Effects of Metals on Measurements of Elemental and Organic Carbon by Evolved Gas Analysis

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Introduction

Carbonaceous PM ranks as some of the most difficult aerosol to measure, with uncertainties of at least 30-50% (e.g., [1]).The thermal/optical transmission method has been widely used for OC and EC quantification [2]. It applies different temperatures for measuring OC and EC contents through programmed, progressive heating in a controlled atmosphere. The sample composition, especially metals, can influence the evolution of carbon from filters, thus affect the OC and EC quantification. In this study, the effect of metal salts on the behavior of diesel EC and OC during EGA is determined.

Experimental Setup

Engine: 4.8 kW direct inject diesel generator run at 100% load
Fuel: California No. 2 ultra-low-sulfur diesel
Metal salts: 2.5% (w/w) in DI H_2O
Diesel Particle Collection: Diesel particles were collected on a quartz filter 10 cm away from the exhaust of the generator
Metal Particle Collection: Nebulizing the metal solution into a 2 m^3 Teflon chamber. Metal particles were collected from the chamber on top of a pre-loaded diesel filter

Methods

Metal size distribution: SMPS
EC/OC: evolved gas analysis (EGA) via the NIOSH methods[3]
BC: dual-wavelength (370nm and 880nm) optical transmissometer (Model OT21, Magee Scientific)
Metal: ICP-AES

(I) Characterization

Pure Diesel Exhaust Particles

	Tox (°C)	split time (s)	EC/OC	Char_trans_%	Char_evol_% (POC/TC%)
Mean	866	504	0.69	4.00	7.63
Median	866	505	0.68	3.22	8.57
S.D	1.48	16.46	0.17	3.33	3.58
RSD(%)	0.2	3.3	25.3	83.3	46.9

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Citations

1.Husberl, B. J.; Charlson, R. J., Uncertainties in data on organic aerosols. Tellus, Ser. B 2000, 52B, (5), 1249-1255.
2.Huntzicker, J. J.; Johnson, R. L.; Shah, J. J.; Cary, R. A., Analysis of Organic and Elemental Carbon in Ambient Aerosols by a Thermal-Optical Method. In Particulate Carbon: Atmospheric Life Cycle; Wolff, G. T., Klimisch, R. L., Eds.; Plenum Press: New York 1982, pp 79-85.
3. NIOSH (Elemental Carbon (Diesel Particulate). NIOSH Manual of Analytical Methods (NMAM) 1999, NIOSH, Method 5040 Issue 3.

(II) Catalytic Effects of Metals in EGA

Ambient Particles

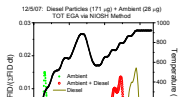

Fig.1: EGA Carbon evolution profile for ambient, diesel, and a combination of ambient and diesel PM. The FID response was normalized to the total FID response. The small amount of ambient aerosol shifts the oxidation temperature of the diesel EC ~100° C earlier. It also changes the evolution of the OC.

Metal Salts

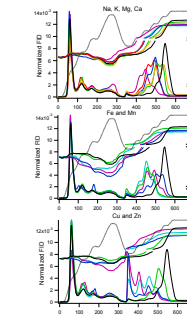

Fig. 2: Average EGA carbon evolution profiles of diesel and metal-loaded diesel PM. The FID response was normalized to the total FID response (Δ FID/ Σ FIDdt). Transmission profiles are shown as percent change relative to the initial transmission signal I_0, i.e. $(\ln I - \ln I_0)/\ln I_0 \times 100$.

- ♦ Affect the laser attenuation in the He phase.
- ♦ More carbon evolves in the lower temperature steps of the oxygen phase.
- ♦ Carbon is oxidized continually in the oxygen phase.

Metal Salts-Average Effects

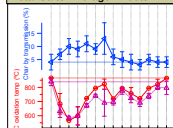

Fig.3: Average and stand deviation of measured parameters for the metal loaded diesel and pure diesel reference samples. Char by transmission is the percent reduction of laser transmission through the filter during the He phase. Char by evolution is the fraction of pyrolized organic carbon (POC).

- Most metals lowered the oxidation temperature of EC: transition > alkaline > alkaline-earth metals; $CuCl_2$>$CuSO_4$, $FeCl_3$>$Fe_2(SO_4)_3$
- Transition metals increase the charring of OC, while alkaline and alkaline-earth metals don't;
- The EC oxidation temperature is strongly correlated the split time.

Metal Salts-Dependence on Metal to Carbon Raito

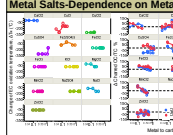

Fig.4 The change of EC oxidation temperature, charred OC, and EC/OC as a function of metal to carbon ratio.
-The catalytic effect on OC charring is dependent on the M/C ratio;
-EC/OC ratios were increased or decreased, from -80 to +80%, dependent on the M/C ratio

Conclusions

These results show that all metals reduce the oxidation temperature of diesel soot, with transition metals, especially Cu, have the largest effect.

Metals were observed to affect the charring of OC and EC/OC ratio; this effect was highly variable and dependent on the M/C ratio.

EGA measurement may either underestimate or overestimate the OC and EC concentrations, depending on the amounts of metals and on the composition and concentration of organic material present in a sample.