Determination of cobalt content, solids content, specific gravity and viscosity in paint driers by Vis-NIR spectroscopy

Introduction to paint drier industry

Paint is generally considered as a mixture of pigment, binder, solvent, driers and other additives. Though the basic function of driers is to decrease the drying time after application, it significantly affects the gloss and clarity of paint coatings. There are many end markets for paints and coatings, ranging from home builders to original equipment manufacturers, many of which are subject to regulations that require testing for compliance. Therefore, producers as well as the end user of paints and additives like paint driers need to control the quality regarding the specification of multiple parameters.

The test procedures are specified by ASTM procedures (see additional poster). The determination of all parameters of interest requires four primary methods – balance & oven, titration equipment, a hydrometer and a viscometer. These four independent analysis methods can be replaced by a single measurement using Vis-NIR spectroscopy: the visible range is used for a direct determination of metal-complex and the near-infrared region for the simultaneous quantification of physical and chemical parameters.

Experimental setup – Cobalt content

5 samples of cobalt octoate with different cobalt content (4%, 6%, 8%, 10%, and 12%) were provided by a producer of paint driers. 10 dilutions were prepared by mixing the 5 initial concentrations by different ratios. Thus, the sample amount was increased from 5 to 15 samples. Each sample was acquired in transmission over the full wavelength range (400–2500 nm) using the NIRS XDS RapidLiquid Analyzer (2.921.1410). The samples were placed in quartz glass cuvettes of 1 mm path length (6.7401.200).

The reference values necessary for the determination of a quantitative model for the prediction of the cobalt content were derived by titration using the Cu ISE (AW TI CH1-1160-012014).

Vision, with its Partial Least Squares (PLS) algorithm, was used to develop quantitative prediction models for cobalt content in paint driers. Therefore, absorption bands of the Vis-range (400–780 nm) were chosen. The spectral data were pre-treated using Standard Normal Variate (SNV) to get rid of light scattering effects. Internal cross validation (leave-one-out method) was applied to verify the performance of the derived quantitative model.

Experimental setup – Physical and chemical properties

4 out of the 5 initial samples were provided with their certificate of specifications for solids content, specific gravity and viscosity. Spectral information of the NIR wavelength region (800–2500 nm) and the provided reference values were correlated to develop three quantitative model. The data was pre-treated using a baseline correction at 800 nm.

Determination of cobalt content

The spectral data, pre-treated with SNV, displays a good correlation between the cobalt content and the absolute absorbance value over the full wavelength range (400–2500 nm). The PLS model with 3 factors based on spectral information of the visible range (400–780 nm) leads to excellent results, see **Fig. 1**.

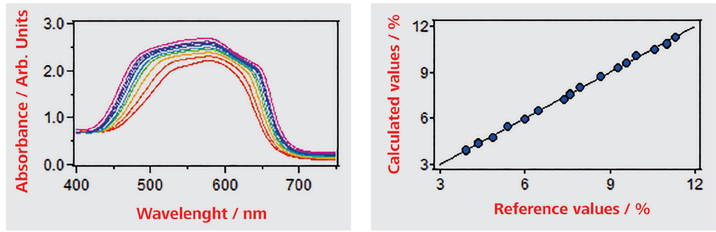

Fig. 1: a) Absorption spectrum of the visible range (400–780 nm) of cobalt octoate with five different cobalt concentrations. b) Correlation of calculated values to reference values as a result of quantitative method development of the cobalt content.

Comparison of results derived from Vis and NIR region

Cobalt octoate is a complex formed by two ethylhexanoate ligands associated to one Co^{2+} ion. In the NIR region, characteristic combination bands can be found of the ligand (NIR active) whereas the bands in the visible range arise due to complexation (Co is NIR inactive; the complex is blue). To verify that the visible range contains the information of interest, the statistical values for three models (Vis, Vis + NIR and NIR) were compared, see **Tab.1**.

	400–780 nm	780–2500 nm	400–2500 nm
R^2	0.999	0.998	0.999
SEC	0.084	0.126	0.096
SECV	0.088	0.132	0.100

Tab. 1: Comparison of results for three quantitative models based on three different wavelength regions

The best statistical values, meaning highest correlation (R^2) and lowest error for calibration (SEC) and validation (SECV), were achieved using the visible range from 400–780 nm. Predicting the cobalt content using the NIR range would be an indirect determination via the ligand and can yield strongly diverging results.

Determination of physical and chemical properties

The NIR wavelength range can be used for the determination of solid content, specific gravity and viscosity of cobalt octoate. **Fig. 2–4** shows the correlation of calculated values to reference values from the developed quantitative methods using the NIR region (800–2500 nm).

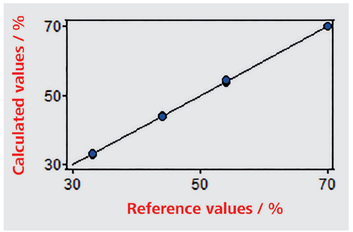

Fig. 2: The provided values for the solids content ranged from 33–67.5%. A PLS model using 3 factors shows a high correlation (R^2 = 0.999, SEC = 0.240%, SECV = 0.285%) between the provided reference values and the calculated values.

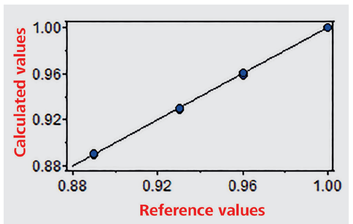

Fig. 3: The provided values for the specific gravity ranged from 0.89–1.00. A PLS model using 3 factors shows a high correlation (R^2 = 0.997, SEC = 0.003, SECV = 0.003) between the provided reference values and the calculated values.

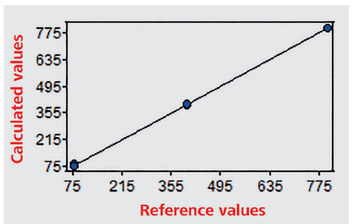

Fig. 4: The provided values for the viscosity ranged from 80–800 mPas. A PLS model using 4 factors shows a high correlation (R^2 = 0.999, SEC = 9.3 mPas, SECV = 10.9 mPas) between the provided reference values and the calculated values.

Conclusion

Paint industry is growing. Vis-NIR spectroscopy has a very high potential in this market segment due to its ability to determine multiple parameters with the same analyzer and on the same time. This analyzer serves the producer and the customer of paints to the same extent for quality control of the raw materials and the final product, respectively.

The visible range (400–780 nm) provides direct prediction results for the cobalt content and can be used to replace the time-consuming and waste-producing wet-chemistry. The NIR region (780–2500 nm) shows excellent results for the simultaneous prediction of three properties (solids content, specific gravity and viscosity). Therefore, Vis-NIR spectroscopy, compared to only NIR spectroscopy, benefits from the extended wavelength range from 400–2500 nm to get all results with higher accuracy and precision.