

Application Note AN-NIR-090

# 磷酸-硫酸-硝酸-氢氟酸混酸工艺质控平台

## Fast and reliable detection of phosphoric, sulfuric, nitric and hydrofluoric 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.

## 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.

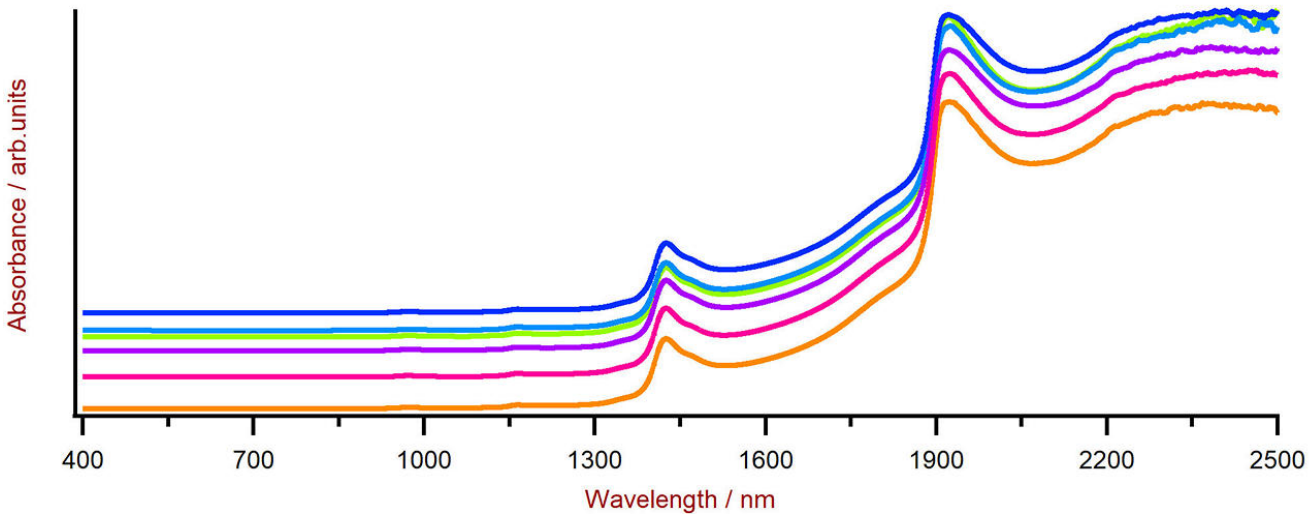



**Figure 2.** Vis-NIR spectra of mixed acids solutions with varying acid content measured on a DS2500 Liquid Analyzer. For display reasons a spectra offset was applied.

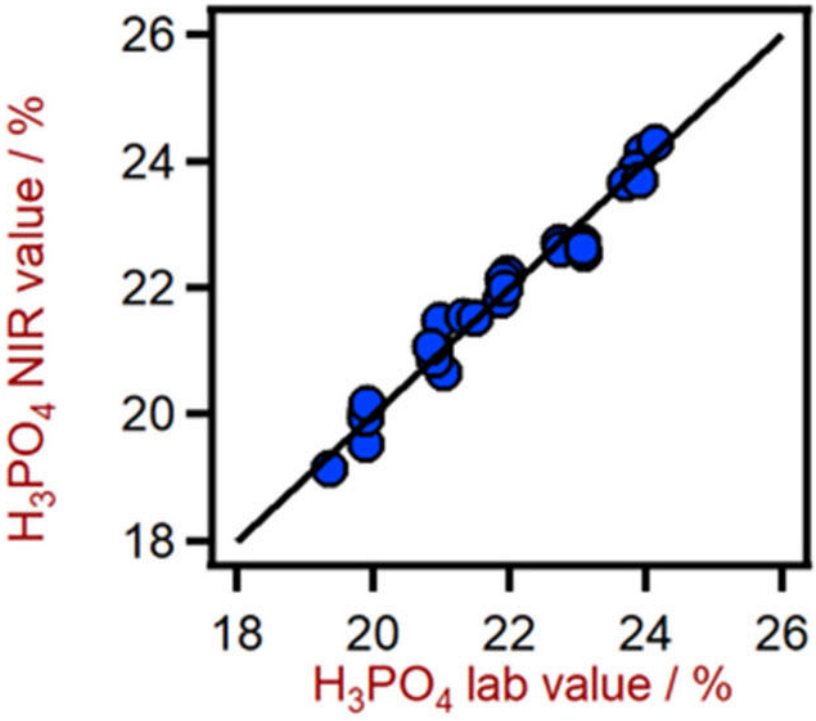



**Figure 3.** Correlation diagram for the prediction of H3PO4 content in a mixed acid solution using a DS2500 Liquid Analyzer.

**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% |

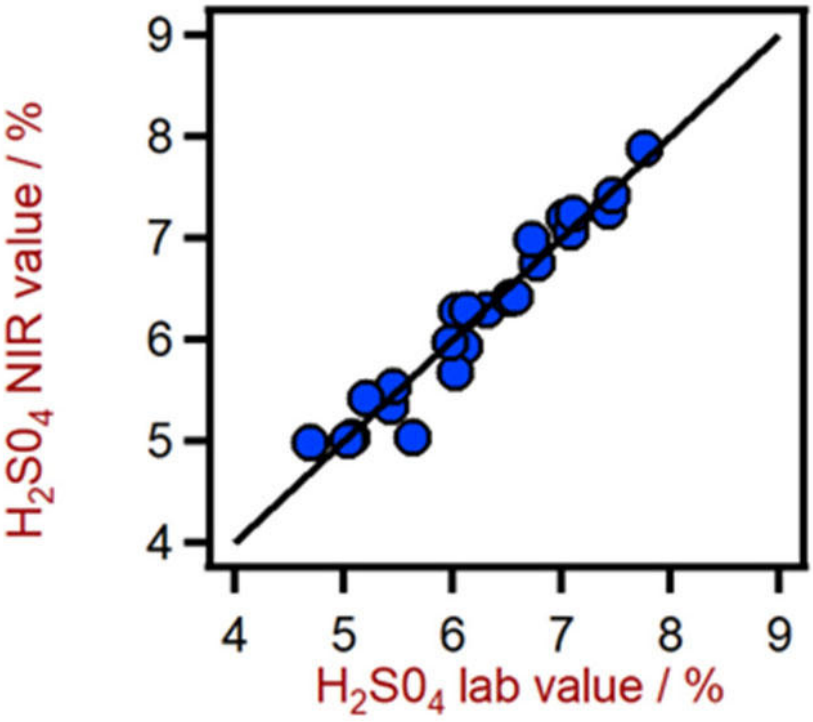



**Figure 4.** Correlation diagram for the prediction of H2SO4 content in a mixed acid solution using a DS2500 Liquid Analyzer.

**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% |

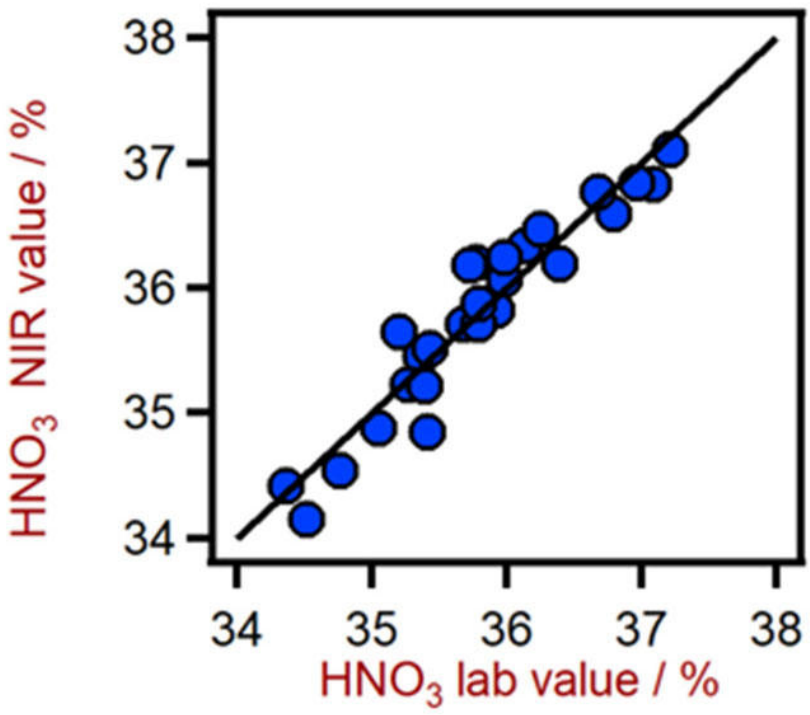



**Figure 5.** Correlation diagram for the prediction of HNO3 content in a mixed acid solution using a DS2500 Liquid Analyzer.

**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% |

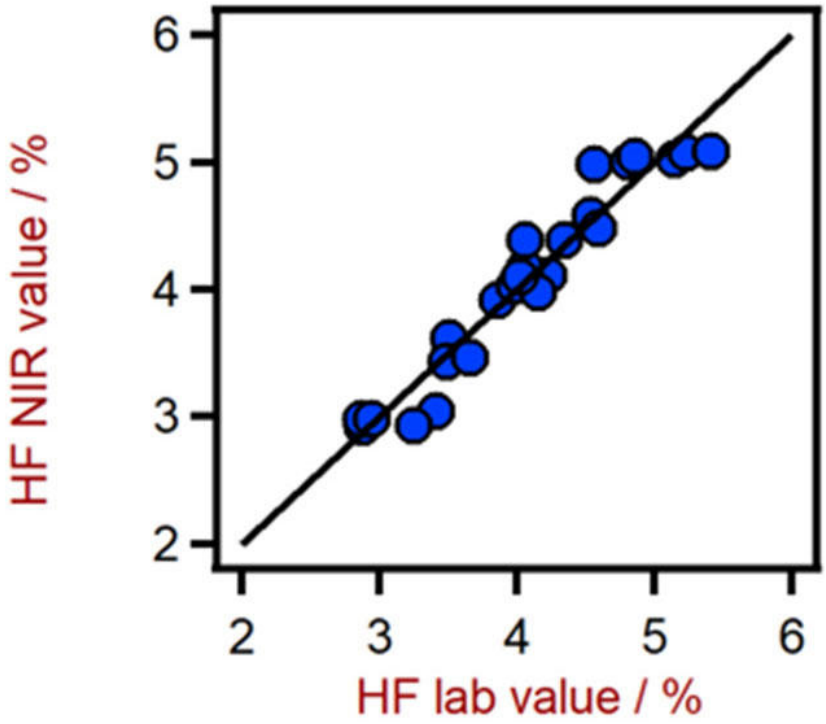



**Figure 6.** Correlation diagram for the prediction HF content in a mixed acid solution using a DS2500 Liquid Analyzer.

**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<br>+ 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

## CONTACT

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## DS2500 Liquid Analyzer

**坚固结实的近红外光谱仪,用于生产环境和试验室中的质量检查。**

DS2500 Liquid Analyzer 是一种成熟且灵活的解决方案,其用于在整个生产链中进行液体常规分析。其坚固结实的设计使 DS2500 Liquid Analyzer 不受灰尘、潮湿、振动的影响,因此非常适用于在恶劣的生产环境中使用。

DS2500 Liquid Analyzer 覆盖 400 至 2500 nm 的整个光谱范围,将样品加热至 80° C 高温,并与各种不同的一次性小瓶和石英比色皿兼容。因此,DS2500 Liquid Analyzer 可适应您的个性化样品要求,帮助您在一分钟内获得精确和具有可重现性的结果。借助集成的样品架识别装置和自带的 Vision Air 软件,还保证了用户能轻松和安全地进行操作。

如果是较大的样品量,则可通过将流通池与一个 Metrohm 机器人自动进样器搭配使用的方法显著提高生产率。



## DS2500 2 mm

直径为 2 mm 且更加智能的一次性玻璃小瓶支架



## 2 mm

200 个可封闭的玻璃(硼硅)一次性样品瓶,直径为 2 mm,适用于分析透射中的液体。

兼容:

- 支架 OMNIS NIR,小管,2 mm (**6.07401.050**)
- DS2500 支架适用于流动池(**6.7492.000**)



## Vision Air 2.0 Complete

**Vision Air – 通用的光谱分析软件。**

Vision Air Complete 是用于监管规范环境的先进易用的软件解决方案。

Vision Air 优点一览:

- 便捷的软件应用和经过适配的用户界面保证了直观简单的操作方式
- 操作过程的创建与维护方式简单
- SQL 数据库,可安全且简单地管理数据

Vision Air Complete (66072208) 版本包含所有用于可见近红外光谱分析质量保证过程的应用:

- 仪器和数据管理应用
- 方法开发应用
- 常规分析应用

其它 Vision Air Complete 解决方案:

- 66072207 (Vision Air Network Complete)
- 66072209 (Vision Air Pharma Complete)
- 66072210 (Vision Air Pharma Network Complete)