

Real time measurements of ash particle emissions

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- Introduction and background
- Results
 - Tests performed
 - Lube oil spray calibration experiments
 - Steady state engine exhaust ash measurements
 - Transient ash measurements
 - Ash measurements downstream of DPF
 - Apparatus and procedure
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Why do we care about ash emissions?

- Degradation of exhaust aftertreatment systems
 - Deposition in Diesel particulate filters (DPF)
 - Plugging exhaust catalysts
- Health concerns with metallic nanoparticles
 - Diesel or SI
 - Mainly a concern for engines without exhaust filters
- Relationship with lube oil consumption



Inlet

Outlet

Ash distribution in exhaust filter channels (Helbel and Bhargava, 2007)

Mid



Accumulation of poorly crystalline Mn_3O_4 on the face of a TWC (Hayhurst, et al., 2006)

Particle formation history – 2 s in the life of an engine exhaust aerosol



Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. "On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results," Journal of Aerosol Science 37, 913–930.

Predicted equilibrium distribution of calcium compounds in diesel engine exhaust



Assumptions: 50 ppm sulfur fuel, equivalence ratio 0.5, lubrication oil containing 5000 ppm Ca, oil consumption 0.1% of fuel consumption.

Ash particles typically "decorate" the surface of soot particles but may also nucleate independently



Without Exhaust Aftertreatment

Engine out, light-load, low soot conditions: Most of the number emissions are solid with Dp < 23 nm



Cummins 2004 ISM engine, BP 50 fuel, AVL modes

Lube oil consumption leads to ash emissions

- Sources: mostly lube oil additives, engine wear, fuel additives
- Principle ash constituents: Ca, Zn, Mg, Fe, P, S



Objectives

- To develop and validate a real-time method to measure engine ash emissions
 - Testing the sensitivity of measurement method to specific metallic lube oil constituents
 - To validate the method for steady-state and transient Diesel engine emission application

High temperature oxidation method (HTOM) overview

Oxidize soot and HC PM within high temperature tube furnace

Cooled particles measured using real/near-real time particle instruments



Stable metal oxides and other refractory metal compounds are formed or survive high temperature tube furnace

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Engine exhaust apparatus



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Lube oil spray calibration experiments

- Investigate high temperature stability of likely ash constituents
- Atomize specially formulated lubricating oils with different additive packages
- Measure particle size distribution upstream and downstream of the furnace
 - Determine penetration vs. temperature
 - Compare with expected solid ash fraction

Specially blended lubricants provided by Castrol

	Base stock	Metal mass fractions in ppm					
_	104A	101A	100A	103A	102A		
B	<5	<5	<5	285	<5		
Ca	<2	<2	3946	<2	3724		
Mg	<2	<2	8	~500	<2		
Ρ	2	976	1052	<10	13		
S	55	1998	802	57	8804		
Zn	<5	1008	<5	<5	<5		

Upstream and downstream volume weighted particle size distributions



Particle volume fraction penetrating the tube oven



Expected metallic mass compared to measured

			_	Metallic Volume Fraction		_
			Concentration			
Blend #	Element	Compound	[ppm]	Expected	Measured	Measured/Expected
100A	Ca	CaCO3	3946	2.9E-03	7.3E-03	2.51
101A	Zn	ZnSO4	1008	5.9E-04	9.6E-06	0.02
102A	Ca	CaSO4	3724	3.4E-03	7.2E-03	2.10
103A	Mg	MgCO3	500	5.3E-04	7.8E-04	1.48

Note: Expected concentrations are based on the assumption of spherical particles of the compounds listed

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Volume weighted particle size distributions from VW TDI engine



Ash volume fraction of exhaust particles for different engine conditions



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Transient engine ash emissions



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Soot and ash particle volume concentration downstream DPF



Soot surface area and ash volume concentrations downstream DPF



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Conclusions

- HTOM calibration experiments lube oil sprays showed that
 - Ash constituents of Ca and Mg additives were conserved
 - Expected Zn compounds were not found apparently due to formation of volatile materials lost to the walls
 - This suggests possible different deposition mechanisms within a DPF
- Steady-state ash measurements showed a slight increase of ash fraction of exhaust particles with load
- Ash emissions under changing engine conditions were highly transient and history dependent
- Ash volume concentrations were successfully measured downstream a loading DPF and were shown to track better with soot surface area than volume concentration
- Ongoing work includes TEM analysis and ATOFMS analysis of particles treated by HTOM

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• Thank you for your attention

References

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Dp [nm]