OFFICE OF MINE SAFETY AND HEALTH RESEARCH

Fuel borne catalysts and aerosol emissions from sintered metal filtration system

Aleksandar D. Bugarski, NIOSH
Jon A. Hummer, NIOSH
Larry D. Patts, NIOSH
Emanuele G. Cauda, NIOSH
Arthur L. Miller, NIOSH
and
Jozef S. Stachulak, Vale

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Introduction

- Extensive research conducted at various underground mining operations and laboratories (Stachulak et al., 2006 & 2012; Bugarski et al., 2009 & 2012) showed that retrofit-type diesel particulate filter (DPF) systems are very effective as a control technology for reducing the exposure of underground miners to aerosols emitted by diesel-powered vehicles.
- However, various operational, reliability, and durability issues so far prevented wide implementation of DPF systems in underground mines.
- The results of long-term evaluation tests (Stachulak and Hensel, 2010) and field and laboratory emission tests (Bugarski et al., 2013) showed that the Mann+Hummel (M+H) SMF-AR® system is potentially a viable control technology that can be used to substantially reduce the exposure of underground miners to aerosols emitted by light-duty underground mining diesel-powered vehicles.

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The operation of the M+H SMF-AR® system requires the use of fuel additives containing iron-based fuel borne catalysts (FBCs).

- Potential emissions of nano-sized metallic aerosols with high surface reactivity and toxicity and their potentially adverse effects (EPA 2008) in underground environments is of concern.
- The NIOSH and Vale conducted a laboratory study to characterize the effects of selected fuel additives on the emission of aerosols (and criteria gases) emitted by a diesel engine equipped with the M+H SMF-AR® system.

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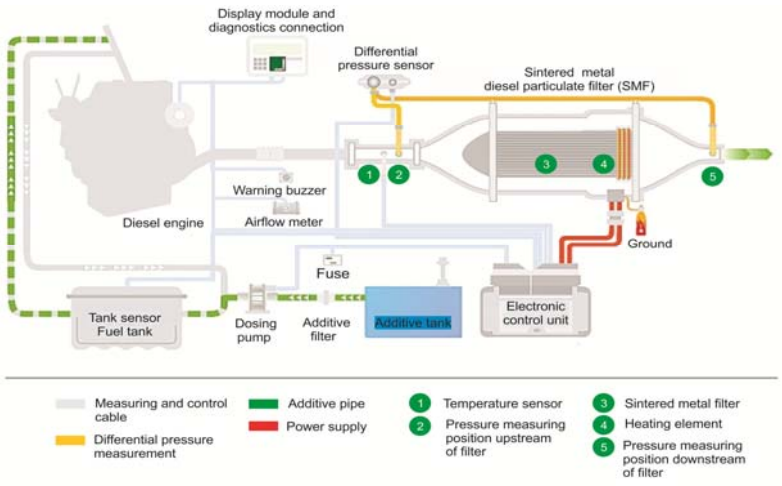
The Mann+Hummel SMF-AR system evaluated in this study is a hybrid (passive/active) DPF system.



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Mann+Hummel SMF-AR System

- The filter element was made of sintered metal plates with 10-µm mean pore size, 45% porosity, and 0.38-mm wall thickness.
- When needed, the electrical heater mounted at the back of the filter element is used to actively regenerate the system.
- The additive plays an important role in the regeneration process and operation of the system.

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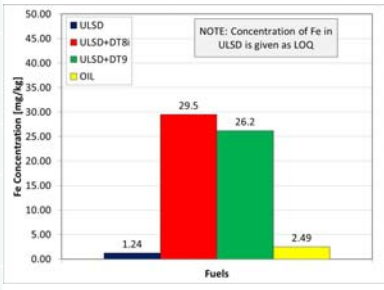
Fuels and Additives

- The emissions were assessed for three fuels:
  - ULSD;
  - ULSD doped with Satacene® (Innospec Ltd., Cheshire, U.K.) and marketed under name DT8i;
  - ULSD doped with Eolys Powerflex®, (Rhodia, La Rochelle Cedes, France) marketed as DT9.
- Both additives introduced approximately 30 ppm of iron in the fuels.

Fuel Property	Test Method	ULSD	ULSD+ DT8i	ULSD+ DT9
Heat of Combustion [BTU/gal]	ASTM D240	14368	14333	14128
API Gravity @ 15.6 °C [°API]	ASTM D1298	35.5	35.5	35.5
Cetane Number	ASTM D613	42.3	40.1	45.4
Sulfur by UV [ppm]	ASTM D5453	5.46	5.14	5.06
Flash Point, Closed Cup [°C]	ASTM D93	59.5	58.5	58.5



Methodology

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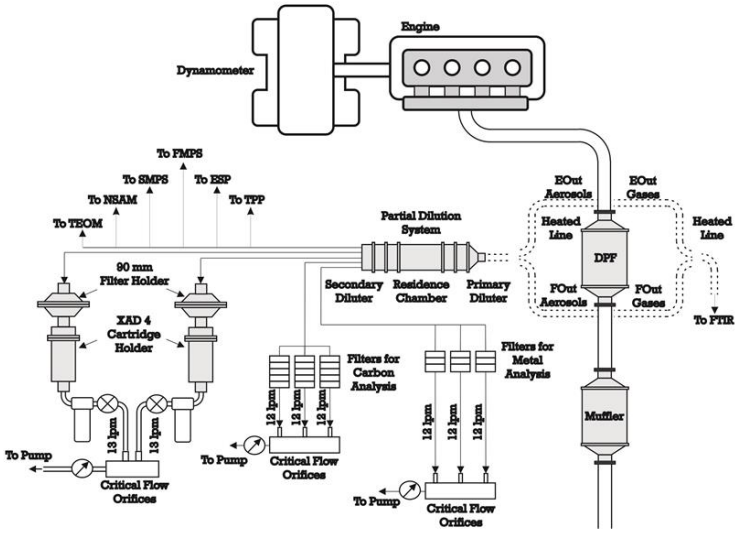
The testing took place at the Diesel Laboratory at NIOSH OMSHR, Pittsburgh, PA.



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Dynamometer and Engines Used for Field and Laboratory Evaluations of the SMF-AR System

Test Vehicle	Specifications
Dynamometer Manufacturer and Model	SAJ SE150
Engine Manufacturer	Isuzu
Engine Model	C240
Number of Cylinders	4 (inline)
Engine Displacement	2.4 l
Engine Type	liquid cooled, naturally aspirated
Engine Output	41.8 KW (56 hp)

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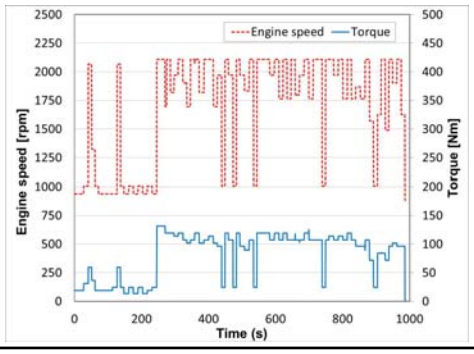
The system was evaluated for four steady-state operating conditions and one transient cycle.

Conditions	Description	Engine Speed	Torque	Power
		rpm	Nm	kW
R50	Rated speed and 50% load	2950	55.6	17.2
R100	Rated speed and 100% load	2950	111.2	34.3
I50	Intermediate speed and 50% load	2100	69.1	14.9
I100	Intermediate speed and 100% load	2100	136.9	30.6



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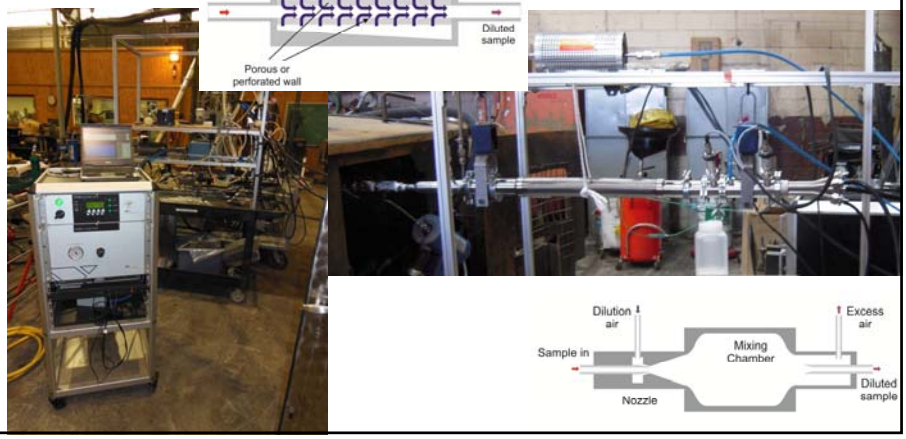
The aerosol sampling and measurements were conducted in the exhaust diluted approximately 30 times using partial dilution system.

- Dekati FPS4000 is designed to dilute exhaust in two stages.
- Primary dilution occurred in perforated disk diluter;
- Secondary dilution was provided by ejector diluter;
- The residence chamber was inserted between those two stages.



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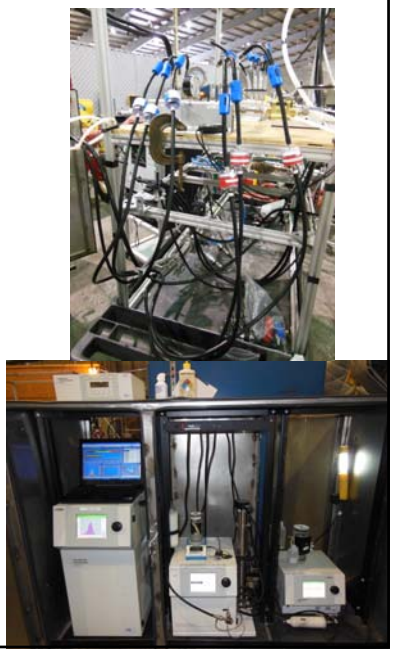
Aerosols Sampling and Measurements

- The effects on mass concentrations of elemental carbon (EC) and total carbon (TC) were determined using the results of thermal optical transmittance-evolve gas analysis (TOT-EGA) performed on the filter samples of the diluted exhaust collected upstream (EOut) and downstream (FOut) of the DPF system.

- Number concentrations and size distributions of aerosols were measured in EOut and FOut diluted exhaust using Fast Mobility Particle Sizer (TSI, Model 3091 FMPS).



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Aerosols Sampling and Measurements

- The effects on selected trace metals were determined using results of the inductively coupled plasma - atomic emission spectroscopy (ICP-AES) analysis performed on the samples collected on 37 mm diameter, 0.8 µm pore, mixed cellulose ester (MCE) filters
- The effects on particle morphology and size resolved elemental composition were determined using the results of the electron microscopy/energy dispersive spectroscopy (EM/EDS) analysis performed on the particulate samples collected using an electrostatic precipitator (ESP) and a thermophoretic precipitator (TPP).

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Results

- Effects of the DPF system and fuel additives on:
  - Integrated mass concentrations of total carbon (TC) and elemental carbon (EC);
  - Aerosol number concentrations;
  - Aerosol size distributions;
  - Integrated total mass concentrations of Fe;
  - Particle morphology

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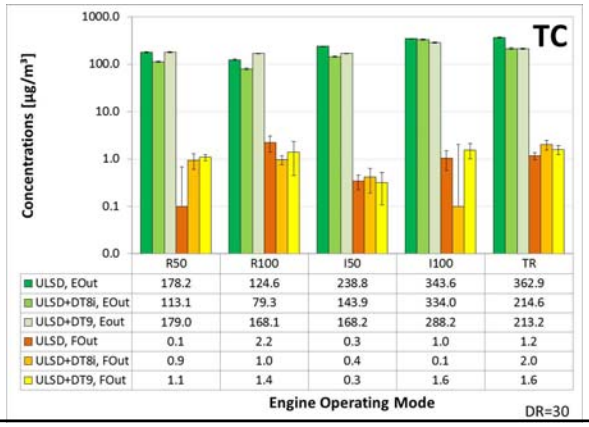
The system dramatically reduced total carbon (TC) and elemental carbon (EC) concentrations in diluted exhaust.

- The FOut TC and EC concentrations were at or below the Limit of Quantification (LOQ) of the TOT-EGA analysis,
- Therefore, the results could not be used to calculate the effectiveness of the system in removal of TC and EC.
- However, it can be concluded that for all test cases, the system filtered more than 99% of TC and EC.



	R50	R100	I50	I100	TR
ULSD, EOut	178.2	124.6	238.8	343.6	362.9
ULSD+DT8i, EOut	113.1	79.3	143.9	334.0	214.6
ULSD+DT9, Eout	179.0	168.1	168.2	288.2	213.2
ULSD, FOut	0.1	2.2	0.3	1.0	1.2
ULSD+DT8i, FOut	0.9	1.0	0.4	0.1	2.0
ULSD+DT9, FOut	1.1	1.4	0.3	1.6	1.6

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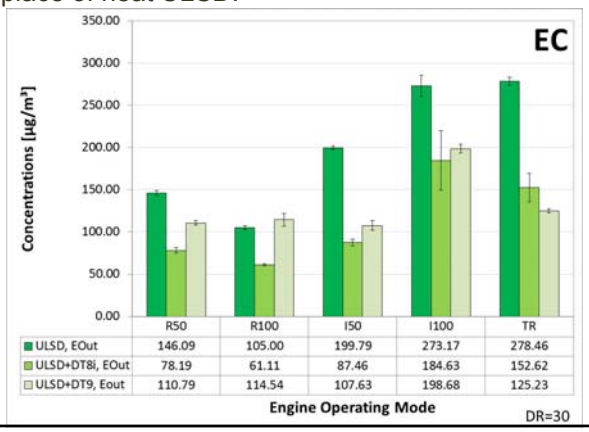
Effects of the additives on total carbon (TC) and elemental carbon (EC) concentrations.

- In the cases of R50, I50, I100, and TR tests, the EOut TC and EC concentrations were substantially lower when fuels treated with ULSD+DT8i and ULSD+DT9 were used in place of neat ULSD.
- In the cases of R100, the EOut TC and EC concentrations were lower when ULSD+DT8i was used, but not when ULSD+DT9 was used in place of neat ULSD.



	R50	R100	I50	I100	TR
ULSD, EOut	146.09	105.00	199.79	273.17	278.46
ULSD+DT8i, EOut	78.19	61.11	87.46	184.63	152.62
ULSD+DT9, Eout	110.79	114.54	107.63	198.68	125.23

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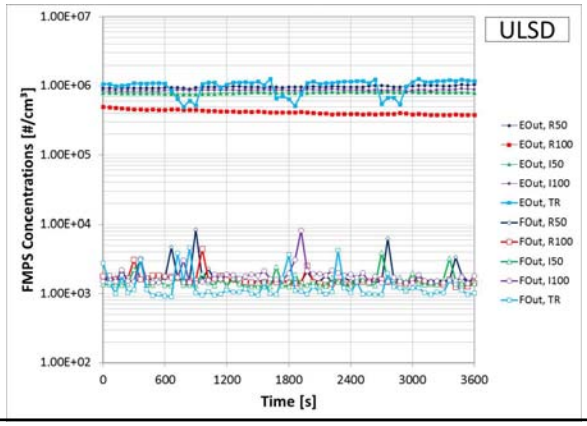
Effects of the system on aerosol number concentrations were examined on the results of FMPS measurements.

- The total number concentrations and size distributions of aerosols in diluted EOut and FOut exhaust were measured continuously with FMPS.
- For each of four steady-state tests, the analysis was performed on the results of FMPS measurements performed during the last hour of the tests.



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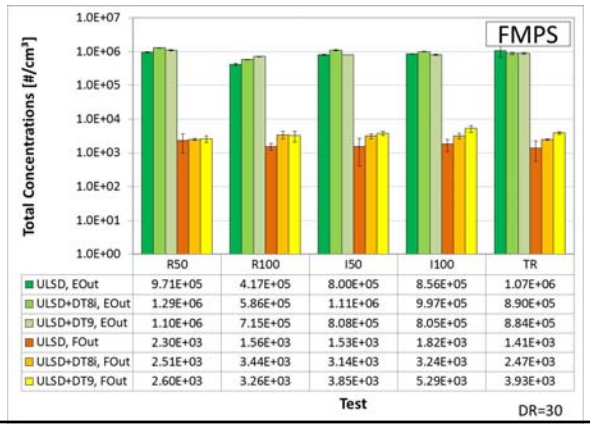
In all studied cases, the FOut concentrations were found to be very low, rarely exceeding dilution system background concentrations of app. 10^3 #/cm^3.

- It appears that the engine operating conditions had only minor effect on the FOut aerosol concentrations.
- For all test conditions, the DPF system filtered more than 99% of aerosols by number.



	R50	R100	I50	I100	TR
ULSD, EOut	9.71E+05	4.17E+05	8.00E+05	8.56E+05	1.07E+06
ULSD+DT8i, EOut	1.29E+06	5.86E+05	1.11E+06	9.97E+05	8.90E+05
ULSD+DT9, EOut	1.10E+06	7.15E+05	8.08E+05	8.05E+05	8.84E+05
ULSD, FOut	2.30E+03	1.56E+03	1.53E+03	1.82E+03	1.41E+03
ULSD+DT8i, FOut	2.51E+03	3.44E+03	3.14E+03	3.24E+03	2.47E+03
ULSD+DT9, FOut	2.60E+03	3.26E+03	3.85E+03	5.29E+03	3.93E+03

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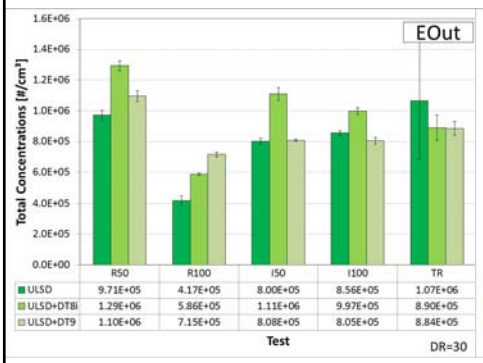
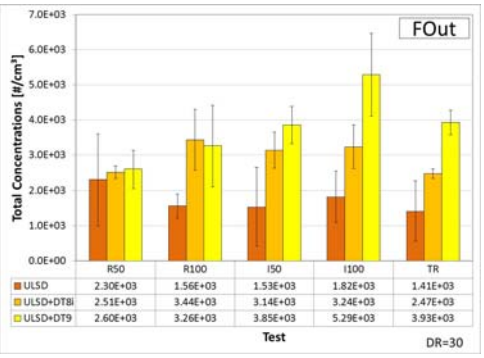
Effects of the additives on aerosol number concentrations were found to be relatively minor.

- With the exception of a couple test conditions, the evaluated additives had adverse effects on the EOut total number concentrations.
- The fuels with additives consistently produced higher FOut concentrations of aerosols.





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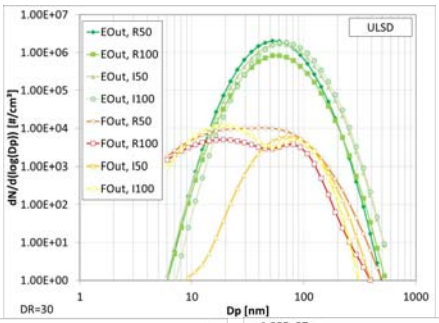
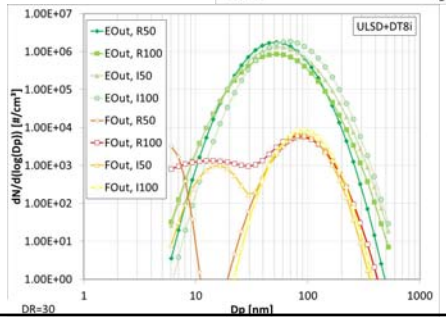
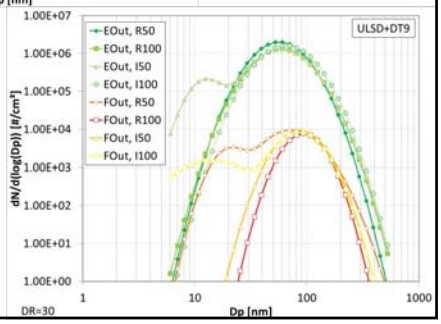
Effects of the system on size distributions of aerosols were examined on the selected results of FMPS measurements.







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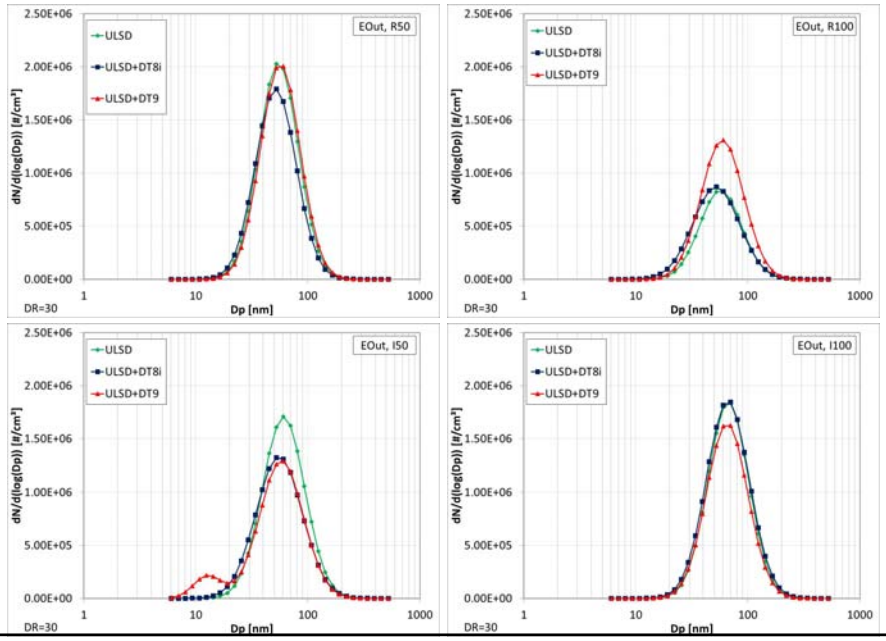
The EOut aerosols were generally distributed in single accumulation mode.



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The CMDs of EOut aerosols in accumulation modes ranged between 51 and 67 nm.

Fuel	Mode	Nucleation Mode			Accumulation Mode		
		CMD	σ	TC	CMD	σ	TC
		nm	-	#/cm³	nm	-	#/cm³
ULSD	R50				54.7	1.503	9.05E+05
	R100				57.1	1.535	3.92E+05
	I50				60.7	1.546	8.10E+05
	I100				66.9	1.516	8.37E+05
ULSD + DT8i	R50				51.7	1.520	8.17E+05
	R100				52.0	1.611	4.52E+05
	I50				55.3	1.609	6.89E+05
	I100				66.2	1.552	8.88E+05
ULSD + DT9	R50				56.7	1.504	9.02E+05
	R100				59.2	1.549	6.25E+05
	I50	12.8	1.338	6.79E+04	58.1	1.565	6.31E+05
	I100				65.3	1.527	7.58E+05

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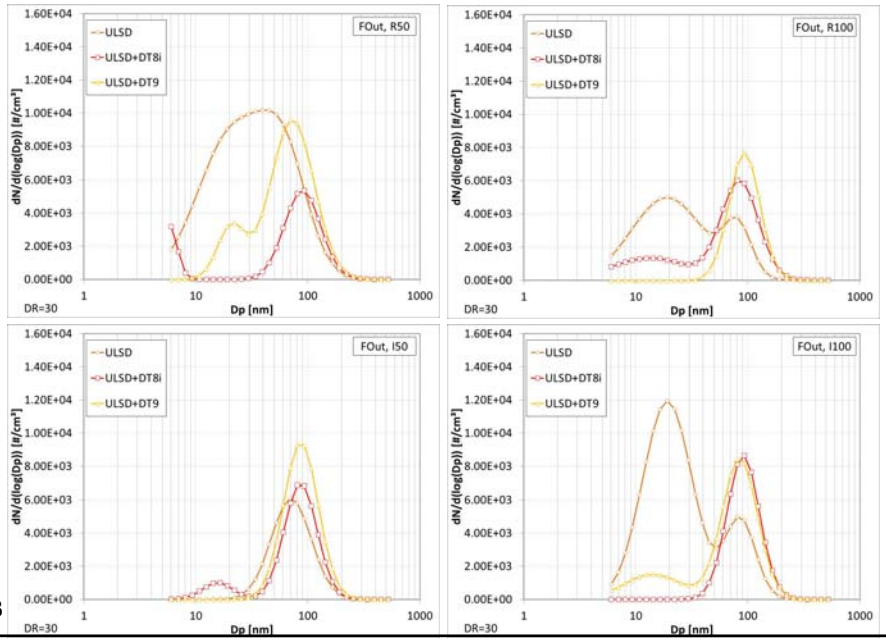
Depending on test conditions, the FOut size distributions were single modal or bimodal.



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The CMDs of FOut aerosols in accumulation modes ranged between 63 and 93 nm.

The CMDs of FOut aerosols in nucleation modes ranged between 13 and 36 nm.

Fuel	Mode	Nucleation Mode			Accumulation Mode		
		CMD	σ	TC	CMD	σ	TC
		nm	-	#/cm³	nm	-	#/cm³
ULSD	R50				81.8	1.441	1.74E+03
	R100	14.2	1.311	4.18E+02	82.5	1.437	1.12E+03
	I50				81.7	1.398	1.45E+03
	I100	36.3	1.793	3.69E+02	87.8	1.305	1.21E+03
ULSD + DT8i	R50	20.7	1.790	5.76E+03	63.1	1.657	8.00E+03
	R100	13.4	2.225	1.16E+03	84.6	1.466	2.48E+03
	I50	15.7	1.359	3.39E+02	86.0	1.401	2.58E+03
	I100				90.9	1.398	3.16E+03
ULSD + DT9	R50				92.2	1.374	2.34E+03
	R100				93.2	1.374	2.67E+03
	I50				86.5	1.430	3.68E+03
	I100	14.3	1.825	9.93E+02	84.7	1.440	3.37E+03

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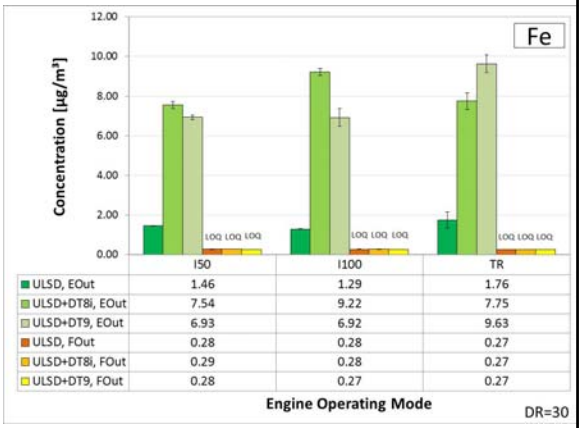
The ICP-AES analysis on the filter samples showed that the system was very effective in trapping iron (Fe).

- For all test conditions, Fe introduced with the additives substantially increased the Fe concentration in the EOut aerosols samples.
- In all cases, the Fe concentrations in the FOut samples were below LOQ of the applied method.
- Importantly, the FOut Fe concentrations were much lower than ULSD EOut concentrations.



	I50	I100	TR
ULSD, EOut	1.46	1.29	1.76
ULSD+DT8i, EOut	7.54	9.22	7.75
ULSD+DT9, EOut	6.93	6.92	9.63
ULSD, FOut	0.28	0.28	0.27
ULSD+DT8i, FOut	0.29	0.28	0.27
ULSD+DT9, FOut	0.28	0.27	0.27

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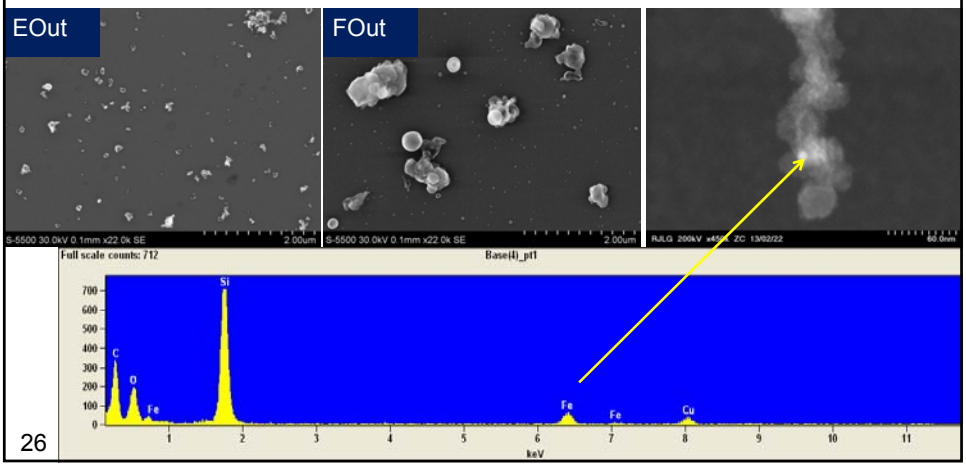
Aerosol Morphology and Chemistry

- Electron microscopy (EM) showed the agglomerated nature of EOut diesel aerosols and nucleation mode aerosols in FOut exhaust.
- EM and energy dispersive spectroscopy (EDS) showed that the Fe particles were in some cases imbedded in the agglomerates and in other cases form nano spheres.



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In Summary:

- The tests showed that the evaluated DPF system was very effective in reducing EC, TC, and total number concentrations of aerosols.
- With the exception of a couple test conditions, the evaluated additives slightly increased EOut total number concentrations.
- The fuels with additives consistently produced slightly higher FOut number concentrations of aerosols.
- In some cases, FOut aerosols were found to be distributed in pronounced nucleation modes.

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In Summary (continued):

- For all test conditions, Fe introduced with the additives substantially increased the Fe concentration in the EOut aerosol samples.
- However, the FOut Fe concentrations were much lower than ULSD EOut concentrations.
- The Fe appears to be distributed between the accumulation and nucleation mode aerosols.

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The effects of the systems on the concentrations of the criteria (CO, CO_2, NO, and NO_2) and other gases were determined using the results of measurements made in undiluted exhaust using the Fourier Transform Infrared (FTIR) analyzer (Gasmet, Model 4000).

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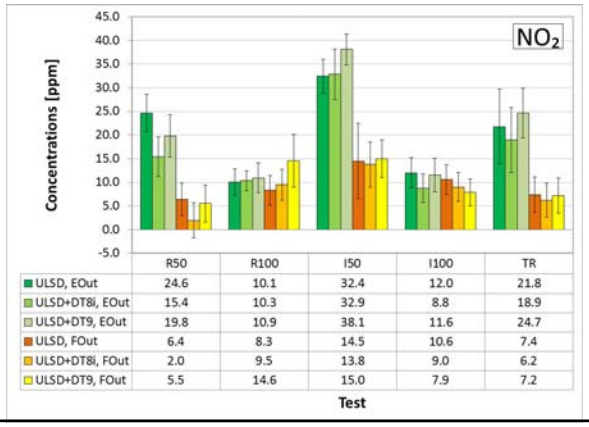
For the majority of the test conditions, the NO_2 concentrations were lower downstream than upstream of the system.

- This can be attributed to the reaction of NO_2 with soot captured in the DPF element.
- That process was not prominent for high load test conditions that generated relatively high exhaust temperatures (>400^{0}C) sufficient to support continuous regeneration.



	R50	R100	I50	I100	TR
ULSD, EOut	24.6	10.1	32.4	12.0	21.8
ULSD+DT8i, EOut	15.4	10.3	32.9	8.8	18.9
ULSD+DT9, EOut	19.8	10.9	38.1	11.6	24.7
ULSD, FOut	6.4	8.3	14.5	10.6	7.4
ULSD+DT8i, FOut	2.0	9.5	13.8	9.0	6.2
ULSD+DT9, FOut	5.5	14.6	15.0	7.9	7.2

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