



Application Note AN-RS-053

Estimation of amine value in epoxies with Raman spectroscopy

A complementary approach to potentiometric titration

Amine value (AV), often used to quantify the amount of reactive amine groups in curing agents, is a critical parameter for optimizing the stoichiometry of epoxy formulations. A resin/hardener epoxy system with optimal AV ensures complete curing, which is essential for achieving the desired properties of the final product [1].

The standard method for determining AV is ASTM D2073, which involves titration with a strong acid [2]. While accurate, this procedure is time consuming, generates hazardous waste, and is not ideal for high-

throughput evaluation. Raman spectroscopy offers a rapid, nondestructive, and contactless alternative. Correlating Raman data with results from a primary method enables the use of Raman spectroscopy as a secondary method for estimating amine value. This supports epoxy quality control by enabling fast, in-process qualitative analysis of intermediate and final products. This proof-of-concept study investigates the feasibility of using Raman spectroscopy to predict the AV of an epoxy hardener through correlation with titration.

INTRODUCTION

Amine value is traditionally determined using strong acid/weak base titration following ASTM methods [3]. While precise, this approach is labor intensive and requires chemicals, sample preparation, and sufficient time for complete titration through the endpoint. In contrast, Raman spectroscopy offers a faster, more efficient alternative and enables rapid,

nondestructive, and contactless analysis of hardeners with no need for sample preparation. This Application Note details the use of Raman spectroscopy to determine the AV of a hardener, with results validated through statistical comparison to conventional titration methods.

SAMPLE PREPARATION

Although AV can be directly assessed from a material using Raman spectroscopy, the hardener was first dissolved in glacial acetic acid (AcOH) following the protocol described in Application Note [AN-T-239](#). This approach ensures that both Raman spectroscopy and potentiometric titration (**Figure 1**) were performed on identical test solutions, enabling a valid comparison between the two methods.

Samples prepared from a commercially available epoxy resin kit were categorized into calibration, validation, and unknown (blind) sets. The calibration set was prepared by dissolving 0 (blank), 68, 116, 208, 315, and 554 mg of the hardener in 25 mL of AcOH. Validation samples were prepared with 308 and 514 mg of the hardener in the same solvent volume. Additionally, five blind samples (A–E) with unknown hardener amounts were prepared to evaluate the model's performance. All samples were prepared in 100 mL beakers.



Figure 1. Metrohm has cutting-edge Raman and titration solutions for all your analysis needs.

Amine value was calculated in this manner:

$$\text{Amine value (mg KOH/g)} = \frac{(V_1 - V_2) \times N \times 56.1}{m}$$

V_1 = volume of HClO_4 consumed by the sample (mL)

V_2 = volume of HClO_4 consumed by the blank (mL)

N = normality of the HClO_4 solution

m = mass of the sample (g)

Calculated AV is independent of the amount of hardener in the solution, as the formula normalizes based on sample mass. Thus, a standard sample mass of 0.5 g was assumed for all AV measurements.

Raman spectra were collected by positioning the probe against the outer wall of the beaker containing test samples. This contactless approach minimizes contamination and ensures reproducible measurement. Instrument and accessory specifications are summarized in Table 1.

Table 1. Raman and titration systems used for the study.

Raman-system	
Laser-excitation	785 nm (preferred)
Accessory	BAC102 Fiber Probe
Software	SpecSuite
Titration system	
Titration	907 Titrando
Burette	Dosino (50 mL)
Electrode	Solvotrode
Software	OMNIS

RESULTS

Titration

According to titration, AVs of the calibration set were 30.8, 54.9, 95.2, 147.7, 196.0, and 258.7 mg KOH/g. The calibration model based on titration volume yielded a near-perfect linear correlation, with $R^2 = 1.0000$, and RMSEC (root mean square error of calibration) of 0.018 (Figure 2). The predicted AVs for the validation samples were 144.1 and 241.9 mg KOH/g for the 308 and 514 mg samples, respectively, deviating $\pm 0.2\%$ from measured values.



Figure 2. Calibration and validation data for Raman-based prediction (green) and titration (red) of amine concentration.

Raman spectra of the hardener and solvent

The hardener exhibited a strong Raman peak at 1002 cm^{-1} which is consistent with aromatic amines such as aniline and phenylenediamine (Figure 3). Glacial acetic acid showed a significant peak attributed to C–C vibration at 893 cm^{-1} . The regions 650–850, 930–1270, and 1550–1630 cm^{-1} demonstrated minimal spectral overlap between the hardener and AcOH, making them suitable vibrational bands for quantitative analysis of AV.

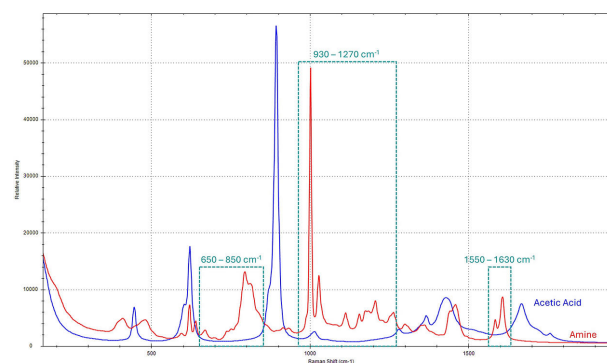


Figure 3. Raman spectra of the hardener and AcOH. Spectral regions used for chemometric analysis are highlighted in green boxes.

Amine quantification with Raman

The intensity of the 1003 cm^{-1} Raman peak increased proportionally with AV, exhibiting a strong linear correlation (Figure 4). Simple linear regression yielded $R^2 = 0.9965$ even without advanced chemometric techniques. This result highlights Raman spectroscopy's intrinsic quantitative capabilities through direct peak intensity/concentration correlation.

A more comprehensive calibration model incorporating key vibrational bands further improved performance, achieving $R^2 = 0.9999$ and RMSEC = 0.79. This model accurately predicted the AV of validation samples with a deviation of $\pm 0.5\%$ from measured values (Figure 2). The Raman-based results were highly consistent with those obtained by titration. These findings support the use of Raman spectroscopy as a reliable secondary technique for the rapid, nondestructive estimation of AV in epoxy formulations.

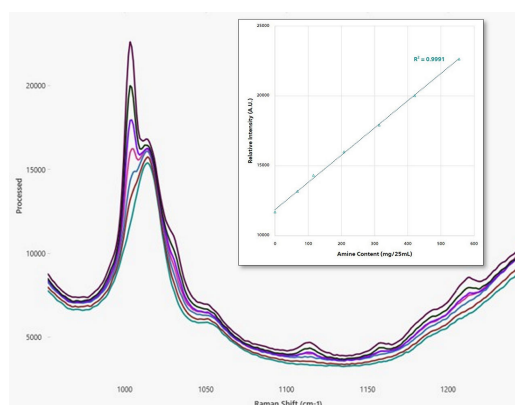


Figure 4. Raman spectra of calibration standards and simple linear regression of Raman intensity versus AV.

Unknown sample evaluation

The AV of the blind samples was predicted using the Raman calibration model and compared to titration results (Table 2). The Raman-predicted AVs closely matched those obtained by titration, with deviation ranging from 0.10–4.4% and RMSE = 2.53. This demonstrates that Raman spectroscopy is a reliable secondary method for AV determination.

Titration in this study has an inherent error margin of approximately ±2%. Because Raman spectroscopy is a secondary method, it inherently carries the uncertainty of the primary method, including sample

preparation variability. As a result, the total error in Raman-predicted AV will generally exceed that of titration, unless Raman is independently validated as a primary method. The actual error attributable to the Raman technique alone is likely smaller than the observed total error, which includes the propagated uncertainty from the titration reference. Furthermore, the accuracy and robustness of the Raman calibration model are expected to improve with the inclusion of a larger and more diverse dataset.

Table 2. Comparison of predicted AV in blind samples using Raman spectroscopy and titration.

Amine value (mg KOH/g)		
Sample	Titration	Raman-predicted
A	245.3	245.5
B	193.0	190.8
C	101.9	97.7
D	96.3	93.9
E	63.5	61.8
RMSE		2.53

CONCLUSION

Raman spectroscopy serves as a rapid and reliable secondary method for estimating the AV of epoxy hardeners. Raman predictions using a calibration model based on characteristic vibrational bands showed excellent agreement with standard potentiometric titration, with deviations within ±3%. Validation with blind samples further confirmed its

accuracy. While titration remains the primary method for determining AV, Raman spectroscopy offers significant advantages with its speed, simplicity, and nondestructive nature, making it well-suited for supplemental use in quality control and process monitoring of epoxy resin systems.

REFERENCES

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2. *Standard Test Methods for Total, Primary, Secondary, and Tertiary Amine Values of Fatty Amines by Alternative Indicator Method*. <https://store.astm.org/d2074-07r19.html> (accessed 2025-06-17).
3. Izumi, A.; Shudo, Y.; Shibayama, M. Network Structure Evolution of a Hexamethylenetetramine-Cured Phenolic Resin. *Polym J* **2019**, *51* (2), 155–160. <https://doi.org/10.1038/s41428-018-0133-8>.

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CONFIGURATION



Sonde Raman haut débit avec déclencheur (785 nm)

Ensemble de sonde Raman à fibre optique à haut débit de qualité de laboratoire avec déclencheur manuel diamètre de 105 μm fibre 0,22NA pour excitation 785 nm diamètre de 300 μm 0,22NA pour capture Raman, densité optique >6 ; jusqu'à 150 cm^{-1} ; longueur de fibre de 1,5 m terminée en FC/PC à l'extrémité côté spectromètre et FC/PC à l'extrémité côté laser. Fenêtre en quartz scellée par un adhésif pour l'échantillonnage sans contact. Distance de travail de 5,5 mm. Pas pour une utilisation en immersion. Cette sonde est compatible avec les familles i-Raman Prime et STRam.

BAC102-785-HT