CHAPTER 3

DETERMINATION OF AEROSOL TYPES

The fine aerosol species at most continental sites can be classified into five major types: sulfates, nitrates, organics, elemental carbon, and soil. Other fine species such as nonsoil potassium, or sea spray and other trace elements, are less important from a visibility standpoint at the majority of the monitoring sites presented here. The value of many of the trace species lies, in part, in their use in identifying origins of different air masses. The fine aerosol types are estimated from the elements and ions measured in IMPROVE samplers based on their presumed or probable aerosol composition. The purpose of this chapter is to define and discuss the compositions assumed for the fine aerosol types and coarse particles. The adequacy and validity of these assumptions are addressed in greater detail in Chapter 4, "Validation".

3.1 Sulfate

Most fine sulfates are the result of chemical processes which convert SO_2 gas into sulfate species. In moist atmospheres, a major process involves the oxidation of SO_2 gas to sulfuric acid in water droplets. If there is inadequate ammonia in the atmosphere to fully neutralize sulfuric acid, as is sometimes the case, then the resulting aerosols are acidic. Under these circumstances solutions of continuously varying acidity are formed. The extremes of this continuum are ammonium sulfate (neutral) and sulfuric acid.

In this report sulfate represents the total concentration associated with elemental sulfur, not just the ion. The multiplicative molar correction factor[2] (mcf) for elemental sulfur depends on the degree of neutralization of the sulfuric acid produced by conversion of SO_2.

SULFATE FORM	**EQUATION**	**NEUTRALIZATION**
$(NH_4)_2SO_4$:	[SULFATE]=4.125[S]	100%
$(NH_4)HSO_4$:	[SULFATE]=3.594[S]	50%
H_2SO_4:	[SULFATE]=3.063[S]	0%

The brackets indicate the mass of the aerosol species or element.

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[2] The mcf is determined by an accounting of the total molar weight of a sulfate species then dividing by the molar weight of sulfur. For example, the mcf for ammonium sulfate is: ((14 + 4)2 + 32 + (16)4)/32 = 4.125.

Based on analysis of high volume filters, many authors have noted the acidity of aerosols in the eastern U.S. (Malm et al., 1991). It is recognized that scattering efficiencies of acidic aerosols in the presence of high RH can be quite different from the scattering characteristics of pure ammonium sulfate (Malm et al., 1990; Tang et al., 1981). However, because acidity was not explicitly measured, all elemental sulfur is presumed to be from ammonium sulfate, as a first approximation. Thus, all elemental sulfur concentrations are multiplied by 4.125. However, a more detailed analysis of assumptions regarding aerosol acidity is presented in Section 4.2.1.

3.2 Nitrates

Nitrate particles are collected on nylon filters. The input stream is denuded to remove nitric acid. The mass of the nitrate ion is determined by ion chromatography. Assuming, as is the case for sulfate, that the collected nitrates are fully neutralized (forming NH_4NO_3), the nitrate mass is estimated by using a mcf of 1.29:

$$[NITRATE] = 1.29[NO_3] \tag{3.1}$$

3.3 Carbons

Both elemental carbon, also called light absorbing carbon (LAC), and the mass of organic species (OM) can be estimated from either Channel A or Channel C (see the discussion in Chapter 2). The LAC and OM are indirectly inferred from Channel A fine aerosols collected on Teflon. LAC is inferred from an absorption coefficient (b_{abs}) as measured using the Laser Integrated Plate Method (LIPM); and OM is inferred from hydrogen (PESA) and sulfur (PIXE) concentrations.

Alternatively, the analysis of Channel C filters attempts to directly quantify the carbon mass from the material collected on quartz filters using the Thermal Optical Reflectance (TOR) combustion method (Chow et al., 1992). The results of the TOR method are the OCLT, OCHT, ECLT, and ECHT variables which depend primarily on the temperature of combustion:

OCLT = Low temperature organic carbon (25^0C to 120^0C);
OCHT = High temperature organic carbon (120^0C to 550^0C);
ECLT = Low temperature elemental carbon (550^0C to 700^0C); and,
ECHT = High temperature elemental carbon (above 700^0C).

Because Channel C carbon determinations represent direct estimates of carbon mass they will be used to describe the ambient aerosol concentrations used in Chapters 6 and 7. The Channel A determinations will be used as quality control variables or checks on the validity of the assumptions used. One assumption that will be examined in detail in Chapter 4 on Validation is the association of ECLT and ECHT with LAC.

3.3.1 Organic Carbon

OM calculated from the concentrations of H and S measured on the Channel A Teflon filter will be denoted as OMH. An average ambient organic particle is assumed to contain constant fractions of carbon (f_{OC}) and hydrogen (f_{OH}) by weight. Furthermore, it is assumed that during exposure to the vacuum of Channel A PIXE and PESA analyses, all nitrates and water volatilize and do not contribute to the mass of H. By assuming a level of neutralization of the sulfate ion, OMH is calculated by:

SULFATE FORM	EQUATION FOR OMH	NEUTRALIZATION
$(NH_4)_2SO_4$:	$[OMH]=(1/f_{OH})([H]-0.250[S])$	100%
$(NH_4)HSO_4$:	$[OMH]=(1/f_{OH})([H]-0.156[S])$	50%
H_2SO_4:	$[OMH]=(1/f_{OH})([H]-0.063[S])$	0%

The sulfur factors are derived from the H/S ratio for each form of sulfate; for example ammonium sulfate has a ratio of 8/32, or 0.25. The value of the factor f_{OH} will be examined in Chapter 4. To be consistent with the assumption of fully neutralized sulfate the top equation would apply; however, Section 4.2.1 will address the ramifications of this assumption.

Organics from Channel C (OMC) is simply the sum of OCLT and OCHT adjusted by the molar correction factor $1/f_{OC}$:

$$[OMC] = (1/f_{oc})([OCLT]+[OCHT]) \qquad (3.2)$$

For this report, a value for f_{OC} of 0.71 is used which gives a reciprocal factor of 1.4 (Watson et al., 1988).

3.3.2 Light Absorbing Carbon (LAC)

LAC, derived from the Channel C TOR analysis is simply the sum of the two elemental fractions:

$$[LAC] = [ECLT]+[ECHT] \qquad (3.3)$$

If the only light absorbing species is elemental carbon, then LAC should compare to Channel A b_{abs} as measured by LIPM.

On Channel A, b_{abs} is quantified directly by the LIPM analysis and is stated in units of $10^{-8}m^{-1}$. To compare the mass of LAC with b_{abs} requires assuming an absorption efficiency. For this report, the relationship used for comparison purposes is:

$$[LAC] = [b_{abs}]/\beta \qquad (3.4)$$

where $\hat{a}$, the absorption efficiency, is assumed to be 10 m^2/g.

3.4 Soil

The soil mass concentration is estimated by summing the elements predominantly associated with soil, plus oxygen for the normal oxides (Al_2O_3, SiO_2, CaO, K_2O, FeO, Fe_2O_3, TiO_2), plus a correction for other compounds, such as MgO, Na_2O, water, and CO_2. The final factors are based on the following observations:

(1) The soil mass can be calculated from the sum of the masses due to the constituent oxides. The mass due to each oxide is seen to be the corresponding measured elemental mass multiplied by the appropriate mcf for that oxide.

(2) Fe is present as both FeO and Fe_2O_3. It is assumed that the two forms are equally abundant (in molar concentrations), giving a mcf of 1.36. This differs from that obtained with average sediment by 1%.

(3) A complicating factor for fine soil particles is that K has a nonsoil component from smoke. Therefore, Fe was used as a surrogate for soil K. Based on the average K/Fe ratio for coarse particles of 0.6 ± 0.2 (Cahill et al., 1986), the following equation was used:

$$[K] = 0.6[Fe] \tag{3.5}$$

which yielded a mcf of 2.08 for Fe.

The final equation for fine soil after dividing by 0.86 to account for other compounds (MgO, Na_2O, water, and CO_2) is:

$$[SOIL] = 2.20[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti] \tag{3.6}$$

3.5 Nonsoil K (KNON)

KNON usually results from combustion processes that produce smoke and can be estimated by the equation:

$$[KNON] = [K] - 0.6[Fe] \tag{3.7}$$

The use of KNON as a tracer for smoke is problematic. This is because the particulate K is probably produced by transformation of volatilized K, while most smoke mass is from primary emissions. In addition, the resulting K is probably smaller than most of the other smoke particles and will have a lower settling velocity. For both reasons, the ratio of K/(smoke mass) will increase with transport time. When close to the source, the particulate K may not have time to form. For long transport, most mass other than K may settle out.

3.6 Salt

In general, NaCl is a significant factor in the reconstructed mass only in marine environments. A significant problem with Teflon filters is that chlorine can be volatilized from the filter during collection. Thus, the relationship:

$$[SALT] = 2.5[Na] \tag{3.8}$$

is used rather than the simple sum of [Na] and [Cl].

3.7 Coarse Mass (CM)

Coarse mass is estimated gravimetrically by subtracting fine mass $PM_{2.5}$ from total aerosol mass PM_{10}:

$$[CM] = [PM_{10}] - [PM_{2.5}] \tag{3.9}$$

No further chemical analysis is available on the individual coarse species. It is assumed that coarse mass consists primarily of insoluble airborne soil particles.

3.8 Reconstructed Fine Mass (RCFM)

The sum of the above fine composites should provide a reasonable estimate of the fine mass measured on the Teflon filter. However, a significant fraction of the nitrate particles can volatilize from the Teflon filter during collection and is not measured by gravimetric analysis. Therefore, nitrate collected on nylon filters is not included in RCFM when comparing RCFM to the gravimetric mass derived from the Teflon filter.

Salt will not be included in RCFM since most of the sites are continental. Moreover, because KNON due to smoke usually exits in trace amounts, and since smoke is measured by its contribution to OM or LAC, KNON will not be included in RCFM. On the other hand, when comparing RCFM to visibility, nitrates are included in RCFM because nitrates can be a significant fraction of fine mass. The equation for RCFM is therefore:

$$[RCFM] = [SULFATE] + [NITRATE] + [LAC] + [OM] + [SOIL] \tag{3.10}$$

As discussed previously, the intent of the design of the IMPROVE sampler was to use Channel C (TOR) measurements to directly quantify both LAC and OM as opposed to using Channel A (PESA, PIXE, and LIPM) to indirectly estimate LAC and OM. Therefore, Channel C determinations of LAC and OM will be used to summarize aerosol conditions. However, in Chapter 4, it will be shown that there are unresolved issues in using Channel C estimates of the carbonaceous species.