

Chemical and Gas Sensors Based on Printed Photopolymers: Sorption, Selectivity, Transduction and Regeneration

Qualifying printed chemical sensors by analyte partitioning, transport, cross-sensitivity, signal transduction and recovery after exposure

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Abstract

Printed photopolymers can serve as structural supports, sorptive matrices, diffusion barriers or active composites in chemical and gas sensors. Sensor output may arise from resistance, capacitance, optical response, mass change or swelling, but all routes begin with analyte transport and partitioning into an active region. High apparent sensitivity can therefore be caused by slow accumulation, humidity interference or irreversible swelling rather than selective transduction. Qualification links concentration, exposure time and environmental state to both analyte uptake and output. Response and recovery time, sensitivity, limit of quantification, cross-sensitivity, baseline drift and regeneration efficiency define the usable sensor state. The engineering outcome is a qualified analyte range, an interference envelope and a regeneration or replacement rule. [1,2]

Keywords: gas sensor; chemical sensor; sorption; chemiresistor; selectivity; regeneration

1. Qualification problem: chemical and gas sensors based on printed photopolymers

Chemical-sensor qualification requires a concentration interval, an interference/environment envelope and a regeneration or replacement rule. Partitioning into the active phase, transport through the printed path and signal relative to baseline noise are treated as distinct stages of the measurement chain.

1.1 Scope boundary.

ER-379 treats gas or chemical recognition through analyte partitioning, transport and a physicochemical transduction step in printed polymer structures. ER-380 owns affinity-based biosensing in liquid matrices, and ER-373 owns humidity as an actuation stimulus; sorption is shared physics but the acceptance variables and calibration problems are different.

2. Governing balances for chemical and gas sensors based on printed photopolymers

Chemical sensing begins before the transducer. External analyte must reach the surface, partition into or react with an active phase, diffuse through the relevant path and then alter a measurable electrical, optical, mass or dimensional property. The rate-limiting stage can change with concentration, flow, thickness and temperature. A response curve therefore conflates transport and transduction unless these stages are independently challenged. [1,2,3]

Gas or vapour first partitions into the polymer or active coating, then diffuses through it and alters an electrical, optical, mass or dimensional property. [1,2]

Conductive-polymer chemiresistors can respond through doping, charge transfer or swelling-driven changes in conductive pathways. [1]

Selectivity is rarely intrinsic to one signal magnitude; it depends on differential response across analytes, humidity, temperature and exposure history. [1,2]

A valid sensing record follows analyte from external concentration through partitioning and diffusion to the transducer output, keeping environmental interferents visible at each stage.

3. Regime boundaries for chemical and gas sensors based on printed photopolymers

At low concentration, performance is limited by signal-to-noise and background drift. In the calibrated regime, response can be related reproducibly to concentration for a defined environmental state. At high loading, sorption sites or transduction can saturate and recovery may become slow or incomplete. Humidity, interferents and mixtures can shift all three boundaries by competing for uptake or changing baseline conductivity. [1,2,3]

Table 1 separates the analyte partition coefficient in the active phase, diffusion time through the printed active path and signal increment per concentration divided by baseline noise. A sensor can fail any one of these even when its nominal sensitivity appears high.

Table 1. Regime indicators and engineering use.

The sensor range is the overlap of partitioning, transport and transduction evidence; concentration limits cannot be extrapolated solely from an electrical response curve.

Indicator	Engineering meaning	Use
analyte partition coefficient in the active phase	Measures how strongly the target analyte is concentrated in the sensing polymer relative to the surrounding phase.	Used to determine whether a concentration calibration can transfer to another polymer state or environment.
diffusion time through the printed active path	Represents the transport delay imposed by active-layer thickness and analyte diffusivity.	Used to set readout time and geometry limits before slow transport is mistaken for weak sensitivity.
signal increment per concentration divided by baseline noise	Combines transduction slope with the background variation that limits useful detection.	Used to set the concentration range and to judge when regeneration or replacement is required.

4. Couplings that move the chemical and gas sensors based on printed photopolymers

Printed geometry couples sensitivity to time response. A thick sorptive region can increase uptake but extends diffusion time; porosity can shorten transport paths while increasing surface contamination and environmental sensitivity. Post-cure can change free volume and polar chemistry, and conductive fillers can alter both sorption and electrical pathways. These couplings mean that calibration belongs to the final printed and conditioned state, not merely to the nominal sensing chemistry. [1,2,3]

Printed porosity and thickness change mass-transfer resistance and therefore response time. [1,2]

Humidity can compete for sorption sites, change ionic conductivity or swell the matrix, creating large cross-sensitivity. [1,2]

Cleaning and post-cure can alter baseline response or analyte uptake; their effect is therefore checked with blanks and calibration standards instead of assumed from nominal chemistry. [1,2]

5. Failure signatures and false diagnoses

A weak signal can originate from poor partitioning, slow diffusion, transducer degradation or competing interferents. A slow recovery can reflect low desorption rate, dead volume or irreversible chemical change. Thickness and flow perturbations distinguish internal diffusion from chamber exchange, while independent uptake measurements separate partitioning from transduction. Interferent-only and blank exposures are essential branches of the fault tree. [1,2,3]

A smaller chemical-sensor signal can result from reduced partitioning, slower transport, transducer drift or competitive interference. Thickness and exposure-time tests, blanks, interferent challenges and independent calibration are used to assign the dominant cause.

Table 2. Failure-mode discrimination and required evidence.

Failure mode	Observable signature	Discriminating evidence
irreversible sorption or swelling	baseline does not recover after purge	extended clean-gas purge with mass or dimensional check
humidity interference	signal follows humidity changes at zero analyte	orthogonal humidity sweep at fixed analyte concentration
sensor poisoning or chemistry drift	sensitivity decreases after repeated high-concentration exposure	calibration before and after challenge exposure
transport-limited false selectivity	slow species appears less sensitive because the exposure is too short	exposure-duration sweep to near-equilibrium

6. Measuring chemical and gas sensors based on printed photopolymers with traceable uncertainty

Calibration should be designed around the complete measurement chain. Gas composition, concentration-generation method, flow, pressure, temperature and humidity need traceable control, and the sensor should be allowed to reach a defined baseline state before exposure. Response magnitude alone is not enough: response time, recovery time, baseline noise and drift determine whether a signal is usable. [1,2,3]

Partitioning and transport should be measured independently whenever possible. Gravimetric uptake, spectroscopy or a reference sorption measurement can establish whether a weak signal reflects poor analyte uptake or an insensitive transducer. Thickness series are especially valuable because diffusion-limited response time should change with transport length, whereas an intrinsic transduction coefficient should not. [1,2]

Use calibrated gas or vapour concentrations with known flow, humidity and temperature. Record the raw transduction variable together with response and recovery times. For sorptive systems, mass change or an independent uptake measurement strengthens mechanism assignment. Calibration should include blanks and interfering species, and baseline noise must be measured over the same timescale used for detection. [1,2]

7. Experiments that discriminate competing mechanisms

Selectivity must be challenged with realistic interferents rather than inferred from a target-gas calibration. The relevant comparison is the sensor output in mixtures, humidity and temperature states that resemble service, including compounds that compete for the same sorption or reaction sites. Modern selectivity reviews emphasize that simple response ratios between isolated analytes can overstate practical discrimination. [3]

Regeneration provides another causal test. If the baseline and calibration slope return after purge, heating or another defined regeneration route, reversible sorption is supported; if sensitivity or baseline shifts cumulatively, irreversible chemistry, residual swelling or transducer ageing becomes more plausible. Multiple regeneration cycles should be evaluated because a single recovery event cannot establish reusability. [1,2,3]

Begin with concentration steps for the target analyte at controlled humidity, then repeat a subset with likely interferents. Vary active-layer thickness to determine whether response is diffusion limited. Challenge the sensor with a high concentration, regenerate under the intended purge or heating protocol and repeat the calibration. A second environmental temperature or humidity state tests whether the calibration transfers. [1]

8. Model identification and validation for chemical and gas sensors based on printed photopolymers

A mechanistic model should separate external mass transfer, partitioning, internal diffusion and transduction. Fitting a single exponential to the sensor output can describe a waveform but cannot identify which stage controls it. Changing flow and active-layer thickness provides the minimum perturbation set needed to distinguish boundary-layer limitation from internal diffusion. [1,2]

For chemiresistive devices, the electrical model should also account for humidity and temperature dependence of baseline conductivity. Sensor-array or multivariate approaches can improve discrimination, but they introduce training-set coverage and drift as new qualification variables. A classifier validated on one environmental distribution should not be treated as selective outside that distribution without new mixture data. [1,3]

A chemical-sensor model is built in layers: analyte partitioning into the active polymer, diffusion time through the printed active path, and conversion of local analyte loading into an electrical, optical or mechanical signal. The transduction calibration is not fitted until transport has been shown not to dominate the response.

Identifiability is tested by varying active-layer thickness and flow or exposure time. A response that scales with diffusion length is not interpreted as a change in intrinsic sensitivity. Interferents are introduced at concentrations relevant to the claimed environment so selectivity is measured rather than inferred from target-analyte calibration alone.

Concentration preparation, environmental state, thickness and signal noise enter separate uncertainty terms. Partitioning controls the concentration-transfer limit, diffusion controls the time-to-reading claim, and baseline noise controls the minimum usable signal. Regeneration is accepted only if repeated calibrations remain inside those uncertainties.

9. Qualification envelope and technology decisions

The qualification envelope should state analyte identity, concentration range, mixture/interference set, humidity, temperature, flow, active-layer geometry, response/recovery criteria, baseline stability and allowed regeneration cycles. Limit of detection is not transferable outside the noise and environmental conditions used to derive it. A sensor is acceptable only when target response remains distinguishable from drift and interferents across the claimed domain. [1,2,3]

Table 3. Technology-decision matrix.

ER-379 separates concentration range, interference/environment envelope and regeneration criterion. A calibration slope is accepted only for the transport state and background composition that produced it, and regeneration is a repeated-calibration question rather than a visual recovery test.

Decision	Minimum evidence	Acceptance logic
qualified analyte concentration range	Calibrated measurements spanning the proposed limit for qualified analyte concentration range, with at least one independent replicate near the boundary and the controlling analyte partition coefficient in the active phase reported with uncertainty.	Accept only while the measured response remains inside the stated boundary and the challenge 'extended clean-gas purge with mass or dimensional check' does not trigger irreversible sorption or swelling or move baseline does not recover after purge outside the qualified range.
interference and environmental envelope	Calibrated measurements spanning the proposed limit for interference and environmental envelope, with at least one independent replicate near the boundary and the controlling diffusion time through the printed active path reported with uncertainty.	Accept only while the measured response remains inside the stated boundary and the challenge 'orthogonal humidity sweep at fixed analyte concentration' does not trigger humidity interference or move signal follows humidity changes at zero analyte outside the qualified range.
regeneration or replacement criterion	Calibrated measurements spanning the proposed limit for regeneration or replacement criterion, with at least one independent replicate near the boundary and the controlling signal increment per concentration divided by baseline noise reported with uncertainty.	Accept only while the measured response remains inside the stated boundary and the challenge 'calibration before and after challenge exposure' does not trigger sensor poisoning or chemistry drift or move sensitivity decreases after repeated high-concentration exposure outside the qualified range.

10. Design consequences for chemical and gas sensors based on printed photopolymers

Design should begin from the required analyte, concentration window and interference set. A highly sorptive matrix can increase sensitivity but also slow recovery and amplify memory effects. Porosity and thin active paths shorten diffusion times but may reduce capacity or increase susceptibility to contamination. The active chemistry, transport geometry and transducer therefore need to be optimized as one system. [1,2,3]

Printed photopolymers add process-state variables that are often neglected in gas-sensor demonstrations. Post-cure can change residual monomer, free volume and polarity; cleaning can remove species that previously contributed to baseline conduction; surface texture changes exposed area. These process steps should be locked in the calibration record, and a process change should trigger at least blank, target and interferent rechecks. [1,2]

Selectivity should be engineered at the system level through active chemistry, diffusion control, sensor arrays or orthogonal signals. Thicker sorptive layers can increase capacity but slow response and recovery. Printed channels should minimize dead volume when rapid gas exchange is required. Regeneration energy and time are part of the device specification, not an afterthought. [1,2]

Chemical-sensor process control links post-cure, porosity, active-path thickness and surface treatment to the relevant transport or transduction test. Cleaning changes are screened with blanks and partitioning checks before calibration reuse, because removal of residual species can shift both baseline and analyte uptake.

11. Evidence gaps for chemical and gas sensors based on printed photopolymers

The largest evidence gap is performance in complex mixtures over long time. Single-analyte chamber tests do not represent environments where humidity, temperature and multiple vapours vary together. Future studies should use mixture matrices and report uncertainty on concentration generation as well as sensor response. [1,2,3]

A second gap is regeneration durability and calibration drift. Repeated adsorption-desorption cycles can alter polymer free volume, conductive pathways or surface chemistry even when the sensor visually recovers. Longitudinal datasets should therefore retain the full baseline and calibration history and specify a replacement criterion when regenerated performance leaves the qualified envelope. [1,2,3]

Printed photopolymer gas sensors need more long-term studies that track post-cure ageing, residual monomer loss and humidity effects on calibration. Real-world mixtures are underrepresented compared with single-analyte demonstrations. Future work should report complete exposure waveforms, environmental conditions, recovery criteria and repeated calibration after regeneration. [1,2]

Chemical-sensor datasets should combine calibrated analyte histories, humidity and temperature, raw transducer output and active-path geometry, with interferent and blank exposures interleaved rather than run separately. Regeneration cycles should preserve the complete baseline history so apparent recovery can be tested quantitatively.

A printed polymer-composite vapour sensor provides a quantitative example of sorption-percolation coupling. Kennedy et al. reported FDM-printed PVDF/MWCNT chemiresistors with conductivity near $3 \times 10^{-2} \text{ S cm}^{-1}$; lower nanotube loading produced resistance changes up to 161% after 3 min for strongly sorbing organic vapours such as acetone and ethyl acetate. The manufacturing route is not vat photopolymerization, so the numbers are not transferable to photocurable matrices, but the experiment directly demonstrates why polymer-analyte partitioning, conductive-network proximity to percolation and regeneration history must be separated. [4]

12. Qualification outcome for chemical and gas sensors based on printed photopolymers

The final engineering claim is therefore calibration-specific. Changes in analyte matrix, humidity range, active-layer thickness, post-cure, cleaning or regeneration protocol modify transport or baseline state and require renewed calibration and interference testing rather than simple reuse of the original sensitivity value.

Qualification is limited to the tested analyte, concentration range, flow, humidity, temperature, active-layer geometry and regeneration history. Sensitivity, selectivity and recovery are independent acceptance limits.

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L.; ER-379 contains no comparative recommendation between commercial products.

Data availability

ER-379 is a literature-based engineering review; no new experimental dataset was generated.