

# Supporting Information

Sareen et al. 10.1073/pnas.1204838110

## Cloud Droplet Number Calculations

Computation of droplet number  $N_c$  is carried out with the Fountoukis and Nenes (FN) (1) droplet activation parametrization [augmented to account for depletion effects from giant cloud condensation nuclei (CCN) (2)]. FN is a comprehensive and efficient formulation which has been evaluated extensively with numerical simulations (1–3), as well as in situ measurements (4, 5). FN is based on the framework of an ascending adiabatic cloud parcel;  $N_c$  is determined by the maximum supersaturation  $s_{\max}$ , which is controlled by the water vapor balance and is obtained by classifying the droplets by proximity to their critical diameter (“population splitting”). The effective water vapor uptake coefficient (which affects the water vapor mass transfer coefficient during droplet formation) is set to 0.06, following Fountoukis et al. (4). The model was integrated for 2 y with present-day emissions of sulfur and sea salt; monthly, grid-by-grid CCN spectra are then derived from the simulations of the second year.

## Kinetics of Methylglyoxal Hydration and Oligomerization

Methylglyoxal (MG) rapidly reacts with water in aqueous aerosols to form hydrated methylglyoxal (HMG) according to



According to the density functional theory calculations of Krizner et al. (6), the corrected free-energy barrier for this process is 17.3 kcal·mol<sup>-1</sup>, and the preexponential factor is 5 × 10<sup>11</sup> M<sup>-1</sup>·s<sup>-1</sup>, yielding a pseudo-first-order rate constant at 298 K of ~6 s<sup>-1</sup>. Hence, the time required for MG to be 98% converted to its singly hydrated form (7) is ~0.7 s. The apparent enhancement in MG uptake due to hydration is already accounted for in the effective Henry’s Law constant reported by Betterton and Hoffmann ( $H^* = 3.2 \times 10^4$  M·atm<sup>-1</sup>) (7).

The kinetics of MG oligomerization in aqueous solutions containing NH<sub>4</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> were presented by Sareen et al. (8) It was found that the rate-limiting step for the formation of oligomers was the protonation of singly hydrated MG by either NH<sub>4</sub><sup>+</sup> or H<sub>3</sub>O<sup>+</sup>, with second-order rate constants  $k_{\text{H}_3\text{O}^+}^{\text{II}} + \leq 10^{-3}$  M<sup>-1</sup>·min<sup>-1</sup> and  $k_{\text{NH}_4^+}^{\text{II}} = 5 \times 10^{-6}$  M<sup>-1</sup>·min<sup>-1</sup>. The conversion rate of HMG is described by the following equation:

$$R = \left( k_{\text{H}_3\text{O}^+}^{\text{II}} [\text{H}_3\text{O}^+] + k_{\text{NH}_4^+}^{\text{II}} [\text{NH}_4^+] \right) [\text{HMG}] \quad [\text{S2}]$$

In the aerosol experiments presented here, [NH<sub>4</sub><sup>+</sup>] = 28 M and [H<sub>3</sub>O<sup>+</sup>] = 7 M. Because the oligomerization reactions are relatively slow compared with the diffusional timescale in the aerosol particle,  $\tau = R^2/D$ , where  $R$  is the characteristic length scale and  $D$  is the diffusion coefficient, we expect that the concentration of HMG in the particle is spatially uniform and maintained relatively constant via MG absorption from the gas phase according to Henry’s Law. Based on a gas-phase MG concentration of 250 parts per billion (ppb), [HMG] = 8 × 10<sup>-3</sup> M. After 3 h of reaction, the total amount of MG sequestered as oligomeric products is between 2.02 × 10<sup>-4</sup> M and 1.03 × 10<sup>-2</sup> M. The total concentration of MG and products is then 0.031–6.06 × 10<sup>-4</sup> mol·C·kg<sup>-1</sup> H<sub>2</sub>O.

## Inorganic:Organic Ratio

This ratio for the chamber filter extracts was calculated based on water-soluble organic carbon (WSOC) and ion chromatography

(IC) analysis. The inorganic on the filter was 1.57 × 10<sup>4</sup> μg and the water-soluble organic matter was 18.928 μg, giving a ratio of 829.4. For comparison, this ratio is also calculated for the particles in the chamber. Based on 250 ppb of MG in the chamber and a Henry’s Law constant of 3.2 × 10<sup>4</sup> M·atm<sup>-1</sup>, the in-particle concentration of MG is 0.008 M. Following Tang and Munkelwitz (9), a 0.2-M ammonium sulfate atomizer solution will lead to an in-particle concentration of 14 M at 65% relative humidity (RH). The inorganic:organic ratio for the chamber based on these numbers is 3,209. The ratio of inorganic:organic material in the filter extracts is lower than that predicted based on Henry’s Law uptake of MG to the particles. This could be due to continued reactive uptake of the gas-phase organic on the filter during particle collection.

## Köhler Theory Analysis

The following equations from Moore et al. (10) were used to infer surface tension of the particles:

$$\sigma = \left[ \frac{\left( \frac{\rho_o}{M_o} \right) \varepsilon_o \nu_o + \frac{\rho_i}{M_i} \varepsilon_i \nu_i}{\frac{256}{27} \left( \frac{M_w}{\rho_w} \right)^2 \left( \frac{1}{RT} \right)^3 \omega^{-2}} \right]^{1/3} \quad [\text{S3}]$$

where the subscripts  $i$ ,  $o$ , and  $w$  refer to the inorganic, organic, and water, respectively.  $M$  is the average molecular weight,  $\rho$  is the density,  $\nu$  is the effective van’t Hoff factor,  $R$  is the universal gas constant,  $T$  is the median temperature of the continuous-flow streamwise thermal gradient CCN chamber (CFSTGC) column,  $\sigma$  is the surface tension, and  $\varepsilon$  is the mass fraction calculated as

$$\varepsilon_i = \frac{\frac{m_i}{m_i + m_o}}{\frac{\rho_i}{\rho_i + \rho_o}} \quad [\text{S4}]$$

$\omega$ , the fitted CCN activity factor, is determined from the critical supersaturation ( $S_c$ ) and the critical dry activation diameter ( $d_d$ ) using the equation

$$S_c = \omega d_d^{-3/2} \quad [\text{S5}]$$

## Surface Tension of the Particle Based on Henry’s Law

The surface tension of the aerosol particles can be estimated using the Szyszkowski–Langmuir equation:

$$\sigma = \sigma_0 - aT \ln(1 + bC) \quad [\text{S6}]$$

where  $\sigma$  and  $\sigma_0$  are the surface tension with and without the organics, respectively,  $T$  is temperature,  $C$  is the carbon content, and  $a$  and  $b$  are fit parameters. Although the particles studied here were composed of ammonium sulfate, we are interested in calculating the surface tension of the particle at the moment of activation. At that point, the particle is composed mostly of water. Therefore, values for  $a$  and  $b$  are taken from the surface tension measurements done on a MG and water solution using pendant drop tensiometry:  $a = 0.0244$  dyn·cm<sup>-1</sup> K<sup>-1</sup> and  $b = 3.050$  kg water (mol·C)<sup>-1</sup>.  $\sigma_0$  was tested in our laboratory using Millipore water and found to be 72.55 dyn·cm<sup>-1</sup>.

$C$  is calculated based on the assumption that the droplet is in Henry's Law equilibrium with the gas phase, and that the total contribution of oligomeric products formed before activation is small. Hence, based on 250 ppb MG in the chamber (and CFSTGC), we calculate an  $8 \times 10^{-3}$  M MG concentration, or 0.0240 mol C (kg water) $^{-1}$ . Plugging these values into the Szyszkowski–Langmuir equation gives a value of 72.02 dyn-cm $^{-1}$  for the surface tension of the MG and ammonium sulfate particles. Surface tension depression will lower the value of  $\kappa$  by a factor of

$$\left(1 - \frac{\Delta\sigma}{\sigma_w}\right)^{-3} \quad [S7]$$

where  $\Delta\sigma$  is the surface tension depression from that of pure water. In our case, the calculated surface tension value of 72.02 dyn-cm $^{-1}$  will lead to a very small (2.2%) increase in  $\kappa$ , much less than the enhancement in CCN activity seen in our chamber studies.

For acetaldehyde, the constants  $a$  and  $b$  are taken from the surface tension measurements done on an acetaldehyde and water solution using pendant drop tensiometry:  $a = 0.0037$  dyn-cm $^{-1}$ ·K $^{-1}$  and  $b = 491.64$  kg water (mol C) $^{-1}$  (11). Based on 250 ppb acetaldehyde in the chamber and a Henry's Law constant of 11.4 M/atm, the acetaldehyde concentration in a particle is  $2.85 \times 10^{-6}$  M, or  $5.7 \times 10^{-6}$  mol C (kg water) $^{-1}$ . These values give a surface tension of 73.16 dyn-cm $^{-1}$  for the surface tension of the acetaldehyde and ammonium sulfate particles and will lead to a negligible change in  $\kappa$  of 0.01%.

#### Concentration of MG at the Moment of Activation

The critical wet diameter  $D_c$  is

$$D_c = \left(\frac{3k}{A}\right)^{0.5} d_d^{1.5} \quad [S8]$$

where  $\kappa$  is the hygroscopicity parameter, calculated from CCN activity data following Petters and Kreidenweis (12), and

$$A = \frac{4\sigma M_w}{RT\rho_w} \quad [S9]$$

Based on the amount of MG in the chamber (250 ppb), we can calculate the number of molecules of MG at each  $d_d$ . Because the number of molecules is constant in the particle, it can be divided by the corresponding volume at  $D_c$  to get the concentration at the activated diameter.

In the chamber experiments, the estimated concentration of MG in the particles at the moment of activation (using Henry's Law) ranged from  $1.17 \times 10^{-5}$  to  $3.22 \times 10^{-5}$  M and for the filter extracts ranged from  $1.24 \times 10^{-4}$  to  $4.53 \times 10^{-5}$  M, orders of magnitude lower than for the atomized bulk solutions (from  $1.59 \times 10^{-2}$  to  $2.86 \times 10^{-3}$  M).

#### Calibration of Supersaturation in the CCN Counter

The effective supersaturation in the CCN instrument depends on the flow rate, pressure, and temperature gradient applied on the column (13). Scanning mobility CCN analysis (SMCA) with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> calibration aerosol is used to determine supersaturation for a given set of operating conditions, following the procedure of Moore et al. (10). Calibration aerosol is generated by atomizing an ammonium sulfate solution in pure water. Atomized droplets were dried in a silica gel dryer and sampled by a differential mobility analyzer (DMA; TSI 3081 Long DMA), which classifies the aerosol, and then introduced into the CFSTGC and a condensation particle counter (CPC; TSI 3010). The voltage applied to the DMA was scanned, and inversion of the time series of CCN and CPC counts yields the fraction of

classified particles that act as CCN ("activation curve"). The dry mobility diameter for which half of the classified particles act as CCN,  $d_{50}$ , is used to characterize instrument supersaturation (being equal to the critical supersaturation of particles with dry diameter equal to  $d_{50}$ ). Köhler theory is used to compute the effective instrument supersaturation, assuming the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles have (at the point of activation) the surface tension and density of pure water, and a variable van't Hoff factor is used as described in Moore et al. (10).

#### Use of Nonacidified (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as the Control

We have used ISORROPIA to compare the apparent hygroscopicity parameter  $\kappa$  for the acidified and nonacidified (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> compositions at pH = 0 and 2 are determined as follows: pure 0.2 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is taken and enough H<sub>2</sub>SO<sub>4</sub> is added so that the pH is 0 and 2, respectively. Assuming that sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (SA) and NH<sub>4</sub>HSO<sub>4</sub> (AB) dissociate completely in solution, we have that the dry material is 37% (by mass) AB + 63% SA for the pH 0 aerosol, and 6% AB + 94% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> for the pH = 2 aerosol.

These compositions are then used in ISORROPIA to determine the amount of water associated with each constituent [SA, AB, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] at various RH values. Given that our dryer reaches 5–10% RH, for the pH = 0 solution there is about 25% (by volume) water. This is justified because H<sub>2</sub>SO<sub>4</sub> is so hygroscopic that it never releases all of its water, even at single-digit RH. The particle sized at 5–10% RH will have 75% volume of salt and the rest is water.  $\kappa$  is then calculated to be ~0.6. Similar results are seen for the pH = 2 aerosol.

In both the acidified cases,  $\kappa$  is predicted to be close to that of pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and hence we can use pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as the control in our studies.

#### Depletion of MG in the Gas Phase

We operate our chamber as a continuous-flow stirred tank reactor. That is, after the initial startup period, conditions are at steady state inside the chamber, and the residence time for gases and particles in the chamber  $\tau$  is given by

$$\tau = \frac{V}{F}$$

where  $V$  is the reactor volume (3.5 m<sup>3</sup>) and  $F$  is the total volumetric flow rate through the reactor.

We calculate the depletion of MG in the chamber in two ways: first, assuming that Henry's Law uptake is valid; and second, based on surface adsorption.

**Henry's Law Uptake.** Assuming Henry's Law describes the uptake of gas-phase MG to the particles, the particle-phase concentration of MG is directly proportional to the gas-phase concentration according to

$$[MG]_{aq} = H^* P_{MG}$$

where  $H^*$  is the effective Henry's Law constant. From Betterton and Hoffman (7),  $H^* = 3.2 \times 10^4$  M·atm $^{-1}$ . Hence, with 250 ppb MG in the gas phase,  $[MG]_{aq} = 8 \times 10^{-3}$  M.

After the particles have equilibrated with MG in the chamber, the maximum amount of MG taken up from the gas phase will be

$$\text{uptake} = N_p V_p [MG]_{aq} N_A = 2.5 \times 10^{11} \text{ molec}/(\text{cm}^3 \text{ gas})$$

Here,  $N_p \sim 10^6$  particles cm $^{-3}$  gas,  $V_p = \frac{4}{3}\pi(231 \times 10^{-7} \text{ cm})^3$  ( $\frac{1 \text{ L}}{1000 \text{ cm}^3}$ ) [=] L particle $^{-1}$ ,  $N_A =$  Avogadro's number, and 250 ppb corresponds to a total initial gas-phase MG concentration

of  $6.15 \times 10^{12}$  molec  $\text{cm}^{-3}$ . Therefore, uptake of MG to the particles will deplete the gas-phase concentration by at most 4%. For the 8 ppb MG case, the depletion is negligible.

**Surface Adsorption.** We may also assume a model of adsorption of gas-phase MG to the particle surface. A reasonable estimate is that each MG molecule occupies  $50 \text{ \AA}^2$  on the surface. In this case, the formation of a full monolayer of MG on one 203-nm (surface-weighted) particle will result in the uptake of  $1.04 \times 10^6$  molecules MG. There are no experimental data available to allow us to predict the surface coverage as a function of MG partial pressure so we will assume full monolayer coverage in these calculations.

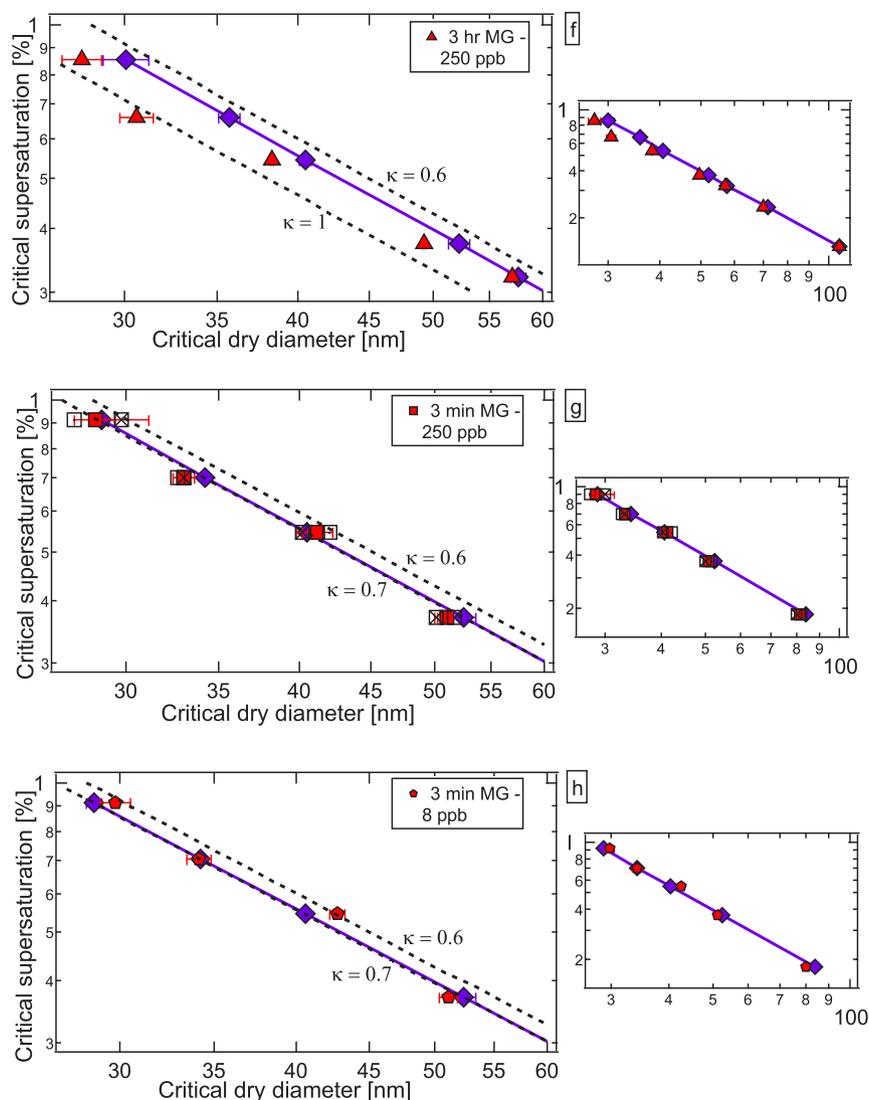
After the particles have equilibrated with MG in the chamber, the maximum amount of MG taken up from the gas phase (per cubic centimeter of gas) will be  $1.04 \times 10^{12}$  molec  $\text{cm}^{-3}$  MG, 5×

that taken up in the Henry's Law scenario. This would result in up to 16% depletion of gas-phase MG. For the 8 ppb MG, we estimate 14% depletion.

We also performed similar calculations for observed concentrations in the atmosphere (urban:  $10^4 \text{ cm}^{-3}$ , 2.5 ppb MG; wet-season Amazon:  $10^2 \text{ cm}^{-3}$ , 0.125 ppb MG). Based on Henry's Law, we calculate negligible depletion for both urban and wet-season Amazon. Taking into account only surface adsorption, we calculate 17% depletion in the urban scenario and 3% depletion in the Amazon. Hence, we do not anticipate depletion effects to be prominent. Given that we are considering full monolayer coverage, these calculations represent the upper limit for depletion. For acetaldehyde, we expect lesser depletion because its Henry's Law constant is 1,000× smaller than MG and it is also slightly more prominent in the atmosphere compared with MG.

1. Fountoukis C, Nenes A (2005) Continued development of a cloud droplet formation parameterization for global climate models. *J Geophys Res* 110(D11):D11212.
2. Barahona D, et al. (2010) Comprehensively accounting for the effect of giant CCN in cloud activation parameterizations. *Atmos Chem Phys* 10(5):2467–2473.
3. Ghan S (2011) Droplet nucleation: Physically-based parameterizations and comparative evaluation. *J Adv Model Earth Sys* 3(M10001):33.
4. Fountoukis C, et al. (2007) Aerosol-cloud drop concentration closure for clouds sampled during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign. *J Geophys Res* 112(D10):D10S30.
5. Meskhidze N, Nenes A, Conant WC, Seinfeld JH (2005) Evaluation of a new cloud droplet activation parameterization with in situ data from CRYSTAL-FACE and CSTRIFE. *J Geophys Res* 110(D16):D16202.
6. Krizner HE, De Haan DO, Kua J (2009) Thermodynamics and kinetics of methylglyoxal dimer formation: A computational study. *J Phys Chem A* 113(25):6994–7001.
7. Betterton EA, Hoffmann MR (1988) Henry's law constants of some environmentally important aldehydes. *Environ Sci Technol* 22(12):1415–1418.
8. Sareen N, Schwier AN, Shapiro EL, Mitroo D, McNeill VF (2010) Secondary organic material formed by methylglyoxal in aqueous aerosol mimics. *Atmos Chem Phys* 10(3):997–1016.
9. Tang IN, Munkelwitz HR (1994) Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance. *J Geophys Res* 99(D9):18801–18808.
10. Moore RH, Nenes A, Medina J (2010) Scanning Mobility CCN Analysis - A method for fast measurements of size-resolved CCN distributions and activation kinetics. *Aerosol Sci Technol* 44(10):861–871.
11. Li Z, Schwier AN, Sareen N, McNeill VF (2011) Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: Surface tension depression and secondary organic products. *Atmos Chem Phys* 11(22):11617–11629.
12. Petters MD, Kreidenweis SM (2007) A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos Chem Phys* 7(8):1961–1971.
13. Lance S, Medina J, Smith JN, Nenes A (2006) Mapping the operation of the DMT continuous flow CCN counter. *Aerosol Sci Technol* 40(4):242–254.





**Fig. S1.** CCN activity data. Humidified, acidified  $(\text{NH}_4)_2\text{SO}_4$  aerosols were exposed to gas-phase MG or acetaldehyde in a  $3.5\text{-m}^3$  Teflon reaction chamber or a glass flow tube for varying residence times. The critical dry diameters observed for each experiment as a function of instrument supersaturation are compared with the  $(\text{NH}_4)_2\text{SO}_4$  control (purple diamonds) to demonstrate the effect of organics. Closed and open symbols represent the first and second trials for each time point, respectively. Small graphs on the right represent the entire range of supersaturations studied, whereas the main plots zoom in on the smaller diameters. Dashed lines show values of constant  $\kappa$ , ranging from our  $(\text{NH}_4)_2\text{SO}_4$  control ( $\kappa \sim 0.6$ ) to the maximum  $\kappa$ -value observed for each experiment. (A and B) Results for particles exposed to 250 and 8 ppb MG for 5 h, respectively. (C and D) Results for particles exposed for 5 h, respectively. (E) Particles were exposed to 8 ppb MG and 8 ppb acetaldehyde for 5 h. (F) Particles were exposed to 250 ppb MG for 3 h. (G and H) Results for particles exposed to 250 and 8 ppb MG for 3 min in the flow-tube reactor, respectively.





**Table S2. Exponents of the power log fits for the supersaturation vs. dry diameter graphs for the various chamber experiments**

Experiment	Average power log fits (exponent)
$(\text{NH}_4)_2\text{SO}_4$	$-1.52 \pm 0.03$
5 h, 250 ppb MG	$-1.34 \pm 0.09$
3 h, 250 ppb MG	$-1.37$
3 min, 250 ppb AC	$-1.42 \pm 0.03$
5 h, 8 ppb MG	$-1.34 \pm 0.09$
3 min, 8 ppb MG	$-1.51$
5 h, 250 ppb AC	$-1.47 \pm 0.06$
5 h, 8 ppb AC	$-1.59 \pm 0.001$
5 h, 8 ppb AC, 8 ppb MG	$-1.57 \pm 0.04$

As expected, these values deviate from the pure  $(\text{NH}_4)_2\text{SO}_4$  calibration curve. AC, acetyldehyde.

**Table S3. Hygroscopicity parameter,  $\kappa$ , values for the different bulk studies**

Experiment	Average $\kappa$
$(\text{NH}_4)_2\text{SO}_4$	$0.60 \pm 0.18$
0.5 M MG	$0.12 \pm 0.04$
0.5 M MG, 3.1 M $(\text{NH}_4)_2\text{SO}_4$	$0.68 \pm 0.09$
0.5 M AC	$0.44 \pm 0.13$
0.5 M AC, 3.1 M $(\text{NH}_4)_2\text{SO}_4$	$0.62 \pm 0.19$
0.5 M MG, 0.5 M AC	$0.11 \pm 0.03$
0.5 M MG, 0.5 M AC, 3.1 M $(\text{NH}_4)_2\text{SO}_4$	$0.59 \pm 0.18$

Bulk aqueous solutions containing 0.5 M of the organic (methylglyoxal and/or acetaldehyde) with and without 3.1 M  $(\text{NH}_4)_2\text{SO}_4$  were allowed to react for 24 h, and were then atomized and analyzed using the CFSTGC.