

## Electronic Supplementary Information

### Analysis of Secondary Organic Aerosols in Air Using Extractive Electrospray Ionization Mass Spectrometry (EESI-MS)

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### **A. Sporadic copper contamination in EESI mass spectra**

As noted in the Experimental section of the paper, mass spectra obtained with the EESI-MS system would sometimes contain peaks at  $m/z$  132/134, 122/124, and 63/65 with a 70:30 ratio. The presence of the peaks at  $m/z$  63/65 and the 70:30 ratio were consistent with the prevalent isotopes of copper, suggesting that the higher mass peaks observed were due to adducts of copper. This was further supported by MS-MS studies of  $m/z$  132 and 122 as described below. Various studies, also described below, led to the conclusion that the copper was in the laboratory air, rather than a contamination in the components of the experimental apparatus, solvents, or instrument. Inductively coupled plasma-mass spectrometry (ICP-MS) was used to confirm that copper was indeed present in the air and to estimate its concentration.

***Tandem mass spectrometry (MS/MS) studies:*** Tandem mass spectra of  $m/z$  132 and 122 both showed a primary fragment at  $m/z$  63, consistent with these peaks being the result of adducts to copper-63. The MS/MS of  $m/z$  132 also showed a fragment at  $m/z$  104, corresponding to loss of 28 Da (perhaps CO), and a peak at  $m/z$  63 corresponding to an additional loss of 41 Da (equal to acetonitrile). Copper has been shown to have a strong affinity for CO,<sup>1</sup> so a copper-CO adduct incorporating acetonitrile is feasible. Similarly, the peaks at  $m/z$  122 and 124 are consistent with species in which a copper ion is bound to one acetonitrile and one water molecule.

***Source of copper contamination:*** The copper peaks were not always present and tended to appear in the afternoon. When present, the peaks would appear as soon as the solvent

stream began flowing into the mass analyzer. Cleaning or changing the tubing had no affect on the appearance or disappearance of the copper peaks, suggesting that the copper source could not be the tubing. Remaking the solvent mixture and trying different bottles of acetonitrile also had no impact on the copper peaks. Given that the peaks would be absent in the morning and sometimes appear in the afternoon, it was not likely that the instrument itself was the source of contamination. This led to the conclusion that the contamination must be a transient component in the laboratory air. A possible source could be the building's air intake as air entering the laboratory building passes through a large series of copper coils. The temporal variability in the  $m/z$  132/134 peaks is also consistent with a common environmental source such as the building air intake. If this is the source of the copper, the particles would likely consist of  $\text{Cu}^{2+}$  in the form of  $\text{CuO}$  or  $\text{CuCO}_3$ . The spectra only showed evidence of  $\text{Cu}^+$ , not  $\text{Cu}^{2+}$ . However,  $\text{Cu}^{2+}$  has been shown to be reduced to  $\text{Cu}^+$  in electrospray ionization systems, particularly in the presence of acidic solvents containing acetonitrile.<sup>2,3</sup> It should be noted that the EESI-MS spectra for the reaction products of the ozonolysis of  $\alpha$ -pinene shown in Figures 2 and 3 were taken when there was no evidence of a copper signal. Hence we would not expect to see any copper adducts for the reaction products, nor did we see evidence of such adducts in the spectra.

***ICP-MS study of copper in laboratory air:*** The presence of copper in the laboratory air was confirmed and quantified by drawing air through a bubbler containing 18.2 M $\Omega$ -cm water for several hours. The copper concentration in the water sample was determined using ICP-MS. Using the blank-corrected concentration of copper from the bubbler and

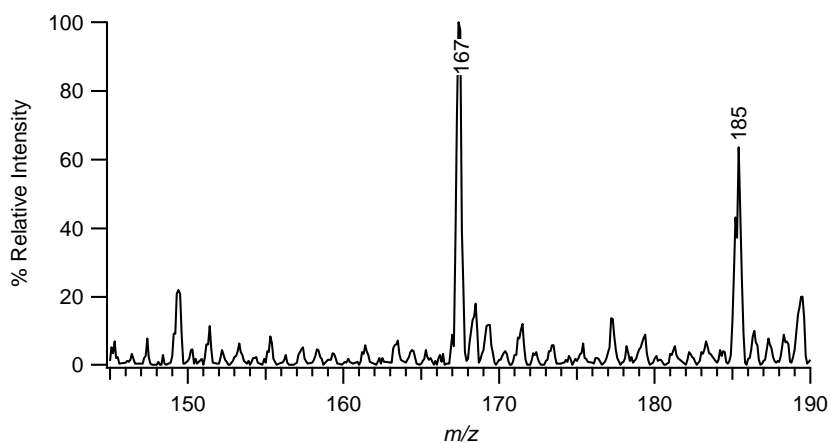
the volume of air that flowed through the bubbler, the concentration of copper in the laboratory air was estimated to be 500-600 ng/m<sup>3</sup>. If the source is small particles becoming dislodged as the air entering the building passes over the copper coils, the particles would be expected to be relatively large, of the order of microns in size. Assuming the particles are spherical with 1 μm diameter, the particle concentration need only be of the order of 0.1 particles/cm<sup>3</sup> in order to generate the observed copper concentrations in air. This type of particle generation would also be expected to be sporadic, as was the case. Using the intensity of the signal at *m/z* 132 in Figure 4 and the intensity of the noise around the signal along with the level of copper in air as determined from ICP-MS, the EESI-MS detection limit is estimated to be 3 ng/m<sup>3</sup> for this particular complex in this solvent system.

#### **B. EESI-MS analysis of *cis*-pinonic standard.**

To estimate the limit of detection of a *cis*-pinonic acid standard, solutions of different concentrations in methanol were atomized to form particles that were analyzed using EESI-MS. Figure S1 shows a typical EESI-MS spectra obtained for a 0.1 mg/mL solution of *cis*-pinonic acid. The peak at *m/z* 185 is attributed to the parent [M + H]<sup>+</sup> ion of *cis*-pinonic acid and the peak at *m/z* 167 is attributed to [M + H - H<sub>2</sub>O]<sup>+</sup>. The intensity ratio of the *m/z* 167 peak to *m/z* 185 peak is 3:2. Solutions at concentrations of 0.2 mg/mL and 0.05 mg/mL produced similar spectra with similar peak ratios. The absolute peak intensities were approximately linearly dependent on solution concentration and particle mass concentration (the latter had a large uncertainty, estimated to be as much as a factor of two, due to some of the size distribution falling outside the SMPS size limit).

In this independent study, peaks attributable to copper contamination were seen at  $m/z$  132/134, and peaks at  $m/z$  247 and 249 (in a 70:30 ratio) were also observed. These peaks can be attributed to copper-63 and copper-65 adducts of *cis*-pinonic acid.

**Figure S1: EESI mass spectrum for the 0.1 mg/mL solution of *cis*-pinonic acid**



#### References cited

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