Rapid Method to Assess Sorbate/Sorbent Reactivity

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Abstract

Novel materials including sorbents for air purification rely on reactivity to partition toxic vapors and liquids. Reactivity of toxic vapors to non-toxic products is preferred for filtration because desorption of the toxic challenge is mitigated.

A number of research programs are focused on development of novel materials for chemical warfare protection. Screening the performance of a large number of these materials is required to develop optimized materials. Both simulants and chemical agents testing is of interest depending on the stage of development.

Prior work to quantify reaction of high volatility vapors such as toxic industrial chemicals (TICs) employed micro-breakthrough methods. Breakthrough testing with low volatility vapors, however, can be difficult to quantify and reactivity cannot be discerned from adsorption. Liquid phase dosing has been used successfully in sorbent studies previously but often with lower throughput analytical methods such as nuclear magnetic resonance and Fourier transform infrared spectroscopy.

Objectives

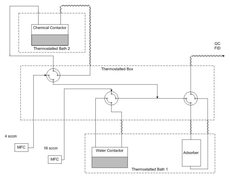
- Support Programs
  - Sorbent Development
  - Multifunctional Materials
- Use commercial analytical materials
- Sorbent and reactant are loaded in vessels, reacted and then analyzed by standard analytical methods and laboratory automation equipment
- Provide low cost method to assess loading = mass chemical/mass sorbent

Materials

- Classes of adsorbents
  - MOFs, Metal Oxides and Hydroxides, Zeolites, Activated Carbons
- Chemical compatibility with solvent is established
- Low volatility vapor to be analyzed

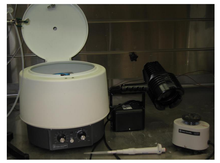
Background

- Filter design driven by loading
  - Ct ~ (loading)*(sorbent mass)/(flowrate)
- Earlier work demonstrated the utility of micro-breakthrough testing for toxic vapor adsorbent performance screening (Mahle et al. J. Phys. Chem. 2010, 114, 20083.)



- Classical chemical warfare agents (CWA) have much lower volatility than toxic gases and MB screening would be prohibitive
- A direct agent/adsorbent dosing approach was studied to improve throughput
- Current CWA filtration relies on physical adsorption but improved adsorbents would promote rapid CWA decomposition
- Method adopted from Roy, et al. (Microporous and Mesoporous Materials 162 (2012) 207) who reported HD and 2-chloro ethyl ethyl sulfide (CEES) degradation on CuBTC metal-organic framework (MOF)
- A universally accessible extraction and (gas chromatograph (GC) analysis was selected

Method



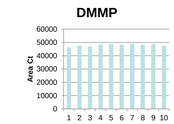
Equipment

Dispensers, autosampler vials, centrifuge and tubes, UV lamp, vortexer

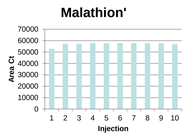
Method, cont.

Condition	Dose	Extract	Analyze
Dry 60 C Humidify 50%RH Check Chemical Purity	Sorbent 10-50 mg Chemical Loading 10wt% Expose 60 minutes	Add Solvent Centrifuge Separate Solvent	Standard Calibration Load Autosampler Compute Mass Balance

- Mass ratio
  - Chemical/Sorbent =10 wt%
- Sample preparation – dry, weigh, humidify
- Chemical Purity
  - Confirmed prior
- Extraction
  - Extraction may decompose or solubilize adsorbent
  - Solvent, acetonitrile non-reactive, quickly eluting
  - Dirty samples can be analyzed
  - Reaction halted by solvent addition
- GC method
  - Agilent 6890 with a flame ionization detector and autosampler
  - Guard column and inlet liner trap non-volatiles
- Mass balance
  - 100% recovery from non-reactive sorbents e.g. BPL carbon
  - Not closed if
    - Bound with adsorbent
    - Insoluble products
    - Non-volatile products
    - Solvent co-eluting products

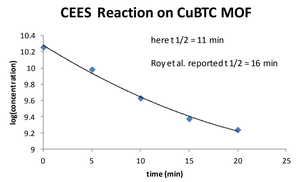


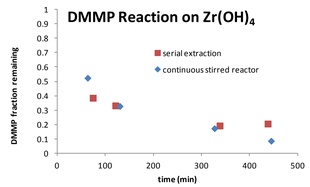
Sampling Repeatability



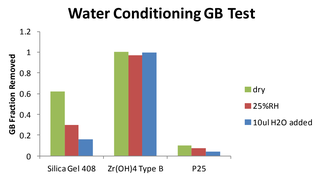
Results

- A mass average fractional conversion of starting chemical is computed
- Samples with high fractional conversion are analyzed further



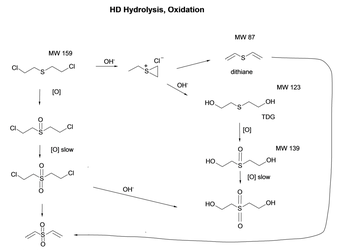


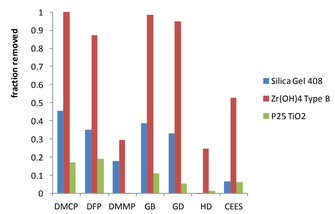
- Using a solvent to disperse agent affects systems differently, so no solvent used as dispersing media

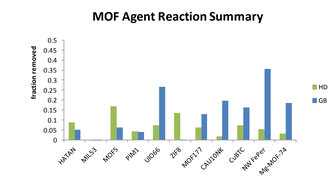


Agent-Simulant Summary

- Products seen in extract by gas chromatography–mass spectrometry
- HD reaction by oxidation and hydrolysis, toxic products formed in some pathways
- Mixed functional sorbents yield a variety of these products
- G acids not volatile (no mass balance closure)

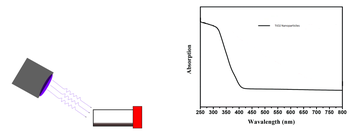


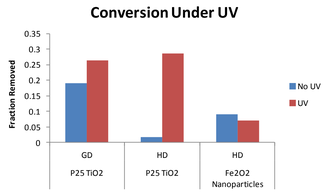




Photocatalysis

- Examine agent conversion for UV exposure
- Samples prepped as usual is glass vials
- Source 100W, 365 nm, UVP Inc
- No temperature rise measured in vial





Conclusions

- A rapid, inexpensive method has been developed to screen adsorbents for activity with low volatility vapors
- Reaction capacity of chemical agents agrees with prior methods
- An agent to simulant correlation has been demonstrated for several reference materials
- Extension of the method to UV reaction studies has been shown

Acknowledgements: The authors wish to thank the Defense Threat Reduction Agency/Joint Science and Technology Office for their assistance and funding of this work under Project CB2198. The views expressed in this presentation are those of the authors and do not necessarily reflect official policy or the position of the Department of Defense or the U.S. Government.