

Quality Control of Mixed Acids

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

Summary

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



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

Mixed acid solutions based on three different acids (AcOH, HF, and HNO₃) 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.

Table 1. Hardware and software equipment overview

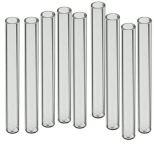
Equipment	Metrohm number
DS2500 Liquid Analyzer	2.929.0010
DS2500 Holder 4 mm vials	6.7492.010
Disposable vials, 4 mm	6.7402.010
Vision Air 2.0 Complete	6.6072.208

**2.929.0010 - DS2500 Liquid Analyzer**

Robust near-infrared spectroscopy for quality control, not only in laboratories but also in production environments. The DS2500 Liquid Analyzer is the tried and tested, flexible solution for routine analysis of liquids along the entire production chain. Its robust design makes the DS2500 Liquid Analyzer resistant to dust, moisture and vibrations, which means that it is eminently suited for use in harsh production environments. The DS2500 Liquid Analyzer covers the full spectral range from 400 to 2500 nm, heats samples up to 80°C and is compatible with various disposable vials and quartz cuvettes. The DS2500 Liquid Analyzer is thus adaptable to your individual sample requirements and helps you obtain accurate and reproducible results in less than one minute. The integrated sample holder detection and the self-explanatory Vision Air Software also ensure simple and safe operation by the user. In the case of larger-sized sample quantities, productivity can be considerably increased by using a flow-through cell in combination with a Metrohm sample robot.

**6.7492.010 - DS2500 Holder 4 mm vials**

Intelligent holder for disposable glass vials with 4 mm diameter



6.7402.010 - Disposable vials, 4 mm diameter, transmission

200 disposable glass vials (borosilicate) with a diameter of 4 mm for analyses of liquid samples in transmission mode. Suitable for the following Analyzers: NIRS XDS RapidLiquid Analyzer; NIRS XDS VialHeater + NIRS XDS Transmission OptiProbe Analyzer;



6.6072.208 - Vision Air 2.0 Complete

Vision Air - Universal spectroscopy software. Vision Air Complete is a modern and simple-to-operate software solution for use in a regulated environment. Overview of the advantages of Vision Air: Individual software applications with adapted user interfaces ensure intuitive and simple operation; Simple creation and maintenance of operating procedures; SQL database for secure and simple data management; The Vision Air Complete version (66072208) includes all applications for quality assurance using Vis-NIR spectroscopy: Application for instrument and data management; Application for method development; Application for routine analysis; Additional Vision Air Complete solutions: 66072207 (Vision Air Network Complete); 66072209 (Vision Air Pharma Complete); 66072210 (Vision Air Pharma Network Complete);

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 HNO₃). 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.

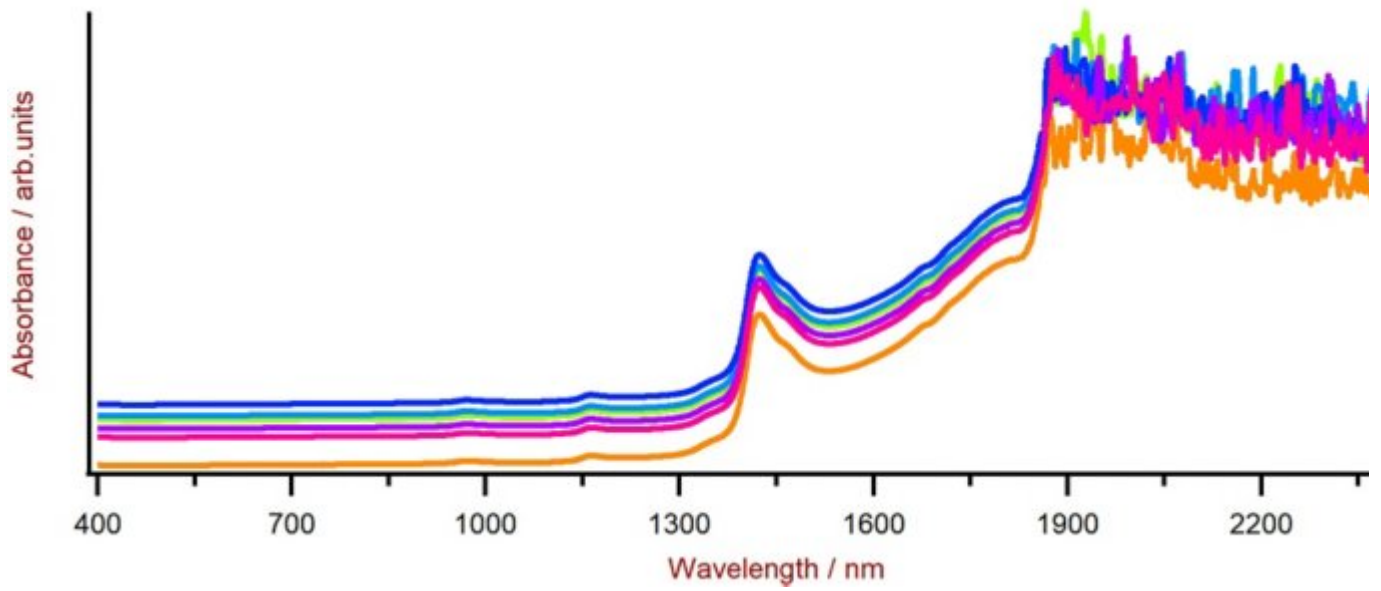


Figure 2. Vis-NIR spectra of mixed acids solutions with varying acid content measured on a DS2500 Liquid Analyzer. For display reasons a spectra offset was applied.

Result AcOH

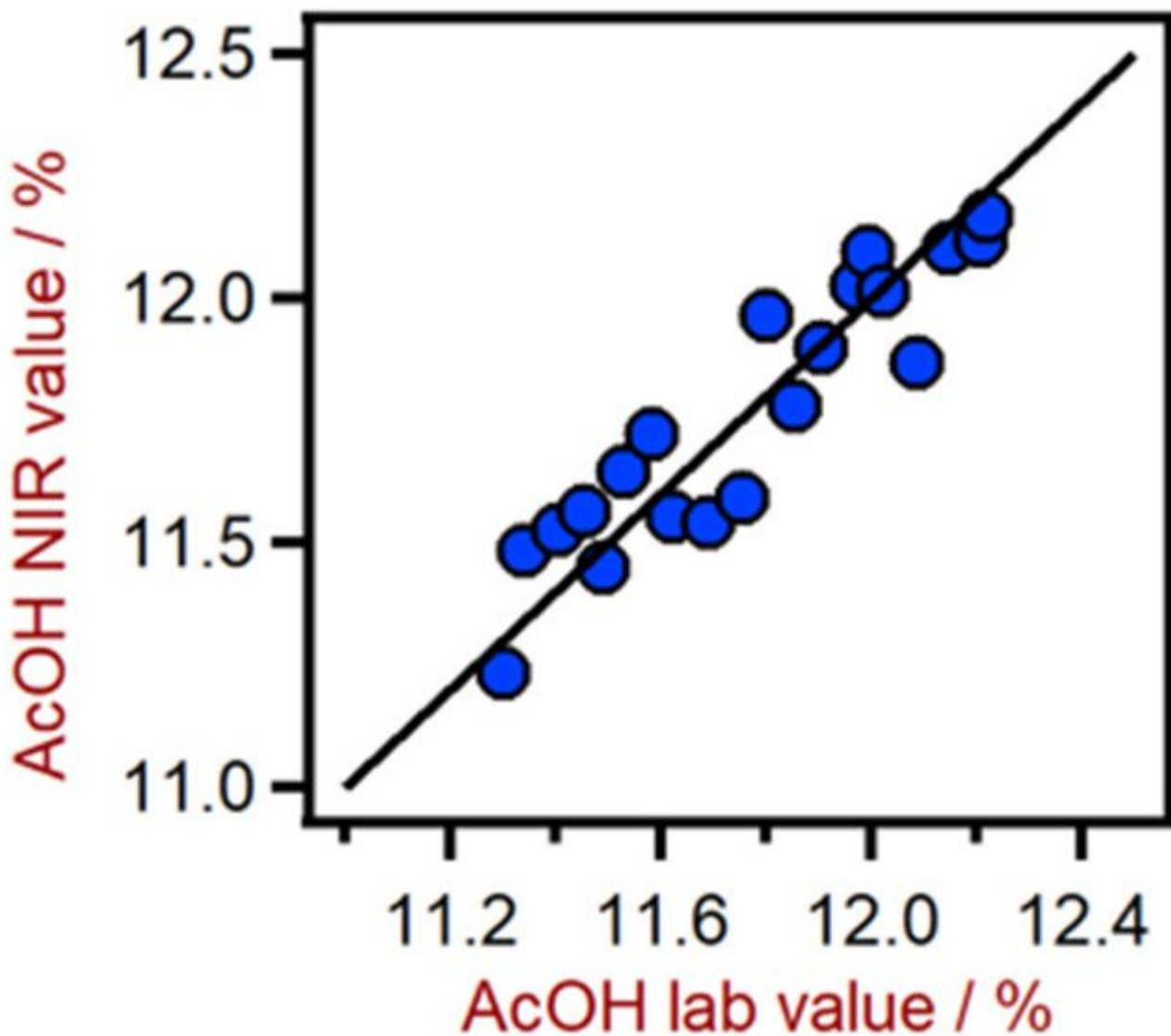


Figure 3. Correlation diagram for the prediction of AcOH content in a mixed acid solution using a DS2500 Liquid Analyzer.

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%

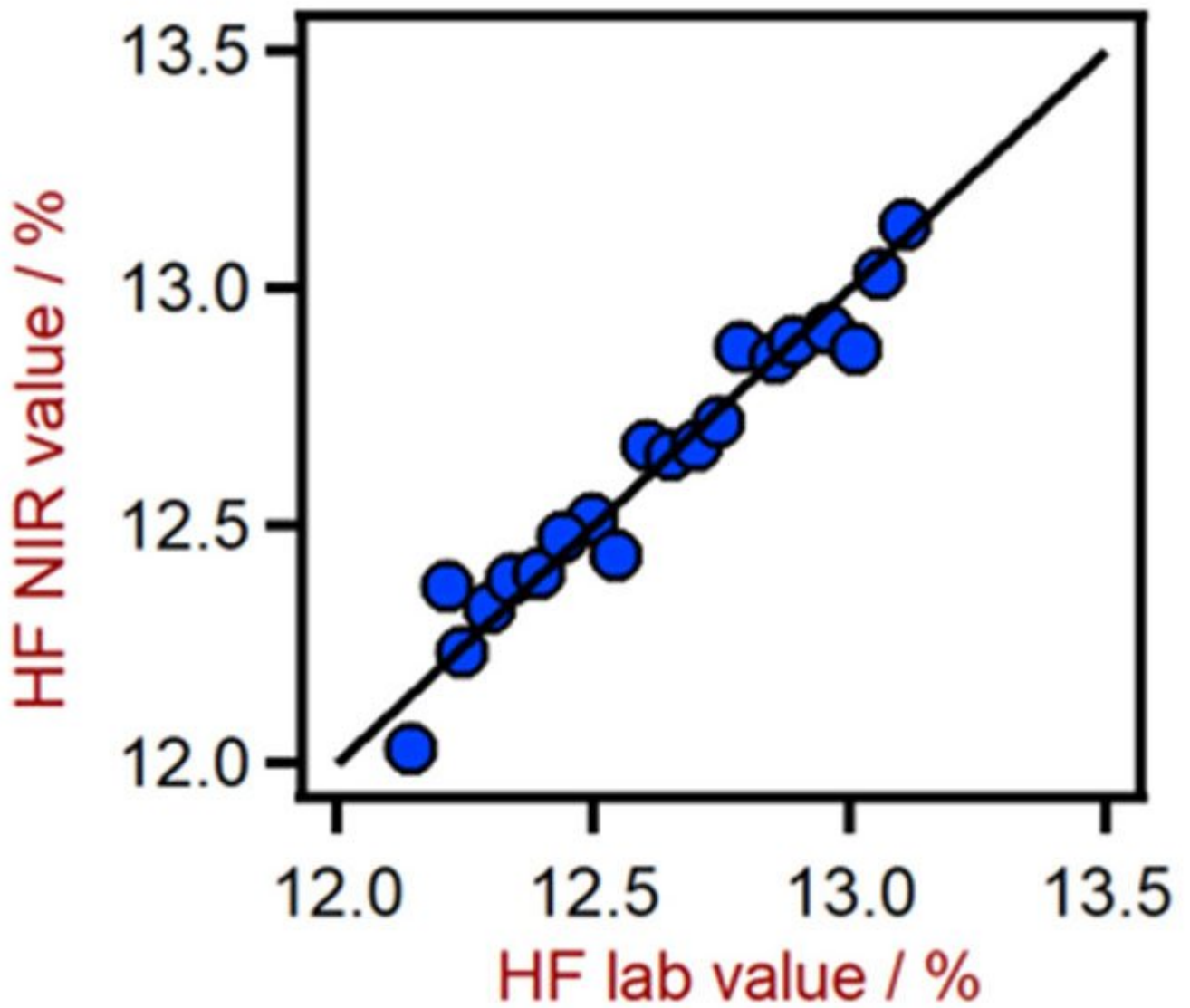


Figure 4. Correlation diagram for the prediction of HF content in a mixed acid solution using a DS2500 Liquid Analyzer.

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%

Result HNO₃

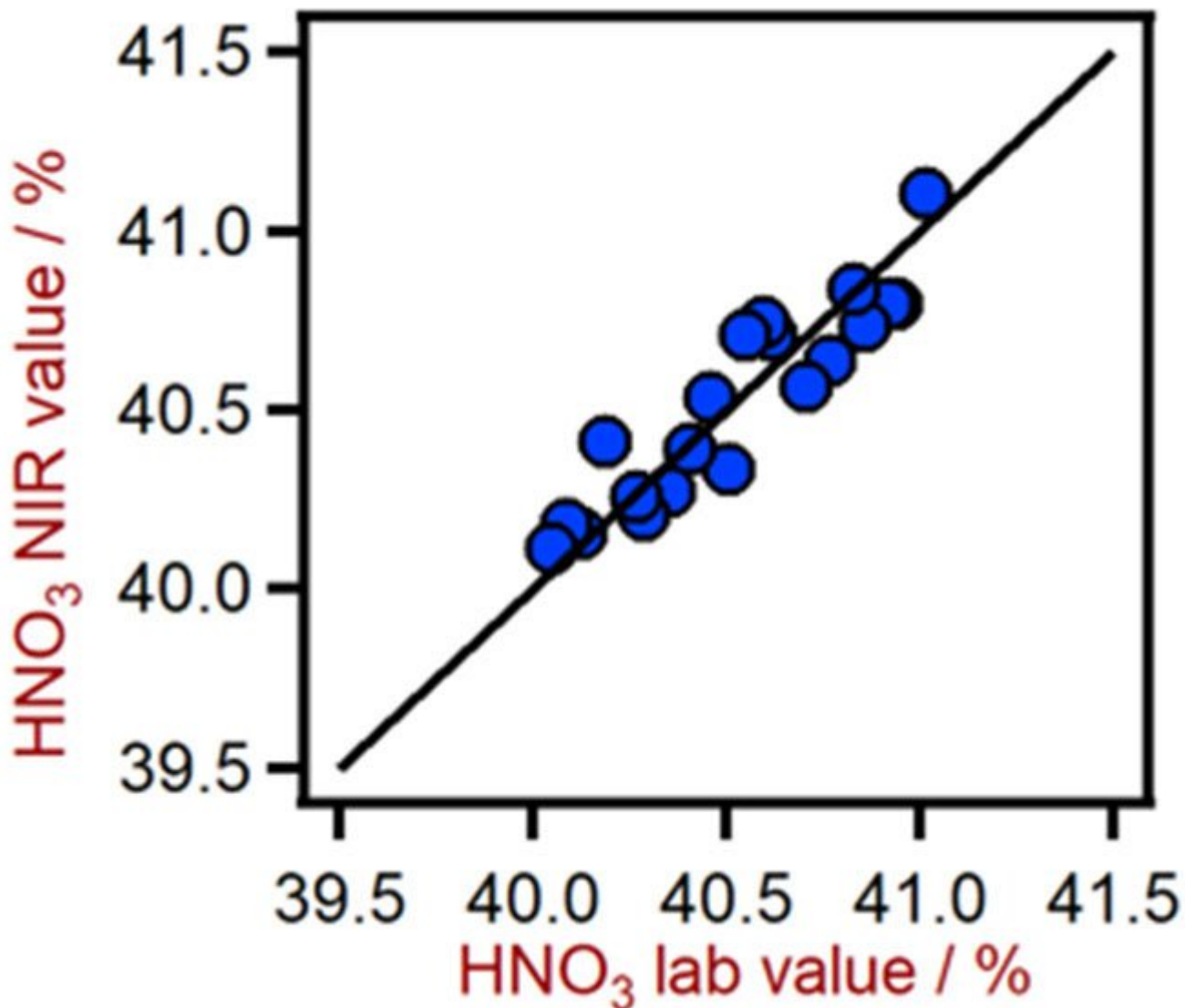


Figure 5. Correlation diagram for the prediction of HNO₃ content in a mixed acid solution using a DS2500 Liquid Analyzer.

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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