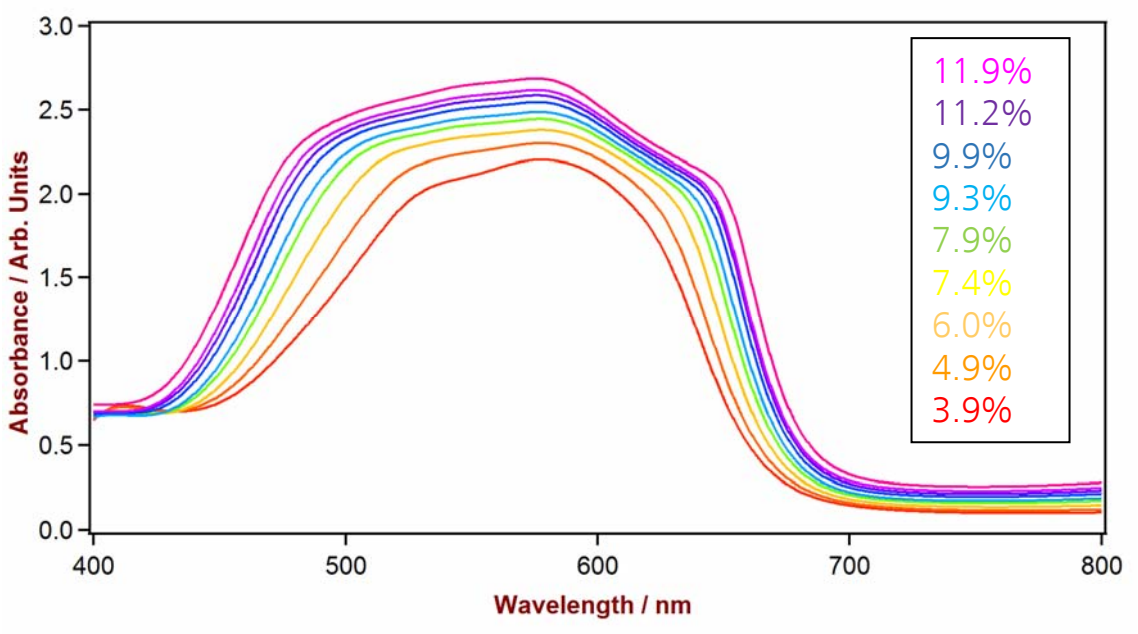
NIR Application Note NIR-33

Cobalt content, solids content, specific gravity, and viscosity in cobalt octoate



This Application Note shows that a Vis-NIR analyzer can simultaneously determine the four most important analytical parameters of paint driers: cobalt and solids content, specific gravity, and viscosity. The visible range correlates proportionally to the metal content; the NIR region gives results on specific gravity, viscosity, and solids content.

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Method description

Introduction

Paint and coatings are generally considered as a mixture of pigments, binders, solvents, and additives, where every component influences significantly the overall end product behavior and performance. Paint driers as one representative of the group of additives do for example decrease the drying time and affect the gloss and clarity of the coating.
Paint and coating products are omnipresent with usage ranging from building construction to original equipment manufacturers. In all application fields customers demand high quality, high-performance products and therefore quality control is a crucial step along the complete production chain, where multiple parameters need to be tested.
In relation with paint driers the parameters of main interest are metal content, solid content, viscosity and specific gravity. All reference test procedures are specified in the ASTM procedures (D2373, D1644, D5125, D2196) which all refer to different analytical instruments: balances & ovens, titrators, hydrometers and viscometers.
Beside these specific ASTM references the general ASTM chapter (D6122) describes near-infrared spectroscopy (NIRS) in combination with Partial Least Squares (PLS) algorithms as a valid complementary analytical technique to evaluate quality control parameters.

This application note presents the potential of Vis-NIR spectroscopy by analyzing a cobalt based paint drier with the help of Metrohm's Vis-NIR spectrometer. In this feasibility study all four parameters or interest are evaluated within one measurement using the visible spectral range for a direct determination of the metal content and the near-infrared region for the simultaneous quantification of the physical and chemical parameters (solid content, viscosity, and specific gravity).

Experimental

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 17 samples. Each sample was acquired in true transmission over the full wavelength range (400 nm – 2500 nm) using a NIRS XDS RapidLiquid Analyzer (Tab.1 / Fig. 1). The samples were placed in sealable quartz glass cuvettes of 1 mm path length to ensure a constant path length and to prevent the samples from evaporating during analysis.

Tab.1: Used equipment

Equipment	Metrohm code
NIRS XDS RapidLiquid Analyzer	2.921.1410
NIRS 12.5 mm quartz cuvette 1 mm	6.7401.200
NIRS Spacer for 12.5 mm cuvettes	6.7403.180
Vision Air 2.0 Software	6.6072.208

Fig. 1: A NIRS XDS Rapid Liquid Analyzer equipped with a NIRS quartz glass cuvette of 1 mm path length was used to record the spectral data.

The reference values necessary for the development of a quantitative model to predict the cobalt content were derived by titration using the Cu ISE (AW TI CH1-1160-012014).
All spectral data were pre-treated using a Standard Normal Variate (SNV) algorithm, which removed light scattering effects. For the development of a quantitative prediction model a Partial Least Squares (PLS) algorithm was applied. Afterwards the model quality was tested using an internal cross validation procedure (leave-one-out method).

Physical and chemical properties

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

Method description

Result

Spectral information

Fig.2 shows the raw data of 17 spectra of cobalt octoate. The baseline shift as a result of scattering effect is clearly visible and has been corrected for the method development by applying a SNV which combines a baseline correction and a scatter correction.

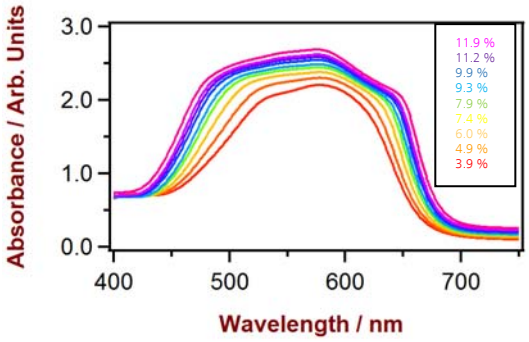

Fig. 2: Non pre-treated spectra of 17 cobalt octoate samples. Only the visible spectral range is displayed. However, with each measurement the full wavelength range (400 – 2500 nm) was collected.

Cobalt content

The spectral data, pre-treated with SNV, displays a good correlation between the cobalt content and the absolute absorbance value. The quality of the figures of merit vary slightly depending on which spectral region is used for the method development. Best results are obtained when only the visible region (400 -800 nm) is taken into account (see **Tab. 2**) with an excellent correlation between reference value and calculate value (see **Fig. 3**).

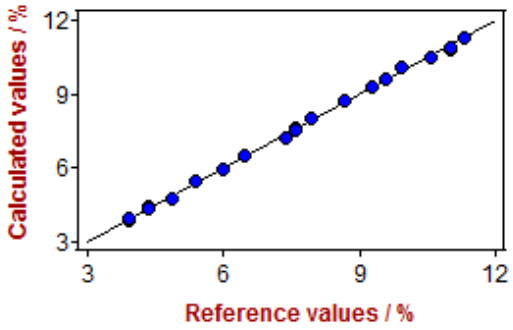

Fig. 3: Correlation plot of the quantitative model displays a good correlation between the calculated values obtained from the absorbance spectra to reference values obtained from the reference method (titration).

Tab. 2: Comparison of results for three quantitative PLS models (each with 3 factors) based on three different wavelength regions.

Wavelength region / nm	400 – 800	800 – 2500	400 – 2500
R^2	0.999	0.998	0.999
SEC / %	0.08	0.13	0.10
SECV / %	0.09	0.13	0.10

Physical and chemical properties

The NIR wavelength range is used to determine the solid content, specific gravity and viscosity of cobalt octoate. **Fig. 4-6** show the correlation of calculated values to reference values from the developed quantitative methods using the full NIR region (800 nm – 2500 nm).

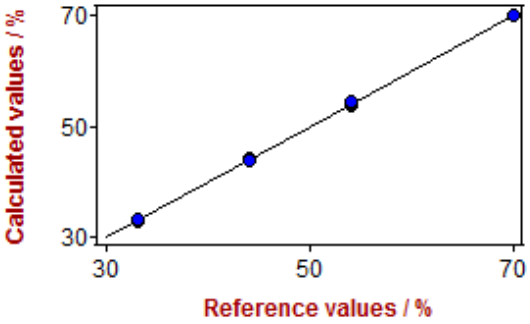

Fig. 4: Correlation of calculated values to reference values as a result of quantitative method development of the solids content.

The provided values for the solids content ranged from 33 % – 67.5 %. A PLS model using 3 factors shows a high correlation between the provided reference values and the calculated values (R^2 = 0.999) and a low SEC = 0.24 % and SECV = 0.29 %.

Method description

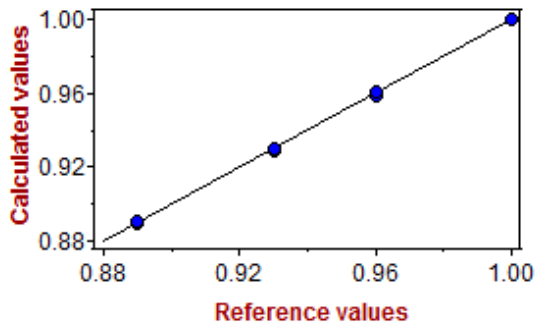

Fig. 5: Correlation of calculated values to reference values as a result of quantitative method development of specific gravity.

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

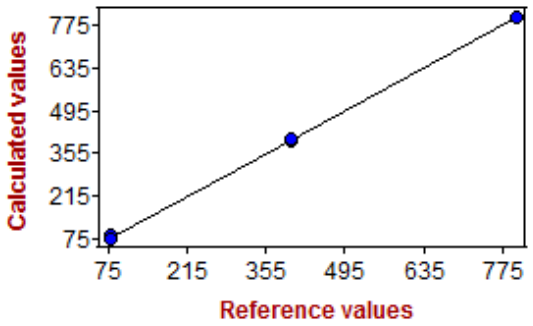

Fig. 6: Correlation of calculated values to reference values as a result of quantitative method development of viscosity.

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

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 at the same time. This analyzer serves the producers and the customers of paints to the same extent for quality control of the raw materials and the final product, respectively.

The visible range (400 nm – 780 nm) provides direct prediction results for the cobalt content. The NIR region (780 nm – 2500 nm) shows good results for the simultaneous prediction of three physical and chemical properties (solids content, specific gravity and viscosity). Therefore, Vis-NIR spectroscopy, compared to only NIR spectroscopy, benefits from the extended wavelength range from 400 nm to 2500 nm to get all results with higher accuracy and precision.

For the parameters solids content, viscosity and specific gravity the model needs to be extended, but the results already give an indication about the feasibility.

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