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Monitoring of pigmented surfaces in accelerated ageing process by ATR–FT-IR spectroscopy and multivariate control charts

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Abstract

This work is an extension of a method for monitoring the conservation state of pigmented surfaces presented in a previous paper. A cotton canvas painted with an organic pigment (Alizarin) was exposed to UV light in order to evaluate the effects of the applied treatment on the surface of the sample. The conservation state of the pigmented surface was monitored with ATR–FT-IR spectroscopy and multivariate control charts.

The IR spectra were analysed by principal component analysis (PCA) and the relevant principal components (PCs) were used for constructing multivariate Shewhart, cumulative sums (CUSUM) and simultaneous scores monitoring and residuals tracking (SMART) control charts.

These tools were successfully applied for the identification of the presence of relevant modifications occurring on the surface of the sample.

Finally, with the aim to more deeply investigate what happened to the sample surface during the UV exposure, a PCA of the residuals matrix of degradation analyses only, not present in the previous paper, was performed. This analysis produced interesting results concerning the identification of the processes taking place on the irradiated surface.

Keywords: ATR–FT-IR spectroscopy; Accelerated ageing process; Multivariate control charts

1. Introduction

There are in literature several applications of infrared spectroscopy [1–7] in the field of cultural heritage preservation as this technique is able to characterise both the inorganic and organic constituents of a wide variety of artworks, giving an insight into the materials and techniques of execution of the artefacts [7].

An important method called internal reflection spectroscopy (IRS) or attenuated total reflection (ATR) for obtaining the infrared spectra of solids or films has been described by Fahrenfort [8] and Harrick [9–11]; this technique is suitable to analyse works-of-art as it does not require any sample pre-treatment and it is a non-destructive analysis.

Chemometric techniques (like principal component analysis, classification methods, cluster analysis and so on) have already been applied in the field of cultural heritage [12–14] as they are able to extract the systematic information from a complex data set, as the spectroscopic ones.

The main problem in the field of cultural heritage is the degradation since artworks, and especially paintings, are very sensitive to environmental damages [15,16].

In this study, a method based on ATR–FT-IR spectroscopy coupled to multivariate control charts is proposed for monitoring the *state-of-health* of pigmented surfaces, with regard to the oxidation processes induced on the medium, the pigment and the canvas, by artificial ageing, caused by the ex-

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posure of the samples to UV rays, simulating an aggressive portion of the sun-light. The principles of statistical process control (SPC) [17–20] can be used in the study of superficial degradation processes as it has already been demonstrated by the monitoring of the conservation state of wooden objects and canvas painted with inorganic pigments, analysed by Raman spectroscopy [21,22]. This paper is an extension of the previous method, applied in the present case to an organic pigment, with a different analytical technique, namely ATR–FT-IR spectroscopy, with an additional statistical treatment devoted to the identification of the changes occurring on the irradiated surface. In this work a cotton canvas strip painted with an organic pigment (Alizarin) mixed with linseed oil, is exposed to an accelerated ageing process, simulated in our laboratories by exposing its surface to UV light produced by a lamp emitting at 254 nm. The aim was to check if the control charts are able to suggest that an effect can be measured, which is obviously related to the applied treatment. The spectroscopic data obtained were analysed by principal component analysis and the relevant PCs were used to build multivariate Shewhart [23–25], CUSUM [26,27] and simultaneous scores monitoring and residual tracking (SMART) [28,29] control charts. The multivariate approach has been preferred rather than the classical monoviariate one, owing to the complexity of the data set.

2. Theory

Chemical data sets are often characterised by a large number of variables, with complex correlation patterns. In these cases, the application of a multivariate approach [28,30,31] represents the best procedure for the process monitoring and identifying trends and systematic behaviours. In this work, the application of a multivariate approach is even more important because of the great number of variables (the peaks' intensities) which are inherently correlated with each other.

A simplification of the problem can be obtained by means of principal component analysis (PCA) [32–35], providing a new set of orthogonal variables, linear combination of the original ones, to describe the system under investigation.

PCA can be applied in order to identify the relevant changes caused by a degradation process, through the analysis of the projections (scores) of the original data (observations at different time) in the PCs space, while the analysis of the composition of each PC in terms of the contribution of the original variables (loadings) may lead to the identification of the causes which produced the changes. Furthermore, the residuals obtained subtracting from the original data the information contained in the set of significant PCs, account for the remaining information; if a treatment leads to a degradation of the studied sample, with production of new species, the related information shall be probably present in the residuals.

Shewhart control charts can be constructed both using the scores of the relevant PCs or the residuals [36–38]; they are not very sensitive to small changes of the process mean and in order to effectively detect the occurrence of such changes, a powerful tool is the so-called cumulative sums (CUSUM) control chart [26].

Multivariate processes can be also analysed by the so-called simultaneous scores monitoring and residual tracking (SMART) charts originally described by Swante Wold [28,29], for monitoring scores and residuals at the same time. The first chart consists of a typical T^2 Hotelling control chart, built with all the significant PCs. The second chart is the DModX control chart, which represents the residuals calculated by the application of the soft independent model of class analogy (SIMCA) [39] classification model based on the significant PCs. These two graphs show the process in its whole, nevertheless a possible disadvantage consists in the more difficult interpretation of the final result due to the combination of the information of all the significant components together.

2.1. The applied procedure

The procedure for monitoring the conservation state of the painted surface under study is the same proposed in a previous paper [17] with the exception of point six:

(1) Characterisation of the painted surface.
(2) Principal component analysis of the characterisation measurements.
(3) Application of the simulated accelerated ageing treatment (UV exposure) and monitoring by regular time IR spectroscopic analyses (treated samples).
(4) Re-projection of each observation of the degradation analyses onto the space given by the relevant PCs calculated from the characterisation measurements.
(5) Multivariate control charts construction.
(6) Principal components analysis of the residuals of degradation analyses: this step is usefull for the comprehension of the phenomena that may occur on the sample surface during the UV exposure: in fact this information is not contained in the characterisation data matrix that is used for first PCA.

3. Experimental

3.1. ATR–FT-IR spectroscopy and software

The IR spectra were registered by an AVATAR 370 FT-IR Thermo Nicolet spectrometer (Thermo Nicolet Corporation, USA) equipped with a He–Ne laser at 50 mW, with a large emission intensity at 630 nm. The spectrophotometer is directly controlled by a PC with the software EZ OMNIC (Thermo Nicolet Corporation, USA). The IR spectra were collected with the SMART Accessory that pressed the sample over the Zn–Se crystal. All spectra were registered from 3600 to 650 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans; the background was collected before each spectrum.

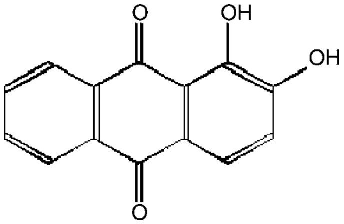

Fig. 1. Chemical structure of alizarin (1,2-dihydroxyanthraquinone).

For principal component analysis and control charts, the following softwares were used: “Statistica” version 6 (StaSoft Inc., USA), “The Unscrambler” version 7.6 (Camo Inc., Norway), “Microsoft Excel 2000” (Microsoft Corporation, USA), “Matlab” version 6.1 (The Mathworks, USA); the spectra transformations were performed by “Origin” version 6.1 (Microcal Software Inc., USA).

3.2. Sample preparation and UV treatment

For this study, Alizarin [40] was chosen (Fig. 1) since it is one of the most stable natural pigments.

In our application Alizarin was mixed with linseed oil [41] 1:1 and spread on a cotton canvas strip (cellulose 98%, lignin–pectine 2% [42]). After the complete drying of the pigment, the characterisation analyses were performed in order to have a description of the sample in its normal conservation state. The IR spectra were always registered on the same point of the canvas strip.

The simulation of the exposure to sunlight was obtained by irradiating the coloured canvas strip with light from a UV lamp (λ: 254 nm, power: 15 W). The analyses were collected every 12 h of exposure (the 12 h of UV irradiation were interrupted for about 5 min to register each IR spectra) for a total of 276 h.

4. Results and discussion

Fig. 2a shows the IR spectrum of the sample before and after the UV exposure; the peaks whose intensity changed during the treatment are pointed out in Fig. 2b–d.

Tables 1–3 report the IR vibrational assignments of linseed oil [41], cotton [42] and Alizarin [43]. It can be seen that there are several common bands among the three materials. The peaks grouped at 2950 cm^{-1}, relative to the alkyl C–H stretch of linseed oil and canvas, are the only ones not in common with Alizarin.

Table 1
IR vibrational assignments of row linseed oil

Band position (cm^{-1})	Assignement[a]
3001	ν(C—H)=CH
2960	ν_a(C—H)CH_3
2926	ν_a(C—H)CH_2
2885	ν_s(C—H)CH_2
1747	ν(C=O)
1658	ν(C=C)
1464	ν(CH_2)
1418	Wagging(CH_2)—CH_2—CO—O—
1378	Wagging(CH_2)
1240	ν_a(C—C—O)
1164	ν(C—O)
1100	ν_a(O—CH_2—C)
990	δ(CH) (alkene)
723	γ—(CH_2)— + wag(C—H)=CH

[a] ν: stretching; δ: bending; γ: rocking; a: asymmetric; s: symmetric.

Table 2
Principal IR vibrational assignments of cotton canvas

Band position (cm^{-1})	Assignement[a]
3012	ν(CH)
2933	ν_a(CH_2)
2853	ν_s(CH_2)
1747	ν(CO)
1657	ν(C=C)
1440	ν_s(OCO)
1302	δ(CH_2) twisting
1266	ν(CH)
990	δ(CH) (alkene)

[a] ν: stretching; δ: bending; a: asymmetric; s: symmetric.

The exposure of the sample to UV light caused a loss of gloss of the surface, and, for what regards the instrumental analysis, a general decrease of the peak intensities with the exception of the peaks at 1027 and at 997 that increased, and of the peak at 1465 cm^{-1} that disappeared during the exposure; these effects could be due to degradation of linseed oil [44], pigment [45] and cotton canvas [46]. The drying of linseed oil, in particular, has been largely studied in the past but it is still far from being completely understood; it seems that in the initial phase an autoxidation of the unsaturated fatty acid components occurs, with the development of an extensive cross-linking and the formation of conjugated unsaturations. In the following phase, a slow consumption of some labile cross-links brings to a very stable network, containing small amounts of low molecular weigh molecules, either formed by fragmentation or as unreacted triglycerides.

The continuation of the hardening process in natural conditions, leads to the oxidative degradation of linseed oil, and only for long periods of artificial ageing (for example UV or high temperatures exposure) corresponding to years of natural ageing, the oxidation takes place on the alkylic segments, leading to partial fragmentation of the structure [41].

Table 3
IR vibrational assignments of Alizarin

Band position (cm^{-1})	Assignement[a]
3300	ν(OH)
3030	Aromatic ν(CH)
1730	ν(C=O)
1600	Aromatic ν(C=C)
1349	δ(C=C)
1268–1000	ν(C—O)
896–600	Aromatic δ(CH)

[a] ν: stretching; δ: bending.

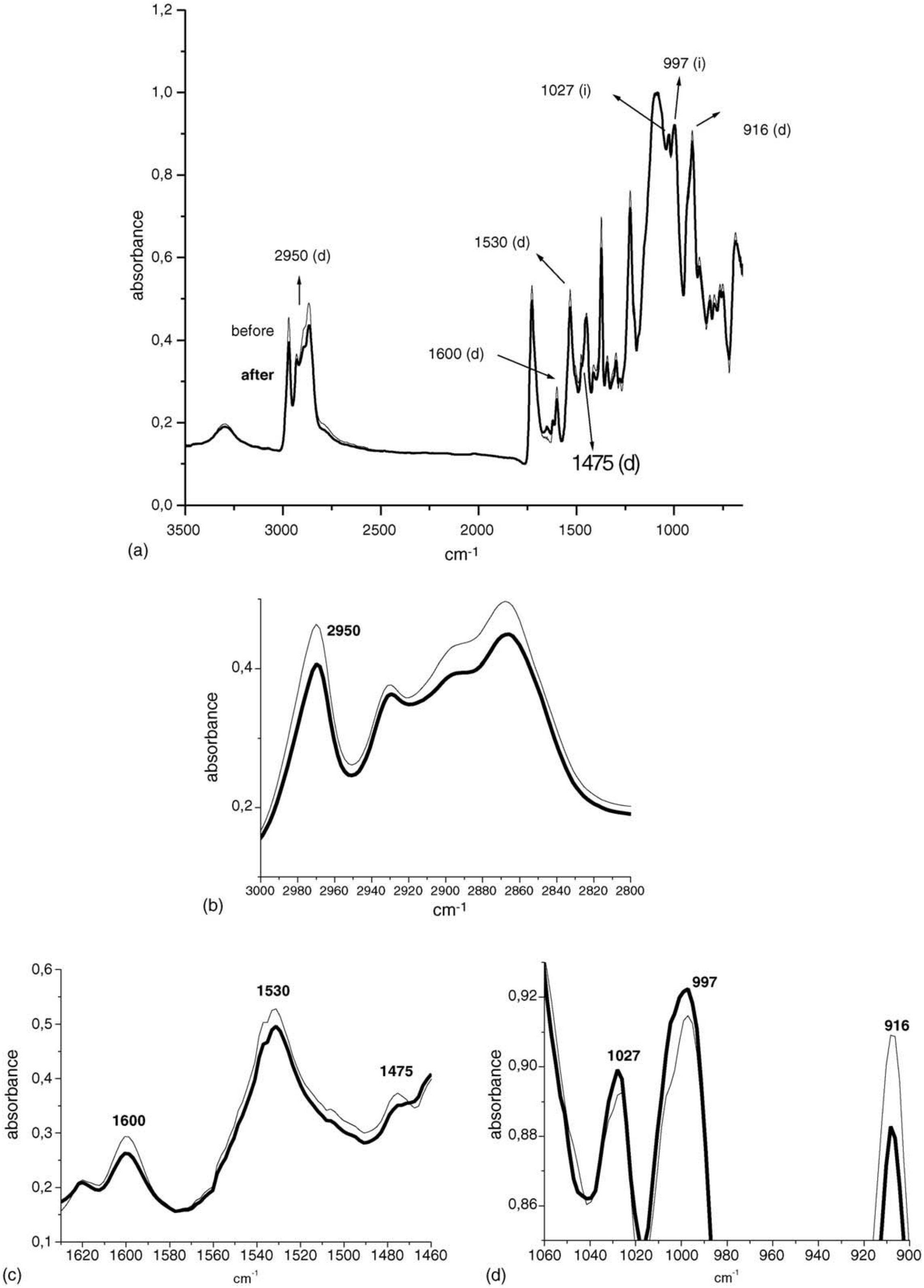

Fig. 2. IR spectra of the studied sample before (thin line) and after (thick line) UV exposure; the peaks which showed relevant changes during UV exposure are indicated (i = increasing while d = decreasing) (a); spectrum details: region between 3000 and 2800 cm^{-1} (b); region between 1630 and 1450 cm^{-1} (c); region between 1060 and 900 cm^{-1} (d).

Table 4
% Explained variance and % cumulative explained variance for the first six PCs calculated for characterisation analyses of the sample

	Characterisation analyses (29 spectra)	
	% Explained variance	% Cumulative explained variance
PC1	67.98	67.98
PC2	19.26	87.24
PC3	7.90	95.14
PC4	1.16	96.30
PC5	0.81	97.11
PC6	0.44	97.55

4.1. Principal component analysis on characterisation analyses

The results of PCA applied to the characterisation samples are reported in Table 4. The first three PCs, accounting for 95% of the total variance, are the significant ones.

In the score plot of PC_1 and PC_2 (Fig. 3a), that account for 87% of the total variance, there is not a clear separation between characterisation and treated analyses.

In the corresponding loading plot, it can be seen that the group of peaks registered at 2950 cm^{-1} (alkyl CH stretch of linseed oil and cotton canvas) has a big weight on PC_1; given that these peaks are not assignable to Alizarin, it can be stated that PC_1 accounts for the information related to linseed oil and/or cotton canvas.

The two peaks around 985 cm^{-1} (alkenyl CH bend) have a large weight on PC_2: it can be remarked that only for the region from 1027 to 997 cm^{-1} the peak intensities increase during the UV exposure. This modification could mean that the UV treatment has caused an oxidation of the unsaturated components of the sample (linseed oil and canvas) [44].

The score plot of PC_1 and PC_3 (Fig. 3b), that accounts for 76% of the total variance, shows a very good separation of the characterisation (at low values) and treated analyses (at high values) along PC_3. The loading plot of PC_3 shows that the peaks at 1600 and 1550 cm^{-1} (alkenyl and aromatic C=C stretch) have a large weight on this PC: the intensities of these peaks decrease during the UV exposure. This means that probably the UV treatment has caused an oxidative effect on the aromatic portion of the sample (pigment) and on the unsaturated components, linseed oil and canvas.

4.2. Multivariate control charts

4.2.1. Shewhart charts

Fig. 4 represents the Shewhart control charts of the relevant PCs. The residual control chart coincides with one of the SMART charts and shall be considered later.

The Shewhart chart of PC_1 (Fig. 4a) shows that after a stable situation corresponding to the characterisation analyses, during the exposure to UV light, the conservation state of the sample went out of statistical control: in fact there is a series of nine point over the average score and, moreover, one analysis is beyond the upper control limit. Besides, the treated analyses are affected by a much larger variability with respect to the characterisation ones. This chart suggests that something happened to linseed oil, namely the component whose PC_1 account for, probably related to the process of drying as a consequence of the exposition to UV light. This shows that taking into account the temporary sequence of the data may add important information on the process status, in fact the analysis of the scores of PC_1 did not suggest evident correlations with the UV exposure.

In the Shewhart chart of PC_2 (Fig. 4b), at the end of the UV exposure, the monitored process went out of statistical control, in fact there is a series of eight points below the mean and one point is beyond the lower control limit. This second chart shows that UV exposure caused a modification of two peaks at 1027 and 997 cm^{-1} whose intensities increased in the last treated analyses (probably an oxidation).

Fig. 4c represents the Shewhart chart of PC_3: this chart shows clearly that UV irradiation caused a significant change of the painted surface: in fact, after a stable behaviour corresponding to the characterisation analyses, the scores suddenly increase and fall beyond the upper control limit. This means that the bonds accounted for by PC_3 (namely the alkenyl and the aromatic C=C stretch at 1600 and 1530 cm^{-1}) have been significantly influenced: it can be supposed that the exposure has probably caused an oxidation of the unsaturated components (linseed oil and canvas) and of the aromatic ring, with subsequent loss of aromaticity (Alizarin) [45].

4.2.2. CUSUM charts

Fig. 5a reports the CUSUM chart for the scores of PC_1. This chart shows that also during the characterisation analyses apparently there were some changes of the surface. In particular four trends of different slope (negative–positive–negative–stable) characterise the first group of analysis in absence of UV irradiation. After the final stable behaviour, the irradiation causes a steep positive trend which then stabilises. This means that the accelerated ageing treatment has caused a change of the process mean towards values higher than the average in the first period, but the process has afterwards returned to its normal values or values slightly smaller than normal. This can be confirmed analysing retrospectively the corresponding Shewhart chart. This can support the assumption of an accelerated drying process of linseed oil.

Fig. 5b reports the CUSUM chart of the scores of PC_2. In this case the evident trend, with negative slope, starts after nine treatment analyses and continues for the whole treated period. This means that the change of the surface accounted for by this principal component does not start with the treatment but needs an induction period, when no effect can be observed. Again the same behaviour can be observed in the Shewhart control chart, but the CUSUM chart is extremely effective in permitting to unequivocally identify the existence of the change of the mean value of the process and the exact

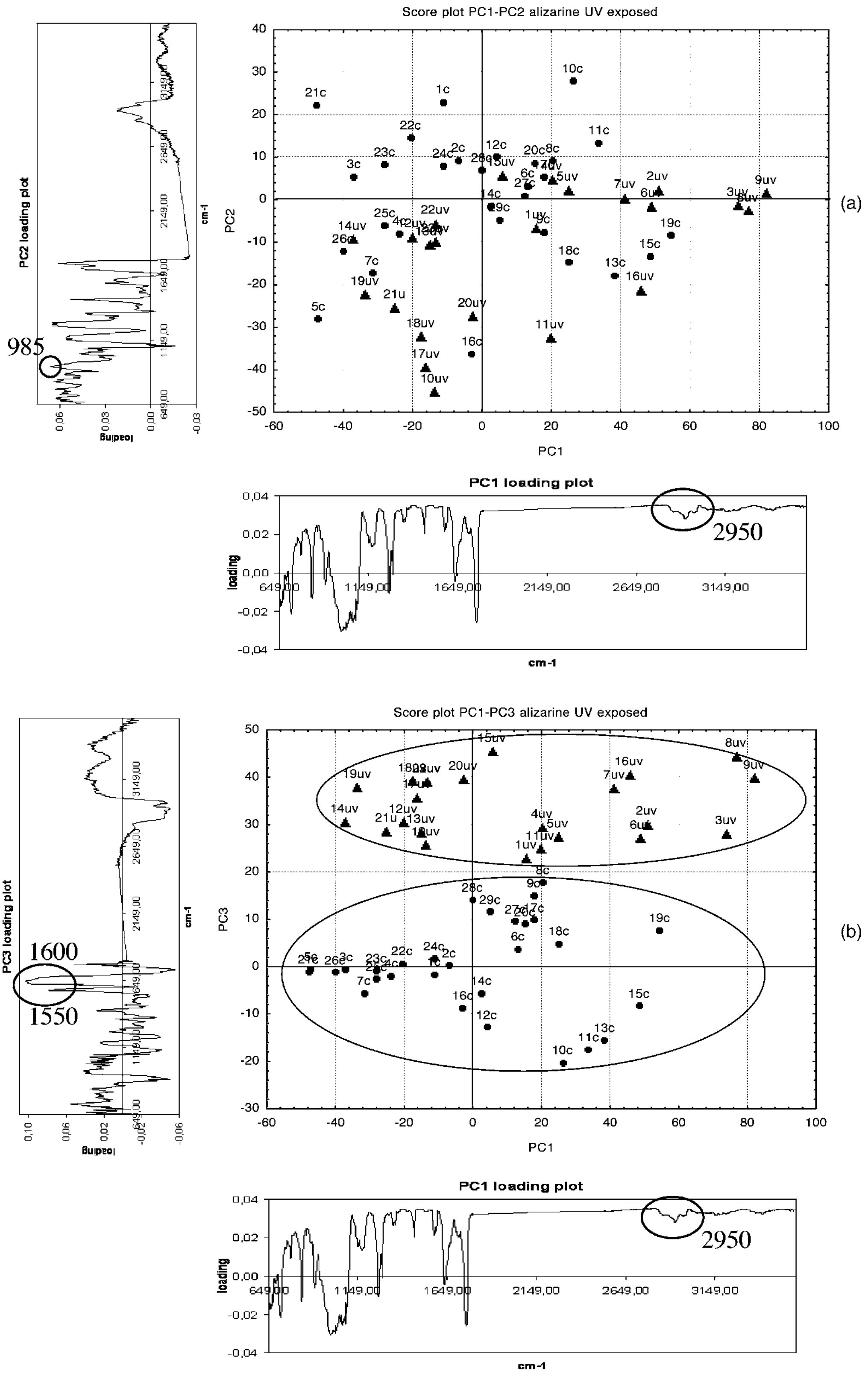

Fig. 3. Score and loading plot of PC_1 and PC_2 (a); score and loading plot of PC_1 and PC_3 (b); the characterisation analyses are represented as black circles, while the treated analyses are represented as black triangles. The peaks showing the larger weight are indicated in the loading plots.

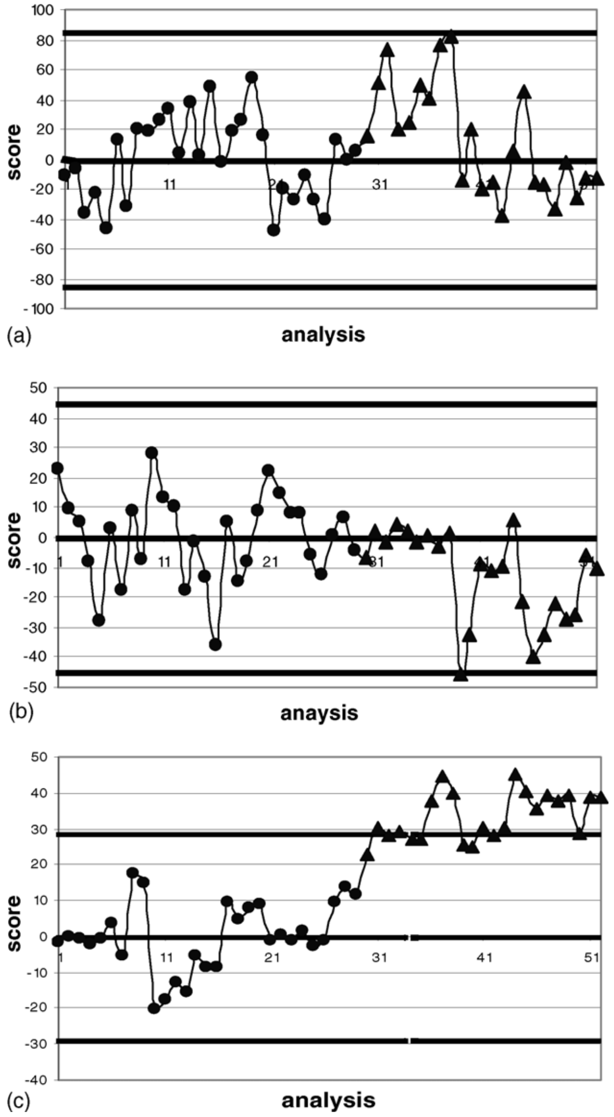

Fig. 4. Multivariate Shewhart control charts for the samples exposed to UV light: Shewhart chart of PC_1 (a); Shewhart chart of PC_2 (b); Shewhart chart of PC_3 (c). The characterisation analyses are represented as black circles, while the treated analyses are represented as black triangles.

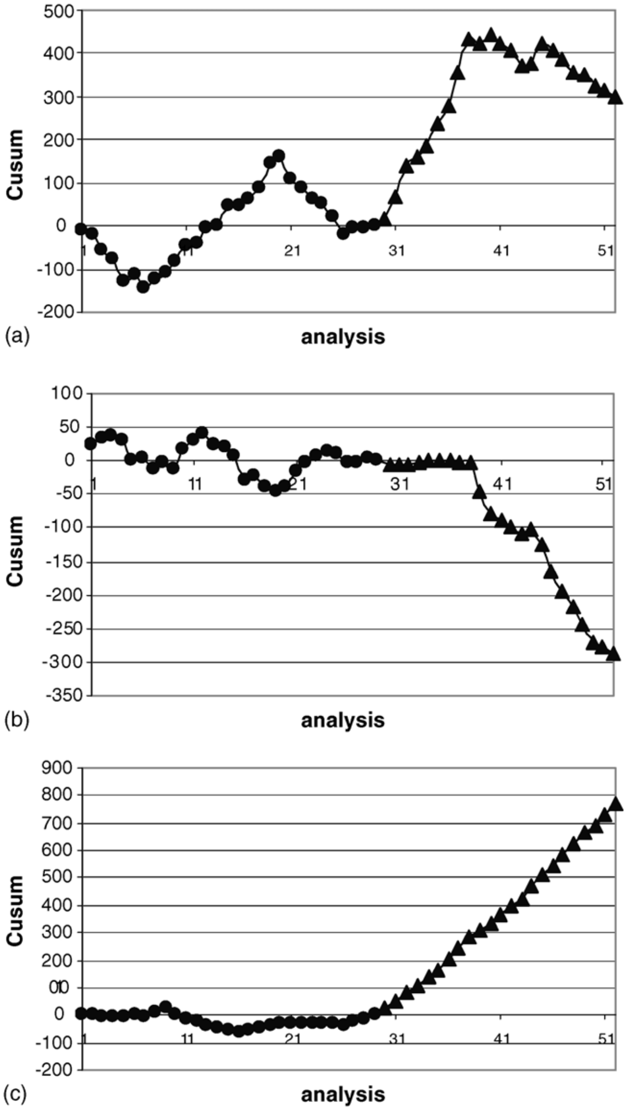

Fig. 5. Multivariate CUSUM control charts for the samples exposed to UV light: CUSUM chart of PC_1 (a); CUSUM chart of PC_2 (b); CUSUM chart of PC_3 (c). The characterisation analyses are represented as black circles, while the treated analyses are represented as black triangles.

instant when this modification started. This can support the assumption of a starting oxidation of the unsaturated fatty acid components of linseed oil in the last degradation analyses.

Fig. 5c shows the CUSUM chart of the scores of PC_3. This chart clearly points out the precise moment when the UV exposure begins, which means that the modification accounted for by PC_3 started immediately after the irradiation with the UV lamp. This can reinforce the assumption concerning the information contained in PC_3, namely the oxidation of the aromatic (Alizarin) and of the unsaturated components (linseed oil and canvas) of the sample surface.

The calculation of the control limits of the CUSUM charts by the V-mask [47] was not necessary, given the evident trends, easily recognisable by visual inspection.

The results obtained with the CUSUM charts have confirmed what already observed analysing the Shewhart charts, but the CUSUM charts allowed to individuate the precise moment when the effect started. The two charts provide complementary information, the CUSUM chart being more sensitive to small changes of the process mean.

4.2.3. SMART charts

Fig. 6 reports the SMART charts, calculated in this case on the basis of a SIMCA classification model built with the first three PCs. The T^2 Hotelling chart, clearly shows that there is a modification of the conservation state of the sample surface during the UV exposure, since all treated analyses fall beyond the T^2_{critical}. Besides, the treated analyses are af-

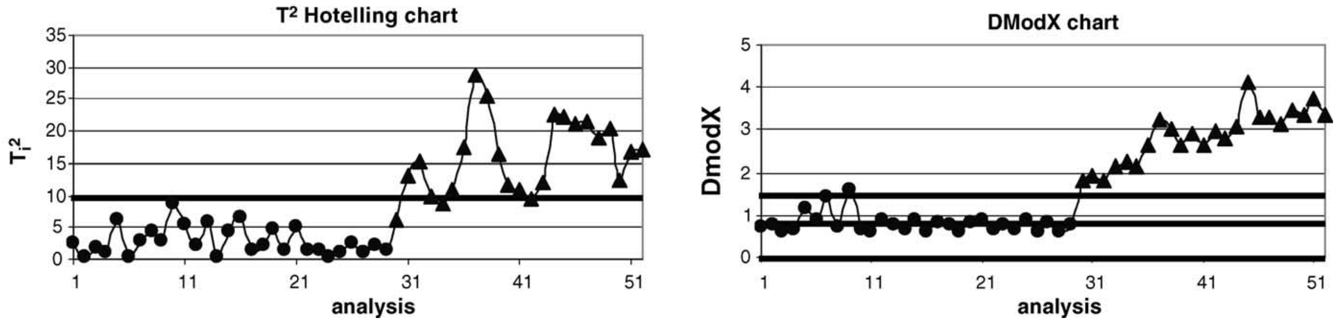

Fig. 6. Multivariate SMART chart for the samples exposed to UV light: T^2 Hotelling chart and DModX chart.

fected by a larger variability than the characterisation ones. This means that the sample surface has been changed by the applied treatment. This chart is effective to recognize out-of-control situations, but the interpretation of the causes is much more difficult. In fact it is not possible, from this chart, to understand immediately which PCs have lead to the out-of-control.

In the DModX chart, i.e. the residual chart, all treated analyses are beyond the upper control limit and they are continuously increasing. Analysis 10 of the characterisation analyses is probably an outlier. The change observed in the DModX chart indicates that some phenomena, not accounted for by the first three PCs, has taken place on the painted surface. The identification of what has happened requires a deeper analysis of the residuals.

In conclusion, we can state that among all control charts, the CUSUM and the SMART ones produced the best results since they allowed to clearly identify a change of the state of the sample surface during the accelerated ageing treatment.

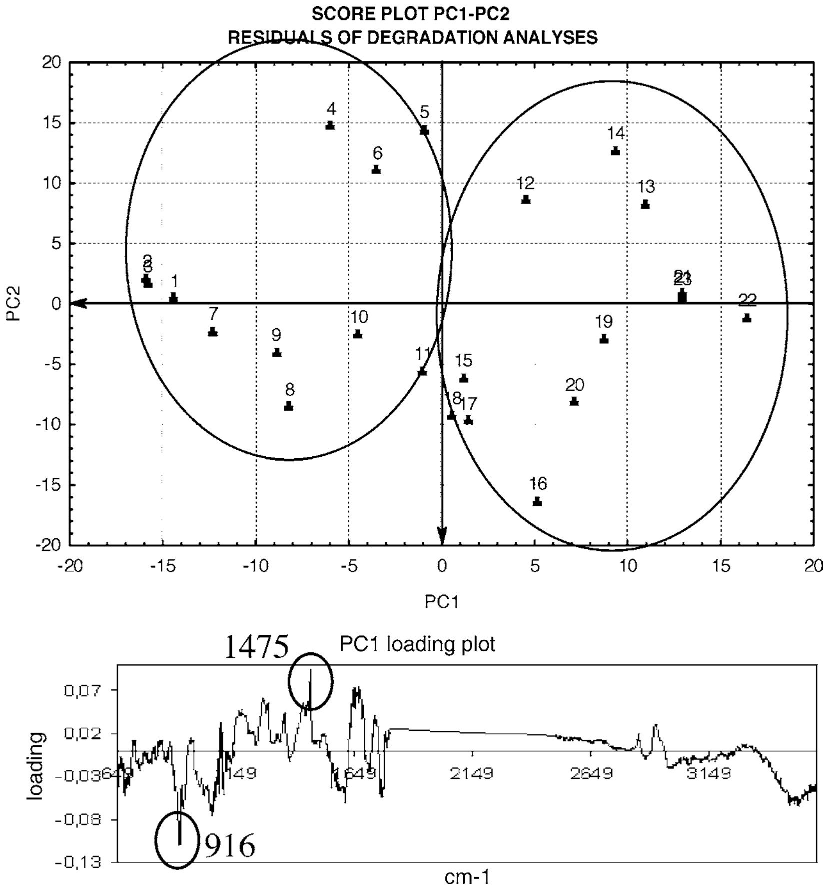

Fig. 7. Score and loading plot of PC_1 and PC_2; the treated analyses are represented as black triangles. The peaks showing the larger weight are indicated in the loading plot.

Table 5
% Explained variance and % cumulative explained variance for the first six PCs calculated for the residuals of analyses corresponding to UV exposure of the sample

	Residuals of degradation analyses (23 spectra)	
	% Explained variance	% Cumulative explained variance
PC1	41.03	41.03
PC2	30.82	71.85
PC3	9.51	81.36
PC4	3.52	84.88
PC5	3.23	88.11
PC6	2.19	90.30

4.3. Principal component analysis on residuals of degradation analyses

The previous PCA had been performed on the characterisation data matrix. However, the three considered PCs showed that the conservation state of the sample surface had changed because the spectral profiles had been modified by the UV exposure. The DModX chart had showed that new information had risen as a consequence of the degradation process. With the aim to analyse the effects of the applied treatment on the sample surfaces, the residuals data matrix was further investigated. The residual of each degradation analysis is a spectrum that contains the peaks not accounted for by the three PCs obtained from the PCA performed on the characterisation analyses. So a new PCA was performed on the residuals data matrix of the degradation analyses. Table 5 shows the result of this PCA. The first PC, accounting for 41% of the total variance, is significant: in fact, looking at the score plot of the first two PCs (Fig. 7), PC_1 separates the degradation analyses in two groups: first analyses (from 1 to 11) at negative values and the last analyses (from 12 to 23) at positive values of PC_1. Looking at the loading plot of PC_1 it can noticed that the peak at 916 cm^{-1} (alkenyl CH bend) has a big negative weight and the peak at 1475 cm^{-1} (alkyl CH bend) has a big positive weight on this PC. Fig. 2d shows that the intensity of the first peak decreased while the second peak disappeared during the UV exposure (Fig. 2c). So, the residuals analysis suggests that the treatment had an effect (probably an oxidation) on the unsaturated (peak at 916 cm^{-1}) and on the saturated (peak at 1475 cm^{-1}) components of the sample surface. These effects could not be observed in the previous analysis since they are not accounted for by the three PCs considered.

5. Conclusions

This work is an extension of a method for monitoring of the conservation state of pigmented surfaces shown in a previous paper; the method is based on the application of ATR–FT-IR spectroscopy coupled to SPC techniques. The aim is to investigate the effect of the exposure to UV light on a canvas strip painted with an organic pigment (Alizarin). The exposure to UV light produced some changes on the sample surface, clearly identified by the multivariate Shewhart, and especially by the CUSUM and SMART charts. The interpretation of the phenomena taking place was very difficult and only a further statistical analysis of the residuals of the treated analyses by PCA could shed light on the effect of the degradation processes.

From the results obtained it can be concluded that the UV exposure has accelerated the natural drying process of linseed oil (namely the autoxidation of the unsaturated component, followed by the formation of the of cross-links) and caused a degradation (oxidation) of the pigment and of the cotton canvas.

The actual results were obtained on a simple model of a painted work-of-art. Work is in progress in our lab to generalise this methodology to more complex systems with several pigments simultaneously present in mixture on the canvas, with the final target of applying the method to a real painting.

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References

[1] C. Balas, et al., J. Cult. Herit. 4 (2003) 330s–337s.
[2] M. Attas, et al., J. Cult. Herit. 4 (2003) 27–136.
[3] M. Fabbri, M. Picollo, S. Porcinai, Appl. Spectrosc. 56 (7) (2002) 420–427.
[4] D.C. Creagh, V. Otieno-Alego, Nucl. Instrum. Meth. B 213 (2004) 670–676.
[5] H. Kuhn, Stud. Cons. 15 (1970) 12–36.
[6] V.J. Birstein, Stud. Cons. 20 (1975) 8–19.
[7] F. Casadio, L. Toniolo, J. Cult. Herit. 2 (2001) 71–78.
[8] J. Fahrenfort, Spectrochim. Acta 17 (1961) 698.
[9] N.J. Harrick, Ann. NY Acad. Sci. 101 (1963) 928.
[10] N.J. Harrick, J. Opt. Soc. Am. 55 (1965) 581.
[11] N.J. Harrick, Internal Reflection Spectroscopy, Wiley/Interscience, New York, 1967.
[12] L. Osete-Cortina, M.T. Domenech-Carbo, R. Mateo-Castro, et al., J. Chromatogr. A 1024 (1/2) (2004) 187–194.
[13] J. Bentley, T.J. Schneider, Comput. Statist. Data Anal. 32 (2000) 465–483.
[14] P. Fermo, et al., Spectrochim. Acta, Part B 58 (2003) 177–184.
[15] G. Spoto, Acc. Chem. Res. 35 (8) (2002) 652–659.
[16] O.F. Van den Brink, G.B. Eijkel, J.J. Boon, Termochim. Acta 365 (1/2) (2000) 1–23.
[17] W.A. Shewhart, Economic Control of Quality of Manufactured Product, Van Nostrand, Princeton, NJ, 1931.
[18] D.C. Montgomery, Introduction to Statistical Quality Control, 3rd ed., Wiley, New York, 1991.
[19] W.H. Woodal, D.J. Spitzner, D.C. Montgomery, et al., J. Qual. Technol. 36 (3) (2004) 309–320.
[20] X. Pan, J. Jarret, J. Appl. Statist. 31 (4) (2004) 397–418.
[21] E. Marengo, et al., Anal. Chem. 75 (2003) 5567–5574.
[22] E. Marengo, et al., Talanta 63 (2004) 987–1002.

[23] F.B. Alt, N.D. Smith, in: P.R. Krishnaiah, C.R. Rao (Eds.), Handbook of Statistics, vol. 7, North-Holland, Amsterdam, 1998, pp. 333–351.

[24] F.B. Alt, in: S. Kotz, N.L. Johnson (Eds.), Encyclopedia of Statistical Sciences, vol. 6, Wiley, New York, 1985, pp. 110–122.

[25] C.T. Chin, F.G. Fan, Instrum. Math. Econ. 32 (3) (2003) 474–474.

[26] R.H. Woodward, P.I. Goldsmith, Cumulative Sum Techniques, Oliver and Boyd, London, 1964.

[27] H.B. Wong, F.F. Gan, T.C. Chang, J. Statist. Comput. Sim. 74 (1) (2004) 47–62.

[28] K.C.S. Pillai, in: S. Kotz, N.L. Johnson (Eds.), Encyclopedia of Statistical Sciences, vol. 3, Wiley, New York, 1983, pp. 668–673.

[29] R.L. Mason, N.D. Tracy, J.C. Joung, J. Qual. Technol. 30 (4) (1998) 423–423.

[30] H. Hotelling, in: Hastay, Wallis (Eds.), Multivariate Quality Control—Techniques of Statistical Analysis, McGraw-Hill, New York, 1947.

[31] P.E. Maravelakis, S. Bersimis, J. Panaretos, et al., Commun. Stat-Theor. M. 31 (12) (2002) 2391–2408.

[32] S. Wold, K. Esbensen, P. Geladi, Chemom. Intell. Lab. Syst. 2 (1987) 37–52.

[33] J.C. Davis, Statistics and Data Analysis in Geology, Wiley, New York, 1986.

[34] D.L. Massart, B.G.M. Vanderginste, S.N. Deming, Y. Michotte, L. Kaufman, Chemometrics: A Textbook, Elsevier, Amsterdam, 1998.

[35] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experimenters, Wiley, New York, 1978.

[36] J.F. MacGregor, T. Kourti, Contr. Eng. Pract. 3 (1995) 403–414.

[37] A.J. Hayter, K.L.J. Tsui, Qual. Technol. 26 (1994) 197–208.

[38] C.M. Mastrangelo, D.C. Montgomery, Qual. Rel. Eng. Int. 11 (1995) 79–89.

[39] S. Wold, Kem. Kemi 9 (1982) 401.

[40] L. Burgio, R.J. Clark, Spectrochim. Acta A 57 (2001) 1491–1521.

[41] M. Lazzari, O. Chiantore, Polym. Deg. Stab. 65 (1999) 303–313.

[42] H.G.M. Edwards, D.W. Farwell, D. Webster, Spectrochim. Acta A 53 (1997) 2383–2392.

[43] A. Holmgren, L. Wu, W. Forsling, Spectrochim. Acta A 55 (1999) 1721–1730.

[44] A. Athanassiou, A.E. Hill, T. Fourrier, L. Burgio, R.J.H. Clark, J. Cult. Herit. 1 (2000) S209–S213.

[45] B. Roig, C. Gonzales, O. Thomas, Spectrochim. Acta A 59 (2003) 303–307.

[46] N. Katsuda, T. Omura, T. Tagagishi, Dyes and Pigments 3 (1997) 231–241.

[47] D.L. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. De Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam, 1997.