

# Exhaust Phosphorous Chemistry

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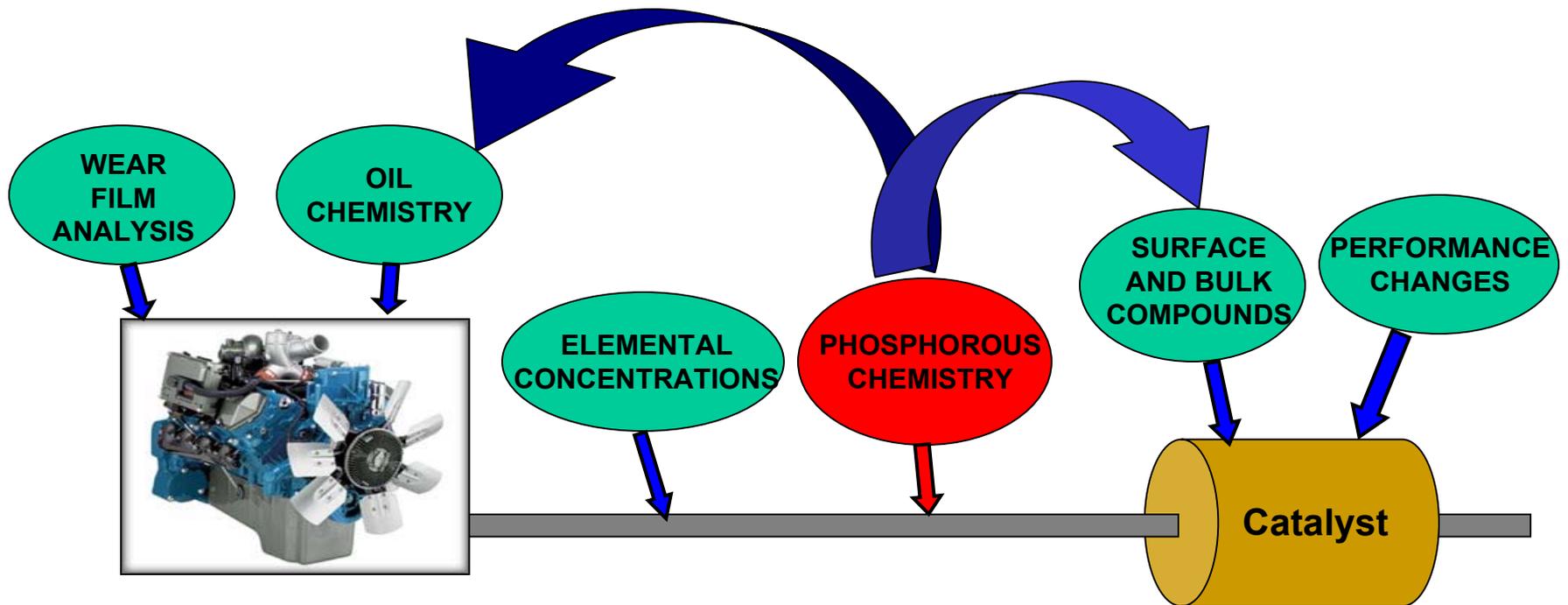
# Phosphorous

- Zinc dialkyldithiophosphate (ZDDP) is used in lube oil
  - Contains zinc, sulfur, and phosphorous
  - Protects oxidation, corrosion, and wear protection
  - Various alcohols can be used to affect activity of ZDDP
- Phosphorous content in lube oil is being reduced
  - 1964 to 1989, no limit
  - 1994, 0.12% maximum
  - 1997 to 2002, 0.10% maximum
  - 2005, 0.08% maximum (proposed)
- Phosphorous is a well documented catalyst poison

# Background

- Most phosphorous found in front 2” of catalyst
  - Affects light-off
- Phosphorous transfer to catalyst is typically high
- 2 to 16 grams of phosphorous per 120,000 miles typical for automotive
- Various ways have been used to study poisoning
  - Long mileage
  - Increased oil consumption
  - Doped fuel
  - Doped lube oil
  - Doped exhaust
  - Direct impregnation
- Phosphorous chemistry is complex and depends on method of introduction and other materials present

# Lube oil additive related measurements



Can exhaust phosphorous chemistry measurements provide a link between additive chemistry and catalyst reactions?

# Exhaust Phosphorous Chemistry

**LUBE OIL  
+ ENGINE**

**EXHAUST  
CHEMISTRY**

**CATALYST**

**ZDDP**

**ZDDP –**

**ZnPO<sub>4</sub>**

**P<sub>2</sub>O<sub>5</sub>**

**Ca**

**Mg**

**Mn**

**Other phosphates**

**NO<sub>x</sub>**

**Nitrates**

**SO<sub>3</sub>**

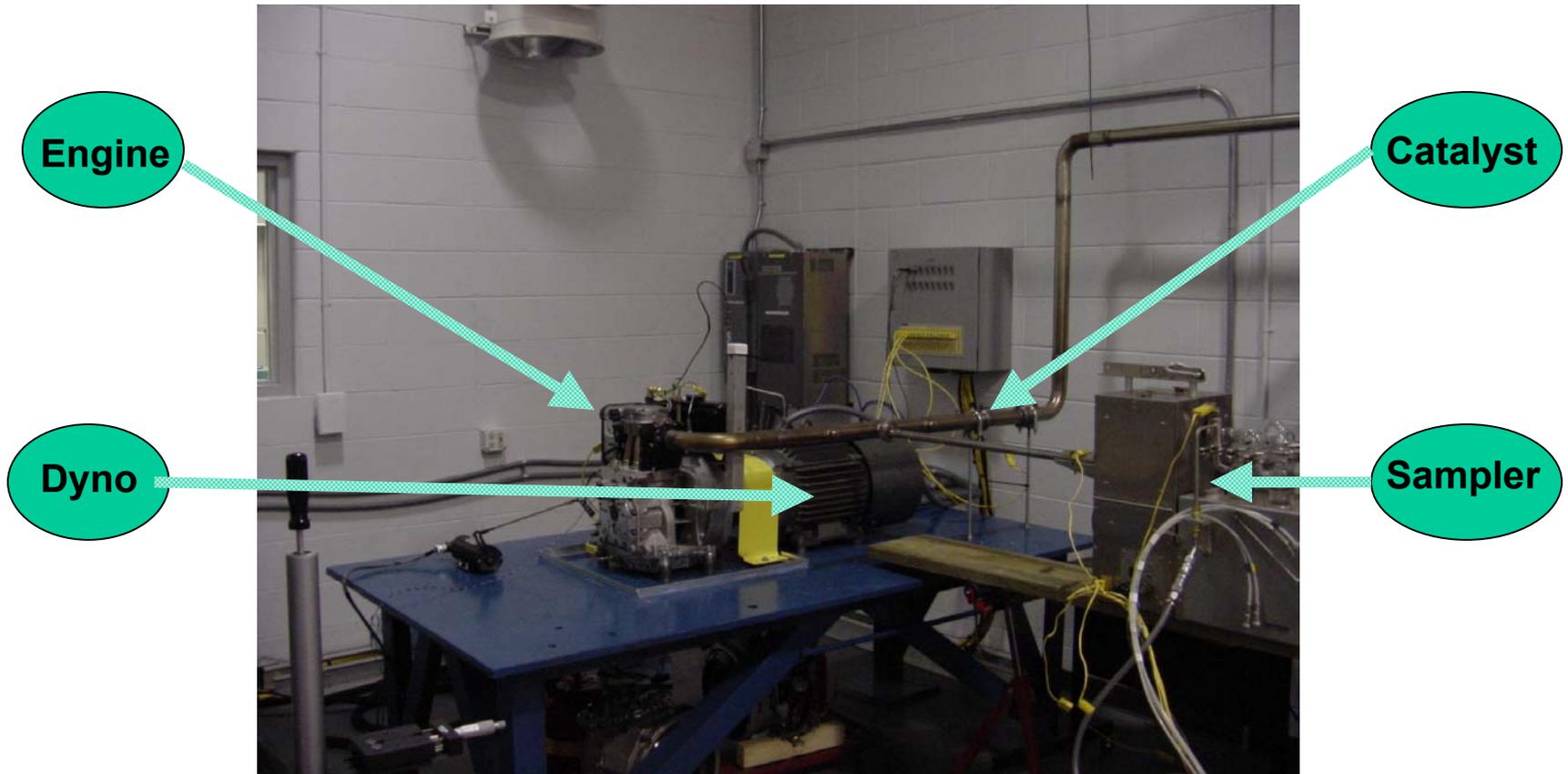
**Sulfates**

**GLASSY  
COATINGS**

**FLUFFY  
COATINGS**

**BULK  
WASHCOAT  
COMPOUNDS**

# Experimental set-up



# Catalyst and holder



# Sources of materials

- Engine
  - Hatz
    - 500 cc single cylinder DI diesel
- ZDDP additives
  - Elco Corporation
    - 4,5,8 primary alcohols
    - 2 secondary alcohols
- Catalyst substrates
  - NGK
    - Cordierite, 200 cpsi, 12 mil, 2” dia x 3” long
- Model catalysts
  - Engelhard Corporation
    - Diesel oxidation catalyst (low PM, alumina, ceria)
    - Diesel NOX adsorber catalyst (Pt, barium, alumina)

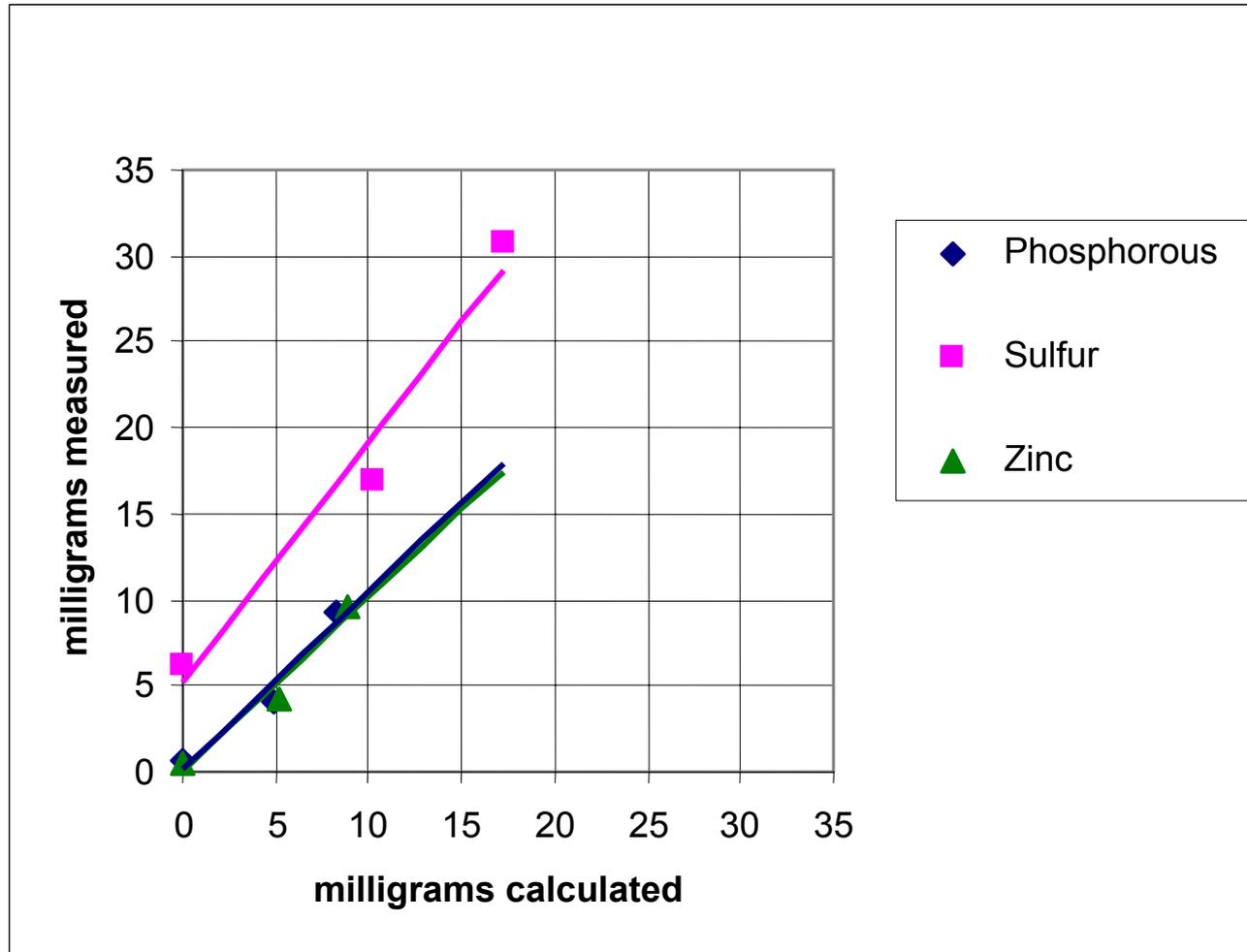
# Sampling and analysis – part 1

- Measurement capability development
  - Dope ZDDP into fuel
  - Vary engine load to vary exhaust temperature
  - Hot exhaust sampling

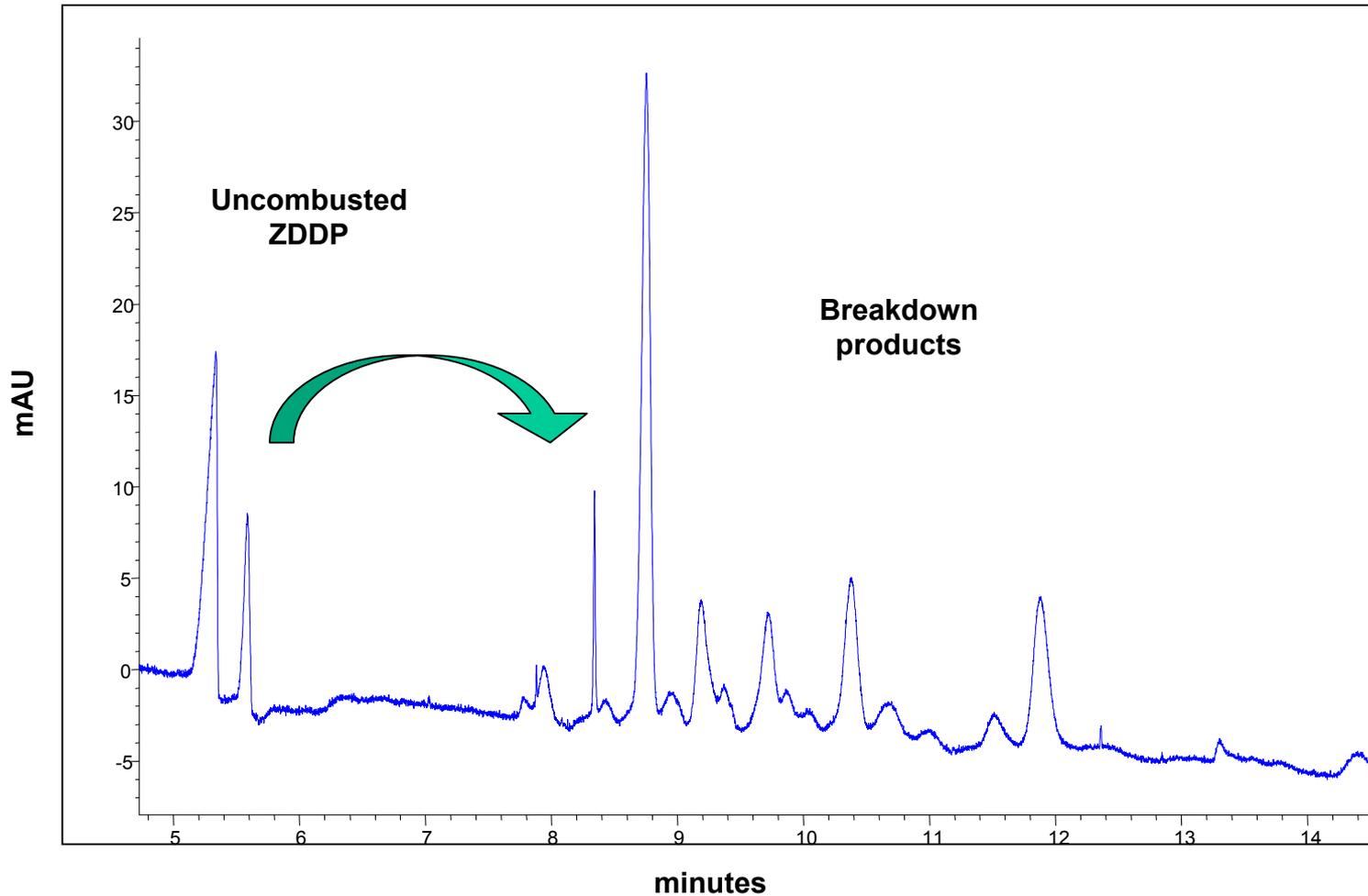
# Phase 1 – measurement development

- Metals analysis
  - Filters and impingers
  - XRF and ICP
- Compound identification
  - Filters and impingers
  - FTIR
  - GC-MS
  - Electrospray MS
  - Capillary-electrophoresis
  - Raman
- Catalyst analysis
  - Raman
  - DRIFTS

# Elemental balances



# CE electropherogram – ZDDP in engine exhaust 230 nm UV adsorption



# Sampling and analysis – part 2

- How do engine / lube oil changes affect exhaust chemistry?
  - Dopant formulation
  - Presence of other metals
  - Path for introduction
- How do exhaust chemistry changes affect catalyst?
  - Surface compounds
  - Bulk reactions
  - Catalytic activity

# Project status

- Literature review and discussions
- Engine set up and running
- Sampling and methods development underway
- Identification of ZDDP breakdown products underway