

LIQUID CRYSTAL SENSORS FOR DOSIMETRY AND RAPID SENSING OF TOXIC GASES

Bart A. Grinwald, Sheila E. Robinson, Timothy G. Burland* & Bharat R. Acharya# Platypus Technologies LLC, 5520 Nobel Drive, Suite 100, Madison, WI 53711, USA

Summary

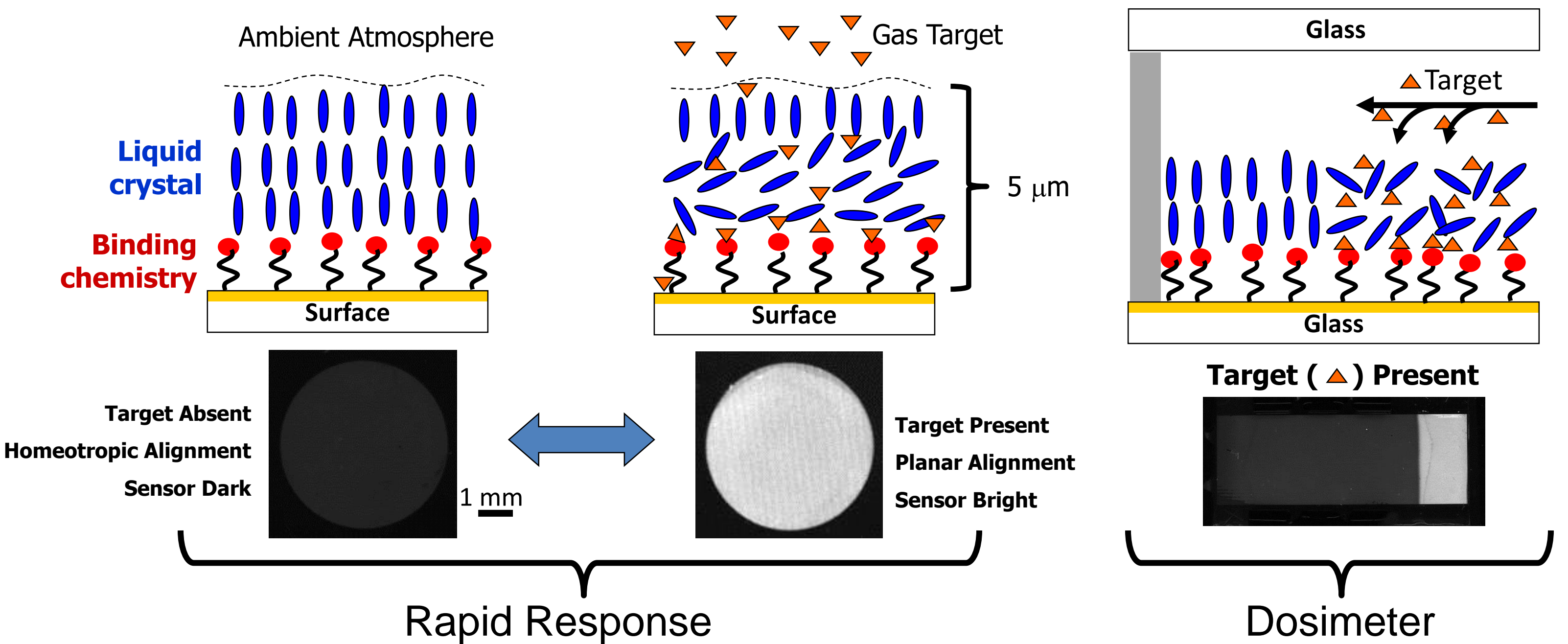
The same liquid crystals (LCs) used in TV and computer screens can also be used for gas sensing. Chemically reactive surfaces are fabricated that (i) align thin films of LC molecules in a specific orientation, and (ii) react with the target gas. Exposure to target gas then disrupts the alignment, and the LC sensors turn from dark to bright.

The ClearSense™ hydrogen sulfide (H₂S) dosimeter, a passive sampling device, detects H₂S more sensitively and with higher specificity than do electrochemical (EC) monitors. The dosimeter can be read with either a zero-power pocket viewer or a USB-powered digital reader. H₂S measurements correlate well with the OSHA-1008 method that pumps air through a sorbent tube, which must be sent to a certified laboratory for analysis. LC dosimeters in contrast provide a sensitive tool for immediate on-site assessment of personal exposure to H₂S, dispensing with the need to wait a week for laboratory analysis.

Fast-response LC sensors use similar surface chemistry principles with a distinct sensor design. Following appropriate chemical and physical optimizations, responses in less than 60 seconds to 100 ppb of H₂S, NO₂, and NH₃ has been achieved.

The light weight, low power requirements and versatile design formats facilitate application of LC sensors to industrial, environmental and defense monitoring needs. These LC sensing capabilities are also ideal for small unmanned vehicles that cannot accommodate traditional electrochemical (EC) sensors, which are either too heavy or too power-hungry or both.

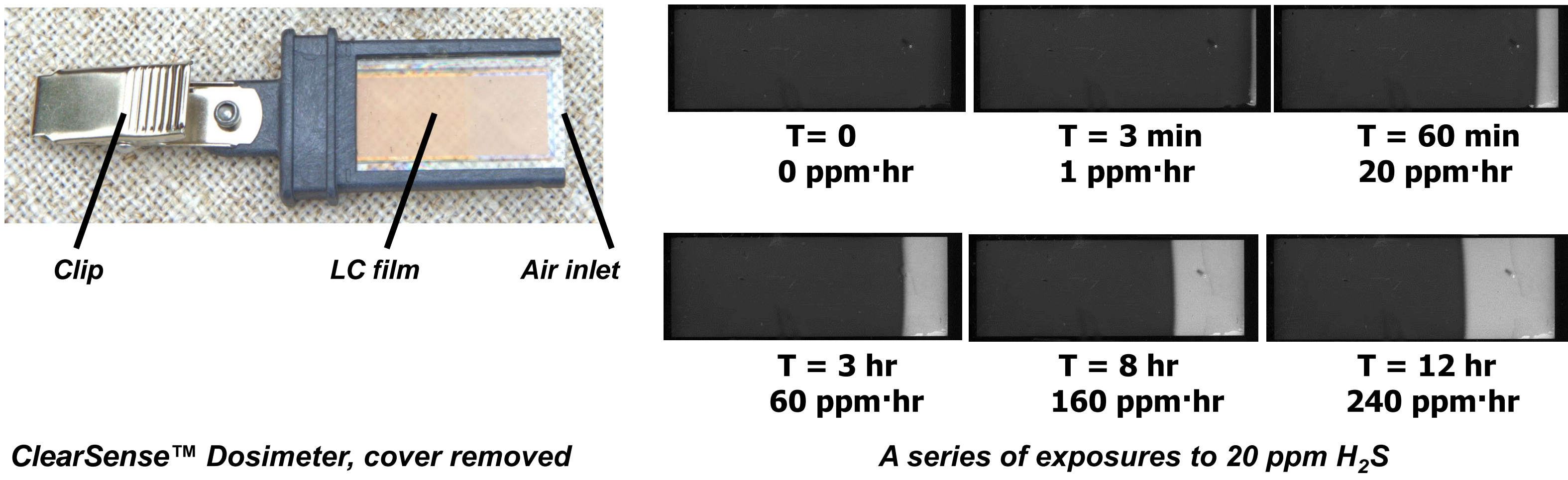
Liquid Crystal Sensing



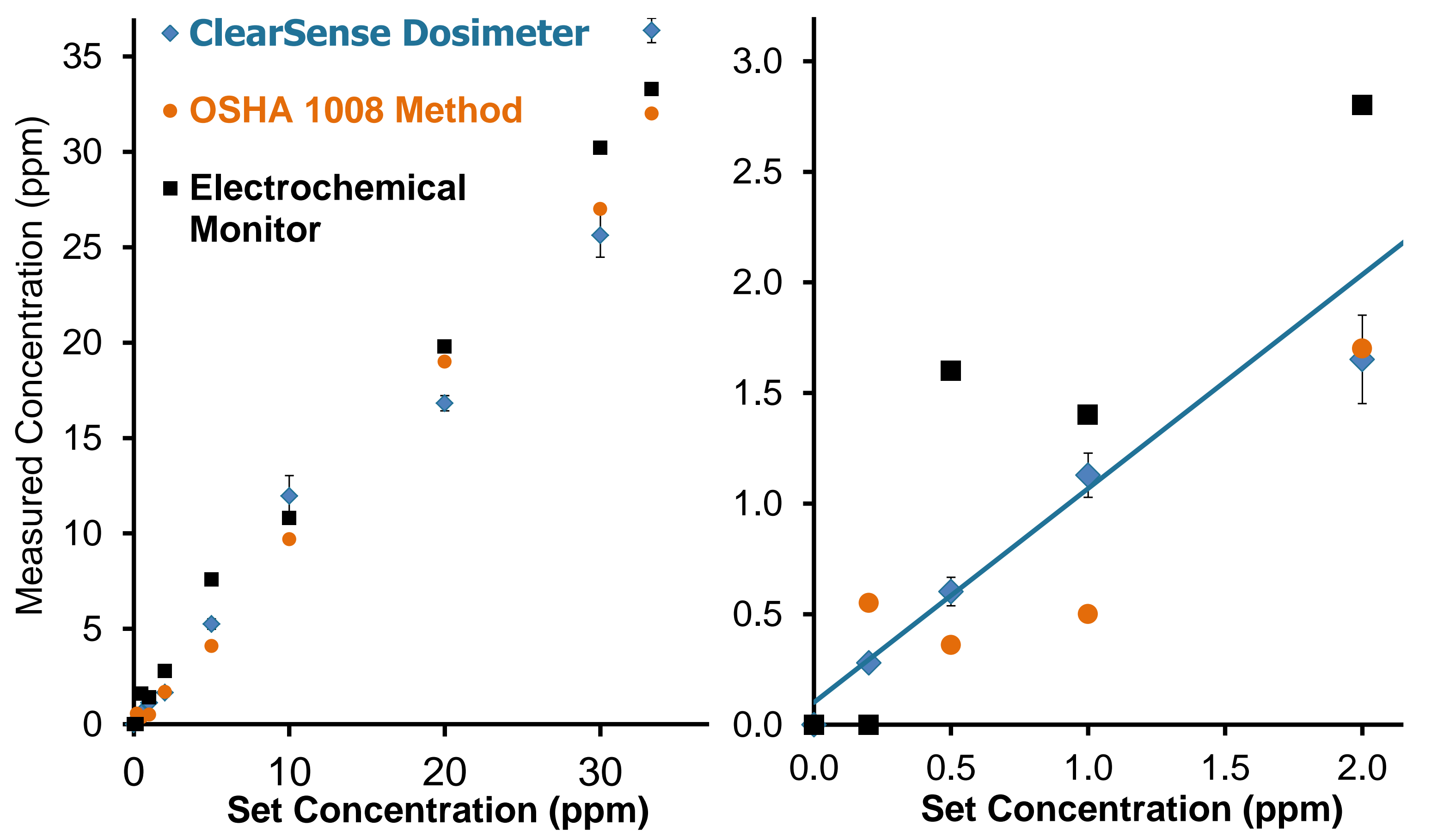
Rapid Response: Gold-coated glass slides are functionalized with reactive chemistries (red) that anchor the LCs (blue bars) in a homeotropic alignment. When viewed through crossed polarizers, the LC sensor appears dark before exposure (left image). When the open-faced sensor is exposed to the target gas, the gas reacts with the surface chemistry, which no longer anchors the LC molecules. As a result, the LC molecules assume a planar orientation and the sensor becomes bright (middle image).

Dosimeter: Using similar surface chemistry, the sensor is enclosed in a housing with only a narrow air inlet that controls diffusion of gas from one end. As the target gas reaches the LCs, the sensor turns bright from the exposed end inwards.

ClearSense™ H₂S Dosimeter

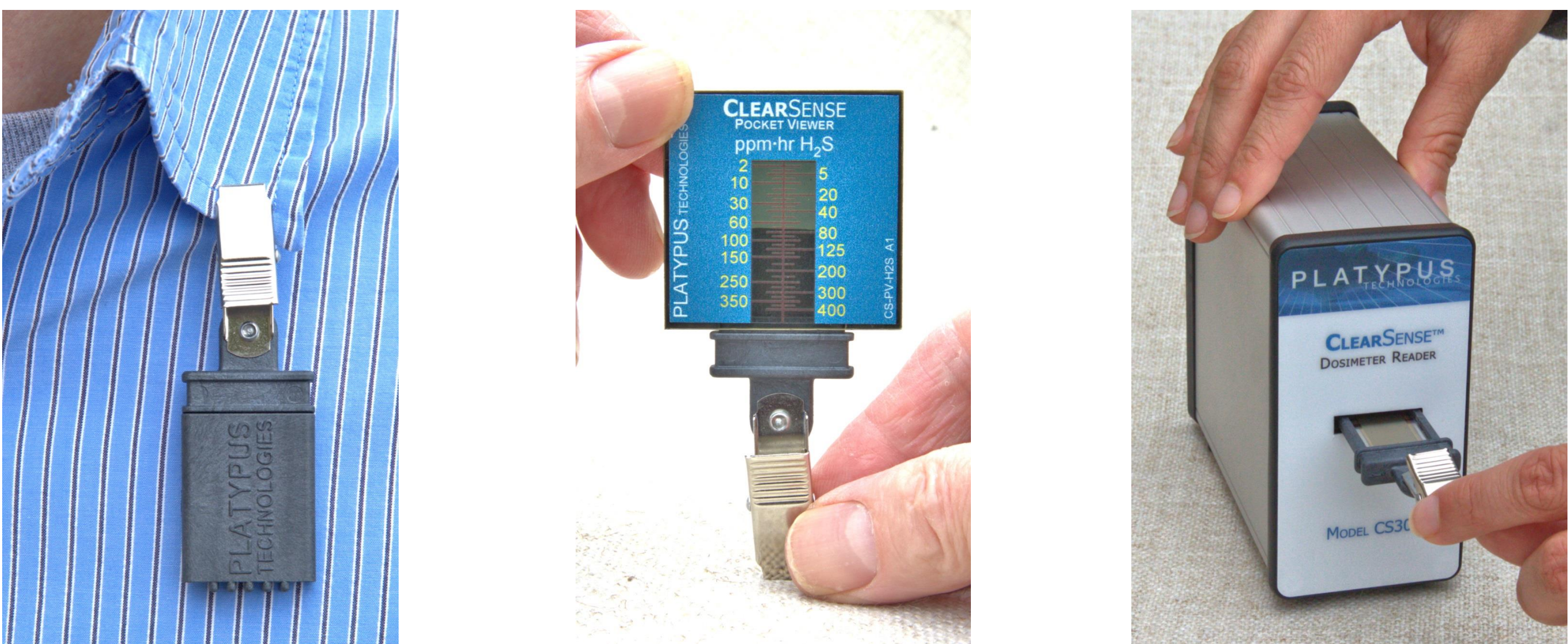


As gas diffuses across the sensor surface, a bright front lengthens in proportion to the dose of H₂S. Shown above left is a dosimeter with the cover removed. Above right is a series of images of dosimeters exposed to 20 ppm H₂S for 0-12 hr., viewed through crossed polarizers.



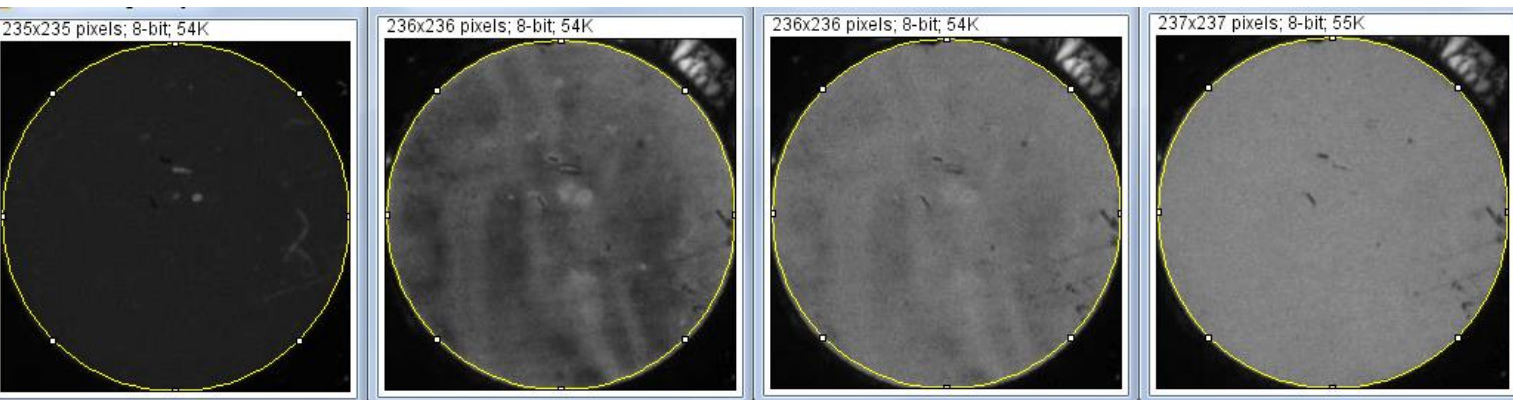
Laboratory validation of ClearSense™ Dosimeters. Five dosimeters each were exposed to nine different concentrations (0.2 to 33.3 ppm) of H₂S for different durations (15 min. to 12 hr.) at 60% RH. Using an algorithm, the concentrations were determined and compared with the concentrations measured using an EC Monitor and the OSHA-1008 method.

The ClearSense™ dosimeter response correlates well with OSHA-1008 measurements and with real-time EC monitor data, and below 5 ppm its linearity is superior to both. The OSHA method requires a sample tube, a calibrated pump, express shipment to a certified lab, and a week's wait for results, while the ClearSense™ dosimeter can be read immediately on site.



Fast-Response Sensors

Fast-response sensors are fabricated as 5-mm LC discs on glass substrates. For exposure the LC surface is completely open to the air. Gas exposures are monitored in real time, collecting camera images every ten seconds.

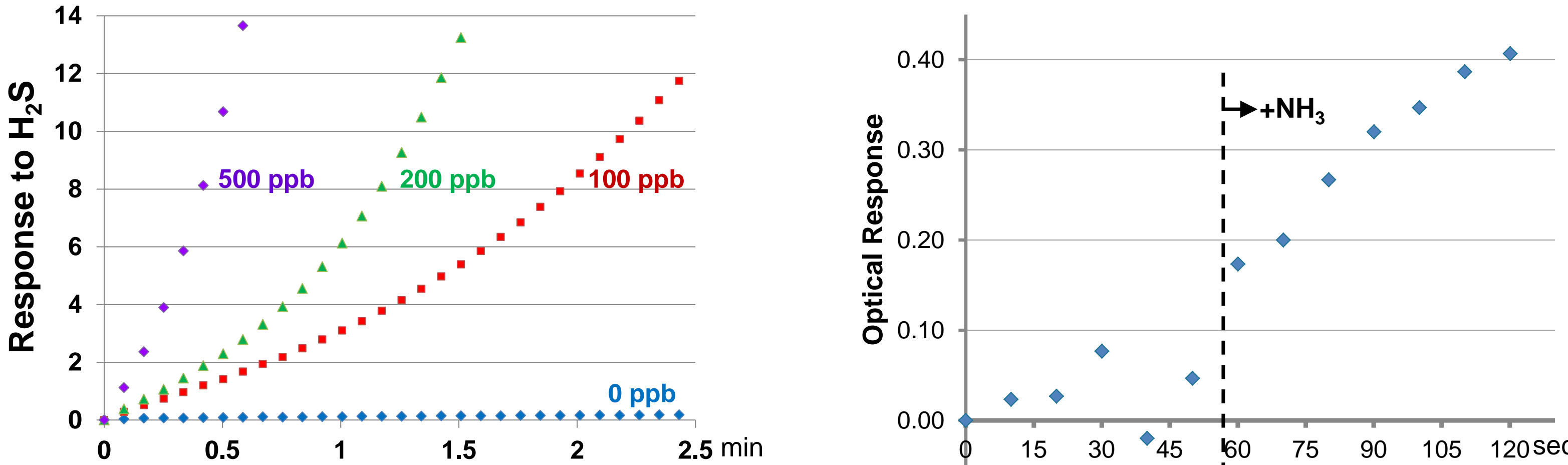


Increasing Sensitivity and Response Times

In order to generate faster responses than dosimeters, the surface chemistry underlying the LCs was modified and optimized, along with other fabrication steps, and LC film thickness was reduced from 5 μm to 1-2 μm.

Surface chemistry optimization centered on (i) screening diverse chemicals for responses to each gas, and (ii) reducing the surface density of LC binding sites.

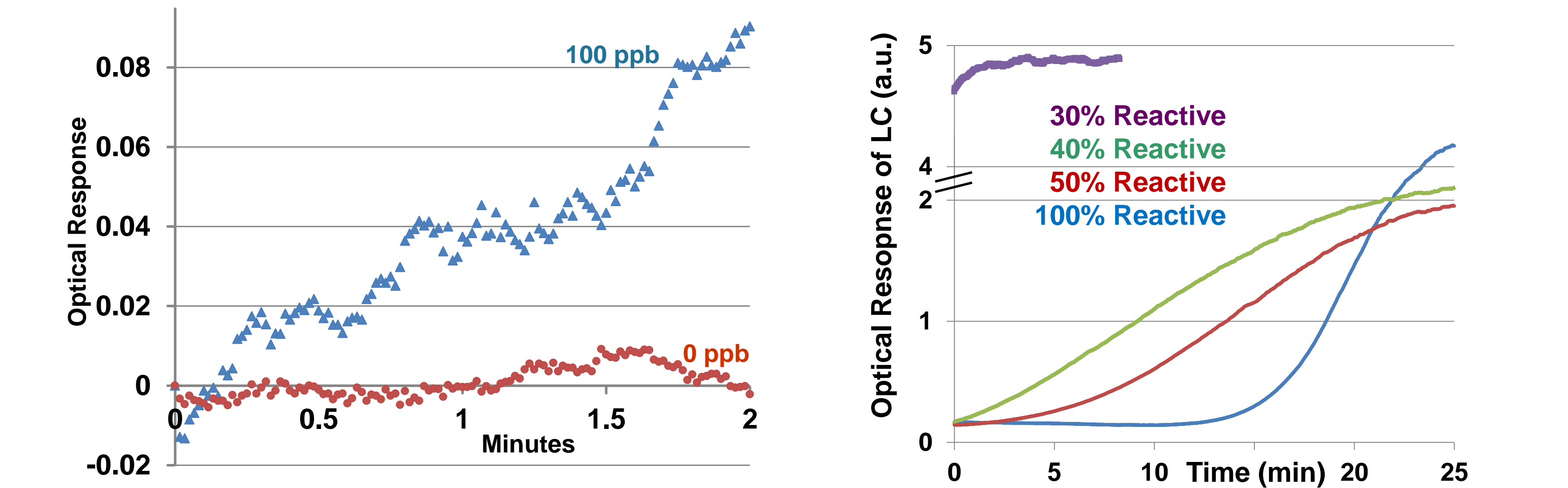
Hydrogen Sulfide & Ammonia



Fast Response Sensors: Left, H₂S sensor responses to 0-500 ppb target. Concentrations down to 100 ppb are detected within a minute, and response rates are a function of target concentration, i.e. the sensors are quantitative. Right, NH₃ sensor response to 100 ppb target again is measurable within a minute.

Nitrogen Dioxide

NO₂ sensor testing was done at 45% relative humidity in nitrogen rather than air since ambient air contains NO₂ levels from 10 - 50 ppb.



Fast Response NO₂ Sensor: Left, NO₂ sensor response to 100 ppb target within a minute. Right: How the proportion of surface binding sites impacts sensor responses to 1 ppm NO₂. As the reactive species is reduced, less energy is available to align the LC molecules, so the target gas more readily disrupts the alignment, generating a more sensitive response. Below a threshold level of reactive species, the LC molecules are not aligned at all and the sensor is bright to begin with.

Acknowledgements

We thank Nicholas Abbott, Jacob Hunter and Marco Bedolla (University of Wisconsin); and Kurt Kupcho, Laura Bremer, Matthew Gajeski and Anthony Moore (Platypus Technologies) for advice and assistance. This work was supported by contract W911SR-11-C-0025 from the US Army Edgewood Contracting Division, contract W911NF-13-P-0030 from the Army Research Office, SBIR Phase I award 1214980 from the National Science Foundation and Research Grant 1R21OH010116-01A1 from the National Institute of Occupational Safety and Health.

*Presenter; tburland@platypustech.com, 608.237.1274. #Present address: 3M Corp., Minneapolis, MN.

