafluoroethylene (PTFE) cap (Thermo Scientific, part no. THC11 14 1906). If a sample contained ceramic residues, these were minimized with a scalpel blade and the sample reweighed. Control samples of commercial CN products from HMG, UHU and Selleys Tarzan's grip (pre 1997) were also weighed. All CN adhesive samples were dissolved in a known volume (0.5 ml) of spectroscopic grade acetone (Merck), and then diluted 20 fold in acetone.

Gas Chromatography Mass Spectroscopy (GC-MS) is a combined analytical technique that employs the resolving power of GC to separate a mixture of organic compounds and MS to identify the unknown organic components (Artioli 2010). Electron impact (EI) ionisation was carried out using a Thermo TRACE Dual Stage Quadrupole (DSQ) GC-MS, with a Scientific Glass Engineering (SGE) 10 m x 0.1 mm ID-SOLGEL-1MS 0.1 mm (micron) Gas Chromatography (GC) column. The GC was programmed: at a flow rate of 0.2 ml/min of Helium, splitless injection was employed, with the injection of 1 µl of adhesive-plasticizer analyte + 1 µl of an internal standard (ISTD) methyl stearate, to allow for corrections due to sample injection variation. Each sample was injected four times to determine reproducibility and confidence limits. Initially the temperature was held at 50°C for 1 minute. Then it was ramped at a rate of 30°C/min to 320°C, where it was held for 2 minutes. The mass spectrometer was employed in full scan mode from 50 to 500 Daltons (Da) at a scan speed of 7298 Da/s.

A stock solution of DBP (2.5 mg dissolved in 1 ml of acetone) was serially diluted to prepare a set of calibration standards, which allowed preparation of a calibration curve (a plot of the response ratio of the peak areas of DBP and the ISTD versus the concentration of DBP) for quantitative analysis purposes (see Figure 4). The Xcalibur quantitative analysis software (Thermo Fisher Scientific) used the linear calibration curve obtained from the control DBP standards (as determined by manual baseline corrected peak area) to determine the amount of DBP in each of the unknown samples. These values were then corrected for dilution, original sample volume and calculated as a percentage of the original weight of the CN adhesive sample.

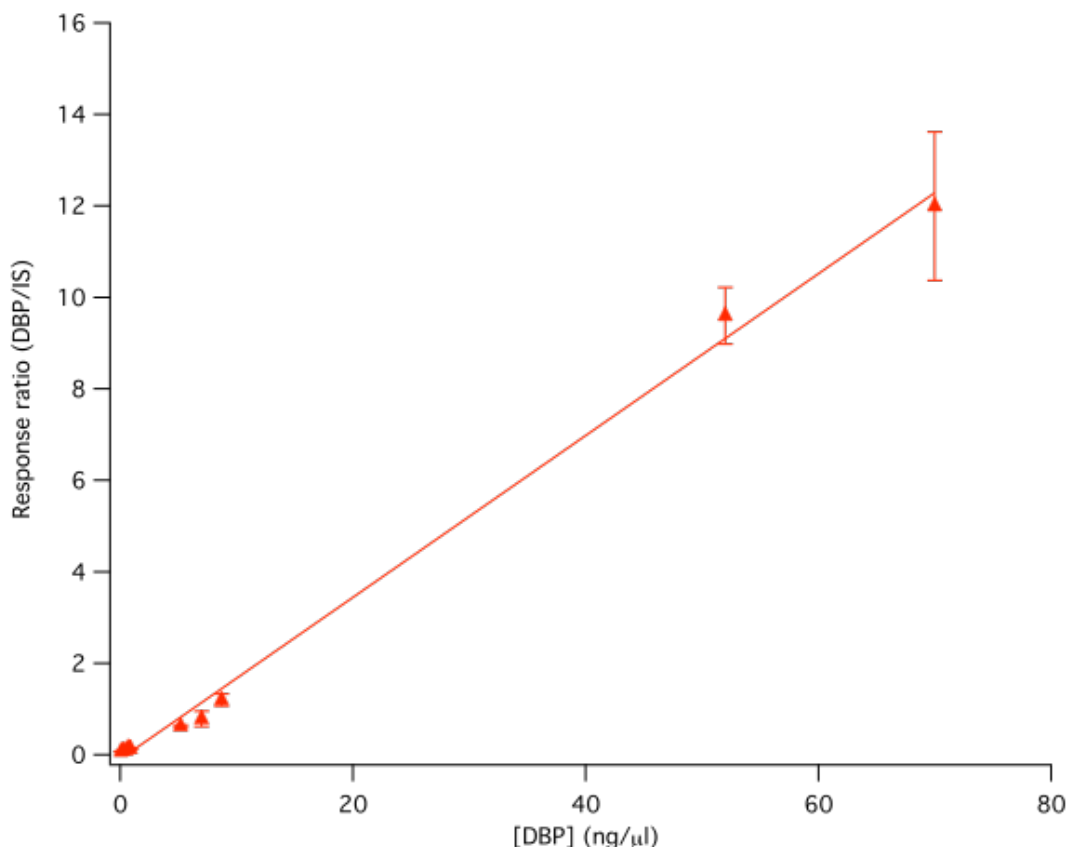


Figure 4. Calibration curve of response ratio of DBP/ISTD versus concentration of DBP in acetone.

Each charged fragment ion of the original molecule is measured as the mass of the fragment divided by its charge (usually +1), or mass to charge ratio (m/z), which represents the molecular weight of the fragment. DBP identification was confirmed by observation of the m/z base peak (which is the highest MW fragment from the original molecule) at 149 in the mass spectrum (Middleditch 1989) of the plasticiser peak. When viewing the mass spectra of samples with low DBP content or acetone alone, m/z peaks were observed at 73, 149, 207, 281 and 355, which are believed to be due to polysiloxane (extracted from the rubber lid of the sample solution glass vial due to the aggressive nature of the acetone solvent system). Another set of m/z peaks

observed at m/z 90-92, but not for the solvent blank, appear to be associated with the low DBP content adhesive samples. The source identity of this molecular ion is being further investigated.

Results and Discussion

Principal component analysis (PCA) of FTIR-ATR spectra

PCA was re-calculated for all 114 CN spectra from the Cypriot pottery survey and control samples, and the scores plots of the principal components (PC) plotted. The first PC (PC1) represents the majority of variance in the data, which is 57% and the second PC (PC2) represents 21% of variance within the data. No distinctions were found in the scores plot of PC1 versus PC2 (not shown). However a scores plot of PC3 (9% variance) versus PC4 (4% variance) separated the CN samples into two distinct groups, referred to as Group 1 and Group 2 (see Figure 5). As all samples were obtained as acetone solvent swabs, the sampling method was not considered to be a contributing factor. A comparison made between the two clusters and the accession numbers of the vessels, found a strong correlation, with 1972 corresponding to group 2 and 1987 to group 1.

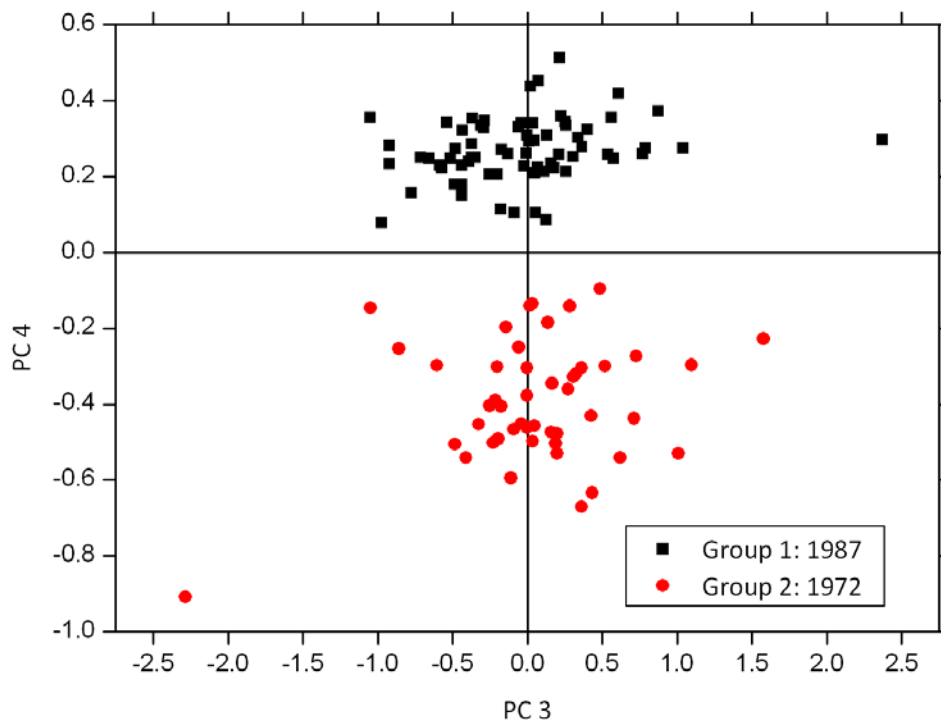


Figure 5. Scores plot of PC4 versus PC3 of FTIR-ATR spectra for CN samples obtained from survey of Cypriot pottery collection. The indiscernible differences within the large spectral set are captured by PCA and observable in this ordination plot.

A visual inspection between the overlaid line plots of IR spectra from Group 1 (1987) and 2 (1972) (see Figure 6a & 6b respectively) found general congruence between the two sets of spectra making it difficult to explain what is differentiating the two groups.

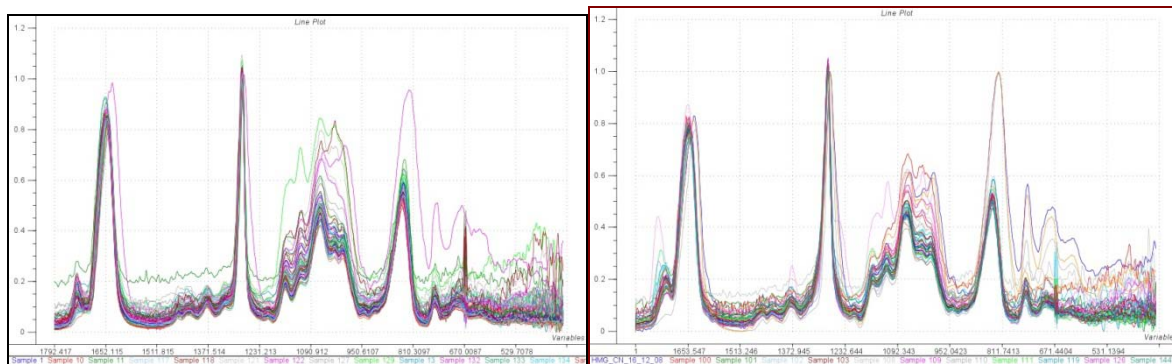


Figure 6. Overlaid line plots of FTIR-ATR spectra of CN samples obtained from Cypriot pottery collection: (a) Group 1 and (b) Group 2.

However loadings plots of PC3 and PC4 (in Figure 7) highlight the specific bands that are attributable to the observed differences. The most significant band in the loading plots of PC3 and PC4 (Figure 7) is the negative peak for PC4 at 1712 cm^{-1} , which corresponds to the carbonyl band of the plasticiser, most likely DBP (1721 cm^{-1}). Superimposition of the IR spectrum for DBP onto the loading plots of PC3 and PC4, demonstrates a strong correlation between the negative peaks of the PC4 loading plot and the peaks of the IR spectrum of DBP at $1721, 1273, 1120, 1072, 742\text{ cm}^{-1}$.

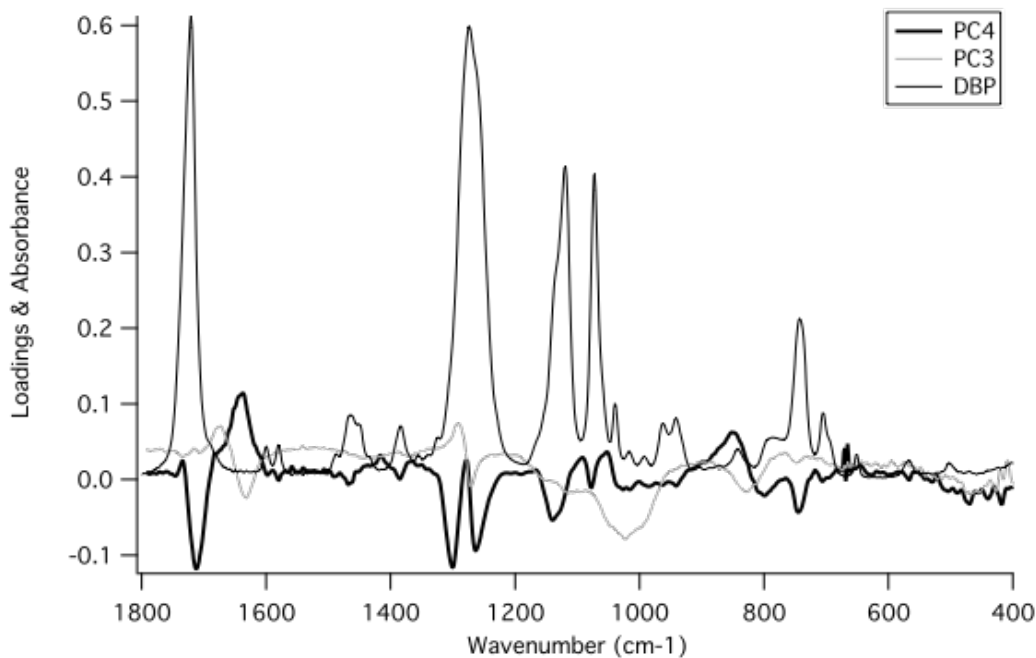


Figure 7. Overlaid loading plots of PC3 and PC4 and IR spectrum of DBP.

Referring back to the IR spectra from the two groups in Figures 6a & 6b, it is discernable that there is a difference in the height of the carbonyl peak at $\sim 1720\text{ cm}^{-1}$ between the two clusters, due to the $\sim 20\%$ wt DBP content in CN adhesives (Horie 1987; Buys & Oakley 1993). However this small difference in plasticizer content, needed to be confirmed by a more sensitive technique, which can both confirm the identity of the plasticizer and allow quantification of plasticizer levels in the CN polymer. As a consequence GC-MS analysis was employed.

GC-MS analysis

Preliminary GC-MS analysis was conducted on samples removed from the 1972 accession period (Lapatsa vessels 1972.0138, 1972.0186 and 1972.0191) and from the 1987 period (Vounous vessels 1987.0068 and 1987.0127). On the chromatogram the retention times for the plasticizer and the internal standard occur at ~ 7.47 and ~ 7.91 minutes respectively. The plasticizer peak concurred with the retention time of a control sample of DBP and with the mass spectrum for DBP with a major molecular ion (base) fragment at m/z 149 (Middleditch 1989). Samples from the 1972 group contained DBP levels high in comparison to the internal standard, while being significantly low for the 1987 samples.

Due to the approximately ten-fold difference in plasticizer levels between the two accession periods, quantitative GC-MS analysis was conducted on samples obtained from a more comprehensive survey of the pottery collection to determine whether the plasticiser identified and its level in CN is consistent across different excavation sites within each of the two clusters (see Figure 8).

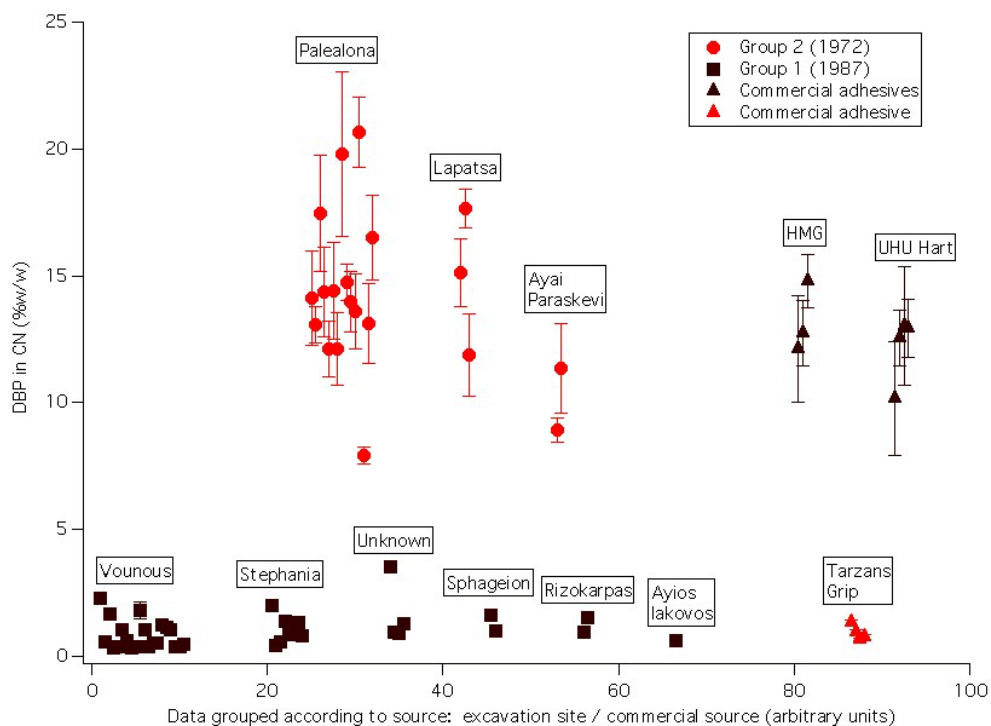


Figure 8. Plasticizer levels (\pm average deviation) in CN adhesives samples removed from pottery vessels in Cypriot pottery collection (grouped according to excavation site) and from three commercial adhesives, as determined by quantitative GC-MS analysis. Red circles and black squares indicate 1972 and 1987 accession periods respectively. Triangles indicate commercial adhesive samples.

From the results there is a clear correlation between the DBP content of ~15% and ~2% (w/w), for vessels from the 1972 and 1987 accession periods respectively, irrespective of excavation site. These results concur with a comparison of three commercial samples: two with a high DBP content (HMG and UHU) and Tarzans Grip (pre-1997), with a low DBP content. Thus the most likely explanation for the difference in DBP levels between the two groups resides with the adhesive formulations that were applied to the vessels.

Another explanation is that vessels from the 1987 acquisition were exposed to elevated temperatures for instance, which caused the volatile loss of DBP, via diffusion to the polymer surface and evaporation (Wilson 1995, p. 80-81). DBP has a low vapour pressure of 0.082 mbar (8.2 Pa) at 100°C and a boiling point of 340°C, which makes volatile loss theoretically possible. Shashoua et al. (1992) heat aged pure DBP at 70°C for 50 days causing it to be reduced by only 1%, due to the loss of water. So exposure to elevated temperatures alone is unlikely to be the explanation of the difference in plasticizer levels between the two groups.

Another issue is the difference in stability between 2% versus 15% (w/w) DBP plasticised CN. Shashoua et al. (1992) conducted a comparative experiment between CN alone and DBP plasticised CN, which determined that the presence of the plasticizer slows degradation of the CN polymer. Thus it would be assumed that 2% (w/w) DBP is more vulnerable to deterioration. However this should be tested, as Shashoua et al. (1992) did not test different levels of DBP content at intermediate concentrations. Wilson (1995) indicates that evaporation controlled loss is independent of plasticiser content, whilst diffusion controlled loss is strongly dependent on plasticiser level, with diffusion being slower through a lightly plasticised polymer than through the more open structure of a highly plasticised polymer.

Conservation implications

Previous work has demonstrated how the unambiguous identification of adhesive types across a whole collection can assist with developing collection management strategies (Nel et al. 2010). Within the 1987 accession period there was a marked contrast between the poor application techniques applied to the Vounous vessels and the neat application techniques used on the Stephania vessels. However PCA of the IR spectra of the CN data set, followed by qualitative and quantitative GC-MS analysis, identified a marked difference in DBP content between the two acquisition periods of the collection. Therefore the Vounous and Stephania vessels, both from the 1987 acquisition period, have equal conservation priority by virtue of the low DBP content in the CN adhesives associated with this acquisition period.

Conclusion

This investigation involved a detailed analysis into the CN adhesive samples associated with the Cypriot pottery collection at the University of Melbourne. The predominant use of CN (~ two thirds of adhesives and three quarters of repaired vessels analysed) (Nel et al. 2010) will have to be taken into account when collection managers prioritise budgets for the conservation and display of the collection. This work has demonstrated how the use of PCA and GC-MS provided invaluable qualitative and quantitative data that led to the identification and

quantification of the plasticiser used in the CN samples, which potentially focuses treatment priorities onto vessels from the 1987 acquisition period.

Acknowledgements

The authors thank the following: Jay Millar and Robyn Hovey from the Ian Potter Museum of Art; and Tony Sagona and Andrew Jamison from the Centre for Classics & Archaeology, for providing access to the Cypriot pottery collection; Robyn Sloggett director of the Centre for Cultural Materials Conservation (CCMC) for providing access to the CCMC adhesive reference collection; Carmela Lonetti and Jean Johnson who assisted with sampling and analysis; and Koman Tam from Biolab (Aust) Pty. Ltd. for providing support for the Bruker Alpha-P diamond FTIR spectrometer. We thank the University of Melbourne and the Australian Research Council (ARC) for financial support of this work.

References

- Artioli, G. *Scientific Methods and Cultural Heritage: an Introduction to the Application of Materials Science to Archaeometry and Conservation Science*. Oxford: Oxford University Press, 2010.
- Barov, Z. "The Reconstruction of a Greek Vase: the Kyknos Krater." *Studies in Conservation* 33 (1988), pp. 165-177.
- Braun, D. *Simple Methods for Identification of Plastics – with the Plastics Identification Table by Hansjurgen Saechtling*, 3rd revised edition. Munich: Hanser, 1996.
- Buys, S. and V. Oakley. *Conservation and Restoration of Ceramics*. Oxford: Butterworth-Heinemann, 1993.
- Derrick, M.R., D. Stulik, and J.M. Landry. *Infrared Spectroscopy in Conservation Science*. Los Angeles: The Getty Conservation Institute, 1999.
- Elston, M. "Technical and Aesthetic Considerations in the Conservation of Ancient Ceramic and Terracotta Objects in the J. Paul Getty Museum: Five Case Studies." *Studies in Conservation* 35 (1990), pp. 69-80.
- Fenichell, S. *Plastic: the Making of a Synthetic Century*. New York: Harper Business, 1996.
- Friedel, R. *Pioneer Plastic: the Making and Selling of Celluloid*. Madison: University of Wisconsin Press, 1983.
- Garner, G. "The Australian Institute of Archaeology." pp. 127-128 in *Ancient Middle Eastern Ceramics and Australian Archaeology in the Middle East Essays on Australian Contributions to the Archaeology of the Ancient Near East*, (edited by C. A. Hope and J. K. Zimmer). Melbourne: RMIT Faculty Art Gallery 1983
- Horie, C.V. *Materials for Conservation: Organic Consolidants, Adhesives and Coatings*. Oxford: Butterworth-Heinemann, 1987.
- Keneghan, B. "Assessing Plastic Collections in Museums by FTIR spectroscopy." pp. 21-24 in *IRUG2 postprints*. London: Victoria & Albert Museum, 1998.
- Koob, S.P. "The Instability of Cellulose Nitrate Adhesives." *The Conservator* 6 (1982), pp. 31-34.
- Middleditch, B.S. *Analytical Artifacts GC, MS, HPLC, TLC and PC*. Amsterdam: Elsevier, 1989.
- Mills, J.S. and R. White. *The Organic Chemistry of Museum Objects*. Oxford: Butterworth-Heinemann, 1994.
- Morgan, J. *Conservation of Plastics: an Introduction*. London: Museum and Galleries Commission, 1991.
- Mossman, S. "Perspectives on the History and Technology of Plastics." *Early Plastics: Perspectives, 1850-1950*, (edited by S. Mossman). London: Leicester University Press, 1997.
- Nel, P. "A preliminary investigation into the identification of adhesives on archaeological pottery." *AICCM Bulletin* 30 (2007), pp. 27-37.
- Nel, P. & A. Jamieson. "Cypriot Pottery at the University of Melbourne: an Examination of Historical Context and Conservation Issues." *Leiden Journal of Pottery Studies* 24 (2008), pp. 141-158.
- Nel, P., C. Lonetti, D. Lau, K. Tam, A.G. Sagona, and R.J. Sloggett. "Analysis of Adhesives used on the Melbourne University Cypriot Pottery Collection using a Portable FTIR-ATR Analyser." *Vibrational Spectroscopy* 53 (2010), pp. 64-70.
- Paist, W.D. "Cellulosics." pp. 212-221 in *Handbook of Adhesives – 2nd edition* (edited by I. Skeist). New York: Van Nostrand Reinhold Company, 1977.
- Paris, C. and C. Coupry. "Fourier Transform Raman Spectroscopic Study of the First Cellulose-Based Artificial Materials in Heritage." *Journal of Raman Spectroscopy* 36 (2005), pp. 77-82.
- Odegaard, N., S. Carroll and W.S. Zimmt. *Material Characterisation Tests for Objects of Art and Archaeology*. London: Archetype Publications, 2000.

- Quye, A. and R. Williamson (editors). *Plastics: Collecting and Conserving*. Edinburgh: NMS Publishing, 1999.
- Roff, W.J. and J.R. Scott. *Fibres, Films, Plastics and Rubbers – A Handbook of Common Polymers*. London: Butterworths, 1971.
- Sagona, A. G. and J. K. Zimmer (editors). *Images of the Ancient World. Archaeology at the University of Melbourne*. Melbourne: Chisholm Institute of Technology, 1988.
- Salter, S. *Cypriot Antiquities at the University of Melbourne*. Melbourne: Macmillan, 2008.
- Selwitz, C. *Cellulose Nitrate in Conservation*. Los Angeles: The Getty Conservation Institute, 1988.
- Shashoua, Y. *Conservation of Plastics: Materials Science, Degradation and Preservation*. Oxford: Butterworth-Heinemann, 2008.
- Shashoua, Y., S.M. Bradley, V.D. Daniels. "Degradation of Cellulose Nitrate Adhesive." *Studies in Conservation* 37 (1992), pp. 105-112.
- Silverstein, R.M. and F.X. Webster. *Spectrometric Identification of Organic Compounds*. Chichester: John Wiley & Sons, 1998.
- Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*. Chichester: John Wiley & Sons, 2001.
- Stuart, B. *Analytical Techniques in Materials Conservation*. Chichester: John Wiley & Sons, 2007.
- Williams, S. "Care of Plastics: Malignant Plastics." *WAAC Newsletter* 24, 1 (2002), pp. 1-11.
- Wilson, A.S. *Plasticisers: Principles and Practice*. London: The Institute of Materials, 1995.

Materials and Suppliers

CN adhesives:

HMG Heat and Waterproof adhesive was obtained from the CCMC reference collection.

UHU Hart (yellow blue tube) was accessed from UHU Sydney Australia office, as distribution in Australia had been discontinued.

Tarzans grip (Selleys, pre-1997 CN formulation) was found in a red-white tube in a drawer at CSIRO Clayton. In 1997 the product changed to a polyurethane (PU) formulation (Nel 2007).

Chemicals and solvents used for GC-MS:

Acetone (analytical grade), used to dissolve adhesive samples, was purchased from Merck.

Dibutylphthalate (DBP, >98%) plasticiser was purchased from Sigma-Aldrich.

Methyl stearate (>99.5%), the internal standard (ISTD) was purchased from Fluka.

Author Biographies and Contact Information

Petronella Nel is a researcher and lecturer at the University of Melbourne's Centre for the Conservation of Cultural Materials (CCMC) in Australia. She has a BSc Honours in Chemistry (1991), a PhD in Chemistry (2000), and an MA in Cultural Materials Conservation in objects conservation (2006) from the University of Melbourne. Petronella is currently working on two research projects: (1) "Archaeological conservation: the development of analysis and assessment protocols for adhesives used on archaeological pottery" (an Australian Research Council Discovery Project) with Associate Professor Robyn Sloggett (CCMC), Professor Antonio Sagona (Classics & Archaeology), and Deborah Lau [Commonwealth Scientific and Industrial Research Organisation (CSIRO)]; and (2) "Compositional study of ochre-earth pigments based on micro-PIXE and micro-XRF/micro-XRD techniques by application of multi-pixel array detector technology" (a University of Melbourne – CSIRO collaborative research program) with Peter Lynch and David Hay (CSIRO). At CCMC, Petronella is subject coordinator for the Chemistry Bridging Course as well as Technical Examination and Documentation, Conservation Materials Chemistry, and Analytical Chemistry in Conservation.

Contact Information:

Academic Teaching and Research
University of Melbourne
Parkville Campus
Victoria 3010, Australia
Tel.: +61 3 8344 0354
E-mail: pnel@unimelb.edu.au

Biographies et coordonnées des auteurs

Petronella Nel est chercheuse et chargée de cours au Centre for the Conservation of Cultural Materials (CCMC) de Melbourne, en Australie. Elle détient un baccalauréat avec spécialisation en chimie (1991), un doctorat en chimie (2000) et une maîtrise en restauration des matériaux culturels en restauration des objets (2006) de l'Université de Melbourne. M^{me} Nel travaille actuellement à deux projets de recherche : 1) le projet « Archaeological conservation: the development of analysis and assessment protocols for adhesives used on archaeological pottery » (un projet de découverte du conseil de recherches de l'Australie) avec la professeure agrégée Robyn Sloggett (CCMC), le professeur Antonio Sagona (humanités et archéologie) et Deborah Lau de l'Organisation australienne de la recherche scientifique et industrielle du Commonwealth (CSIRO) et 2) le projet « Compositional study of ochre-earth pigments based on micro-PIXE and micro-XRF/micro-XRD techniques by application of multi-pixel array detector technology » (un programme de recherche conjoint de l'Université de Melbourne et de la CSIRO) aux côtés de Peter Lynch et David Hay (CSIRO). Au CCMC, M^{me} Nel est coordinatrice de la matière du cours de transition en chimie et de la documentation et de l'examen technique, en chimie des matériaux de restauration et en chimie analytique en restauration.

Coordonnées :

Academic Teaching and Research
Université de Melbourne
Parkville Campus
Victoria 3010, Australie
Tél. : +61 3 8344 0354
Courriel : pnel@unimelb.edu.au

Deborah Lau is a materials scientist. She has a BAppSc and MSc from RMIT University in Melbourne, Australia and is in the final stage of PhD candidature at the University of Melbourne. She is currently Program Leader of the Surfaces and Nanoscience Program at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Division of Materials Science and Engineering, Clayton. Her research interests include cultural heritage, chemometrics, informatics, and synchrotron science, and involve non-destructive and micro/nano-analytical methodologies using a wide variety of X-ray and spectroscopic characterization approaches. She is actively engaged in implementing strategies to improve the efficiency of examining large data sets. Deborah has an ongoing interest in developing the field of conservation science in Australia.

Contact Information:

CSIRO Materials Science and Engineering
Private Bag 33
Clayton South, Victoria 3169, Australia
Tel.: +61 3 9545 2830
E-mail: Deborah.Lau@csiro.au

Carl Braybrook is a mass spectroscopy specialist for the Commonwealth Scientific and Industrial Research Organisation (CSIRO) operating from the Clayton Campus (Australia). He received a BSc Honours in Physics for Advanced Technology from Salford University (United Kingdom) in 1983 and, following graduation, collaborated with Rolls Royce in a joint research project involving the theoretical and practical characterization of novel composite materials. In 1986, he joined VG Analytical Ltd. (now Waters) as Product Manager and spent the next decade in the Organic Mass Spectrometry R&D team developing hybrid (quadrupole/sector) organic mass spectrometers for the world market. He relocated to the Australian National University (ANU) in 1995, setting up and managing the ANU mass spectrometry core facility for 4 years. He moved into his current role in 1999, where he now provides a world-class mass spectrometry service to the CSIRO scientific community.

Contact Information:

CSIRO Materials Science and Engineering
Ian Wark Laboratories
Bayview Ave.
Clayton, Victoria 3169, Australia
Tel.: +61 3 9545 2546
E-mail: carl.braybrook@csiro.au

Deborah Lau est une spécialiste en science des matériaux. Elle possède un baccalauréat ès sciences appliquées et une maîtrise ès sciences de l'Université RMIT de Melbourne, en Australie, et en est à la dernière étape de la défense de sa thèse de doctorat à l'Université de Melbourne. Elle est actuellement la directrice du programme des surfaces et de la nanoscience à la division des sciences des matériaux et du génie de l'Organisation australienne de la recherche scientifique et industrielle du Commonwealth (CSIRO), à Clayton. Ses domaines de recherche de prédilection sont le patrimoine culturel, la chimométrie, l'informatique et la synchrotronique, et ses travaux portent sur les méthodes non destructives et de micro/nano-analyse reposant sur un large éventail d'approches de caractérisation radiographique et spectroscopique. Elle participe activement à la mise en œuvre de stratégies qui devraient permettre d'examiner plus efficacement de grands ensembles de données. M^{me} Lau travaille sans relâche à favoriser l'expansion du secteur australien des sciences de la restauration.

Coordonnées :

CSIRO Materials Science and Engineering
Private Bag 33
Clayton South, Victoria 3169, Australie
Tél. : +61 3 9545 2830
Courriel : Deborah.Lau@csiro.au

Carl Braybrook est spécialiste de la spectrométrie de masse et travaille pour le compte de l'Organisation australienne de la recherche scientifique et industrielle du Commonwealth à partir du campus de Clayton (Australie). En 1983, il a obtenu un baccalauréat avec spécialisation en physique pour le secteur de la technologie de pointe de l'Université de Salford (Royaume-Uni). À sa sortie de l'université, en collaboration avec Rolls Royce, il mène un projet de recherche conjoint sur la caractérisation théorique et pratique de nouveaux matériaux composites. En 1986, il entre chez VG Analytical Ltd. (désormais Waters) comme chef de produit, et il passe la décennie suivante au sein de l'équipe de recherche et développement sur la spectrométrie de masse organique, qui met au point des spectromètres de masse organiques hybrides (quadrupolaires et à secteur) pour le marché international. En 1995, il est passé à l'Australian National University (ANU), où il a mis en place et géré pendant quatre ans la principale installation de spectrométrie de masse de l'ANU. Il a commencé à exercer ses fonctions actuelles en 1999, dans le cadre desquelles il fournit des services de spectromètre de masse de calibre mondial à la collectivité de scientifiques de la CSIRO.

Coordonnées :

CSIRO Materials Science and Engineering
Ian Wark Laboratories
Bayview Ave.
Clayton, Victoria 3169, Australie
Tél. : +61 3 9545 2546
Courriel : carl.braybrook@csiro.au