Table S1. Sampling information for all UAS samples.

Sample name	Collection media	Ground or air	Sampling time, start	Sampling time, end	PM collection duration (h)	Total air vol. sampled (m ³)
PNNL_F1	Filter	Ground	12/06/2021 19:30	12/06/2021 22:30	3	0.45
PNNL_F2	Filter	Ground	12/06/2021 22:30	12/07/2021 01:30	3	0.45
PNNL_F3	Filter	Ground	12/07/2021 01:30	12/07/2021 04:30	3	0.45
PNNL_F4	Filter	Ground	12/07/2021 04:30	12/07/2021 07:30	3	0.45
PNNL_F5	Filter	Ground	12/07/2021 07:30	12/07/2021 10:30	3	0.45
PNNL_F6	Filter	Ground	12/07/2021 10:30	12/07/2021 13:30	3	0.45
PNNL_F7	Filter	Ground	12/07/2021 13:30	12/07/2021 16:30	3	0.45
PNNL_F8	Filter	Ground	12/07/2021 16:30	12/07/2021 19:30	3	0.45
PNNL_I1	Impactor	Ground	12/06/2021 19:30	12/07/2021 14:30	19	0.342
PNNL_I2	Impactor	Ground	12/07/2021 14:30	12/07/2021 16:30	2	0.036
PNNL_I3	Impactor	Ground	12/07/2021 16:30	12/07/2021 19:30	3	0.054
SGP_I1	Impactor	Ground	11/15/2021 16:40	11/16/2021 16:26	24	0.432
SGP_I2	Impactor	Ground	11/16/2021 16:54	11/17/2021 14:18	23.7	0.426
SGP_I3	Impactor	Ground	11/17/2021 14:46	11/18/2021 14:32	24	0.432
SGP_F1	Filter	Multiple UAV flights	11/15/2021 16:40	11/18/2021 14:32	15.38	2.31

Table S2. HR-AMS fragmentation table used in this study. Unique differences related to the use of ³⁴SO₄ can be found in the "HR frag sulphate 34" column.

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HR_specMassAlgebra	HR_frag_sulphate	HR_frag_sulphate_34	HR_frag_organic
С			{C},-HR_frag_blackcarbon[{C}]
j13C			0.0108157*HR_frag_organic[{C}]
N			
j15N			
0	0.04*HR_frag_sulphate[{H2O}]	0.04*HR_frag_sulphate_34[{H2O}]	0.04*HR_frag_organic[{H2O}]
НО	0.25*HR_frag_sulphate[{H2O}]	0.25*HR_frag_sulphate_34[{H2O}]	0.25*HR_frag_organic[{H2O}]
j18O	0.00205499*HR_frag_sulphate[{O}]	0.00205499*HR_frag_sulphate_34[{O}]	0.00205499*HR_frag_organic[{O}]
H2O	0.67*HR_frag_sulphate[{SO2}],0.67*HR_frag_sulphate[{SO}]	0.67*HR_frag_sulphate_34[{j34SO2}],0.67*HR_frag_sulphate_34[{j34SO}]	0.225*HR_frag_organic[{CO2}]
Hj18O	0.00205499*HR_frag_sulphate[{HO}]	0.00205499*HR_frag_sulphate_34[{HO}]	0.00205499*HR_frag_organic[{HO}]
H2j18O	0.00205499*HR_frag_sulphate[{H2O}]	0.00205499*HR_frag_sulphate_34[{H2O}]	0.00205499*HR_frag_organic[{H2O}]
CO2plus2			{CO2plus2}
со			0.75*{CO2}
j13CO			0.0108157*HR_frag_organic[{CO}]
Cj18O			0.00205499*HR_frag_organic[{CO}]
S	0.21*HR_frag_sulphate[{SO2}],0.21*HR_frag_sulphate[{SO}],		
j33S	0.00789557*HR_frag_sulphate[{S}]		
j34S	0.0447416*HR_frag_sulphate[{S}]	{j34S}	
CO2			{CO2}
j13CO2			0.0108157*HR_frag_organic[{CO2}]
Cj18OO			0.0041099871*HR_frag_organic[{CO2}]

15 Table S3. Analytical parameters for the MN-AMS, derived from the analysis of standard mixtures. Reported nebulization efficiency is for a solution containing 3 mg L⁻¹ of each of the listed components and syringe pump flow rate of 52 μL min⁻¹. "Required sampling time" gives an estimate of the sampling time needed to reach the limit of quantification (10*standard deviation), based on an average ambient PM concentration of 10 μg m⁻³ and a sampler flow rate of 2.5 L min⁻¹.

Component	Nebulization efficiency (%)	Detection limit (ng)	HR-AMS recovery (%)	Required sampling time (h)
Organic	0.934	2.19	94.0	0.166
SO4	1.24	0.189	104	0.01
NO3	0.775	0.751	87.1	0.074



Figure S1. Comparison between organic and inorganic data derived from a standard collision-type atomizer and the MN-AMS system. a) Organic and sulfate mass spectra derived from atomizing a solution of sucrose and ammonium sulfate. b) The strong correlation ($r^2 = 0.99$) between the systems indicates the micronebulizer and standard atomizer behave similarly with no clear artifacts introduced by the micronebulization procedure.



Figure S2. The HR-AMS measured particle size distribution is modified by the total solute concentration, but not by sample volume nebulized. a) The organic size distribution measured at decreasing total solute concentrations at a syringe pump flow rate of 53
μL/min. The particle size distribution shifts to lower diameters as the total solute concentration decreases, but remains within the 100 % transmittance efficiency range of the HR-AMS. b) The organic and c) sulfate size distributions measured using decreasing syringe pump flow rates. Lower flow rates lead to lower sampled mass, but the mode diameter is not significantly affected.



Figure S3. The HR-AMS-measured mass concentration of different component is highly reproducible across a range of solute concentrations using very low sample volumes (\sim 53 µL) using the Fast-MS mode. The ³⁴SO₄-normalized solution concentrations of organics and SO₄ are well-correlated to the known solution concentrations of sucrose and SO₄.



50 Figure S4. Comparisons of ambient PM_{2.5} samples collected using a UxS filter sampler and a Water-CPC Impactor Sampler at PNNL during the same time period. a) Mass spectra of the filter and impactor, normalized by the total measured PM mass. b) Comparison between the organic mass spectra of the filter and impactor. c) Fraction contribution of the measured PM components in the filter and impactor sample.



Figure S5. ACSM data for the filter and impactor sampling periods indicated in Fig. 4a. The ACSM data is the companion data for Figs. 4b-e, and were used to determine the r^2 shown in Figs. 4b-e.



60 Figure S6. Recreation of Figs. 5 b-e showing only the CHN⁺ and CHON⁺ ions.





Figure S7. a) A typical ToF-SIMS unit mass resolution, positive ion spectrum of an SGP impactor 2. CHN^+ and $CHON^+$ ions are colored in blue, while all other organic species (e.g. CH^+ , CHO^+) are in green. CHN^+ and $CHON^+$ ions are offset by 0.2 *m/z* for clarity when there is overlap with other organic ions. b) A selection of *m/z* values and the high-resolution fittings for the SIMS and AMS. Note that the large differences in instrument sampling and ionization mechanisms precludes specific chemical comparisons. High-resolution fittings are shown to illustrate the similar abundance of nitrogen-containing organics detected by each instrument.