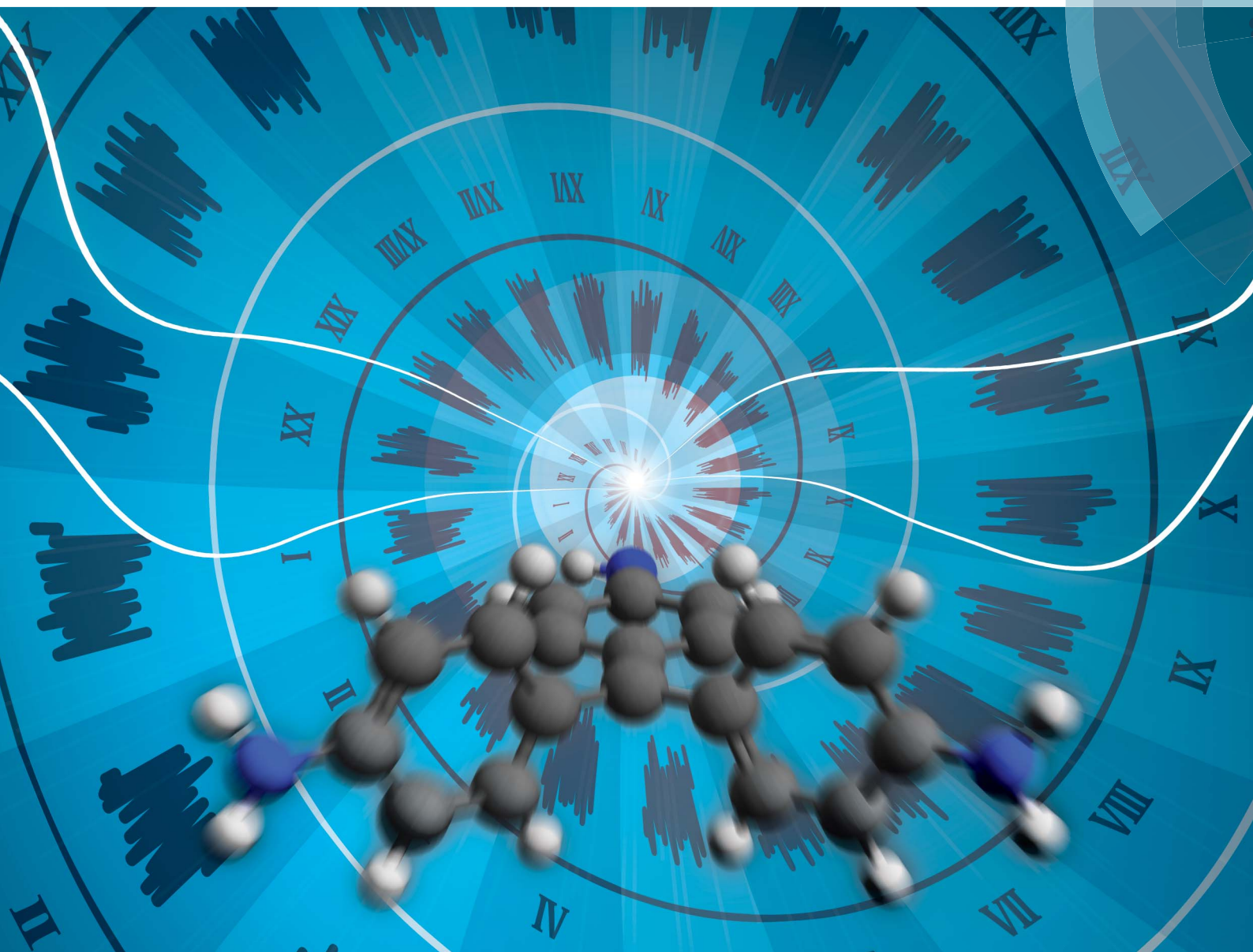


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PAPER

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A study into the ageing and dating of blue ball tip inks on paper using *in situ* visible spectroscopy with chemometrics

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A study into the ageing and dating of blue ball tip inks on paper using *in situ* visible spectroscopy with chemometrics†

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This paper presents a study into the potential of visible spectroscopy with chemometrics as an approach to dating blue ball tip inks on paper documents. Analysis of six inks left under various conditions found that the majority of those kept in the dark could still be matched to the source pen after 32 months of ageing. Conversely, the majority of those exposed to light exhibited rapid spectral changes that continued throughout the 32 month period. Partial least squares regression (PLSR) was used to generate dating models for inks aged with exposure to light. Evaluation using an external test set found absolute dating to be challenging for these ink deposits within the first 2–6 months of ageing. However, predictive accuracy was found to improve for long-term ageing, with two-year old samples yielding age estimates with a maximum error of 6 months. This rapid, non-destructive methodology could assist document examiners in the relative ageing or approximate age determination of questioned documents, as well as the identification of document alterations.

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Introduction

Civil and criminal cases involving fraud or forgery remain a significant concern to society. The Western Australia Police identified fraud as the largest and most expensive category of federal offences from Australian courts in 2015, despite only an estimated 25% of cases being reported.¹ Such offenses may involve the falsification or alteration of handwritten documents, which remain prevalent in financial, legal or identity matters.²

Ink analysis can play an important role in the forensic investigation of such cases. Modern writing inks are complex mixtures consisting of multiple dyes or pigments suspended in a solvent, along with various additives designed to regulate properties such as viscosity or adhesion.^{3–5} The most common ink formulations in use today are those associated with ball tip pens; namely ballpoint, rollerball and gel inks.

Contemporary ballpoint inks usually consist of synthetic dyes dissolved in a glycol- or benzyl alcohol-based solvent.^{6,7} This results in a high viscosity formulation that is fast-drying,

water resistant and provides a controlled ink flow. In contrast, rollerball inks are typically water or xylene based; the latter being water resistant.⁸ These inks are attractive due to their smoother flow and rich colour saturation compared to ballpoint inks, although the lower viscosity makes them more susceptible to smudging or bleeding. Gel inks combine characteristics of both ballpoint and rollerball inks by using a water-based gel rather than a liquid solvent.⁵ This results in a thixotropic ink that is semi-solid until liquified by the movement of the ball tip. Gel inks are usually pigment-based to increase colour permanence and opacity, although newer gel formulations may be dye-based.^{9,10} More recently, ‘low viscosity’ gel inks have also been developed as a hybrid between ballpoint and typical gel inks.

The complexity and variety of modern ink formulations, whilst challenging for analysis, potentially allows for discrimination based on their distinctive compositions. The chemical and physical examination of ink components can therefore provide valuable information regarding document authenticity. These analyses can be used to determine the source of an unknown ink, to identify additions or alterations made to handwritten ink entries, or to estimate the date at which an entry was produced.

Ink dating in particular is a highly complex challenge in questioned document examination. Once deposited on a substrate, inks can undergo rapid compositional changes due to factors such as solvent evaporation, chemical interactions with the substrate, or dye degradation.^{11–13} The exact rates at which these processes occur vary according to several factors,

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including the initial ink composition, paper properties and the storage environment.^{14–16} Several studies have attempted to utilise the changes observed in ink deposits over time to establish a reliable means of ink dating, as reviewed by Ezcurra *et al.*⁷ These studies can be broadly divided into three approaches; those based on the evolution of resins,^{17–19} loss of volatile components,^{15,20,21} or variations in the dyes.^{12,22,23} The latter is of specific interest as many inks contain unique combinations of dyes and pigments, making colour a highly distinguishing feature.

More recent studies have investigated the practicality of ink dating using various approaches to chemical analysis in combination with chemometrics. Senior *et al.* used principal component analysis (PCA) with ultraviolet-visible (UV-vis) spectroscopy and high performance thin layer chromatography to study the ageing of ten blue ballpoint inks up to 18 months after deposition on paper.²⁴ The aged deposits were found to produce significantly different PCA scores, which could be correlated with time using multiple linear correlation analysis. The resulting equations were used to estimate the age of three samples aged for four months, with two samples yielding predictions accurate to within ten days.

Sharma and Kumar later demonstrated the use of UV-vis with multiple linear regression (MLR) to model the degradation of blue ballpoint inks aged up to approximately nine months.²⁵ The final model was able to estimate the age of tested ink entries to within an accuracy of 14 days. Diaz-Santana *et al.* similarly employed gas chromatography-mass spectrometry and high performance liquid chromatography in conjunction with MLR, modelling the concentration changes in solvents or dyes from blue and black ballpoint inks over 45 months. The resulting models provided dating estimates with a maximum error of 4–7 months.²⁶

Although promising, it should be noted that the methodologies described above required extraction of the ink into a solvent, rather than analysis *in situ* on the paper substrate. Given the legal or financial nature of documents that may be submitted for examination, non-destructive testing is vital in order to preserve the document's integrity. Additionally, these previous studies utilised the same ink deposits for both the construction of the models and their validation. This fails to consider possible heterogeneity in the ink composition or variations in the ageing process between ink deposits and may therefore result in an over-estimation of the model's capabilities.

Most recently, Ortiz-Herrero *et al.* presented a non-invasive methodology for ink dating based on UV-vis-NIR reflectance spectra.²⁷ 48 samples of a commercial ink were artificially aged for up to 11 days, and the resulting data used to construct regression models using partial least squares analysis. These models were tested using a selection of five inks aged under the same conditions for up to nine days, achieving relative standard deviations as low as 16%. Additional samples of these inks were also exposed to natural ageing for up to 45 days in order to establish a correlation between natural and artificial ageing.

This approach addresses many of the limitations associated with previous studies as described above. However, as noted by

the authors, artificial ageing does not necessarily provide a complete representation of ink ageing processes under natural conditions. Additionally, as the regression model was constructed using a single brand of commercial ink, predictions were found to be inaccurate for inks of substantially different composition. The authors thus acknowledge the need to develop separate predictive models for each class of ink in order for this method to be more broadly applicable.

In previous research by the authors Sauzier *et al.*, diffuse reflectance visible spectroscopy was utilised with chemometrics to examine the classification and chemical changes upon ageing of blue ball tip inks on paper.²⁸ As highlighted by Ortiz-Herrero *et al.*,²⁷ diffuse reflectance spectroscopy is highly advantageous for this purpose as it is rapid, requires minimal sample preparation and is non-destructive when applied *in situ*. A discriminant model was constructed from a sample set of 35 inks using PCA and linear discriminant analysis (LDA), then evaluated using an external validation set of 12 inks. The resultant model was able to assign 71.7% of spectra to the correct pen model, and a further 16.7% to the correct supplier.

Six of these inks were then selected for ageing under various office conditions over a two-month period. It was found that ink deposits stored in a dark environment (either open to air or in polypropylene sleeves) remained chemically stable, whereas those exposed to light could undergo significant spectral changes in as little as one week. It was proposed that these changes were due to the photodegradation of triarylmethane dyes in the ink; a process further accelerated by the presence of titanium dioxide in the paper substrate.^{29,30} However, this study was focussed solely on how ageing could affect the classification of inks using the chemometric model, rather than establishing a means of age determination. Additionally, this work was limited to the ageing of ink deposits over two-months. As questioned documents encountered in forensic casework may be several months or years old, it is of relevance to investigate what additional changes occur over a long-term ageing period.

This study expands upon the previous work by examining the continued natural ageing of blue ball tip ink deposits between 2–32 months, and how this affects their classification using the established predictive model. Partial least squares regression (PLSR) was subsequently used to establish individualised dating curves for each of the light-exposed ink deposits, and these models evaluated using a separate validation set aged for up to 24 months.

Experimental

Sample collection and preparation

In previous work by the authors, 35 blue ball tip pens were obtained from existing stationery supplies and Western Australian retailers (Table S1†).²⁸ The sample set was intended to consist solely of ballpoint inks, as ballpoint pens are generally considered to be the most common writing implement in current use.³¹ However, during the course of this study it was found that one ink, originating from a Pilot G-2 05 retractable pen, was in fact a gel formulation. It was decided to retain this



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Table 1 Number of misclassified spectra for inks stored in polypropylene archive sleeves in the dark, at various intervals following ink deposition. Labels in brackets indicate assigned groups. Inks that did not yield any misclassified spectra throughout the ageing period have been omitted for clarity

| Ageing period | Pen 10 | Pen 11 | Pen 23 | Pen 26 |
|---------------|------------|------------|------------|------------|
| 4 months | — | 1 (pen 13) | — | — |
| 6 months | 1 (pen 18) | 1 (pen 13) | — | — |
| 8 months | — | 1 (pen 13) | — | — |
| 10 months | — | 1 (pen 13) | 1 (pen 10) | — |
| 13 months | — | 3 (pen 13) | 1 (pen 1) | — |
| 14 months | — | 1 (pen 13) | 1 (pen 10) | — |
| 19 months | 1 (pen 18) | 2 (pen 13) | — | — |
| 25 months | — | 2 (pen 13) | 1 (pen 10) | — |
| 28 months | — | 1 (pen 13) | — | — |
| 32 months | — | 2 (pen 13) | 1 (pen 10) | 1 (pen 10) |

Table 2 Number of misclassified spectra for ink samples stored open to air in the dark, at various intervals following ink deposition. Labels in brackets indicate assigned groups. Inks that did not yield any misclassified spectra throughout the ageing period have been omitted for clarity

| Ageing period | Pen 8 | Pen 11 | Pen 23 |
|---------------|------------|------------|------------|
| 4 months | — | — | 1 (pen 10) |
| 6 months | — | — | 1 (pen 10) |
| 8 months | — | — | — |
| 10 months | — | — | — |
| 13 months | — | — | — |
| 14 months | — | — | 1 (pen 1) |
| 19 months | — | — | — |
| 25 months | — | — | — |
| 28 months | 3 (pen 13) | — | — |
| 32 months | 5 (pen 13) | 1 (pen 33) | — |

28 months of exposure, the Celco Retractable ink was misclassified as originating from a J.Burrows ballpoint pen. This indicates that despite the lack of exposure to light, the dyes in this ink are still undergoing a gradual degradation process, likely due to oxidation. Aginsky found that even in the absence of light, triarylmethane dyes can undergo an oxidative process with atmospheric oxygen to form diphenylmethane derivatives and phenol.³⁵ This theory is supported by the fact that these changes were not observed for the deposits stored in polypropylene sleeves with limited air exposure.

The classification results were corroborated through projection of the aged ink deposits onto the original PCA model, which revealed the samples to remain largely clustered with their equivalent fresh deposits (Fig. 1). Exceptions were noted for single replicates of the Pentel Rolly ink stored in polypropylene at 32 months, and Office Basics ink kept open to air at 14 months. Visual inspection revealed these spectra to significantly differ from the typical spectra of their respective deposits, and so these replicates were identified as outliers.

Interestingly, spectra from the Celco Retractable ink at 32 months showed little apparent shift from the fresh deposits, despite being misclassified by the LDA model. It should be

noted that the remaining 29 inks in the population, though not shown in the projection plot, may lie close to inks subjected to ageing. As a result, even seemingly minor changes in sample distribution may produce incorrect classifications. However, these misclassified samples can be identified as atypical through inspection of their discriminant values, as discussed in previous research.²⁸

It can be seen from Fig. 1 that the Celco, PaperMate and Keji inks exposed to air displayed a greater spread compared to those in polypropylene sleeves, reinforcing the idea that these inks are vulnerable to oxidative dye degradation. Conversely, the Office Basics ink shows a greater shift when stored in polypropylene sleeves. In this instance, it is possible that the solvent trapped within the polypropylene sleeve is undergoing a chemical interaction with the dyes, as previously suggested by Grim *et al.*¹⁴ In both cases however, the variation between spectra obtained at different ageing periods was no greater than the variation between spectra collected on the same date. As the overall classifications of these samples remain unchanged using LDA, it cannot be stated with certainty whether these variations are indicative of a current compositional change, or rather due to instrumental variation and inhomogeneity within the ink deposits.

Inks exposed to light exhibited varying misclassifications throughout the ageing period (Table 3). The Pentel Rolly remained correctly classified until 25 months of exposure, indicating that this formulation is relatively slow-ageing. This suggests that the Pentel Rolly ink formulation uses a colourant with greater photostability, such as copper phthalocyanine, in order to provide increased fade resistance. In contrast, the Pilot G-2 05 gel ink exhibited misclassifications within the first four months of ageing, suggesting that this formulation is dye-rather than pigment-based and thus vulnerable to photodegradation.

Notably, the classifications of the inks change several times, indicating that the ageing process is still ongoing. This is evident in the PCA projection plot (Fig. 2), where the aged deposits continue to drift further from the baseline samples with time. The direction of this shift is consistent with the short-term ageing results previously reported, with samples attaining more positive scores along PC1 and negative scores along PC3.²⁸ Though compositional changes pose a challenge in the identification of an unknown ink formulation, they may facilitate the identification of altered documents, as discussed in initial research.²⁸ The recognition of handwritten document alterations may be difficult if changes have been made using the same pen as the original entry. However, this research demonstrates that handwritten ink entries completed using the same pen at different times may be readily differentiated if the document has been exposed to light.

Examination of the spectra revealed an increasing red reflectance and decreasing blue reflectance over time, consistent with preliminary findings that shifts along PC1 and PC3 are due to changes in these regions.²⁸ This spectral shift can also be related to the anticipated degradation pathway of the ink dyes. One of the main proposed mechanisms for triarylmethane dye degradation is oxidative *N*-demethylation, wherein methyl



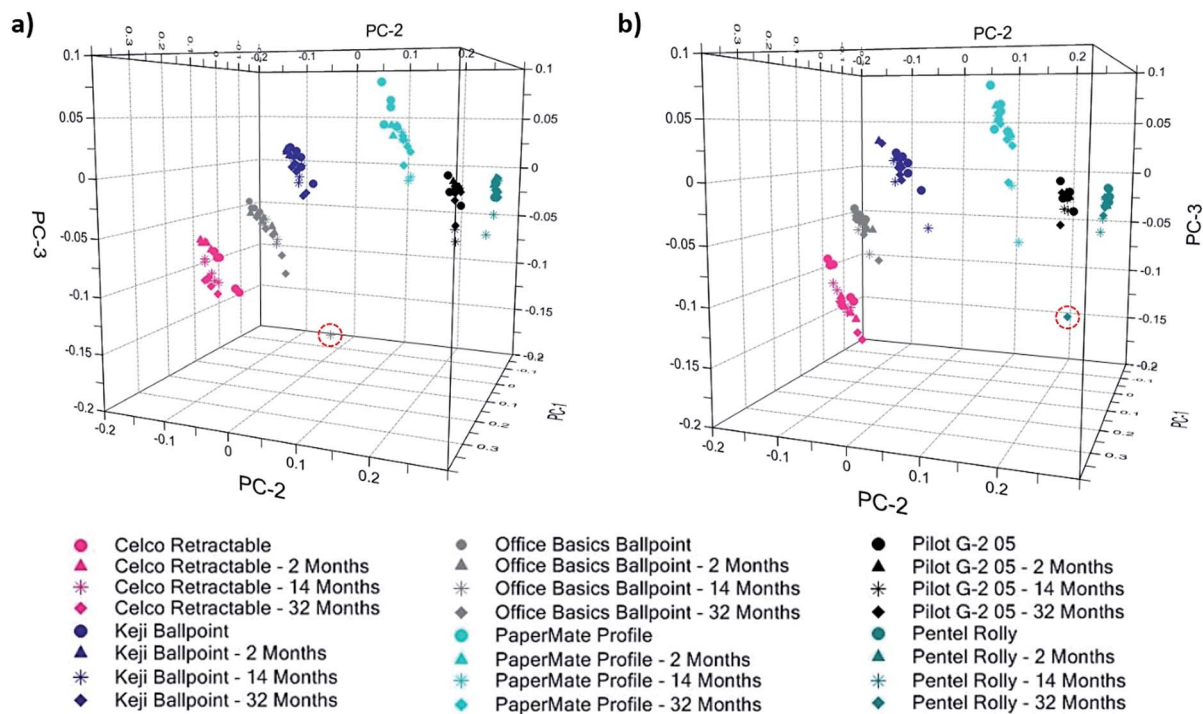


Fig. 1 3-Dimensional PCA projection plot showing the distribution of fresh ink deposits and those stored in the dark; (a) in polypropylene archive sleeves and (b) open to air; for 2 months, 14 months and 32 months. Red circles indicate spectra identified as outliers.

groups are successively substituted by hydrogen atoms.^{36,37} The degree of methylation of triarylmethane dyes affects their shade, with greater methylation resulting in blue-violets and lower methylation leading to red-violets.³⁸ The red shifts observed in the spectra of the aged inks is therefore consistent with dye degradation occurring *via* *N*-demethylation. Interestingly, the spectral changes and PCA shifts observed in the Pilot G-2 05 ink were comparable to those in the ballpoint deposits. These results again suggest a dye-based gel formulation,

containing the same or structurally similar dyes as the ballpoint inks.

Although the ageing process appears to still be ongoing, analysis of the spectra from a single ink deposit indicates that the rate of ageing is slowing. Fig. 3 shows the distribution of spectra obtained from the Celco Retractable ink at each analysis interval. It is evident that the shift in sample scores between intervals becomes smaller as the deposits age, with overlap observed for spectra obtained after 8–10 months. This follows

Table 3 Number of misclassified spectra for inks stored open to light, at various intervals following ink deposition. Labels in brackets indicate assigned groups

| Ageing period | Pen 8 | Pen 10 | Pen 11 | Pen 19 | Pen 23 | Pen 26 |
|---------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------|
| 4 months | 5 (pen 13) | 5 (pen 13) | 5 (pen 13) | 5 (pen 30) | 4 (pen 22), 1 (pen 30) | — |
| 6 months | 5 (pen 13) | 2 (pen 13) | 5 (pen 13) | 5 (pen 27) | 5 (pen 22) | — |
| 8 months | 5 (pen 13) | 1 (pen 33) | 5 (pen 13) | 3 (pen 27), 2 (pen 13) | 4 (pen 22), 1 (pen 30) | — |
| 10 months | 4 (pen 13), 1 (pen 34) | 1 (pen 33) | 5 (pen 13) | 3 (pen 29), 1 (pen 13), 1 (pen 33) | 2 (pen 16), 2 (pen 22), 1 (pen 30) | — |
| 13 months | 3 (pen 19), 2 (pen 34) | 5 (pen 33) | 4 (pen 33), 1 (pen 30) | 3 (pen 13), 2 (pen 29) | 4 (pen 16), 1 (pen 19) | — |
| 14 months | 3 (pen 19), 2 (pen 34) | 3 (pen 33), 1 (pen 16), 1 (pen 24) | 2 (pen 30), 2 (pen 33), 1 (pen 19) | 5 (pen 13) | 4 (pen 16), 1 (pen 19) | — |
| 19 months | 3 (pen 34), 1 (pen 29), 1 (pen 32) | 5 (pen 16) | 5 (pen 16) | 2 (pen 12), 2 (pen 21), 1 (pen 2) | 5 (pen 10) | — |
| 25 months | 4 (pen 29), 1 (pen 30) | 5 (pen 16) | 5 (pen 16) | 2 (pen 2), 2 (pen 12), 1 (pen 32) | 3 pen (10), 1 (pen 1), 1 (pen 11) | 1 (pen 27) |
| 28 months | 2 (pen 29), 2 (pen 32), 1 (pen 30) | 5 (pen 16) | 5 (pen 16) | 2 (pen 2), 2 (pen 33), 1 (pen 32) | 3 (pen 1), 1 (pen 9), 1 (pen 10) | 1 (pen 27) |
| 32 months | 5 (pen 30) | 4 (pen 24), 1 (pen 16) | 5 (pen 24) | 5 (pen 13) | 3 (pen 1), 1 (pen 9), 1 (pen 11) | 3 (pen 27) |



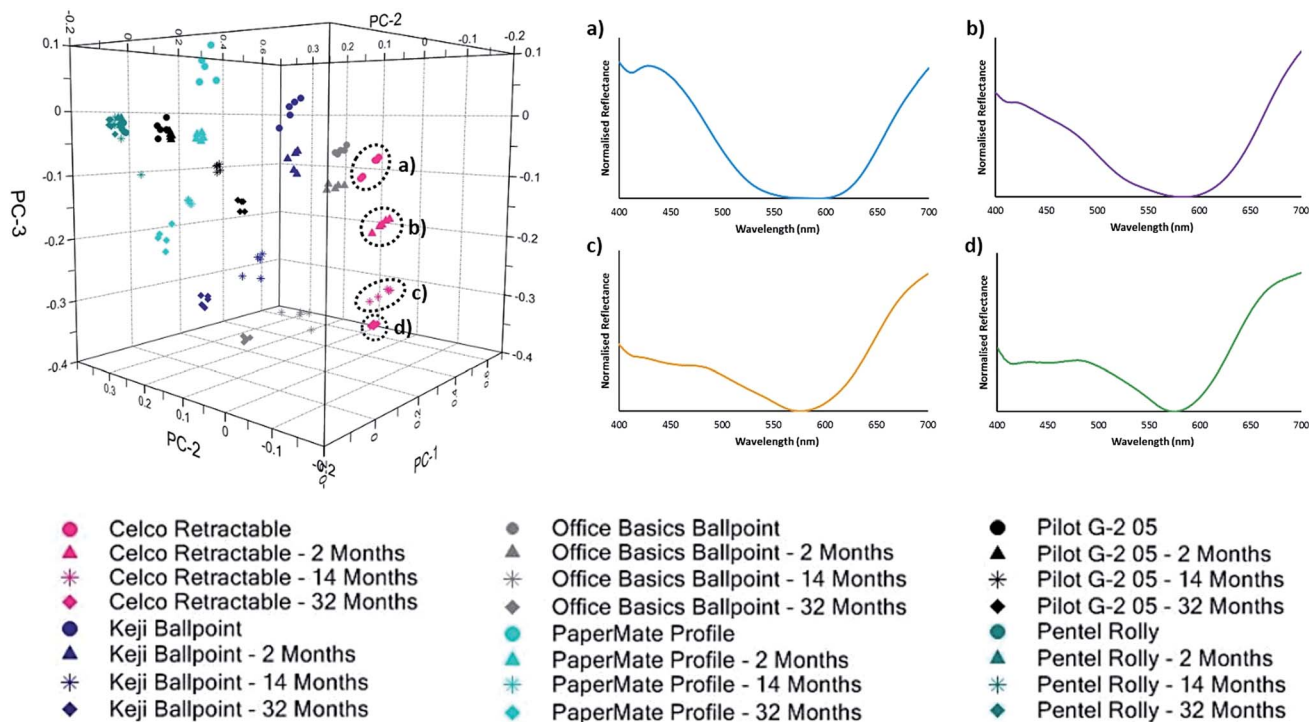


Fig. 2 3-Dimensional PCA projection plot showing the distribution of (a) fresh ink deposits; and those stored open to light for (b) 2 months; (c) 14 months; and (d) 32 months, with normalised spectra obtained at each interval for the Celco Retractable ink.

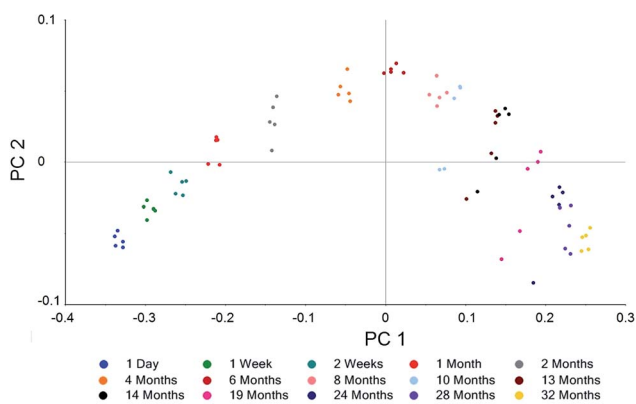


Fig. 3 2-Dimensional PCA plot showing the distribution of fresh and aged blue ball tip inks exposed to light following various periods for the Celco Retractable ink.

the expectation that the rate of dye degradation would be most rapid in the immediate months following exposure to light, with the rate of change then decreasing over time. These findings are also consistent with literature suggestions that the degradation of triarylmethane dyes can be detected up to approximately 30 months of ageing.³⁷

Development of dating models for light-exposed samples

The results obtained from both PCA and LDA indicate that the ageing of ink deposits under ambient light is a dynamic process, with changes continuing to occur over at least a 32

month period. These changes could potentially be used to develop chemometric models for the age estimation of unknown ink entries. With this in mind, calibration curves were generated for the inks using partial least squares regression (PLSR).

PLSR is a multivariate regression method that first reduces the original predictor set into a lesser number of orthogonal factors, in a similar fashion to PCA.^{39,40} These factors are calculated in such a way that covariance between the predictor and response variables is maximised.^{41,42} That is, greater weight is applied to wavelengths that display variation highly correlated with sample age, under the assumption that these will be the most accurate for predictive purposes.

Separate PLSR models were constructed for each of the light-exposed inks using the spectra acquired over the 32 month ageing period. For each model, a Scree plot was used to select the optimal number of factors to retain for regression, as summarised in Table 4 below. Dispersion graphs of the actual and predicted ageing intervals for the calibration set are provided in the ESI (Fig. S2[†]). Excellent agreement was observed between the actual and estimated values, with correlation coefficients greater than 0.97 obtained for all models including the Pentel Rolly ink. Based on this high correlation, the resultant models would be expected to demonstrate good predictive capability in estimating the age of an unknown ink deposit.

The regression models were evaluated using a separate validation set of ink deposits aged for up to 24 months. As these deposits were prepared approximately seven months after the initial ageing samples, baseline spectra from each deposit were



Table 4 Number of selected factors and corresponding percentage of total variance for PLSR models of blue ball tip inks exposed to light over a 32 month period

| Ink | Factors | % variance |
|-------------------|---------|------------|
| Celco Retractable | 4 | 99.3 |
| Keji Ballpoint | 2 | 98.0 |
| Office Basics | 2 | 99.1 |
| Pilot G-2 05 | 1 | 98.3 |
| PaperMate Profile | 3 | 98.3 |
| Pentel Rolly | 6 | 98.8 |

first predicted using the discriminant model, in order to determine whether any significant compositional changes in the inks had occurred whilst in storage. All spectra were correctly assigned, indicating the inks to have remained chemically stable within the pen cartridges during storage. These results are consistent with research by Andrasko and Kunicki, who found no evidence of dye degradation in ink entries produced from the same pen up to 6 years apart.⁴³ Grim *et al.* similarly found that dyes within the ink cartridges of pens stored for up to 20 years remained predominantly unchanged, although a small number of inks exhibited ageing at a greater rate than when deposited on paper.⁴⁴

Age estimations for the validation samples are summarised in Table 5. The predicted and actual ages for deposits within the first 2–6 months of ageing were substantially different, with some inks obtaining negative age estimations. Closer inspection of the data revealed a high level of variability between replicate spectra of any given deposit acquired on a single analysis date, resulting in poor predictive performance. This was evidenced by the high relative standard deviations (RSDs) associated with the dating estimates, which in several instances exceeded the actual age of the ink (Table S2†). It is likely that the rapid chemical changes occurring during this initial ageing period are too variable to be precisely modelled for dating purposes.

Interestingly, model performance was observed to improve with increasing sample age. In particular, 24 month-old deposits

Table 5 Mean estimated ageing periods for validation ink deposits exposed to light, compared to actual ageing periods. Values are averaged over five replicate spectra

| Actual ageing (days) | Estimated ageing (days) | | | | | |
|----------------------|-------------------------|--------|--------|--------|--------|--------|
| | Pen 8 | Pen 10 | Pen 11 | Pen 19 | Pen 23 | Pen 26 |
| 1 | −47 | −13 | 25 | −7 | 15 | 15 |
| 6 | −35 | −64 | 19 | −2 | −15 | −12 |
| 21 | −12 | −42 | 35 | 4 | 9 | −16 |
| 42 | −4 | −62 | 44 | 39 | 47 | 43 |
| 98 | 39 | −28 | 91 | 74 | 126 | 159 |
| 147 | 93 | −8 | 135 | 126 | 164 | 207 |
| 504 | 453 | 357 | 463 | 411 | 417 | 551 |
| 596 | 432 | 416 | 511 | 432 | 461 | 544 |
| 617 | 588 | 435 | 599 | 484 | 520 | 569 |
| 672 | 633 | 513 | 623 | 549 | 594 | 609 |

Table 6 RMSEC values obtained for PLSR models of blue ball tip inks exposed to light over a 32 month period

| Ink | RMSEC |
|-------------------|-------|
| Celco Retractable | 12.6 |
| Keji Ballpoint | 13.9 |
| Office Basics | 16.8 |
| Pilot G-2 05 | 27.5 |
| PaperMate Profile | 15.6 |
| Pentel Rolly | 11.2 |

were predicted with an absolute error between 1–6 months. The RSDs associated with these predictions (Table S2†) were also noted to decrease with time. These results suggest that age estimation using this approach is more readily achieved based on subtle changes occurring during mid- to long-term ageing. Ortiz-Herrero *et al.*, similarly observed that one ink analysed yielded lower RSDs over time, although other inks displayed no clear correlation between ageing period and predictive accuracy.²⁷

Closer inspection of the scores plots for each ink found that although there is a clear change in scores over time, the shift between spectra recorded at different time intervals is similar to that amongst spectra obtained on the same date. The similar magnitudes of intra-group and inter-group variance are likely to have reduced the discrimination between deposits of different ages. Additionally, the calibration and validation samples were separately prepared approximately seven months apart. It is thus possible that heterogeneity between deposits or uncontrolled environmental variations (*e.g.* ambient light intensity or humidity) may have caused the ageing process to occur at different rates.

A further figure of merit is the root mean square error of calibration (RMSEC), which measures the level of dispersion about the regression line. Table 6 shows the RMSEC values for each model to be in the range of 1–2 months, leading to a disproportionately high prediction error for inks within the first six months of ageing.

Despite these limitations, the regression models demonstrate potential in establishing the approximate age of an unknown ink entry, which may be sufficient to prove or disprove a point of contention in court. Additionally, these results indicate that the models can distinguish relatively fresh deposits (within six months of ageing) from those that are at least a year old, even when the same ink has been used in both instances. This approach could therefore still be applicable to the relative ageing of two or more ink entries of the same formulation. This could be valuable in determining the order in which two or more documents were written, or again to identify whether an alteration has been made to a document using the same ink formulation at a later date. Furthermore, the comparable results obtained for both the ballpoint and gel inks demonstrate the potential applicability of this approach to multiple ink types, such as gel, rollerball or hybrid formulations.

Conclusions

This study demonstrates the utility of diffuse reflectance visible spectroscopy for the analysis of inks *in situ* on paper, providing



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