

Draft PM_{2.5} Chemical Speciation Program

Thermal Optical Analysis Issue Paper

Carbon represents a major constituent of fine PM_{2.5} mass in many parts of the country; therefore, mass balance and quality assurance require determination of PM_{2.5} particulate carbon. Differentiation of organic, elemental, and carbonate carbon, provides a useful characterization for source attribution and trends analysis. For the PM_{2.5} speciation trends program, total, organic, elemental, and carbonate carbon will be determined by thermal-optical transmittance (TOT) and the method specified in NIOSH 5040. The specific instrument chosen was based on commercial availability and the work done by Turpin, Cary and Huntzinger, 1990. Method selection was reviewed by the Chemical Speciation expert panel (Koutrakis, 1998) and based on data use objectives and the availability of standard operating procedures.

The differentiation of organic from elemental carbon, and elemental from carbonate carbon is dependent on the specific analytical technique and operational procedures used. There are currently no reference standards or a standardized method for distinguishing between organic and elemental carbon; therefore, differing results can be obtained for the same sample depending on the analytical method used. Because of these limitations, it is extremely important that a consistent analytical method be used for the Chemical Speciation program's trends sites.

Two thermal-optical methods are currently in use for the analysis of carbonaceous aerosols, they are the NIOSH (TOT) and DRI/OGC (Desert Research Institute/Oregon Graduate Center thermal-optical reflectance, TOR) methods. The NIOSH method has typically been used for analysis of diesel particulate. The DRI/OGC method has historically been used for the EPA IMPROVE (Interagency Monitoring of Protected Visual Environments) program for mostly federal class I areas. The measurement principal is fundamentally the same; however, the methods differ with respect to analysis time, temperature profile (temperature vs. time), types of carbon speciated, and the pyrolysis correction technique (see below for a more detailed discussion). The pyrolysis correction feature allows correction for the "char" that forms on the filter during analysis of some materials (e.g., cigarette and wood smoke). Correction for pyrolysis is made by continuously monitoring the filter transmittance or reflectance throughout the analysis.

Although it is understood that comparison between organic and elemental carbon is highly variable and not necessarily expected since they are operationally-defined, recent intercomparison analyses by Chow (PM2000) and Norris (in progress) identify significant differences between the elemental carbon results provided by the NIOSH and IMPROVE methods. Given that the PM_{2.5} Speciation and IMPROVE programs characterize the aerosol in both urban and rural environments and provide data for use in the EPA PM_{2.5} program, there is a necessary linkage and need for comparability of data. Although many carbonaceous aerosol sampling issues remain, this paper focuses only on the analytical method and outlines the operational differences, method issues and the near-term plan for resolving the analytical issues.

Thermal Optical Analysis Issues

Organic and elemental carbon by thermal optical analysis have meaning only in the operational

sense. That is, the results reflect the method used and the appropriateness of a method depends on the data use objectives. Operational-based methods differ from those used for specific, identifiable analytes (e.g., sulfate or sulfur), where a well-defined entity is quantified and laboratory standards are available for its determination. Because organic and elemental carbon are operationally defined, the details of the method must be rigorously prescribed. Organic and elemental carbon fractions are defined when using the operating parameters in NIOSH 5040. Total carbon is the sum of these two and the carbonate carbon (as simple carbonate, not a bicarbonate) can be estimated by integrating the carbonate peak. In contrast, four types of organic carbon and three types of elemental carbon are defined by the IMPROVE technique. Total carbon is the sum of all fractions and carbonate is typically determined by the acidification technique. In both cases, different classes of carbon are evolved from the sample during the analysis. The division into fractions reflects the data use and purpose of the method (i.e., occupational monitoring of diesel particulate using the NIOSH method and visibility monitoring using DRI/OGC for IMPROVE).

Results from intercomparison studies of DRI-TOR versus Sunset Labs-TOT methods by Countess (1990), Birch (1998), Chow (PM2000), and Norris (in progress) are consistent. Results for total carbon are in fairly good agreement (generally < 10 %), while the agreement for organic and elemental carbon is highly variable. As mentioned previously, agreement between organic and elemental carbon is generally not expected since these components are operationally defined. The difference between organic carbon measurements has been shown to be as much as 17.5±15% (Chow, PM 2000). Elemental carbon as determined by the DRI/OGC EC method has been shown to be as much as a factor of 2 higher (Norris, 2000) when comparing to the NIOSH EC method. Data on specific comparisons of the carbonate carbon results were not available.

Generally, the analytical differences between the NIOSH and DRI/OGC methods are as follows:

- **Temperature profile and subsequent total run time** - the total run time is approximately 12 minutes for the NIOSH method and 35 minutes for DRI/OGC. Refer to the table below for a comparison of the temperature profiles.

NIOSH -OC	DRI/OGC -OC	NIOSH - EC	DRI/OGC - EC
Helium	Helium	2% O₂ in He	2% O₂ in He
250° C, 30 sec.	<i>OC1</i> : 120° C, 3-10 min.*	650° C, 1 min.	<i>EC1</i> : 550° C, 3-10 min.*
500° C, 30 sec.	<i>OC2</i> : 250° C, 3-10 min.*	750° C, 1 min.	<i>EC2</i> : 700° C, 3-10 min.*
650° C, 1 min.	<i>OC3</i> : 450° C, 3-10 min.*	850° C, 1 min.	<i>EC3</i> : 800° C, 3-10 min.*
850° C, 1.5 min.	<i>OC4</i> : 550° C, 3-10 min.*	940° C, 2 min.	--

* Based on time required for FID to return to baseline.

OC - organic carbon
EC - elemental carbon

- **Procedure for quantifying organic carbon (OC) and elemental carbon (EC) peaks** - Two different procedures are used to quantify organic and elemental carbon. For NIOSH, OC is the sum of carbon before the split between OC and EC (determined as the point where the transmittance reaches the initial value) and EC is the sum of the remainder. For DRI/OGC, it is the sum of the organic and elemental carbon fractions; $OC = OC1 + OC2 + OC3 + OC4 + \text{Pyrolyzed carbon}$ and $EC = EC1 + EC2 + EC3 - \text{Pyrolyzed carbon}$ as shown in the Table above.
- **Optical measurement of pyrolysis correction** - This feature corrects for the pyrolysis-generated EC or “char” formed during the analysis of some materials. The NIOSH method uses transmittance and DRI/OGC uses reflectance. The point at which the transmittance or reflectance reaches its initial value is where the OC/EC definition or split occurs. The carbon evolved prior to the split is considered OC (including carbonate) and the carbon volatilized after the split, and prior to the methane calibration peak, is considered EC. The method definition of the “split” has an impact on the amount of EC and OC determined.
- **Procedure for determining carbonate carbon** - The DRI/OGC procedure involves a more specific determination of carbonate carbon from a second filter punch that is acidified then analyzed. The NIOSH method can provide an estimation of the total carbonate-source carbon (i.e., potassium carbonate, sodium carbonate, magnesium carbonate, calcium carbonate) by integrating the last peak that occurs just before pyrolytic carbon. Verification of the carbonate carbon present in the sample can also be done by taking a second filter punch, acidifying and then analyzing.
- **Higher sample loadings** - higher sample loading require special care during analysis and can affect the results from either thermal optical method.

Availability of NIST Calibration Materials

Another important issue that remains unresolved is the availability of National Institute of Standards and Technology (NIST) or other calibration standards for OC, EC and carbonate carbon aerosols. Without these materials, there is no reliable way to determine method bias or true concentrations of the carbon fractions. Thermal-optical methods are currently calibrated using sucrose. Potassium acid phthalate (KHP) is sometimes used as an alternative to sucrose and the injection of a known volume of methane with every sample, is used as quality control check of the sucrose calibration.

Near-term Plan

Given that the measurement of carbon is operationally-based and dependent on the specific analytical technique and operational procedures used, the ultimate goal is to determine and finalize the operational details of the method used for the PM_{2.5} Speciation program. It is important to generate data of acceptable quality and consistency in order to meet the primary data use objectives (trends, SIP development, source attribution, and linkage with IMPROVE).

Collaboration between the OAQPS and ORD/NERL has resulted in the proposal to quantify and report the fraction of OC evolved from 550-850 (prior to addition of O₂) using the NIOSH

Speciation method. This fraction will be referred to as “OCX” or organic carbon X and will be reported as a separate fraction for the Chemical Speciation program. No changes to the operational conditions or temperature profile will be made. To achieve comparability with data being generated for IMPROVE, data users will add this fraction to the EC reported by the Speciation program and subtract it from the OC fraction. No adjustments to the reported TC or CC measurements are required. Preliminary review of the proposal and feedback from CASAC provides concurrence of this approach with a recommendation for further study of the carbon sampling and analysis issues.

OAQPS and ORD staff collaboration continues in order to identify and discuss the thermal-optical method issues. We continue to gather information relative to the intercomparison of the two methods. This information will be used to provide feedback to the program manager, policy and scientific decision makers, and program participants regarding the specific method parameters needed for the PM_{2.5} Speciation program. This group will convene as information becomes available to discuss next steps and a further course of action.

Summary of Preliminary Findings

- **Carbon Fractions:** Initially, there was concern that separate OC and EC fractions generated by DRI/OGC are also necessary for PM_{2.5} Speciation source attribution. A limited number of discussions with data users so far indicates that these fractions are not currently being used for source attribution modeling. In addition, the identification of the actual constituents of each of these carbon fractions is still uncertain.
- **Source Profiles:** If most of the PM carbon profiles used for source attribution were generated primarily with one method, then consistency with this method should be considered. To obtain a snapshot of available profiles, the EPA SPECIATE 3.0 data base was reviewed for the PM source profiles with *elemental carbon* as a component. SPECIATE is EPA’s repository of total organic and PM speciated profiles for a wide variety of sources. Interestingly, most of the profiles were generated in the late 70's and during the 80's by John Cooper and other investigators, including John Watson’s thesis from the Oregon Graduate Center. The most recent series of profiles in the data base were generated by Hildemann, Markowski and Cass (1991). The Geographic coverage of profiles in SPECIATE is limited and appears to be focused on the west coast, with the exception of some work done in the Denver area.
- **Calibration Standards (non-NIST):** Promising work is being done by the ORD/NERL staff to generate EC calibration materials suitable for thermal optical analysis. A technique, which uses graphitic carbon sublimation and vacuum deposition to apply carbon as a thin film on quartz filters, is being evaluated as a viable option. SEM analysis of a few filters shows that the film is deposited as a very uniform layer on the filter substrate. Additional filters will be prepared at three different loadings and analyzed by thermal optical analysis. Purity of the carbon rods used is greater than 99 %.

References

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