

Inline Spectroscopy as Process Analytical Technology for Photoresins: Identity, Concentration, Conversion and Drift

Turning spectra into manufacturing decisions: sensor placement, calibration transfer, chemometrics and state attribution

Juan Segurola

3Dresyns by Resyner Technologies S.L.

© 2026 Juan Segurola. All Rights Reserved.

Correspondence: info@3Dresyns.com · www.3Dresyns.com

ER-342 · Engineering Review · Version 0.5 · 28 September 2026

Abstract

Inline spectroscopy becomes process analytical technology only when the optical interface, sampling volume, preprocessing and calibration model are controlled well enough to relate a spectrum to a declared material state. Window fouling, path length, bubbles, pigment scattering and local flow can dominate apparent spectral change. Chemometric models should declare calibration domain, reference method, preprocessing and prediction uncertainty. Real-time Raman can track depletion of reactive bands and reveal initiation, rate changes and endpoint behaviour. A spectrum can confirm that a material belongs to the expected class while still missing a concentration shift within that class. Qualification therefore depends on preserving the measured state, configuration and exception history needed to distinguish these mechanisms in production rather than relying on nominal recipe identity alone.

Keywords: inline spectroscopy; Raman; NIR; process analytical technology; photoresin; chemometrics; conversion; drift

1. Significance and scope

Inline spectroscopy becomes process analytical technology only when the optical interface, sampling volume, preprocessing and calibration model are controlled well enough to relate a spectrum to a declared material state. The engineering question is whether inline spectroscopy can distinguish material identity, concentration, conversion and drift within a validated calibration domain while remaining robust to optical-path and process changes. The review focuses on evidence that supports repeatable manufacturing decisions and excludes proprietary recipes, supplier-specific settings and undocumented operator heuristics.

1.1 Corpus boundary

ER-342 owns inline or at-line spectroscopic measurement used to infer photoresin identity, concentration, conversion or drift during manufacturing. It does not own standalone laboratory spectroscopy as a generic analytical technique or printer optical-dose calibration. ER-341 owns blending scale-up and ER-343 owns machine-health monitoring and predictive-maintenance decision logic; ER-342 is limited to spectroscopic inference of material state, calibration-domain validity and spectral drift.

2. A spectrum is not yet a process measurement

Inline spectroscopy becomes process analytical technology only when the optical interface, sampling volume, preprocessing and calibration model are controlled well enough to relate a spectrum to a declared material state. Raman is especially useful for reactive-group tracking in photopolymerisation, while NIR can support composition and cure-state monitoring where broad overtone bands are handled by multivariate models [1-3].

3. Probe geometry defines what is being measured

Window fouling, path length, bubbles, pigment scattering and local flow can dominate apparent spectral change. The installation must therefore document probe location, optical geometry, cleaning state and whether the sampled volume is representative of the bulk. A calibration developed on cuvette spectra cannot be assumed transferable to an immersed fibre probe [1,3].

4. Calibration models require bounded use

Chemometric models should declare calibration domain, reference method, preprocessing and prediction uncertainty. Drift detection is not the same as concentration prediction: a residual or distance metric may be the correct tool when the objective is to detect departure from a qualified spectral population rather than estimate a constituent [3,4].

5. Conversion monitoring needs kinetics-aware interpretation

Real-time Raman can track depletion of reactive bands and reveal initiation, rate changes and endpoint behaviour [1,2]. However, the spectroscopic conversion measured at the probe is local and may not represent the whole vessel or a cured part. Temperature, light distribution and oxygen exposure must be recorded when conversion is used as a process-state variable.

6. Identity and concentration are separate claims

A spectrum can confirm that a material belongs to the expected class while still missing a concentration shift within that class. Conversely, a quantitative model can predict one constituent while remaining blind to an unexpected contaminant. Qualification should therefore separate identity classification, constituent prediction and out-of-model detection [3,4].

7. Qualification architecture

A robust implementation links spectral acquisition to a traceable reference method, challenges the model with expected sources of variation and defines rules for recalibration. The acceptance logic should be frozen before production data are reviewed to avoid moving thresholds to fit historical batches [3-5].

8. Evidence hierarchy and transfer

The strongest transfer evidence uses independent reference assays, multiple batches and deliberate variation in temperature, turbidity and probe condition. Successful transfer between instruments requires wavelength, intensity and preprocessing comparability rather than simply loading the same regression coefficients [3-5].

Table 1. Qualification matrix for inline spectroscopy as process analytical technology for photoresins.

PAT function	Model output	Primary validation
Identity	Class membership / spectral distance	Known-positive and challenge materials
Concentration	Predicted constituent level	Independent assay
Conversion	Reactive-band or multivariate endpoint	Reference conversion method
Drift	Distance/residual statistic	Historical and induced drift sets
Probe health	Signal quality indicators	Window/fouling challenges

9. Interpretation matrix

For inline spectroscopic PAT, a spectral excursion may reflect real chemistry, probe fouling, optical-path change or calibration-domain failure. Interpretation should combine spectral residuals with reference-standard checks, probe condition and the applicable calibration model before material drift is concluded.

Table 2. Diagnostic interpretation matrix for inline spectroscopic PAT.

Failure mode	Misleading interpretation	Required control
Window fouling	False composition drift	Probe-health metric
Bubbles/scatter	Baseline or intensity change	Flow/degassing challenge
Temperature shift	Spectral displacement	Temperature compensation
Out-of-domain sample	Confident but invalid prediction	Leverage/residual alarm

10. Limitations and evidence gaps

Inline spectroscopic performance depends strongly on probe geometry, optical path, scattering, temperature and the calibration population used to build the model. Published photoresin studies do not yet establish universal detection limits or transfer rules across instruments and formulations. A PAT model should therefore be treated as valid only inside a declared calibration domain and requalified when the optical interface or material family changes.

11. Conclusions

Inline spectroscopy can become a useful PAT layer for photoresins when identity, concentration or conversion signals are linked to a controlled optical interface and a bounded calibration model. Its value lies in detecting material-state drift early, not in replacing independent reference measurements. Transfer requires explicit verification of probe geometry, preprocessing and model domain.

References

1. Jessop JLP. A Practical Primer: Raman Spectroscopy for Monitoring of Photopolymerization Systems. *Polymers*. 2023;15(18):3835. doi:10.3390/polym15183835.
2. Bai YR, Chai KL. Real-Time Raman Monitoring of Photopolymerization in Rubber-Acrylate Networks for Assessing the Impact of Initiator Concentration on Grafting, Kinetic and Thermal Stability. *Journal of Physical Chemistry B*. 2026;130(24):6198-6207. doi:10.1021/acs.jpcb.5c08542.
3. Chang C, Feng L-F, Gu X-P, Zhang C-L, Dai L-K, Chen X, Hu G-H. In Situ Raman Spectroscopy Real-Time Monitoring of a Polyester Polymerization Process for Subsequent Process Optimization and Control. *Industrial & Engineering Chemistry Research*. 2022;61(49):17993-18003. doi:10.1021/acs.iecr.2c02933.
4. ISO/ASTM 52920:2023. Additive manufacturing - Qualification principles - Requirements for industrial additive manufacturing processes and production sites. ISO, Geneva, 2023.
5. ANSI/ISA-95.00.01-2025 (IEC 62264-1 Modified). Enterprise-Control System Integration - Part 1: Models and Terminology. International Society of Automation, 2025.

Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated for this review.