



STANDARD OPERATING PROCEDURES

Reconstructing Fine Particulate Matter Mass from Measured Chemical Components

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1.0 SCOPE AND APPLICATION

This SOP describes the method used by SPARTAN to reconstruct the fine particulate matter (PM_{2.5}) mass measured on sampled PTFE filters. Chemical constituents measured through ion chromatography, sulfate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), and sodium (Na⁺), are used along with measured trace element concentrations to infer major constituent such as ammonium nitrate and soil. Equivalent black carbon (EBC) is determined as described in SPARTAN SOP EBC SSR Revision 2.0. The particle-bound water in the total PM_{2.5} is estimated based on the chemical constituent concentrations using κ-kohler theory and described herein. The inferred residual matter (RM), taken as the difference between the total PM_{2.5} and the sum of measured components, is used as a surrogate for organic matter that is not yet directly measured by SPARTAN.

| REVISION HISTORY | | | |
|------------------|---|-----------------|----------------|
| Revision No. | Change Description | Date | Authorization |
| 2.0 | General reorganization and clarification; update to CM calculation and RM mass growth factors | August 20, 2018 | Crystal Weagle |
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2.0 RECONSTRUCTING WATER-SOLUBLE CONSTITUENTS

2.1 Dry inorganic species from water-soluble ions

As described in SPARTAN SOP Anion/Cation Revision 2.0, there are seven anions and six cations quantified by ion chromatography. The determined amount of individual water-soluble ions is used to infer the concentrations of ammonium nitrate, sea salt, sodium sulfate, and ammoniated sulfate contained in the measured PM_{2.5} mass. References for each method are provided in Table 1 in section 5.0. Here, the term “dry” refers to components with no associated water (0% relative humidity).

To account for the sodium associated with crustal material, 10% of measured aluminum is taken to be associated with sodium and removed from the total sodium concentration. To account for the associated Cl, the dry sea salt concentration is represented as 2.54[Na⁺]_{ss}, based on the 1:1 molar ratio of Na⁺:Cl⁻.

Sodium sulfate is calculated as a fraction of the measured sodium, 0.18[Na⁺]_{ss}. To account for sulfate in the form of sodium sulfate, 12% of the measured sodium concentration is removed from the total measured sulfate. Nonetheless, sodium sulfate is found to contribute negligibly to the total PM_{2.5} mass (< 0.1%) at all sampling sites and is not included in the reconstructed mass.

All measured nitrate is treated as neutralized by ammonium to form ammonium nitrate when in the aerosol form. The corresponding mass of dry ammonium nitrate is defined as $1.29[\text{NO}_3^-]$ based on the 1:1 molar ratio of $\text{NH}_4^+:\text{NO}_3^-$. Ammonium that is not in the form of ammonium nitrate, and sulfate that is not in the form of sodium sulfate, are assumed to be a mixture of ammonium bisulfate and ammonium sulfate. Thus, this mixture is referred to as ammoniated sulfate (ASO_4 , dry). The sum of dry ammonium nitrate and dry ammoniated sulfate is equal to the sum of measured sulfate, nitrate, and ammonium.

2.2 Accounting for water associated with inorganic species

Under the weighing conditions used, where the relative humidity is between 30 and 40 %, there is water associated with the inorganic species. This particle-bound water (PBW) contributes to the total $\text{PM}_{2.5}$ mass and must be accounted for. The PBW is estimated based on the mass of the chemical component X , as:

$$PBW_X = [X] \kappa_{m,X} \frac{RH}{100 - RH} \quad (1)$$

where $[X]$ is the concentration of the chemical component, $\kappa_{m,X}$ is the mass growth factor for the chemical component, and RH is the relative humidity of the weighing conditions. Since the RH of the clean room during weighing is 30 – 40 %, an RH of 35 % is used for PBW calculations. The estimated mass growth factors for the three relevant inorganic species are estimated based on the volume growth factors and densities of the species:

$$\kappa_{m,\text{NH}_4\text{NO}_3} = \kappa_{v,\text{NH}_4\text{NO}_3} / \rho_{\text{NH}_4\text{NO}_3} = 0.67/1.72 = 0.39$$

$$\kappa_{m,\text{ASO}_4} = \kappa_{v,\text{ASO}_4} / \rho_{\text{ASO}_4} = 0.53/1.77 = 0.30$$

$$\kappa_{m,\text{NaCl}} = \kappa_{v,\text{NaCl}} / \rho_{\text{NaCl}} = 1.12/2.17 = 0.52$$

To obtain the concentration of a component at 35 % RH :

$$[X]_{35\%} = [X]_{\text{dry}} \left(1 + \kappa_{m,X} \frac{RH}{100 - RH} \right) \quad (2)$$

The total PBW associated with inorganic components, $PBW_{\text{IN_mass}}$, can be calculated as the sum of the difference between the $[X]_{35\%}$ and $[X]_{\text{dry}}$ terms of all inorganic components. The EBC determined as described in SPARTAN SOP EBC SSR Revision 2.0 is assumed to be hydrophobic and have no associated water.

3.0 ADDITIONAL CONSTITUENTS FROM TRACE ELEMENTS

As described in SPARTAN SOP Trace Metals ICP-MS there are over 20 elements that are quantified by analysis of filter extracts with ICP-MS. The concentrations of elements determined through this method are used to estimate contribution of crustal material and trace element oxides to total PM_{2.5}. The water uptake of crustal material and trace element oxides is treated as negligible.

Concentrations of elements Al, Fe, and Mg are used to estimate the crustal material component of PM_{2.5} mass. Crustal material (CM) consists of resuspended road dust, desert dust, soil, and sand. Following the work of Wang (2015) that describes the elemental composition of natural desert dusts, it is generalized in this study that natural CM concentration is represented by 10*([Al] + [Fe] + [Mg]). CM is represented by elemental aluminum, iron, and magnesium due to their consistency in natural mineral dust samples and frequency above detection limits. Silicon and titanium are commonly included in equations inferring crustal material, however silicon is not available in the ICP-MS analysis and titanium was found to contribute negligibly (< 1%) to CM mass.

Trace elemental oxides (TEO) are the sum of the masses of trace elements measured by ICP-MS, less those used in other calculations, in their oxide form. TEO concentrations are a function of the measured elemental mass and typical oxides of that element found in nature. For example, there are many oxides of vanadium (V₂O₅, V₃O₇, etc.), but V₂O₃ is found to be representative. The total mass contributed from TEO is typically 1 – 2 % of total mass and is calculated as follows:

$$[TEO] = 1.47[V] + 1.27[Ni] + 1.25[Cu] + 1.24[Zn] + 1.32[As] + 1.2[Se] + 1.07[Ag] + 1.14[Cd] + 1.2[Sb] + 1.12[Ba] + 1.23[Ce] + 1.08[Pb] \quad (3)$$

4.0 CALCULATION OF RESIDUAL MATTER

Currently the organic components of the collected PM_{2.5} is not directly measured by SPARTAN. However, the residual matter (RM) component is assumed to be predominately organics based on comparison with independent measurements as reported by Snider et al. (2016). The RM component at 35 % RH is calculated by mass balance by subtracting the total of the measured inorganic chemical components (IN_{mass,dry}) and associated water (PBW_{IN_mass}) from the total PM_{2.5} mass:

$$RM_{35\%} = PM_{2.5,35\%} - [IN_{mass,dry}] - [PBW_{IN_mass}] \quad (4)$$

where $[IN_{mass,dry}] = [NH_4NO_3]_{dry} + [ASO_4]_{dry} + [NaCl]_{dry} + [CM] + [TEO] + [EBC]$

Negative $RM_{35\%}$ values are retained if the reconstructed inorganic mass at 35 % RH ($IN_{mass,35\%}$) exceeds the total $PM_{2.5}$ mass by less than 10 %, otherwise values are flagged. Flagged negative $RM_{35\%}$ values may result from an overestimation of an inorganic component. Thus, reconstructing $PM_{2.5}$ mass acts as a Level 2 data validation of other analysis methods by leading to investigation of obtained values.

Identifying a representative organic hygroscopic parameter is challenging, as many are available from laboratory studies and field campaigns and vary by site and season. Value of κ_v for organic matter ($\kappa_{v,OM}$) range from 0 to 0.2, thus a single $\kappa_{v,OM}$ value of 0.1 is chosen based on an O:C ratio of 0.5 to represent the urban, populated nature of SPARTAN sites. Therefore, following the calculation of the RM contribution at 35 % RH, the dry RM concentration can be determined following the method outlined in section 2.2 using an estimated mass growth factor as follows:

$$\kappa_{m,RM} = \kappa_{v,OM} / \rho_{OM} = 0.1 / 1.4 = 0.07$$

5.0 SUMMARY OF SPECIATION DEFINITIONS

Table 1 provides a summary of the speciation definitions used to reconstruct $PM_{2.5}$ mass, the measurement method used to obtain relevant species, and the reference used to inform component definitions.

Table 1. Summary of speciation definitions and associated references.

| Species | Method | Species mass (μg) | Reference |
|--|---|--|--|
| SS | IC | $2.54[\text{Na}^+]_{\text{SS}}$, where $[\text{Na}^+]_{\text{SS}} = [\text{Na}^+]_{\text{total}} - 0.1[\text{Al}]$ | Malm et al., 1994; Remoundaki et al., 2013 |
| NH_4NO_3 | IC | $1.29[\text{NO}_3^-]$ | Malm et al., 1994 |
| ASO_4 | IC | $[\text{SO}_4^{2-}]_{\text{non-SS}} + [\text{NH}_4^+] - 0.29[\text{NO}_3^-]$, where $[\text{SO}_4^{2-}]_{\text{non-SS}} = [\text{SO}_4^{2-}]_{\text{total}} - 0.12[\text{Na}^+]$ | Dabek-Zlotorzynska et al., 2011; Henning, 2003 |
| Na_2SO_4 | IC | $0.18[\text{Na}^+]_{\text{SS}}$ | Dabek-Zlotorzynska et al., 2011; Henning, 2003 |
| CM | ICP-MS | $10 \times ([\text{Al}] + [\text{Mg}] + [\text{Fe}])$ | Wang, 2015 |
| EBC | SSR | $20.7 \times \ln(R/R_o)$ | Taha et al., 2007 |
| TEO | ICP-MS | $1.47[\text{V}] + 1.27[\text{Ni}] + 1.25[\text{Cu}] + 1.24[\text{Zn}] + 1.32[\text{As}] + 1.2[\text{Se}] + 1.07[\text{Ag}] + 1.14[\text{Cd}] + 1.2[\text{Sb}] + 1.12[\text{Ba}] + 1.23[\text{Ce}] + 1.08[\text{Pb}]$ | Malm et al., 1994 |
| $\text{PBW}_{\text{IN}_{\text{mass}}}$ | $\kappa_{m,X}$ | $\sum_X [f_{m,X}(\text{RH}) - 1][X]$ | Kreidenweis et al., 2008 |
| PBW_{RM} | $\kappa_{m,OM}$ | $\text{RM} (1 - 1/f_{m,RM})$ | Jimenez et al., 2009 |
| RM (35 % RH) | Mass balance | $[\text{PM}_{2.5}] - \{ [\text{EBC}] + [\text{CM}] + [\text{TEO}] + [\text{NH}_4\text{NO}_3] + [\text{SS}] + [\text{ASO}_4] + [\text{Na}_2\text{SO}_4] + [\text{PBW}_{\text{IN}_{\text{mass}}}] \}$ | This study |
| RM (0 % RH) | Mass balance, $\kappa_{m,OM} = 0.07$ | $\text{RM}(35\%) - \text{PBW}_{\text{RM}}$ | Jimenez et al., 2009; Sun et al., 2011 |

Measurement methods: IC = Ion Chromatography, ICP-MS = Inductively Coupled Plasma – Mass Spectrometry, SSR = Smoke Stain Reflectometer, $\kappa = \kappa$ -Kohler hygroscopicity theory