

Review report (acp-2010-440)

Title: The effect of metal salts on quantification of elemental and organic carbon in diesel exhaust particles using thermal-optical evolved gas analysis

Authors: Y. Wang, A. Chung, and S. E. Paulsen

General comments:

Metal salts have long been suspected to catalyze EC oxidation in the thermal analysis of EC and OC, but there has not been a systematic investigation. This work has filled in this gap. The authors did a systematic study on the comparative catalytical behaviors of 13 metal salts in the quantification of EC and OC in diesel exhaust particles using thermal/optical transmittance methods. They have clearly shown that metals reduce the oxidation temperature of EC and enhance the charring of OC. The experiments are well designed. I only have a few minor points for authors to consider in their next revision of the manuscript.

Specific comments

1. Figure 1 shows the thermogram in the form of normalized FID signal versus elapsed analysis time. In the ambient sample, OC dominates while in the combined ambient+diesel particle sample, EC dominates due to the larger carbon loading from the preload diesel particles. It is difficult to tell from the normalized thermogram how the OC evolution pattern changes when ambient particles and diesel particle co-exist on the filter. It will be helpful to include in this figure the normal thermograms, i.e., absolute FID signal as a function of elapsed analysis time and the transmittance variation curves. The normal thermograms will allow a better visual comparison of the OC evolution patterns in the He stage and eyeball whether the thermograms are additive.

2. Section 3.1: The authors discuss in this section the effect of ambient aerosols on thermal analysis of diesel particles. They report that the weighted EC/OC ratio of the ambient+diesel particle mixture sample would be 3.72; however my calculation using the information given leads to a value of 2.51 (see the table below for my calculation). Please check.

Sample	Measured values				
	TC	EC/OC	EC/TC	EC	OC
diesel	171	4.31	0.812	138.8	32.2
ambient	28	0.14	0.123	3.4	24.6
diesel+ambient	199	1.49	0.598	119.1	79.9
	Expected values if assuming additive behavior of the ambient and diesel particles				
diesel+ambient	199	2.51	0.715	142.2	56.8

3. In the discussion of effects on EC/OC ratio (page 16955, 1st paragraph), the authors are right in pointing out that POC and EC likely have different absorption coefficients of the monitoring laser. The correct speciation of OC and EC in thermal/optical methods depends on one of the following two assumptions: (1) pyrolytically-generated EC evolves before native EC evolves in the analysis or (2) pyrolytically-generated EC and native EC have the same apparent light absorption coefficient (σ) at the monitoring light wavelength (Yang and Yu, EST, 2002, v36, 5199-5204). The work by Yang and Yu is relevant here and can strength the authors' argument on why EC/OC is shifted despite the use of transmittance-based charring correction.

4. Towards the end of the manuscript, the authors discussed the atmospheric implication that metal salts cause early EC oxidation, which then causes underestimates of EC in ambient samples. This important atmospheric implication should be mentioned in the abstract, since many readers of this journal are interested in measurements of ambient EC and OC.