



Evaluation of
elemental ratios
measured by aerosol
mass spectrometry

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Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Elemental compositions of organic aerosol (OA) particles provide useful constraints on OA sources, chemical evolution, and effects. The Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) is widely used to measure OA elemental composition. This study evaluates AMS measurements of atomic oxygen-to-carbon (O : C), hydrogen-to-carbon (H : C), organic mass-to-organic carbon (OM : OC), and carbon oxidation state (\overline{OS}_C) for a vastly expanded laboratory dataset of multifunctional oxidized OA standards. For the expanded standard dataset, the “Aiken-Explicit” method (Aiken et al., 2008), which uses experimentally measured ion intensities at all ions to determine elemental ratios, reproduces known molecular O : C and H : C ratio values within 20 % (average absolute value of relative errors) and 12 % respectively. The more commonly used “Aiken-Ambient” method, which uses empirically estimated H_2O^+ and CO^+ ion intensities to avoid gas phase air interferences at these ions, reproduces O : C and H : C of multifunctional oxidized species within 28 % and 14 % of known values. These values are systematically biased low, however, with larger biases observed for alcohols and simple diacids. A detailed examination of the H_2O^+ , CO^+ , and CO_2^+ fragments in the high-resolution mass spectra of the standard compounds indicates that the Aiken-Ambient method underestimates the CO^+ and H_2O^+ produced from many oxidized species. Combined AMS-vacuum ultraviolet (VUV) ionization measurements indicate that these ions are produced by dehydration and decarboxylation on the AMS vaporizer (usually operated at 600 °C). Thermal decomposition is observed to be efficient at vaporizer temperatures down to 200 °C. These results are used together to develop an “Improved-Ambient” elemental analysis method for AMS spectra measured in air. The Improved-Ambient method reduces the systematic biases and reproduces O : C (H : C) ratios of individual oxidized standards within 28 % (13 %) of the known molecular values. The error in Improved-Ambient O : C and H : C values is smaller (12 % and 4 % respectively) for synthetic mixtures of the oxidized organic standards, which are more representative of the complex mix of species present in ambient

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



follows:

$$\text{O} : \text{C} = \alpha_{\text{O}:\text{C}} \cdot (M_{\text{O}}/M_{\text{C}}) \cdot (\text{MW}_{\text{C}}/\text{MW}_{\text{O}}) \quad (1)$$

$$\text{H} : \text{C} = \alpha_{\text{H}:\text{C}} \cdot (M_{\text{H}}/M_{\text{C}}) \cdot (\text{MW}_{\text{C}}/\text{MW}_{\text{H}}) \quad (2)$$

5 MW_{C} , MW_{O} and MW_{H} are the atomic weights of C, O, and H respectively. Since AMS ion intensities are proportional to the mass of the original molecules present (Jimenez et al., 2003), M_{C} , M_{O} , and M_{H} are obtained as a sum of the appropriate ion intensities across the complete organic spectrum (including H_2O^+ , CO^+ , and CO_2^+) as follows:

$$M_{\text{C}} = \sum_{j=m/z_{\min}}^{m/z_{\max}} I_j F_{\text{C}} \quad (3)$$

$$10 \quad M_{\text{O}} = \sum_{j=m/z_{\min}}^{m/z_{\max}} I_j F_{\text{O}} \quad (4)$$

$$M_{\text{H}} = \sum_{j=m/z_{\min}}^{m/z_{\max}} I_j F_{\text{H}} \quad (5)$$

where I_j is the ion intensity of the j th ion in the spectrum and F_{C} , F_{O} , F_{H} are the relative carbon, oxygen, and hydrogen mass fractions for that ion. Calibration parameters ($\alpha_{\text{O}:\text{C}}$ and $\alpha_{\text{H}:\text{C}}$) account for preferential losses of some atoms to neutral rather than ion fragments during the fragmentation processes. The tendency of hydrocarbon fragments to form positive ions more readily than those containing the more electronegative O atom, for example, can result in such a detection bias. Aiken et al. (2008) obtained slopes of 0.75 and 0.91 (i.e. $\alpha_{\text{O}:\text{C}} = 1/0.75$ and $\alpha_{\text{H}:\text{C}} = 1/0.91$), respectively, by comparing measured and known O : C and H : C values for a range of organic standards according to Eqs. (1) and (2).

**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

In AMS elemental analysis, Eqs. (1) and (2) are applied in two different ways which we refer to here as the Aiken-Explicit and Aiken-Ambient methods (Aiken et al., 2008). The Aiken-Explicit method is used when organic signals at CO^+ and H_2O^+ can be directly measured. Laboratory measurements performed in an atmosphere of dry argon, for example, do not contain the interfering H_2O or N_2 species and allow for direct measurement of the organic signals at H_2O^+ and CO^+ . The organic signals at CO^+ have also been obtained under ambient conditions from AMS size distributions and by monitoring changes in the m/z 28 intensities (Zhang et al., 2005; Takegawa et al., 2007). Calibrations have also been carried out in laboratory chamber experiments under controlled relative humidity to determine the interference signals and obtain the organic signals at CO^+ and H_2O^+ by subtraction (Chen et al., 2011; Nakao et al., 2013).

The Aiken-Ambient method is used for measurements performed in air where the interferences from gaseous N_2 and H_2O are difficult to estimate. Since most field measurements and laboratory chamber measurements are performed under the latter conditions, this method has in practice been the most widely used method of obtaining elemental ratios from AMS measurements. In the Aiken-Ambient method the organic H_2O^+ and CO^+ intensities used in Eqs. (3)–(5) are empirically estimated rather than directly measured. The $\text{H}_2\text{O}^+/\text{CO}_2^+$ and $\text{CO}^+/\text{CO}_2^+$ ratios recommended by Aiken et al. (2008) were empirically estimated from limited ambient OA measurements available at the time to be 0.225 and 1 respectively. The $\text{CO}^+/\text{CO}_2^+$ ratio was determined from AMS size distribution measurements where the gas-phase signal from N_2 can be separated from the particle phase CO signal intensities (Zhang et al., 2005; Takegawa et al., 2007). The $\text{H}_2\text{O}^+/\text{CO}_2^+$ mass ratio was empirically estimated to conserve OA mass concentrations that resulted from the $\text{CO}^+/\text{CO}_2^+$ ratio. This $\text{H}_2\text{O}^+/\text{CO}_2^+$ empirical mass ratio corresponds to a raw ion signal ratio of either 0.225, assuming H_2O^+ and CO_2^+ were each formed with a relative ionization efficiency (RIE) of 1.4 or 0.321, using a recently-determined RIE of 2.0 for the formation of H_2O^+ (Mensah et al., 2011).

3 Results and discussion

3.1 Evaluation of Aiken-Explicit and Aiken-Ambient methods

We evaluated the performance of both Aiken-Explicit and Aiken-Ambient methods over a large range of species, including those with higher O:C and more multifunctional moieties than originally studied by Aiken et al. (2008). Panels a and b in Fig. 1 show elemental ratios obtained with the Aiken-Explicit method for the laboratory standards studied here. The Aiken-Explicit method results reproduce known molecular O:C and H:C ratios for all the standard molecules with an average absolute value of the relative error (referred to as “error” in the rest of this manuscript) of 20 % and 12 % respectively. This is consistent with the accuracies reported by Aiken et al. (2008) and confirms that the Aiken-Explicit method can be used for a wide range of OA species.

Figure 1c and d shows Aiken-Ambient results for the laboratory standards. In general the Aiken-Ambient O:C values are biased low for all the standards and observed errors are dependent on the functional groups contained in the different standard molecules. The Aiken-Ambient values for multifunctional standard molecules are biased low by 28 % and those for diacids and alcohols are biased low by 46 %. The error in Aiken-Ambient H:C values for all standards is smaller, but alcohols and diacids are still biased low compared to multifunctional species.

3.2 Measurements of H_2O^+ , CO^+ and CO_2^+ signal intensities with Electron Ionization (EI)

The only difference between the Aiken-Explicit and Aiken-Ambient methods is the measured vs. estimated H_2O^+ and CO^+ ion intensities. Since these ion intensities are estimated based on assumed H_2O^+ and CO^+ ratios to CO_2^+ , we investigate trends in the relative signal intensities of these 3 key ions in the observed standard mass spectra. Figure 2 shows the fractional AMS ion intensities (relative to the total ion signal for each standard) measured for these key thermal decomposition products in the spectra of the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



different laboratory standards. The standards are separated according to functionality, and they are arranged according to increasing molecular O : C. Measurements of the same standard on different instruments are shown as separate bars on the graph. The general agreement between different instruments supports the reproducibility and transferability of the results obtained here to other AMS instruments. The relative intensities of the three ions vary according to specific differences in the decomposition mechanisms including those shown in Reactions (R1) and (R2) above. Spectra from carboxylic acids, esters, polyacids, and multifunctional acids have higher $f_{\text{CO}_2^+}$ (defined as the intensity of CO_2^+ divided by the total ion intensity) and f_{CO^+} than alcohols, indicative of decarboxylation. On the other hand, spectra from alcohols have negligible $f_{\text{CO}_2^+}$ and significant $f_{\text{H}_2\text{O}^+}$, indicative of dehydration (Reaction R2).

Figure 3a shows the f_{CO^+} vs. $f_{\text{CO}_2^+}$ scatter plot for all the standards in this study. For most multifunctional systems, the $f_{\text{CO}^+}/f_{\text{CO}_2^+}$ ratio is relatively consistent with the assumed value of 1 from Aiken et al. (2008). The measured $f_{\text{CO}^+}/f_{\text{CO}_2^+}$ ratios for alcohols and most diacids are ≥ 2 which likely contributes to the additional underestimation in O : C that is observed for these species with the Aiken-Ambient method. These measurements are generally consistent with previous studies that have shown that most laboratory SOA (thought to contain a mixture of multifunctional species) yield $f_{\text{CO}^+}/f_{\text{CO}_2^+}$ values around 1 (Chhabra et al., 2010; Chen et al., 2011) with exceptions of SOA produced by isoprene photooxidation (2.63; Chen et al., 2011) and glyoxal uptake under dark, humid conditions (5.0; Chhabra et al., 2010), both of which contain products that are rich in hydroxyl functional groups but poor in carboxyl groups (Hastings et al., 2005; Lin et al., 2012). Ambient estimates are also in the similar range of 0.9–1.3 (Takegawa et al., 2007; Zhang et al., 2005). The $f_{\text{CO}^+}/f_{\text{CO}_2^+}$ ratios discussed above are summarized in Table 2.

The relationship between $f_{\text{H}_2\text{O}^+}$ and $f_{\text{CO}_2^+}$ for the standard spectra are shown in Fig. 3b and Table 2. The observed signal intensity ratios in the spectra are larger than those calculated from the empirical mass ratios of Aiken et al. (2008). The mea-

**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

5 sured $f_{\text{H}_2\text{O}^+}/f_{\text{CO}_2^+}$ ratio of multifunctional species varies from near 0 to over 2, and many diacids are between 1 and 2 (although some are substantially lower than 1). Polyols and alcohol spectra have even higher ratios, mainly due to their lack of CO_2^+ . As shown in Table 2, similar departures from the assumed $f_{\text{H}_2\text{O}^+}/f_{\text{CO}_2^+}$ ratios were originally observed for chamber SOA by Chen et al. (2011) (0.84–3.91) and more recently by Nakao et al. (2013) (0.33–1.23). We note that in mixed ambient aerosols the $f_{\text{H}_2\text{O}^+}/f_{\text{CO}_2^+}$ ratios would be moderated by the presence of species other than alcohols. However, high values for this ratio (1.0) were also reported for ambient measurements from Whistler mountain (Sun et al., 2009). It is clear from Fig. 3 that the biases in the elemental ratios obtained with the Aiken-Ambient method are due to underestimations of the assumed $f_{\text{H}_2\text{O}^+}/f_{\text{CO}_2^+}$ and $f_{\text{CO}^+}/f_{\text{CO}_2^+}$ values. The H_2O^+ and CO^+ intensities observed for alcohols, in particular, are severely underestimated in the current assumptions since the estimates are tied to CO_2^+ , an ion that is not produced in any significant intensity in spectra of species that do not contain -C(O)OR moieties (e.g. alcohols).

15 In the Aiken-Ambient method the intensities of the OH^+ and O^+ fragments of H_2O^+ are estimated according to the ratios measured for gas-phase H_2O . Figure S3 in the Supplement shows the scatter plots of measured f_{OH^+} vs. $f_{\text{H}_2\text{O}^+}$ and f_{O^+} vs. $f_{\text{H}_2\text{O}^+}$ for all the laboratory standards. The empirical estimate used in the default AMS fragmentation table (Allan et al., 2004) for the $\text{OH}^+/\text{H}_2\text{O}^+$ ratio is very consistent with the observed relative intensities, indicating that the OH^+ ion indeed arises from the fragmentation of molecular water from thermal decomposition of the standards. The consistency in these fragmentation patterns also holds for various chamber SOA (Chen et al., 2011). The $\text{O}^+/\text{H}_2\text{O}^+$ ratio, in contrast, shows substantial scatter, as the dominant source of the O^+ for our standards appears to be fragmentation of CO_2^+ rather than H_2O^+ (Supplement Fig. S3c). Alcohols, which do not produce CO_2^+ , are an exception with $\text{O}^+/\text{H}_2\text{O}^+$ ratios that are much closer to the empirical estimates. Fragmentation of CO_2^+ to yield O^+ ($\text{O}^+/\text{CO}_2^+ \sim 6\%$) is currently not accounted for in the AMS elemental ratio analysis and will contribute to the underestimation observed in AMS O : C values.

3.3 Measurements of H_2O^+ , CO^+ and CO_2^+ with VUV ionization

The H_2O^+ , CO_2^+ , and CO^+ signals observed in the AMS are produced by dehydration and decarboxylation processes that take place before ionization (i.e. on the vaporizer surface or in the gas-phase after evaporation) and/or after 70 eV electron-impact ionization (i.e. fragmentation of thermally excited ions). VUV-AMS measurements were used to examine the production mechanisms of these ions in more detail. VUV-AMS data were obtained for many standards with the AMS vaporizer set to both 200 °C and 600 °C (see Table 1). All experiments were carried out under an argon atmosphere. A VUV-AMS spectrum of glutaric acid is shown in Fig. 4a as an example. This spectrum was observed with the AMS vaporizer at 200 °C and a VUV photon energy of 10.5 eV. Since VUV is a “softer” ionization method than EI, this spectrum would be expected to contain only the glutaric acid molecular ion if thermal decomposition on the vaporizer was negligible. However, even at this lower vaporizer temperature, the molecular ion of glutaric acid (m/z 132) has very low intensity and organic ion fragments corresponding to loss of neutral H_2O , CO , and CO_2 from glutaric acid are observed instead. CO_2^+ , CO^+ , and H_2O^+ are negligible in this spectrum at this VUV photon energy.

Figure 4b shows the CO_2^+ , CO^+ , and H_2O^+ signals observed from glutaric acid as a function of VUV energy. The onsets of CO_2^+ , CO^+ , and H_2O^+ signals are observed to occur at VUV energies that correspond to the ionization energies of neutral H_2O , CO_2 , and CO molecules (12.62 eV, 13.77 eV, and 14.01 eV respectively), rather than the 10.5 eV ionization energies of the observed organic ions. This indicates that these ions are formed by VUV ionization of neutral CO_2 , CO , and H_2O molecules rather than by dissociative ionization of glutaric acid. Neutral CO_2 , CO , and H_2O fragments formed upon photoionization of glutaric acid could further ionize to give rise to these signals. This process requires the absorption of two photons in the ionization region, however, and is therefore unlikely. Instead, the most likely source of the CO_2^+ , CO^+ , and H_2O^+ signals is direct VUV ionization of neutral CO_2 , CO , and H_2O molecules formed from thermal decomposition of organic species on the AMS oven. VUV-AMS measurements

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

of the other organic standards also show a lack of parent ions and fragments corresponding to loss of CO₂, CO, or H₂O moieties, indicating that a wide range of oxidized organic species undergo dehydration and decarboxylation upon heating to temperatures greater than 200 °C.

3.4 Effect of vaporizer temperature on H₂O⁺, CO⁺ and CO₂⁺

Thermal denuder measurements have shown that ambient OA needs to be heated to a minimum temperature of ~ 225 °C for several seconds in order to insure quantitative vaporization of a significant fraction of ambient oxidized OA (Huffman et al., 2009). Supplement Fig. S3 compares the trends in $f_{\text{H}_2\text{O}^+}$, f_{CO^+} and $f_{\text{CO}_2^+}$ observed with the AMS (using EI) at vaporizer temperatures of 600 °C and 200 °C. The total CO₂⁺ / CO⁺ / H₂O⁺ decomposition fragment intensities observed for both temperatures is remarkably similar across the standards. In most cases, $f_{\text{H}_2\text{O}^+}$ is slightly higher at 200 °C compared to 600 °C, while f_{CO^+} follows the opposite trend and $f_{\text{CO}_2^+}$ changes little between the two temperatures. This indicates that dehydration is facile for these acids and alcohols even at 200 °C, which is also consistent with the VUV results shown in Fig. 4. The extent of thermal decomposition observed in the AMS is likely influenced by its specific vaporization conditions (i.e. porous tungsten hot surface and high-vacuum conditions). For example, Lloyd and Johnston (2009) reported that in laser-desorption–electron-ionization analysis of SOA, the signal due to CO₂⁺ was much lower than in AMS spectra of the same aerosol type, and attributed the difference to differences in the vaporization conditions. Our measurements suggest that thermally-induced decomposition could affect the interpretation of organic measurements from other aerosol chemistry measurement techniques that utilize thermal desorption on surfaces, even if temperatures of only 200 °C are reached. Such techniques include aerosol Gas Chromatography–Mass Spectrometry (GC-MS) and thermal-desorption Chemical Ionization mass Spectrometry (CIMS) (e.g. (Lopez-Hilfiker et al., 2014; Williams et al., 2006; Yatavelli and Thornton, 2010; Holzinger et al., 2013). Proton Transfer Reaction–Mass Spectrometry

**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(PTR-MS) measurements of heated ambient filters by Holzinger et al. (2010), for example, show low molecular weight fragments at higher thermal desorption temperatures, consistent with this finding. The specific impact of the surface materials, vaporization temperatures, and pressure conditions on the decomposition reactions of OA should be the focus of future studies.

3.5 Improved-Ambient method

It is clear from Fig. 3 that the relationships among $f_{\text{CO}_2^+}$, $f_{\text{H}_2\text{O}^+}$, and f_{CO^+} are variable and cannot be well prescribed with a single empirical relationship. Furthermore, as discussed in Sects. 3.2 and 3.3, O : C and H : C calculated with the Aiken-Ambient method are biased low because the empirical estimates used in this method often underestimate the intensities of the H_2O^+ and/or CO^+ fragments. Acidic species are observed to be a large source for CO^+ and H_2O^+ fragments while alcohols are a significant source of H_2O^+ fragments.

A correction that is dependent on both acid and alcohol content of the OA is needed to address this composition dependence in the OA fragmentation. Previous AMS measurements have shown that $f_{\text{CO}_2^+}$ can be used as a surrogate for acid content (Duplissy et al., 2011; Takegawa et al., 2007). An AMS surrogate for alcohol moieties has not been identified before, but spectra obtained during this study indicate that f_{CHO^+} (m/z 29) can be used as a surrogate for alcohol content. As shown in Fig. S4, spectra of standard species with no alcohol content have minimal $f_{\text{CHO}^+} < 0.05$ while those with non-zero alcohol content show f_{CHO^+} values ranging from 0.05 to 0.15. High f_{CHO^+} values are found for polyols as well as multifunctional species with non-acid OH groups. Some esters are also observed to yield f_{CHO^+} similar to species with non-acid OH groups. Previous studies have shown that CHO^+ is also an atmospherically significant ion and a key oxygen-containing ion in many types of ambient and chamber aerosol (Ng et al., 2010a). The $f_{29}(f_{\text{CHO}^+})$ fragment has also been used to monitor photooxidation of glyoxal and related species in the aqueous phase (Lee et al., 2011).

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

H₂O in aerosol samples such as aerosol water or dehydration of inorganic acids (Kroll et al., 2011).

The corrected elemental analysis values will have implications for the interpretation of Van Krevelen diagrams (i.e. plots of H : C vs. O : C), which have been used to obtain insights into the chemical transformations of ambient OA. Heald et al. (2010) first showed the utility of this diagram for bulk total OA (including POA and SOA) composition analysis, and demonstrated that for some datasets bulk ambient OA evolved with a slope of -1 , suggesting composition changes with aging that are consistent with simultaneous increases in both carbonyl and alcohol moieties. Ng et al. (2011) used the Van Krevelen diagram to follow the oxidative transformations of ambient OOA (as opposed to total OA) from multiple field campaigns and showed that they clustered along a slope of approximately -0.5 . This slope was interpreted as being indicative of simple oxidative mechanisms that involve net additions of both C(O)OH and -OH / -OOH functional groups without fragmentation (i.e. C-C bond cleavage), and/or the addition of C(O)OH groups with fragmentation. The Improved-Ambient method yields Van Krevelen slopes that are approximately 20 % shallower than those determined with the Aiken-Ambient method. Details are discussed in Chen et al. (2014). These slopes (-0.8 for total OA, and -0.4 for OOA) suggest that the ambient OA oxidative mechanisms involve different net addition of -OH and/or -OOH functionalities and fragmentation than previously assumed.

3.8 Effect of Improved-Ambient method on empirical parameterizations of OA elemental ratios from unit mass resolution data

Empirical methods relating unit mass resolution (UMR) AMS ion tracers with Ambient-Aiken elemental ratios obtained from high-resolution AMS data have been previously reported by Aiken et al. (2008) and Ng et al. (2011). Here we reassess these relationships for elemental ratios calculated with the Improved-Ambient method.

Aiken et al. (2008) presented a parameterization to estimate O : C from measured f_{44} values. High-resolution AMS measurements indicate that the UMR signal at m/z 44 is

Figure 8b compares the parameterization from Eq. (12) with the measured Improved-Ambient H : C values. The figure indicates that as in Ng et al. (2011), the measured H : C values for secondary OA components, secondary chamber OA, and several standard molecules are reproduced to within $\pm 10\%$ by Eq. (12).

4 Conclusions

This manuscript evaluates the accuracy of the AMS elemental analysis approach over a wider range of OA species than has been studied before. Thermally-induced dehydration and/or decarboxylation of OA species is observed to be efficient in the AMS not only at the standard vaporizer temperature of 600°C but also at much lower vaporizer temperature (even 200°C , the lowest feasible vaporization temperature). These processes likely also play a role in other heated surface vaporization-based aerosol measurement techniques even if they limit heating to $\sim 200^\circ\text{C}$. The H_2O , CO , and CO_2 molecules produced by these decomposition processes must be taken into account in order to obtain accurate elemental composition information.

The accuracy of elemental ratios obtained with the AMS depends on the exact method that is used. The Aiken-Explicit method reproduces known O : C and H : C ratios to within 20 % and 12 % respectively. These results validate the use of this methodology for calculating elemental ratios across a range of OA molecular compositions. This method is recommended for laboratory experiments and smog-chamber measurements as well as ambient measurements when sufficient signal is available (e.g. at very polluted sites). Careful control of the sampling conditions and/or calibration experiments that enable unambiguous extraction of the organic signal contributions to measured H_2O^+ and CO^+ ion intensities are recommended for these situations (see for example Chen et al., 2011). The Aiken-Ambient method (used for most measurements of aerosols obtained in air) produces O : C (H : C) ratios for multifunctional species that are within 28 % (14 %) of known ratios respectively. These values are biased low, however, with larger biases observed for some highly functionalized species (e.g., polyols

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Evaluation of
elemental ratios
measured by aerosol
mass spectrometry

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Table 1. A list of standards analyzed in this study and their molecular O : C and H : C ratios. Standards are categorized according to their functionality into broad groups. All standards were studied with EI AMS, while standards also studied with VUV-AMS are noted in the last column.

	Name	Formula	O : C	H : C	VUV-AMS
Multifunctional	<i>Cis</i> -Pinonic Acid	C ₁₀ H ₁₄ O ₃	0.3	1.4	X
	2-Oxooctanoic Acid	C ₈ H ₁₄ O ₃	0.37	1.75	
	Acetylsalicylic Acid	C ₉ H ₈ O ₄	0.44	0.89	X
	Homovanillic Acid	C ₉ H ₁₀ O ₄	0.44	1.11	X
	4-Acetylbutyric Acid	C ₆ H ₁₀ O ₃	0.5	1.67	
	5-Oxoazaleic Acid	C ₉ H ₁₄ O ₅	0.55	1.56	X
	Levulinic Acid	C ₅ H ₈ O ₃	0.6	1.6	
	Gamma Ketopimelic Acid	C ₇ H ₁₀ O ₅	0.71	1.43	X
	3-Hydroxybutyric Acid	C ₄ H ₆ O ₃	0.75	2	
	2-Ketobutyric Acid	C ₄ H ₆ O ₃	0.75	1.5	
	3-Hydroxy-3-Methylglutaric Acid	C ₆ H ₁₀ O ₅	0.83	1.67	
	1,3-Acetonedicarboxylic Acid	C ₅ H ₆ O ₅	1	1.2	
	α -Ketoglutaric Acid	C ₅ H ₆ O ₅	1	1.2	X
	Lactic Acid	C ₃ H ₆ O ₃	1	1.67	
	Pyruvic Acid	C ₃ H ₄ O ₃	1	1.33	
	Citric Acid	C ₆ H ₈ O ₇	1.16	1.33	X
	Diglycolic Acid	C ₄ H ₆ O ₅	1.25	1.5	
	Malic Acid	C ₄ H ₆ O ₅	1.25	1.5	X
	Oxaloacetic Acid	C ₄ H ₄ O ₅	1.25	1	
	Glycolic Acid	C ₂ H ₄ O ₃	1.5	2	
	Tartaric Acid	C ₄ H ₆ O ₆	1.5	1.5	X
Alcohols	<i>Cis</i> -3-methyl-3,4-dihydroxytetrahydrofuran	C ₅ H ₁₀ O ₃	0.6	2	
	Racemic mixture of ?-Isoprene Epoxydiols	C ₅ H ₁₀ O ₃	0.6	2	
	<i>Trans</i> -3-methyl-3,4-dihydroxytetrahydrofuran	C ₅ H ₁₀ O ₃	0.6	2	
	Mannitol	C ₆ H ₁₄ O ₆	1	2.33	
	Mannose	C ₆ H ₁₂ O ₆	1	2	X
	Sucrose	C ₁₁ H ₂₂ O ₁₁	1	2.09	X
	Xylitol	C ₅ H ₁₂ O ₅	1	2.4	X
	Diacids	Sebacic Acid	C ₁₈ H ₁₆ O ₄	0.4	1.8
Azalaic Acid		C ₉ H ₁₆ O ₄	0.44	1.78	
Pimelic Acid		C ₇ H ₁₂ O ₄	0.57	1.71	X
Adipic Acid		C ₆ H ₁₀ O ₄	0.66	1.67	X
Glutaric Acid		C ₅ H ₈ O ₄	0.8	1.6	X
Malaic Acid		C ₄ H ₄ O ₄	1	1	X
Succinic Acid		C ₄ H ₆ O ₄	1	1.5	X
Malonic Acid		C ₃ H ₄ O ₄	1.33	1.33	X
Oxalic Acid		C ₂ H ₂ O ₄	2	1	
Polyacids		1,3,5-Cyclohexanetricarboxylic Acid	C ₆ H ₉ O ₆	1	1.5
	Tricarballic Acid	C ₆ H ₆ O ₆	1	1.33	X
	1,2,4,5-Benzenetetracarboxylic Acid	C ₆ H ₆ O ₆	1.33	1	X
Esters	Dibutyl Oxalate	C ₈ H ₁₈ O ₄	0.5	2.25	
	Gamma Ketopimelic Acid Dilactone	C ₆ H ₈ O ₄	0.57	1.14	X
	Ethyl Pyruvate	C ₅ H ₈ O ₃	0.6	1.6	
	Dimethyl 1,3-Acetonedicarboxylate	C ₇ H ₁₀ O ₅	0.71	1.43	

Table 2. Summary of fragment ion ratios observed for standard molecules, chamber SOA, and ambient SOA. The entry * denotes the use of default assumptions for the ratio.

	Obs H ₂ O ⁺ / CO ₂ ⁺	Obs CO ⁺ / CO ₂ ⁺	Frag Wave H ₂ O ⁺ / CO ₂ ⁺ RIE H ₂ O = 1.4	Frag Wave H ₂ O ⁺ / CO ₂ ⁺ RIE H ₂ O = 2	Literature reference
AMS Frag Table					
Default Assumptions	0.32	1	0.32	0.225	Aiken et al. (2008)
OA Standards					
Multifunctional	0.5–1.5	1–2	0.5–1.5	0.35–1.05	This study
Polyacids	1	1–2	1	0.7	
Diacids	2	2	2	1.4	
Esters	0.5–1	1	0.5–1	0.35–0.7	
Alcohols	> 10	> 4	> 10	> 7	
Ambient Aerosol					
Pittsburgh, USA	*	1.3	*	*	Zhang et al. (2005)
Tokyo, Japan	*	1	*	*	Takegawa et al. (2007)
Whistler Mtn, Canada	1	*	1	0.7	Sun et al. (2009)
Chamber SOA					
Isoprene Photooxidation (Low NO _x)	3.9	1.03–2.6	3.9	2.7	Chhabra et al. (2010), Chen et al. (2011)
Isoprene Photooxidation (NO _x)	0.3	*	0.3	0.2	Nakao et al. (2013)
α-pinene + O ₃	0.8–1	1–1.1	0.8–1	0.6–0.7	Chhabra et al. (2010), Chen et al. (2011), Nakao et al. (2013)
β-caryophyllene + O ₃	0.7–1.3	1.2	0.7–1.3	0.5–0.9	Chen et al. (2011), Nakao et al. (2013)
Toluene Photooxidation (NO _x)	1.8	1	1.8	1.3	Hildebrandt et al. (2014)
Aromatics Photooxidation (NO _x , Low NO _x)	0.3–1.3	*	0.3–1.3	0.2–0.9	Nakao et al. (2013)
Naphthalene Photooxidation (Low NO _x)	*	1.2	*	*	Chhabra et al. (2011)

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 3. Summary of elemental composition information obtained for chamber and ambient OA.

	Improved-Ambient				Change (with respect to Aiken-Ambient)				Literature reference
	O:C	H:C	OM:OC	Osc	O:C (%)	H:C (%)	OM:OC (%)	OSc (Absolute)	
Ambient OA									See Supplement Table S1 for full list
Total OA	0.52	1.65	1.84	-0.60	27	11	9	0.06	
Primary Components									
HOA	0.13	1.96	1.34	-1.69	27	8	4	-0.09	
BBOA	0.36	1.76	1.64	-1.04	34	11	9	0.01	
COA	0.22	1.81	1.45	-1.37	32	11	6	-0.06	
Secondary Components									
SV-OOA	0.53	1.62	1.84	-0.57	32	12	11	0.07	
LV-OOA	0.84	1.43	2.25	0.25	25	12	12	0.19	
Total OOA	0.67	1.54	2.03	-0.19	28	12	11	0.13	
Chamber SOA									
Isoprene	0.87	1.94	2.33	-0.19	57	23	24	0.27	Chen et al. (2011)
α -pinene	0.41	1.48	1.67	-0.65	24	9	7	0.04	Chen et al. (2011)
β -caryophyllene	0.47	1.52	1.75	-0.58	29	11	10	0.06	Chen et al. (2011)
Toluene	0.85	1.67	2.28	0.10	50	25	22	0.30	Hildebrandt Ruiz et al. (2014)

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

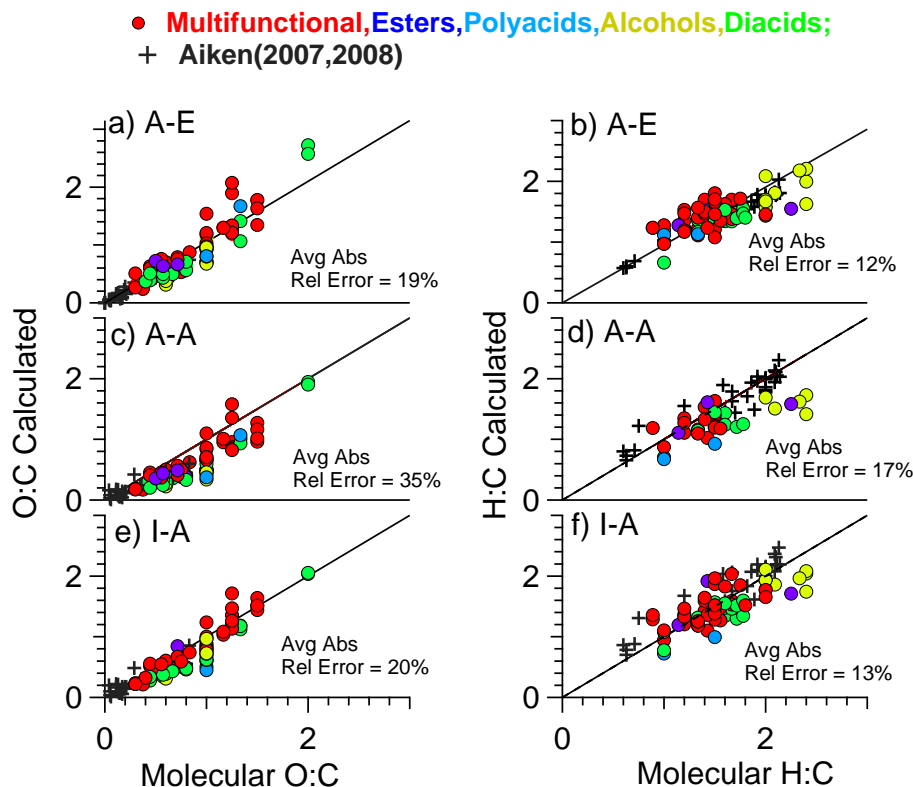


Figure 1. Scatter plots between known molecular elemental ratios and AMS elemental ratios obtained with the Aiken-Explicit (A-E; panels **a** and **b**), Aiken-Ambient (A-A; panels **c** and **d**), and Improved-Ambient methods (I-A; panels **e** and **f**). A 1 : 1 line is shown for reference in all plots. The standards examined in this study are colored according to their chemical functionality. Also shown are previously published standard molecule data from Aiken et al. (2007).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

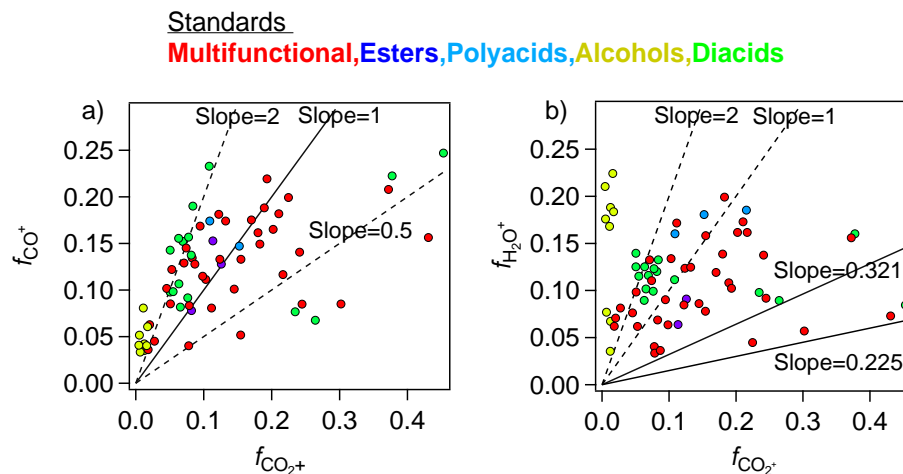


Figure 3. Scatter plots between AMS fractional ion intensities for CO⁺ and CO₂⁺ (panel **a**) and H₂O⁺ and CO₂⁺ (panel **b**). The empirical ratios used for each of these relationships in the Aiken-Ambient calculations are shown as solid lines with the appropriate slopes. In panel (**b**) two solid lines are shown to reflect the measured ratios that correspond to possible H₂O RIE values ranging from 1.4 to 2 (see Sect. 2 for more information). Dashed lines on both panels are included for reference to visualize the range of slope values.

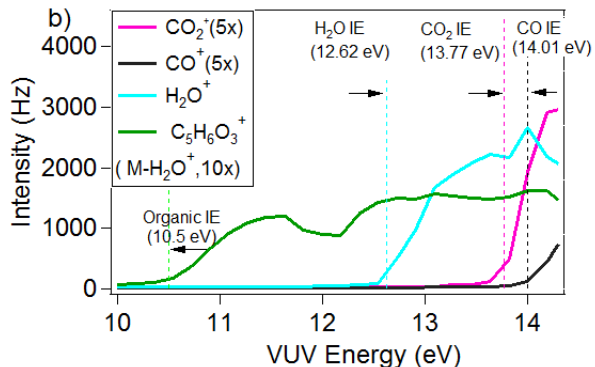
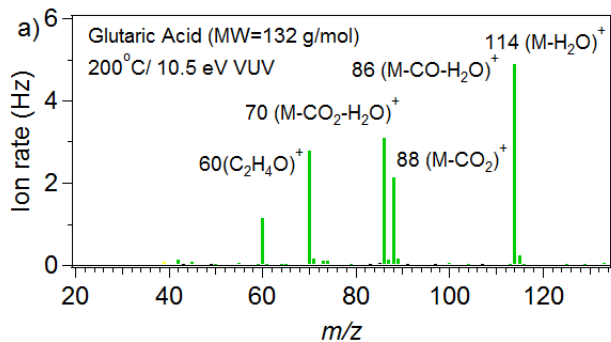


Figure 4. (a) VUV-AMS spectrum of glutaric acid obtained under an argon atmosphere. The spectrum was obtained at a VUV energy of 10.5 eV and a vaporizer temperature of 200 °C. Ions corresponding to loss of CO₂, CO, and H₂O moieties from the parent ion (M⁺) are observed. (b) Glutaric acid VUV-AMS signals as a function of VUV monochromatic photon energy. The signal intensity of C₅H₆O₃⁺ which corresponds to the [M-H₂O]⁺ ion, and the signal intensities of CO₂⁺, CO⁺, H₂O⁺ are shown. The gas phase ionization energies (IE) for neutral CO₂, CO, and H₂O molecules are shown as colored vertical lines.

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

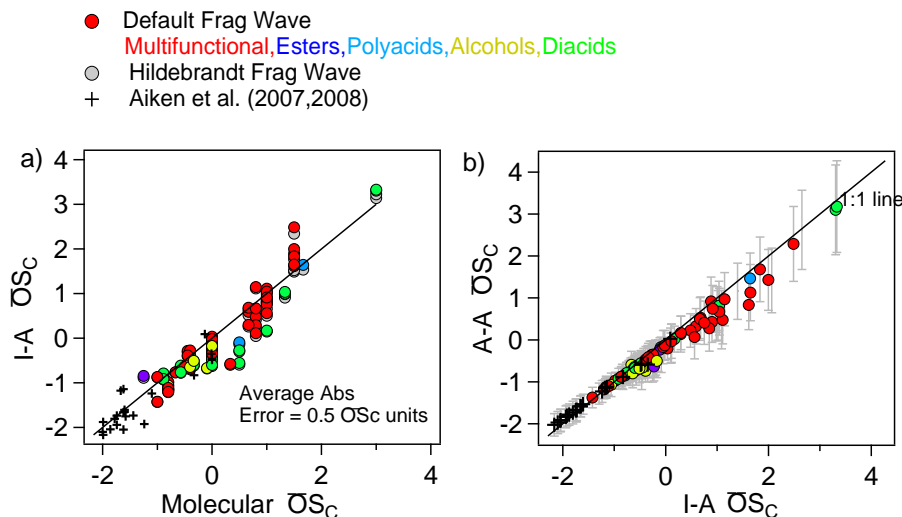


Figure 5. (a) Scatter plot of Improved-Ambient \overline{OS}_C values ($2 \times O:C - H:C$) of the organic standards vs. their known molecular \overline{OS}_C values. The Improved-Ambient method was applied with the default AMS organic fragmentation wave (colored solid circles) as well as with the Hildebrandt et al. (2014) changes to the organic fragmentation wave. (b) Scatter plot of Aiken-Ambient \overline{OS}_C values of the organic standards vs. the corresponding Improved-Ambient method values. The error bars denote the propagated uncertainty in the Aiken-Ambient \overline{OS}_C values due to the uncertainties in the Aiken-Ambient O:C and H:C values. The solid line shows the 1:1 relationship.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

**Evaluation of
elemental ratios
measured by aerosol
mass spectrometry**

M. R. Canagaratna et al.

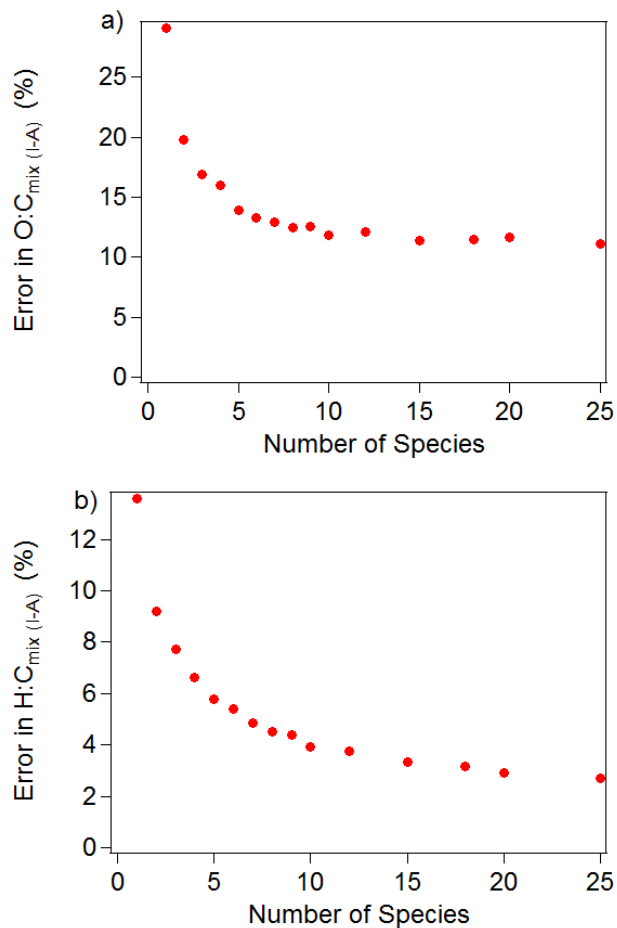


Figure 6. (a) Errors in Improved-Ambient O : C ratio of organic standard molecule mixtures as a function of number of species in the mixture. (b) Errors in Improved-Ambient H : C ratio of the organic standard molecule mixtures as a function of number of species in the mixture.

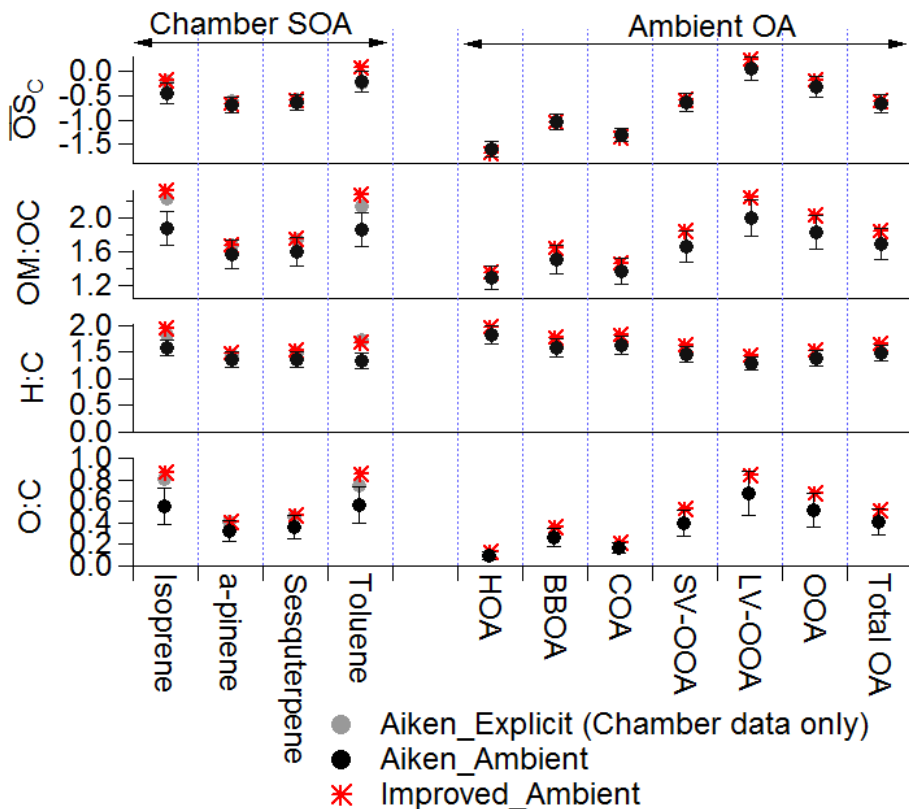


Figure 7. Summary of elemental composition information obtained across chamber and ambient OA measurements. The figure shows values obtained with the Improved-Ambient method as well as the Aiken-Ambient method. Aiken-Ambient elemental ratios are shown with errors from Aiken et al. (2007, 2008) for reference. For the chamber data, Aiken-Explicit values measured by Chen et al. (2011) and Hildebrandt Ruiz et al. (2014) are also shown.

Evaluation of elemental ratios measured by aerosol mass spectrometry

M. R. Canagaratna et al.

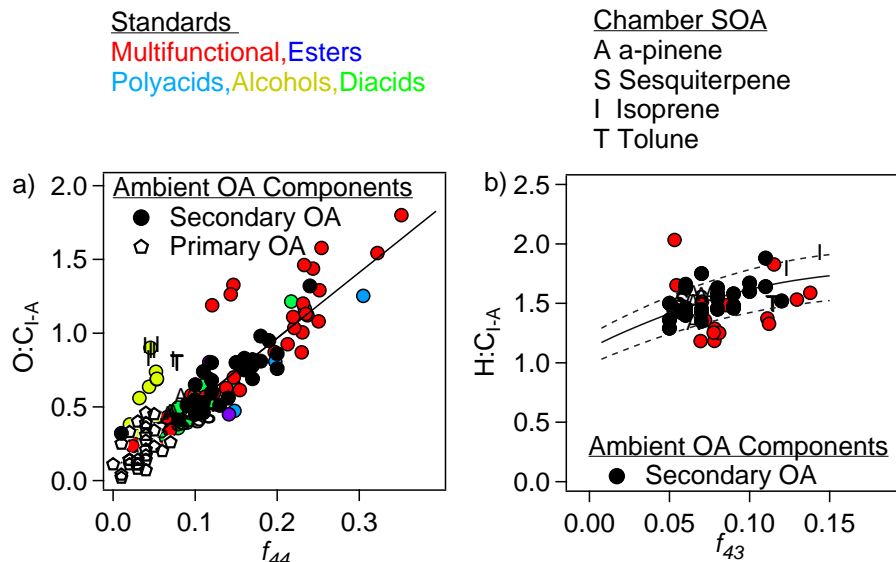


Figure 8. Scatter plot between Improved-Ambient O:C values and f_{44} (fractional ion intensity at m/z 44 from unit mass resolution data). Ambient OA component data from field campaigns are shown as black points. The black line shows the linear fit through the ambient OA ($O:C_{I-A} = 0.079 + 4.31 \cdot f_{44}$). Chamber SOA and standard OA data are also shown in the figure. **(b)** Scatter plot between Improved-Ambient H:C values and f_{43} for ambient secondary OA components and chamber SOA. OA standard data is shown for the few multifunctional species which fit the criteria for this parameterization ($f_{44} > 0.05$ and $f_{43} > 0.04$). The solid line shows a scaled version of the Ng et al. parameterization ($H:C_{\text{Improved Ambient}} = 1.12 + 6.74 \cdot f_{43} + 17.77 \cdot f_{43}^2$) and the dotted lines show $\pm 10\%$ deviations from the parameterization.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	