Rapid identification of cellulose nitrate and cellulose acetate film in historic photograph collections

Elizabeth A. Carter1,2*, Brad Swarbrick2, Thérèse M. Harrison1 and Lucilla Ronai3

Abstract
Cellulose nitrate transparent plastic film was used by photographers and movie filmmakers from its release in the 1880s to the 1950s. The storage of this material is a challenge for cultural institutions because of its instability and hazardous nature, as nitrate is highly flammable and deteriorates over time. Historically, cellulose acetate gradually began to replace cellulose nitrate as it is not flammable. Despite its non-flammable properties, leading to cellulose acetate being called ‘safety’ film, over time it became clear that it also deteriorates in hazardous ways. Identification of cellulose nitrate and cellulose acetate in collections is necessary for preservation and risk management to collections and humans. Both cellulose nitrate and cellulose acetate are found in gallery, library, archive and museum photographic collections. As a result, identification and management of this material might be the responsibility of curators, librarians, archivists, collection managers, registrars or conservators, depending on the institution staffing and structure. Currently, there is no single identification method readily available to heritage institutions that meets the requirements to identify and distinguish between cellulose nitrate and cellulose acetate reliably, non-destructively and rapidly. In this study samples from both the Sydney University Museums and Australian National Maritime Museum collections have been analysed using infrared total reflectance spectroscopy, a novel approach which demonstrates great potential for rapid and non-invasive identification particularly when combined with multivariate statistical analysis methods. Principal component analysis (PCA) allowed for non-subjective data mining and the development of a model which is hoped to be used in the future for predicting sample identification. After calculation of the PCA model, the novel application of the Parsimax orthogonal rotation method potentially provides a means of determining the level of chemical deterioration in the cellulose nitrate film.

Keywords: Infrared spectroscopy, Total reflectance, Cellulose nitrate, Cellulose acetate, Deterioration, Parsimax rotation, Multivariate analysis

Introduction
The Historic Photograph Collection (HPC), part of the Macleay Collections of the Chau Chak Wing Museum1 of the University of Sydney, includes over 70,000 photographic objects with a wide variety of formats dating from the mid-nineteenth to mid-twentieth centuries, a tenth of these are on a cellulose nitrate or cellulose acetate film base. With its images of people, landscape and town views, family albums, images from travels and expeditions, scenes of university life, scientific work and ethnographic photographs, it is a rich historical resource. The Australian National Maritime Museum (ANMM) collection has over 24,000 negatives and positives on transparent plastic film bases. The collection spans from

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*Correspondence: elizabeth.carter@sydney.edu.au

1 Sydney Analytical, Vibrational Spectroscopy Facility, The University of Sydney, Madsen Building, Level 2, Camperdown, NSW 2006, Australia

Full list of author information is available at the end of the article

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the 1890s to the early 2000s with photographs by many notable maritime photographers. A reliable and rapid method for the identification of the plastic film base for the items within these collections is needed to manage this material due to the unstable nature of the plastic film bases.

**Plastic film bases**

Cellulose nitrate was used by photographers and movie filmmakers as a flexible plastic film base for their images and movies from its release in the 1880s to the 1950s. However, it was possibly still used some years after manufacture ceased by photographers and filmmakers who had a stockpile of film [1]. The use of cellulose nitrate as a film base was driven by its flexibility, transparency, low weight and strength. The production of a thin, light and flexible cellulose nitrate film in the 1880s was praised for the resulting luminous, high-contrast images, that were attributed to a silver rich emulsion and the excellent transparent nature of the film [2]. It allowed the industry to move away from the heavy glass plates being used and made the process more accessible [1, 3]. During the 20th century, amateur and professional photographers and filmmakers used cellulose nitrate more frequently than any other film support [1].

Initially used in the manufacture of military explosives, cellulose nitrate was stabilised with camphor to produce celluloid. However, the instability and highly flammable nature of the plastic film material resulted in many fires and subsequent deaths where cellulose nitrate was housed and where motion picture films were screened [4, 5]. As a result it was gradually replaced from the 1920s, and production ceased in the 1950s [6]. From the 1920s cellulose acetate was a new transparent plastic film base in use for photography and filmmaking. Over the twentieth century multiple forms were chemically developed including cellulose diacetate, cellulose acetate propionate, cellulose acetate butyrate and cellulose triacetate (collectively referred to as cellulose acetate) [6]. It was dubbed ‘safety’ film due to its comparatively non-flammable properties and began to gradually replace cellulose nitrate. However, it was also found to have stability issues. Some forms of cellulose acetate are still used as a film base today.

Polyester, a synthetic polymer, was used as a plastic base for photographic material from the 1950s onwards due to its superior dimensional stability and mechanical strength. During the 1960s and 1970s it gradually replaced cellulose acetate as it was found to be more chemically and physically stable than cellulose nitrate and cellulose acetate [7]. More than 50 years after its first began to be used in the photography industry it is still demonstrating little to no deterioration.

**Film composition and structure**

The image of a black and white still or sheet photograph on a plastic support, known as the emulsion layer, is comprised of fine silver particles embedded in a thin transparent binder which is typically gelatin, see Fig. 1a [7, 8]. A colour photograph image on a plastic support contains yellow, magenta and cyan dyes suspended in three distinct layers of gelatin that contain silver halide crystals, see Fig. 1b. Black and white photographs on plastic supports were either a cellulose nitrate, cellulose acetate or polyester base. Colour photographs were only on cellulose acetate or polyester base [9].

Cellulose nitrate film bases were made by reacting cellulose polymers with nitric acid in the presence of sulphuric acid to produce nitrate esters, which were then combined with a plasticiser (for example phthalates, aryl phosphates, or camphor) to provide flexibility and allow for the casting of thin films and sheets [7, 10]. Between the image layer and plastic film base is a coating of diluted nitrocellulose, called subbing, used to enhance the adhesion of the layers. An anti-curl layer of gelatin with anti-halation dyes was also applied to the non-image side of cellulose nitrate bases to prevent light reflecting from the back of the support and exposing the silver salts. Early cellulose nitrate film occasionally had varnishes applied including a shellac containing borax and glycerine or a dammar varnish [7].

Cellulose acetate is a generic term used for cellulose diacetate, mixed esters of cellulose acetate including butyrate and propionate, and cellulose triacetate bases. The composition of these vary, however, generally cellulose polymers undergo an acetylation reaction with acetic acid and an excess of acetic anhydride in the presence of sulphuric acid. A plasticiser (triphenyl phosphate or dimethoxyethyl phthalate) was then added to the polymer to enable flexibility [7, 10]. As with cellulose nitrate, a subbing of diluted thin cellulose nitrate was used, a gelatin anti-curl layer with anti-halation dyes applied to the non-image side of the base and occasionally it had a shellac or dammar varnish [7].

**Deterioration**

The preservation of cellulose nitrate and cellulose acetate film presents numerous challenges for institutions due to their hazardous and inevitable deterioration. Acidic and hazardous vapours that off-gas from cellulose nitrate (nitric acid) and cellulose acetate (acetic acid) are a by-product of their deterioration. These vapours pose a risk to humans and to other material that is stored with it. Table 1 lists the different levels of physical and visual deterioration of cellulose nitrate and cellulose acetate film which in some cases can be characteristic and aid identification (Fig. 2).
Deterioration of cellulose acetate can be detected and measured using the Acid Detection (AD) strip test, which requires 24–48 h to collect a measurement. The AD strips, developed specifically for cellulose acetate films, are acid–base indicator paper strips that change colour in the presence of acidic vapour. Following exposure, the colour of the strips are then compared to a reference scale. AD strips are not recommended for use with cellulose nitrate films and they cannot distinguish between cellulose nitrate and cellulose acetate [11]. Currently, there is no non-destructive chemical technique that can be used to determine the level of cellulose nitrate deterioration. Although there are many studies which have investigated the mechanism of deterioration [12–15] there are no published studies which correlate the visible and physical signs, as outlined in Table 1, with the degree of chemical deterioration.

The deterioration of cellulose nitrate and cellulose acetate cannot be reversed. Low temperature storage is used by many heritage institutions to delay or slow down deterioration. Not all institutions have access to low temperature storage and this film still poses a risk to staff and to the rest of the collection. Another option is to copy the photographic films to another analog or digital format that is more stable to prevent image and information loss. High levels of deterioration of both cellulose nitrate and cellulose acetate film bases can result in the total loss of the image. However, copies are not a replacement for the original, and reproduction and digitisation are time consuming and costly processes. Whether physical or digital, the copies still need to be stored and maintained.

### Table 1 Characteristic physical and visual signs of cellulose nitrate and cellulose acetate deterioration [6, 25]

| Level | Cellulose nitrate                                      | Cellulose acetate                                      |
|-------|--------------------------------------------------------|--------------------------------------------------------|
| 1     | No visible deterioration                                | No visible deterioration                                |
| 2     | Film base turns yellow, and image shows signs of mirroring | Film base begins to curl and can turn red or blue       |
| 3     | Film base becomes sticky and gives off a strong smell of nitric acid | Film base shrinks, becomes brittle and produces acetic acid (vinegar smell) |
| 4     | Film base becomes amber in colour and the image begins to fade | Film base can begin warping                             |
| 5     | Film softens and can weld to adjacent material or enclosure | Film base forms bubbles and crystals                     |
| 6     | Film turns into a brown acid powder                     | Film base forms channels                                |
One of the most essential approaches is to segregate cellulose nitrate and cellulose acetate from larger collection stores, separate them from each other and even isolate highly deteriorated film from those in good condition. Therefore, cellulose nitrate and cellulose acetate film in collections needs to be identified, isolated and their condition checked routinely.

**Identification challenges**

The main challenge in identifying cellulose nitrate and cellulose acetate in heritage collections is the huge scale of unidentified material and a lack of resources. A 2017 survey of Australian heritage institutions found that most state and national galleries, libraries archives and museums hold cellulose nitrate and cellulose acetate in their photographic collections. Cumulatively, 28 Australian institutions hold approximately 1.5 million identified cellulose nitrate and 5.8 million identified cellulose acetate [16]. Furthermore, these institutions have approximately 1.8 million photographic materials on unidentified, unknown plastic bases that would be cellulose nitrate or cellulose acetate. One institution alone holds half a million unidentified items and this sheer quantity applies to other collections [7]. These items require identification on a large scale, for preservation and risk management purposes.

Currently, no single method readily available to heritage institutions meets their requirements to identify and distinguish between cellulose nitrate and cellulose acetate reliably, non-destructively and rapidly (see Table 2). The known methods are unreliable due to a lack of information (such as dates), absence of identifying or unambiguous features (such as notches, edge printing or diagnostic deterioration) and in the case of destructive tests, false positives. Furthermore, the available destructive tests have related Work Health and Safety issues with the solvents used or resulting hazardous by-products (see Table 2).

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**Fig. 2** Photographic images showing examples of characteristic deterioration used to identify known cellulose nitrate and cellulose acetate samples that were analysed. They have been graded based on the signs of physical and visible deterioration outlined in Table 1. **a** Cellulose acetate showing level 2 blue coloured anti-halation dye separation deterioration **b** cellulose acetate showing level 6 channelling deterioration **c** cellulose nitrate showing level 2 iridescent mirroring **d** cellulose nitrate showing level 4 amber discolouration
There is no standard within the national or international cultural heritage industry to identify cellulose nitrate and cellulose acetate. Upon consultation with Australian institutions, it was found they currently use visual examination, the float test, diphenylamine test, or a limited number had access to spectroscopic instrumentation (L. Ronai 2017 and 2019, personal communication). Discussions with international institutions revealed that the burn, diphenylamine or float test (despite the associated issues) as well as spectroscopic analysis were used by different institutions in the United States of America (L. Ronai 2019, personal communication). The variation in identification methods is, in part, due to different attitudes towards destructive testing, and available resources.

A new identification method is required that is:

- Reliable and repeatable.
- Rapid to deal with the scale of collections that require identification.
- Safe with no associated Work Health and Safety issues.
- Non-destructive, non-invasive and no sample removal to meet the cultural heritage industry preference.
- Readily available to institutions who already have the required equipment, or can gain access to the equipment through collaborations with facilities or other institutions.

### Exploring a possible solution

Vibrational spectroscopy is an ideal tool for the analysis of photographic plastic film material because it is relatively inexpensive and is produced as accessible portable or hand-held equipment. In addition, some of the available sampling techniques are non-contact with non-destructive and rapid data collection capabilities.

Vibrational spectroscopy has been used to study a range of cellulose nitrate and cellulose acetate containing materials including museum artefacts [17–24], X-rays [25], cinematographic film [12, 15, 26] and photographic film [27–29]. These materials have been studied with a range of infrared (IR) sampling techniques including IR microscopy [15, 17, 20, 27], attenuated total reflectance (ATR) [22, 24–26, 28], diffuse reflectance (DRIFT) [19, 27], diamond anvil cell (DAC) [17, 24], external (mostly specular) reflection [21, 22, 30] and near infrared (NIR) spectroscopy [23, 29]. There are limited studies which use Raman spectroscopy for the analysis of cellulose

### Table 2 Traditional methods used by cultural heritage institutions for identification of photographic plastic film bases

|                         | Cellulose nitrate | Cellulose acetate | Polyester | Evaluation of technique                                      |
|-------------------------|-------------------|-------------------|-----------|-------------------------------------------------------------|
| **Contextual information** |                   |                   |           |                                                            |
| Date [6]                | ?                 | ?                 | ?         | Requires verification: periods of use overlap.              |
| **Visual examination**  |                   |                   |           |                                                            |
| Edge printing [6]       | ✔️ Nitrate        | ✔️ Safety         | ✔️ Estar ‘Cronar’ | Non-invasive No WHS Concerns Physical characteristics not always present |
| Notches [47]            | x                 | x                 | ?         | Requires verification: film duplication (for example from nitrate to polyester) can include previous edge printing |
| Deterioration [48]      | ?                 | ?                 | x         | Requires verification: some deterioration is common to both Only identifies polyester |
| Polarisation test [48]  | x                 | x                 | ✔️       | Shows interference colours Requires verification: does not distinguish between cellulose nitrate and cellulose acetate |
| **Chemical testing**    |                   |                   |           |                                                            |
| Float test [48]         | ✔️                | ✔️                | ✔️        | Invasive & destructive (requires sample) WHS concerns (solvents or by products) Requires verification: results can be difficult to interpret, since there are many different types of cellulose nitrate and acetate manufactured, and deteriorated film behaves diversely |
| Diphenylamine spot test [49] | ✔️         | x                 | x         | Requires verification: cellulose acetate and polyester sometimes have a subbing layer of cellulose nitrate — can create a false positive. |
| Burn test [48]          | ✔️                | x                 | x         | Requires safety measures: must be performed outdoors, requires bucket of water, and is generally no longer conducted |
studies using ATR spectroscopy reported on the inability of the technique to detect the film base, particularly if both sides of the film were coated in a layer containing gelatin [25, 28]. This is not surprising because ATR spectroscopy is a surface sensitive technique probing only to a depth of 1–3 µm into the sample. Therefore, in order to analyse the film base using this technique it is necessary to remove the anti-curl or image layer and thereby the gelatin. However, most institutions require item-by-item justification and approval by all stakeholders to allow destructive analysis or sample removal. Therefore, analysis that requires sample removal (such as the burn or float test) or removal of the gelatin containing layers is generally not an option.

Recently, there have been a number of studies that have used external reflection spectroscopy for analysis of a range of cultural heritage objects such as paper [32], pigments [33, 34], varnishes [35] and plastics (including cellulose nitrate and cellulose acetate) [21, 22, 30]. The instrument used in these studies is a portable Bruker ALPHA FTIR spectrometer equipped with an external reflection module (ERM). The design of the instrument allows for the measurement of both specular and diffuse reflection which has been termed by some researchers as total reflection (TR) [21, 30]. Specular reflection occurs when the IR light is reflected from a sample whereby the angle of incidence equals the angle of reflection and this sampling mode is typically used for smooth mirror-like surfaces. Diffuse reflection occurs from rough surfaces and the IR light is reflected in all directions [36]. Therefore, the resulting spectrum that is collected using this total reflection configuration will be highly dependent upon the nature of the sample surface, with the sample spectrum potentially a composite of both specular and diffuse reflections.

This study aims to develop a methodology allowing for the rapid identification and differentiation of cellulose nitrate and cellulose acetate by exploring the potential of infrared reflectance spectroscopy. The data will be investigated with multivariate data analysis to establish if a valid statistical model could be developed and implemented to allow for point of use data analysis resulting in a straightforward yes/no or a true/false output. This would provide a technique that could be easily implemented by various professionals working with this material in the cultural heritage industry.

Experimental Samples
A total of 56 samples including 32 cellulose nitrate, 9 cellulose acetate and 15 unknowns were provided by the Macleay’s HPC and the ANMM. The analysed samples were in either sheet (flat—has notch) or still photo (rolls including cut into strips or single images, perforated 35 mm, slide transparencies) formats. All handing of collection samples was undertaken by trained professionals with required skills, including conservators and registrars. This is to limit safety risks to the persons involved and damage to collection items which can be in a deteriorated condition.

The samples were identified using a combination of techniques due to no single method being completely reliable (see Table 2). This included the date range, notch (if present), format, polarisation test and visual examination of characteristic deterioration features (see Table 1). The majority of the Macleay’s HPC samples had been previously subjected to destructive testing. Only non-destructive and non-invasive/non-sample removal identification methods were used for the ANMM samples as they are part of the National Maritime Collection and destructive testing is not permissible. However, destructive testing had previously occurred on some samples before they became part of the ANMM collection. Unknown samples did not exhibit any visual signs of characteristic deterioration, have a date that fell within a range that both cellulose nitrate and cellulose acetate were manufactured and in use, was in a format that was used for production of both types, and did not show any red or green interference pattern which is obtained during the polarisation test.

Data collection
IR reflectance spectra were collected using a Bruker ALPHA portable FTIR spectrometer (Bruker Optiks, Ettlingen, Germany) equipped with a QuickSnap™ ERM and integrated video camera to assist in the location of the region of interest to be sampled. The module has a magnetically mounted reference cap with a gold coated mirror which is used to collect the background spectrum. Once the background spectrum was collected the gold coated mirror was replaced with a sample cap aperture with a 3 mm diameter for sample analysis. Infra-red reflectance spectra were collected in triplicate, at a minimum, from three regions of the non-image side of a sample. Both the background and sample spectra were collected with the co-addition of 32 scans, at a 4 cm⁻¹ spectral resolution, over a spectral range from 4000 to 400 cm⁻¹. After collection the reflectance spectra were processed in the OPUS software package (Version 7.5, Bruker Optiks, Ettlingen, Germany) with the Kramers– Kronig transformation (KKT) to calculate the absorbance spectrum.
Data analysis

Infrared reflectance spectra were imported into The Unscrambler (Version 10.4, CAMO, AS, Norway) and the triplicate spectra collected from each sampled area were averaged. Prior to the application of scatter correction, a Savitzky-Golay smoothing filter (11-point smooth) was applied, followed by the Standard Normal Variate (SNV) transformation [37]. A Savitzky-Golay 1st derivative was applied to the data to remove residual baseline effects. The application of SNV to a noisy data set will result in extraneous noise being carried over to the derivative pre-processing, therefore smoothing prior to scatter correction removes inherent detector noise and with the chosen resolution no reduction in spectral information was expected. SNV was then applied to remove the scatter effects caused by the reflectance measurement, and a low bandpass derivative was used to enhance spectral features caused by overlapping of peaks.

Principal component analysis (PCA), using the spectral range from 1850–410 cm\(^{-1}\), was applied followed by the factor rotation method of Parsimax rotation leading to simple structure in the data [38–40] that produce components with enhanced chemical interpretability.

Results and discussion

Spectral processing and interpretation

Figure 3a presents a typical spectrum collected from a film sample investigated in this study. Two features were commonly observed in the film spectra including interference fringes, sinusoidal modulations that result from reflections within the sample [41], and reststrahlen bands which results from a change in the refractive index (RI) and is associated with strongly absorbing bands. A rapidly changing RI produces a derivative shaped band and a Kramers–Kronig Transform (KKT) algorithm is used to calculate an absorbance spectrum, see Fig. 3b.

As discussed earlier photographic plastic film is composed of a number of layers including an anti-curl layer containing gelatin, the film base (cellulose nitrate, cellulose acetate or polyester), subbing, image layer/s (gelatin) with silver particles and/or dyes and sometimes a surface coating. The plastic base is approximately 90% of the films composition. Using the external reflection technique the signal is comprised of both specular and diffusion reflection contributions, also known as total reflection. Figure 4 presents the spectra collected from the image and non-image containing sides of a cellulose nitrate film base sample using total reflection. The spectrum presented in Fig. 4a has a number of characteristic features attributable to gelatin including the Amide I, II and III bands observed at ~1658, 1552, 1243 cm\(^{-1}\), respectively. The spectrum collected from the non-image side, for this particular sample, appears to be predominately arising from cellulose nitrate. Therefore, as part of the experimental optimisation it was decided that all spectra would be collected from the non-image side of the film samples where the gelatin-containing coating, if present, is likely to be thinner.

Spectra of the known samples clustered into four distinctive groups, the averaged spectrum of each group is presented in Fig. 5 and a table of assignments is provided in Table 3. The spectra shown in Fig. 5a is comprised of cellulose nitrate 35 mm roll film samples, Fig. 5b contains cellulose nitrate sheet film, Fig. 5c is cellulose acetate sheet film and Fig. 5d contains
cellulose acetate roll film. The distinctive features in Fig. 5a at 1654, 1282 and 843 cm\(^{-1}\) are attributed to the \(\nu_{as}(NO_2)\), \(\nu_s(NO_2)\) and \(\nu(NO)\) modes of cellulose nitrate, respectively [20, 24]. In Fig. 5b the spectrum is dominated by features at 1654 and 1554 cm\(^{-1}\) which are attributed to the proteinaceous Amide I and II bands of the gelatin. In fact, the spectral features of the gelatin not only dominate the spectrum but mask the \(\nu_{as}(NO)\) mode of cellulose nitrate at 1654 cm\(^{-1}\). Other notable features include the absence of the \(\nu_{s}(NO_2)\) band at 1282 cm\(^{-1}\) and the presence of a weak \(\nu(NO)\) mode at 843 cm\(^{-1}\). Figure 4d presents a spectrum with the characteristic features of cellulose acetate referred to as the rule of three. These bands are observed at 1757, 1238 and 1054 cm\(^{-1}\) and are assigned to \(\nu(C=O)\), \(\nu(CCO)\) and \(\nu(COC)\), respectively [42, 43]. Figure 5c, similar to Fig. 5b, is dominated by the Amide bands of gelatin however the distinctive cellulose bands at 1760 and 1052 cm\(^{-1}\) are easily observed.

### Multivariate statistical analysis

The primary aim of this research project was to develop a robust and objective methodology that can be used by various professionals working with cellulose nitrate and cellulose acetate within the cultural heritage industry. The majority of this material is found in galleries, libraries, archives and museum collections and therefore its identification and management resides with staff with various expertise. Therefore, the development of a valid statistical model which results in a straightforward yes/no or a true/false output on the basis of a simple, rapid, non-destructive and inexpensive methodology is vital.

The infrared data collected from all samples was subjected to a variety of pre-processing techniques, outlined in the experimental section, prior to undergoing principal component analysis (PCA) and factor analysis. PCA is an unbiased exploratory data analysis technique that eliminates subjectivity and is used to find the latent (hidden) structure in complex multivariate data tables. The main

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**Table 3 Assignments of IR reflectance bands of photographic film based on literature [21, 24, 42, 50–52]**

| Cellulose nitrate | Position (cm\(^{-1}\)) | Assignment | Intensity |
|-------------------|-------------------------|------------|-----------|
| 1727              | \(\nu(C=O)\) camphor     | Weak       |
| 1654              | \(\nu_s(NO_2)\)         | Strong     |
| 1453              | \(\delta(CH_2)\)        | Weak       |
| 1420              | \(\delta(CH)\)          | Weak       |
| 1375              | \(\delta(CH_2)\)        | Weak       |
| 1282              | \(\nu_s(NO_2)\)         | Strong     |
| 1161              | \(\nu(COC)\)            | Weak       |
| 1120              | \(\nu(COC)\)            | Weak       |
| 1070              | \(\nu(COC)\)            | Medium     |
| 1024              | \(\nu(COC)\)            | Weak       |
| 1004              | \(\nu(COC)\)            | Weak       |
| 920               | \(\delta(CH)\)          | Weak       |
| 843               | \(\nu(NO)\)             | Medium     |
| 750               | \(\delta(NO_2)\)        | Weak       |
| 694               | \(\delta(NO_2)\)        | Weak       |

| Cellulose acetate | Position (cm\(^{-1}\)) | Assignment | Intensity |
|-------------------|-------------------------|------------|-----------|
| 1751              | \(\nu(C=O)\)            | Strong     |
| 1588              | Additive                | Weak       |
| 1488              | Additive                | Weak       |
| 1432              | \(\delta(CH_3)\)        | Weak       |
| 1369              | \(\delta(CH)\)          | Medium     |
| 1234              | \(\nu_{CCO}_{ester}\)   | Strong     |
| 1187              | \(\delta(CH_3)\)        | Weak       |
| 1162              | \(\nu(COC)\)            | Weak       |
| 1123              | \(\nu(COC)\)            | Weak       |
| 1052              | \(\nu(COC)\)            | Strong     |
| 963               | Additive                | Weak       |
| 903               | \(\delta(CH)\)          | Weak       |

\(\nu\), stretching; \(\delta\), bending; \(a\), anti-symmetric; \(s\), symmetric
outcomes of PCA are the scores plot (map of sample relationships) and loadings (variable correlations). The scores and loadings plots are assessed together to provide interpretability to the model. PCA is highly visual and provides validation statistics that allow for an assessment of model quality. This provides PCA with properties that are highly desirable for complex data analysis.

Figure 6 provides the PCA Scores and Loadings plot for principal components (PC’s) 1 and 2. The use of sample grouping shows a distinction exists between the cellulose nitrate and cellulose acetate film. More importantly, the variance is distributed over 2 PCs in a near orthogonal relationship that is not solely described by either PC1 or PC2 alone. This variance pattern, as is highlighted by the lines placed through the data, indicated that the data would benefit from more advanced multivariate statistical analysis such as factor analysis.

Jackson [38] describes the concept of simple structure as an orthogonal rotation of the principal components (PC’s) that leads to less abstract and more physical/chemical interpretability of the components. The ability to orthogonally rotate factors into pure axes provides for enhanced chemical interpretability of the data. In the analysis of data in this study, the Parsimax rotation method was used as it distributes the variance more evenly over rotated components compared to alternatives such as Varimax [44] or Equimax [45] produced components with high chemical interpretability [39]. For an overview of orthogonal rotation methods, the interested reader is referred to Mulaik [46], Esbensen and Swarbrick [40].

Figure 7a presents the results after application of the Parsimax rotation in the form of the rotated Scores plot for Factor 1 vs. Factor 2, and the corresponding rotated Loadings plots are shown in Fig. 7b. Examination of the rotated Scores plots reveals that there are four distinctive groups of clustered data, the averaged spectra of each group can be found in Fig. 5. The most important observation, however, is that the cellulose acetate films now lie exclusively along the rotated PC1 direction. This indicates that the rotated Factor 1 loading is a pure cellulose acetate component and can be interpreted in terms of its chemistry. In Fig. 7a the samples separate along PC1 due
to the variables at 1756 and 1653 cm$^{-1}$ as shown in the Loadings plot in Fig. 7b. These variables are assigned to the ν(C=O) mode of cellulose acetate and gelatin, respectively. Rotated Factor 2 shows that the cellulose nitrate samples do not exactly line up with the rotated PC2 axis, however, this axis can be interpreted as changes in the cellulose nitrate films with little loss of generality. Along Factor 2 separation of the group labelled a in Fig. 7a with respect to the other groups is due to the variable at 1278 cm$^{-1}$, which is attributed to the ν$_s$(NO$_2$) mode of cellulose nitrate.

To validate the model’s predictive ability, the method of projection [40] was used. Figure 8 shows the unknown samples not included in the modelling process and projected onto the rotated model. Although this is a small data set and not all of the sample variability would have been captured it is evident from the figure that these samples lie in their expected clusters, as was confirmed when the individual spectra were examined and compared against the known reference samples. Although the data could be viewed as potentially lying outside of an expected class, there is no overlap with other classes, and it would be anticipated that the chances of ambiguous classification would be small. This observation suggests that there is good potential of applying the model for the prediction of future sample types.

**Investigating the potential for determining deterioration levels**

The data that was collected in this study suggests that correlating the visible and physical signs with the degree of chemical deterioration may be possible using the combination of IRS and multivariate analysis. Figure 9 presents the rotated Factor 1 vs Factor 4 scores plots with corresponding Factor 4 loadings plot. Interestingly, the cluster that contained the spectra which were identified as cellulose nitrate but contained a significant spectral component due to gelatin are observed to spread along PC4. The three remaining groups, one cellulose nitrate and two cellulose acetate, remain tightly clustered.

Examination of the Factor loadings plots in Fig. 9b reveals that this separation is due to the band at ~843 cm$^{-1}$ which is attributable to the ν(NO) mode of cellulose nitrate.

The sample grouping capability within The Unscrambler software allows for data to be plotted and assigned specific colours, or symbols, which allows for visualisation of trends or the distinction between classes, or groups, of samples to be easily made. Sample grouping was used to understand why one cluster of cellulose nitrate data spread along PC4, and the grouping was based on the value of the variable at 843 cm$^{-1}$ identified...
in Fig. 9b. The grouping is based on the pre-processed data and as a result of the use of the first derivative the values are a mixed range of negative and positive values as can be seen in the legend of Fig. 9a. Spectra from samples within this cluster were plotted (data not shown) with data taken from the extremes and the middle of the group to examine the spectral region containing the band at 843 cm\(^{-1}\). Notably, the \(\nu(\text{NO})\) band was absent in the spectra of the samples at the top of the group along the PC4 axes but was present in the other sample spectra to varying degrees. The intensity of this band was largest in the sample spectra from the bottom of the group. A significant shift in the position of the band which varied from 829 to 856 cm\(^{-1}\) was also observed. Further work is needed to understand if this could be used to establish a correlation between the visual, physical and chemical signs of cellulose nitrate deterioration.

Conclusions
The research presented in this paper outlines the development of a methodology based on infrared total reflectance spectroscopy, for rapid identification of cellulose nitrate and cellulose acetate. Identification of cellulose nitrate and cellulose acetate in collections is necessary for preservation management and risk management to collections and humans due to its hazardous and unstable nature. Cellulose nitrate and cellulose acetate are found in gallery, library, archive and museum photographic collections. As a result, identification and management of this material might be the responsibility of curators, librarians, archivists, collection managers, registrars or conservators, depending on the institution staffing and structure.

Infrared reflectance spectroscopy allowed for film samples to be rapidly and non-destructively analysed with no sampling needed, a methodology that meets the cultural heritage industry’s requirements. Approximately 12 samples were measured in triplicate within an hour, once confident that the established methodology is robust there is potential for upwards of 30–40 samples per hour to be analysed as single measurements. Spectra of well-preserved cellulose nitrate and cellulose acetate could easily be identified by visual inspection of the data. However, the eventual aim of the method development is to allow for non-experienced users to collect data and obtain a simple true/false or yes/no answer. The application of multivariate statistical analysis allowed for a model to be developed that in the future could have a simple graphic user interface to enable the simple true/false type of answer.

Principal component analysis provided an opportunity to distinguish between different sub-groups within the data and it is hoped that in the future it can be used to detect specific levels of film deterioration. In particular, the use of the orthogonal rotation method of Parsimax resulted in chemically interpretable loadings plots which contained information that potentially provide a more objective means of ascertaining the level of chemical deterioration in the cellulose nitrate film.

All samples analysed in this preliminary study were either sheet or still photographic film. Other formats, such as motion picture film, magnetic soundtrack, aerial, microfilm or x-rays were not analysed in this study and are necessary for future research and testing the validity of this method.
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