Supplemental Information

Secondary Organic Aerosol Composition from C$_{12}$ Alkanes

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Overview of Supplemental Information

This supplemental section contains further information on our DART-MS method validation; our GC/MS methods; and a review of the equations used to relate the DART-MS signal to ion abundance.

DART-MS Analysis

The use of DART-MS to enable the detection of low-volatility species is well-established in literature; its application to SOA is recent, however. A common mass calibrant for DART-MS are polypropylene or polyethylene glycols. We have analyzed polypropylene glycol by (+)-DART-MS using the same method we used to analyze SOA (Figure S1). Dipropylene glycol has, as calculated using the EVAPORATION model, a vapor pressure of 5.9×10^{-6} atm; as shown in Figure S1, the highest polymer of polypropylene glycol measured by us was the 10-mer, with a calculated vapor pressure of 6.8×10^{-20} atm.

DART-MS is routinely used to identify pharmaceuticals and drugs such as ibuprofen (calculated P_{vap} of 0.11 atm), cocaine (calculated P_{vap} of 1.4×10^{-3} atm), and heroin (calculated P_{vap} of 5.6×10^{-7} atm). We reproduced a test of this nature in Figure S2, also conducted with the same method as used to analyze SOA in the manuscript.

These standards demonstrate the viability of DART-MS for the analysis of compounds spanning a broad range of volatilities and structures. Works cited in the manuscript (Cody et al., Harris et al., etc.) illustrate the utility of DART-MS in the analysis of many classes of compounds and are part of the literature foundation for the application of DART-MS to the qualitative and quantitative analysis of organic compounds.
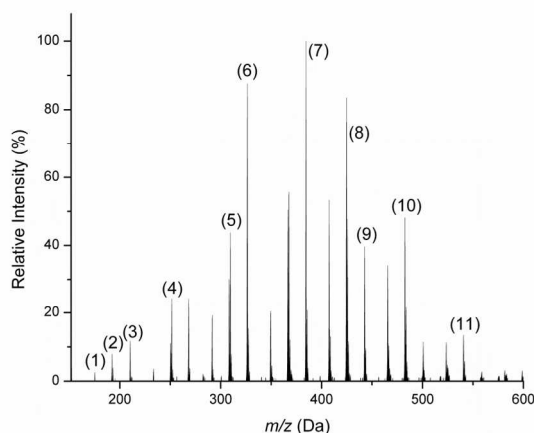

Figure S1: (+)-DART mass spectrum of polypropylene glycol ($H[OCH(CH_3)CH_2]_nOH$). Labeled peaks indicate: (1) n =2, $[M+NH_4]^+$; (2) n = 3, $[M+H]^+$; (3) n = 3, $[M+NH_4]^+$; (4) n=4, $[M+H]^+$; (5) n = 5, $[M+H]^+$, (6) n = 5, $[N+NH_4]^+$; (7) n = 6, $[M+NH_4]^+$; (8) n = 7, $[M+H]^+$; (9) n = 7, $[M+H_3O]^+$; (10) n = 8, $[M+H]^+$; (11) n = 10, $[M+H]^+$.
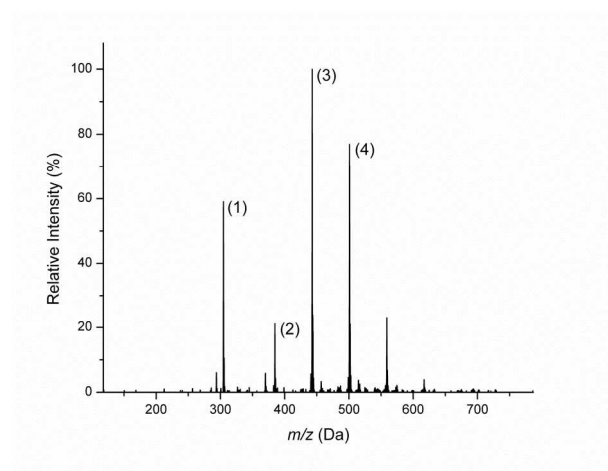
Figure S2: (+)-DART mass spectrum of the surface of a randomly chosen five-dollar bill. Labeled peaks are assigned as: (1) cocaine, $[M+H]^+$; (2) heroin, $[M+H]^+$; (3) (1R,9S)-1-acetoxy-N-acetyl-1,9-dihydro-anhydronornarceine (major alkaloidal impurity in heroin), $[M+H]^+$; (4) N-acetylanhydronornarceine or N-acetylnornarcotine (major isobaric alkaloidal impurities in heroin), $[M+H]^+$.

We detect peroxide standards as ammonium adducts, as well as proton- and ammonium-bound dimers and trimers, and hydronium adducts (Figure S3a). The complexation with ammonium occurs with all forms of peroxides, including acyl, alkyl, and cyclic peroxides. Adding 18-crown-6 introduces an ammonium ion sink, removing the major ionization pathway for peroxides of all kinds. Tert-butyl peroxybenzoate was analyzed as shown in Figure S3a; in Figure S3b, 18-crown-6 is co-introduced into the DART stream with t-butyl peroxybenzoate, and nearly none of the peroxide is detected. Figure S3b demonstrates the effectiveness of 18-crown-6 at complexing with ammonium ions in the DART stream and thereby halting peroxide detection. Cumene hydroperoxide is commercially available at 80% purity. We did test it, but the interferences from these impurities (methylstyrene, acetophenone, and cumyl alcohol, along with some unidentified high-concentration impurities) lead to less clear and lower quality mass spectra.
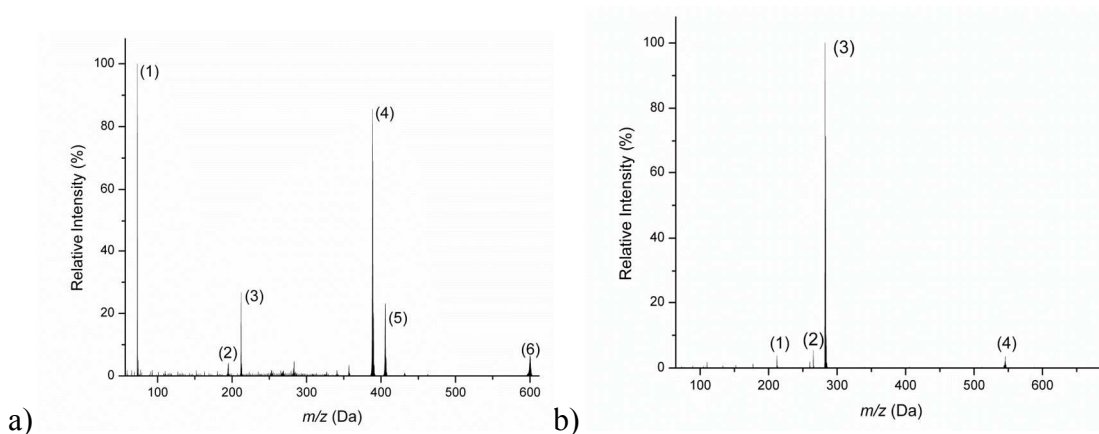

a)   b)

Figure S3: (a) (+)-DART mass spectrum of t-butyl peroxybenzoate. Labeled peaks are assigned as: (1) tBuO$^+$; (2) protonated t-butyl peroxybenzoate, $[M+H]^+$; (3) $[M+NH_4]^+$; (4) $[2M+H]^+$; (5) $[2M + NH_4]^+$; (6) $[3M+NH_4]^+$. (b) (+)-DART mass spectrum of t-butyl peroxybenzoate + 0.2

mM 18-crown-6 in methanol. Labeled peaks are assigned as: (1) [t-butyl peroxybenzoate + NH$_4$]$^+$; (2) [18-crown-6 + H]$^+$; (3) [18-crown-6]+ NH$_4$]$^+$; (4) [2(18-crown-6)+NH$_4$]$^+$.

GC/MS Analysis Details: Accounting for Thermally Labile Analytes

Molecular decomposition in the GC is difficult to account for in unknown samples, so we studied it with standards. We optimized instrumental methods to reduce sample degradation to the lowest possible level for both GC/MS and DART-MS analysis. We analyzed standards by both GC/MS and DART-MS to assess the instrument's performance with different classes of expected compounds; these standards included aldehydes, ketones, alcohols, carboxylic acids, 1,4-hydroxyketones, furans, dihydrofurans, amines, and hydroperoxides. DART-MS did not produce significant dehydration of alcohols or hydroperoxides. We focused then on minimizing dehydration in our GC/MS analyses.

We used a programmed temperature vaporization (PTV) inlet, instead of a standard split/splitless inlet, to achieve the softest possible volatilization of analytes for GC/MS. PTV injectors are capable of transferring many thermally labile compounds intact onto the column for separation and of concentrating a larger volume of a complex mixture of trace organic species. The most advanced deactivation coatings for both the column (Agilent DB5-MSUI) and inlet liner (Restek Sky liners) were used to prevent loss and tailing of active hydrogen-containing species. We used Agilent's DB-5 column test mix (Agilent, P/N 200-0185) to assess instrument performance, especially peak shape and tailing that would indicate degrading separatory ability for active hydrogen-containing species. The DB-5 standard test mix contained n-tetradecane, n-tridecane, 1-undecanol, 1,6-hexanediol, 2-ethylhexanoic acid, 4-chlorophenol, dicyclohexylamine, and 1-methylnaphthalene.

These measures to reduce artifactual dehydration were effective because we were able to observe in GC/CI-MS data dehydration steps occurring due to protonation by the methanol reagent gas (see new Supplemental Figure S4). In addition to water loss, nitric acid loss is another possible method artifact. We did not detect nitric acid loss or formation during analysis. We would have been able to detect nitric acid (63 amu) by DART and GC/MS, had it formed, but it was not observed.
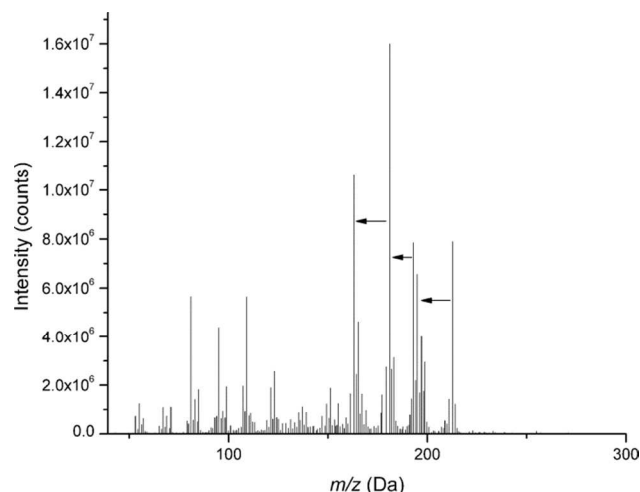
Figure S4: Chemical ionization mass spectrum at 22.73 min during GC/MS runs of SOA derived from dodecane low-NO photooxidation with ammonium sulfate seed. Arrows indicate water loss (-18 Da).

Equations for Calculating Weighting Factors from DART-MS

Relationship between Ion Current Intensity and Concentration, written for an Analyte, *i*:

$$(1) \qquad I_i = A_i P_{vap,i} C_i$$

Ratio of Equation 1 Written for an Analyte, *i*, and the Internal Standard (IS):

$$(2) \qquad \frac{I_i}{I_{IS}} = \frac{A_i P_{vap,i} C_i}{A_{IS} P_{vap,IS} C_{IS}}$$

Solving Equation 2 for Ratio of Concentrations, $\frac{C_i}{C_{IS}}$:

$$(3) \qquad \frac{C_i}{C_{IS}} = \frac{P_{vap,IS}}{P_{vap,i}} \frac{I_i}{I_{IS}}$$

Expressing the Sum of the Relative Concentrations of All Analytes, *i*, for a Given SOA Sample:

(4) Total concentration of SOA components $= \sum_i \frac{C_i}{C_{IS}}$

Finding Percent Contribution (*w*) of Each Analyte, *i*:

$$(5) \quad w = \frac{\frac{c_A}{c_{IS}}}{\sum_i \frac{c_i}{c_{IS}}} * 100\%$$

Obtaining the Mean Molecular Weight (M$_w$) of a Given SOA Sample Containing *i* Analytes, using a Weighted Average Formula and the Percent Contribution as the Weighting Factor:

$$(6) \quad \text{Mean } M_w = \sum_i w M_{w,i}$$