Application Note AN-NIR-090

Quality Control of Mixed Phosphoric, Sulfuric, Nitric, and Hydrofluoric Acids

Fast and reliable detection of different acids in mixtures with NIR spectroscopy

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.

EXPERIMENTAL EQUIPMENT

Mixed acid solutions based on four different acids (H_3PO_4, H_2SO_4, HNO_3, and HF) were measured in transmission mode with a DS2500 Liquid Analyzer over the full wavelength range (400–2500 nm). Disposable vials with a pathlength of 2 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 2 mm vials	6.7492.000
Disposable vials, 2 mm diameter, transmission	6.7402.070
Vision Air 2.0 Complete	6.6072.208

RESULTS

27 measured Vis-NIR spectra (Figure 2) were used to create a prediction model for quantification of the different acid concentrations (H_3PO_4, H_2SO_4, HNO_3, and HF). 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.

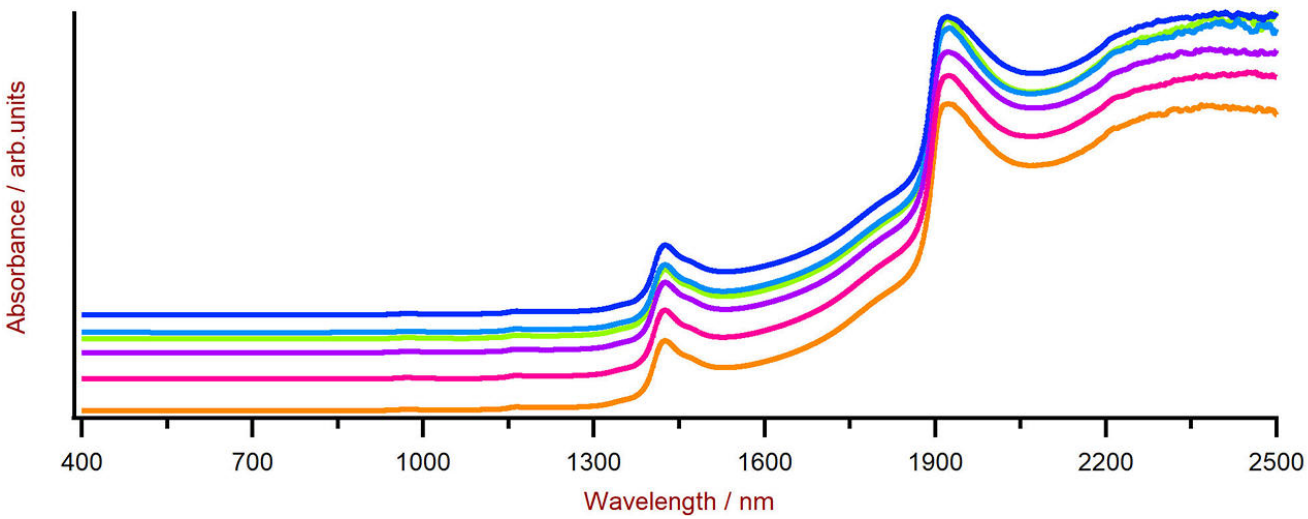

Figure 2. Vis-NIR spectra of mixed acids solutions with varying acid content measured on a DS2500 Liquid Analyzer. For display reasons a spectra offset was applied.

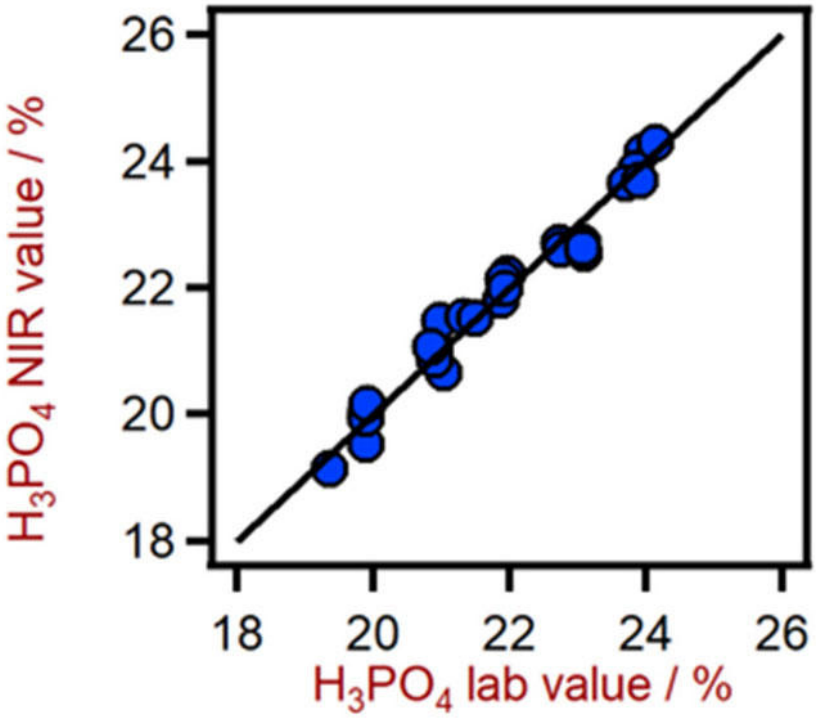

Figure 3. Correlation diagram for the prediction of H3PO4 content in a mixed acid solution using a DS2500 Liquid Analyzer.

Table 2. Figures of merit for the prediction of H3PO4 content in a mixed acid solution using a DS2500 Liquid Analyzer.

Figures of merit	Value
R^2	0.969
Standard error of calibration	0.290%
Standard error of cross-validation	0.410%

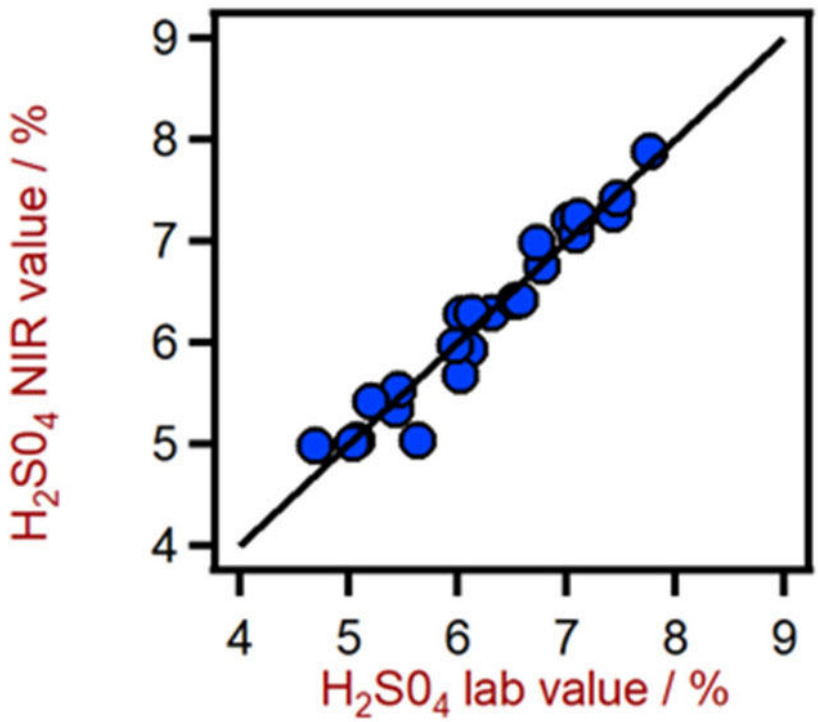

Figure 4. Correlation diagram for the prediction of H2SO4 content in a mixed acid solution using a DS2500 Liquid Analyzer.

Table 3. Figures of merit for the prediction of H2SO4 content in a mixed acid solution using a DS2500 Liquid Analyzer.

Figures of merit	Value
R^2	0.9448
Standard error of calibration	0.243%
Standard error of cross-validation	0.297%

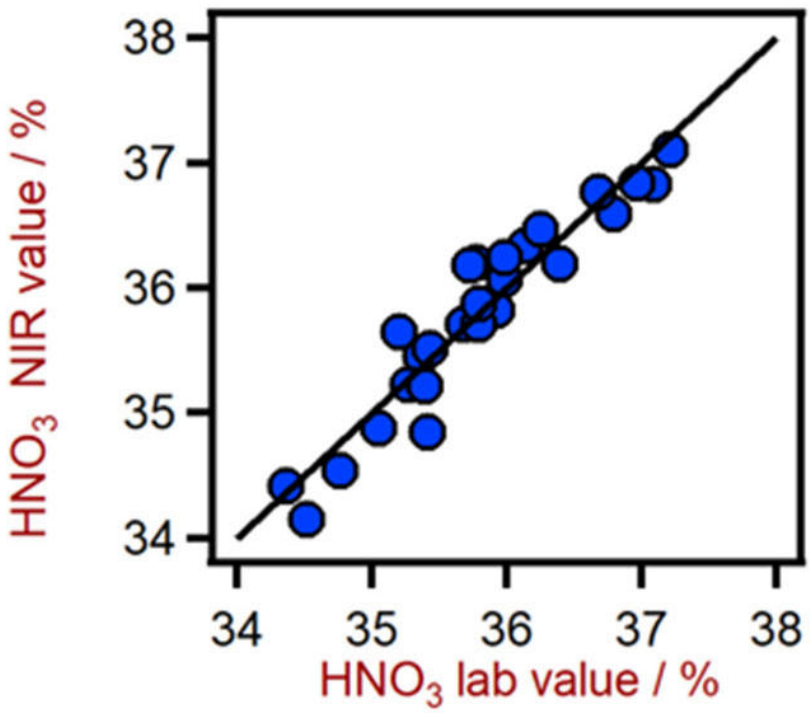

Figure 5. Correlation diagram for the prediction of HNO3 content in a mixed acid solution using a DS2500 Liquid Analyzer.

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	0.901
Standard error of calibration	0.279%
Standard error of cross-validation	0.345%

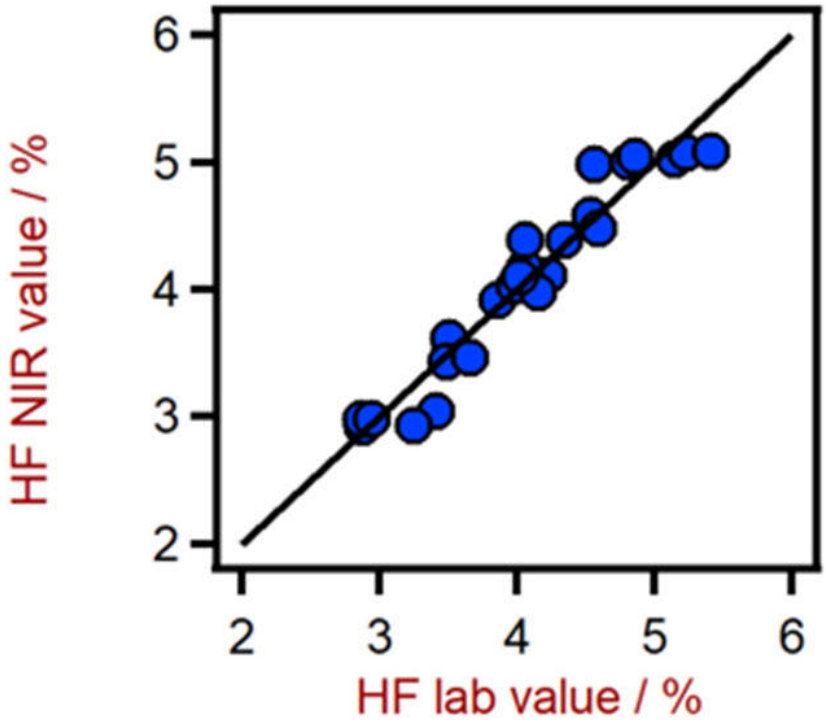

Figure 6. Correlation diagram for the prediction HF content in a mixed acid solution using a DS2500 Liquid Analyzer.

Table 5. 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	0.936
Standard error of calibration	0.211%
Standard error of cross-validation	0.276%

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 6).

Table 6. 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
H_3PO_4, H_2SO_4, HNO_3, and HF content	Thermometric titration (three-fold determination)	25 min. preparation for the determination of the titer and blank value + 12 min. (3 times 4 min.) for the titration measurement
H_3PO_4, H_2SO_4, HNO_3, and HF content	NIR Spectroscopy	1 minute for NIR spectroscopy measurement

Internal reference: AW NIR CN-0018-092020

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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.

DS2500 Holder 2 mm vials

Intelligent holder for disposable glass vials with 2 mm diameter

Disposable vials, 2 mm diameter, transmission

200 lockable disposable glass vials (borosilicate) with a diameter of 2 mm for analyses of liquids in transmission mode.

Compatible with:

- Holder OMNIS NIR, vial, 2 mm (6.07401.050)
- DS2500 holder for flow cells (6.7492.000)

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)