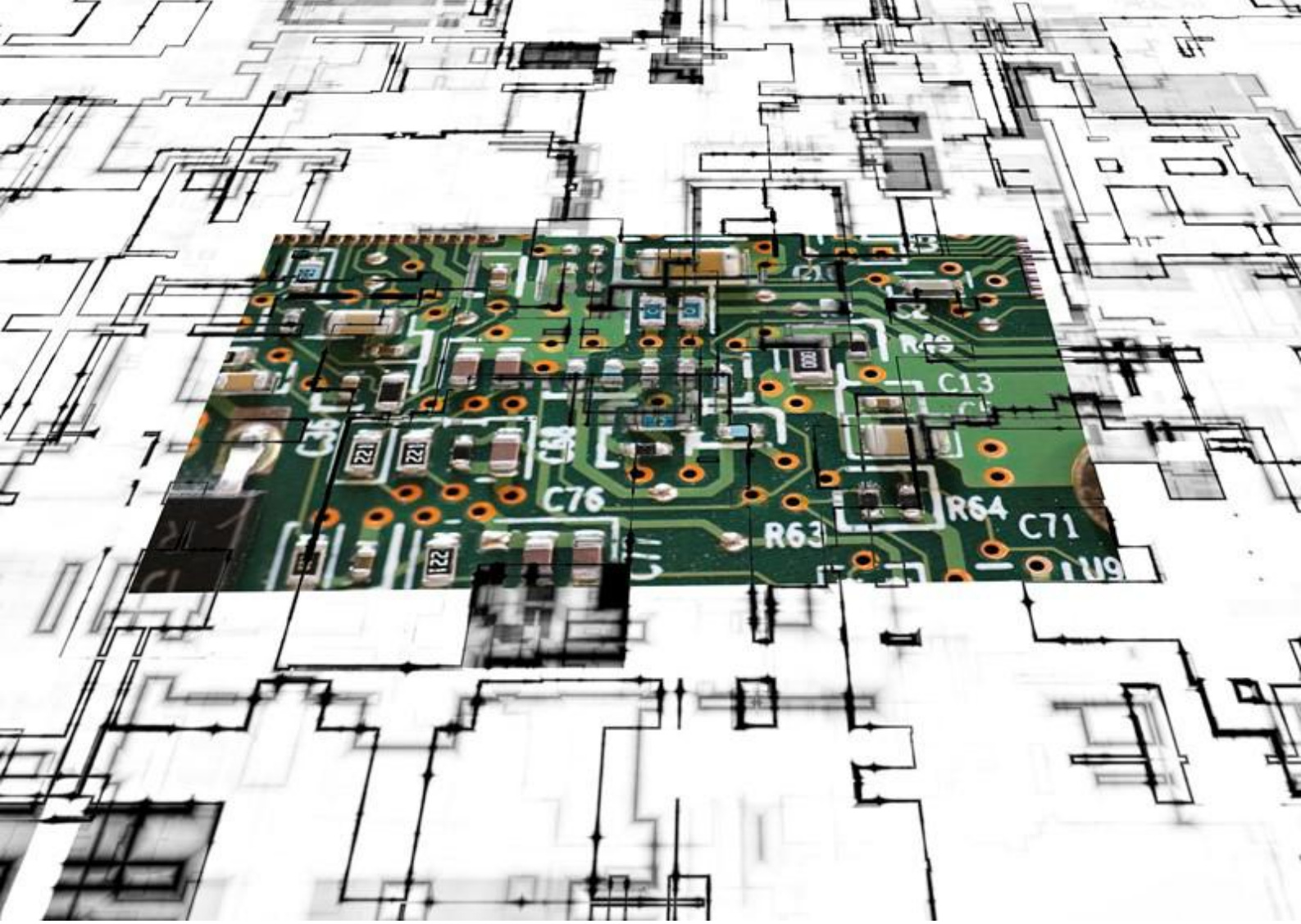

Application Note AN-NIR-091

Quality Control of Mixed Acids

Fast and reliable detection of acetic, hydrofluoric, and nitric acids

Determination of the acid concentration in mixed acid solutions is a critical quality control step for successful etching processes. While primary analytical methods such as thermometric titration are well known, difficulties arise when mixtures of three or more acids need to be analyzed or if the time to result is a critical aspect. This application note discusses an alternative near-infrared (NIR) spectroscopy method that can reliably determine all parameters within a minute, even in complex acid mixtures.

EXPERIMENTAL EQUIPMENT

Mixed acid solutions based on three different acids (AcOH, HF, and HNO_3) were measured in transmission mode with a DS2500 Liquid Analyzer over the full wavelength range (400–2500 nm). Disposable vials with a pathlength of 4 mm were used for convenient and fast measurement. The Metrohm software package Vision Air Complete was used for all data acquisition and prediction model development.

Figure 1. DS2500 Liquid Analyzer and a sample filled in a disposable vial.

Table 1. Hardware and software equipment overview

Equipment	Metrohm number
DS2500 Liquid Analyzer	2.929.0010
DS2500 Holder 4 mm vials	6.7492.010
Disposable vials, 4 mm	6.7402.010
Vision Air 2.0 Complete	6.6072.208

RESULTS

20 measured Vis-NIR spectra (Figure 2) were used to create a prediction model for quantification of the different acid concentrations (AcOH, HF, and HNO_3). The quality of the prediction models was evaluated using correlation diagrams, which show a very high correlation between Vis-NIR prediction and primary method values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis.

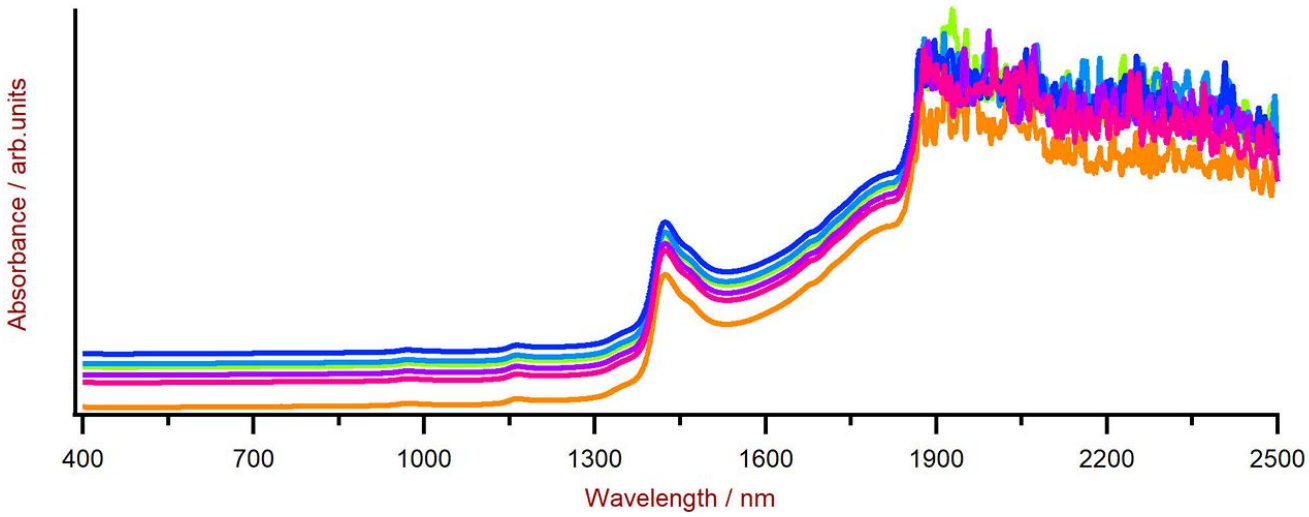

Figure 2. Vis-NIR spectra of mixed acids solutions with varying acid content measured on a DS2500 Liquid Analyzer. For display reasons a spectra offset was applied.

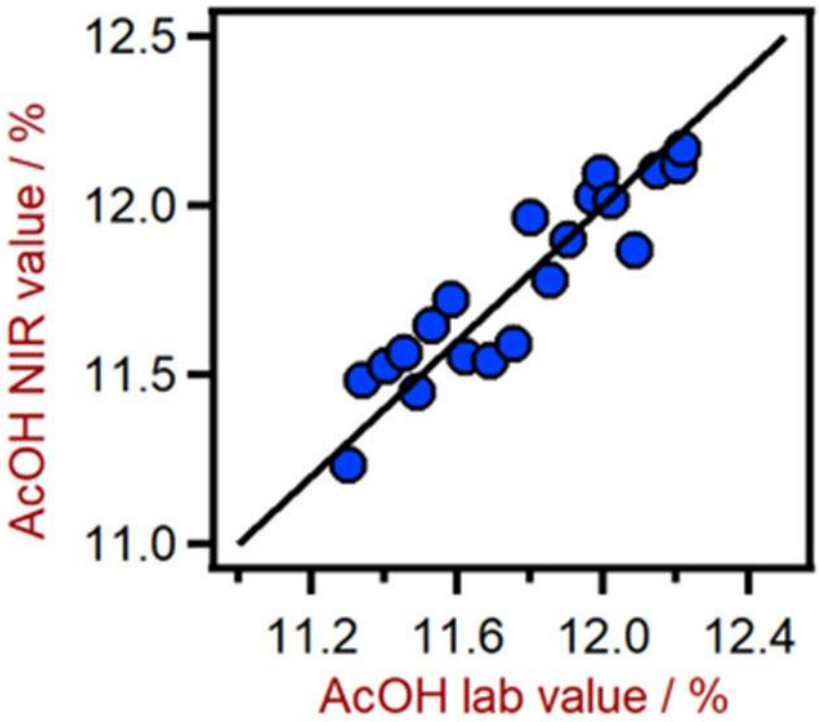

Figure 3. Correlation diagram for the prediction of AcOH content in a mixed acid solution using a DS2500 Liquid Analyzer.

Table 2. Figures of merit for the prediction of AcOH content in a mixed acid solution using a DS2500 Liquid Analyzer.

Figures of merit	Value
R^2	0.852
Standard error of calibration	0.124%
Standard error of cross-validation	0.147%

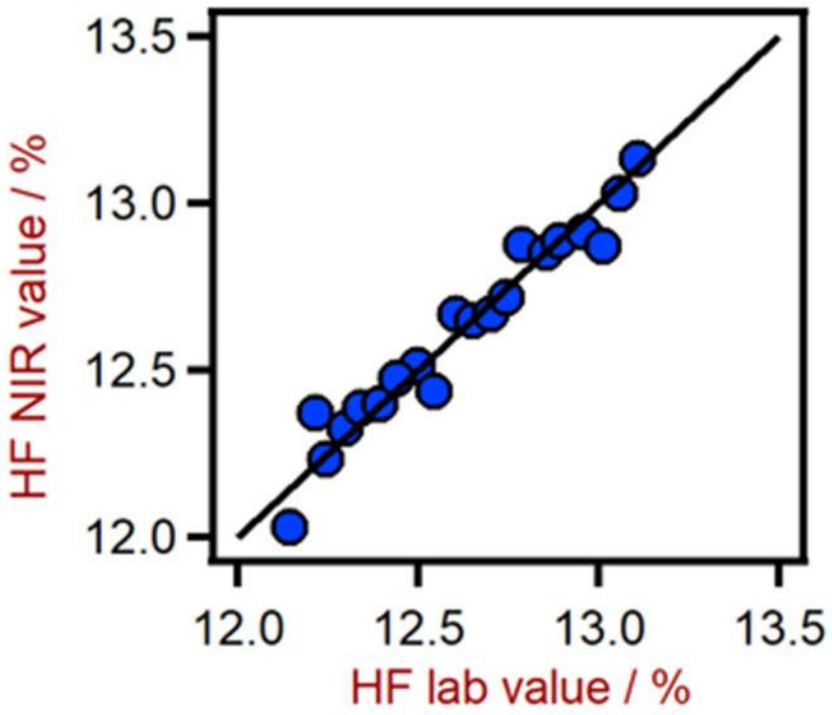

Figure 4. Correlation diagram for the prediction of HF content in a mixed acid solution using a DS2500 Liquid Analyzer.

Table 3. Figures of merit for the prediction of HF content in a mixed acid solution using a DS2500 Liquid Analyzer.

Figures of merit	Value
R^2	0.947
Standard error of calibration	0.080%
Standard error of cross-validation	0.133%

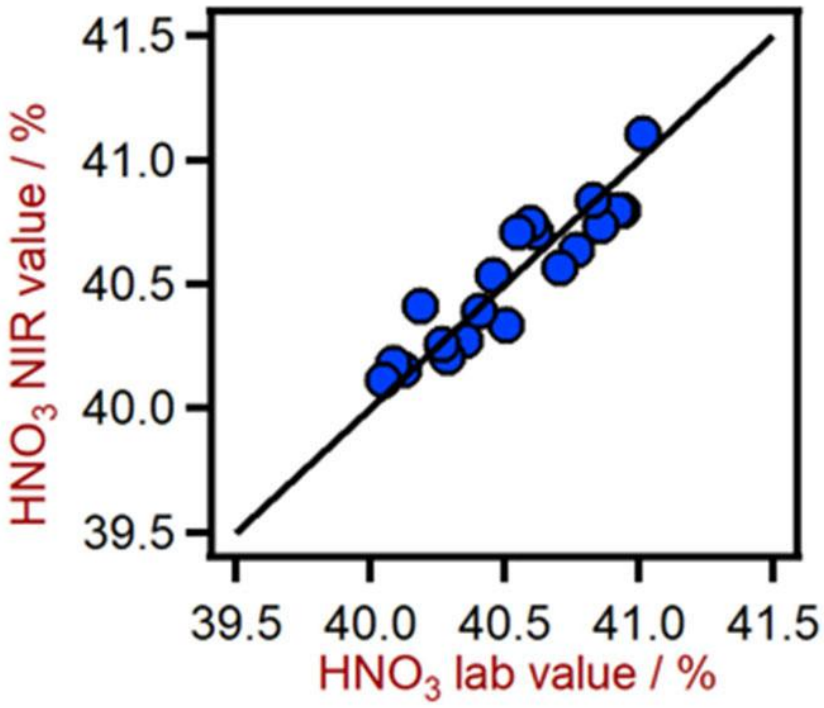

Figure 5. Correlation diagram for the prediction of HNO3 content in a mixed acid solution using a DS2500 Liquid Analyzer.

Table 4. Figures of merit for the prediction of HNO3 content in a mixed acid solution using a DS2500 Liquid Analyzer.

Figures of merit	Value
R^2	0.849
Standard error of calibration	0.128%
Standard error of cross-validation	0.139%

CONCLUSION

This application note demonstrates the feasibility of the DS2500 Liquid Analyzer for the determination of individual acid concentrations in a mixed acid solution. Vis-NIR spectroscopy enables fast determinations with high accuracy, and therefore represents a suitable alternative to the standard method (Table 5).

Table 5. Time to result for the acid content determination of a mixed acid solution using thermometric titration and NIR spectroscopy.

Parameter	Method	Time to result and workflow
AcOH, HF, and HNO_3	Thermometric titration (three-fold determination)	25 min. preparation for the determination of the titer and blank value + 6 min. (3 times 2 min.) for the titration measurement
AcOH, HF, and HNO_3	NIR Spectroscopy	1 minute for NIR spectroscopy measurement

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