Novel Approaches for Speciation of Platinum and Vanadium in Mobile Source Emissions

Martin Shafer¹, James Schauer¹, Water Copan², Alberto Ayala³, Shaohua Hu³, Jorn Herner³

¹University of Wisconsin-Madison
Environmental Chemistry & Technology
²Clean Diesel Technologies Inc.
³California Air Resources Board

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Motivation

- Controlling emissions from mobile sources are critical for continued reduction in health impacts of air pollution, and for addressing regional and global climate impacts.
- Most current and proposed emission control strategies for diesel and gasoline engines employ metal catalysts to reduce tailpipe emissions of regulated species.
  - Gasoline Three-Way-Catalysts (Pt, Pd, Rh)
  - Diesel Fuel Based Catalysts (Pt-FBC)
  - Diesel Particulate Filters (Pt-Catalyzed)
  - Diesel Selective Catalytic Reactors (V-SCR)
- The use of these metals raises concerns about potential environmental contamination and the health implications of widespread trace metal dissemination.
The toxicological responses of many metals (e.g. Cr, Cu, Mn, Pt, V) are determined by the specific chemical & physical speciation in the emissions.

- **Platinum**: soluble, oxidized, halogenated (e.g. chloroplatinic acids) species are 500 fold more toxic than metallic species.
- **Vanadium**: pentoxide V(V) species exhibits much greater toxicity than the lower oxidation state species.

**Problem and Challenge:**

- 😞Extant modern methodologies provide little relevant speciation information.
- 😞Traditional techniques that are speciation capable lack the required sensitivity, particularly in the context of lower emissions from vehicles equipped with modern control devices.
Engine Exhaust PM Characterization

- Elemental & Isotopic Characterization
  - Magnetic sector (high resolution) ICP-MS
  - Sensitivity and Interference Isolation

- Chemical & Physical Speciation of PM
  - Solubility
  - Oxidation State
    - Soluble Species:
      - Long-path (100 cm) Spectrophotometry with Characteristic Ligand e.g. Fe(II)/Fe(III), Mn(II)/Mn(>III), Cr(III)/Cr(VI)
      - Immobilized Ligand – Selective Extraction and Elution
    - Direct Solids:
      - Synchrotron X-ray Absorption Spectroscopy
  - Colloid Charge: Ion Chromatography (DEAE, SAX micro-columns) → ICP-MS
  - Colloid Size: Ultrafiltration (10, 100 kDa) → ICP-MS

Complementary Total and Extractable Methods
Speciation Background

- **Platinum**
  - Oxidation States (0, II, IV). Group 8 transition metal.
  - Higher oxidation states may be more soluble.
  - Chloroplatinic/um salts (H, NH$_4$, K, Na) are very soluble.

- **Vanadium**
  - Oxidation States: (0,II,III,IV,V).
  - Higher oxidation states more soluble in water due to hydrolysis.
    - V(V): (high pH) VO$_4^{3-}$, HVO$_4^{2-}$, H$_2$VO$_4^-$, H$_3$VO$_4$, VO$_2^+$ (low pH).
    - V(IV): cationic (VO$^{2+}$)
Platinum: Sources and Receptors Under Study

- Three-Way-Catalysts
- Size-Resolved PM from Engines burning Platinum-Amended Diesel Fuel
- PM from Platinum-Catalyzed DPF
- Roadside Dust / Soils

25 mm PCIS Substrate

Gasoline Engine Catalytic Converter
What is a Fuel-Borne Catalyst?

- Catalyst dosed directly into diesel fuel
  - Pt / Ce fuel-soluble bimetallic catalyst
  - delivered *in situ*
- Active in high temperature combustion zone
  - higher efficiency of fuel HC combustion
- FBC intimate contact with PM
  - more complete combustion of solid C, HC
  - uniformly distributed across PM size range
  - no increase in ultra-fines
- Delivers Catalyst to DOC / DPF
  - fresh catalyst surface replenishment
  - same active forms
  - permits lower lifetime use of Pt
Platinum: Analytical Speciation of Engine PM

- **Solid Phase**
  - Total: microwave/acid digestion – HR-ICP-MS
  - **Oxidation State: Synchrotron XAS**

- **Extractable Species**
  - Primarily oxidized and halogenated species
  - Total “soluble” - HR-ICP-MS
    - Water
    - Methanol
    - DCM
  - Ultra-filtration: colloidal versus “dissolved”
  - Ion Chromatography: anionic versus cationic
  - HPLC-IC-HR-ICP-MS: specific chemical species

- **Particle Size Distribution**
  - Sioutas PCIS (5 size-cuts)

Analytical Challenge: <1 ng extractable platinum (10-30 pg in specific fractions).
Speciated Water Soluble Platinum in Diesel PM

FTP Cycle Means

Extractable fraction = < 3%.

Large colloidal fraction (44% of extractable species).

Dissolved (<10 kDa) species exhibit significant anionic character on DEAE (42%).

Vanadium: Analytical Speciation of Engine PM and Urban Aerosol

- **Solid Phase**
  - Total: microwave/acid digestion – HR-ICP-MS
  - **Oxidation State: Synchrotron XAS**

- **Extractable Species**
  - Primarily V(V) and V(IV)
  - Total water and acetate soluble: HR-ICP-MS
  - $[\text{V(II), V(III)}]$ V(IV), V(V): Immobilized ligand speciation

- **Particle Size Distribution**
  - Sioutas PCIS (5 size-cuts)

**Significant Analytical Challenge:** 0.2-2 ng total vanadium from Dyno Trials for speciation studies.
Vanadium Catalyst: Total Vanadium

Particle Size (µm)

- dM/dlogDp
- 0.0
- 0.5
- 1.0
- 1.5
- 2.0

14.3 µg V g⁻¹

Vanadium Catalyst: Soluble Vanadium

Particle Size (µm)

- dM/dlogDp
- 0.0
- 0.1
- 0.2
- 0.3
- 0.4
- 0.5
- 0.6

3.5 µg V g⁻¹

Vanadium Catalyst: Soluble V (% of Total)

Particle Size (µm)

- Percent Soluble
- 0
- 20
- 40
- 60
- 80
- 100

Aggregate = 24%

SCRT® System Schematic

- Urea Tank
- SCR Control Unit
- Diesel Engine
- SCR Catalyst System
- Diesel Oxidation Catalyst
- SCR Catalyst System
- SCR Catalyst for Reduction of NOₓ to N₂
- Ammonia Slip Oxidation Catalyst

Table:

<table>
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<th>NOₓ (g/kWh)</th>
<th>PM (g/kWh)</th>
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<tr>
<td>Engine out</td>
<td>6.0</td>
<td>0.15</td>
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<tr>
<td>Engine + SCRT</td>
<td>0.95</td>
<td>0.005</td>
</tr>
<tr>
<td>Euro 5 targets</td>
<td>2.00</td>
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* 12 litre turbocharged (310 kW)
Vanadium Oxidation State Speciation with Chelex

Chelex: cation exchanger at higher pH, anion exchanger at lower pH. In pH range of 4 to 7.4 both cations and anions are adsorbed.

- **Preparation & Extraction**
  - Micro-columns of Chelex (immobilized iminodiacetate)
    - 0.2 g of perchloric acid cleaned and acetate buffered (pH=4.5) resin
  - Samples extracted in 2 mM sodium acetate buffer
    - 1.5 mL nitrogen purged buffer in purged cryo-vial
    - 60 minutes with defined agitation (under nitrogen canopy)

- **Separation – Speciation**
  - 1.0 mL of sample loaded onto column
  - Process through column at 1.0 mL per minute – collect fraction
  - Elute column with 4 x 1 mL of 0.1 M ammonium hydroxide – collect fraction = V(V).
  - Elute column with 2 x 1 mL of 0.2 M perchloric acid – collect fraction = V(IV)

- **Vanadium Quantification**
  - Magnetic Sector ICP-MS in medium resolution with on-line standard addition
  - 10,000 cps/ppb V. Background = ~2 cps (0.2 ng L\(^{-1}\)). 1-5% RSD.
Vanadium Oxidation State Speciation with Chelex

Method Blanks

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<tr>
<th>Vanadium Oxidation State</th>
<th>Standard Deviation</th>
<th>Detection Limit</th>
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<tr>
<td>(IV)</td>
<td>0.044 ± 0.037 ng</td>
<td>0.11 ng (0.44 ppm)</td>
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<tr>
<td>(V)</td>
<td>0.016 ± 0.011 ng</td>
<td>0.03 ng (0.14 ppm)</td>
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n=17
Vanadium Speciation – Defined Standards

((V) - V₂O₅)

(V) = 96.4 ± 2.2 %

((IV) - VO₂ and VOSO₄)

(IV) = 89.3 ± 3.3 %

V2O5-A
V2O5-B
V2O5-C
V2O5-D

VO2-A
VO2-B
VO2-C

VOSO4-A
VOSO4-B
VOSO4-C

4.2 ng each trial
1.2 ng each trial
1.2 ng 2.4 ng 3.6 ng

Percent

0
20
40
60
80
100

Percent

0
20
40
60
80
100

V(V)
V(IV)
Not-Retained
Vanadium Speciation – Environmental Matrices

Urban Dust (NIST SRM)

- UD-A: 2.7 ng
- UD-B: 5.3 ng
- UD-C: 10.6 ng
- UD-D: 10.6 ng

Los Angeles Aerosol

- LA-Fire-A: 0.64 ng
- LA-Fire-B: 1.2 ng
- LA-Fire-C: 1.1 ng

V (IV) = 53.9 ± 5.5 %
V (V) = 43.8 ± 5.8 %

V (IV) = 56.6 ± 5.7 %
V (V) = 42.0 ± 5.6 %
Vanadium Speciation – Engine Exhaust PM

**ADVANCES**
1. Micro-scale
2. DLs improved by 10-50x
3. Coupling to HR-ICP-MS

**Vanadium Speciation – Engine Exhaust PM**

**Diesel Engine PM**
Vanadium Pentoxide SCR

0.33 ng 0.39 ng

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<th>Percent</th>
<th>TAL-03</th>
<th>TAL-07</th>
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V (IV) = 3.3 ± 2.3 %
V (V) = 96.6 ± 2.6 %

**SCR Mechanism: Vanadia**
- Riedel-Eley mechanism: reaction of strongly adsorbed NH₃ with NOₓ
- Involves acid vanadium and redox vanadium species

Synchrotron X-Ray Absorption Spectroscopy

- Direct Solids Analysis – complementary to solution phase tools.
- XANES – (oxidation state) and/or EXAFS – (nearest neighbor chemical bonding environment). XRD – (characteristic diffraction)
- Range of spatial scales (with/without micro-focused beamline).

\[ L_{III} \text{ Edge (2p sublevel) of Pt in PtO}_2 \]

EXAFS Spectra of Platinum Reference Materials

Pt-foil = platinum foil; Pt-alumina = 5% platinum on alumina; Pt-C = 5% platinum on graphite; Pt(II)Cl2 = platinum(II) chloride; TCP = potassium platinum(II) tetrachloroplatinate; PtO2 = platinum(IV) oxide; Pt(IV)Cl4 = platinum(IV) chloride; HCP = potassium platinum(IV) hexachloroplatinate

LBL-Advanced Light Source
Pt speciation was studied in a 4 year old 3-way automobile catalyst. A 30 µm thick, quartz slide mounted, longitudinal section of the center of the catalyst was prepared.

(A) Light microscope image; outlined area was examined with XRF mapping.

(B) Red (Pt) – green (Cu) – blue (Ce) XRF-derived tricolor map. Pt L3-edge extended-XANES spectra were collected at spots 0-2.

(C) The e-XANES spectra (11,466-12,077 eV) were fit with reference spectra - Pt foil, 5% Pt in alumina matrix, 5 % Pt in carbon matrix, Pt(II)Cl₂, Pt(IV)Cl₄, PtO₂, K₂Pt(IV)Cl₆·H₂O, and K₂Pt(II)Cl₄ – by linear least squares method

(D) Select reference spectra and an example fit shown in C and D).

Modeled fraction of oxidized Pt is significant.
XRF Map, and Extended-XANES Fitting Results, of Diesel Exhaust Particulates Trapped on a Diesel Particulate Filter (engine running a Pt-FBC)

Large heterogeneities in particle composition are observed with many particles exhibiting a significant oxidized platinum component.

**Strong evidence for PtO₂** (14-25% in many spots, up to 40% when associated with Ca and S), and less compelling evidence for presence of chloroplatinates.
Platinum bulk-XANES
XAS Spectra of Platinum Standards and Diesel Engine Exhaust PM (Running Pt-FBC Fuel)

XRF Maps of Diesel Exhaust Particulates Impacted on Teflon PCIS Substrates (engine running with a **vanadium SCR**)

Strong evidence of V, Ti–rich particles in engine PM

Preliminary e-XANES suggests V(V)
Acknowledgments
Significantly more Pt extracted with MeOH (28 ± 1.4%) than with DCM (0.79 ± 0.15%) or water.

DCM should not extract ionic Pt species (except via physical process).

DCM more selective in isolating any Pt associated with organic matter.

Methanol (MeOH) extracts and disperses both polar and non-polar species. Breaks up diesel PM soot matrix. High MeOH extractables fraction does not indicate the presence of a large pool of organo-Pt species.