



U.S. Department  
of Transportation

Pipeline and  
Hazardous Materials  
Safety Administration

# Safe Transport of Energy Products Session

# Risk Assessment of Surface Transport of Liquid Natural Gas



*presented to*

**PHMSA Office of Hazardous Materials Safety  
Research and Development Forum May 16, 2018**

*presented by*

**Cambridge Systematics, Inc.**

**David O. Willauer**



**U.S. Department of Transportation  
Pipeline and Hazardous Materials  
Safety Administration**

# Presentation Outline

- Introduction
- Natural Gas Background
- LNG Outlook and Emerging Markets
- Supply Chain Analysis
- Quantitative Risk Assessment
- Rail LNG Risk Assessment
- Emergency Response
- Truck LNG and LPG Risk Factors
- Findings



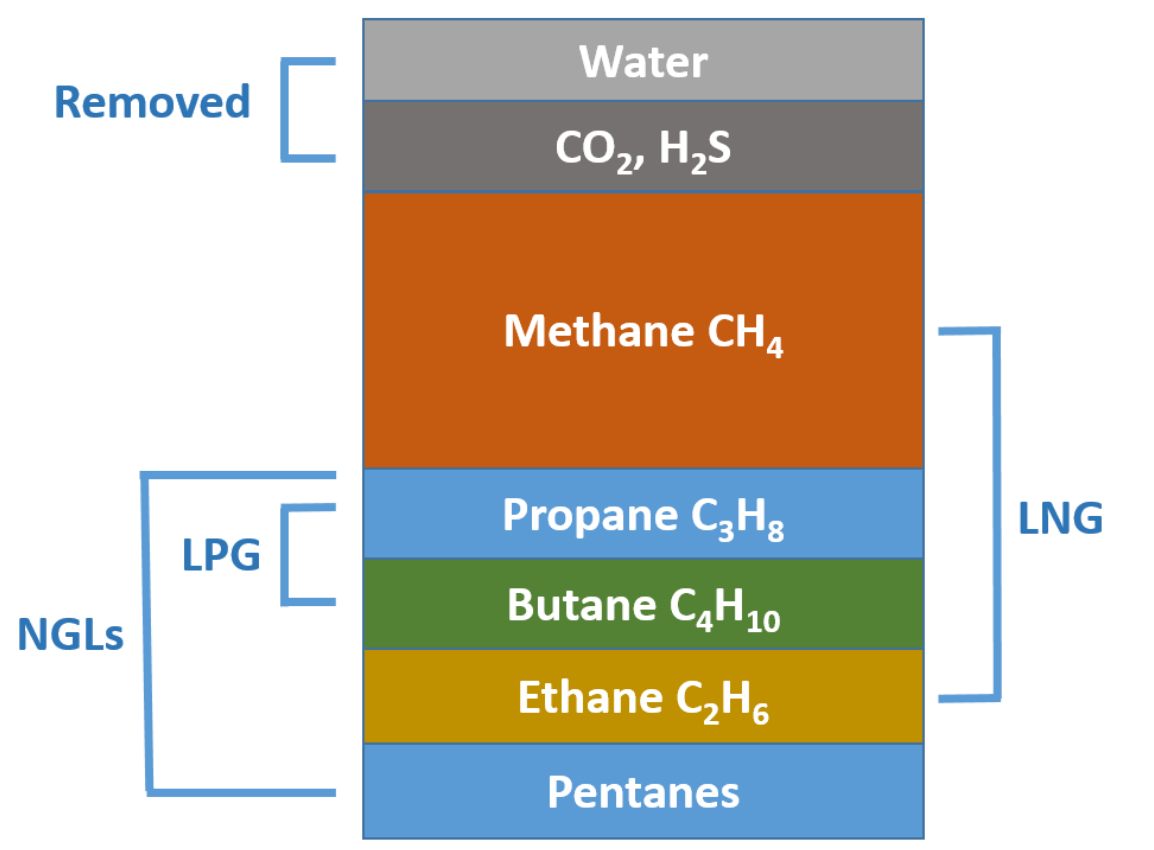
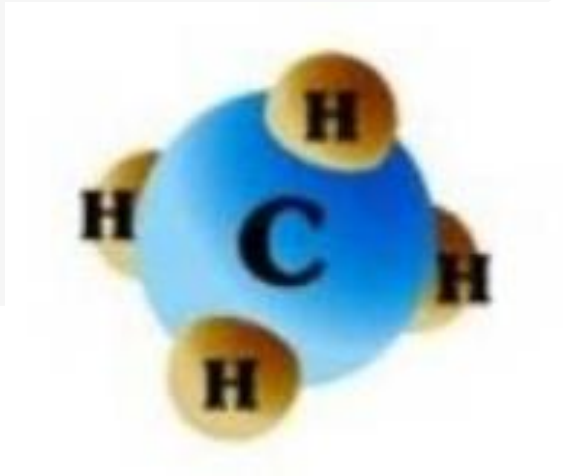
DistriGas, Everett, MA

# Study Purpose

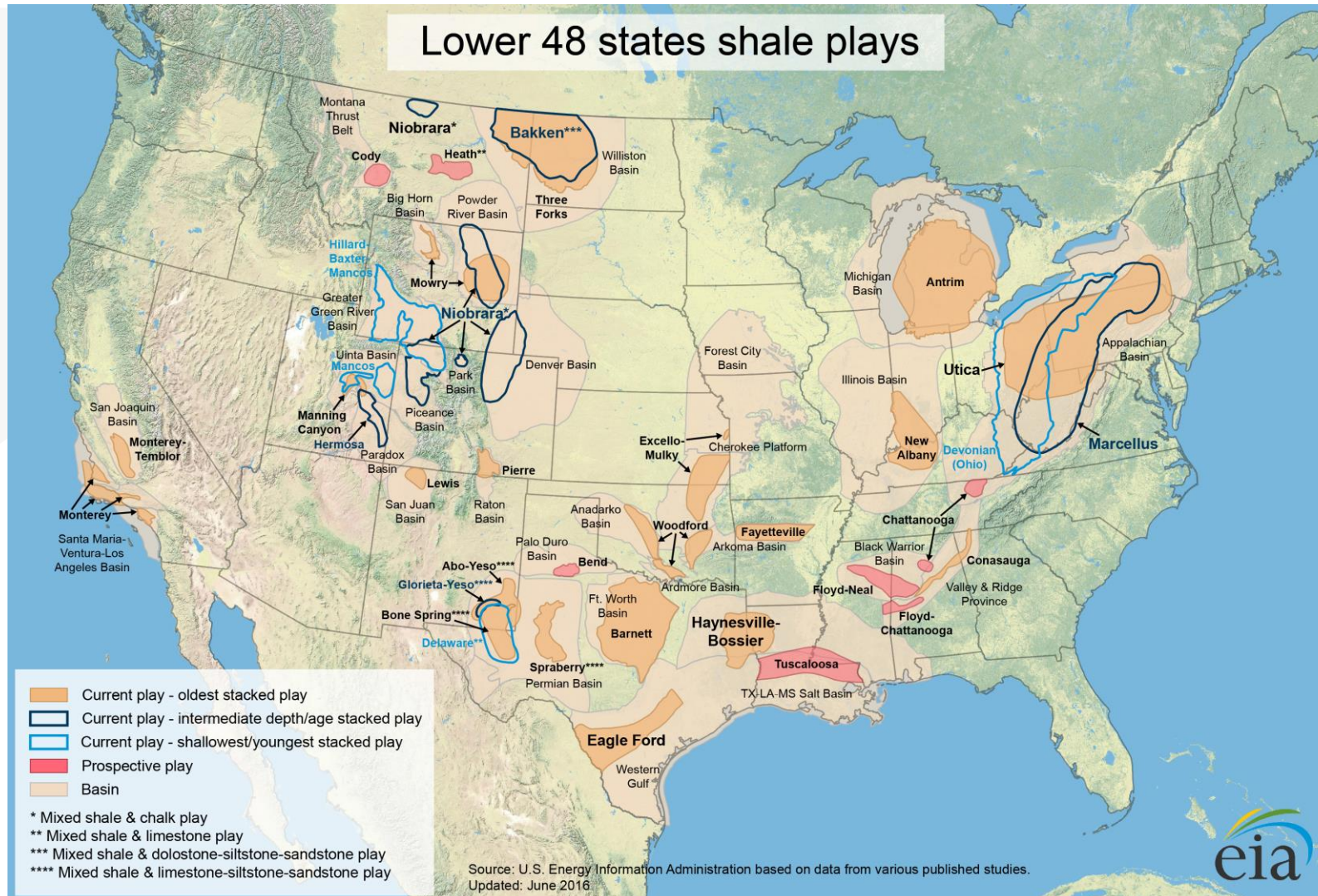
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- The purpose of the study was to assess the risks of transporting Liquid Natural Gas (LNG) by surface modes with an emphasis on rail. Study products included a Literature Review, Comprehensive Risk Plan, Factors and Parameters required for the LNG Risk Model, and a Final Report.

# Natural Gas Properties



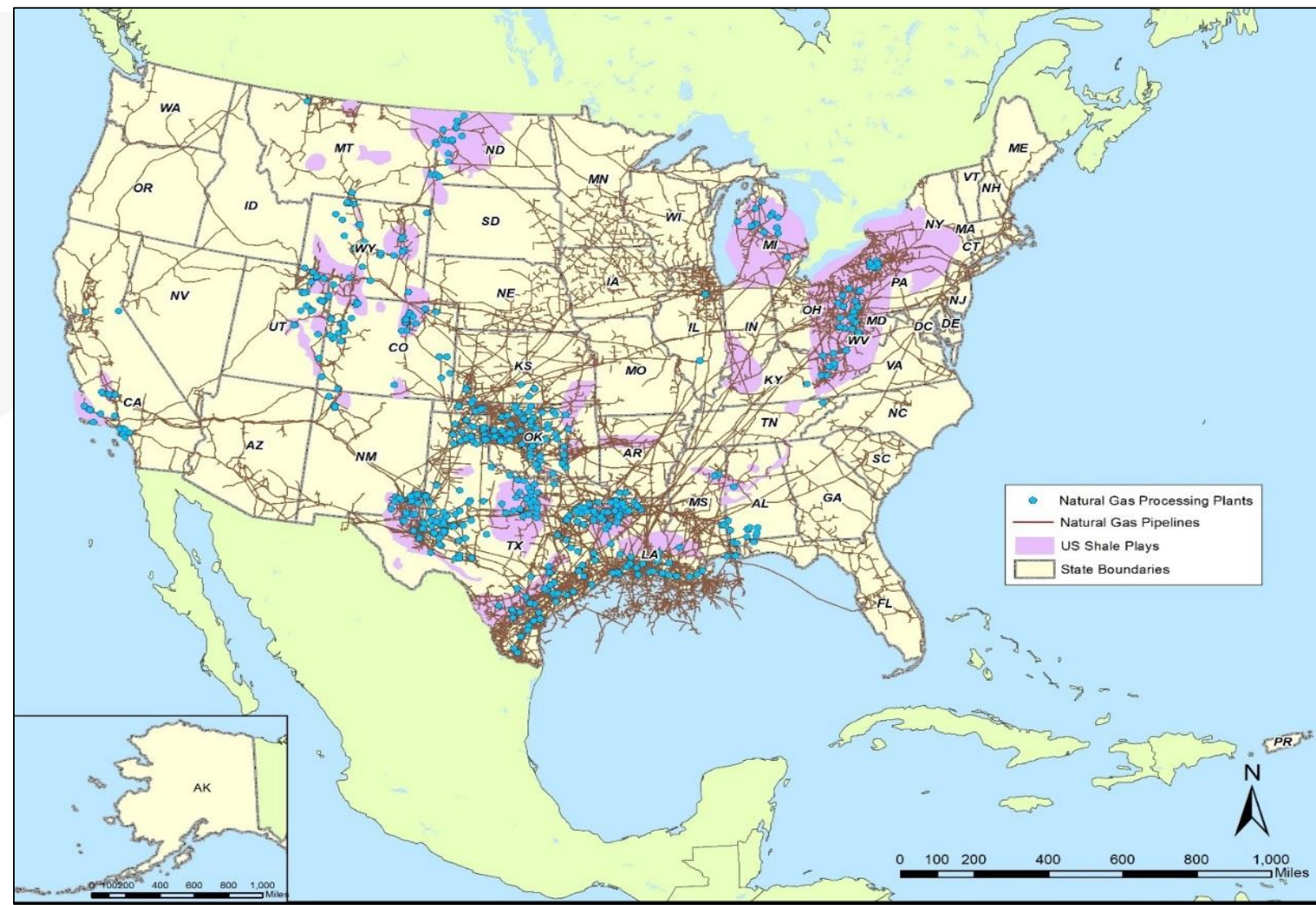
# U.S. Shale Gas and Oil Plays



Source: EIA, 2016

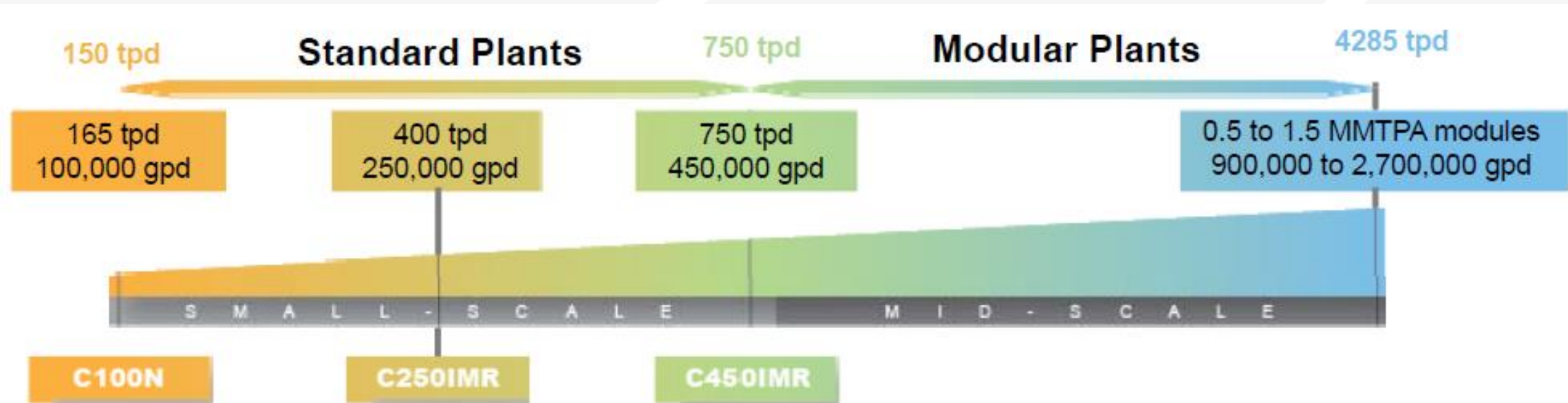


# Natural Gas Processing Regions & Pipeline Network



Sources: EIA,  
Cambridge  
Systematics

# Liquefaction Facility Capacities



Source: Chart Industries.



## New Fortress Energy LNG Liquefaction Plant, Hialeah, FL



## Cheniere LNG Liquefaction Plant, Sabine Pass, LA



Sources: Cheniere Energy, New Fortress Energy

# LNG Exports and Imports (millions of tons per annum) 2017

Top 5 Countries Exporting LNG	Volume (MTPA)
Qatar	77.2
Australia	44.3
Malaysia	25.0
Nigeria	18.6
Indonesia	16.6

Top 5 Countries Importing LNG	Volume (MTPA)
Japan	83.3
South Korea	33.7
China	26.8
India	19.2
Taiwan	15.0

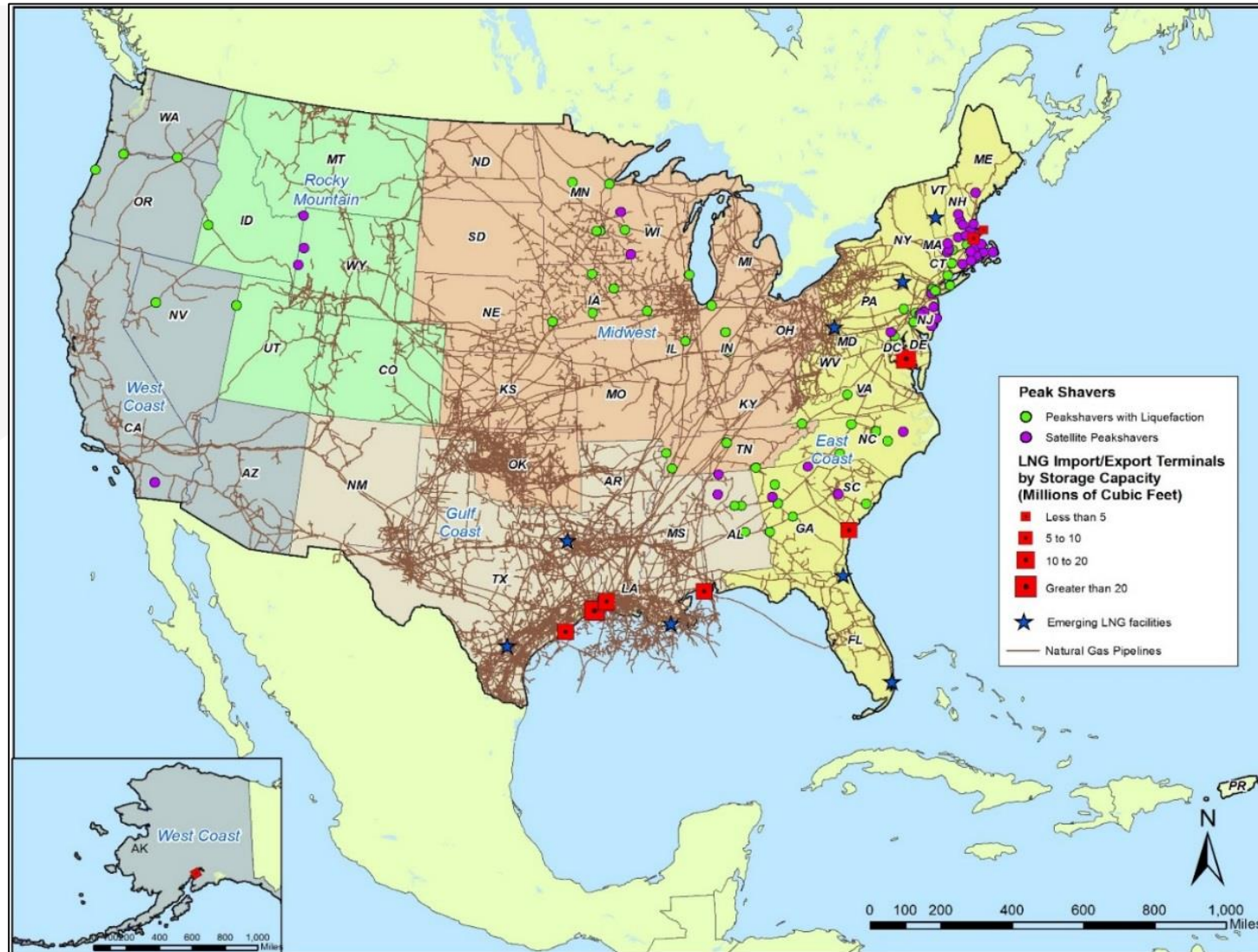
Source: International Gas Union World LNG Report, 2017 Edition

# Emerging Markets: Mining, Maritime, Rail Fuel, Cargo



Sources: Chart Industries, FECR, Tote Marine, CN Railroad

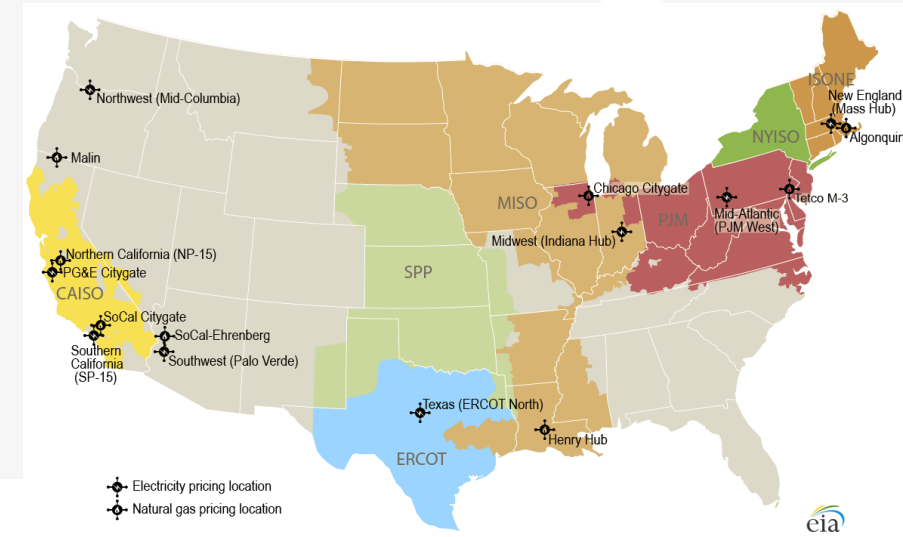
# U.S. LNG Facilities



Sources: PHMSA Annual Report 2016, FERC, EIA, Cambridge Systematics

# LNG Economics

Supply-Side Factors	Demand-Side Factors
Production amounts	Seasonal variations
Storage levels	Economic growth
Import-Export Volumes	Competing fuel prices



Sources: EIA, Cambridge Systematics

# LNG Cryogenic Containers

Rail Tank Car  
DOT 113



Cargo Tank Trailer  
MC-338

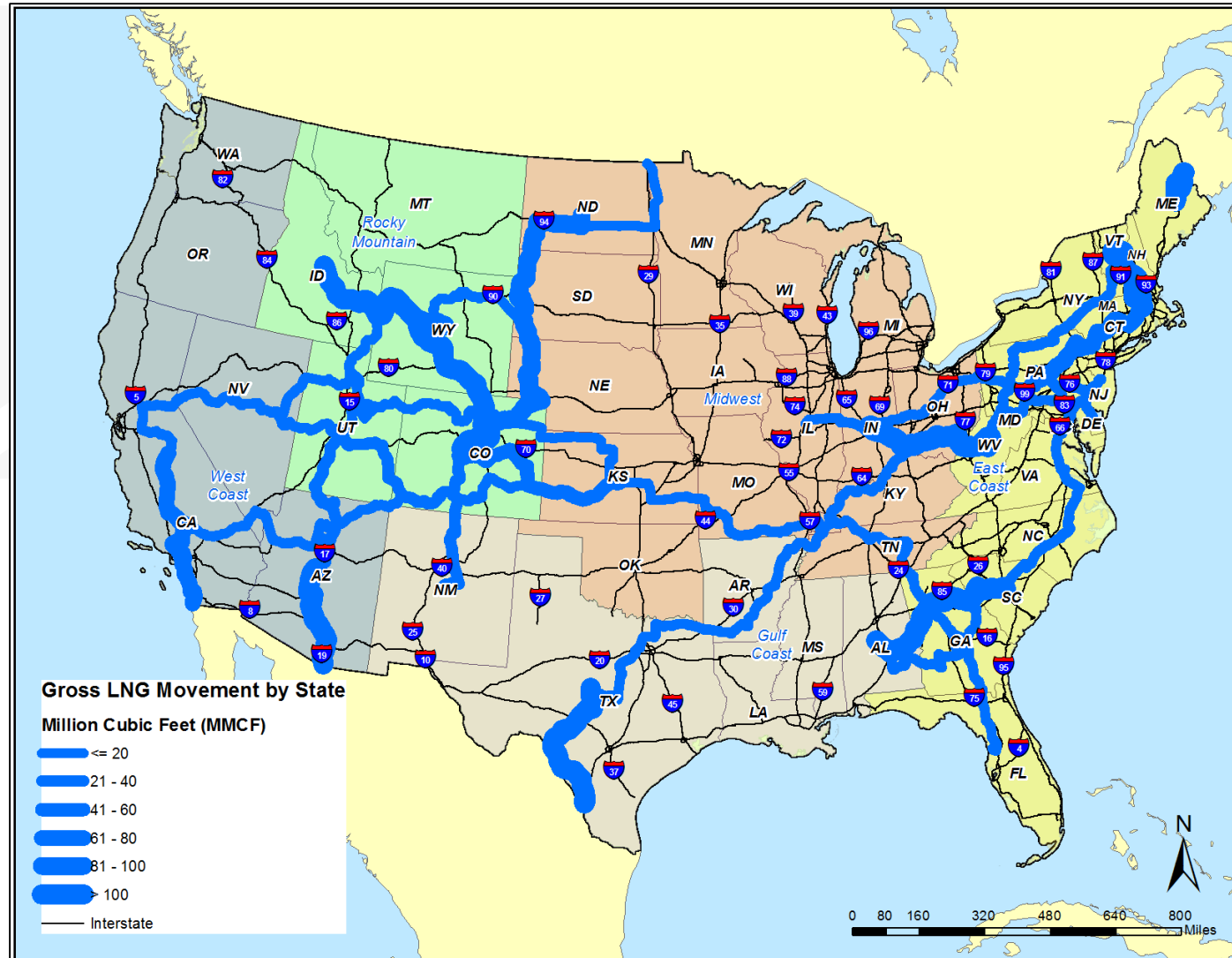


Portable Container  
ISO T-75



Source: Chart Industries

# U.S. LNG Interstate Movements

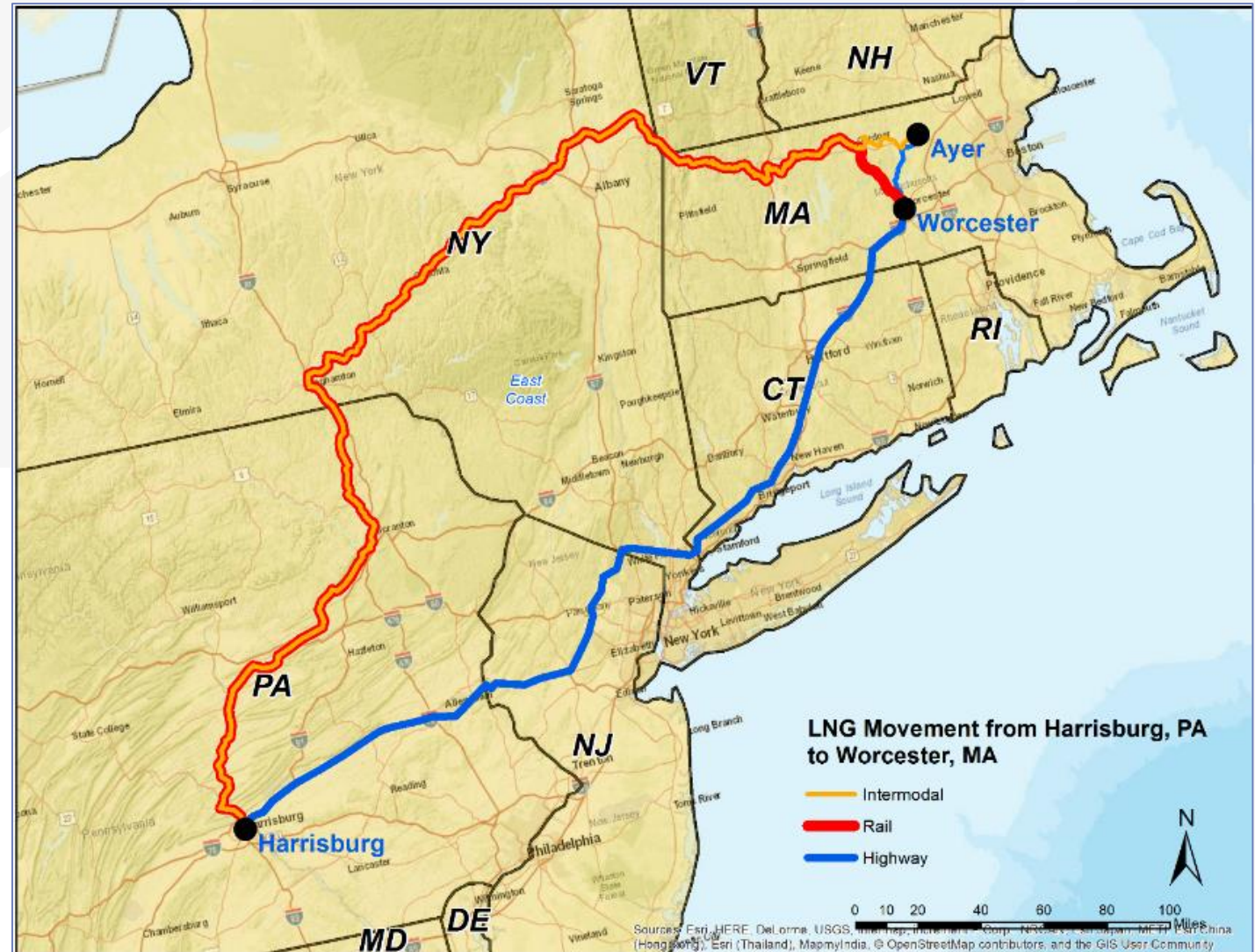


Sources: EIA 2016  
 Annual Report,  
 Cambridge Systematics

# LNG Transportation Case Study PA to MA

- **Rail:** 507 miles
- **Truck** 353 miles
- 72,041 MCF gas
- **80 Trucks**  
12,700 gals (10,943)
- **91 ISO Tanks**  
12,200 gals (9,571)
- **28 Rail Cars**  
34,500 gals (30,680)

Sources: Cambridge Systematics, NS





# Quantitative Risk Assessment (QRA)

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- QRA is used to evaluate risk and provide information needed to make decisions about risk exposure
- History shows considerable variation in the outcomes of the QRA studies (industry, government)
- There are various ways to do a QRA

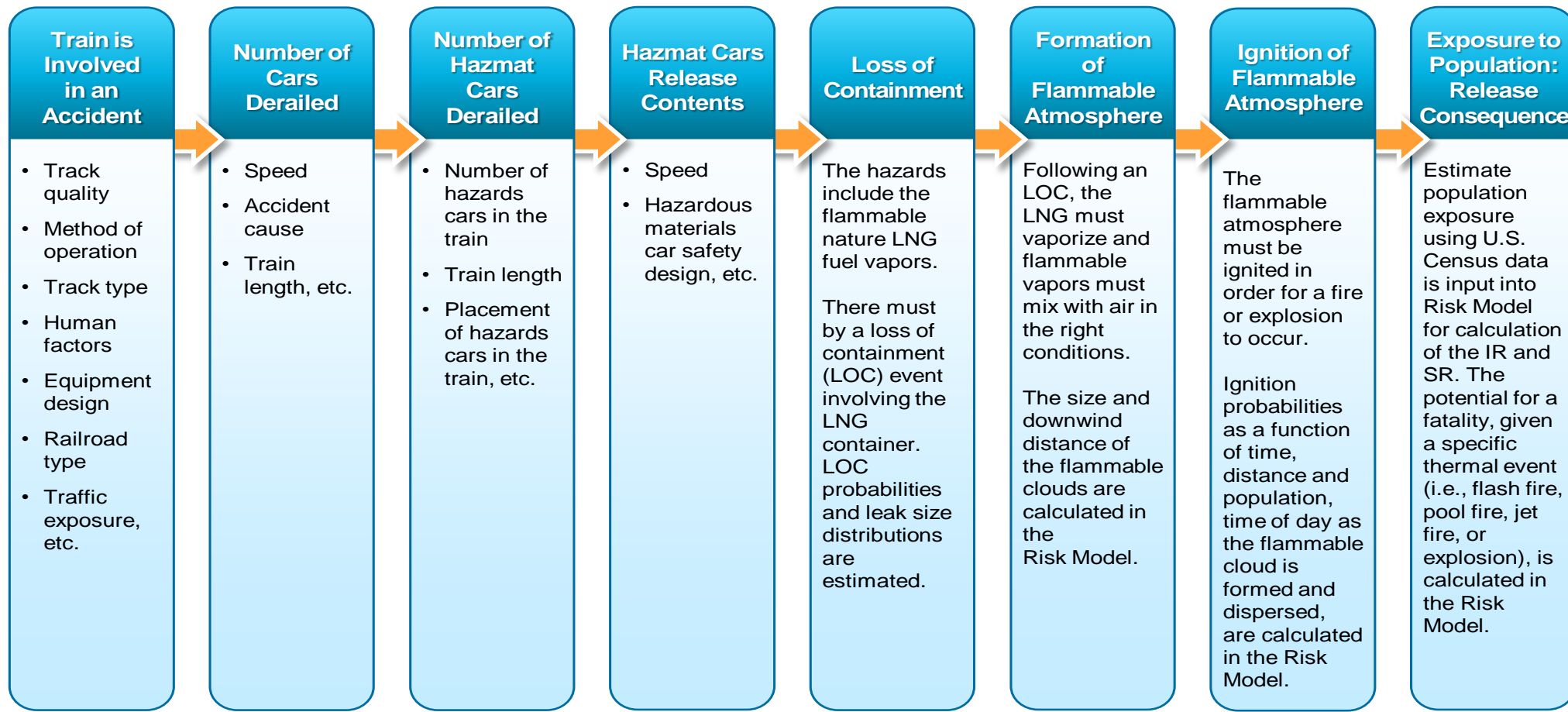
# NFPA Individual and Societal Risk, NFPA 59A

- **Individual Risk:** the frequency at which an individual may be expected to sustain a serious or fatal injury.
- **Societal Risk:** the cumulative risk exposure by all persons sustaining serious or fatal injury from an event in the LNG plant.



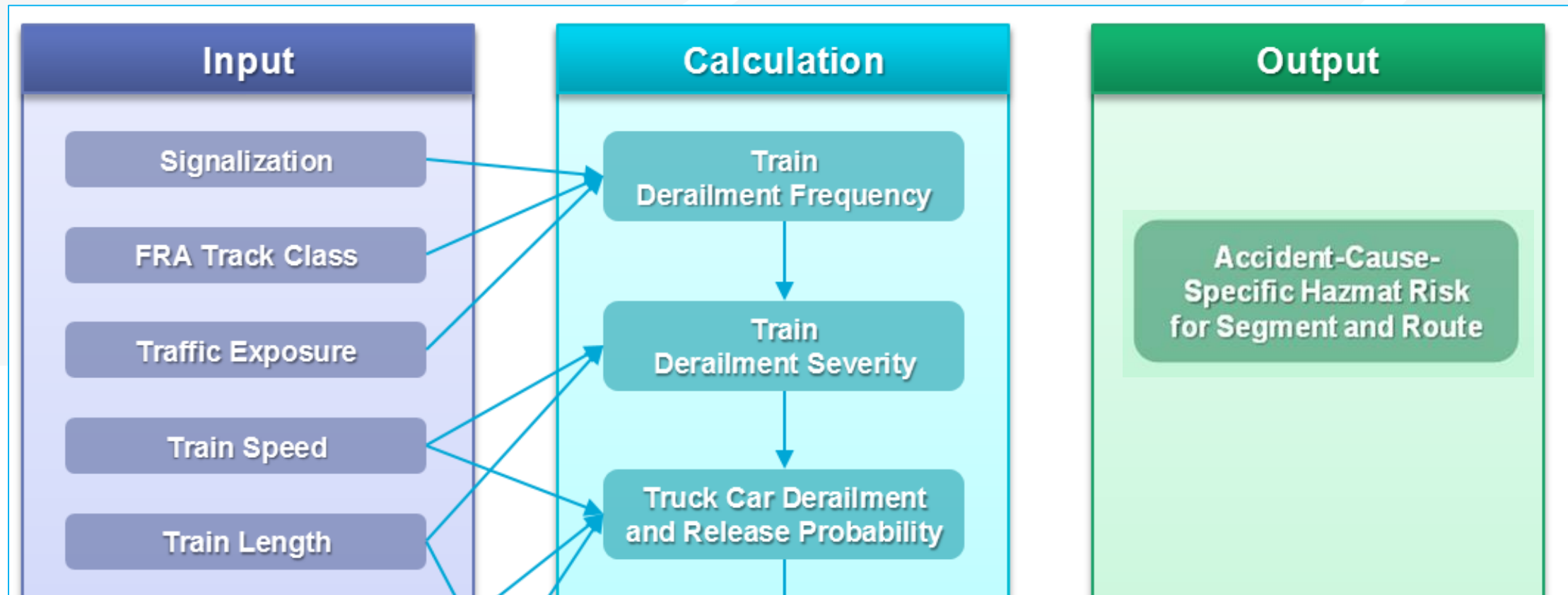
Source: NFPA Standard for the Production, Storage, and Handling of LNG, 2016.

# Event Chain Diagram for Rail LNG



Sources: Arthur D. Little, Xiang Liu, Exponent, Cambridge Systematics

# Factors and Parameters: (partial) Rail Inputs Example



Source: Xiang Liu

# LNG Emergency Response

- LNG – the next priority
- High hazard flammable trains (HHFT)
- NGLs associated with liquefaction facilities
- Alaska and Florida LNG Training completed

- ❖ Cannot cap off a leak or interact with container
- ❖ Immediate Evacuation of area and securing of facilities
- ❖ Cannot put water on a cryogenic release
- ❖ LNG must gas off naturally, and ignition sources eliminated

# Comparing Truck and Rail Risk Factors



- Trucks transporting LNG have historically very low crash rates
- Truck risk factors include driver behavior, traffic congestion, truck speed, and truck volume
- Rail risk factors include FRA track class, method of operation and traffic density

Photo: Chart Industries

# Findings

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- Natural gas is capturing a larger share of the energy market
- LNG complements the distribution of natural gas by pipeline, particularly in remote locations
- Demand exists for shipping LNG by rail, which can be both competitive and complementary to the truck and pipeline networks
- LNG Exports will increase through 2022 as import facilities are converted to export facilities
- Emerging LNG markets include maritime, rail and truck fuel operations

# Findings

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- LNG transportation has a good safety record, with minimal maritime, facility, and motor carrier incidents relative to other flammable liquids
- Developing a QRA with risk factors and parameters will help to evaluate the derailment and release probability of LNG rail cars
- When the probability of LNG tank car derailment is understood, better decisions can be made regarding the crashworthiness, placement, and operation of rail cars
- Further study for modeling the probability and consequences of transporting LNG by rail and truck will be beneficial to understanding risks to the public



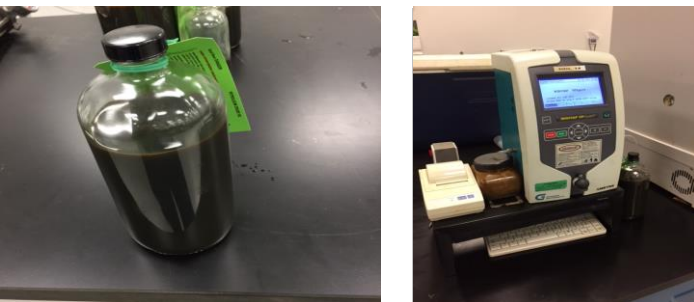
# Questions, Discussion

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# Crude Oil Characterization Research Study

Project Update

## Task 2: Sampling and Analysis Methods Evaluation

*Office of HAZMAT Safety Research & Development Forum*

NTSB Conference Center  
420 10<sup>th</sup> St SW  
Washington, DC  
May 16, 2018

*Project manager*

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SAND 2018-4600 PE

# Participants

- Sponsoring Agencies
  - US Department of Energy
  - US Department of Transportation
  - Transport Canada
- Technical Team
  - David Lord, Sandia National Laboratories
  - Ray Allen, Allen Energy Services
  - David Rudeen, GRAM, Inc.
- Peer Reviewers
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  - Dr. Kesavalu Bagawandoss, Ph.D., J.D.
  - Thomas Hurstell, P.E.
  - Robbie Lansangan, Ph.D.
- Technical Support
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  - Chad Wocken, University of North Dakota EERC
  - Ted Aulich, University of North Dakota EERC

# Presentation Outline

- Problem Statement
- Sampling Methods
- Analysis Methods
- Results
- Ongoing Work
- Future Research Areas

# Project Publications

 Today's presentation is a high-level summary of SAND2017-12482

- Lord, D. L., R. Allen and D. Rudeen (2017). "DOE/DOT Crude Oil Characterization Research Study, Task 2 Test Report on Evaluating Crude Oil Sampling and Analysis Methods." *Unlimited Release SAND2017-12482*. Sandia National Laboratories, Albuquerque, NM 87185.
- Lord, D., A. Luketa, C. Wocken, S. Schlasner, R. Allen and D. Rudeen (2015). "Literature Survey of Crude Properties Relevant to Handling and Fire Safety in Transport." *Unlimited Release SAND2015-1823*. Sandia National Laboratories, Albuquerque, NM 87185.

# Drivers for Conducting this Work

- Crude transport by rail poses risks recognized by US and Canadian regulators and stakeholders
- Hazards have been realized in a number of high-profile train derailments leading to oil spills, environmental contamination, fire, property damage, and fatalities
- Open debate on whether the types of crude (tight oil vs. conventional production) have significant bearing on severity of transportation accidents
- Additional uncertainty around which sample capture and analysis methods are appropriate for crude that could indicate potential combustion hazard levels in an accident



TSBC (2014). "Runaway and Main-Track Derailment Montreal, Maine & Atlantic Railway Freight Train Lac-Megantic, Quebec 06 July 2013." **R13D0054**. Transportation Safety Board of Canada, Gatineau QC K1A 1K8. Railway Investigation Report.

# Problem Statement

- Crude Oil Characterization Research Study
  - Objective: Evaluate whether crude oils currently transported in North America, including those produced from “tight” formations, exhibit:
    - physical or chemical properties that are distinct from conventional crudes, and
    - how these properties associate with combustion hazards that may be realized during transportation and handling
  - Findings may help improve crude oil transportation safety by providing objective scientific data to inform decisions on classifying hazardous materials
- Project Structure
  - Task 1: Project Administration and Outreach
  - **Task 2: Sampling & Analysis Methods Evaluation** ← Today's focus
  - Task 3: Combustion Experiments and Modeling
  - Task 4: Crude Characterization, Tight vs. Conventional

# Closer Look: Task 2 Objectives

- Problem
  - Unclear from current literature which crude oil capture and analysis methods are suitable for measuring vapor pressure and light ends content for oils to be compared in Tasks 3 and 4
- Task 2 Objectives
  - Investigate which commercially available methods can accurately and reproducibly:
    - capture, transport, and deliver hydrocarbon fluid samples from the field to the analysis laboratory, and furthermore
    - analyze for properties related to composition and volatility of the oil, including true vapor pressure, gas-oil ratio, and dissolved gases and light hydrocarbons
  - Performance will be directly compared to a well-established mobile laboratory system that currently serves as the baseline instrument system for the U.S. Strategic Petroleum Reserve Crude Oil Vapor Pressure Program
  - Methods that perform well in Task 2 will be utilized in Tasks 3 and 4



# Approach

- Select two crude oil sampling sites within the domestic supply chain to obtain a continuous, reasonably homogeneous sample for up to three consecutive sampling days
  - North Dakota Bakken terminal
  - Texas Eagle Ford terminal
- Capture samples by an assortment of open and closed industry standard sampling methods
  - Treat the sampling method as an independent variable
- Measure those samples with an assortment of industry standard analysis methods
  - Treat the analysis method as an independent variable
- Compare analytical results across sampling methods, analysis methods, and laboratories
  - Compare to a baseline “gold standard” flash separator system that currently serves (1995-present) as the primary analysis system supporting the crude oil vapor pressure program at the US Strategic Petroleum Reserve
- Move forward in Tasks 3 & 4 with methods found to give acceptable performance for accuracy, reproducibility, and self-consistency

# Sampling Methods

## Baseline System

- Closed methods

- “Tight Line” to on-site test separator

- ASTM D3700 floating piston cylinder (FPC)

- ASTM D8009 manual piston cylinder (MPC)

- GPA 2174 water displacement cylinder (WD)

- Open methods

- ASTM D4057 bottle sample, Boston Round (BR)

- BR ambient fill: vacuum pull used to draw sample straight from ambient P/T bottle into 6377 VP tester

- BRMPC: sample was chilled & transferred to MPC prior to pressurized injection into D6377 VP tester. Sample then pre-conditioned to 6377 test cell temperature prior to injection.



# Analysis Methods Listing

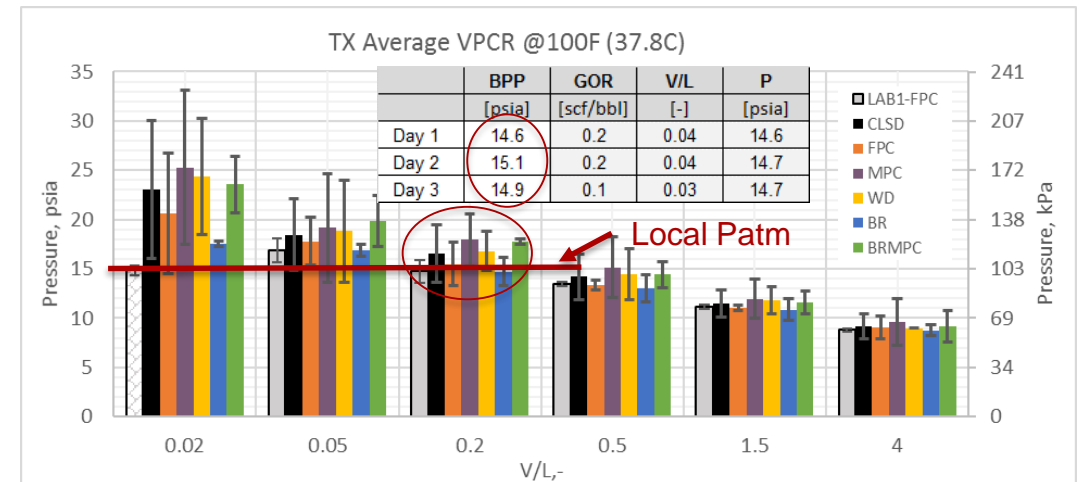
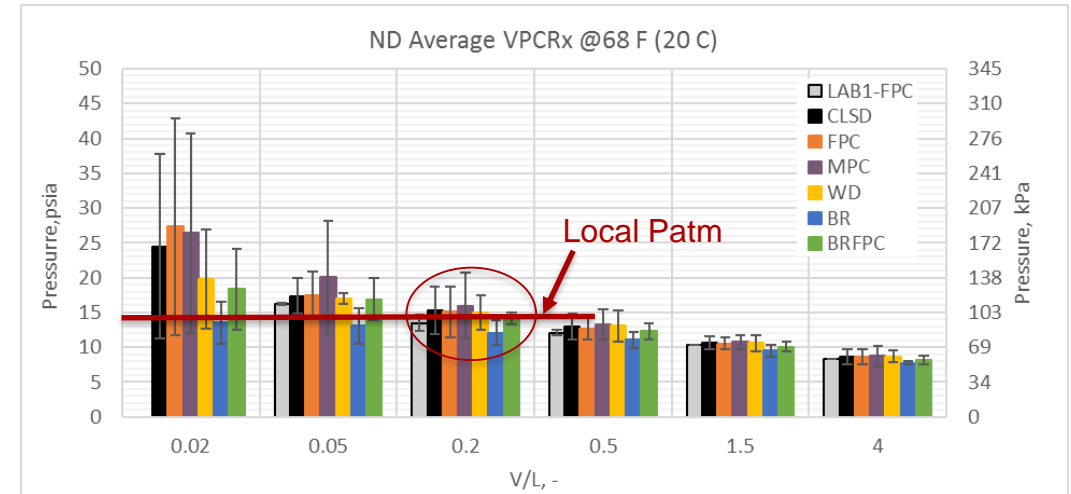
- Crude Oil Vapor Pressure VPCR<sub>x</sub>(T) by ASTM D6377-16-M
  - “M” requires sample pre-conditioning and minimum equilibration criteria
  - V/L = 0.02 through 4.0; T = 68, 100, 122 F
- TVP-95 mobile separator unit for bubblepoint pressure (BPP) and gas-oil ratio (GOR) at T = 100 F
- Pressurized compositional analyses
  - TM1: BPP and GOR flash gas analysis with C30+ with numerical merge
  - TM3: GOR flash + ASTM D8009 + ASTM D7169 with numerical merge
  - TM4: GPA 2103-M + physical shrink + ASTM D2887 C7+ analysis with numerical merge
- Selected physical properties
  - Total sulfur mass %, relative density, average molecular weight, kinematic viscosity, flashpoint, initial boiling point

Baseline Flash  
Separator System

# TASK 2: RESULTS

# Oils Exhibit BPP = 1 atm at Line T

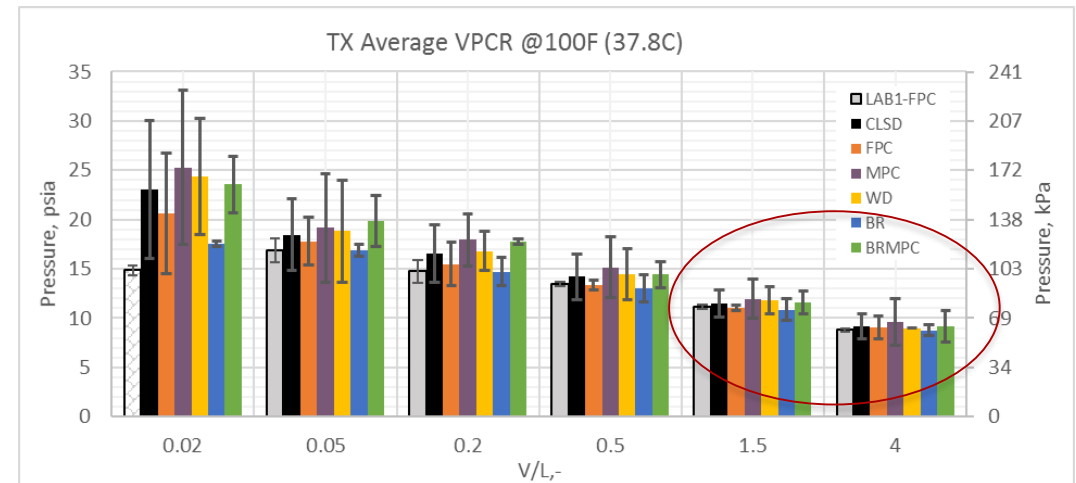
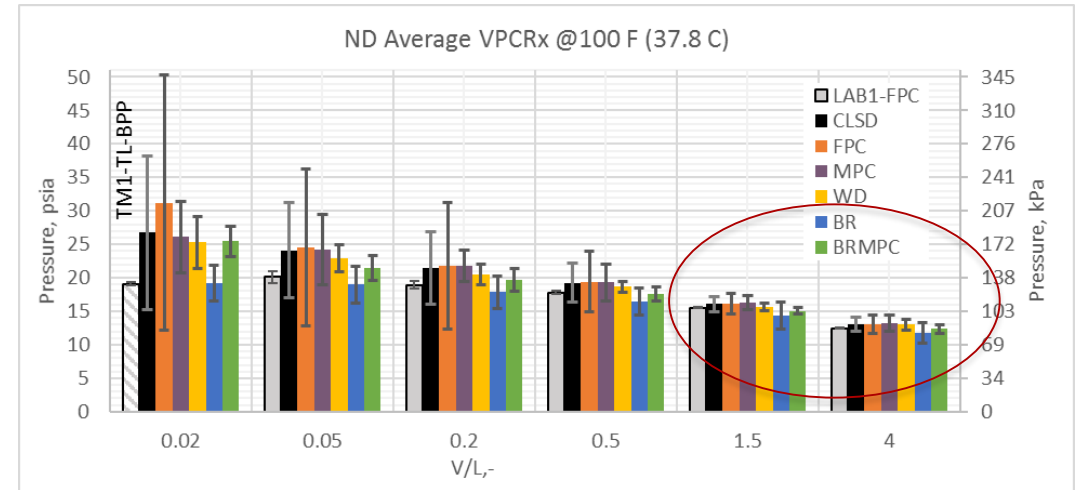
- Both oil samples appeared to have been equilibrated with ambient conditions in atmospheric tanks elsewhere in the supply chain before they were sampled.
- This was evidenced by bubblepoint pressures (BPP) at or near local atmospheric pressure at line sampling temperature.
- **Implication: VPCR of a crude oil in unpressurized storage will likely reflect local ambient conditions**



VPCR<sub>0.2</sub> compares well to BPP at same temperature<sub>37</sub>

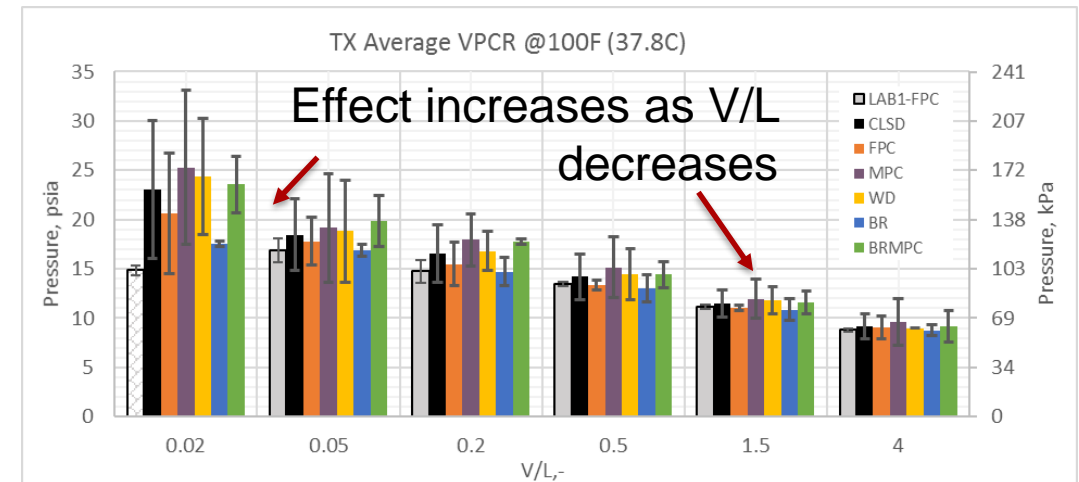
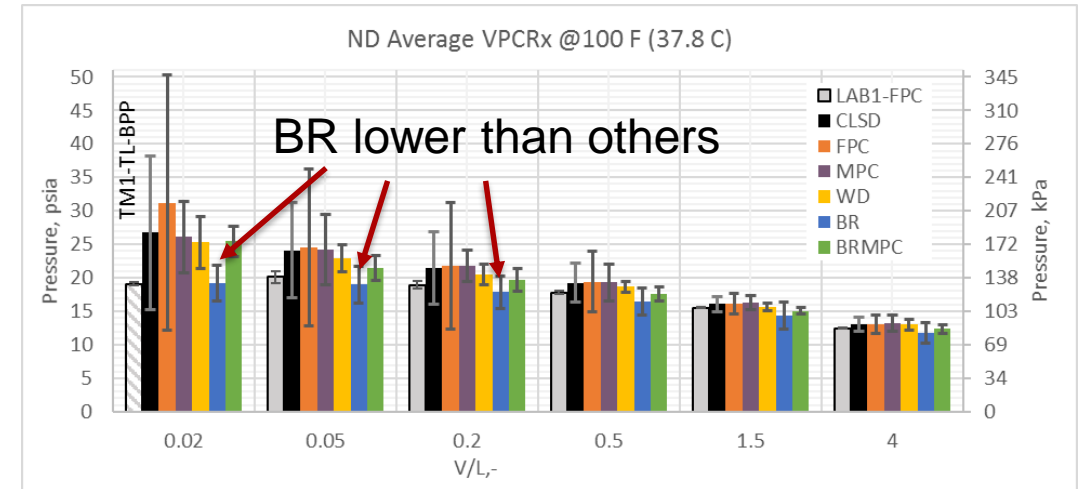
# Sampling Methods Equivalent for VPCR at High V/L

- All open and closed methods for sourcing VPCR give comparable results to baseline tight-line system for high V/L (1.5, 4.0)
- **Implication:** Oils sampled from a supply chain point equilibrated with ambient conditions and tested for VPCR at high V/L (1.5, 4.0) will likely be relatively insensitive to sampling method



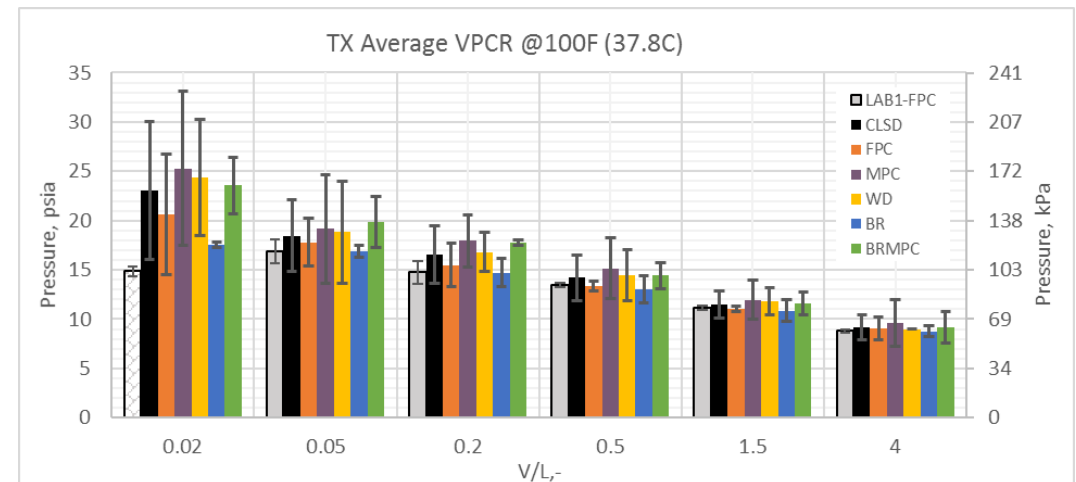
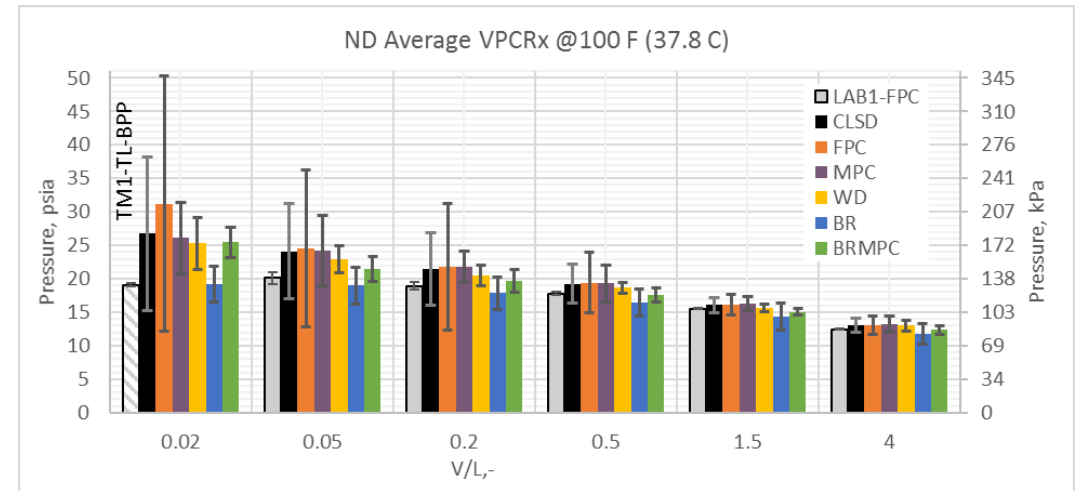
# Methods not Equivalent for VPCR at Low V/L

- Open and closed methods were not equivalent in their ability to deliver appropriate samples to the ASTM D6377 vapor pressure instrument for vapor-liquid ratio (V/L) < 1.
- Samples must be introduced into the VPCR instrument from pressurized containers (BRMPC) for testing at V/L < 1.
- Implication: VPCR sample acquisition and handling for V/L < 1 require higher level of rigor than V/L > 1**



# VPCR Uncertainty at Low V/L

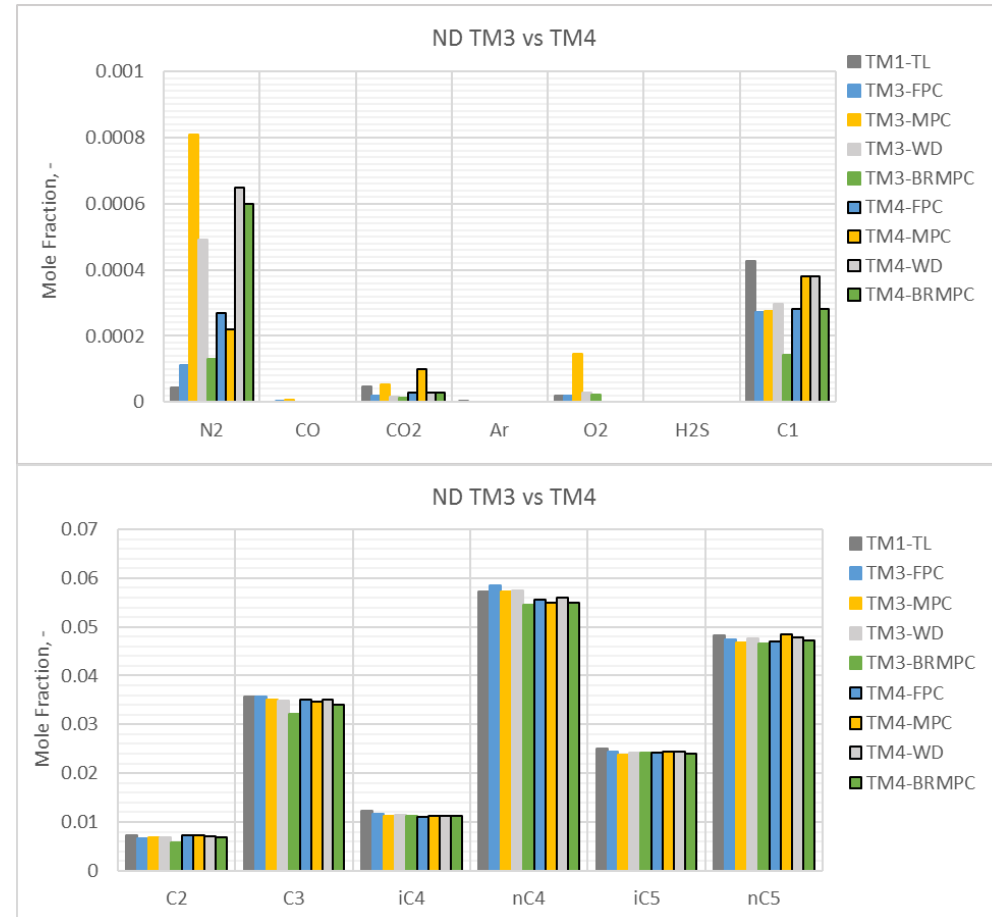
- All sampling methods generally showed high standard deviations and poor reproducibility at low V/L, especially 0.02 and 0.05
- **Implication: Current capabilities for measuring VPCR of crude at low V/L (0.02, 0.05) are not sufficient to produce reliable property measurements**





# Compositional Analysis

- All spot sampling and pressurized analysis methods for hydrocarbon composition compare well to baseline tight-line system
- Exception is noted for inert gases, which may enter spot samples from handling procedures
- **Implication:** There are several commercially available options for obtaining pressurized compositional analysis (N<sub>2</sub>, CO<sub>2</sub>, C<sub>1</sub>-C<sub>30</sub>+) for crude oil spot samples that compare well with a baseline flash separator approach. Required sample volume and analysis costs for spot samples are generally lower than with a flash separator.



- TM1: BPP and GOR flash gas analysis with C<sub>30</sub>+ with numerical merge
- TM3: ASTM D8003 + GOR flash + ASTM D7169 with numerical merge
- TM4: GPA 2103-M + physical shrink + ASTM D2887 C<sub>7</sub>+ analysis with numerical merge

- In summary, the study found that there are a number of viable options for sample capture and analysis to accurately determine VPCR and composition of crude oils that exhibit bubblepoint at or below local atmospheric pressure
- There are issues with reproducibility of VPCR at low V/L (0.02, 0.05) and inert gas content in spot sampling that appear to be related, which could potentially be mitigated with improved spot sample handling methods
- Regarding later phases (Tasks 3,4) of this research
  - Use closed methods for acquiring samples for VPCR<sub>x</sub>(T) and whole oil composition
  - Use open methods for properties that are not subject to effects of volatiles (i.e., sulfur, viscosity)
  - Since performance of the pressurized compositional methods examined here are all acceptable, factors such as cost and availability will influence method selection going forward

- Revision to SAND 2017-12482 is in review and should be published later in 2018 addressing:
  - Additional Compositional Analyses
    - Two more compositional analysis methods (TM2, TM4a) were applied to Bakken and Eagle Ford samples for comparison against the data shown in prior slides (TM1, TM3, TM4)
  - Winter Sampling
    - Both ND and TX locations were sampled with open and closed methods in March 2017 to explore possible seasonal effects on sampling performance
- Combustion Testing at Sandia
  - Crude oils representing a measurable range of vapor pressure and light ends content are being subjected to pool fire and fireball experiments to determine if these properties relate to measurable differences combustion properties that control hazards in large-scale combustion events

# Standards Work

- Peer review panel reached consensus that that current shortcomings in sampling and analysis standards associated with crude oil vapor pressure determination has some role in the variations that were observed in the VPCR data presented in this report
- Outcomes from this work will be taken to industry standards drafting committees as revision points moving forward
  - Sampling methodology issues
  - Testing standards

# Future Research Areas

- Improve reproducibility of D6377 VPCR at low V/L for spot sampling. Need to isolate sample handling effects from instrument limitations.
- Reduce frequency/magnitude of introducing inert gas into VPCR and compositional samples that create a lab sample different from the parent material
- Explore the viability of VPCR(V/L =0.2) or similar as an estimate for bubblepoint pressure or true vapor pressure
- Determine where in the supply chain open versus closed sampling really does and does not matter for collecting VPCR and compositional samples

# Project Contacts

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**END OF PREPARED SLIDES**

# Rapid Identification of Hazardous Materials in Transportation

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Sean Lazaro<sup>1</sup>

<sup>1</sup>School of Engineering and Applied Sciences, Harvard University, Cambridge, MA

<sup>2</sup>Validere Technologies Inc., Toronto, Canada





# Project Purpose

- Development of a user-friendly, low-cost diagnostic device that can rapidly classify hazardous liquids in the field.
- Can be used by shippers, hazardous waste handlers or PHMSA inspectors directly on site
- Requires no training or expertise to use



# Device Concept

Instant results displayed

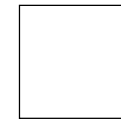


Disposable container with multiple indicator materials

## Indicator materials



Property 1



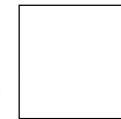
Property 2



Property 3



Property 4



Property 5



Property 6

Camera



- Computer vision readout
- Combinatorial analytics
- Machine learning

# Classification of hazardous waste

- Flammability
- Volatility
- Corrosiveness (pH)
- Water content
- Caloric value (heat of combustion)
- Contains halogenated organic compounds?
- Contains heavy metals?
- Reactivity

**Many important properties are hard to measure rapidly in the field**



**HARVARD**

John A. Paulson  
School of Engineering  
and Applied Sciences

# Making waste classification more accessible

**1. Predict hard-to-measure properties from easy-to-measure ones**

**2. Measuring new properties with simple optical tests**

# Making waste classification more accessible

**1. Predict hard-to-measure properties from easy-to-measure ones**

2. Measuring new properties with simple optical tests

# Property prediction using chemical data library

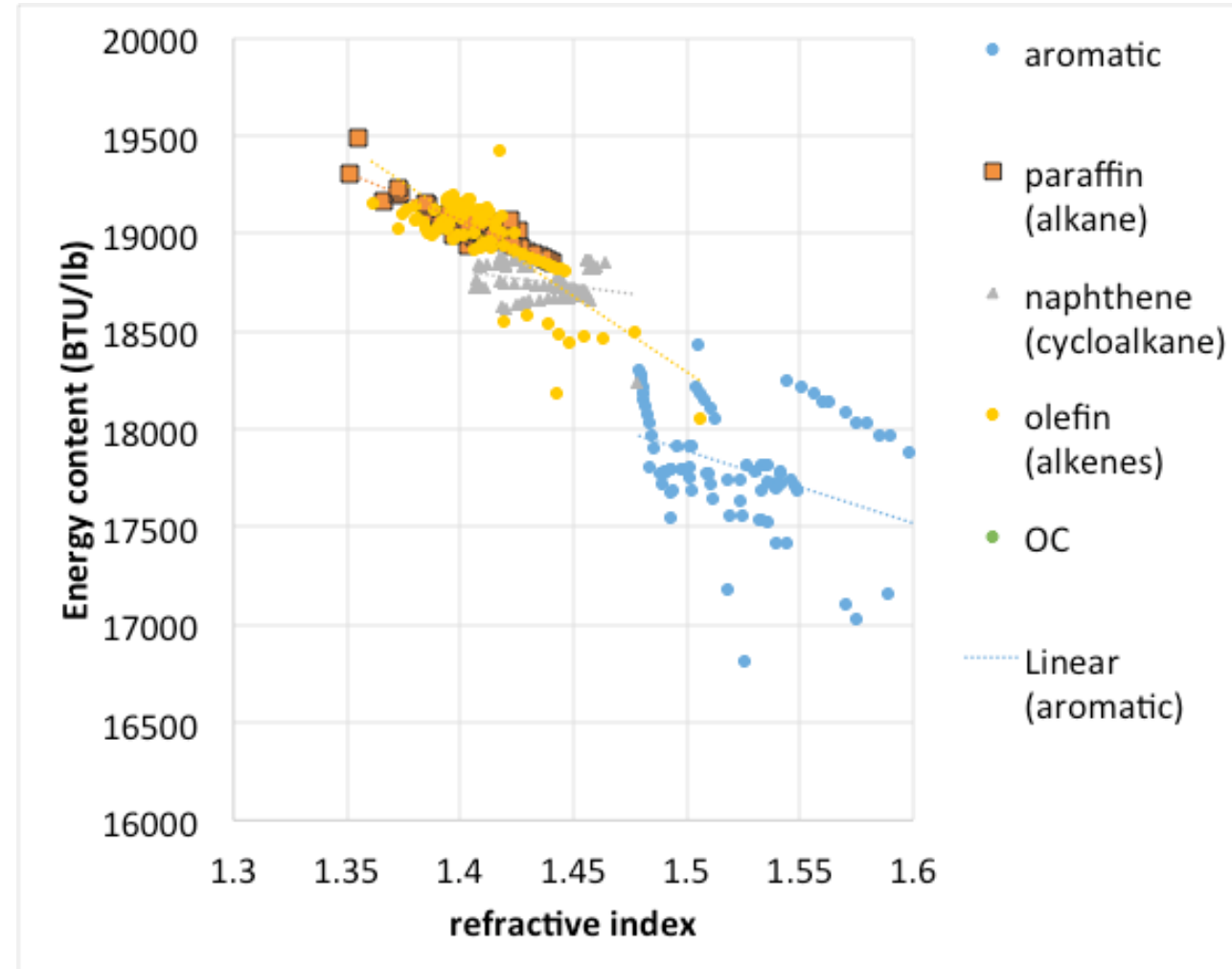
## 1. Build large data library of chemical properties

1. Contains over 600 common compounds
2. Built from measurements and public sources

## 2. Identify simple measurements that predict important hard-to-measure properties

1. Ex. refractive index predicts heat of combustion

## 3. Specificity through measurement combinations



HARVARD

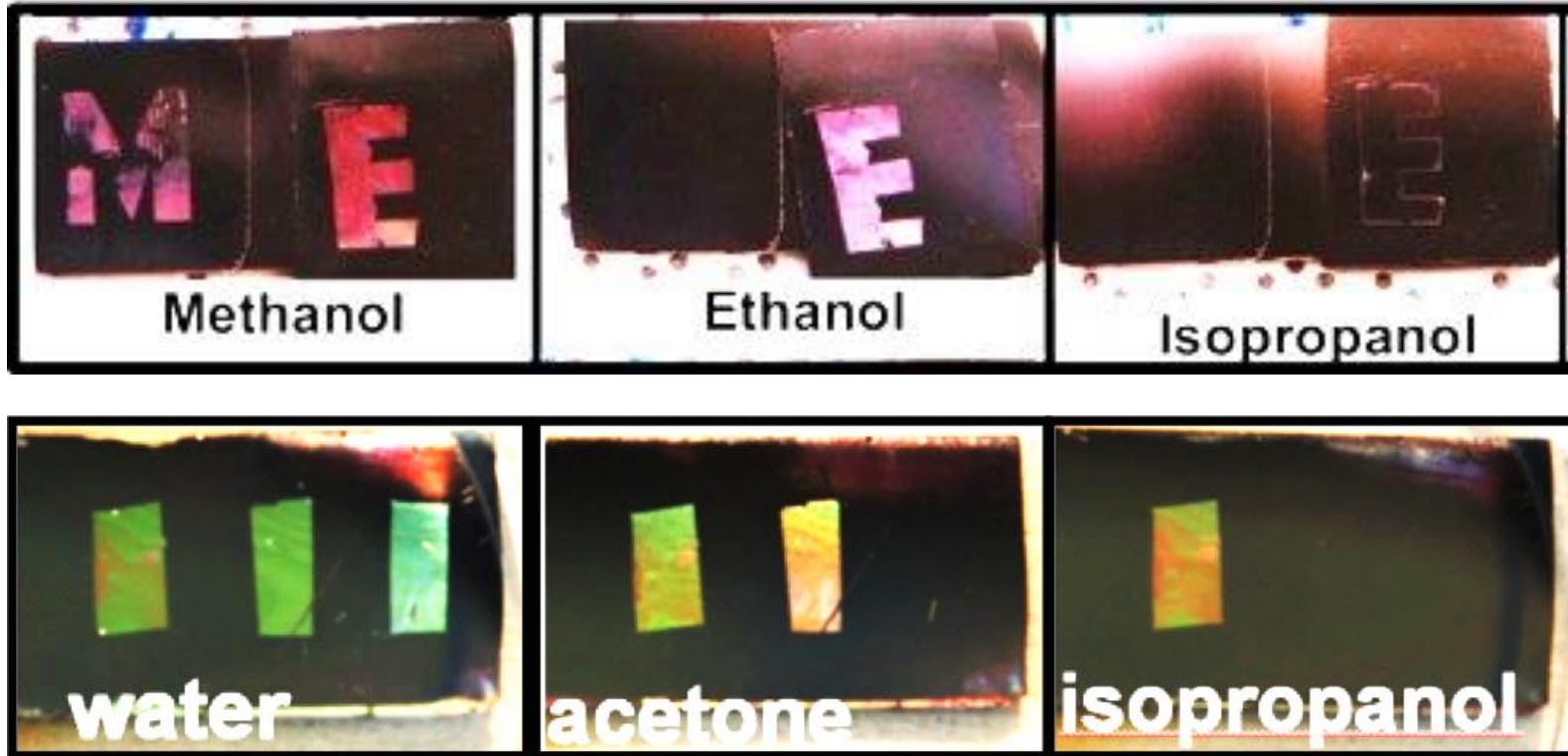
John A. Paulson  
School of Engineering  
and Applied Sciences

# Making waste classification more accessible

1. Predict hard-to-measure properties from easy-to-measure ones

**2. Measuring new properties with simple optical tests**

# Measuring surface interactions with color patterns



**Rapid colorimetric distinction of liquids based on physical properties**



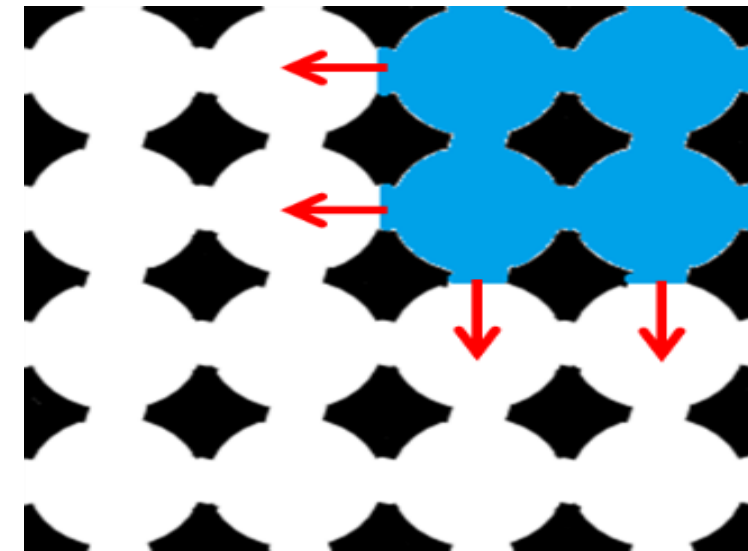
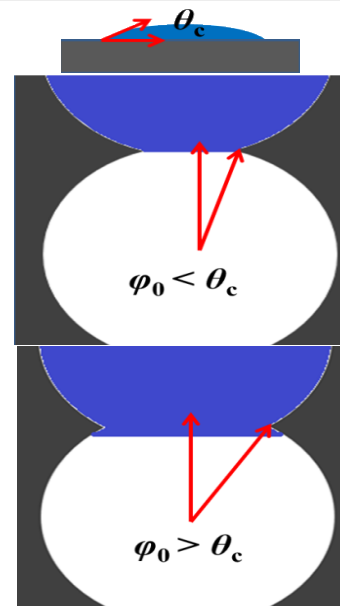
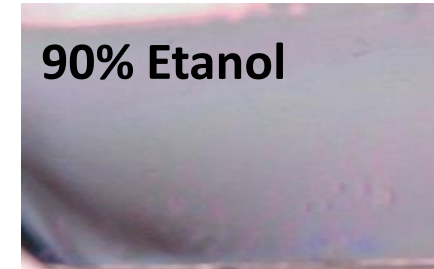
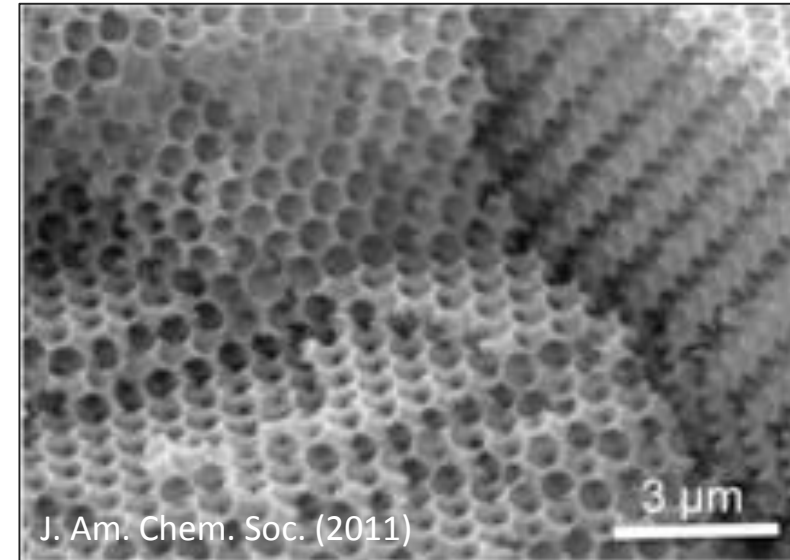
## 1. Thin film with highly regular nm-scale pores

1. Pores scatter visible light – iridescent color

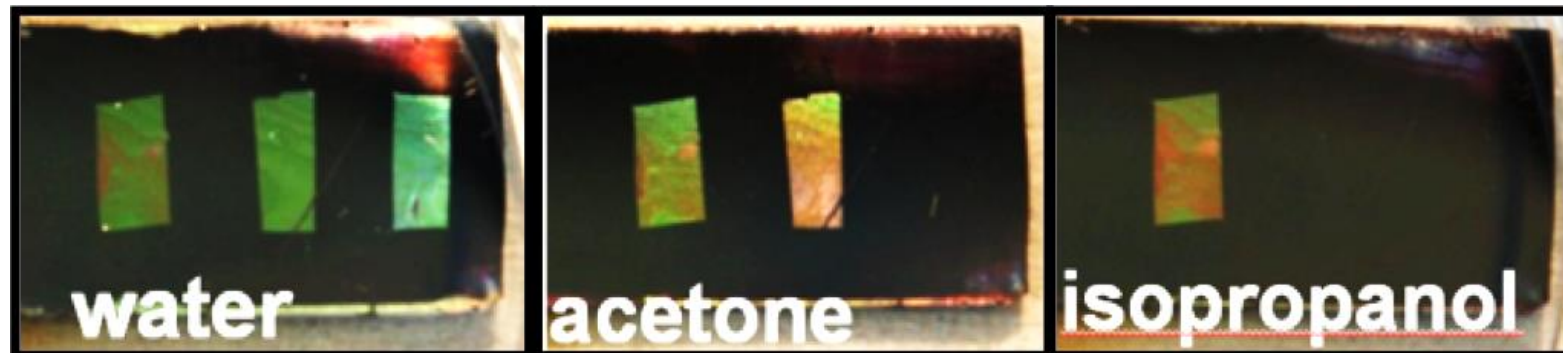
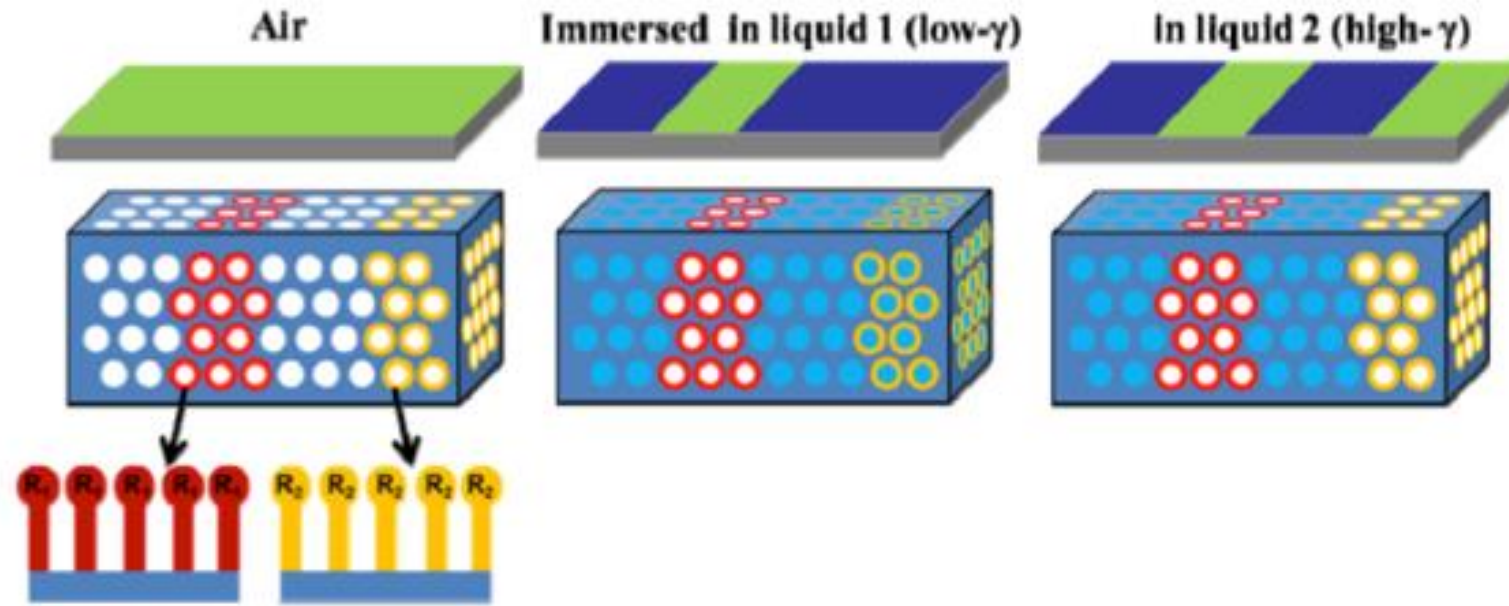
## 2. Each pore lets liquid fill below a critical surface energy

1. Critical value depends on pore shape
2. All pores have about the same shape

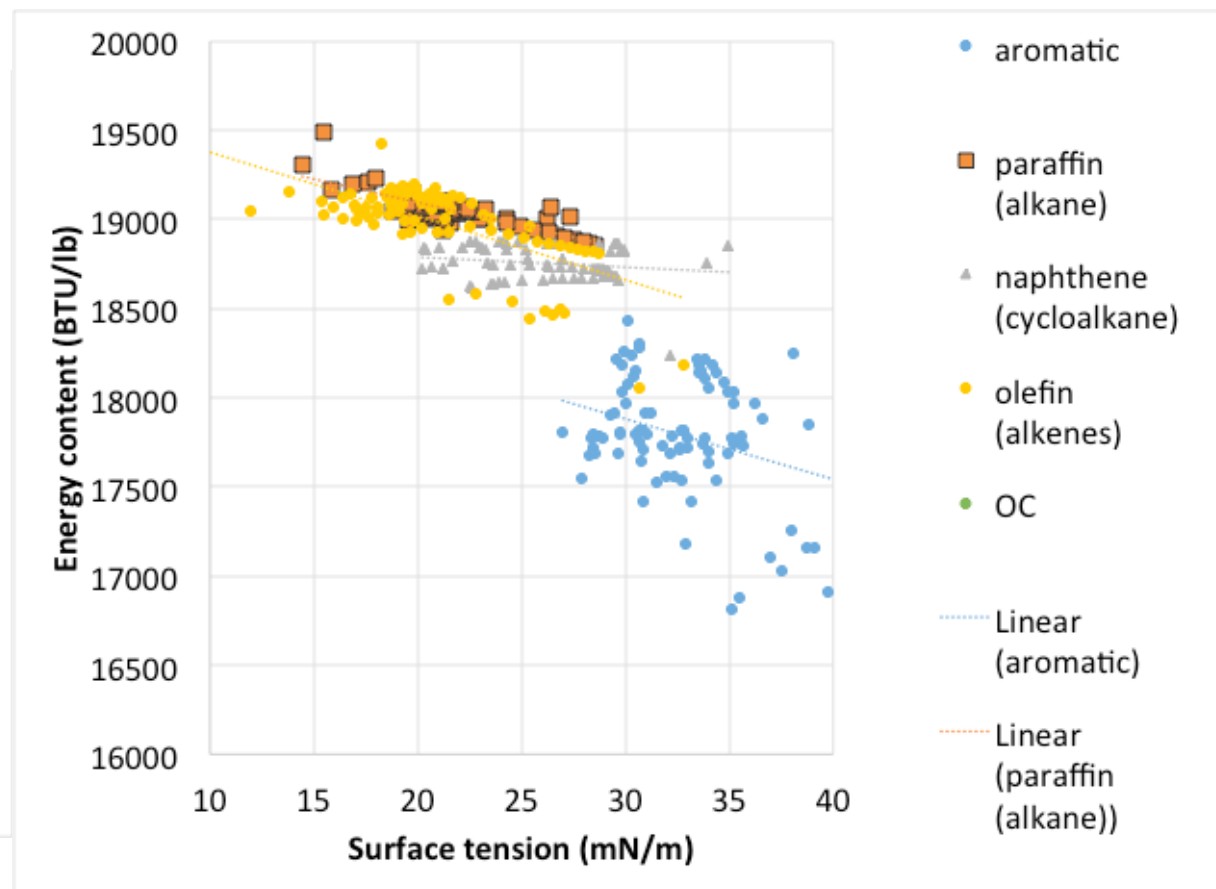
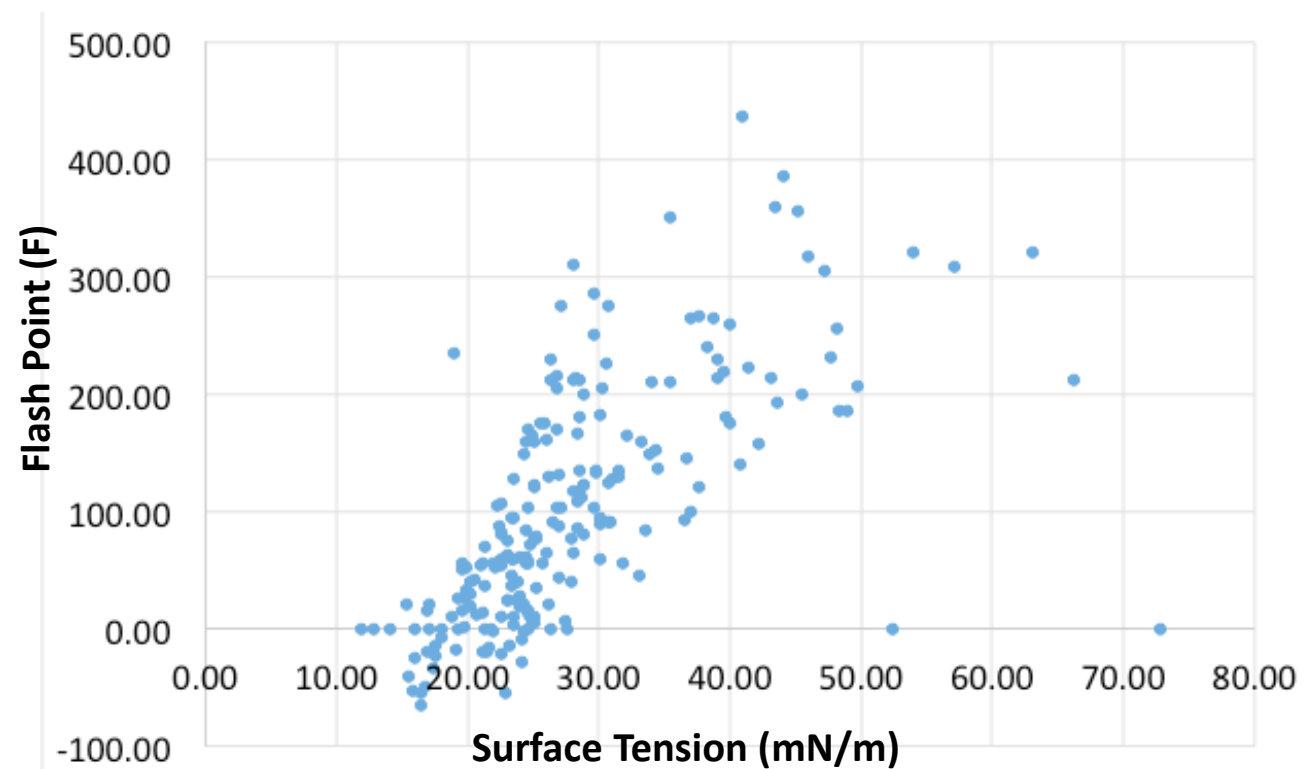
## 3. Tiny change in surface tension creates large visible color change



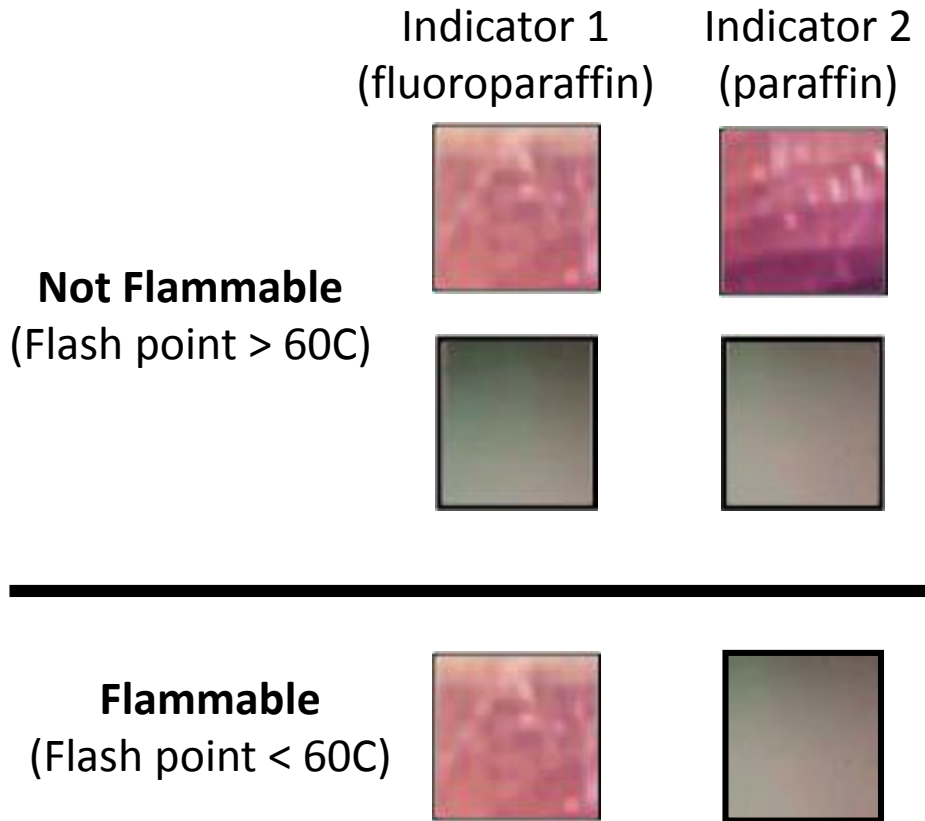
# Patterned surface chemistry: Multiple selective responses



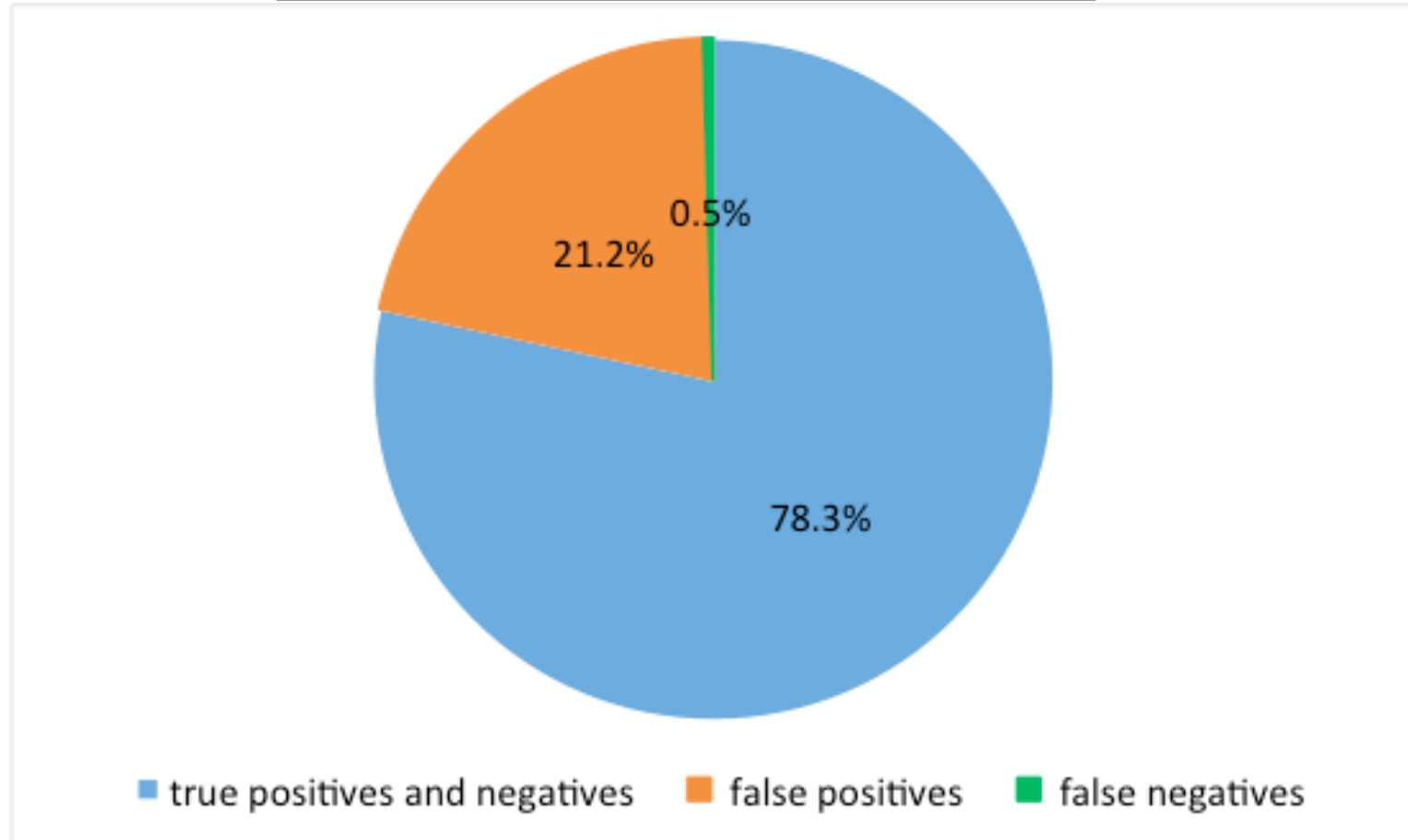
# Surface tension correlates with flammability



# "pH paper" for Flammability



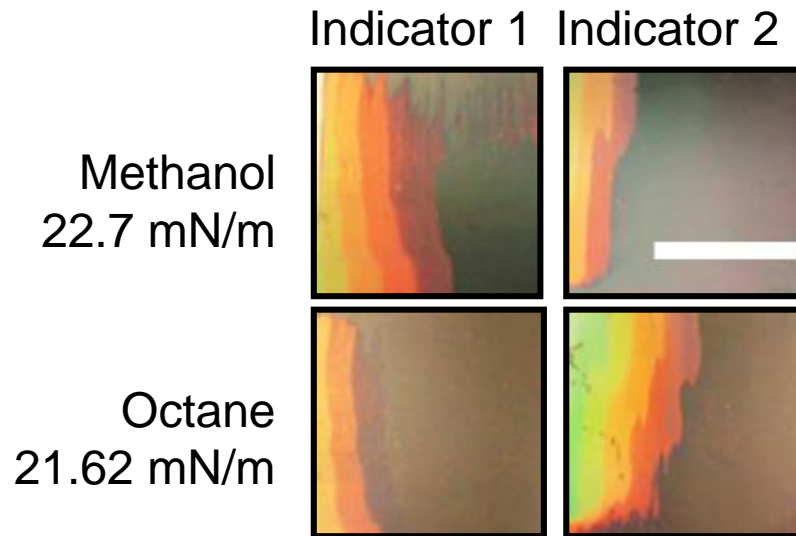
## Tested on 217 common chemicals



**Two indicators with different functionalization (paraffin and fluoroparaffin) combine to identify flammables with 99.4% sensitivity and 78% specificity**

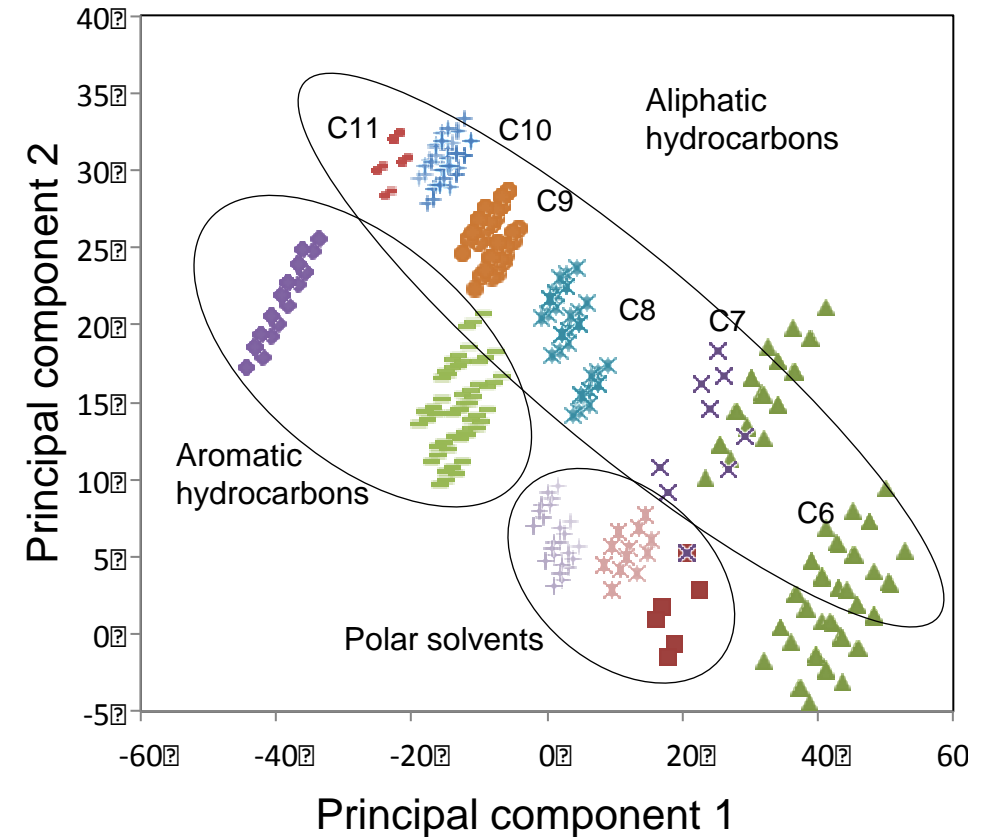


# More complex indicator arrays reveal chemical properties



Reversed relative wetting on two different gradients yields more information about their compositions than just their relative surface tension.

## Chemical classification of liquids in 6-indicator array

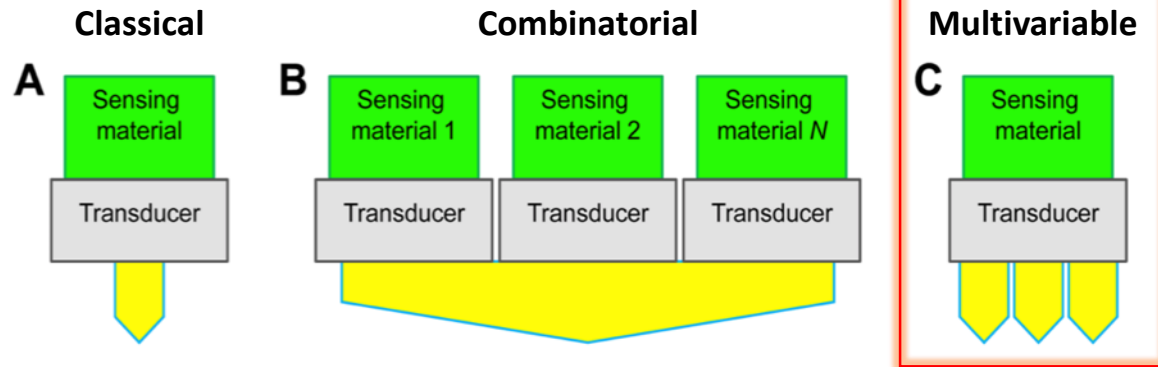
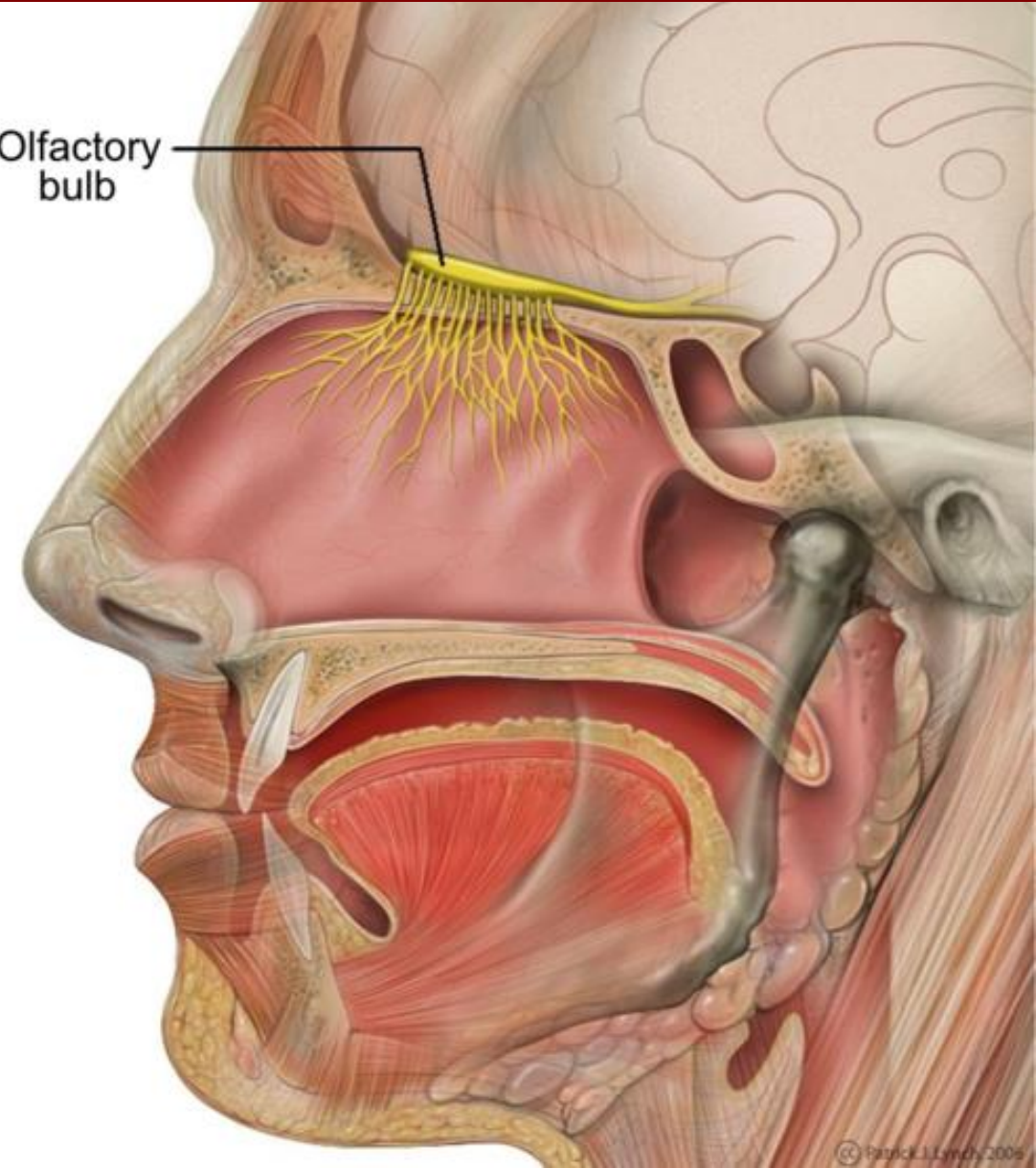


# Bio-inspired spatio-temporal approach mimicking the olfactory system for sensing volatiles

**Non-equilibrium odor delivery:  
Spatio-temporal approach**

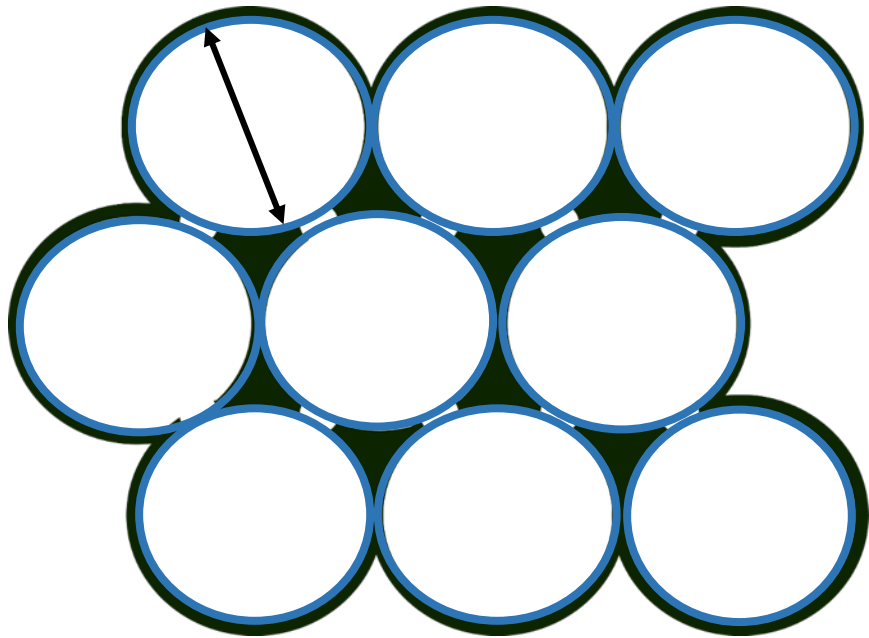
**Interpretation of the odor  
by the neural network**

Olfactory bulb

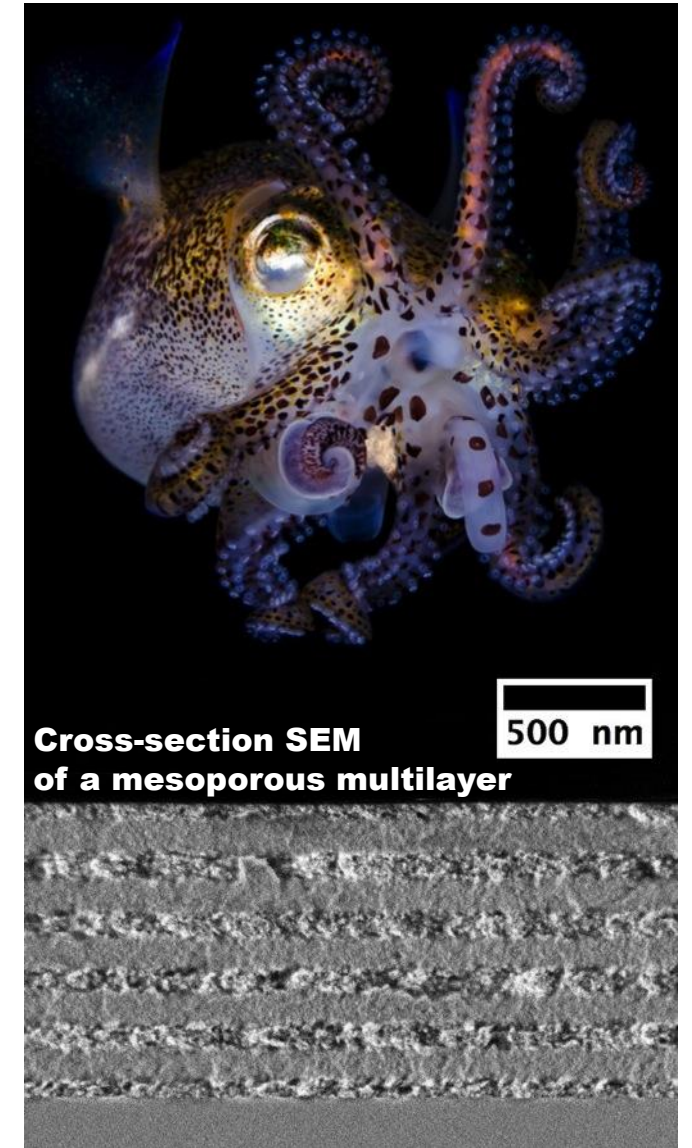
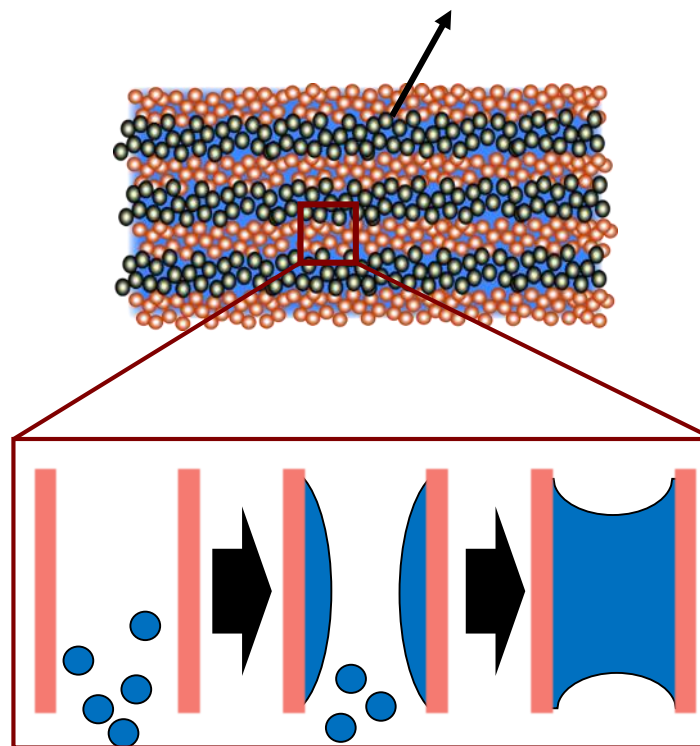


# Mesoporous colorimetric indicators allow for volatile sensing

Macropores ~ 200-350 nm



Mesopores ~ 2-50 nm

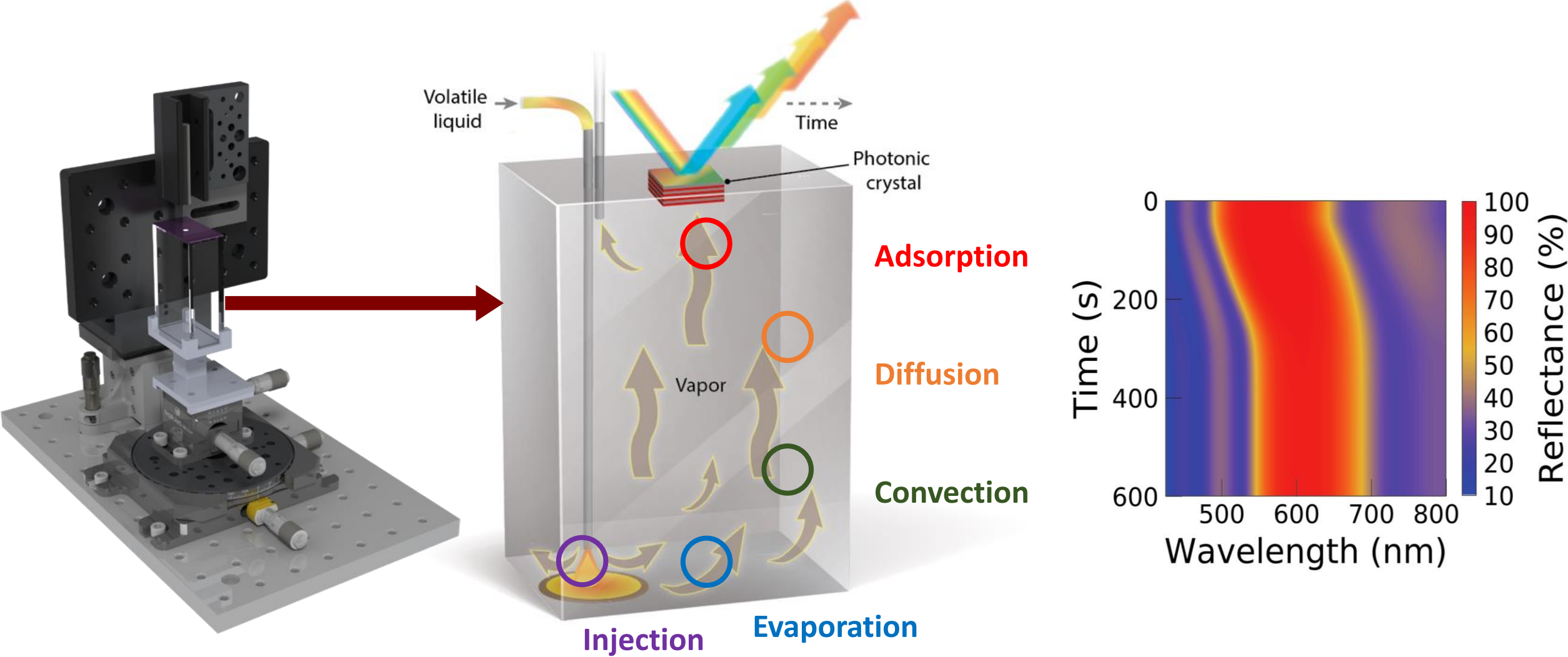


Cross-section SEM of a mesoporous multilayer

Photo by Todd Bretl



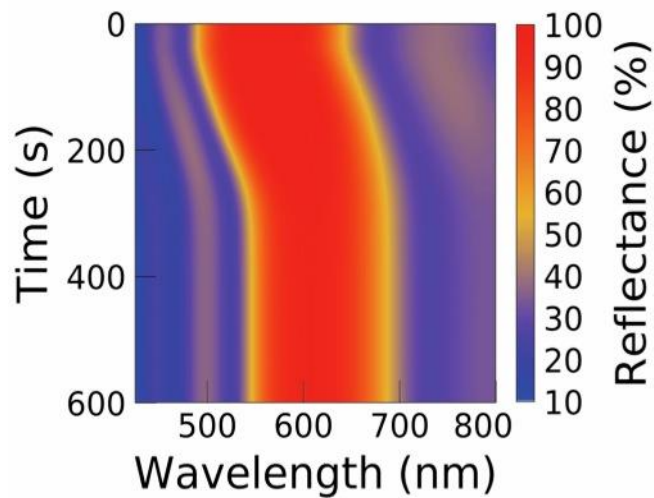
# A multivariable platform for detecting volatile components





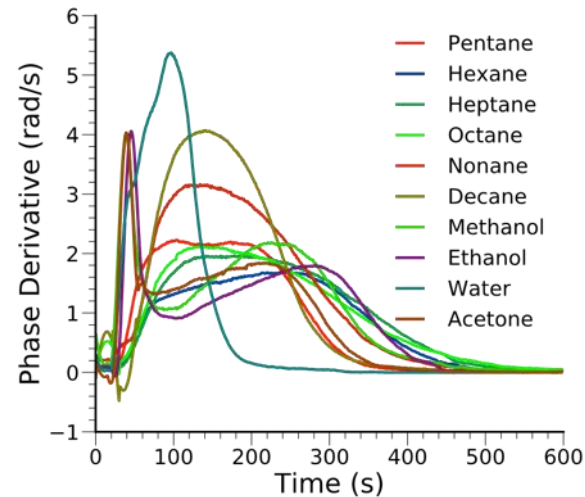
# Data processing pipeline

## 1. Collect dynamic data



## 2. Reduce Dimensionality

- Fourier Transform
- Fourier Phase
- Phase Derivative



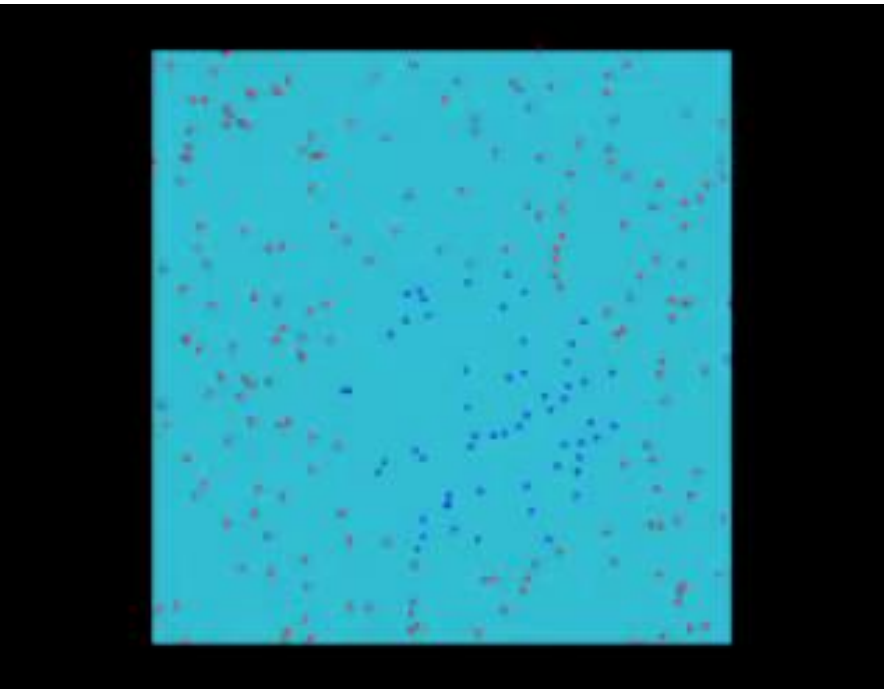
## 3. Analyze with machine learning



**Classification**

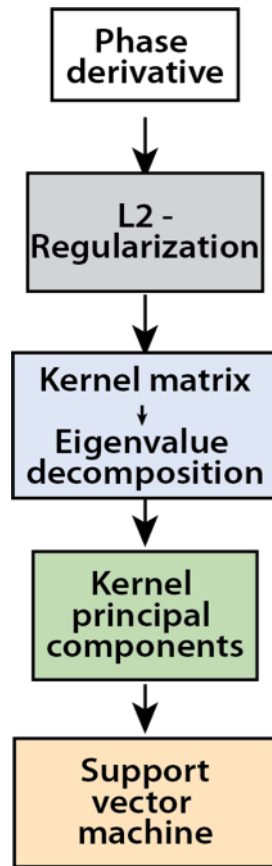
**Prediction  
(regression)**

# Classification works better when using the SVM with kernel principal components

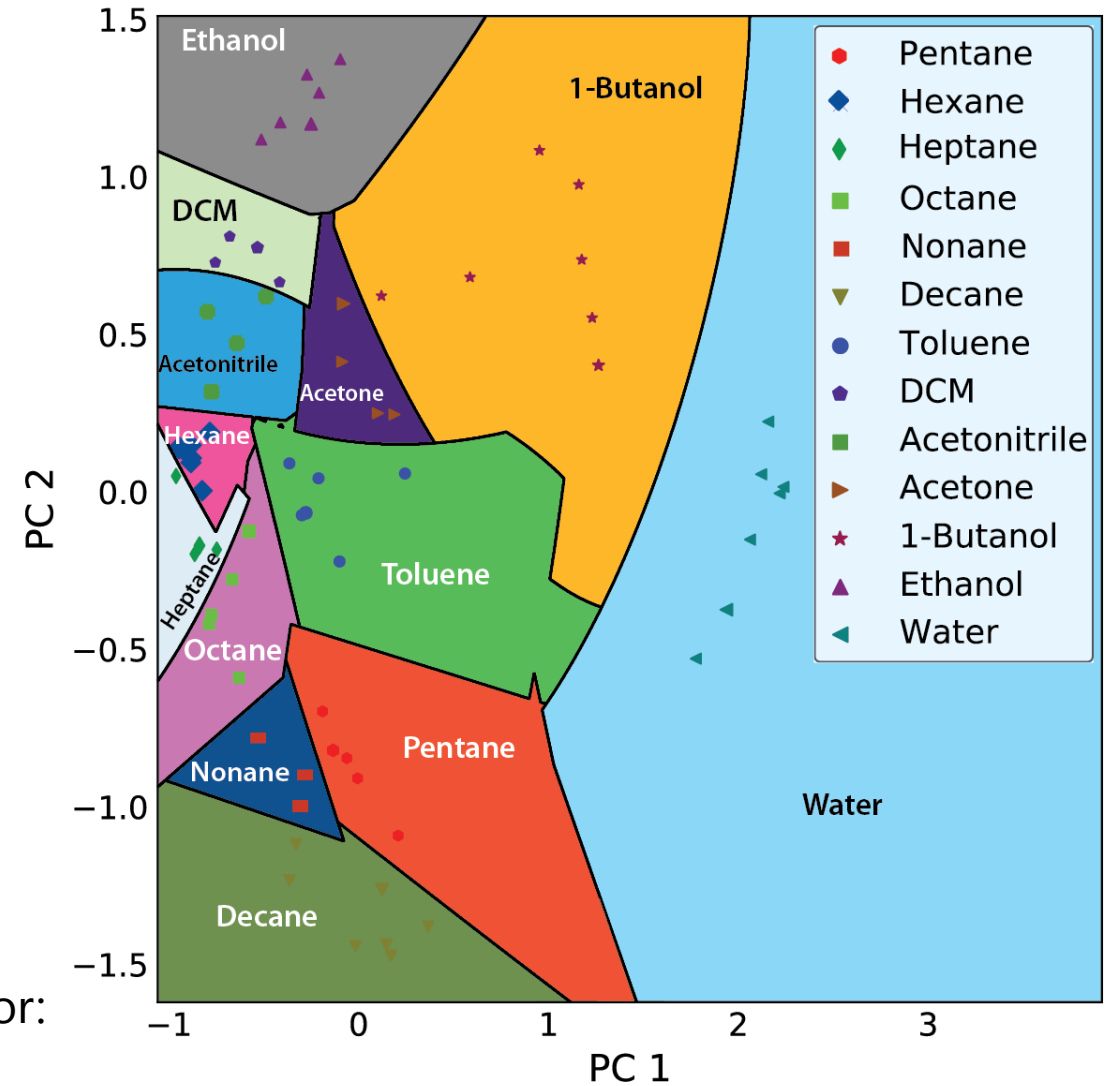


SVM with polynomial kernel visualization  
@udiproduct

Data pipeline:

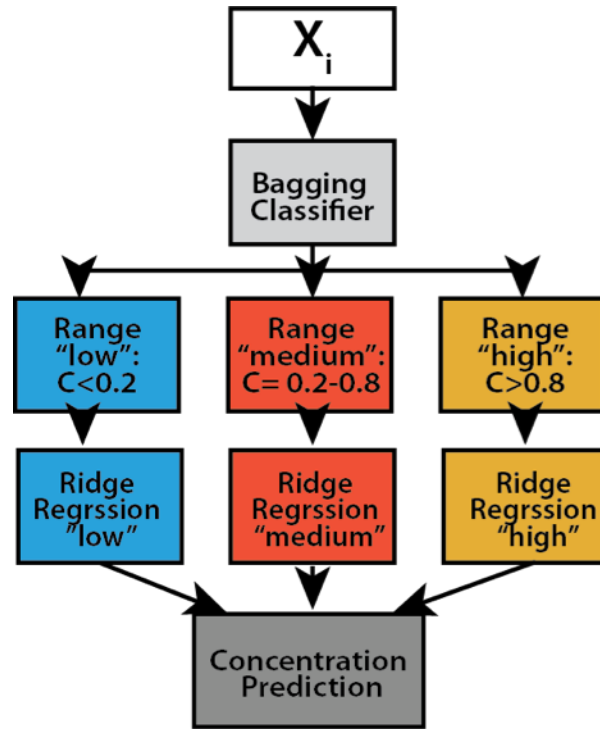


Random permutation cross-validator:  
20% test – 80% training



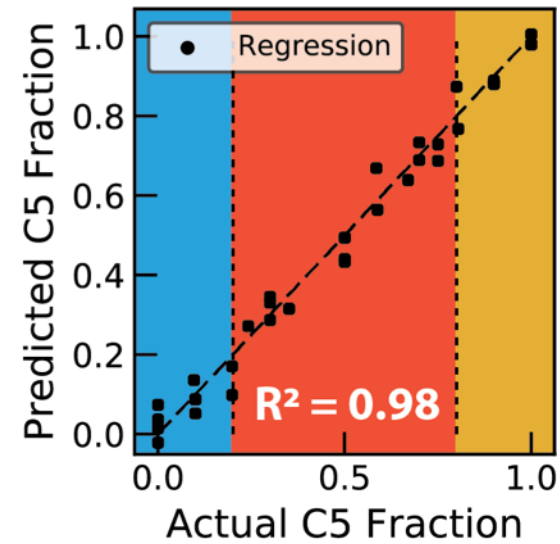
# Concentration prediction using the regression models for hydrocarbon mixtures

Data pipeline:

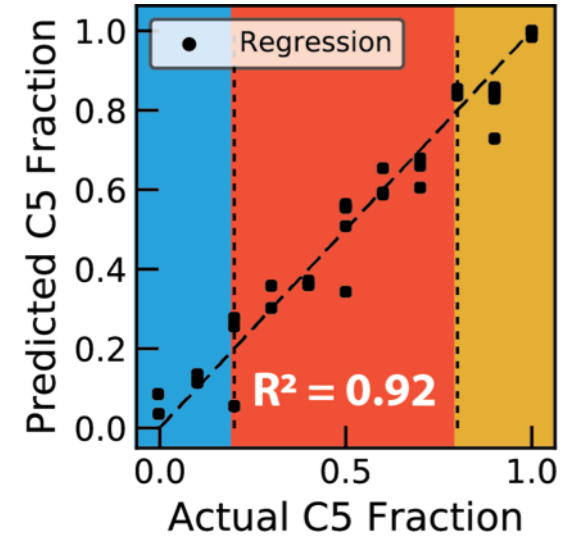


Analysis of  
*pentane/hexane*  
and  
*pentane/octane*  
mixtures

*Pentane/octane*

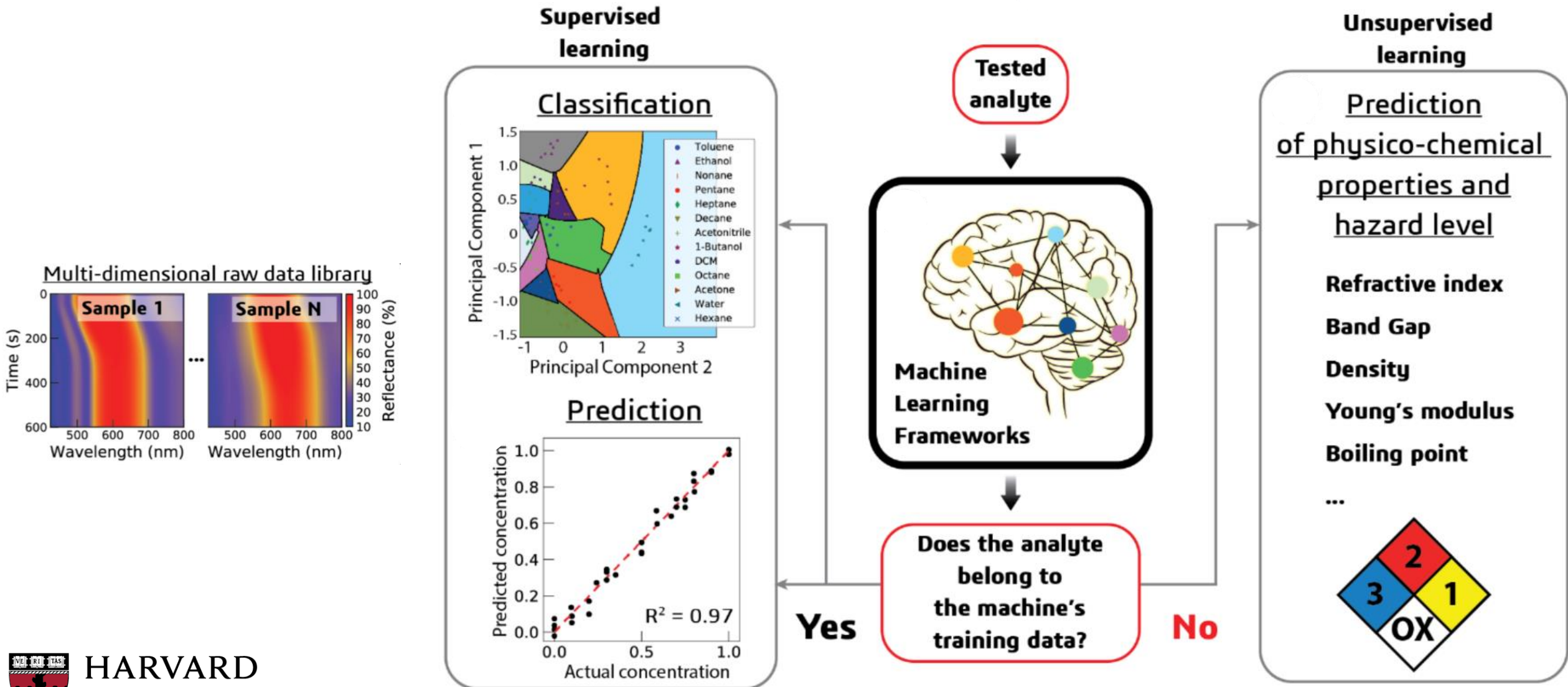


*Pentane/hexane*



Polynomial kernel ridge regression in each region

# Future goal: Unsupervised learning of analyte properties



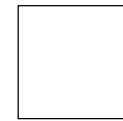
# Device Concept

Instant results displayed

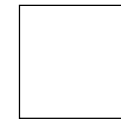


Disposable container with multiple indicator materials

## Indicator materials



Property 1



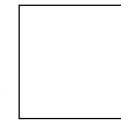
Property 2



Property 3



Property 4



Property 5



Property 6

Camera



- Computer vision readout
- Combinatorial analytics
- Machine learning



# Improving classification of hazardous waste

- Flammability
- Volatility
- Corrosiveness (pH)
- Water content
- Caloric value (heat of combustion)
- Contains halogenated organic compounds?
- Contains heavy metals?
- Reactivity

**Many important properties are hard to measure rapidly in the field**



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School of Engineering  
and Applied Sciences

# Improved classification of hazardous waste

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- Reactivity

## Where improvements came from:

- **Develop new simple optical tests to measure different properties**
  - Surface tension
  - Wettability
  - Differential adsorption of volatiles
- **Develop algorithms that predict hard-to-measure properties from easy-to-measure ones**
  - Flammability and water content from wettability
  - Caloric value from refractive index
  - Volatility from surface adsorption

**Ongoing improvements to sensors and algorithms aim to achieve full hazard classification in a single device**



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School of Engineering  
and Applied Sciences

Questions?





U.S. Department  
of Transportation

**Pipeline and  
Hazardous Materials  
Safety Administration**

**END Day 1**