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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The effect of metal salts on quantification of elemental and organic carbon in diesel exhaust particles using thermal-optical evolved gas analysis" *by* Y. Wang et al.

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Reviewer: "On Page 16943 Line 19 the authors claim that 'a handful of recent studies have suggested', but in the following paragraphs the authors themselves show that the most of the cited papers are from the 90s, some are even from the early 80s, so the problem is absolutely not new to the aerosol community. In fact, it is as old as the first thermal studies on atmospheric soot."

» Our study focuses on the effects of metals on the OC and EC determination by thermal-optical methods. The problem has been little studied. Previous studies we cite beginning in the early 80s mostly discuss the oxidation of soot and graphitic car-

bon and were aimed at finding an effective catalyst to reduce the soot emissions from diesel fuel combustion. A few studies reported the evolution of carbon during evolved gas analysis. These studies were largely based on thermal methods other than the (now common) thermal-optical method used in this study. The previous studies provide the foundation of the hypothesis that metals might affect the OC and EC determination by thermal-optical methods. However, no study has reported systematically the effects of metals on the OC and EC determination by thermal-optical methods as we show here. Additionally, unsolved and/or poorly understood existing problems are worth addressing; indeed they constitute the majority of scientific research. Completely new problems are rare. Perhaps the reviewer objects to our word choice: we agree, "recent" is a debatable term in this context. We are happy to omit it.

Reviewer: "Basically, the authors try to study two separate effects: lowered EC oxidation temperature and increased charring due to the presence of metals. Both effects are well known in the field and have been thoroughly studied for decades."

» We are not trying to study two separate effects, but are rather attempting to break down the problem of quantifying EC and OC with thermo-optical evolved gas analysis into its contributing factors. The effects of metals on EC oxidation and OC charring help us to understand their effects on OC and EC quantification. The effects of metals on EC oxidation and OC charring in thermo-optical analyses are not well known in the field. The two effects have received some attention for decades, but they have been studied separately and for different purposes. The studies on the effects of metals on EC oxidation focus on the reduction of soot emission from diesel exhaust, while the studies on OC charring focus on the use of metals to catalyze the pyrolysis of cellulose, wood and coals. Few studies have discussed the two effects together, and none is as systematic as ours; we compare the effect of 13 metal salts over a wide range of metal : carbon ratios.

Reviewer: "First, pure diesel particulates are usually not sampled separately in the atmosphere, they always mixed with a suite of other components, especially in TSP.

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Therefore, it is not particularly relevant that metals significantly lower the EC oxidation temperature of pure diesel emission particulates since EC is always determined in the presence of metals from ambient aerosol."

» As the reviewer states, EC in ambient particles is always determined in the presence of metals thus it is very important to understand the effects of various metals (present in ambient aerosols) on EC quantification. Ambient aerosols are uncontrolled mixtures that would be difficult to interpret and would be very difficult to use to address the problem systematically. To understand the behavior of ambient aerosols, lab studies frequently take the tactic of using a single components, and many sound insights have been garnered from such approaches. Our results show that the presence of metals generally reduces the reported EC/OC ratio of diesel exhaust particles, a consequence of reducing the EC oxidation temperature and increasing charring. The results are relevant to quantification of ambient aerosols, because it suggests that the EC/OC ratio of ambient aerosols quantified by thermal-optical method is generally lower than the true EC/OC ratio due to the presence of metals.

Reviewer: "It would have been more interesting how stable the split point is with varying loads of ambient aerosol."

»Without an absolute measure of EC and OC or TC it is not possible to test out mixtures of ambient aerosol and EC, because there is no way to accurately assess the EC and OC present in the ambient sample initially. Further there is no method to assess the interaction between the added EC and OC, existing EC and OC and other components of the aerosols. Some of the effects are dependent on the metal-to-carbon ratio as we show here. Over a wider range of EC to OC than studied here, effects are likely dependent on the EC/OC ratio as well, and this would change together with the metals as the ambient : diesel ratio was varied. Further, it is completely unclear what the correct measure of metals in the ambient aerosols would be for comparisons for thermo-optical analyses. We speculate that digestion in nitric acid may underestimate the quantity of metals that become active while the sample is heated to several

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hundred degrees, above the melting point of many forms of metals commonly found in ambient particles. Mixtures of metals may also act in ways that are not simply additive. As reviewer mentioned it would have been more interesting how stable the split point is with varying loads of ambient aerosols. This is addressed in the manuscript, which states: "TOEGA results for the samples from 6 December and 7 December were very similar to 5 December; higher M/C did not further reduce the oxidation temperature of diesel EC." Importantly, the effects of ambient aerosol collected at any given point in space and time doesn't necessarily inform the effects of other ambient aerosols, because ambient aerosols are so variable. With a truly enormous amount of sampling, one might make headway by collecting many large ambient samples and mixing them with diesel PM at different ratios, characterizing their metal content measuring carbonaceous material with EGA. The effect of the metals as components in mixtures as a function of metal : carbon ratio and the type of EC and OC might eventually emerge. Our current work would provide as a framework to interpret the results of such an undertaking by providing insights such as which metals are most active (copper, transition metals) and which other factors are important (metal : carbon ratio etc.) and so on. Such an experimental program would likely require attempting several methods of metal characterization to find the one that gives predictive ability. Also we note that in our manuscript we have used the convention that "split point" refers to the time of the split between OC and EC. The reviewer may be referring to the split between OC and EC. The split point (time) should change as the charring and temperature dependent evolution of carbon changes, thus by itself it is of little interest.

Reviewer: "On the other hand, the 'effective' chemical forms of the metals in TSP are more critical but have not been addressed in the manuscript. Among the salts used in the experiments, perhaps sodium chloride is the only one which might be atmospherically relevant, the availability of the others is at least highly questionable."

»What ever the chemical forms of the metals present in ambient particles or the metal salts we used, they change repeatedly during the heating process of thermo-optical

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analysis. Characterizing the forms of the metals during heating is an enormous undertaking beyond the scope of the present study. Our results shows that the anions (chloride or sulfate) associated with metals affect the OC and EC quantification to a lesser extent than cations (metals). The use of representative metal salts is very common in lab research. We selected the metals based on the speciation, oxidation state and metal/carbon ratios commonly reported for ambient aerosols. The effects we see with ambient aerosols are roughly what we would expect from the metal salt data.

Reviewer: "The authors adjust the metal-to-carbon ratio with soluble salts to the bulk concentrations commonly observed in ambient aerosol (TSP), though several of metals in TSP are definitely bound to dust particles largely in their mineral forms which are barely soluble in dilute nitric acid. Even if some metals are present in the ambient TSP which can be liberated and determined following prolonged exposure of the samples to nitric acid, but are the same metals in the same quantities (and chemical forms) similarly available as catalysts for a few seconds in the course of thermal determination? I would doubt so, since different properties and time scales come into play (solubility vs. melting point, day vs. seconds)."

»Currently there is not sufficient information in the literature to compare the behavior of metals dissolving in nitric acid solution over hours to days with metals being strongly heated, in most cases to above their melting points both in the absence and presence of oxygen. However, the metals do appear to melt or change phase, as we observe a strong inverse relationship between melting point and OC charring (Fig. 6). The reviewer is correct that it is difficult to create a 1:1 predictive model of ambient aerosols from our results, but this is also true for the majority of other possible experimental designs. There are numerous variables that would need to be addressed. From our experiments, one can begin to unravel the source of the aerosol-dependent variability associated with thermo-optical methods: clearly some metals, such as transition metals change the analysis substantially. Some other metals and anions are much less active. Further our results suggest EC in high EC/OC samples is more likely to be

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underestimated if there is a significant amount of metal in the aerosol.

Reviewer: “Another concern is that the manuscript relies on only three consecutive daily samples, which do not provide a firm experimental background to draw the conclusions.”

»We have not relied on the three daily TSP samples to draw the conclusions. The conclusions are drawn primarily from the data of 13 representative metal salts mixed with diesel particles. The data from TSP mixed with diesel particles confirm the earlier result from the literature (e.g. Turner and Hering 1994) that chemical components in TSP likely affect the carbon analysis of diesel particles, and provide motivation for the single metal measurements.

Reviewer: “The experimental method of generating metal salts particles raises additional problems since admittedly crystalline metallic particles form during particle generation (page 16950 line 1) which likely have little if any relevance in atmospheric particles.”

» Again, the original chemical forms of metals present in particles are not, as far as we can tell, critical. The chemical forms of metals in our samples (mixture of metal salts with diesel particles) change during the heating process. They may go from crystalline particles to metal hydroxide, metal oxides, and other forms. Similarly, the metals present in ambient aerosols will also go through different forms during the heating process.

Reviewer: “Minor comment: The authors quote (e.g. on page 16952) that in biomass burning aerosol EC is combusted at lower temperature because of the presence of metals: in fact biomass burning EC in its chemistry and structure is vastly different from diesel particulates.”

»Novakov and Corrigan, 1995b, concluded that the presence of K or Na in biomass smoke samples lowered the combustion temperatures of black carbon in biomass sam-

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ples. Their results are based on the comparison between the original samples and samples after removal of water-soluble components. We agree that biomass burning EC in its chemistry and structure is different from diesel particles. We are addressing the different effects of metal catalysts on the OC and EC measurements for variety types of carbonaceous aerosols in another manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 16941, 2010.