



Positive and Nondestructive Identification of Acrylic-Based Coatings

Using Partial Least Squares Discriminant Analysis with the Agilent 4300 Handheld FTIR

Application Note

Materials Testing and Research

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Introduction

Acrylic-based coatings are produced in formulations to suit all the major markets within the coatings industry. Industrial, decorative, printing inks, powder, and wall coverings are some of the market areas where acrylic-based coatings are widely used. Water emulsion and film-forming acrylic-based coatings are of particular importance due to their relative high performance and extremely low volatile organic compound (VOC) emissions.

To ensure performance and longevity, it is critical to properly apply the correct acrylic coating in the substrate. Equally important is the ability to assess changes in the chemical composition of the coating under actual use. For this reason, a portable analyzer is of great interest to engineers who are responsible for ensuring that coatings meet their performance claims.



Agilent Technologies

In this application note, we used the Agilent 4300 Handheld FTIR (Figure 1) to analyze 14 industrial acrylic coatings that have the same binder type and similar chemical composition. First, we used an extended library method to identify the acrylic coatings. However, the library search method was not sensitive enough to clearly distinguish between similar coatings. To clearly separate these we used a partial least squares discriminant analysis (PLS-DA) multivariate classification method for more sensitive discrimination of the coatings, since they have similar binder types. We combined the PLS-DA algorithm with unique Agilent MicroLab PC Component Reporting to provide precise identification of each acrylic coating.



Figure 1. Agilent 4300 Handheld FTIR spectrometer with external reflectance (diffuse and specular) and internal reflectance (ATR) sampling interfaces. Interfaces can be changed in seconds, with no realignment required.

Experimental

The acrylic coatings were individually spray-coated onto separate 4 × 9 inch Q panels (~10 × 23 cm), and 10 spectra were collected randomly from each panel. Acquisition of multiple spectra across the coating was important to account for paint inhomogeneity and paint application variance. To develop the library for each acrylic coating, eight of these randomly collected spectra were used to populate the library, and the remaining two spectra were used as the test unknowns.

The 4300 Handheld FTIR spectrometer, coupled with a diffuse reflectance interface, was used to measure the 14 proprietary acrylic coatings (labeled A to N) using spectral acquisition conditions of 128 co-added interferograms at 8 cm⁻¹ resolution from 5,200 to 650 cm⁻¹. The total spectral measurement time was less than 40 seconds per spectrum. Similar measurements were collected using the 4300 FTIR equipped with the attenuated total reflectance (ATR) sample interface for comparison.

Library searches were carried out using the software similarity match algorithm of the 4300 FTIR MicroLab PC. PLS-DA calibration models were developed using eight spectra for each acrylic coating out of 10 collected spectra. The two spectra that were not included in building the PLS-DA model were used as test spectra to assess the final MicroLab method for coating identification. For each calibration model development, spectra were preprocessed using mean centering, multiplicative scatter correction, and a nine-point Savitzky-Golay first derivative.

Results and Discussion

The diffuse reflectance spectra of 14 acrylic coatings were used to build the library of coatings, and also to perform PLS-DA classification. Diffuse reflectance measurement is preferred since more spectral information related to binder, pigment, and additives is obtained as a result of the higher penetration of the IR beam into the coating, as compared to surface-sensitive ATR measurement (Figure 2). In addition, diffuse reflectance measurement of coatings is nondestructive and highly reproducible, compared to ATR measurement.

The library method for coating identification was developed using a similarity search algorithm in the MicroLab PC software. The library search results for the test spectra for each coating are shown in Table 1. The library was constructed by multiple entries of spectra per coating. The primary hit group (1st, best matching, A) and the secondary hit group (2nd, best matching, E) are listed in the library hit column. Figure 3 displays the advantages of having multiple entries where the hit quality value for the primary group and the secondary group ranges from 0.99986 to 0.99952 and 0.99134 to 0.99045, respectively.

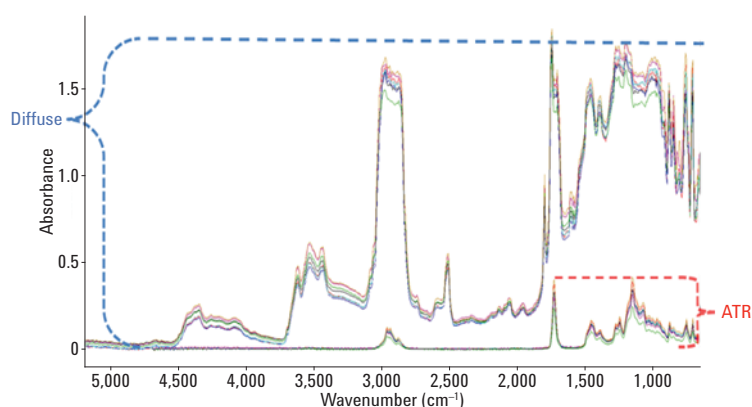


Figure 2. ATR and diffuse reflectance spectra of the same acrylic-based paint A. The diffuse reflectance spectra provide more information from overall stronger absorbance bands, as well as the ability to record bands that are too weak to observe by ATR. The maximum absorbance for the diffuse reflectance and ATR are indicated by the blue and red lines, respectively.

Table 1. Fourteen Acrylic-based Coatings, A to N, and Their Primary and Secondary Hit Sets

Coating	ID	Library hit	Coating	ID	Library hit
A	✓	1st = A, 2nd = E	H	✓	1st = H, 2nd = D
B	✓	1st = B, 2nd = A spectra 8, C	I	✓	1st = I, 2nd = F
C	✓	1st = C, 2nd = A spectra 8, E	J	✓	1st = J, 2nd = D
D	✓	1st = D, 2nd = J	K	✓	1st = K, 2nd = I
E	✓	1st = E, 2nd = A	L	✓	1st = L, 2nd = C
F	✓	1st = F, 2nd = I	M	✓	1st = M, 2nd = A
G	✓	1st = G, 2nd = A	N	✓	1st = N, 2nd = G

Note that a green tick was attributed only if both test spectra gave correct positive identification of coating type. For coatings B and C, a single spectrum (A, spectra 8) separated the groups.

The individual spectral primary hit quality value in all cases was better than >0.998 for both test spectra when checked against all 14 acrylic-based coatings in the library. The top eight library search results for two test spectra for each coating formulation A to N indicated the correct match. In all cases, the next best hit (that is, the 9th ranked hit) was not the correct coating, and the hit quality value ranged from 0.892 to 0.997. In some cases, the secondary hit quality value was as high as 0.997, indicating that the library search result may not be sufficient for the proper identification of the coatings with high confidence, especially when the hit quality values differ very slightly between the correct and incorrect match-coating results. Therefore, for the coatings with similar chemical formulations, a more rigorous statistical analysis method is needed to gain confidence on identification of the correct coating.

Multivariate discriminant analysis techniques, which capture more spectral variance than library search algorithms, are needed to provide confidence on coating identification of similar formulations. Multivariate analysis methods (MVA) are used both to discriminate (qualitative analysis), and to measure the extent of processes (quantitative analysis) such as degree of cure, days in a weatherometer, or even amount of trapped solvent remaining in an analysis of coating-plus-mixture ratios.

We have examined both the PCA and PLS-DA approaches and, though both are effective, we implemented the latter method in the 4300 FTIR MicroLab PC software. PLS-DA is considered a more sensitive discriminant analysis technique compared to PCA when separating spectra that are nearly identical. PLS-DA is a supervised classification technique where the analyst assigns an arbitrary membership value to each group of spectra, which are used for classification. Once values are assigned to define a class, the calibration model is developed in a similar manner to building a PLS quantitative calibration model. Finally, after a calibration plot is obtained, a threshold y-value is chosen from the PLS plot to classify the groups based on their distribution profile. The calibrated classification model can then predict the identity of the unknown samples relative to one of the defined classes.

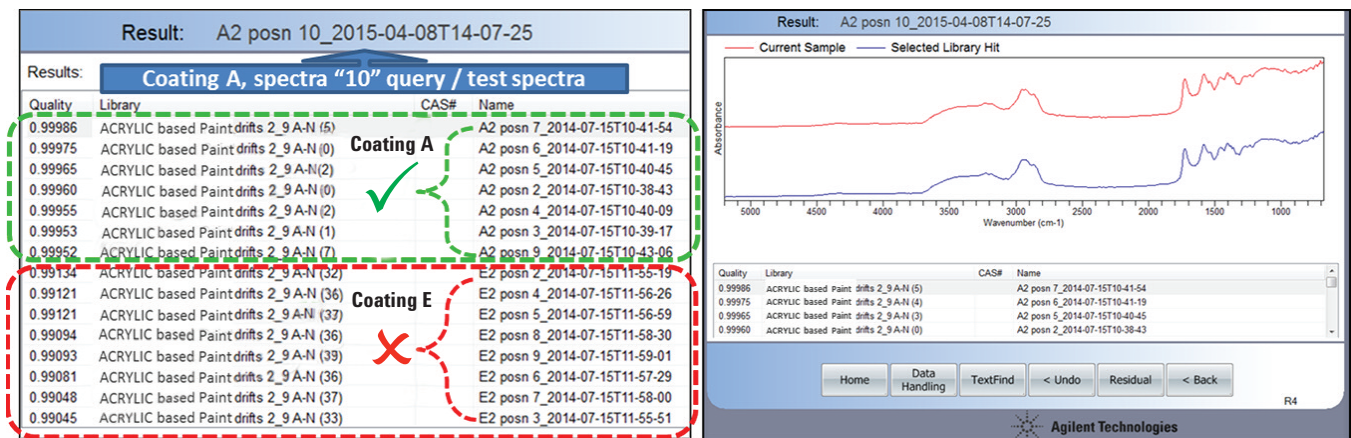


Figure 3. Library search results with hit quality value of acrylic coating type A test spectra (left); spectrum of test sample (red) and best match from the spectral library (blue) (right). Note: A2 = coating A by diffuse and posn. 10 = 10th position on Q-panel.

Eight spectra, collected from eight different spots of the painted Q panel, were used to represent the individual acrylic-based coatings while building the PLS-DA models. Five PLS-DA calibration models were needed to obtain proper classification between the 14 coatings. The calibration models were developed sequentially to have well-defined separation between the groups of spectra for each coating. The calibration parameters obtained for each calibration model

are shown in Table 2. Based on the visual spectral similarity, the 14 acrylic coatings were first divided into three groups. The first group consisted of spectra representing D, H, J, and M coatings, the second group of spectra of A, B, C, E, F, G, I, K, and L coatings, and third group of spectra of coating N (Figure 4). As an example (Figure 4), the first calibration model was able to classify coating N from the rest of coatings.

Table 2. PLS-DA Calibration Model Parameters

Calibration model	R ²	No. of factors required	Arbitrary value assigned for each coating group	Coatings separated
1	0.984	6	[D, H, J, M] = "0" [A, B, C, E, F, G, I, K, L] = "1" [N] = "2"	N
2	0.997	3	D = "0", H = "1", J = "2", M = "3"	D, H, J, and M
3	0.994	5	[A, B, C, E] = "0" [F, G, I, K, L] = "1"	[A, B, C, E] and [F, G, I, K, L]
4	0.999	3	A = "0", B = "1", C = "2", E = "3"	A, B, C, and E
5	0.998	4	F = "0", G = "1", I = "2", K = "3", L = "4"	F, G, I, K, and L

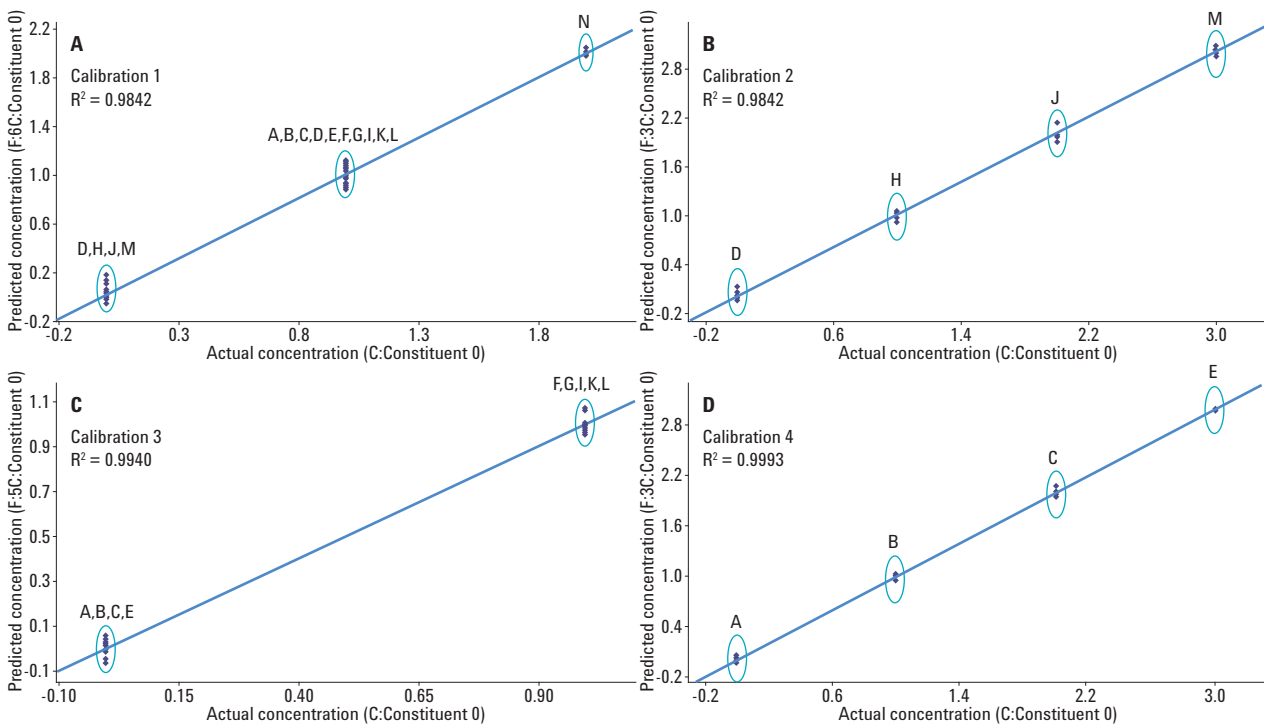


Figure 4. Four PLS-DA calibration plots (the fifth calibration plot looked similar to Calibration 4).

The second calibration plot was able to classify between four coatings D, H, J, and M. The third calibration plot classified between two groups, [A, B, C, E] and [F, G, I, K, L]. The fourth calibration plot classified between four coatings A, B, C, and E. Similarly, the fifth calibration plot classified between the remaining five coatings F, G, I, K, and L. Therefore, with five separate PLS-DA calibration plots, the classification of all 14 acrylic-based coatings was successfully obtained. However, and most importantly, the next step combined all calibration models into one method for the identification of an unknown sample.

The innovative Agilent MicroLab PC Software, with a unique Component Reporting feature, is able to incorporate five calibration models into one single method. The final method can positively identify all 14 acrylic coating test spectra successfully. In Component Reporting, the threshold y-value from each calibration plot was used to set the logic so that the appropriate calibration models were executed as necessary to predict the unknown spectra (Figure 5). Several conditions can be placed on each component using logic statements. For example, coating N uses the Mahalanobis distance (MDistance) to determine if the sample is statistically within the calibration set. Component Reporting allows several pieces of information taken from the five distinct calibrations to be combined to yield a single informative result (Figure 6). In effect, the specialty knowledge usually required to differentiate closely related coatings can be built into the method, making an advanced analysis automatic and field deployable.

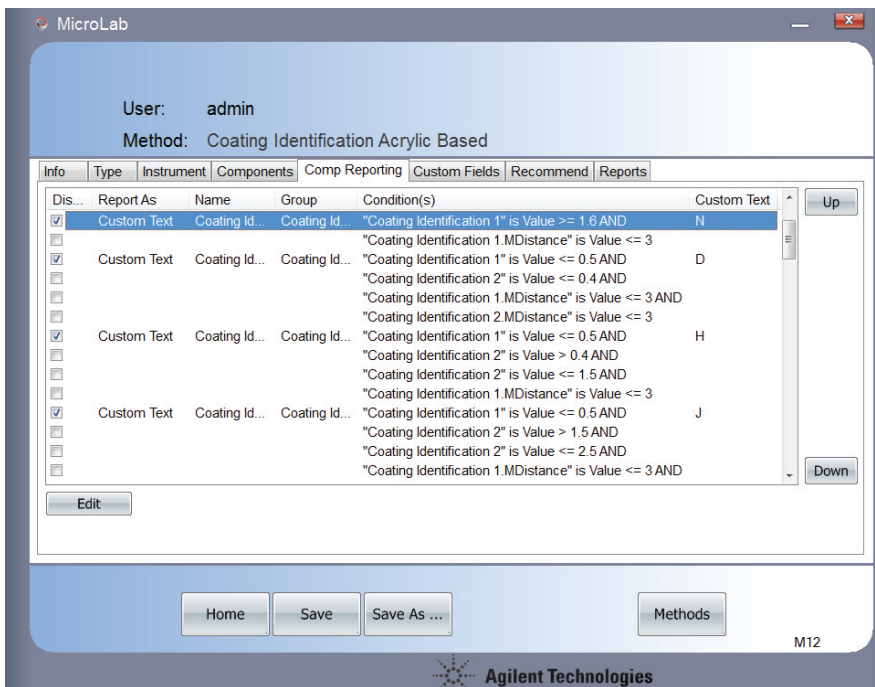


Figure 5. The Component Reporting feature of Agilent MicroLab PC Software allows conditions to be set to select the correct calibration model, and to choose the component to be reported in the final result.

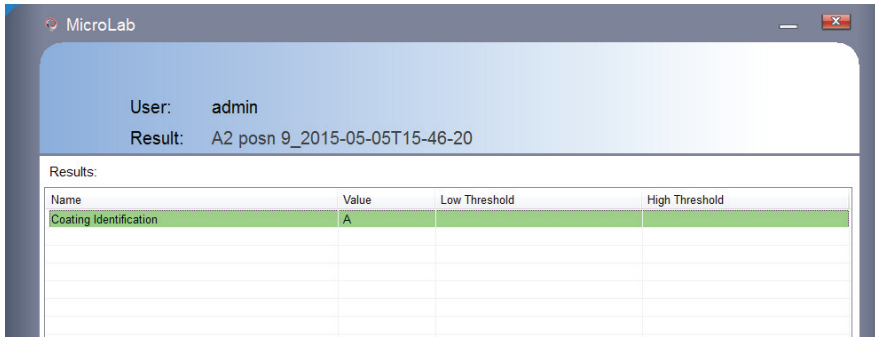


Figure 6. Final result display screen where the coating spectrum is identified as coating A.

Conclusions

The identification of specific acrylic coatings was performed using two different methods of discrimination. A similarity match algorithm was used to correctly identify specific acrylic coatings. Although they were correctly identified, the limited statistical basis of the library search did not provide the means to positively identify closely related coatings. Discriminant techniques, such as PLS-DA are statistically based, providing greater confidence in the match found. A series of PLS-DA calibration models were combined into one method using the Agilent 4300 MicroLab PC Component Reporting capability. This method quickly and successfully differentiated and identified these very similar coatings. The PLS-DA methods provide an extra layer of security and confidence in the identification of closely matched acrylic coatings.

We have shown that the Agilent 4300 Handheld FTIR, equipped with the diffuse sample interface, is well suited for positive material identification of coatings. The spectrometer is particularly useful because of its portability and available sample interfaces, which enable the analysis and identification of specific formulations on a coated article regardless of location, size, and shape. Since the spectrometer is taken to the sample, we have a truly nondestructive method for analyzing coatings. In addition, a sample does not need to be excised for measurement in a lab. We have shown that the diffuse reflectance measurement is preferable since more spectral information is gained, and the measurement is truly nondestructive because the coating surface is not marred or stressed in any way during spectral analysis.

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