

# Elemental Analysis of Organic Species with Electron Ionization High-Resolution Mass Spectrometry

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We present a new elemental analysis (EA) technique for organic species (CHNO) that allows fast on-line analysis (10 s) and reduces the required sample size to ~1 ng, ~6 orders of magnitude less than standard techniques. The composition of the analyzed samples is approximated by the average elemental composition of the ions from high-resolution electron ionization (EI) mass spectra. EA of organic species can be performed on organic/inorganic mixtures. Elemental ratios for the total organic mass, such as oxygen/carbon (O/C), hydrogen/carbon (H/C), and nitrogen/carbon (N/C), in addition to the organic mass to organic carbon ratio (OM/OC), can be determined. As deviations between the molecular and the ionic composition can appear due to chemical influences on the ion fragmentation processes, the method was evaluated and calibrated using spectra from 20 compounds from the NIST database and from 35 laboratory standards sampled with the high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). The analysis of AMS (NIST) spectra indicates that quantification of O/C is possible with an error (average absolute value of the relative error) of 30% (17%) for individual species. Precision is much better than accuracy at  $\pm 5\%$  in the absence of air for AMS data. AMS OM/OC has an average error of 5%. Additional calibration is recommended for types of species very different from those analyzed here. EA was applied to organic mixtures and ambient aerosols (sampled at 20 s from aircraft). The technique is also applicable to other EI-HRMS measurements such as direct injection MS.

Elemental analysis (EA) of complex organic mixtures (C, H, N, O) is of interest in many fields such as environmental and food chemistry. Traditional EA generally requires a few milligrams of sample and ~10 min per sample analysis. Thermal methods are the most common type of EA for CHN analysis, which decompose the sample using high-temperature oxidation followed by thermal

conductivity detection.<sup>1</sup> Oxygen content must be measured separately using pyrolysis and reduction of the sample,<sup>1</sup> adding additional instrument reconfiguration and analysis time. For organic/inorganic mixtures, either the sample needs to be subjected to some type of separation (which could introduce biases), inorganic species need to be analyzed separately for every sample, or the results obtained will average both types of species. As these techniques were designed for off-line analysis, time resolution was not a concern.

Due to the limitations of existing organic EA techniques, the development of new techniques that require much smaller samples and provide much faster analysis is of great interest in, for example, environmental analyses. One potential method is to use the elemental composition of the ions formed from electron ionization (EI) high-resolution mass spectrometry (HRMS), which is very fast and sensitive, to approximate the composition of the molecules analyzed. This potential technique has not been explored to our knowledge, which may be due to the lack of widespread availability of HRMS instruments until recently and also to the perception of widespread chemical biases in the fragmentation process.<sup>2,3</sup> After a molecule is ionized into a positive ion, it may undergo one or several fragmentation reactions, each producing an ion and a neutral fragment. Various chemical properties such as ionization potential, ion and neutral stability, etc., as well as kinetic effects influence the pathways of fragmentation reactions,<sup>2</sup> which could lead to biases between the molecular and the ion elemental compositions, e.g., if electronegative groups preferentially become the neutral fragment rather than a positive ion during fragmentation.

Organic aerosols are one type of environmental sample that is currently receiving considerable attention from the scientific community. Aerosols are responsible for important effects on climate, health, and visibility,<sup>4</sup> and organic species comprise a large fraction of the mass at most locations.<sup>5</sup> They are an example of a complex organic mixture found in the environment for which

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standard chemical analysis techniques such as GC/MS can only identify a small fraction (~10%) of the total species present.<sup>6</sup> The aerosol mass spectrometer (AMS) has become a “de facto” standard for studying ambient aerosol size-resolved composition due to its ability to quantitatively characterize submicrometer nonrefractory particles with high sensitivity and time and size resolution.<sup>7–9</sup> AMS spectra of standards have been shown to be similar to those from EI databases, albeit with more fragmentation.<sup>10,11</sup> The most notable difference is the greatly enhanced intensity of the CO<sub>2</sub><sup>+</sup> ion for species such as carboxylic acids in the AMS, likely due to pyrolysis occurring on the vaporizer.<sup>10</sup> With the recently developed high-resolution time-of-flight AMS (HR-ToF-AMS),<sup>12</sup> elemental composition of organic ions can be directly determined, especially for the lower  $m/z$  (<100) where most of the signal appears for the AMS.

EA of the total organic aerosol is of great interest but is difficult to perform with traditional CHNO instrumentation due to the large sample size needed, which limits time resolution to several hours. It would require filtering 1000–10 000 m<sup>3</sup> of air per sample at typical ambient particle concentrations, in addition to the potential for gas adsorption or particle evaporation artifacts when collecting samples on a filter for offline analysis using traditional techniques.<sup>13</sup> Some recent mass spectrometric instruments have demonstrated EA of individual particles by ablating the particles into atomic ions.<sup>14–16</sup>

This paper describes the first application of electron ionization high-resolution mass spectrometry (EI-HRMS) to EA of organic molecules (rather than just individual ions) to our knowledge. Using EI mass spectra of small molecules from the NIST database, we demonstrate that it is possible to determine atomic ratios for O/C, H/C, and N/C, as well as the ratio for total organic mass to organic carbon mass (OM/OC). The EA method is further validated and characterized with pure-component aerosol standards and their mixtures sampled with the HR-ToF-AMS. We then apply the method to ambient aerosols as sampled from aircraft to highlight its advantages of high precision, high time resolution, and small sample size for EA.

## METHODS

**Elemental Analysis Procedure.** It is a property of EI for molecules containing small atoms such as C, H, N, O, and S that the sum of the ion signal intensities from all fragments is approximately proportional to the mass concentration of the original species.<sup>8,17,18</sup> This dependence arises because of the roughly linear increase of the electron ionization cross section with the number of electrons in the molecule, combined with the proportionality between the number of electrons and molar mass (MM) for molecules with the small atoms mentioned above.<sup>8</sup> The proportionality constant can change for various groups of molecules such as sulfate or oxygenated organics, but these changes are smaller than a factor of 2 and can be calibrated.<sup>8</sup> Thus, species can be directly quantified from the measured ion currents, a result that has been verified through multiple intercomparisons with quantitative instruments operating based on other principles.<sup>8,9,19</sup>

If the elemental composition of each fragment ion signal in a mass spectrum can be identified (as with HRMS), the average composition of the ions can be calculated. Since the ion current produced by EI is approximately proportional to the total molecular mass present, the same ion current at different  $m/z$ 's represents the same original mass. For example, if there is 1-kHz signal at both  $m/z$  60 and 300, each being the molecular ion from one of two species, approximately the same mass of both species was present in the ionization region. Therefore, 5 times more molecules of the lighter molecule must have been present. The average elemental composition in that case would be the weighed average of the composition of the two observed ions, with each ion carrying the same weight (since their ion currents are the same). For a complex spectrum from an unknown molecule or mixture, the best approximation for the elemental composition of the original species that each ion represents is the composition of that ion. The best estimate of the molecular or mixture composition can then be found by summing the ion contributions across the whole mass spectrum. For an organic spectrum, the relative mass concentrations of C and O ( $M_C$  and  $M_O$ , respectively) can be estimated as

$$M_C = \sum_{j=m/z_{\min}}^{m/z_{\max}} I_j F_C$$

$$M_O = \sum_{j=m/z_{\min}}^{m/z_{\max}} I_j F_O \quad (1)$$

where  $I_j$  is the ion current at the  $j$ th peak in the spectrum (corrected for any  $m/z$  dependences of the mass spectrometer or detector) and  $F_C$  and  $F_O$  are the mass fractions of C and O in each ion (e.g.,  $F_C = 12/29$  and  $F_O = 16/29$  for CHO<sup>+</sup>. Note that average elemental masses should be used, but integer masses are shown here for simplicity). The O/C mass ratio can then be calculated as  $M_O/M_C$ . Isotopic peaks (e.g., ions with <sup>13</sup>C) need to be included in the calculations. Hereinafter, we will only present O/C atomic ratios, calculated as  $(M_O/16)/(M_C/12)$ , as these are

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**Table 1. List of Pure Compounds Sampled with the HR-ToF-AMS Grouped by Organic Category<sup>a</sup>**

no.	class	subclass	compound	MM	formula	
1	hydrocarbon	alkane	hexadecane	226.27	C <sub>16</sub> H <sub>34</sub>	
2		PAH	fluoranthene	202.08	C <sub>16</sub> H <sub>10</sub>	
3		PAH	pyrene	202.08	C <sub>16</sub> H <sub>10</sub>	
4		PAH	benzo[e]pyrene	252.09	C <sub>20</sub> H <sub>12</sub>	
5	alcohol	alkanol	1-octadecanol	270.29	C <sub>18</sub> H <sub>38</sub> O	
6		alkanol	1-icosanol	298.32	C <sub>20</sub> H <sub>42</sub> O	
7		alkanol	1-docosanol	326.35	C <sub>22</sub> H <sub>46</sub> O	
8		dialkanol	1,2-tetradecanediol	230.22	C <sub>14</sub> H <sub>30</sub> O <sub>2</sub>	
9	carboxylic acid	phenol	pyrogallol	126.03	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	
10		sterol	cholesterol	386.35	C <sub>27</sub> H <sub>46</sub> O	
11		alkanoic acid	decanoic acid	172.15	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	
12		alkanoic acid	pentadecanoic acid	242.22	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	
13		alkanoic acid	hexadecanoic acid	256.24	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	
14		alkanoic acid	stearic acid	284.27	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	
15		alkenoic acid	oleic acid	282.26	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	
16		dicarboxylic acid	glutaric acid	132.04	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	
17		dicarboxylic acid	adipic acid	146.06	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	
18		dicarboxylic acid	undecanedioic acid	216.14	C <sub>11</sub> H <sub>20</sub> O <sub>4</sub>	
19		hydroxy-carboxylic acid	15-hydroxypentadecanoic acid	258.22	C <sub>15</sub> H <sub>30</sub> O <sub>3</sub>	
20		hydroxy-carboxylic acid	16-hydroxyhexadecanoic acid	272.24	C <sub>16</sub> H <sub>32</sub> O <sub>3</sub>	
21		aldehyde	alkanal	nonyl aldehyde	142.14	C <sub>9</sub> H <sub>18</sub> O
22			phthalate	dioctyl phthalate	390.28	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>
23	ester	alkanoate	dioctyl sebacate	426.37	C <sub>26</sub> H <sub>50</sub> O <sub>4</sub>	
24		peroxide	alkyl peroxide	lauroyl peroxide	398.34	C <sub>24</sub> H <sub>46</sub> O <sub>4</sub>
25	anhydride	benzyl peroxide	benzoyl peroxide	242.06	C <sub>14</sub> H <sub>10</sub> O <sub>4</sub>	
26		alkyl anhydride	heptanoic acid, anhydride	242.19	C <sub>14</sub> H <sub>26</sub> O <sub>3</sub>	
27		cyclic anhydride	glutaric anhydride	114.03	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	
28	carbohydrate	monosaccharide	levoglucosan	162.05	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	
29		amine	amino acid	4-aminobenzoic acid	137.05	C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>
30	amide	amino anhydride	<i>N</i> -methylisatioc anhydride	177.04	C <sub>9</sub> H <sub>7</sub> NO <sub>3</sub>	
31		alkaloid	quinine	324.18	C <sub>20</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub>	
32		alkyl amide	bis-acrylamide	154.07	C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	
33	organic nitrite	phenyl nitrite	3-methyl-4-nitrophenol	153.04	C <sub>7</sub> H <sub>7</sub> NO <sub>3</sub>	
34		pyridine	<i>trans</i> -1,2-bis(4-pyridyl) ethylene	182.08	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub>	
35		cyclic acid	nicotinic acid (niacin)	123.03	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	

<sup>a</sup> General organic class and subclass are included for each compound along with MM (g/mol) and molecular formula.

more meaningful than mass ratios to characterize the chemical properties (e.g., functionality) of a molecule or mixture. The measured “raw” ratios are converted to estimated ratios by using a calibration factor ( $\alpha_{O/C}$ ) determined below with laboratory standards, for example, for the O/C ratio:

$$O/C_{\text{measured}} = \alpha_{O/C} \times O/C_{\text{raw}} \quad (2)$$

The same procedure is applied to estimate the H/C and N/C ratios.

**EA Method Validation with Spectra from the NIST EI Database.** Ideally, one could use existing high-resolution EI spectra to evaluate the EA method proposed here, but currently no high-resolution EI spectra databases are available to our knowledge. Data from unit mass resolution (UMR) EI databases can be used to test the method, but only for molecules in which the elemental composition of all ions contributing appreciably to the total signal can be unambiguously determined from the ion mass and the molecular composition (i.e., only one combination of the atoms present in the molecule can produce each ion fragment). This requirement limits the technique to small molecules ( $16 \leq \text{MM} \leq 90$  in our case) for UMR data. Spectra for 20 individual compounds were obtained from the NIST Standard Reference Database 1A, version 2.0, 1998, (NIST/EPA/NIH Mass Spectral Library), which contains UMR spectra with complete mass and intensity data. The complete mass spectra included in the database were used. Multiple replicate spectra (from different instruments/contributing groups) were used for a total of 58 spectra sampled with  $\sim 3$  spectra per compound.

**EA Method Validation with HR-ToF-AMS Data.** The HR-ToF-AMS has been described in detail elsewhere,<sup>12</sup> so only a brief description follows. Particles are sampled into a differentially pumped vacuum chamber through an aerodynamic focusing lens inlet, sized by measuring particle time-of-flight under vacuum, and compositionally analyzed by thermal desorption under high vacuum followed by EI and time-of-flight mass spectrometry. The HR-ToF-AMS differs from the original quadrupole-based AMS<sup>7,8</sup> in that the quadrupole mass spectrometer has been replaced with a custom TOFMS (H-TOF series, ToFwerk, Thun, Switzerland) with two reflectron configurations, known as V- and W-mode. All laboratory data presented here were acquired using the W-mode configuration as the longer flight path, enabled by two passes through a reflectron and one hard mirror, yields the highest mass resolution for this TOFMS,<sup>12</sup> facilitating the determination of ion composition and the correct assignment of ion signals. The data acquisition software used was ToF-AMS DAQ v 1.7.2B.<sup>20</sup> Data were analyzed in Igor Pro 5.0 (Wavemetrics, Lake Oswego, OR) using the standard ToF-AMS data analysis program (SQUIRREL),<sup>21</sup> with additional custom Igor software for extracting ion intensities from HR-ToF-AMS spectra<sup>12</sup> and for performing the EA calculations.

**Laboratory Experiments with the HR-ToF-AMS.** Laboratory experiments were conducted using the HR-ToF-AMS on 35 organic compounds. Mass spectra were acquired from  $m/z$  11 to

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**Table 2. EI Oxalic Acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>; MM 89.995 g/mol) Spectrum from the NIST Database (Main Library) As Processed by the EA-HRMS Method<sup>a</sup>**

<i>m/z</i>	frag ID	A (%)	no. of C's	no. of H's	#no. of O's	C signal	H signal	O signal
12	C	20	1	0	0	20.00	0.00	0.00
16	O	30	0	0	1	0.00	0.00	30.00
17	OH	100	0	1	1	0.00	5.88	94.12
18	H <sub>2</sub> O	210	0	2	1	0.00	23.33	186.67
28	CO	610	1	0	1	261.43	0.00	348.57
29	CHO	320	1	1	1	132.41	11.03	176.55
44	CO <sub>2</sub>	280	1	0	2	76.36	0.00	203.64
45	CHO <sub>2</sub>	999	1	1	2	266.40	22.20	710.40
46	CH <sub>2</sub> O <sub>2</sub>	800	1	2	2	208.70	34.78	556.52
47	<sup>13</sup> CH <sub>2</sub> O <sub>2</sub>	20	1	3	2	5.11	0.85	13.62
56	C <sub>2</sub> O <sub>2</sub>	50	2	0	2	21.43	0.00	28.57
72	C <sub>2</sub> O <sub>3</sub>	10	2	0	3	3.33	0.00	6.67
90	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	20	2	2	4	5.33	0.44	14.22
total signal						1000.50	98.53	2369.54
EA mass ratio						1.00	0.10	2.37
EA mass (%)						28.84	2.84	68.31
EA atomic ratio						1.00	1.18	1.78
nominal ratio						1.00	1.00	2.00

<sup>a</sup> Signal is apportioned to each element at each fragment within the mass spectrum and then summed for the whole spectrum. The ARs can be estimated from the ratios of the summed elemental signals. The nominal O/C and H/C for oxalic acid are 2 and 1, respectively.

**Table 3. List of 20 Compounds Analyzed by EA from the NIST Database Grouped by Organic Classification, Including Molecular Formulas, MM (g/mol), Nominal and Calculated ARs (O/C, H/C, N/C) with One Standard Deviation ( $\sigma$ ) from All Replicates**

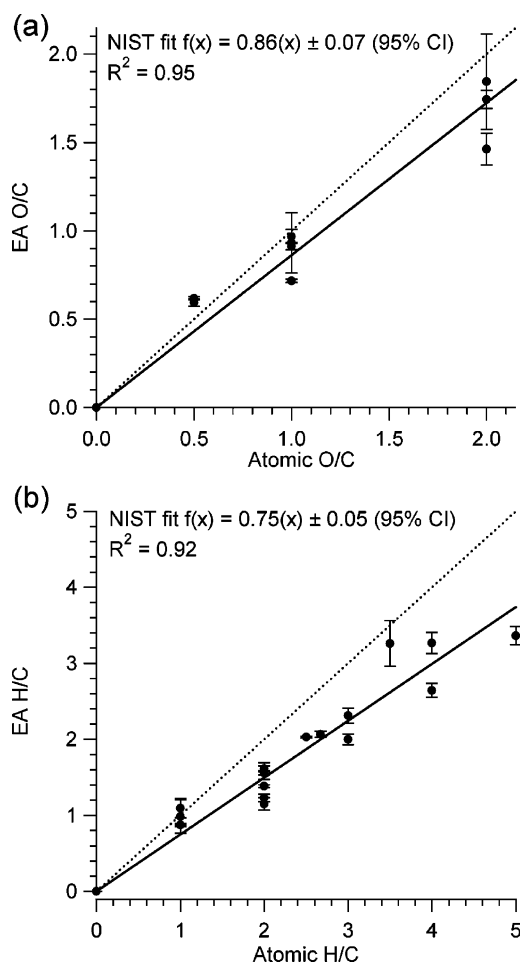
no.	compound	class	formula	MM	O/C	O/C <sub>EA</sub> ± $\sigma$	H/C	H/C <sub>EA</sub> ± $\sigma$	N/C	N/C <sub>EA</sub> ± $\sigma$
1	methanol	alcohol	CH <sub>3</sub> OH	32.03	1	0.93 ± 0.17	4	2.64 ± 0.09		
2	ethanol	alcohol	C <sub>2</sub> H <sub>6</sub> O	46.04	0.5	0.59 ± 0.02	3	2.31 ± 0.10		
3	formaldehyde	aldehyde	CH <sub>2</sub> O	30.01	1	0.97 ± 0.04	2	1.23 ± 0.05		
4	acetaldehyde	aldehyde	C <sub>2</sub> H <sub>4</sub> O	44.03	0.5	0.62 ± 0.01	2	1.38 ± 0.02		
5	methylamine	amine	CH <sub>5</sub> N	31.04			5	3.36 ± 0.12	1	1.00 ± 0.00
6	ethylamine	amine	C <sub>2</sub> H <sub>7</sub> N	45.06			3.5	3.26 ± 0.30	0.5	0.81 ± 0.04
7	formic acid	carboxylic acid	CH <sub>2</sub> O <sub>2</sub>	46.01	2	1.46 ± 0.09	2	1.15 ± 0.08		
8	acetic acid	carboxylic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60.02	1	0.72 ± 0.01	2	1.61 ± 0.04		
9	oxalic acid	carboxylic acid	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	90.00	2	1.74 ± 0.05	1	1.10 ± 0.13		
10	methane	hydrocarbon	CH <sub>4</sub>	16.03	0	0.00 ± 0.00	4	3.27 ± 0.14		
11	ethane	hydrocarbon	C <sub>2</sub> H <sub>6</sub>	30.05			3	2.00 ± 0.07		
12	propane	hydrocarbon	C <sub>3</sub> H <sub>8</sub>	44.06			2.67	2.07 ± 0.04		
13	butane	hydrocarbon	C <sub>4</sub> H <sub>10</sub>	58.08			2.5	2.03 ± 0.01		
14	ethene	hydrocarbon	C <sub>2</sub> H <sub>4</sub>	28.03			2	1.58 ± 0.11		
15	propene	hydrocarbon	C <sub>3</sub> H <sub>6</sub>	42.05			2	1.56 ± 0.03		
16	acetylene	hydrocarbon	C <sub>2</sub> H <sub>2</sub>	26.02			1	0.87 ± 0.01		
17	benzene	hydrocarbon	C <sub>6</sub> H <sub>6</sub>	78.05			1	0.87 ± 0.02		
18	hydrogen cyanide	N-containing	HCN	27.01			1	0.98 ± 0.22	1	0.87 ± 0.01
19	carbon monoxide	other	CO	27.99	1	0.91 ± 0.02	0	0.00 ± 0.00		
20	carbon dioxide	other	CO <sub>2</sub>	43.99	2	1.84 ± 0.27				

440 from compounds (114 ≤ MM ≤ 426; Table 1 and Supporting Information Table S-1) that were dissolved in either 2-propanol or ethyl acetate. All standards were supplied by Fisher Scientific or Sigma-Aldrich, most with minimum purities of >98%, a few at 95%, and one at 90%. Solvents were from Fisher, both with >99.5% minimum purities. Solutions were atomized using a modified TSI atomizer (model 3076, Shoreview, MN) using only metal, glass, and Teflon components. After atomization, the aerosol was dried through four diffusion driers in series filled with activated carbon. Atomization was carried out using prepurified (minimum purity 99.998%) argon (Airgas, Inc., Radnor, PA) in order to eliminate interferences from air ions. It is especially important to accurately determine the signal from the OH<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, and CO<sup>+</sup> fragment ions, which can be major fragments from oxygenated organic species in the AMS but suffer from interferences from gas-phase H<sub>2</sub>O and N<sub>2</sub> in air.

## RESULTS AND DISCUSSION

**NIST EI Database Analysis.** In order to evaluate the potential effect of chemical biases during the fragmentation process and to determine if the fragment ions comprising a mass spectrum approximately retain the atomic ratios (ARs) of the original compound, EA was initially applied to standard EI mass spectra from the NIST database. ARs were calculated and compared to the ARs of the original compound. The calculation method is demonstrated using one of the replicate spectra of oxalic acid (NIST) as an example in Table 2. The example calculation yields an O/C of 1.78 (−11% relative error) and an H/C of 1.18 (+18% relative error).

The EA procedure was repeated for NIST spectra from 20 molecules (listed in Table 3) from six types of carbon-containing molecules: alcohols, aldehydes, amines, carboxylic acids, hydrocarbons (saturated, unsaturated, and aromatic), nitrogen-containing, plus carbon monoxide and carbon dioxide. All replicate



**Figure 1.** Scatter plot of (a) O/C and (b) H/C ratios determined by EA of spectra from the NIST EI database vs the nominal ARs. Error bars are one standard deviation ( $\sigma$ ) derived from all available replicate spectra for each species.

spectra in the database for each given molecule (from different groups or instruments) were used for EA. Figure 1 shows the scatter plots of the EA calculated versus atomic O/C and H/C ratios. Both O/C ( $R^2 = 0.95$ ) and H/C ( $R^2 = 0.92$ ) show high correlation between the nominal and EA calculated ratios, showing that chemical biases during fragmentation are not large enough to suppress this information for these small molecules.

The O/C regression line lies below the 1:1 line, indicating a weak tendency for fragments without (or with less) oxygen to retain the positive charge during fragmentation, as expected based on the electronegativity of oxygen.<sup>2</sup> However, the slope of the O/C line is  $0.86 \pm 0.07$  (95% confidence interval (CI)), indicating that this effect is not overwhelming. While some EI-MS practitioners would expect this effect to be stronger based on, for example, frequent losses of neutrals such as  $H_2O$  and  $CO_2$  from molecular ions and large fragments, a unique feature of our analysis is that it is not focused on the largest fragments but includes all of the ions produced by a given molecule. The small fragments that are often lost as neutrals may also retain the charge a fraction of the time, leading to a compensating effect for the estimated ARs. We quantify the relative error for each compound between the calibrated O/C ratio and the real O/C ratio. We use the average across all species sampled of the absolute value of the relative error to characterize the measurement. For example, for formic

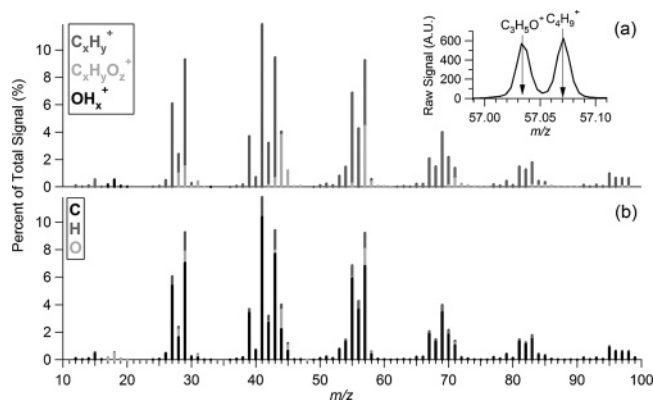
acid the actual O/C is 2.0, the raw O/C from the spectrum is 1.46, the calibrated O/C is 1.70, the relative error is  $-15\%$ , and its absolute value is  $15\%$ . When the last number is averaged over all compounds, the average error of the O/C measurements is  $17\%$ . Note that this is a lower limit when applying to other species since the calibration and error were determined with the same data points.

The calculated H/C ratios show a larger underestimation. This is likely due to frequent neutral losses of H and  $H_2$  during fragmentation<sup>2</sup> and is also partially due to the fact that lower  $m/z$  ions are not reported for the majority of the spectra in the NIST database. Of the 58 spectra sampled in the NIST database, 13 do not include fragments below  $m/z$  20; only 11 include data for  $m/z$  2, 4 of which report  $m/z$  1. If the spectra that include  $m/z$  2 are analyzed separately, the “raw” measured H/C ratio is  $5\%$  higher than for the rest of the spectra. The average error after calibration is  $14\%$ . The calibration lines determined here show that the estimation of the O/C and H/C ratios of molecules analyzed by EI is possible.

**HR-ToF-AMS Standard Analysis.** A total of 35 standards were sampled with the HR-ToF-AMS in the laboratory, and their spectra were analyzed as described above. Compounds were selected in an attempt to represent the types of species that have been reported previously in ambient aerosols.<sup>4</sup> A broad range of organic functionality is represented, including hydrocarbons (saturated, unsaturated, aromatic, PAH), alcohols, carboxylic and dicarboxylic acids, aldehydes, esters, peroxides, anhydrides, carbohydrates, amines, amides, organic nitrites, and pyridine derivatives ( $114 \leq MM \leq 426$ ). A full list of the compounds analyzed can be found in Table 1. The Supporting Information (Table S-1) contains a more detailed list that includes structures and known primary organic aerosol sources when applicable.

The ability to quantify ARs with the HR-ToF-AMS depends critically on a high-accuracy calibration of the  $m/z$  axis, the accurate characterization of the detailed peak shape of an isolated ion,<sup>12</sup> and the correct identification of all fragment ions present. The organic fragments were first apportioned into four organic categories ( $C_xH_y^+$ ,  $C_xH_yO_z^+$ ,  $C_xH_yN_p^+$ ,  $C_xH_yO_zN_p^+$ )<sup>12</sup> before applying EA to separate signal from individual elements. An example of the separated HRMS from nonyl aldehyde is shown in Figure 2. The consistency of the subspectra of each organic category across the  $m/z$  range was used to identify potential errors in the ion assignments. The UMR mass spectra were also compared to the NIST database, as AMS spectra are typically similar as discussed above, in order to check for the potential effect of impurities in the standards. Both methods were also useful to detect the presence of residual solvent in the particles. While a small amount of residual solvent can have a disproportionate effect on some properties such as cloud activation,<sup>22</sup> in most cases, the solvent mass fraction could be made negligibly small by adding a sufficient number of diffusion dryers in series. In two cases (1-eicosanol and 1-docosanol), a significant interference from 2-propanol remained, but atomization in ethyl acetate allowed the recording of spectra without solvent interferences. The effect of remaining

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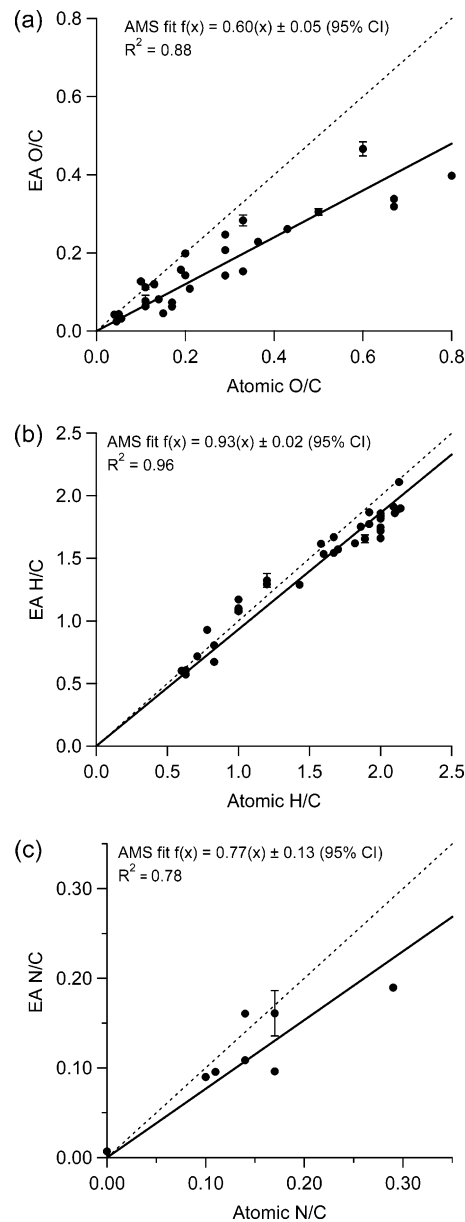
**Figure 2.** HR-ToF-AMS mass spectra shown as summed to UMR for nonyl aldehyde with the signal divided into (a) organic categories of  $C_xH_y^+$ ,  $C_xH_yO_z^+$ , and  $OH_x^+$  (with an inset of the raw spectrum for  $m/z$  57) and (b) elemental signals (C, H, O) by the EA method. As only 3.4% of the signal is above  $m/z$  100, the abbreviated spectrum is shown for simplicity.

interferences, such as peaks from impurities that were part of the standards and thus could not be separated or contamination introduced by the particle generation system, is estimated to be on the order of 5%.

The raw ARs for O/C, H/C, and N/C derived from the spectra of laboratory standards are shown as scatter plots against the ratios of the pure standard molecules in Figure 3. (The data set is also included as a table in the Supporting Information (Table S-2). The clear correlation between the raw estimated and nominal ARs indicates that, after calibration, our technique should be able to provide reasonable estimates of elemental ratios for complex mixtures such as ambient secondary organic aerosol (SOA) for which other methods are ill-suited. All of the EA calculated O/C ratios are below the 1:1 line. The raw AMS AR estimates underestimate the oxygen content more than was observed for the NIST spectra. The reasons for the difference in the NIST versus AMS slopes are not clear, but may be related to the larger size of the molecules sampled with the AMS, to an effect of pyrolysis during the flash vaporization process in the AMS, or to enhanced fragmentation in the AMS due to the higher internal energy gained during vaporization at 600 °C. No clear trends in the O/C underestimation were found versus organic functionality or molecular mass.

The raw estimated H/C and N/C ratios are also lower than the nominal ratios but are not as underestimated as the O/C ratio. As O is more electronegative than N and H, it may have a larger tendency to be lost as a neutral fragment during fragmentation. Note that the tendency to underestimate the H/C ratio and the scatter in the graph is reduced when compared with the NIST database, likely due to the inclusion of ions down to  $m/z$  11 for all spectra in our analysis, and the use of larger molecular masses, which leads to a lower fraction of the ion signal being below  $m/z$  20.

The quantification of the N/C is explored in Figure 3c. Although we sampled less N-containing species, as our focus for this paper is on the O/C ratio, the clear correlation indicates that the method is also promising for the quantification of N in organic species. Nitrogen typically represents a small fraction of the organic aerosol, and therefore, the N/C range explored here is smaller. Nicotinic acid produced a signal at  $N^+$ , comprising 14%



**Figure 3.** Scatter plots of raw elemental ratios (O/C, H/C, and N/C) estimated from HR-ToF-AMS spectra of laboratory standards atomized in argon vs the nominal ARs. The data include error bars of one standard deviation ( $\sigma$ ) and are fit by linear regression through zero.

of the total nitrogen signal. This standard exemplifies a potential problem in which ambient or laboratory particles, which are analyzed in air with this method, could have more uncertainty in the estimation of their elemental ratios than suggested by Figure 3, due to a portion of the signal being present at peaks that have a large contribution from ionization of air molecules such as  $N^+$ . This signal can be separated using particle time-of-flight AMS data such as for  $CO^{+23}$  and may also require the subtraction of the estimated inorganic signal (as for  $N^+$ )<sup>24</sup> based on laboratory calibrations.

The average error in the estimated O/C ratios after applying the calibration (as defined above) is 30%, while the uncertainty in

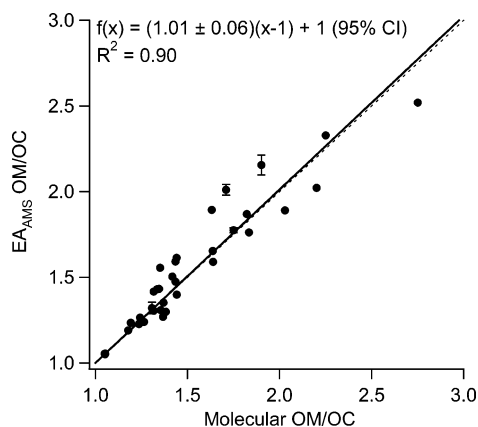
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**Table 4. EA of Mixtures of Pure Organic Compounds after Applying the Laboratory-Derived Calibrations<sup>a</sup>**

no.	compound				O/C			H/C		
	1	2	3	4	real	EA ( $\pm\sigma$ )	% error	real	EA ( $\pm\sigma$ )	% error
1	adipic acid	levoglucosan			0.75	0.66 $\pm$ 0.000	-11.8	1.67	1.92 $\pm$ 0.000	15.3
2	levoglucosan	stearic acid			0.38	0.46 $\pm$ 0.004	22.8	1.88	2.05 $\pm$ 0.003	9.1
3	adipic acid	levoglucosan	stearic acid		0.46	0.46 $\pm$ 0.001	0.2	1.82	1.93 $\pm$ 0.011	6.2
4	levoglucosan	stearic acid	1,2-tetradecanediol		0.29	0.31 $\pm$ 0.013	7.4	1.98	2.06 $\pm$ 0.015	4
5	adipic acid	levoglucosan	stearic acid	16-hydroxyhexadecanoic acid	0.38	0.38 $\pm$ 0.004	-0.3	1.87	1.94 $\pm$ 0.012	3.7

<sup>a</sup> Results are presented with  $\pm 1\sigma$  (precision) and the absolute error.



**Figure 4.** Scatter plot of OM/OC determined from the calibrated ARs of the HR-ToF-AMS laboratory standards with error bars of one standard deviation ( $\sigma$ ) versus the OM/OC of the pure compounds.

the slope of the line is  $\sim 9\%$  (95% confidence interval). The reproducibility of each measured value is high (better than 5%), indicating a higher precision than accuracy. For classes of compounds, such as SOA, which are chemically similar, this suggests the possibility to characterize smaller changes in O/C within a sample, which could be indicative of processes such as oxidative aging in the atmosphere. The average errors for the H/C and N/C are 7 and 20%, respectively. Finally, as the range of compounds used in this method demonstration is limited, additional calibration of the method is desirable before it is applied to types of organic species very different from those presented here, or with mass spectrometer systems that could have significant mass discrimination or other similar effects.

**Estimation of OM/OC.** Estimates of OM/OC for atmospheric organic aerosols have been used in the past to quantify the total mass of organic compounds since only OC could be quantified directly.<sup>13</sup> A value of OM/OC = 1.4 was used in the literature for many years, which was determined as an average of samples from 2 days in the Los Angeles area.<sup>25</sup> Recent studies, using a wider variety of techniques, report 1.4 to be a lower bound<sup>26</sup> and support larger values up to 2.5,<sup>27</sup> differing with location and based mainly on the oxygen content as the OM/OC excluding oxygen appears relatively low and constant across different locations.<sup>27</sup>

OM/OC values can be calculated from the relative masses of the elements defined above:

$$\text{OM/OC} = \frac{M_C + M_H + M_O + M_N}{M_C} \quad (3)$$

or reconstructed from the measured elemental ratios:

$$\text{OM/OC} = \frac{(16 \times \text{O/C}) + (1 \times \text{H/C}) + (14 \times \text{N/C}) + 12}{12} \quad (4)$$

The second equation can be used to determine OM/OC directly from the calibrated ARs. Figure 4 shows the comparison of the OM/OC calculated from the calibrated ARs of the laboratory standards versus the nominal OM/OC values for each compound. When fit through ( $x = 1, y = 1$ ), the linear regression has a slope of  $1.01 \pm 0.06$  (95% CI), with an average error (as defined above) of 5% for individual compounds.

#### Application of the Method to Mixtures of Organic Species.

Mixtures of standards were prepared using 1:1 mass ratios of two to four standards as shown in Table 4. Small differences in the relative ionization efficiencies (RIEs) of different organic species in a mixture<sup>8</sup> may result in additional inaccuracies with respect to individual compounds, as can differences in the solubilities to the solvents used or in surface adsorption in the mixing and atomization systems. The raw ARs were calibrated using the linear regressions from the pure laboratory standards. The accuracy and precision observed for these mixtures are similar to those of the individual compounds (Figure 2a).

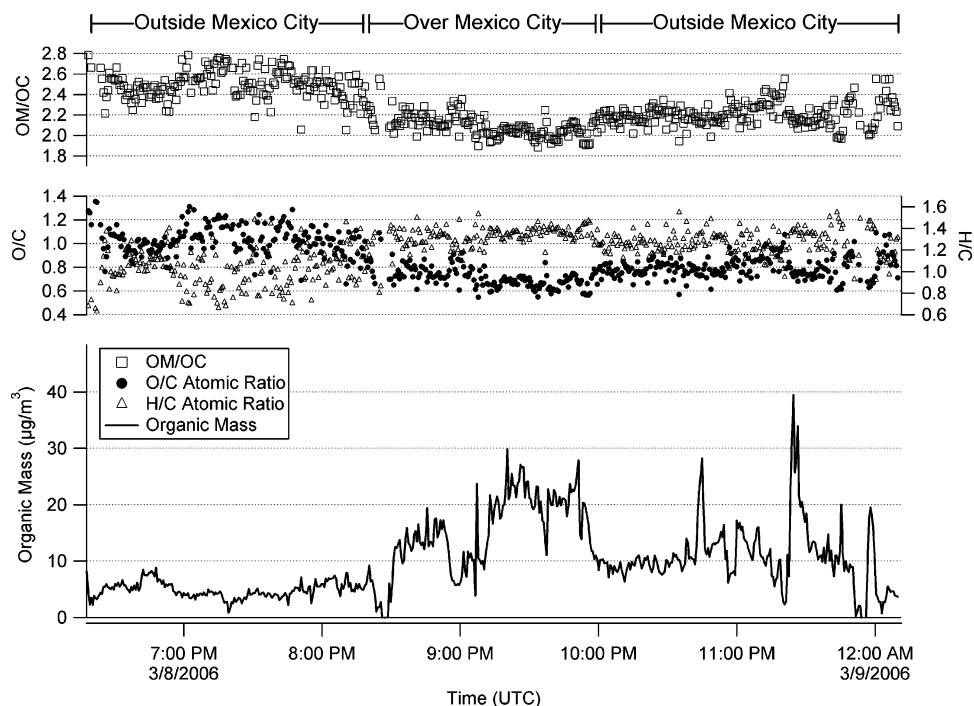
**Other Issues for Organic Aerosols.** In ambient air, the aerosol signals for  $\text{CO}^+$  and  $\text{H}_2\text{O}^+$  have a significant interference from air or other aerosol species. Several techniques to address this problem will be presented in a future publication. Another possible source of error in the EA of ambient organic aerosols arises if one fails to account for signals produced by organic species at nominally inorganic fragment ions in the AMS (e.g.,  $\text{NO}^+$ ,  $\text{NO}_2^+$ , which can arise from organic nitrates, or  $\text{SO}^+$ ,  $\text{SO}_2^+$ , from organosulfates).<sup>28</sup> Neglecting these signals would lead to the underestimation of the organic O/C, N/C, and S/C ratios. The fraction of the signals from these organic compounds appearing at nominally inorganic ions in the AMS<sup>24</sup> should be a focus of future research by analyzing pure standards. However, during many field campaigns, the large majority of the nominally inorganic ions in the AMS are indeed due to inorganic species, based on the stoichiometric ratios of ammonium to nitrate and sulfate showing neutralization of the inorganic salts. During periods when neutralization of the inorganic acids by ammonium

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**Figure 5.** ARs of O/C and H/C and the mass ratio OM/OC vs time calculated for ambient aerosol sampled from the NCAR C-130 aircraft during the MILAGRO Field Experiment. Each point represents 20 s of sampling time. The following assumptions were applied to estimate the ions with large interferences from air peaks, based on previous work<sup>23,31</sup> and on conserving organic mass:  $\text{CO}^+ = 1.0 \times \text{CO}_2^+$ ,  $\text{H}_2\text{O}^+ = 0.225 \times \text{CO}_2^+$ .<sup>24</sup>

is observed within measurement precision,<sup>29,30</sup> the errors in the estimated organic elemental composition arising from this reason should be small.

Additionally, possible larger RIEs for reduced versus oxidized compounds<sup>8</sup> could cause a negative bias on the O/C and OM/OC ratios of mixtures containing significant amounts of both types of species and should be the focus of future research. Applying the EA method separately to spectral components separated by principal component analysis techniques<sup>5,23</sup> should reduce the impact of such biases.

**Application to Fast Ambient Aerosol Measurements from Aircraft.** Although the accuracy of the new method described in this paper is not as high as for most offline EA methods for organic samples, it does have the advantage of being able to use much smaller sample sizes and sample at much higher time resolution while retaining good precision and reproducibility. Also, the absence of evaporation or adsorption artifacts for organics in the AMS and the ability to eliminate inorganic interferences greatly reduce potential errors introduced in the elemental composition of filter samples<sup>13</sup> and may partially compensate for the lower nominal accuracy of our analysis method when applied to ambient aerosols. Note that while the absolute accuracy of the method is lower than standard methods, the precision of the technique is better than its accuracy. To demonstrate the application of our method to real world measurements, we analyzed ambient aerosol data collected with the HR-ToF-AMS data in V-mode over Mexico City from the NCAR C-130 aircraft as a part of the MILAGRO (Megacity Initiative: Local and Global Research Observations)

field campaign in March 2006. O/C, H/C, and OM/OC ratios were calculated for the 20-s data and are shown in Figure 5. Each data point represents the analysis of  $\sim 0.2\text{--}1.5$  ng of organic aerosol. The figure demonstrates the high sensitivity, precision, and time resolution achievable with this EA technique. A less oxidized aerosol is present over the city, where many sources of reduced carbon such as traffic are present,<sup>29</sup> while the more regional aerosol outside of the city shows a higher degree of oxidation, consistent with recent results at many locations in the Northern Hemisphere.<sup>5</sup> Note that assumptions based on our results and previous studies<sup>23,31</sup> were made for peaks such as  $\text{CO}^+$ , which suffer from large interferences from air ions, which do reduce the accuracy of the method for ambient samples.

## CONCLUSIONS

While commercial instrumentation exists to measure elemental composition of organic species (CHNOS), we propose an alternative method based on EI mass spectra. Our method is less accurate than standard thermal methods, but it has a precision of  $\sim 5\%$ , can be used online with high time resolution and small sample size, and avoids interferences from inorganic species. The method can be applied to spectra from unknown molecules or mixtures obtained from other EI techniques such as direct injection MS when high-resolution mass spectrometry is used. It can also be applied to organic aerosols and to the nonvolatile fraction of particles suspended or dissolved in water samples, both of which are subjects of great interest in environmental chemistry.

Our elemental analysis method was first demonstrated using 58 EI spectra of 20 compounds from the NIST database, showing

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good correlation between known and estimated elemental ratios (O/C and H/C) with average errors of 17 and 14%, respectively. The method was then calibrated with atomized aerosol standards and a HR-ToF-AMS, which produced qualitatively similar but quantitatively different calibrations, likely due to the larger molecules used or additional pyrolysis and fragmentation. Additional calibration is recommended when analyzing types of species very different from those used here. Our method also allows the estimation of OC (organic carbon) mass and OM/OC directly from AMS data. An average error of 30% and a precision better than 5% is observed for O/C, while the average errors for H/C, N/C, and OM/OC are 7, 20, and 5%, respectively.

The application of EA to ambient aerosols sampled from aircraft demonstrates that the method has high precision for very small sample sizes and very high time resolution data, neither of which is possible with standard EA instrumentation. The method is sensitive enough for the precise measurement of samples of less than 1 ng in 20 s. This small sample size represents an improvement of ~6 orders of magnitude over the minimum sample sizes for thermal CHNO analyzers, which are on the order of 1 mg.<sup>32</sup>

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(32) Elementar; Americas; Inc. Vario MICRO Cube brochure ([www.CH-NOS.com](http://www.CH-NOS.com)), 2007.

## ACKNOWLEDGMENT

This research was supported by funding from the following grants: NSF CAREER ATM-0449815, NSF ATM-0513116, EPA STAR RD-83216101-0, NASA NNG04GA67G, NASA Earth System Science Graduate Fellowship NNG04GR06H, and EPA STAR Fellowship FP-91650801. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not reflect the views of the funding agencies. We also thank Ken Docherty and Joel Kimmel (CU-Boulder) for assistance with acquisition of the laboratory data, Donna Sueper for data analysis software development, and Aerodyne, Tofwerk, the rest of the Jimenez Group for technical support and useful discussions, in addition to an anonymous reviewer for useful suggestions.

## SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Supporting Information for Elemental Analysis of Organic Species with Electron Impact  
High-Resolution Mass Spectrometry**

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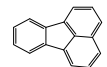

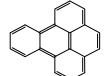



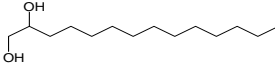

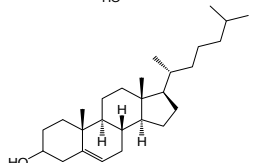
Two Supporting Tables are included:

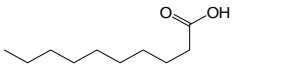
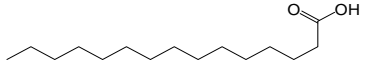
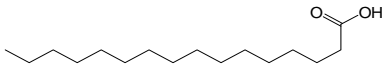
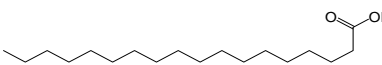
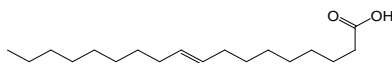
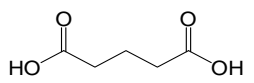
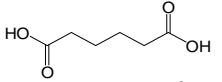
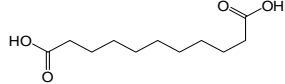
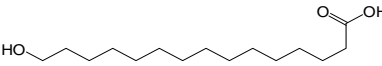
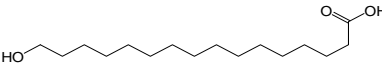
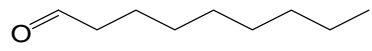
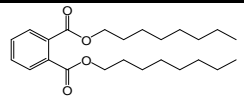
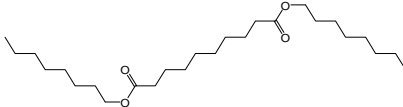
**Table S-1**\* characterizes the 35 pure compounds analyzed by elemental analysis using the High-Resolution Time-of-Flight Aerosol Mass Spectrometer.

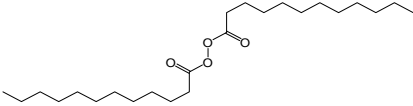
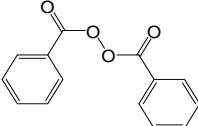
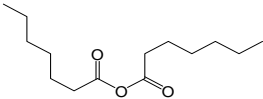
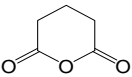
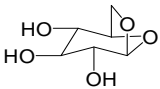
**Table S-2**\* includes the nominal ratios and the calculated atomic ratios determined by elemental analysis of the 35 pure compounds detailed in the previous table.

\*Both tables are divided into two categories (a) 28 Carbon, Hydrogen and Oxygen-containing compounds, (b) 7 Nitrogen-containing organic compounds.

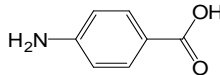
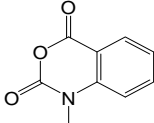
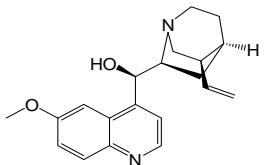
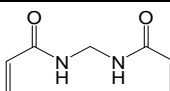
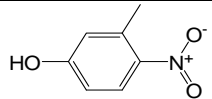
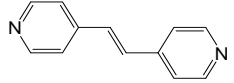
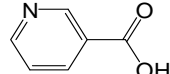
22 **Table S-1(a).** List of pure compounds sampled with the HR-ToF-AMS grouped by organic category:  $C_xH_y$  and  $C_xH_yO_z$ . General organic  
 23 class and subclass are included for each compound along with structures, molar mass (g/mol), molecular formula, atmospheric presence\* (as  
 24 reported by Seinfeld and Pandis). \* (Atmospheric presence symbols from Seinfeld and Pandis: M, meat cooking; A, automobiles; RD, road  
 25 dust; V, vegetation; G, natural gas home appliances; C, cigarette smoke; AS, asphalt; B, boilers; W, wood burning.)

Class	Subclass	Name	Structure	MM (g/mol)	Formula	Atmospheric Presence
Hydrocarbon	Alkane	Hexadecane		226.27	$C_{16}H_{34}$	
	PAH	Fluoranthene		202.08	$C_{16}H_{10}$	M,A,RD,G,C,A S,B,W
	PAH	Pyrene		202.08	$C_{16}H_{10}$	M,A,RD,G,C,A S,B,W
	PAH	Benzo[e]pyrene		252.09	$C_{20}H_{12}$	M,A,RD,G,AS, B,W
Alcohol	Alkanol	1-Octadecanol		270.29	$C_{18}H_{38}O$	C
	Alkanol	1-Eicosanol		298.32	$C_{20}H_{42}O$	C
	Alkanol	1-Docosanol		326.35	$C_{22}H_{46}O$	C
	Dialkanol	1,2-Tetradecanediol		230.22	$C_{14}H_{30}O_2$	
	Phenol	Pyrogallol		126.03	$C_6H_6O_3$	
	Sterol	Cholesterol		386.35	$C_{27}H_{46}O$	M,C

Class	Subclass	Name	Structure	MM (g/mol)	Formula	Atmospheric Presence
Carboxylic Acid	Alkanoic Acid	Decanoic Acid		172.15	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	M,A,RD,V,G,C, AS,B,W
	Alkanoic Acid	Pentadecanoic Acid		242.22	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	M,A,RD,V,G,C, AS,B,W
	Alkanoic Acid	Hexadecanoic Acid		256.24	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	M,A,RD,V,G,C, AS,B,W
	Alkanoic Acid	Stearic Acid		284.27	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	M,A,RD,V,G,C, AS,B,W
	Alkenoic Acid	Oleic Acid		282.26	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	M,A,RD,V,C,A S,W
	Dicarboxylic Acid	Glutaric Acid		132.04	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	M,C,W
	Dicarboxylic Acid	Adipic Acid		146.06	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	M,W
	Dicarboxylic Acid	Undecanedioic Acid		216.14	C <sub>11</sub> H <sub>20</sub> O <sub>4</sub>	
	Hydroxy-carboxylic Acid	15-Hydroxypentadecanoic Acid		258.22	C <sub>15</sub> H <sub>30</sub> O <sub>3</sub>	
	Hydroxy-carboxylic Acid	16-Hydroxyhexadecanoic Acid		272.24	C <sub>16</sub> H <sub>32</sub> O <sub>3</sub>	
Aldehyde	Alkanal	Nonyl Aldehyde		142.14	C <sub>9</sub> H <sub>18</sub> O	M
Ester	Phthalate	Diethyl Phthalate		390.28	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	
	Alkanoate	Diethyl Sebacate		426.37	C <sub>26</sub> H <sub>50</sub> O <sub>4</sub>	

Class	Subclass	Name	Structure	MM (g/mol)	Formula	Atmospheric Presence
Peroxide	Alkyl Peroxide	Lauroyl Peroxide		398.34	C <sub>24</sub> H <sub>46</sub> O <sub>4</sub>	
	Benzyl Peroxide	Benzoyl Peroxide		242.06	C <sub>14</sub> H <sub>10</sub> O <sub>4</sub>	
Anhydride	Alkyl Anhydride	Heptanoic Acid, anhydride		242.19	C <sub>14</sub> H <sub>26</sub> O <sub>3</sub>	
	Cyclic Anhydride	Glutaric Anhydride		114.03	C <sub>5</sub> H <sub>6</sub> O <sub>3</sub>	
Carbohydrate	Monosaccharide	Levoglucozan		162.05	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	

29 **Table S-1(b).** List of pure compounds sampled with the HR-ToF-AMS grouped by organic category:  $C_xH_yO_z$  and  $C_wH_xO_yN_z$ . General  
 30 organic class and subclass are included for each compound along with structures, molar mass (g/mol), molecular formula, atmospheric  
 31 presence\* (as reported by Seinfeld and Pandis). \*(Atmospheric presence symbols from Seinfeld and Pandis: M, meat cooking; A,  
 32 automobiles; RD, road dust; V, vegetation; G, natural gas home appliances; C, cigarette smoke; AS, asphalt; B, boilers; W, wood burning.)

Class	Subclass	Name	Structure	MM (g/mol)	Formula	Atmospheric Presence
Amine	Amino Acid	4-aminobenzoic acid		137.05	$C_7H_7NO_2$	
	Amino Anhydride	N-methylisatioc Anhydride		177.04	$C_9H_7NO_3$	
	Alkaloid	quinine		324.18	$C_{20}H_{24}N_2O_2$	
Amide	Alkyl Amide	bis-acrylamide		154.07	$C_7H_{10}N_2O_2$	
Organic Nitrite	Phenyl Nitrite	3-Methyl-4-nitrophenol		153.04	$C_7H_7NO_3$	
Pyridine	Alkyl Pyridine	trans-1,2-bis(4-pyridyl) ethylene		182.08	$C_{12}H_{10}N_2$	
	Cyclic Acid	Nicotinic Acid (Niacin)		123.03	$C_6H_5NO_2$	C

34 **Table S-2(a).** Actual and calculated ARs of 28 pure organic compounds (containing Carbon,  
 35 Hydrogen, and Oxygen) from EI mass spectra taken with the HR-ToF-AMS. Standard  
 36 deviations of  $\pm 1\sigma$  are provided for multiple samples.

Class	Name	O/C	O/C calc $\pm \sigma$	H/C	H/C calc $\pm \sigma$
Hydrocarbon	Hexadecane			2.13	2.11
	Fluoranthene			0.63	0.61
	Pyrene			0.63	0.57
	Benzo[e]pyrene			0.60	0.60
Alcohol	1-octadecanol	0.06	0.03	2.11	1.88
	1-Eicosanol	0.05	0.04	2.10	1.86
	1-Docosanol	0.05	0.03	2.09	1.91
	1,2-Tetradecanediol	0.14	0.08	2.14	1.90
	Pyrogallol	0.50	$0.31 \pm 0.008$	1.00	$1.08 \pm 0.011$
	Cholesterol	0.04	0.04	1.70	1.57
Carboxylic Acid	Decanoic Acid	0.20	0.20	2.00	1.66
	Pentadecanoic Acid	0.13	0.12	2.00	1.83
	Hexadecanoic Acid	0.13	0.12	2.00	1.85
	Stearic Acid	0.11	$0.11 \pm 0.005$	2.00	$1.86 \pm 0.001$
	Oleic Acid	0.11	$0.08 \pm 0.014$	1.89	$1.66 \pm 0.032$
	Glutaric Acid	0.80	0.40	1.60	1.54
	Adipic Acid	0.67	0.34	1.67	1.54
	Undecanedioic Acid	0.36	0.23	1.82	1.62
	15-Hydroxypentadecanoic Acid	0.20	0.14	2.00	1.75
	16-Hydroxyhexadecanoic Acid	0.19	0.16	2.00	1.72
Aldehyde	Nonyl Aldehyde	0.11	$0.06 \pm 0.002$	2.00	$1.82 \pm 0.001$
Ester	Diethyl Phthalate	0.17	0.07	1.58	1.62
	Diethyl Sebacate	0.15	0.05	1.92	1.87
Peroxide	Lauroyl Peroxide	0.17	0.06	1.92	1.77
	Benzoyl Peroxide	0.29	0.25	0.71	0.72
Anhydride	Heptanoic Acid, anhydride	0.21	0.11	1.86	1.75
	Glutaric Anhydride	0.60	$0.47 \pm 0.018$	1.20	$1.32 \pm 0.055$
Carbohydrate	Levoglucosan	0.83	$0.53 \pm 0.002$	1.67	$1.67 \pm 0.001$

38 **Table S-2(b).** Actual and calculated ARs of 7 Nitrogen-containing compounds from EI mass spectra taken with the HR-ToF-AMS. Standard  
 39 deviations of  $\pm 1\sigma$  are provided for multiple samples.

Class	Name	O/C	O/C calc $\pm \sigma$	H/C	H/C calc $\pm \sigma$	N/C	N/C calc $\pm \sigma$
Amine	4-aminobenzoic acid	0.29	0.21	1.00	1.09	0.14	0.16
	N-methylisatoic Anhydride	0.33	0.15	0.78	0.93	0.11	0.10
	Quinine	0.10	0.13 $\pm$ 0.003	1.20	1.29 $\pm$ 0.001	0.1	0.09 $\pm$ 0.000
Amide	Bis-acrylamide	0.29	0.14 $\pm$ 0.001	1.43	1.29 $\pm$ 0.001	0.29	0.19 $\pm$ 0.000
Organic Nitrite	3-Methyl-4-nitrophenol	0.43	0.26	1.00	1.10	0.14	0.11
Pyridine	trans-1,2-bis(4-pyridyl) ethylene			0.83	0.81 $\pm$ 0.001	0.17	0.10 $\pm$ 0.001
	Nicotinic Acid (Niacin)	0.33	0.28 $\pm$ 0.014	0.83	0.67 $\pm$ 0.006	0.17	0.16 $\pm$ 0.025

40