

Chemistries for Protection and Decontamination

**Organic and Inorganic
Chemistry Workshop
Cambridge, MA
18-19 March 2008**

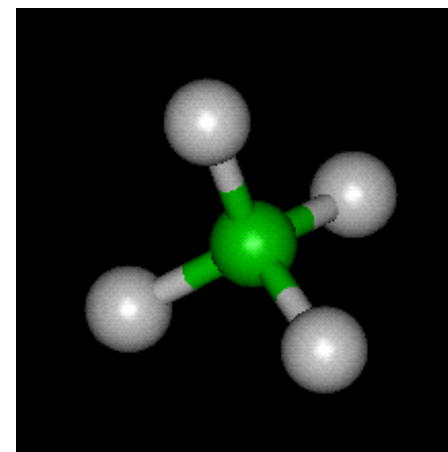
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Outline of Presentation

- **Protection**
 - Conductive polymer CW agent sensors for protective clothing
- **Hazard mitigation**
 - Electrochemically generated decon solution
 - Decon assurance spray
 - Catalytic self-decontaminating coatings



Conductive Polymer Sensors

- **Develop nerve agent sensors on an RFID platform for protective clothing**
 - Replace or augment heavy / bulky CWA sensing equipment with active RFID sensors

Integrated with uniform

Replace (or augment)
Gas chromatographs



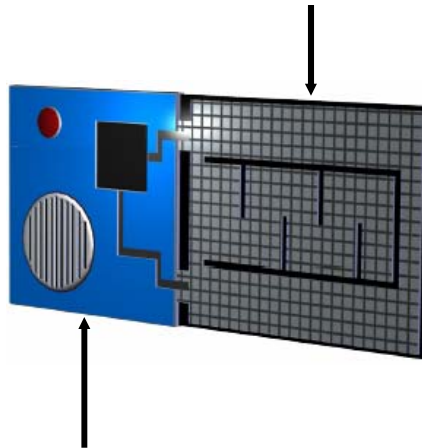
With RFID sensors



Technical Approach

Sensor concept:

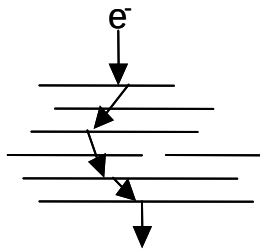
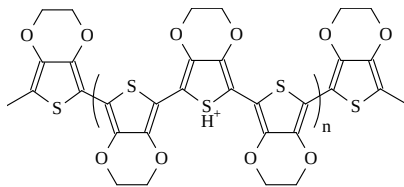
- (1) an easily printed conducting polymer thin film
- (2) that has a selective resistance response to the CWA



Existing RFID technology used to monitor resistance, record data, communicate

Conducting Polymers: Solubility Problem

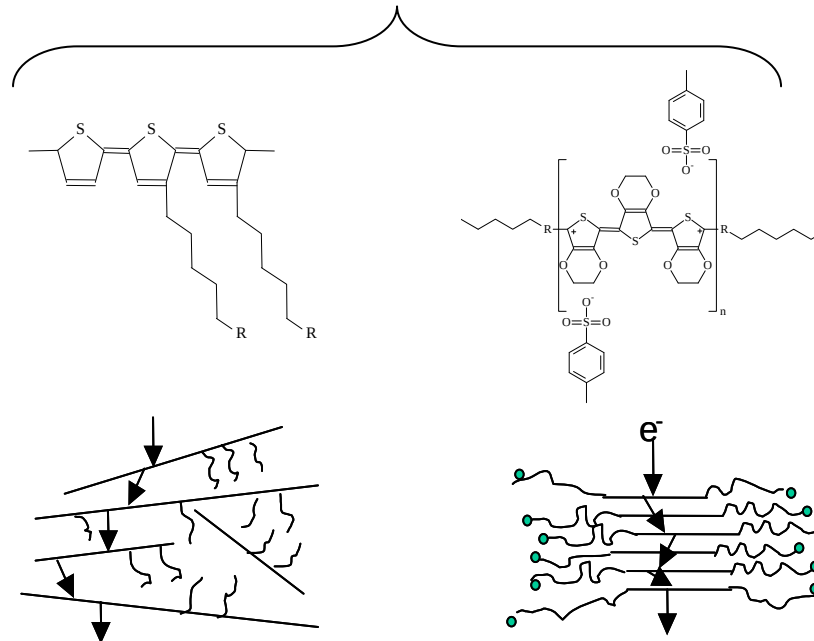
PEDOT
conducting polymer



Rigid Rods
crystallize

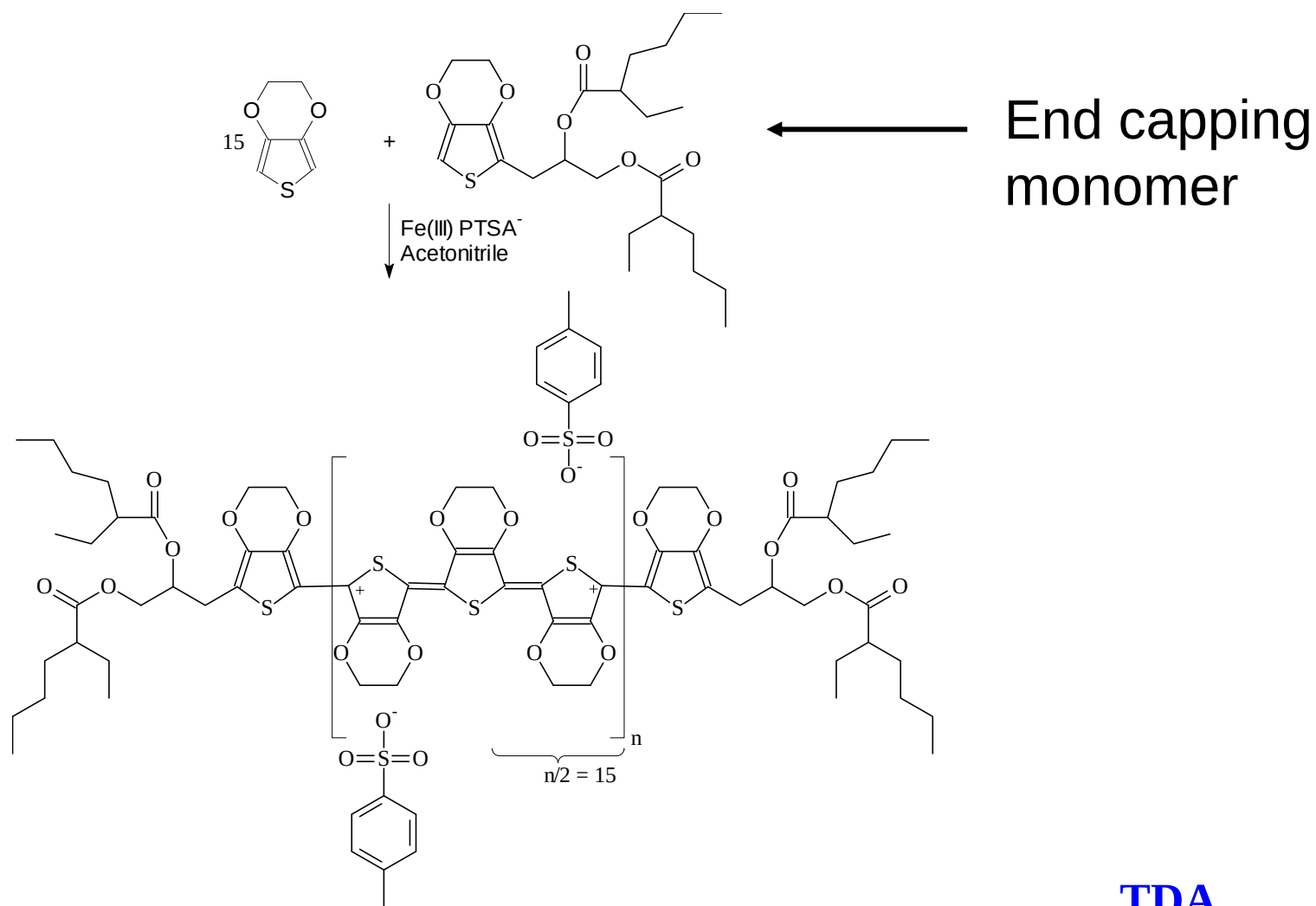
Insoluble
non-dispersible
intractable

Dispersible forms of polythiophenes

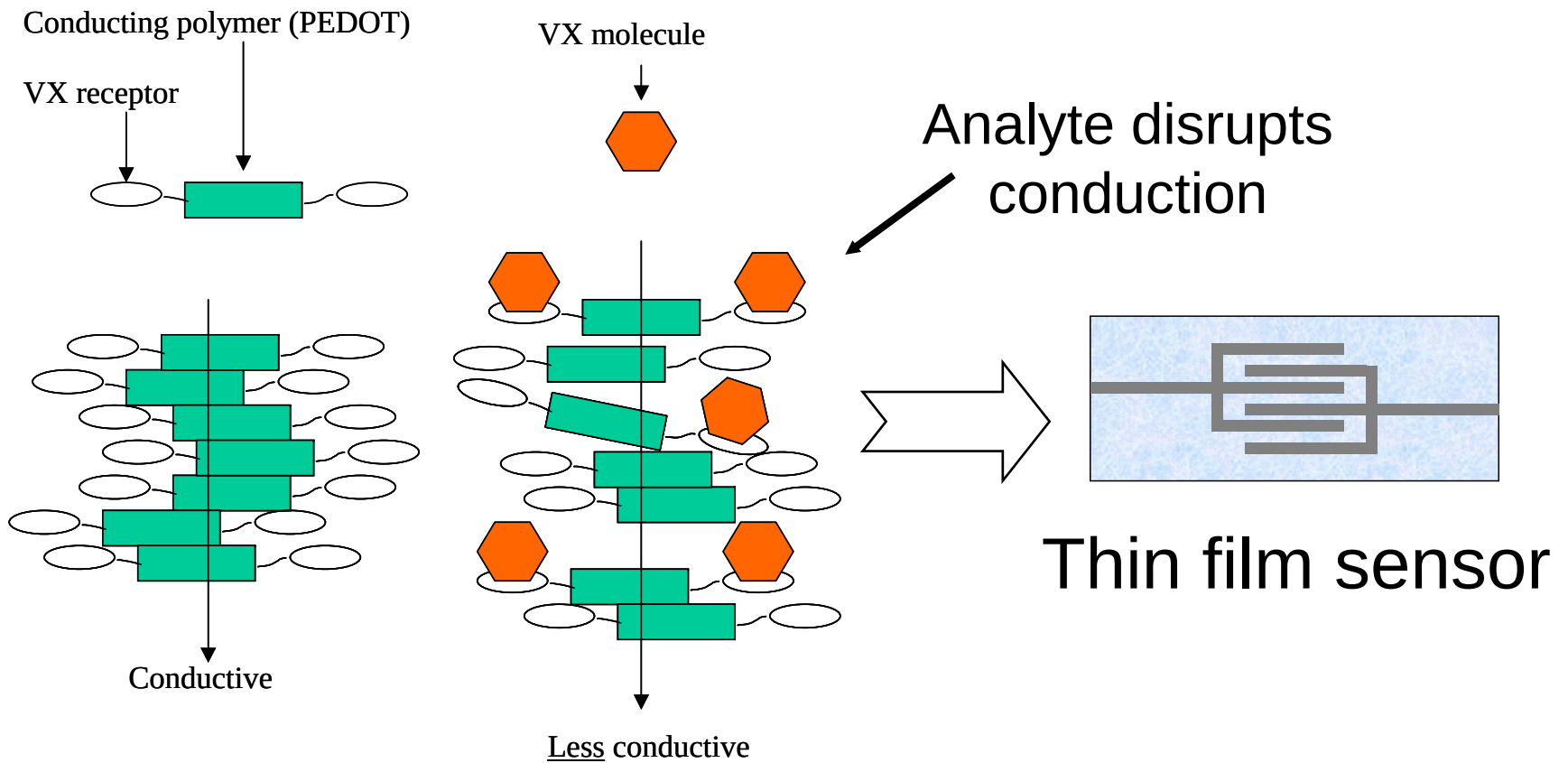


Pendant groups or side groups
promote dispersion in some solvents

Conducting Oligomers: Co-polymerization of Monomers with End-caps



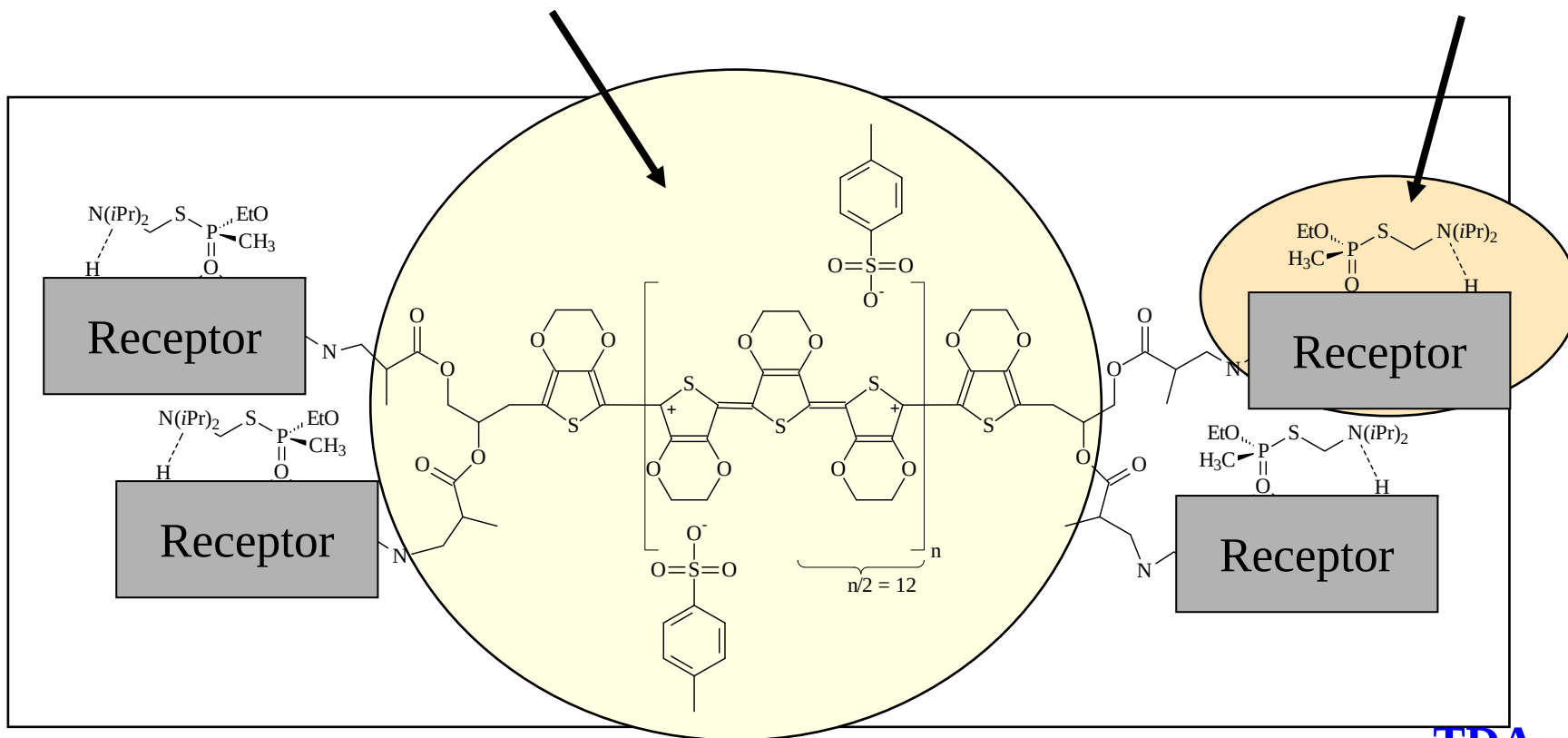
Sensor Concept



Synthetic Approach – Modify a Commercial Product with Receptors

Central core is based on existing TDA conducting polymer materials

Many different receptors can be added and tested



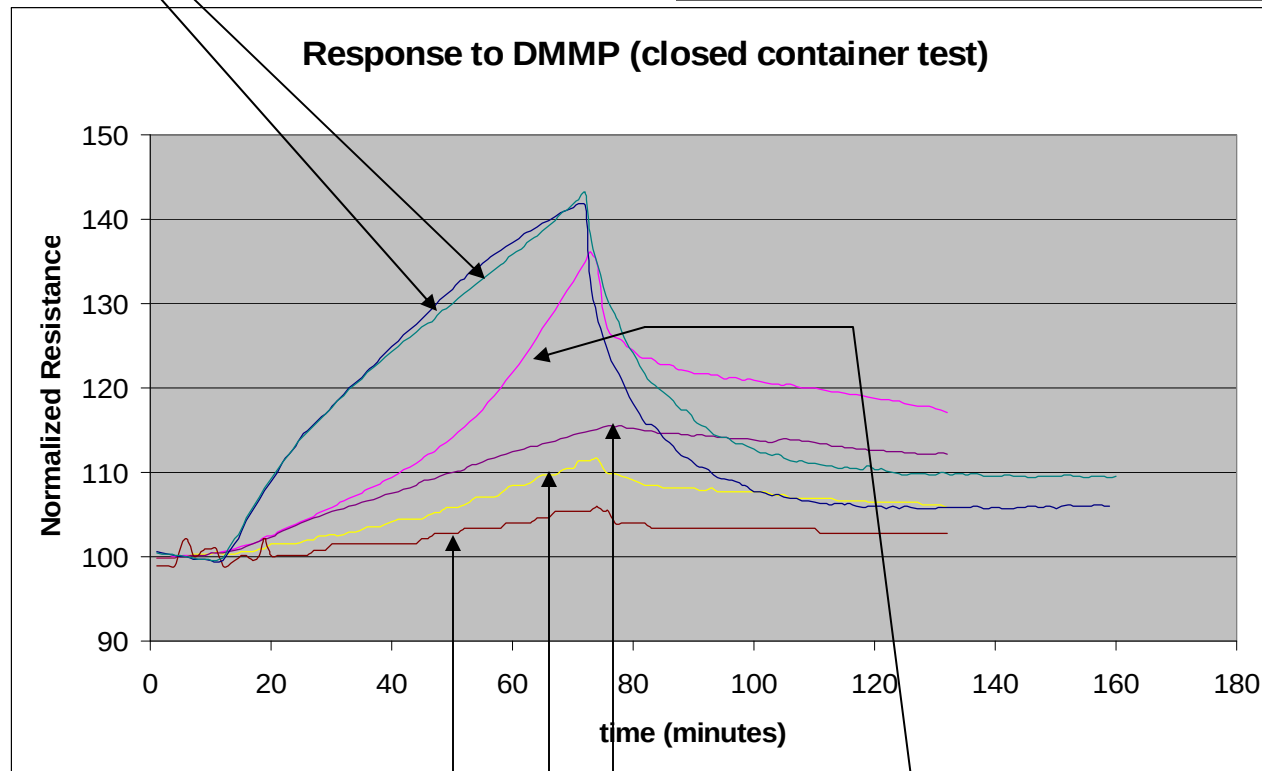
Conducting Polymer Sensors

- **New receptors are conjugated to conducting polymer**
 - Good selectivity
 - Strong function of receptor type
 - Varying the binding strength gives significant DMMP selectivity.
- **Live agent GB test soon for new receptors**
 - Sequential exposure / recovery at two concentrations
 - 500 mg/m³ and 2500 mg/m³
- **Humidity effects have been quantified**
- **New RFID tags will be designed and acquired**
 - Measure and compare two sensor films
 - One with a receptor and one with no receptor (control)
 - Control film will eliminate temperature and humidity effects

Selectivity of Receptors

Class 2 / type b

“Class 2” and type “b”
receptors are best



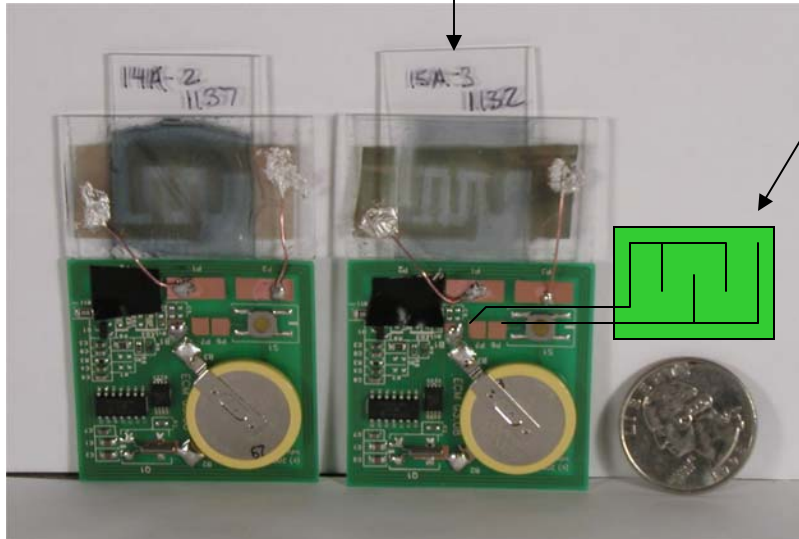
Class 1 / type b

No receptor

Class 1 / type a

Sensor Corrected for Temperature and Humidity

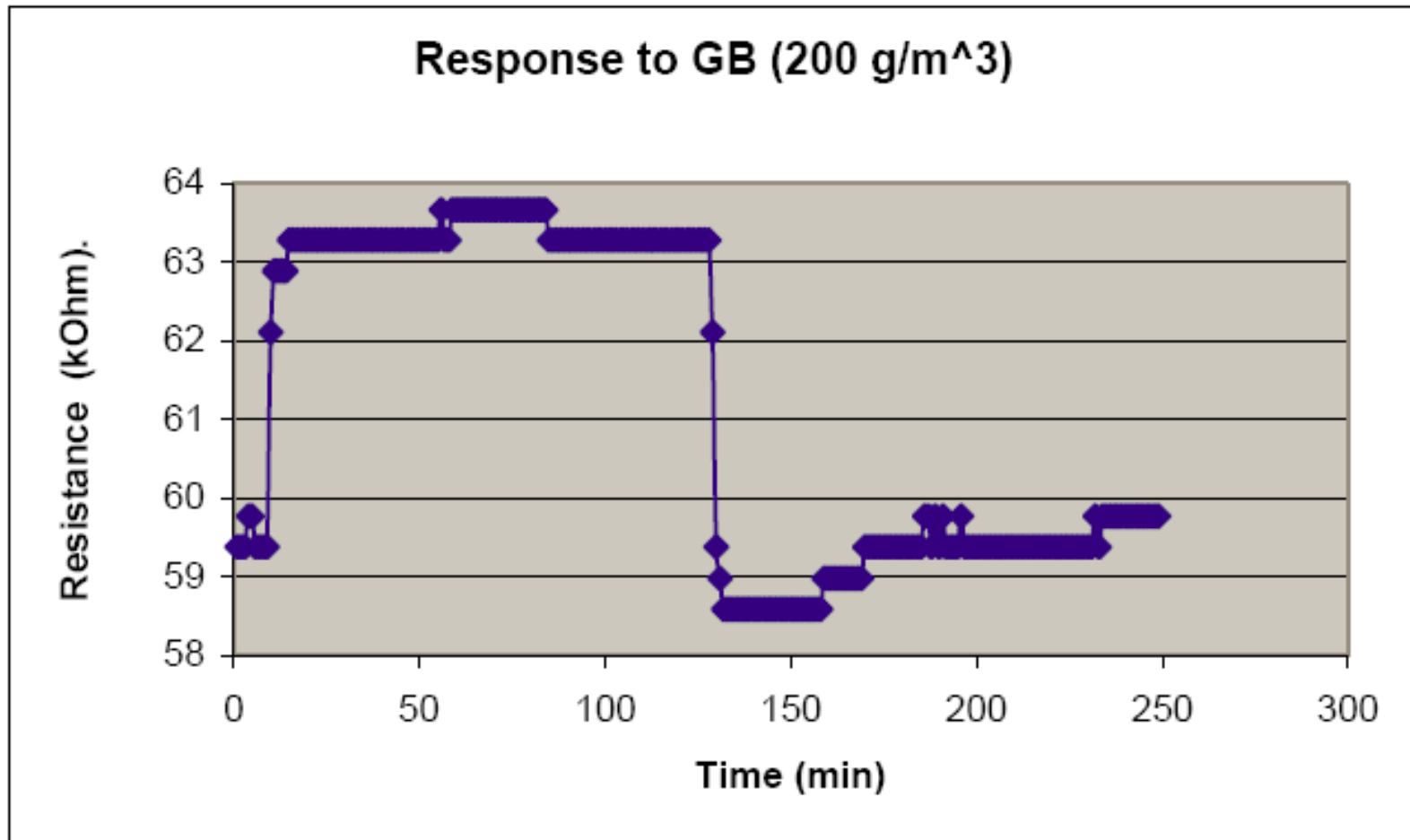
Current tags measure one film (with receptor)



New tags will add a second film (with no receptor)

Both films will respond nearly the same to temperature and humidity, but the film with the receptor will have a much stronger response to the CW agent.

Sensor Response to Live Agent



Electrochemically Generated Liquid Decon Solution

- **Technology objective: water-based system for operational decon**
 - Rapidly neutralize against CW and BW agents
 - Stable to long-term storage
 - Readily transported
 - Quickly activated
 - Minimal environmental impact
- **Operational decon objectives:**
 - Neutralize classical CW agents in five minutes to below limit of detection with M8/M9 paper
 - Neutralize biological threats, including bacterial spores

Operational Decon

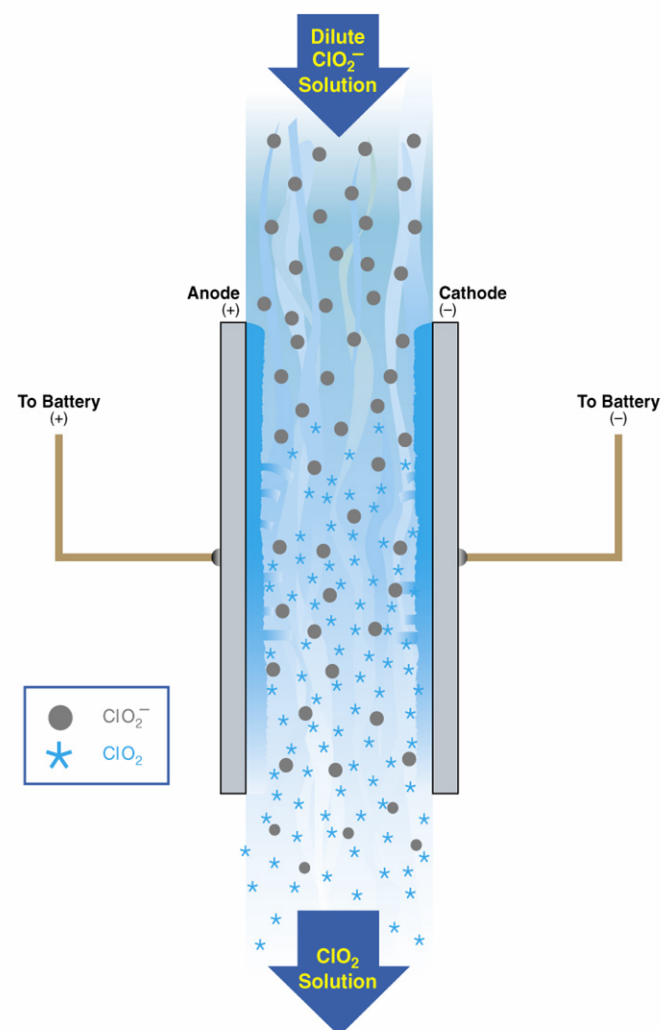
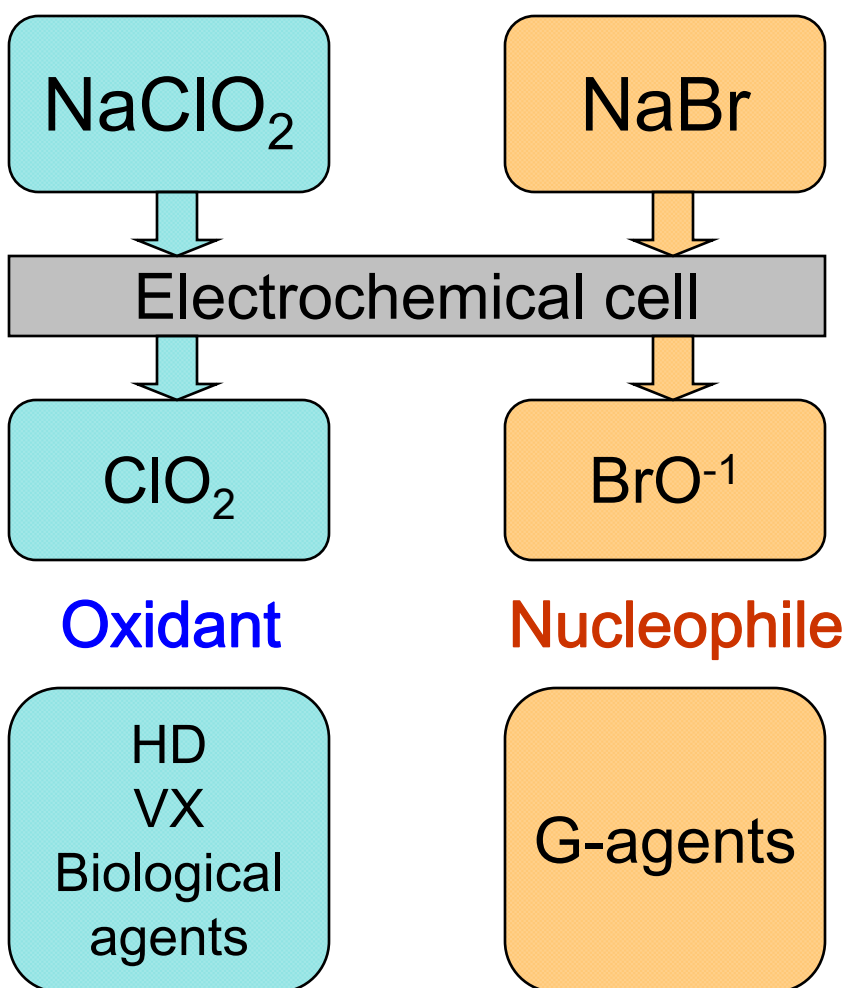
Minimize Contact and Transfer Hazards to Sustain Operations



Approach

- **Generate active species as needed using battery-powered electrochemical cell**
- **Store and transport a powder solid, not a highly reactive species**
 - Shelf stable and readily transportable
 - Add water on site
- **Active species are generated on demand**
 - Highly reactive and do not persist
 - No hazardous residue, environmentally friendly
- **Liquid decon, simple spray on application**

Technology Summary



Why ClO_2 ?

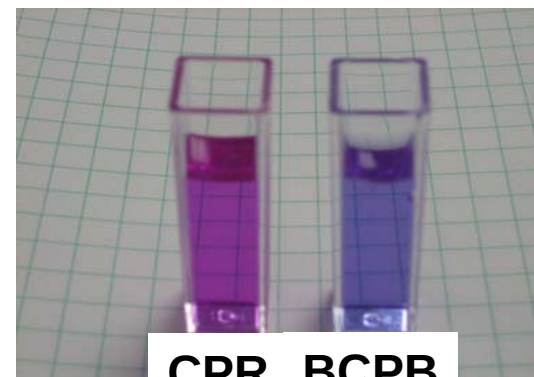
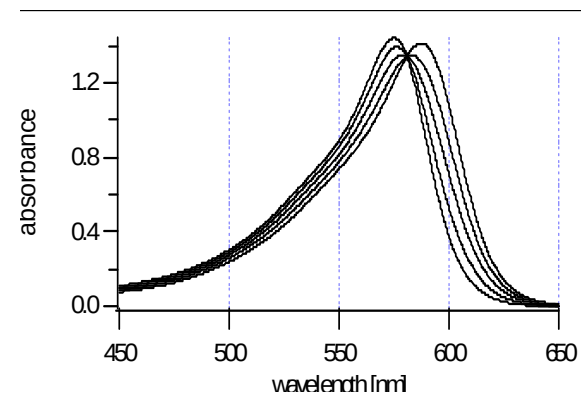
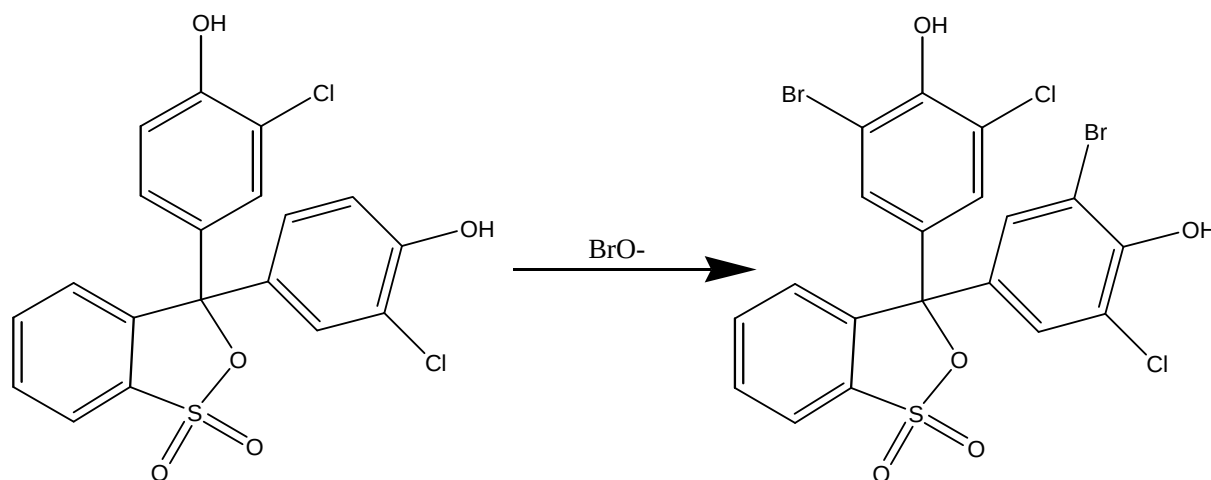
- Neutralizes HD & VX
- Gas is soluble in water and organics
- Decomposes completely in a short time, minimizing environmental hazard
- Chemically effective over a broad pH range
- Known sporicide, bactericide, and viricide

Why BrO^- ?

- Rapid GD hydrolysis
- Alpha-effect nucleophile

Analytical Method Development

- TDA developed methods to quantify BrO^- in presence of ClO_2
 - Cannot use oxidative property of species to detect BrO^- , ClO_2 is a stronger oxidant
 - Spectrophotometric method uses chlorophenol red (CPR): oxidized in presence of ClO_2 , brominated by BrO^-



Project Status (1)

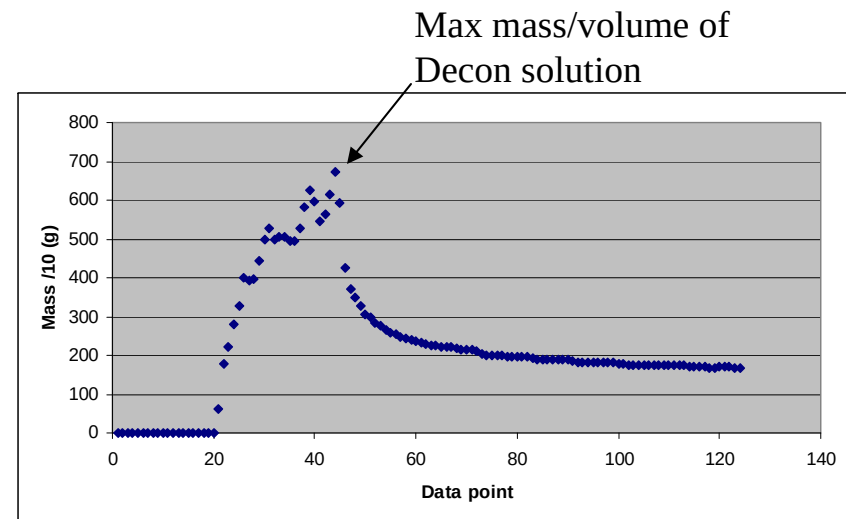
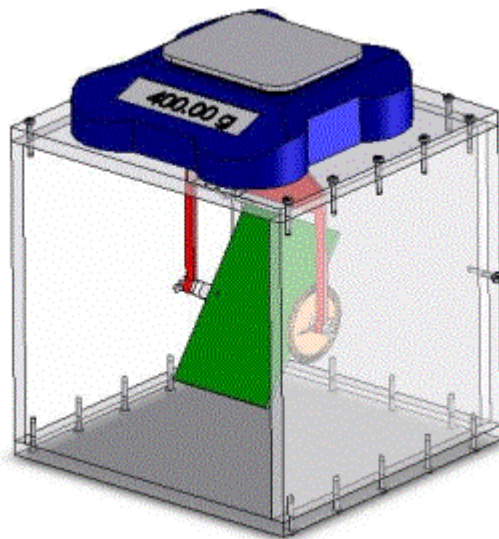
- **Formulation defined**
 - NaClO₂, NaBr, plus additives
- **CW agent efficacy for operational decon confirmed through tests with live agents on multiple surfaces**
 - Limited data on efficacy to thorough decon levels
- **Efficacy against biological threats confirmed**
 - Active against bacteria (vegetative cells and spores), viruses. Tests to verify activity against anthrax spores are planned; required for EPA approval as sporicide under FIFRA

Project Status (2)

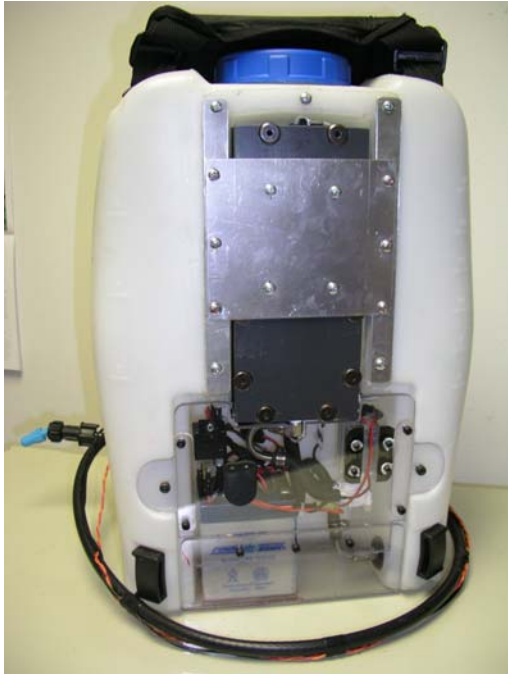
- **Prepared and evaluated test units**
 - Handheld, backpack; larger units feasible
- **Extensive tests of materials compatibility**
- **Optimized spray application; tests underway to compare spray vs. brush**
- **Tests and analysis confirmed that system is stable on storage, readily transported per DOT regulations**
- **System is versatile**
 - Can be used with other solutions, range of sizes

Surface Coverage

- **Tests determined the amount of solution on a CARC-painted surface at different orientations**
 - Determine film volume, thickness. Compare with test data showing efficacy against live agents on same surface, orientation.
- **Determine the volume of solution required for operational decon of a given surface area**
 - Analysis confirmed that a backpack-size unit has capacity to treat one vehicle



Backpack EC Decon Test Unit



Backpack includes battery, pump, flow controller, electrochemical cell, spray wand. Field test with full strength solution.

Decontamination Assurance Spray

- **Post decon treatment to identify problem areas**
- **Designed to be compatible with available sprayers**
- **Apply to all types of surface**
- **Current systems, such as M8/M9 papers and test kit, must be applied to a specific spot; this system could cover an entire vehicle or piece of equipment**

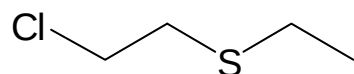
Design Parameters

- Color change in contaminated areas
- Visible on all surfaces
- Non-Staining
- Responsive to CW agents
- Responsive to many TICS?
- **Answer: develop a white powder-supported colorimetric indicator**

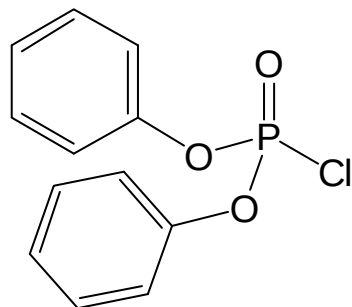
Approach to Development of Colorimetric Indicator

- **Formulate from commodity chemicals**
 - Lower cost, faster time to product
- **Design a complex that releases a dye after reacting with CW agents (and TICs)**
- **Study reactivity with simulants**
- **Multiple colors possible**
 - Possible selective color responses to identify different agents
- **Measure reaction rates**
 - Both absorbance and reflectance
- **Formulate as spray**

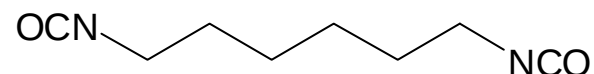
Simulants



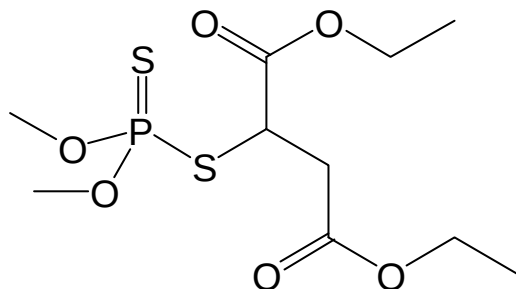
CEES



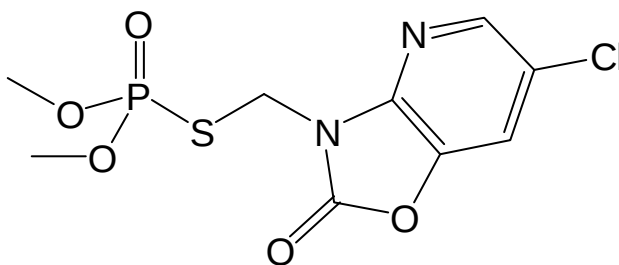
Diphenyl Chlorophosphate



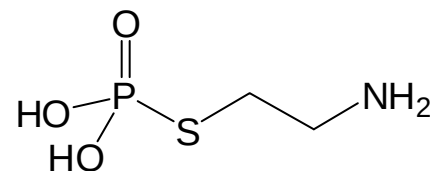
HMDI



Malathion



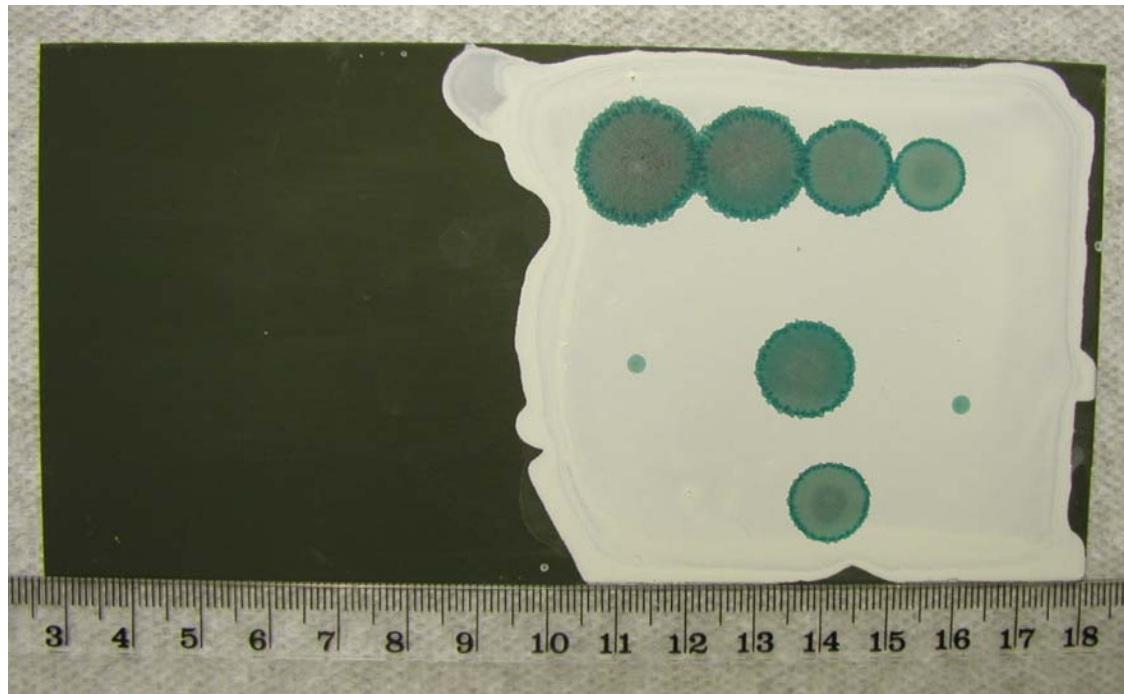
Azamethiphos



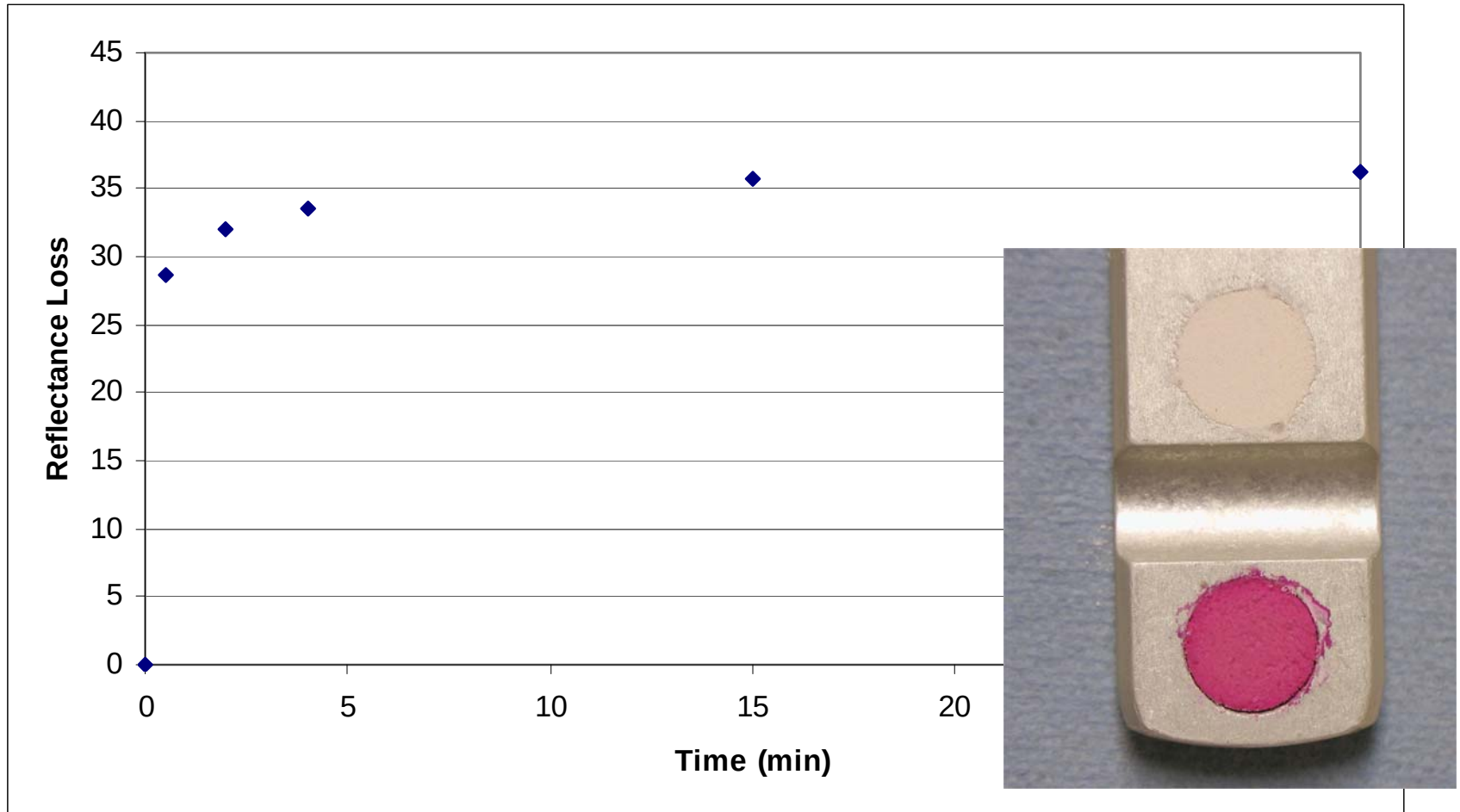
Cysteamine S-Phosphate

Support Indicators on a White Powder

- A white powder provides color contrast so that color changes are visible on all surfaces
 - The powder retains all of the colored material to avoid staining
 - Agent is absorbed into the powder support, increasing the interaction with the indicator



Red Indicator with 4% Azamethiphos in Ethanol



Further Directions

- Improved loading of the indicator on supports
- Improved reactivity of supported indicator
- Live agent validation
- Development of a sprayable formulation

Catalytic Self-Decontaminating Coatings

- **Goal: coating that will self-decontaminate through catalytic reaction at ambient temperature**
- **Effective against VX, G-agents, and HD**
 - Activity against BW agents not considered here
- **Objective is non-hazardous products, not complete mineralization**
 - TDA's effort does not consider photochemical processes
- **Focus on selective oxidation of HD to sulfoxide**

Application: Military Ground Vehicles

Aircraft, Other Sensitive and High-value Assets

- **Currently use chemical agent resistant coating (CARC)**
 - Absorbs minimal amount of CW agents
 - Epoxy primer for corrosion protection
 - Polyurethane topcoat; light-stable, camouflage (visible and NIR)
 - Any modifications must maintain current features of CARC coating system



HMMWV could benefit from catalytic coating

Structured Surface

An Approach to Increasing Effective Catalyst Surface Area

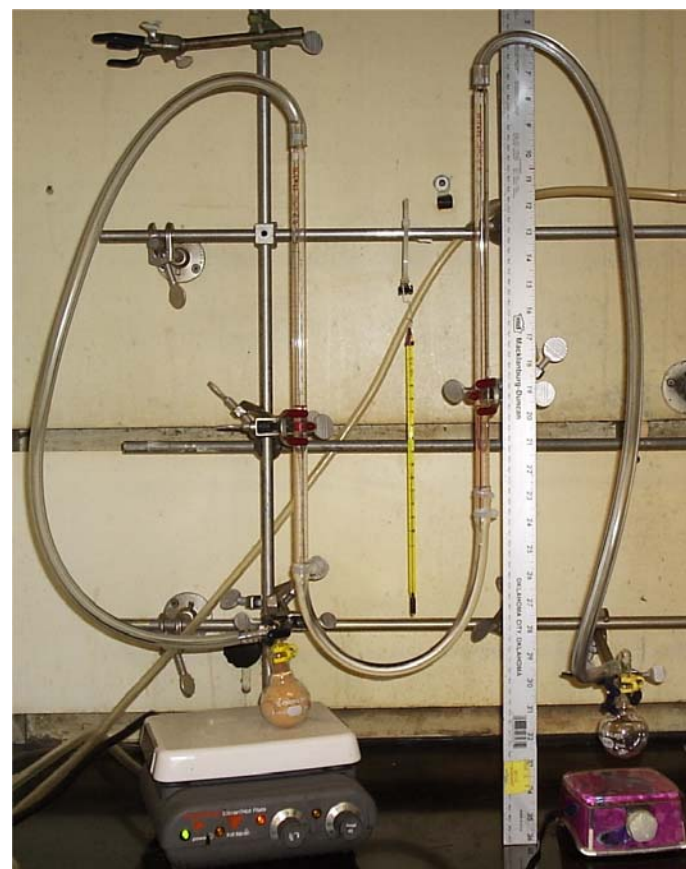
- **Advantage of a catalytic coating with a porous surface is improved mole ratio of HD to catalyst compared to non-structured surface**
 - Heavy coverage: 400
 - Light coverage: 100
- **Increase the number of accessible catalyst sites per nominal surface area by a factor of 80 or more**
 - Corresponding decrease in turnover number required for complete decontamination
- **Structured catalyst consistent with signature management**
 - CARC uses particulate materials (flattening agents) to lower gloss
- **Simplify experimental challenge of evaluation**
 - Lower turnover rates are measurable

Test Methods

- **Test with simulants, then live agents**
 - Identify reaction products
- **Test sequence:**
 - Stirred homogeneous solution
 - Stirred dispersion (substrate soluble, not catalyst)
 - Solvent-free (stirred dry powder)
 - Coated metal panels
- **Challenge: follow reaction progress in sealed vessel**
 - Monitor changes in volume or pressure
 - In oxidation reactions, O_2 is converted to a non-volatile product, so the pO_2 and total pressure will change
- **At 5:1 mole ratio O_2 :CEES, 13% of CEES is in vapor phase**
 - At this loading, 4% of the air will be consumed at the end of the reaction

Oxygen Uptake Apparatus

- Dual gas burettes partially filled with oil
- One flask holds the stirred catalyst/substrate and the other is a reference flask
- Both flasks sealed at same time with identical initial volume, temperature and pressure
- Uptake measured by change in volume at constant pressure

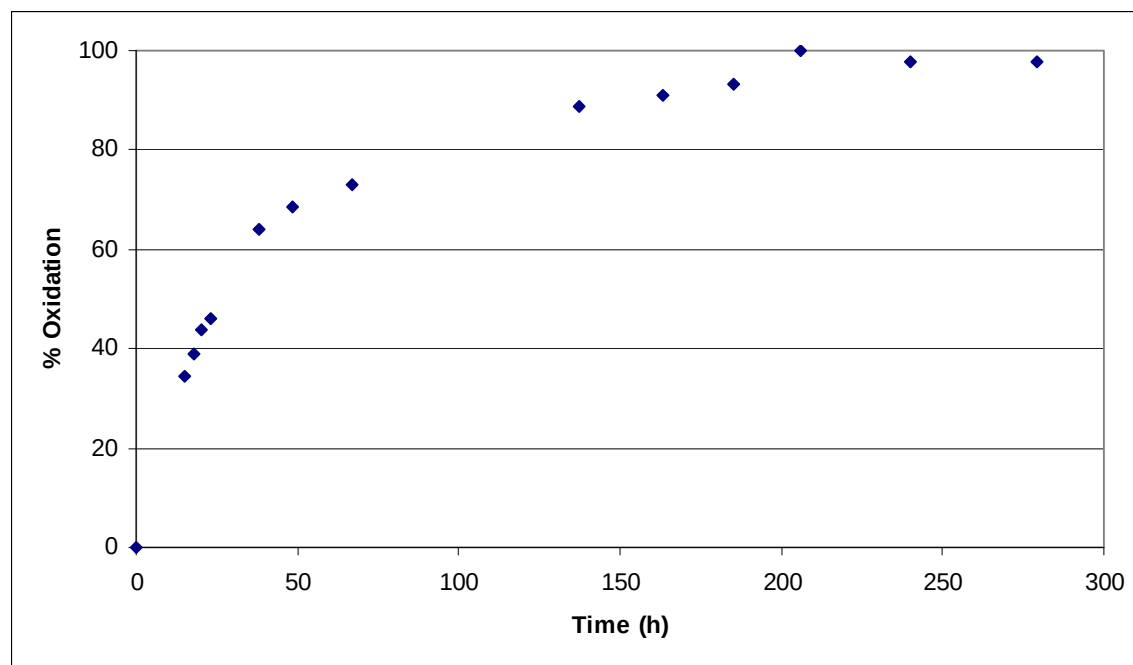


Measurement of Catalyst Activity, Supported Catalyst in Solvent

- Stirred heterogeneous mixture
- CEES as simulant
- Monitored reaction by GC analysis of aliquots
- Observed 55% removal in 2 hours, 100% removal (~23 catalyst turnovers) in 3 days.
- CEES sulfoxide detected after reaction

Measurement of Oxygen Uptake, Supported Catalyst and CEES in Solvent-Free System

- Supported catalyst as powder, neat CEES; mechanical agitation
- Catalytic oxidation of CEES; ~20 turnovers
- Oxidation stops after conversion of sulfide to sulfoxide



Tests with HD

- At CUBRC (Buffalo)
- Supported catalyst as powder, neat HD; mechanical agitation.
- Ambient temperature, sealed vessel under air, 28-hour test
- Only partial recovery (~40%) of HD in control (support only); much lower recovery in presence of supported catalyst (~5%)

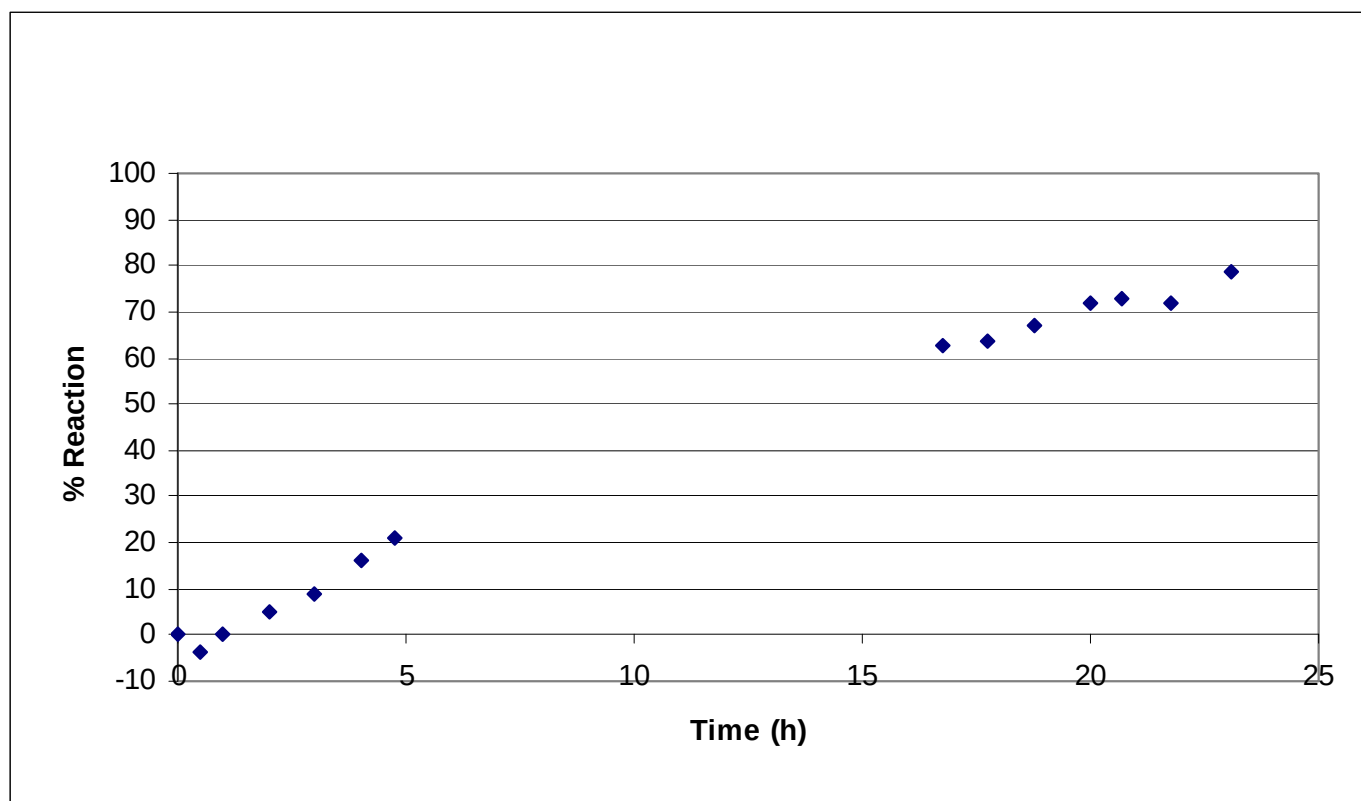
Tests with HD



Assembly of two dual gas burettes for HD tests at CUBRC. The dual burette on the left was connected to a flask with the catalyst and HD (and to an empty flask as a pressure reference). The dual burette was connected to a flask that held untreated catalyst support and HD.

Measurement of Oxygen Uptake, Supported Catalyst and HD in Solvent-Free System

- Supported catalyst as powder, neat HD; mechanical agitation
- Based on difference between HD recovery with catalyst and control, 6 to 7 turnovers
- After extraction, HD-sulfoxide found in supported catalyst sample, not in control
- Faster rate than earlier test with CEES; modified catalyst



Catalytic Coatings: Summary

- **Structured surfaces could improve catalyst loading and performance in reactive coatings**
- **Use of O₂ uptake measurement to follow course of oxidation reactions**
 - TDA tested catalysts in fluorocarbon slurry and dry powder, with CEES and HD
 - Test with HD showed oxygen uptake and sulfoxide formation consistent with aerobic oxidation
- **Preparation of catalyst samples on epoxy-coated metal coupons**
 - Demonstrated activity with CEES

Acknowledgements and Disclaimer

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- **Disclaimer**

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