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Profiling of Liquid Crystal Displays with Raman Spectroscopy: Preprocessing of Spectra

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Raman spectroscopy is applied for characterizing paintable displays. Few other options than Raman spectroscopy exist for doing so because of the liquid nature of functional materials. The challenge is to develop a method that can be used for estimating the composition of a single display cell on the basis of the collected three-dimensional Raman spectra. A classical least squares (CLS) model is used to model the measured spectra. It is shown that spectral preprocessing is a necessary and critical step for obtaining a good CLS model and reliable compositional profiles. Different kinds of preprocessing are explained. For each data set the type and amount of preprocessing may be different. This is shown using two data sets measured on essentially the same type of display cell, but under different experimental conditions. For model validation three criteria are introduced: mean sum of squares of residuals, percentage of unexplained information (PUN), and average residual curve. It is shown that the decision about the best combination of preprocessing techniques cannot be based only on overall error indicators (such as PUN). In addition, local residual analysis must be done and the feasibility of the extracted profiles should be taken into account.

Index Headings: Liquid crystal displays; LCD; Raman spectroscopy; Preprocessing; Depth profiling; Polymeric films; Residual analysis.

INTRODUCTION

Raman spectroscopy for depth profiling of polymeric layers and films currently attracts a lot of attention.^{1–13} The sub-micrometer “spatial” resolution and 1–2 μm depth resolution are considered to be major advantages of confocal Raman spectroscopy for profiling. Other general advantages of Raman spectroscopy are the fact that composition information can be extracted relatively quickly and that no additional sample pre-treatment is needed even for analysis below the surface of a structure.¹⁴

In this study confocal Raman spectroscopy is used to characterize so-called paintable displays. The ‘classical’ way of producing liquid crystal (LC) displays¹⁵ counts 14 (!) stages. In the production of paintable displays many of these stages can be avoided.¹⁶ This means that paintable displays are easier, faster, and cheaper to produce. Equally important is the fact that they can be produced on any material of choice, opening the way towards highly flexible displays.

The challenge is to develop a method with which the distribution of the liquid crystal and a number of polymer components in a single display cell can be determined. The composition information that can be extracted in this way will give a better understanding of the paintable dis-

play manufacturing process and gives the opportunity for further improvement and fine-tuning.

Most analytical techniques cannot be used for characterizing LC displays, because sample preparation is almost impossible without influencing the device properties. This is due to the liquid nature of the monomers and the LC material. So, only a non-contact technique can be used. The high spatial resolution of Raman spectroscopy makes it a much better choice than, for example, infrared (IR) spectroscopy.

The main question is, how reliable is the obtained picture of the chemical composition of the display cell? The fact that measurements in depth are performed could distort the composition picture. Moreover, band overlap in Raman spectra in combination with all kinds of irrelevant spectral variation caused by cosmic spikes, spectral baseline drift, and small shifts between measured spectra may give a wrong picture of the composition.

Everall and others^{2–6} described the mismatch in confocal Raman spectroscopy between actual and apparent depth when metallurgic objectives are applied for depth profiling. The underlying reasons for this effect also lead to a reduced depth resolution for high NA objectives. Better results can be achieved with oil immersion objectives,^{5,12,13} but the overall intensity of the measured Raman spectrum might still depend on the depth of measuring. This implies that the intensity of the bands in the Raman spectrum is not only determined by the composition of the polymer film but also by the depth of measurement. The relation between the depth of measurement and the reliability of the extracted picture of the chemical composition is, however, not addressed here.

The classical least squares approach (CLS)¹⁷ is used to study the measured Raman spectra. CLS is selected, because (1) the component spectra of the monomer and the liquid crystal are available and (2) those component spectra have a considerable band overlap. This band overlap makes it impossible to quantify the contribution of one component independently of the others. By adopting a CLS model, it is assumed that the measured Raman spectra are a full linear combination of the available component spectra. The raw measured display cell spectra, however, are not (and in fact never will be) an exact linear combination. Except for noise there will always be other non-modeled spectral variation present. This spectral variation invalidates the CLS model and will lead to a distorted compositional picture of the display cell. Preprocessing of the spectra thus plays an important role in obtaining the true compositional picture of the paintable display.

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The focus of this study will be on the spectral preprocessing of Raman spectra that is necessary to remove and suppress this non-modeled spectral variation. It will be shown *how* to select the combination of preprocessing methods that supplies the best picture of the display cell composition. This selection is done using the remaining spectral variation after preprocessing and the CLS modeling of the spectra. The effect of each combination of preprocessing methods is judged with performance measures that supply information about size and shape of the remaining spectral errors. Additionally, a feasibility criterion is used to do a check on the results of the analysis. So, in the end the combination of CLS and preprocessing is used as a tool to analyze the measured spectra and to extract valuable compositional information.

Two sets of Raman spectra are analyzed. Both are measured on essentially the same type of display cell; however, the experimental setup in each case was different. The first set is measured using a confocal setup with a metallurgic (air) objective and the second set with an oil immersion objective. It will be shown that data preprocessing of the measured Raman spectra is critical in both cases and ultimately determines the quality of the emerging picture.

THEORY

Model of the Data and the Figures of Merit. The spectral data model is a straightforward CLS model. The display cell spectra ($\mathbf{S}_{\text{cell}}$) are modeled as a linear sum of the measured component spectra ($\mathbf{S}_{\text{comp}}$):

$$\mathbf{S}_{\text{cell}} = \mathbf{C}_{\text{comp}} \mathbf{S}_{\text{comp}} + \mathbf{E} \quad (1)$$

in which: $\mathbf{E}$ is the residual matrix ($N_{\text{spec}} \times N_w$); $\mathbf{S}_{\text{cell}}$ is the measured mixture spectra ($N_{\text{spec}} \times N_w$); $\mathbf{S}_{\text{comp}}$ is the measured component spectra ($N_{\text{comp}} \times N_w$); $\mathbf{C}_{\text{comp}}$ is the predicted amount of components ($N_{\text{spec}} \times N_{\text{comp}}$); N_{spec} is the total number of spectra measured in the display cell; N_w is the total number of wavenumbers in the Raman spectrum; and N_{comp} is the number of chemical components.

Several quantities are used to judge the model performance:

- (1) The residual matrix $\mathbf{E}$.
- (2) The mean sum of squares of the residuals for one measured display cell spectrum (i) is calculated as:

$$MSS_i = \frac{1}{N_w - N_{\text{comp}}} \sum_{j=1}^{N_w} (\mathbf{E}_{ij})^2 \quad (2)$$

in which j is an index running over the wavenumbers.

- (3) The Percentage of UNexplained information, PUN. For each measured spectrum (i), this is defined as:

$$PUN_i (\%) = \frac{\frac{1}{N_w - N_{\text{comp}}} \sum_{j=1}^{N_w} (\mathbf{E}_{ij})^2}{\frac{1}{N_w} \sum_{j=1}^{N_w} (\mathbf{S}_{\text{cell}_{ij}})^2} \cdot 100 \quad (3)$$

Also, overall PUN numbers for all display cell spectra

(for all i) are calculated that measure the overall performance of the model:

$$PUN (\%) = \frac{\frac{1}{N_w - N_{\text{comp}}} \sum_{i=1}^{N_{\text{spec}}} \sum_{j=1}^{N_w} (\mathbf{E}_{ij})^2}{\frac{1}{N_w} \sum_{i=1}^{N_{\text{spec}}} \sum_{j=1}^{N_w} (\mathbf{S}_{\text{cell}_{ij}})^2} \cdot 100 \quad (4)$$

The factor $N_w - N_{\text{comp}}$ in Eqs. 2–4 is used because a measured spectrum is modeled as the sum of the component spectra. Therefore, N_{comp} degrees of freedom are lost.

The mean sum of squares of the residuals measures the absolute modeling error, while the PUN number measures the relative modeling error. From Eqs. 3 and 4 it is clear that the PUN number decreases for a better model that yields smaller residuals. Even for a “perfect” model the lower limit of the PUN number would not be zero, but it is equal to the ratio of the spectral noise relative to the analytical signal. If the analytical signal is very small it is important to realize that the PUN number will approach 100%.

The PUN numbers and MSS_i supply an error measure for the *whole* selected wavenumber range that is used for modeling. These numbers represent a global error measure and do not give information concerning at which wavenumbers the model fails. Inspection of the residual matrix supplies that information. Also, the shape of the residual curve is important. From the shape it can, for example, be seen whether shifts between the component and the display cell spectra exist. In that case the residual curve looks like the first derivative of the original spectrum. When there is a slight difference between the width of a band in the component spectra and a band in the measured cell spectra a second-derivative shape appears in the residual curve.

To get a better estimate of the shape of the residual curve it is proposed to use the *averaged residual curve*, which is calculated as:

$$\bar{e}_j = \frac{1}{N_{\text{spec}}} \sum_{i=1}^{N_{\text{spec}}} E_{ij} \quad (5)$$

For each wavenumber (j) the average residual over all spectra is calculated. This average residual curve is a tool to find overall small modeling errors that would otherwise be undetected. It allows detection of wavenumber ranges where the data model fails.

Used Preprocessing Methods. Several preprocessing methods are used for correcting the measured Raman spectra: cosmic spike removal (SPIKE), removal of baseline and fluorescence signal (BASECOR), alignment of measured display cell spectra (ALIGN), and an additional (small) shifting of each component spectrum (SHIFT) with respect to *all* display cell spectra.

SPIKE. Cosmic spikes are removed using a moving median filter with window width of 5 points.¹⁸ Parts of the spectra that contain bands are excluded from this correction, because the median filter also has a small smoothing effect on the measured spectra. This smoothing effect is undesirable for spectra having sharp bands. The spectra after spike removal were inspected and no spikes were left.

BASECOR. Fluorescence expresses itself as a slow

FIG. 1. Scheme explaining ALIGN. The solid line shows the measured display cell spectrum with the highest band intensity at LC position, while the dashed lines show some other measured display cell spectra. Spectra 1 and 2 are moved to the right and 4 is moved to the left.

broad band-like phenomenon underlying the Raman spectrum. This phenomenon and the instrumental baseline variations are modeled as a sixth-order polynomial. This polynomial is estimated for every spectrum separately. Only parts of the spectrum without bands are used. Correction consists of subtracting the estimated baseline from the measured spectra.

ALIGN. Aligning is performed on all measured display cell spectra. Inspection of the display cell spectra showed that they are not completely aligned. The isolated bands in the spectra are not at exactly the same position. The aligning procedure corrects this.

An isolated LC band (located approximately at 2227 cm^{-1}) is selected for the aligning. This band is suitable because it is characteristic only for the cyano-functionality in the LC material. By checking the pure compounds spectra (see Fig. 4B below) it was verified visually that other components do not disturb this band.

The display cell spectrum with the maximal band intensity is selected as a reference spectrum. All other display cell spectra are aligned by placing the band maximum of the LC band exactly on the same position as in the reference spectrum. A schematic picture of the ALIGN procedure is shown in Fig. 1. All display cell spectra are aligned using an equidistant wavelength base. Note that using one band in the alignment procedure allows only for the correction of linear shifts.

To improve the accuracy of the alignment procedure a parabola is fitted to the band maximum and the two neighboring data points. The maximum of the parabola is taken as the band position. To put the band of the cell spectra on exactly the same position as the reference spectrum band, interpolation between the original data points is needed. A cubic spline interpolation is used to do this.

SHIFT. The shift procedure is performed only on component spectra. A more careful look at the relationship between component and display cell spectra (in the region chosen for modeling) showed that display cell spectra are not a linear combination of component spectra

FIG. 2. Normalized measured display cell spectra (solid) and component spectra: LC material (dashed), Stilbene (dotted), and Iboma (dashed-dotted) after SPIKE and BASECOR for the AIR set. The band at $\sim 1635\text{ cm}^{-1}$ of the display cell spectra cannot be explained by the component spectra. The Stilbene and Iboma spectra are shifted to the left and the LC spectrum is shifted slightly to the right (see Table I, spike, basecor, and shift columns).

(Fig. 2). This is caused by shifts of the component spectra. These shifts of the component spectra are corrected by using a modified simplex¹⁹ optimization in which the shift of the three components is adapted so that the *overall* sum of squares of the residuals (matrix **E**) is minimized. The optimization is done with respect to all the cell spectra together. In that way some protection against over-fitting the data is achieved. To actually shift a component spectrum a cubic spline interpolation is used.

Summarizing, both ALIGN and SHIFT correct for shifts in measurements. In the ALIGN procedure every display cell spectrum is corrected separately and independently with respect to the reference spectrum. The SHIFT procedure is done only on the component spectra. The component spectra are shifted with respect to the whole set of measured display cell spectra.

EXPERIMENTAL

The Paintable Display Cell. A mixture of two monomers, stilbene dimethacrylate (Stilbene) and isobornyl-methacrylate (Iboma), and the LC material is deposited on a thin glass substrate ($170\text{ }\mu\text{m}$). To obtain a display cell, first the walls are made by using a mask. The polymerization of Iboma and Stilbene is initiated by UV irradiation ($360\text{--}400\text{ nm}$, 2 min curing). After formation of the walls the mask is removed and a second UV irradiation ($320\text{--}360\text{ nm}$, 30 min curing) is used, now to form the top layer of the display cell by stratification. Finally, the whole process results in the formation of polymer cells filled with LC material. Each display cell consists of polymer walls formed in the first step and the polymer lid (top layer) formed in the second step. The LC cell is $500 \times 500\text{ }\mu\text{m}$ squared and $20\text{ }\mu\text{m}$ deep. Figure 3A shows a scheme of a cross-section of an LC cell (pixel). The results are discussed for the center layer and Fig. 3B shows the scheme of that layer. More details

FIG. 3. (A) Scheme of the cross-section of the display-cell. (B) Scheme of the center layer in the LC cell. The black spots represent the measurement positions.

about the production of the material can be in found in Penterman et al.¹⁶

Raman Measurements. Two sets of measurements were done. (1) AIR set, using an Olympus 100× long working distance NA = 0.8 objective; and (2) OIL set, using a Zeiss 100× long working distance NA = 1.3 oil immersion objective. The Raman instrument used in both setups was a standard Jobin Yvon LabRam set up for high confocality. An 1800 lines/mm grating was used. For the AIR set the laser excitation wavelength used was 632.8 nm and the ambient temperature was not controlled. The measurements in depth were started from the top (polymer side) of the display cell. For the OIL set the excitation wavelength was 514.5 nm. In that way higher spatial resolution in depth is expected due to improved diffraction limited spot size. Contrary to the AIR set, the depth measurements started from the glass side of the display cell and the room temperature was stabilized within 0.5 °C.

In both cases, the depth at which the spectrum with highest intensity is measured is taken as the middle of the cell (z-position (depth) = 0). For the AIR set, measurements are done every 0.5 μm, while for the OIL set the target step size was 1 μm. The total measurement range was 40 μm. More details about production of the LC cell and Raman measurements on the cell can be found in Mank et al.²⁰

Description of Data Sets. The spectra of all three components are measured (the Stilbene and Iboma homopolymers and the LC material) and used for analyzing the spectra of the AIR and OIL set. Note that the measured component spectra cannot be turned into molar spectra because the molar mass and density of the polymers are not known. Therefore, it is not possible to calculate absolute concentration profiles for the components.

FIG. 4. (A) Some of the measured display cell spectra. (B) Normalized spectra of LC material (blue), Stilbene (red), and Iboma (green).

For this reason the contour plots of the components (Figs. 5, 7, and 8) are scaled between the lowest and highest amount of the component plotted. For each plot the red color corresponds to the highest amount and the blue color to the lowest amount of the component (Fig. 3B, color bar).

RESULTS AND DISCUSSION

Exploratory Analysis. Normalized† Raman spectra of the three components are shown in Fig. 4B. Band overlap of the component spectra can be seen in all important wavelength ranges. It appears that the Iboma polymer has two bands at around 1460 and 1727 cm⁻¹ that are almost free of interference from the other two components. Still, the real measured intensity of these two bands is extremely small and is therefore easily obscured by the tails of neighboring bands of LC material and Stilbene. This makes the quantification of the amount of Iboma difficult. For the LC material one clearly separated band can be found at around 2227 cm⁻¹. This band will be used for aligning the display cell spectra (as explained in the Used Preprocessing Methods subsection). Some of the measured display cell spectra are shown in Fig. 4A. The spectra contain spikes, fluorescence, and baseline drift. The LC bands are easily seen, Stilbene bands are already more difficult to discern, and Iboma bands are hardly visible (look in the range 1440–1510 cm⁻¹ and 1710–1750 cm⁻¹). Shifts between these spectra and the component spectra are also present and they are corrected with the SHIFT procedure.

The CLS model¹⁷ (Eq. 1) is used to analyze the spectra of the AIR and the OIL set.

Processing of the AIR set ($N_w = 113$, $N_{\text{spec}} = 664$). All depths and the wavenumber range from 1438 to 1767 cm⁻¹ are selected for modeling. This range is chosen after inspection of the component spectra (Fig. 4B). In that range all components have intense bands. However, there is band overlap. For example, the two bands of Stilbene are overlapping with a band of the LC material. The region above 1767 cm⁻¹ does not seem to contain any im-

† Normalize spectra (s_{norm}): $s_{\text{norm}} = s/\|s\|$, s is one spectrum.

TABLE I. Results for the AIR set. *PUN* = Percentage unexplained spectral variation (see Eq. 2). Shifts of component LC material, Iboma, and Stilbene spectrum in nanometers after optimization.

Preprocessing:	none	spike, basecor	spike, basecor, shift	spike, basecor, align	spike, basecor, align, shift
<i>PUN</i> (%)	23.51	8.71	0.39	1.30	0.30
LC material <i>shift</i> (nm) ^a	—	—	−0.11	—	0.014
Iboma <i>shift</i> (nm)	—	—	0.27	—	−0.48
Stilbene <i>shift</i> (nm)	—	—	0.39	—	0.51

^a Shifts in the tables are given in nm, because ALIGN and SHIFT procedures are performed on *equidistant wavelength* base. Figures are plotted on wavenumber scale; in that way two sets can be compared.

portant information about polymers. The LC band at 2227 cm^{−1} is used for aligning the mixture spectra with the LC component spectrum of the LC material. The LC spectrum dominates the mixture spectra and the chosen part for modeling gives good results in predicting the amount of LC material.

As already mentioned, the spectra are disturbed by spikes and by a drifting spectral baseline (Fig. 4A). Also, the spectra proved to not be fully aligned. Different combinations of preprocessing methods are tried and the figures of merit are calculated in each case (Table I). Using the SPIKE, BASECOR, and ALIGN preprocessing considerably improved the *PUN* (about a factor 18). The SHIFT correction leads to further decrease of the *PUN* number (about a factor 4). Now, 99.7% of the total measured spectral variation is modeled. The shifts of the component spectra that are determined in this way are 0.45, −15.27, and 16.20 cm^{−1} for LC material, Iboma, and Stilbene, respectively (positive shift: spectrum is shifted to the left). The most probable cause for these shifts is that the component spectra and the display cell spectra are collected on different days without performing a wavenumber calibration of the instrument each day. Moreover, the room temperature was not controlled.

Contour plots of the estimated amounts of the components are shown in Fig. 5 for the worst case (no preprocessing) and for the best case (after SPIKE, BASECOR, ALIGN, and SHIFT). The plots in Figs. 5A, 5C, and 5E are made for the worst case, while the plots in Figs. 5B, 5D, and 5F are for the best preprocessing method. The picture for the LC material is almost the same in both cases. The reason is that the LC spectrum is the most dominant spectral component. Preprocessing therefore hardly has any effect on the picture (Figs. 5A and 5B). On the contrary, the polymer images are completely different without (see Figs. 5C and 5E) and with preprocessing (see Figs. 5D and 5F). The results obtained for Iboma and Stilbene without any preprocessing are unrealistic. It appears that Iboma has the highest concentration in the glass substrate, but this obviously cannot be true.

The essential plots needed for the analysis of the modeling error are supplied in Fig. 6. Spectral preprocessing improves the model considerably. This can be seen by comparing the averaged residual curves with and without preprocessing (Fig. 6C). For the best case the curve is mostly close to zero and only around the major band (1600 cm^{−1}) does it differ from zero. Figure 6B shows that absolute residuals are largest at positions where the

FIG. 5. Set AIR: Contour plots of amounts of components for the central layer. (A, B) LC material. (C, D) Stilbene. (E, F) Iboma. (A, C, and E) No preprocessing. (B, D, and F) After SPIKE, BASECOR, ALIGN, and SHIFT.

amount of the major spectral contributor (LC material) is also high. The relative modeling error *in* the display cell is, however, very constant, as is shown by Fig. 6D. This figure also shows where the relative modeling error (*PUN*) is high. It is high outside the display cell itself, viz. in the glass substrate. The reason is that the denominator of the *PUN* number (Eq. 4) decreases. The spectral measurements are done (partially) in glass substrate and therefore the analytical signal is getting smaller. Additionally, the glass also causes small modeling errors. This error increases the numerator of the *PUN*.

The influence of *not* using a SHIFT correction can be seen in Fig. 7A. Compared to Fig. 5D the Stilbene profile is blurred. The average residual curves with and without shift correction (Fig. 7E) explain this. The spectral residuals without SHIFT correction (black line) are clearly higher. The pattern of these residuals is also informative. The residuals clearly show a derivative pattern indicating that a shift exists between component spectra and display

FIG. 6. Set AIR: (A) measured display cell spectra; (B) contour plot of residuals for the best case; (C) (wavenumber) averaged residuals for the worst case (blue) and for the best case (red); (D) contour plots of *PUN* numbers for the best case.

FIG. 7. Set AIR: (A, B) profiles for Stilbene and (C, D) profiles for Iboma. (A, C) Without SHIFT (same wavenumber range used as for Fig. 5). (B, D) All preprocessing methods used, but (slightly) different wavenumber range (1500–1767 cm^{-1}) is used. (E) (Wavenumber) averaged residuals for the best case (red) and for the case without SHIFT (black). One of the measured display cell spectra (blue).

cell spectra. In order to see this derivative pattern as a reference the spectral shape of the measured spectrum is plotted (Fig. 7E).

Even for the best preprocessing some shape in the residuals is still left. The remaining shape is similar to a second-order derivative under LC material band (Fig. 7E). This indicates that a small difference in band width between component spectra and mixture spectra exists.

Figures 7B and 7D also show the effect of slightly changing the wavenumber range used for modeling. The total picture is changed. In the shown case, the modeling range is 1500–1767 cm^{-1} . In this way the Iboma band in the range 1438–1500 cm^{-1} is excluded (Fig. 4B) and as a consequence the Iboma profile is severely affected. Again, it appears that the higher concentration of Iboma is at the bottom of the cell and this is obviously wrong.

Processing of the OIL Set ($N_w = 224$, $N_{\text{spec}} = 1092$). To make results comparable with the AIR set the same wavenumber range is selected for modeling (1438 to 1767 cm^{-1}). All preprocessing methods are again considered. Table II shows the results. The lowest PUN number (0.43) is reached without any preprocessing. This value is much lower than the same value for the AIR set, indicating that measurements are better. Indeed, fewer

TABLE II. Results for the OIL set. PUN = Percentage unexplained spectral variation (see Eq. 2). Shifts of component LC material, Iboma, and Stilbene spectrum in nanometers after optimization.

Preprocessing:	none	spike, basecor	spike, basecor, shift	spike, basecor, align	spike, basecor, align, shift
PUN (%)	0.43	0.52	0.49	1.47	0.74
LC material <i>shift</i> (nm) ^a	—	—	0.005	—	−0.03
Iboma <i>shift</i> (nm)	—	—	0.50	—	0.43
Stilbene <i>shift</i> (nm)	—	—	−0.07	—	−0.08

^a Shifts in the tables are given in nm, because ALIGN and SHIFT procedure are performed on *equidistant wavelength* base. Figures are plotted on wavenumber scale; in that way two sets can be compared.

FIG. 8. Set OIL: contour plots for amounts of components for the central layer. (A, B) LC material. (C, D) Stilbene. (E, F) Iboma. (A, C, and E) No preprocessing. (B, D, and F) After SPIKE, BASECOR, and SHIFT.

spikes and a less pronounced spectral drift are found in the measurements. However, the extracted Iboma profile remains unrealistic (Fig. 8E). Again, a large amount of Iboma is found in the glass. For the OIL set the glass is on the top of the figures because measurements are started from the glass side.

As for the AIR set, the pictures of the LC material do not depend on the type of preprocessing used. Contrary to the AIR set, however, the Stilbene profile is stable and not much affected by preprocessing. For the Iboma profile the selected preprocessing method, however, is critical.

Drift correction improves the Iboma picture considerably, although the PUN number increases (0.52). An explanation can be found by looking at the wavenumber averaged residual curve in Fig. 9C. On average, higher residuals are found for wavenumbers below 1500 cm^{-1} . This is exactly the range (1440–1500 cm^{-1}) where the major Iboma band is present (Fig. 4B). Without baseline correction, the uncorrected baseline of the raw spectra masks the presence of the Iboma band. This is a good

FIG. 9. Set OIL: (A) measured display cell spectra; (B) contour plot of residuals for the best case; (C) (wavenumber) averaged residuals for the worst case (blue), after SPIKE and BASECOR (green), and for the best case SPIKE, BASECOR, and SHIFT (red); (D) contour plots of PUN numbers for the best case.

example to show that the average residuals curve supplies additional information about the fit quality. Overall, the fit may get slightly worse (PUN number), but local improvements might lead to a better picture of composition.

Adding more preprocessing leads to only slightly better results. With SHIFT correction the residual patterns hardly change (Fig. 9C). Also, the retrieved shifts for the LC material and Stilbene are very small (compare these with shifts for the AIR set). Figure 8F shows the Iboma profile after SPIKE, BASECOR, and SHIFT. This picture is acceptable.

Aligning the display cell spectra on the LC band in this case does not improve the model fit, as can be seen by the increase in PUN number to 1.47% (Table II). Inspection of the spectra after aligning showed that near perfect alignment is achieved at the LC band position, but in the modeling range 1438–1767 cm^{-1} , alignment makes things worse. There are two possible explanations. It might be that for this data the spectral shift is also nonlinear. The ALIGN method used here cannot correct for this, because only one isolated LC band is found. Another explanation could be that the spectra are already very well aligned. The ALIGN procedure then starts to overcorrect and aligns on the noise present at the LC band position. Each spectrum would be shifted slightly by a random shift. This increases residual errors.

For each set the type of preprocessing does not affect the picture of the LC material (compare Fig. 5A with Fig. 5B and Fig. 8A with Fig. 8B). This means that differences in the picture for LC between the OIL and AIR sets are only caused by the way the measurements are performed. The objective used is the main difference between the two sets of measurements. The LC picture of the AIR set (Fig. 5A) is more blurred compared to the LC picture of the OIL set (Fig. 8A). So, very likely the oil immersion objective has a better depth resolution. This is in agreement with recent literature^{5,12,13} that indicates that oil immersion objectives give much better results than metallurgic objectives for measurements in depth.

For both sets of measurements the absolute residuals are highest in the center of the cell (Figs. 5B and 8B), where a lot of LC material is present. The spectral signal there is much higher. Still, the relative residuals (Figs. 5D and 8D) are almost the same for the whole display cell (blue in the middle). The high PUN values at the bottom for the AIR set and also at the top for the OIL set are expected to be due to measurements in the glass substrate. For the OIL set high PUN numbers are also found for the bottom because hardly any spectral signal and only noise is found there.

CONCLUSION

A paintable display cell is characterized with Raman spectroscopy using two different experimental setups. The goal is to obtain the chemical composition of the cell. The measured display cell spectra are analyzed using a combination of classical least square (CLS) modeling and spectral preprocessing. The focus is on the selection of the best combination of preprocessing methods in order to remove unwanted and unmodeled spectral variations (caused by fluorescence, baseline drift, and instrumental variations) and to obtain the best compositional picture of the display cell.

In the paintable display the liquid crystal (LC) material is the dominant component in the Raman spectrum. Preprocessing of the spectra hardly influences the strong spectral signal of the LC component. Preprocessing is therefore not needed to get a good picture of the LC component distribution in the display cell.

For the set measured with a metallurgic (AIR) objective, the preprocessing (align and shift procedure) is essential for obtaining compositional information about components that have a small contribution to the overall display cell spectrum (Stilbene and Iboma). Even for the measurements under improved experimental conditions and using an oil immersion objective, preprocessing is important. Alignment of measured display cell spectra is, however, no longer needed. This shows that the amount and type of preprocessing varies with the quality of the measurements and that no standardized procedure can be used.

To select the best combination of preprocessing methods it is important to pay attention to residual analysis after preprocessing and CLS modeling of the measured spectra, as well as to look at the feasibility of the resulting compositional profiles. For quantitative purposes the percentage of unexplained information (PUN numbers) is proposed. In general, a preprocessing method that yields a lower PUN number is expected to supply a more reliable compositional picture. However, when differences between PUN numbers are small, a more detailed residual analysis should be performed. The average residual curve is proposed as a tool to inspect the shape and size of residuals. It allows one to check whether or not local modeling errors still exist. In all cases the resulting compositional pictures should be checked for feasibility. Clearly, knowledge about the sample and the way in which measurements are performed is needed to do this.

1. L. Baia, K. Gigant, U. Posset, R. Petry, G. Schottner, W. Kiefer, and J. Popp, *Vib. Spectrosc.* **29**, 245 (2002).
2. L. Baia, K. Gigant, U. Posset, G. Schottner, W. Kiefer, and J. Popp, *Appl. Spectrosc.* **56**, 536 (2002).
3. K. J. Baldwin and D. N. Batchelder, *Appl. Spectrosc.* **55**, 517 (2001).
4. J. L. Bruneel, J. C. Lassegues, and C. Sourisseau, *J. Raman Spectrosc.* **33**, 815 (2002).
5. N. J. Everall, *Appl. Spectrosc.* **54**, 1515 (2000).
6. N. J. Everall, *Appl. Spectrosc.* **54**, 773 (2000).
7. C. A. Froud, I. P. Hayward, and J. Laven, *Appl. Spectrosc.* **57**, 1468 (2003).
8. S. Michielsen, *J. Appl. Polym. Sci.* **81**, 1662 (2001).
9. H. Reinecke, S. J. Spells, J. Sacristan, J. Yarwood, and C. Mijangos, *Appl. Spectrosc.* **55**, 1660 (2001).
10. J. Sacristan, H. Reinecke, C. Mijangos, S. Spells, and J. Yarwood, *Macromol. Chem. Phys.* **203**, 678 (2002).
11. Ch. Sammon, S. Hajatdoost, P. Eaton, C. Mura, and J. Yarwood, *Macromol. Symp.* **141**, 247 (1999).
12. J. Vyorykka, M. Halttunen, H. Iitti, J. Tenhunen, T. Vuorinen, and P. Stenius, *Appl. Spectrosc.* **56**, 776 (2002).
13. J. Vyorykka, J. Paaso, M. Tenhunen, J. Tenhunen, H. Iitti, T. Vuorinen, and P. Stenius, *Appl. Spectrosc.* **57**, 1123 (2003).
14. M. J. Pelletier, *Appl. Spectrosc.* **57**, 20A (2003).
15. S. Morozumi, "Materials and assembling Process of LCDs", in *Liquid Crystals: Application and Uses*, B. Bahadur, Ed. (World Scientific, London, 1990), vol. 1, p. 181.
16. R. Penterman, S. I. Klink, H. de Koning, G. Nisato, and D. J. Broer, *Nature (London)* **417**, 55 (2002).
17. H. Martens and T. Naes, *Multivariate Calibration* (John Wiley and Sons, New York, 1989).
18. D. Zhang and D. Ben-Amotz, *Appl. Spectrosc.* **56**, 91 (2002).
19. J. A. Nelder and R. Mead, *Comp. J.* **7**, 308 (1965).
20. A. J. G. Mank, I. Vorstenbosch, R. Penterman, J. P. A. Vogels, S. I. Klink, and D. J. Broer, *Appl. Spectrosc.*, paper to be submitted (2005).