Composition Analysis of Fine Particles from Diesel Vehicles using PIXE

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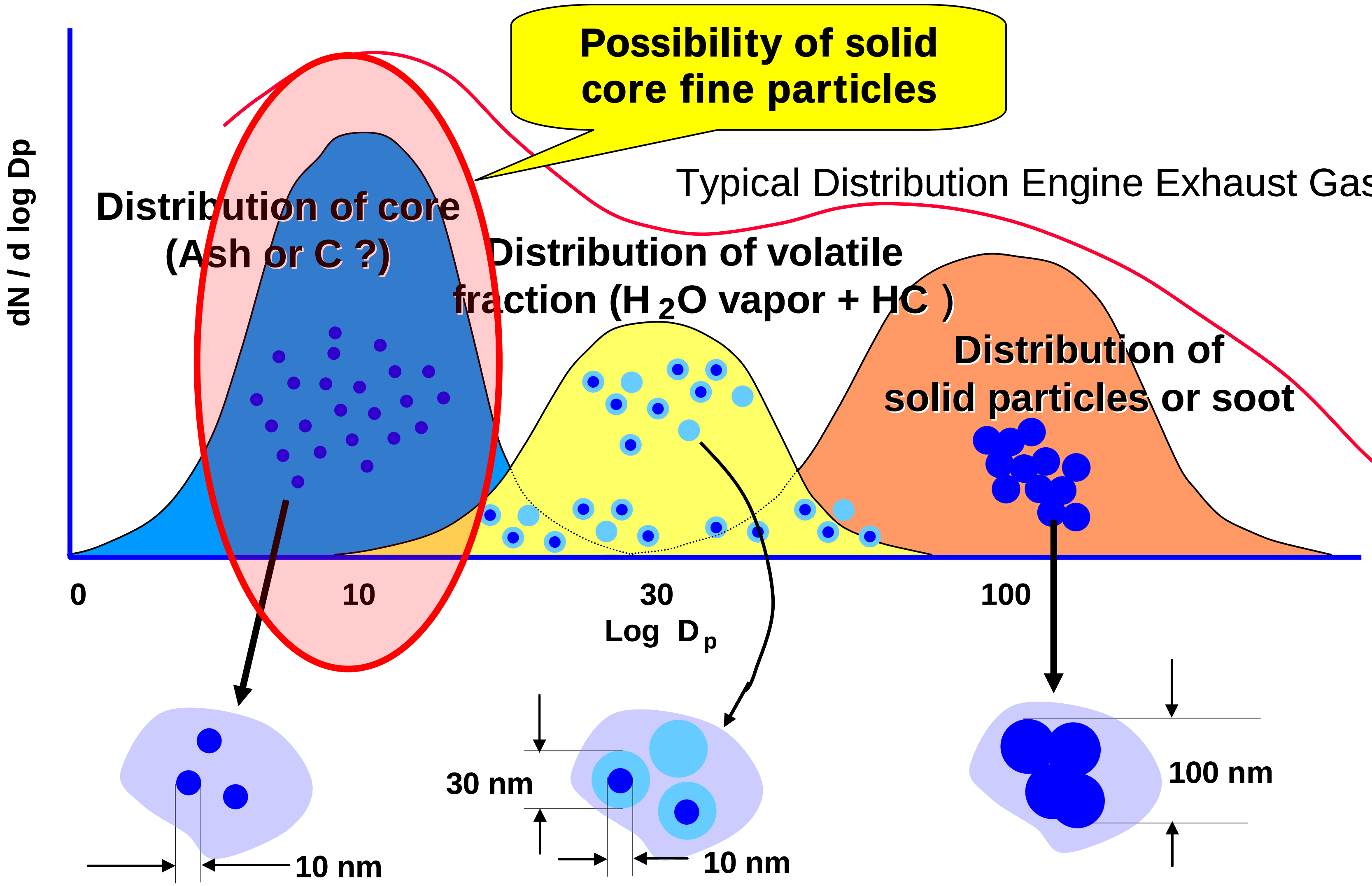
Introduction

- Distributions of diesel exhaust particles have been investigated in much detail by many researchers. And also the behaviors of emission particles have been examined in various driving conditions. During idling or deceleration, fine particles are emitted from diesel vehicles.
- However, compositions of fine particles emitted from diesel vehicles with DPF have not been investigated enough yet. We presented Nano-Particle model for DEP in 8th ETH Conference, 2004. This model estimated the possibility of solid fine particles, so we focus on elements' analyses of fine particles.
- In this study, compositions of fine particles in each size have been analysed by PIXE (Particle Induced X-ray Emission) analyses in air under various driving conditions.

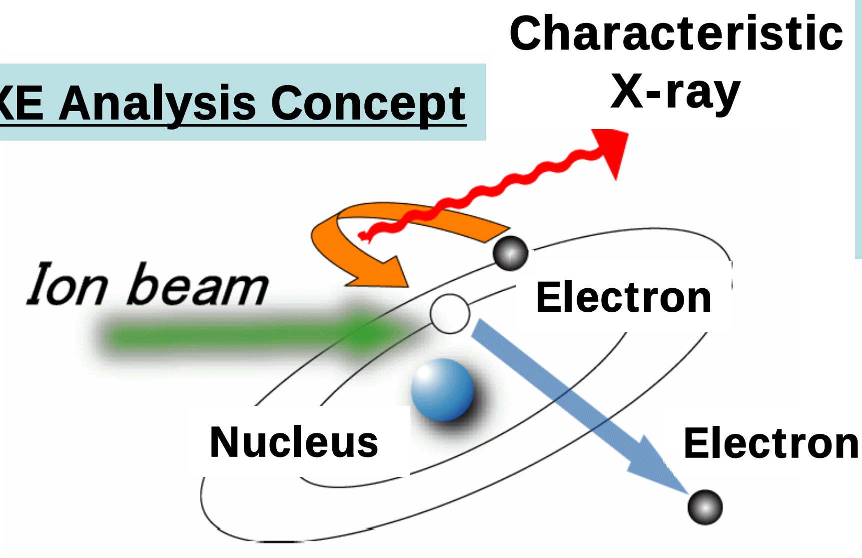
Nano-Particle Model



ETH 2004 T.Kawai, R.Montajir, Y.Goto, M.Odaka

What is PIXE?

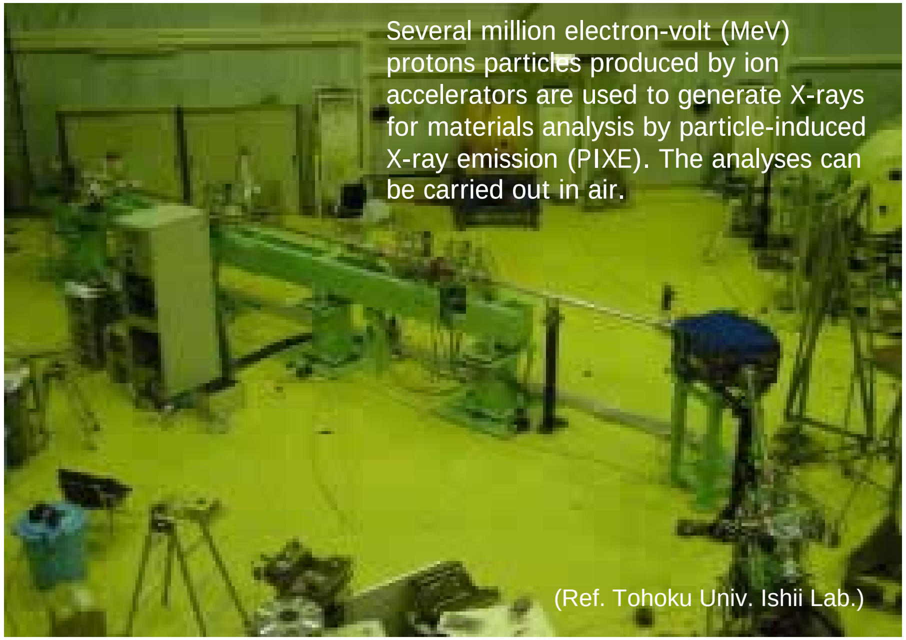
PIXE Analysis Concept



- High sensitivity
- Measurement in the air
- Wide elements

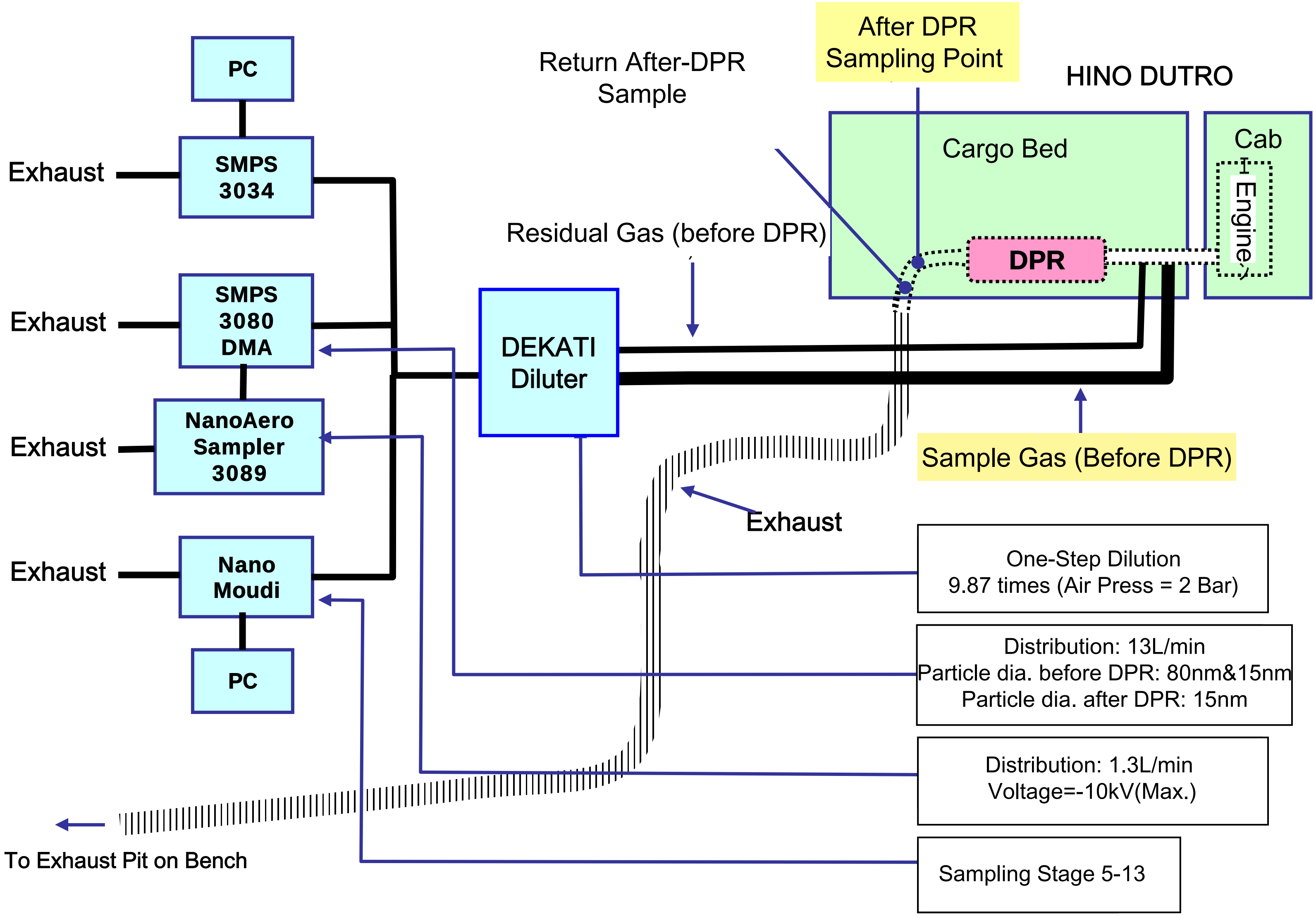
PIXE (Particle Induced X-ray Emission)

PIXE is a technique used in determining the elemental make-up of a material or sample. When a material is exposed to an ion beam, atomic interactions occur that gives off wavelengths of EM radiation in the x-ray part of the spectrum specific to an element.



Methods

Schematic of Experiment Setup



Specifications of Instruments

Engine Specification

Displacement (L)	4.009
Cylinder No.	4 cylinders
Combustion chamber	Reentrant, Direct inj.
Bore× Stroke (mm)	104.0 × 118.0
Compressin ratio	18.0
Turbo system	Weast gate
After-treatment system	Cont. regen. Type DPF
Fuel supply	Common rail
Maximum power (kW/ rpm)	110/ 3000 (net)
Maximum torque (Nm/ rpm)	392/ 1600 (net)
Idling speed (rpm)	650

S=10ppm Diesel fuel

Item		Unit	Value
Density 15℃		g/cm^3	0.8183
Viscosity 30℃		mm^2/s	3.067
CFPP		℃	-17
S contents		mass%	0.0004
Cetane value			56.5
HFRR		μm	287
CHN analysis	C	mass%	86.0
	H	mass%	13.9
	N	mass%	<0.1
GHV		J/g	46040
NHV		J/g	42900
Cetane index			58.7

Nano Moudi-II TM Specifications

	Impactor
Configuration	Impactor only
Flow Rate(at the inlet)	10l/min
Pressure Drop (without filter)	90kPa(360 in wg)
Size(D× H)	83× 521mm
Weight	4.7kg(10.3lb)

Stage No.	Size(nm)
1	10,000
2	5,600
3	3,200
4	1,800
5	1,000
6	560
7	320
8	180
9	100
10	56
11	32
12	18
13	10

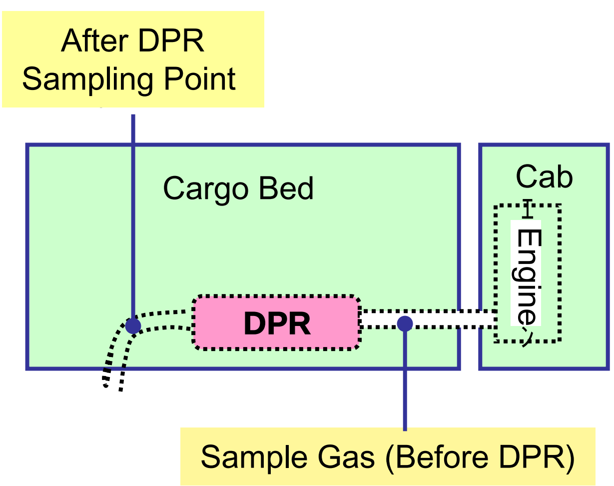
Sampling Stages

Test conditions

Fine particles are emitted under idling conditions.
Impact on fine particle emissions were investigated under regeneration condition.

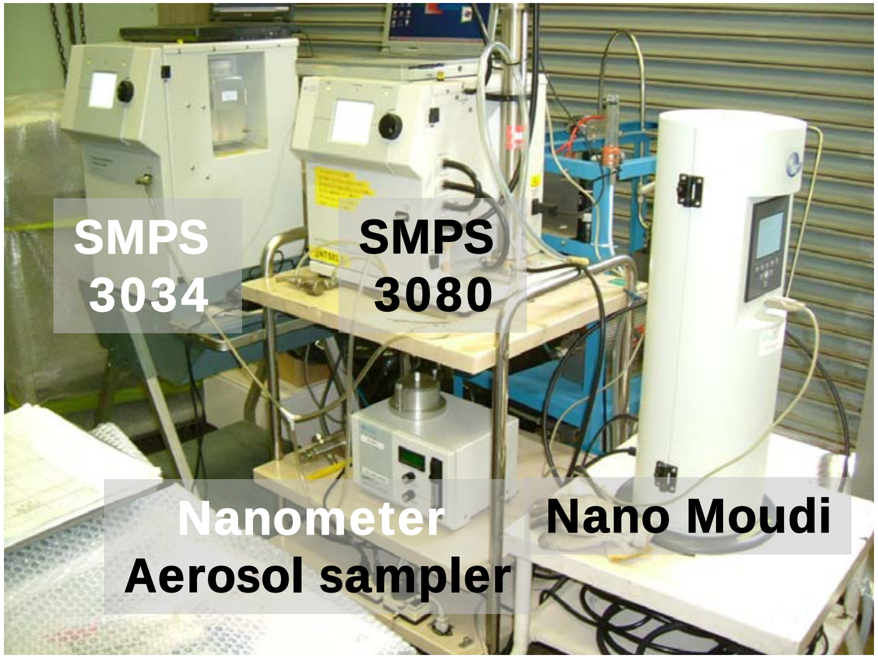
Test No.	Sampling point	Engine condition	Particle size	Sampling time
①	Before DPR	Idling (650rpm)	80nm	1Hr
②	Before DPR	Idling (650rpm)	15nm	1Hr
③	after DPR	Idilng (650rpm)	15nm	6Hr
④	after DPR	Regeneration (950rpm	15nm	30Min (10Min× 3)

Nanometer Aerosol sampler (TSI 3089)



- **Test No.①② of Before DPR are short sampling time because of high particle concentration.**
- **Test No.③④ of After DPR are long sampling time because of low particle concentration.**
- **DPR is forcibly regenerated at intervals in the condition of long idling.**

Testing setup



Measurement Instruments

Test Vehicles

Results

Inorganic Compositions of Size-resolved DEP (Before DPF) - Idling by Nano Moudi

	NN1-5 1800 nm - 1000 nm Stage No. 5	NN1-6 1000 nm - 560 nm Stage No. 6	NN1-7 560 nm - 320 nm Stage No. 7	NN1-8 320 nm - 180 nm Stage No. 8	NN1-9 180 nm - 100 nm Stage No. 9	NN1-10 100 nm - 56 nm Stage No. 10	NN1-11 56 nm - 32 nm Stage No. 11	NN1-12 32 nm - 18 nm Stage No. 12	NN1-13 18 nm - 10 nm Stage No. 13
Elemental composition (ng/m^3)									
Mg	659	1620	758	1700	798	<LOQ	1950	5170	5090
Si	<LOQ	1260	<LOQ	416	642	1090	1020	1940	1760
S	<LOQ	<LOQ	<LOQ	818	<LOQ	639	<LOQ	<LOQ	<LOQ
Cl	338	1260	655	<LOQ	<LOQ	384	1460	2180	1290
K	<LOQ	<LOQ	63.6	117	57.1	70.4	<LOQ	<LOQ	<LOQ
Ca	11.3	249	1510	2590	1400	824	307	26.6	227
Fe	1.53	17.7	15.5	2160	54.0	36.6	21.4	54.9	64.5
Ni	0.44	6.52	<LOQ	<LOQ	2.48	1.55	<LOQ	19.4	2.93
Cu	<LOQ	<LOQ	<LOQ	4.96	7.14	13.6	15.8	14.5	12.7
Zn	3.06	35.1	261	469	395	448	211	50.0	65.4
Pb	<LOQ	3.10	1.55	20.8	<LOQ	38.8	<LOQ	<LOQ	27.3
Ionic composition (μg/m^3)									
NO_2^-	17.4	9.47	10.0	2.37	6.32	6.58	18.2	13.2	5.26
NO_3^-	8.42	6.05	6.58	3.42	4.74	5.26	12.4	8.42	5.00
SO_4^{2-}	0.26	0.53	1.32	0.79	0.79	1.58	0.79	1.05	0.79

LOQ is below limit of quantification. Indication of italic and under bar is value of under the determination limit.

Mg, Si, Ca, Zn are emitted before DPF in Idling.

Inorganic Compositions of Size-resolved DEP (After DPF) – Idling by Nano Moudi

	NNA1-5 1800 nm - 1000 nm Stage No. 5	NNA1-6 1000 nm - 560 nm Stage No. 6	NNA1-7 560 nm - 320 nm Stage No. 7	NNA1-8 320 nm - 180 nm Stage No. 8	NNA1-9 180 nm - 100 nm Stage No. 9	NNA1-10 100 nm - 56 nm Stage No. 10	NNA1-11 56 nm - 32 nm Stage No. 11	NNA1-12 32 nm - 18 nm Stage No. 12	NNA1-13 18 nm - 10 nm Stage No. 13
Elemental composition (ng/m^3)									
Mg	268	267	7.70	175	296	<LOQ	280	826	584
Si	<LOQ	48.1	<LOQ	307	93.1	<LOQ	131	<LOQ	45.6
S	<LOQ	160	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	157	249
Cl	120	98.1	<LOQ	<LOQ	98.2	148	90.9	<LOQ	549
K	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ca	<LOQ	<LOQ	<LOQ	70.6	<LOQ	5.69	11.0	<LOQ	63.2
Fe	0.51	51.8	3.52	3.98	3.57	4.55	0.54	96.6	15.0
Ni	0.15	<LOQ	0.16	<LOQ	0.57	0.47	<LOQ	1.75	0.49
Cu	0.47	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.02	<LOQ
Zn	0.73	<LOQ	<LOQ	1.24	1.60	1.09	<LOQ	<LOQ	<LOQ
Pb	<LOQ	<LOQ	<LOQ	1.09	<LOQ	<LOQ	<LOQ	1.48	<LOQ
Ionic composition (μg/m^3)									
NO_2^-	1.00	1.80	4.47	1.40	0.96	2.63	0.66	1.14	0.96
NO_3^-	0.92	1.32	2.15	0.79	0.79	1.49	0.88	0.96	1.01
SO_4^{2-}	<0.04	0.09	0.09	<0.04	0.04	0.04	<0.04	<0.04	0.04

LOQ is below limit of quantification. Indication of italic and under bar is value of under the determination limit.

Mg, Si, Ca, Fe, Ni are emitted after DPF in Idling.

Inorganic Compositions of Size-resolved DEP (After DPF, Regeneration) – Idling by Nano Moudi

	NNT1-5 1800 nm - 1000 nm Stage No. 5	NNT1-6 1000 nm - 560 nm Stage No. 6	NNT1-7 560 nm - 320 nm Stage No. 7	NNT1-8 320 nm - 180 nm Stage No. 8	NNT1-9 180 nm - 100 nm Stage No. 9	NNT1-10 100 nm - 56 nm Stage No. 10	NNT1-11 56 nm - 32 nm Stage No. 11	NNT1-12 32 nm - 18 nm Stage No. 12	NNT1-13 18 nm - 10 nm Stage No. 13
Elemental composition (ng/m^3)									
Mg	2350	1850	<LOQ	<LOQ	1720	1640	619	9600	7410
Si	1450	174	2340	1260	552	459	<LOQ	1060	332
S	628	952	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Cl	<LOQ	<LOQ	1060	<LOQ	<LOQ	1550	<LOQ	<LOQ	5700
K	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ca	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Fe	142	<LOQ	<LOQ	16.7	31.0	42.8	56.9	728	25.4
Ni	7.42	8.07	4.34	21.1	13.6	8.69	10.3	46.8	37.1
Cu	<LOQ	<LOQ	8.69	11.2	6.83	<LOQ	<LOQ	<LOQ	37.1
Zn	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	35.5	<LOQ
Pb	<LOQ	2.48	<LOQ	<LOQ	<LOQ	<LOQ	20.5	38.7	<LOQ
Ionic composition (µg/m^3)									
NO_2^-	8.4	9.5	33.2	16.8	3.2	15.8	14.2	16.8	11.6
NO_3^-	12.1	12.6	21.6	15.8	11.0	13.2	16.3	11.0	13.2
SO_4^{2-}	<0.5	2.1	<0.5	2.1	<0.5	0.5	0.5	<0.5	<0.5

LOQ is below limit of quantification. Indication of italic and under bar is value of under the determination limit.

Mg, Si, Fe, Ni, Cu are emitted after DPF in Regeneration.

Inorganic Compositions of Size-resolved DEP– Idling by Nanometer Aerosol sampler

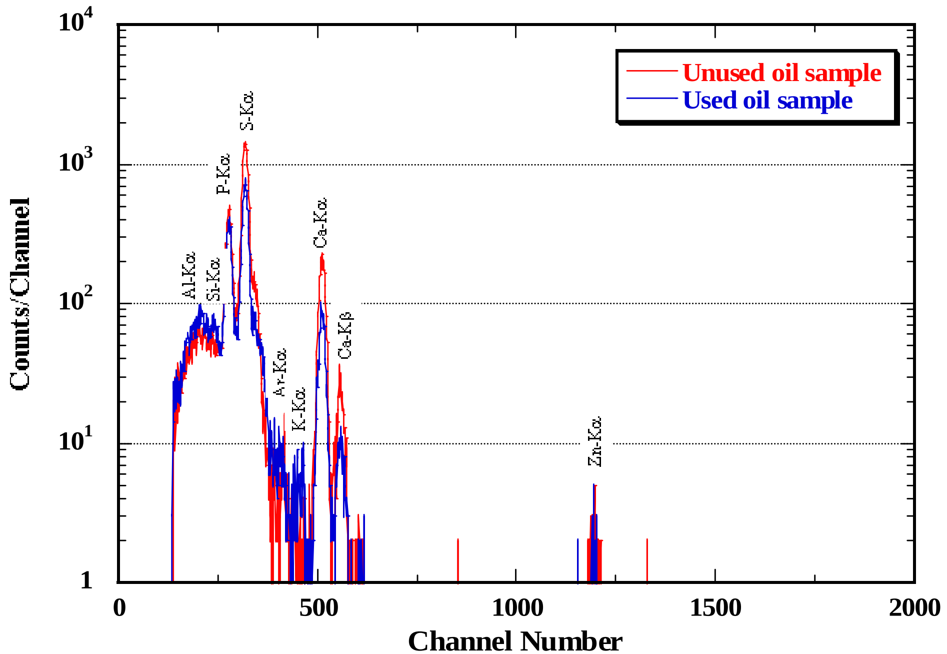
	Before		After	
				Regeneration
Sample No.	NN-80	NN-15	NNA-15	NNT-15
Particles size	80 nm	15 nm	15 nm	15 nm
Elemental composition (ng/m^3)				
Mg	<LOQ	<LOQ	15400	146000
Si	42800	23700	<LOQ	162000
S	<LOQ	32900	<LOQ	<LOQ
Cl	59000	<LOQ	10200	89800
K	<LOQ	5790	<LOQ	<LOQ
Ca	<LOQ	505	<LOQ	<LOQ
Fe	<LOQ	724	113	5490
Ni	593	680	43.9	659
Cu	<LOQ	<LOQ	<LOQ	615
Zn	<LOQ	<LOQ	65.9	<LOQ
Pb	<LOQ	<LOQ	<LOQ	<LOQ
Ionic composition (µg/m^3)				
NO_2^-	6.1	22.3	2.0	76.9
NO_3^-	14.2	32.4	4.0	93.1

NN-80 and NN-15 are soure; NNA-15 is after DPR & catalyst; NNT-15 is teatment of DRP. LOQ is below limit of quantification.

Emissions of Mg, Si, Fe, Ni, Cu increase Under regeneration.

PIXE analysis of Lubricants

Both lubricant used by test and fresh same lubricant were analyzed by PIXE.



X-ray spectra of the engine lubricating oil samples obtained by 5.1 MeV Helium ion bombardment.
Oil target samples were fixed by making the oil sample sandwiches with 1% collodion solution based ethyl alcohol.

- **P, S, Ca, Zn were detected from unused oil sample.**
- **P, S, Ca, Zn, Al, Si, K were detected from used oil sample. It was estimated that P and S 300 – 500 mg/L, Ca 20 – 30 mg/L, Zn some mg/L, Al, Si and K 0.05 – 0.1 mg/L.**
- **Usually Lubricants contain antioxidant, detergent and antifoam additives.**
- **Generally speaking, P, S and Zn are contained in ZDTP (zinc dialkyldithiophosphate) as antioxidant additive , Ca in Antifoam additive, Si in antifoam additive.**

Conclusions

- In investigating physical and chemical characteristics of fine particles from a diesel vehicle with DPF, three factors - size distribution, concentration and chemical composition - are usually most important.
- Fine particles were sampled by using a nano-moudi sampler (MSP) and a nanometer aerosol sampler.
- Various elements (Mg, Si, Ca, Zn, Fe, Ni, Cu) in fine particles were determined by PIXE analyses. Part of these elements are used as additives in lubricant oil. It will be reasonable that some of these elements come from lubricant oil.
- Metallic elements detected by PIXE seem to be some of solid core in fine particles. Emission of these elements increased under regeneration condition.

Thank you for your attention.

My acknowledgment for Dr.Saito's substantial contribution to PIXE analyses.