WHITE PAPER

Quality control of semiconductor acid baths as per ASTM E1655 – Time- and cost-efficient with NIRS

The semiconductor industry, comprising microelectronics, photovoltaics, flat panel displays, LED manufacturing, and printed electronics, is an essential intermediate for consumer products in the economy [**1**]. The demand for microelectronics and printed circuit boards (PCBs) has steadily increased due to digitalization in general, and has further accelerated during the COVID-19 pandemic as people were forced to find other ways of working and interacting.

Although this increased demand may be favorable for PCB manufacturers, challenges arise to deliver on time while upholding high quality standards. To be successful, several processes must be optimized in order to increase production efficiency.

This White Paper describes the capabilities of the modern analytical method near-infrared (NIR) spectroscopy for assessing the quality of acid baths for etching of microelectronics and printed electronics. Not only are analysis times sharply reduced to less than a minute, the related running costs are also significantly lower – certainly a boost in efficiency that should not be overlooked!

Metrohm

IMPORTANCE OF ACID BATH QUALITY CONTROL: COMPARISON OF METHODS

Maintaining the proper concentrations of all components in an acid bath ensures a repeatable etching process, which for the manufacturing of printed or microelectronics means the correct production of specified patterns on the semiconductor wafer.

A commonly used method to test the concentration of mixed acids is thermometric titration. While this method works reliably for simple solutions consisting of **up to three acids**, it requires proficiency, time, and additional attention for more complex acid mixtures. Aside from the usual titer determination, typical steps of a thermometric titration involve the calculation of the method blank.

As an example, for the thermometric titration of a mixture of three acids: sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrofluoric acid (HF), three different titers have to be used (namely $AlNO_3$, $BaCl_2$, and NaOH) to determine the individual acid concentrations [**2**]. Although a single thermometric titration is fast, the increasing complexity as presented in Metrohm **Application Note H-114** results in waiting times of at least 12 minutes for the results (nine thermometric titrations are required when a three-fold determination is performed).

As shown below, near-infrared (NIR) spectroscopy can be a reliable alternative to wet chemical methods to increase laboratory efficiency.

Figure 1 displays the time-to-result difference between acid content measurements in a mixed acid bath with NIR spectroscopy and the previously described thermometric titration. The time savings with NIR spectroscopy are already quite significant when comparing the determination times alone. **NIR spectroscopy can determine all parameters within one minute**.

Also shown is the time required to carry out the preparation steps needed for thermometric titration (standardization and blank determination). If these steps are also taken into consideration, then the time-to-result difference is extreme (42 minutes compared to 30 seconds). Luckily, these preparation steps are not required before each titration measurement (only 1–2 times per week), but a regular test of the titer concentration (standardization), and the determination of the blank are highly recommended and needed for the most accurate results.

Beside the time-to-result aspect, cost saving potentials should also be considered. **Table 1** compares the costs per analysis when using thermometric titration methods and when NIRS is used. Calculations for the thermometric measurement are based on the workflow description in **Application Note H-114** with 20 analyses per day and 225 working days per year [**2**]. **Figure 2** highlights the potential savings over a period of 10 years. As shown, the pure chemical saving potential is roughly $66,000 USD over this time period ($6645 USD per year).

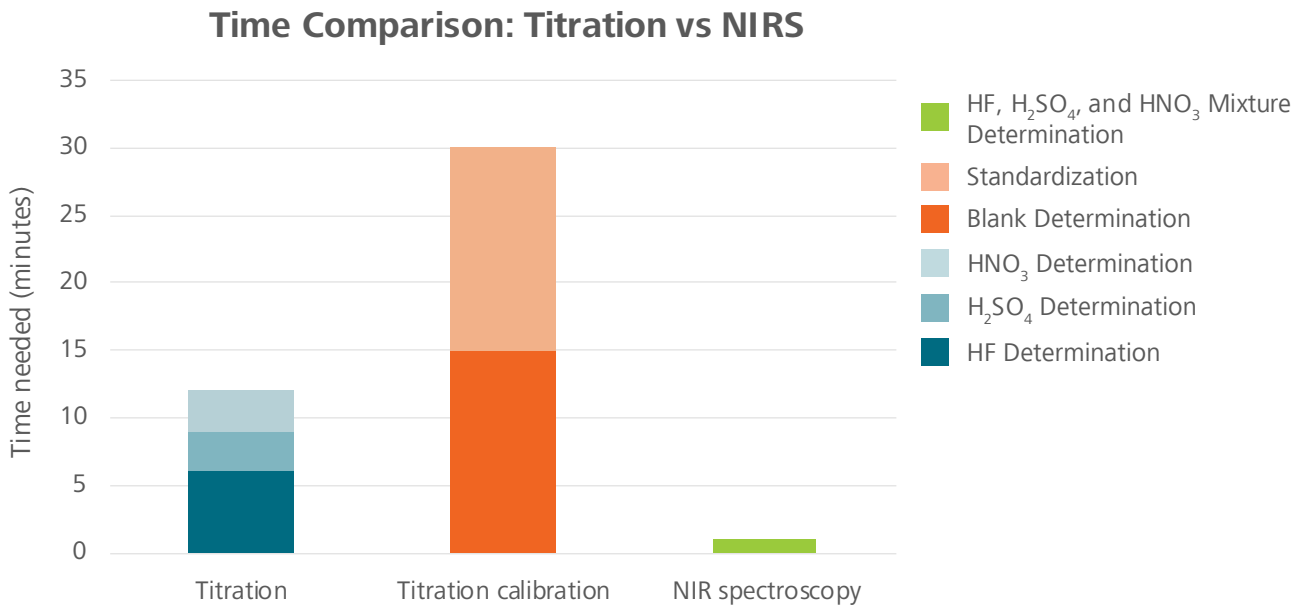


Figure 1. Time-to-result comparison when using thermometric titration vs. NIR spectroscopy. In less than a minute, all three acid concentrations can be determined using NIR spectroscopy.

Table 1. Overview of related costs per analysis and per year for the determination of H_2SO_4, HNO_3, and HF using thermometric titration and NIRS. Chemical disposal costs are not included.

Working days per year	225	
Analyses per day	20	
Total analyses per year	4500	
Consumables ($USD): chemicals / analysis	**Titration**	**NIRS**
HF Concentration	$1.04	$0.50
H_2SO_4 Concentration	$0.42	
HNO_3 Concentration	$0.34	
Blank and Standardization	$3.63	
Total consumables costs ($USD) per year	**$8,895**	**$2,250**

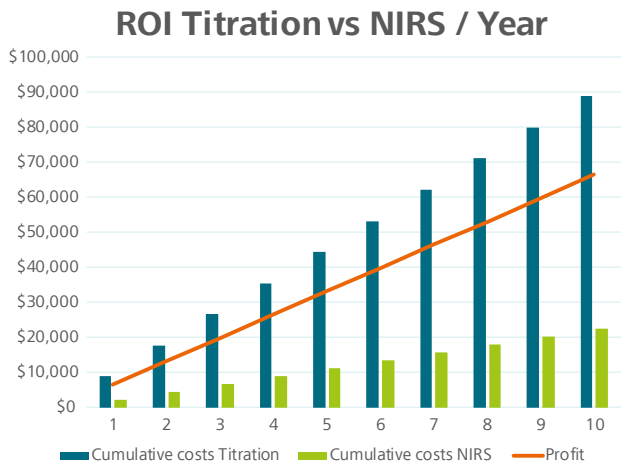


Figure 2. Graph displaying the savings potential (profit) over a period of 10 years when using near-infrared spectroscopy.

After presenting the potential cost and time savings by using NIR spectroscopy, the following section briefly explains the basics of NIRS and how to set up such a system in accordance with ASTM E1655 [**3**].

NIR SPECTROSCOPY BASICS

– WHAT IS NIR SPECTROSCOPY?

NIR spectroscopy is the analysis of the interaction between light and matter. This light-matter interaction is a well-known process most people have already encountered—a sunburn is just one example. However, contrary to UV-light which causes the sunburn, **near-infrared light is lower in energy and therefore non-destructive**.

Instruments such as the Metrohm NIRS DS2500 Liquid Analyzer can accurately measure light-matter interactions and will generate spectra as displayed in **Figure 3**. The spectral data allows extraction of the parameter of interest.

NIR spectroscopy is especially sensitive to the presence of certain functional groups like -CH, -NH, -OH, and -SH (**Figure 3a**), and is an ideal method for the quantification of chemical parameters including the acid concentration, moisture content, or the acid number.

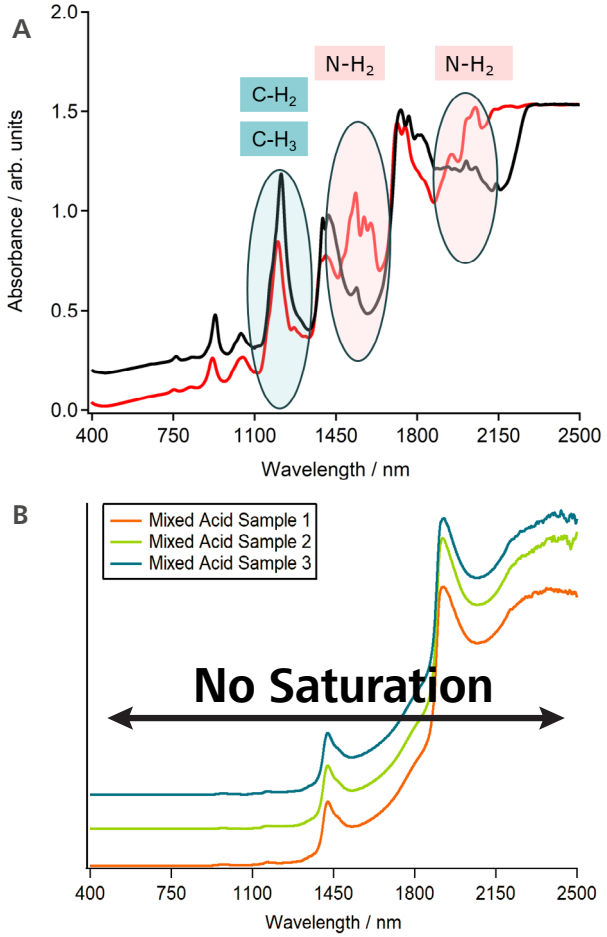


Figure 3. A) Display of the relation between absorbance bands and the absorbance of functional groups in molecules. B) Overlay of three mixed acid Vis-NIR spectra. All spectra are not saturated in the NIR wavelength region and can be used for analysis.

An advantage of NIRS compared to other spectroscopic technologies (e.g., infrared (IR) spectroscopy) is that this method is also suitable for the analysis of aqueous mixtures (up to 15 % water). As shown in **Figure 3b**, the NIR spectra do not saturate, which would be the result of an overabundance of absorbed light, which is a common problem with IR spectroscopy. Therefore, NIR spectra can be used to quantify acid concentrations in mixed acid solutions.

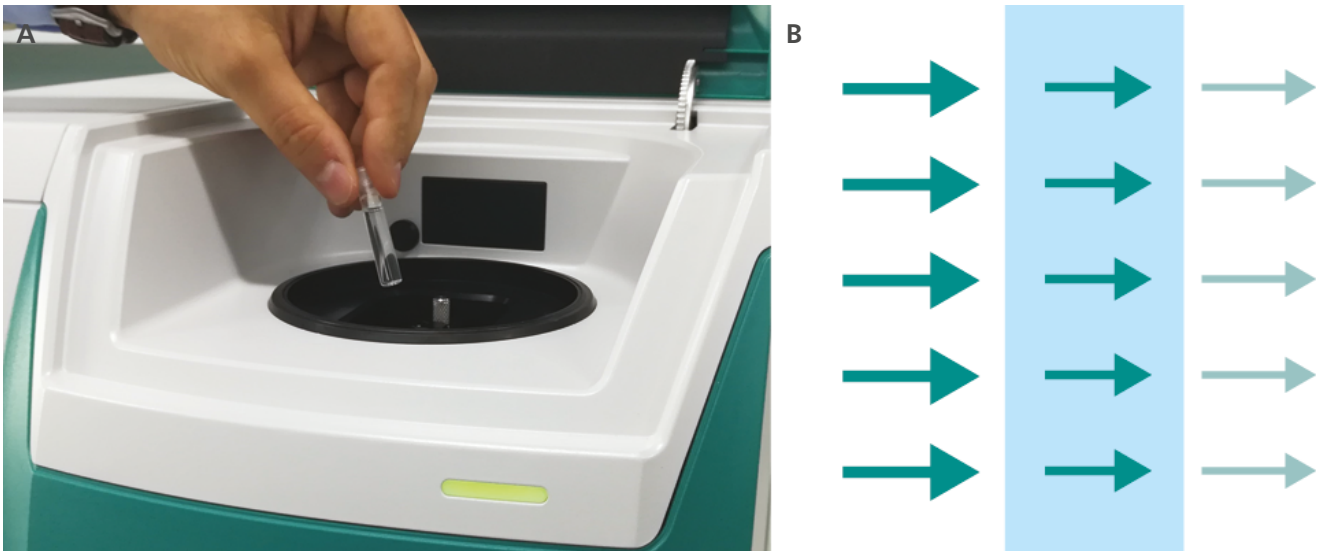


Figure 4. A) Metrohm NIRS Analyzer with a filled disposable vial. B) Transmission measuring principle: light passes through the samples (represented in blue) and the remaining light is detected.

– NIRS MEASUREMENT SETUP

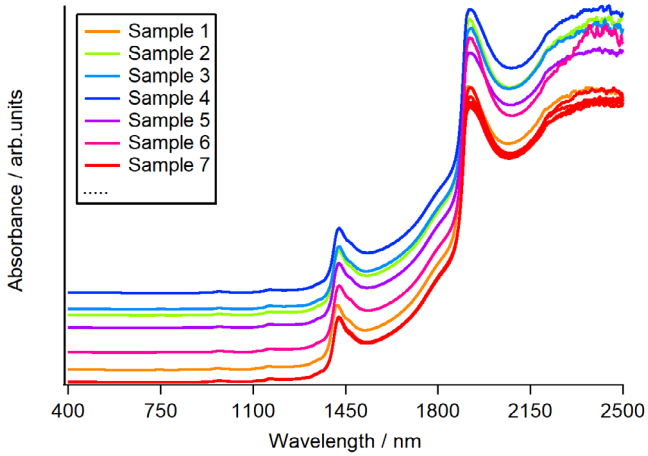
As **Figure 4a** illustrates, the preferred sample vessels for liquid measurements are vials or cuvettes. Disposable vials are typically used for convenience, eliminating any need for sample vessel cleaning, and allowing a full analysis in less than a minute.

The measuring mode of choice for liquid analysis is known as **transmission**. In this case, the NIR radiation travels through the solution before reaching the detector (**Figure 4b**).

– CALIBRATING A NIRS METHOD TO ANALYZE ACID CONCENTRATIONS

To evaluate the parameters of interest from a spectrum, a calibration is needed. Such a calibration is called a **prediction model**, which is a mathematical function applied automatically during routine quality control measurements. The following section describes the workflow and requirements mentioned in the ASTM E1655 guideline for the creation of prediction models.

To create prediction models, the system needs to be «trained» to determine how different values of a parameter (e.g., acid concentration) will affect the spectrum. Training of the system is achieved by using a calibration data set, which consists of spectra from

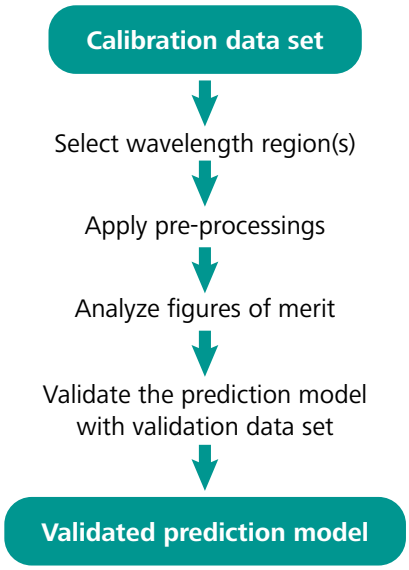


Sample	H_2SO_4 Concentration (%)	HF Concentration (%)
Sample 1	6.41	3.69
Sample 2	7.06	5.14
Sample 3	5.35	4.22
Sample 4	5.04	4.8
Sample 5	6.76	3.54
Sample 6	5.94	3.91
Sample 7	4.99	3.51
.....	.....	.....

Figure 5. Example of a calibration set consisting of spectra and reference values for the parameters of H_2SO_4 and HF acid concentration to create the prediction model.

representative samples and the related reference values (ideally consisting of a minimum of 20 samples). Reference values are the values of the parameter of interest (e.g., acid concentration) measured with a primary method such as thermometric titration as displayed in **Figure 5**.

Four successive steps are done with the training set to create the prediction model:



1. User selects the wavelength region where the absorbance values correlate with the change of the parameter of interest.

2. User intensifies the signals by applying mathematic pre-treatment (e.g., a derivative).

3. The software calculates the correlation between absorbance values of the selected wavelength region and reference values of the parameter of interest.

   User evaluates the results (Figures of Merit, FOM). Ideally, the software displays a high correlation $R > 0.9$ between calculated (predicted) NIR result and the reference values. Furthermore, the accuracy of this prediction model based on the calibration set (shown as SEC) is in the range of the accuracy of the error of the reference method.

4. Another data set of spectra and reference values is used to validate the prediction model. The software also displays the accuracy of the prediction of this validation set (SEP). Both accuracies, SEC and SEP, should be similar.

If the correlation is high ($R > 0.9$) with similar SEC and SEP values, the prediction model can be used as a replacement for the reference method.

It is recommended that for the first prediction model development the user is assisted by the vendor of the spectroscopy system. Metrohm offers this service to support analysts – ensuring that using the system is comfortable and that results obtained by the NIR analyzer are reliable.

Additionally, some starter prediction models for the analysis of acid mixtures are available that can be used to simplify the development of tailored prediction models.

SUMMARY

Near-infrared spectroscopy is a time- and cost-efficient alternative to other analytical methods for the determination of different acid contents in semiconductor acid baths. As a secondary method, NIRS uses prediction models to interpret the interaction between light and matter. The development of a prediction model consists of four main steps—a process typically supported by vendors of NIR spectrometers, such as Metrohm.

Especially for more complex mixtures, differences between the reference method (thermometric titration) and NIR spectroscopy become obvious. NIRS allows users to analyze acid mixtures within 30 seconds without any consumption of chemicals during the analysis.

Detailed application examples of the analysis of mixed acid solutions with NIR spectroscopy can be found in the related **Application Notes NIR-090** and **NIR-091** [**4,5**].

References

[1] Wittmann, J. *Introduction to quality management in the semiconductor industry*. CreateSpace Independent Publishing/Amazon Media EU S. à.r.l.: Luxembourg, 2016; Vol. 1.

[2] Metrohm AG. *Determination of sulfuric acid, nitric acid, and hydrofluoric acid in etch solutions*, Metrohm AG: Herisau, Switzerland, 2011. **AN-H-114**

[3] *ASTM E1655-17 Standard Practices for Infrared Multivariate Quantitative Analysis;* ASTM International: West Conshohocken, PA. (**https://www.astm.org/Standards/E1655.htm**)

[4] Metrohm AG. *Quality Control of Mixed Acids – Fast and reliable detection of phosphoric, sulfuric, nitric and hydrofluoric acids*, Metrohm AG: Herisau, Switzerland, 2021. **AN-NIR-090**

[5] Metrohm AG. *Quality Control of Mixed Acids – Fast and reliable detection of acetic, hydrofluoric, and nitric acids*, Metrohm AG: Herisau, Switzerland, 2021. **AN-NIR-091**

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