



## Application Note AN-H-140

# Titration of phosphoric, nitric, and acetic acid mixtures

## Fast and reliable analysis of phosphoric etchants used in the semiconductor industry by thermometric titration

Aluminum and its alloys are used for wiring in microchips [1]. To selectively wet etch aluminum, an etching bath made of phosphoric acid, nitric acid, and acetic acid (PAN etchant) is used. This acid mixture must be analyzed and monitored for optimal and efficient etching.

The SEMI C37 standard uses potentiometric titration to measure total acidity and phosphoric acid content. However, nitric acid must be analyzed by UV/VIS

spectroscopy, while acetic acid content is calculated from the other results [2]. Thermometric titration (TET) is an alternative PAN etchant analysis method which can determine all three acids quickly.

In this Application Note, the acid concentrations are determined in sequence using a single titration. Compared to potentiometric titration, TET is faster and more convenient. On a fully automated system, the complete analysis takes about 95 seconds.

# SAMPLE AND SAMPLE PREPARATION

This application is demonstrated on a simulated aqueous etching solution composed of phosphoric

acid, acetic acid, and nitric acid.  
Sample preparation is not required.

# EXPERIMENTAL

The determinations are carried out on an OMNIS Professional Titrator equipped with a dThermoprobe (**Figure 1**). To avoid manually handling chemicals, all solutions are automatically added using an OMNIS Dosing Module.  
An appropriate amount of sample is pipetted into the titration vessel and deionized water is added. Afterwards, the solution is titrated until after the third exothermic endpoint with standardized sodium hydroxide (**Figure 2**).



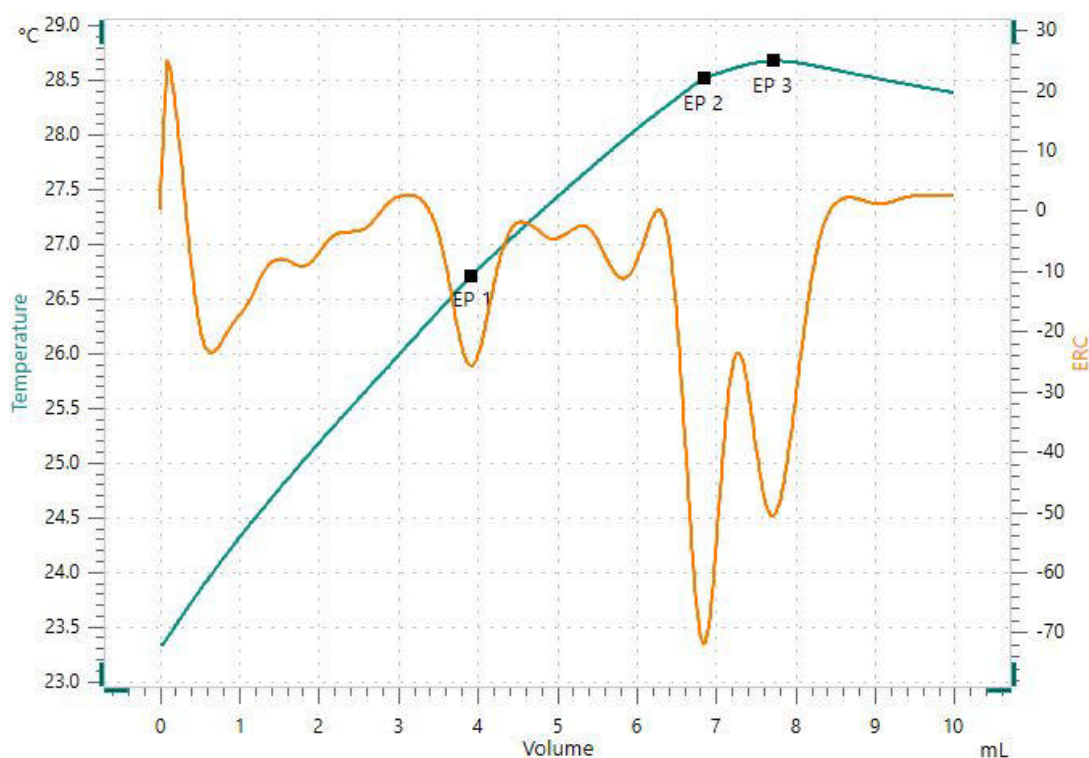
**Figure 1.** OMNIS Titrator Professional equipped with a dThermoprobe and a rod stirrer.

# RESULTS

This method offers very accurate results for PAN etchant, as displayed in **Table 1**.

**Table 1.** Results of the thermometric titration of a mixture containing 10.5% acetic acid, 24.5% phosphoric acid, and 35% nitric acid (n = 3).

Sample (n = 3)	Mean value in %	SD(rel) in %
CH <sub>3</sub> COOH (10.5%)	9.82	0.5
H <sub>3</sub> PO <sub>4</sub> (24.5%)	25.4	0.7
HNO <sub>3</sub> (35%)	36.1	0.5



**Figure 2.** Titration curve showing the thermometric determination of a three-acid mixture. The EPs are explained in Table 2.

**Table 2.** Explanation of TET endpoints from Figure 2.

EP1	EP2	EP3
HNO <sub>3</sub> (fully dissociated)	CH <sub>3</sub> COOH (pK <sub>a</sub> = 4.75)	–
H <sub>3</sub> PO <sub>4</sub> (pK <sub>a1</sub> = 2.12)	H <sub>3</sub> PO <sub>4</sub> (pK <sub>a2</sub> = 7.21)	H <sub>3</sub> PO <sub>4</sub> (pK <sub>a3</sub> = 12.36)

## CONCLUSION

Thermometric titration is a very fast and accurate method that can determine the concentration of acetic, phosphoric, and nitric acids in one titration. This method can differentiate between the three acid

components with a determination time of **less than two minutes**. No sensor maintenance is required, making TET a robust alternative to other PAN etchant analysis methods.

## REFERENCES

1. Hilleringmann, U. *Silicon Semiconductor Technology: Processing and Integration of Microelectronic Devices*; Springer Fachmedien: Wiesbaden, 2023.  
<https://doi.org/10.1007/978-3-658-41041-4>.
2. SEMI C37 - Specification for Phosphoric Etchants; SEMI C37; SEMI: Milpitas, CA, USA, 2011.

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## CONFIGURATION



OMNIS  
OMNISOMNIS3S

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- 4
- 
- : 5102050 mL
- 3S:
- 
- : Basic ()
- (/): Advanced ()
- (/): Professional ()



dThermoprobe  
OMNIS TET  
Thermoprobe  
HF :

- ASTM D8045 (TAN)
- (TBN)
- 
- Ca/Mg
-



OMNIS 10 mL

OMNIS Titrator 10 mL:

- 
- 5
- 
- 
- 
- EDTA

# OMNIS

A WHOLE NEW LEVEL OF PERFORMANCE

OMNIS Titrator

- (TET)
- MEAS U / T / pH
- OMNIS Titrator