

Characterization of Liquid Smoke by Size Distribution and Kappa Values

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Abstract

Liquid smoke has potential to be a proxy for biomass burning in aerosol research. Liquid smoke can be successfully run through a variety of aerosol research instruments to get the size distribution and kappa values. The size distribution of Wright's Mesquite liquid smoke has a peak around 40.0 nm and has kappa values around 0.81 that show that it is more hygroscopic than ammonium sulfate which has a kappa value of 0.61 but less hygroscopic than salt which has a kappa value of 1.28.

1. Introduction

Biomass burning is an important part of the Earth's global carbon cycle (Bowman et al. 2009). The aerosols and greenhouse gasses emitted during burning can alter atmospheric processes such as the warming of the earth and changes in the microphysics of clouds (Petters et al. 2009). Additionally, biomass burning is important because it can affect human health and living conditions. Research has been conducted where biomass is burned, and emissions measured to study interactions between biomass burning and the atmosphere. The difficulty in these studies is that there is no laboratory standard for the emissions. In each biomass burning experiment, different biomass substances are used which leads to different results since each substance produces aerosols with different properties. One important property is the hygroscopicity parameter of the biomass emissions. Kappa is a hygroscopicity parameter that relates dry diameter of a particle and the cloud condensation nuclei (CCN) activity (Petters and Kreidenweis 2008). Calculating Kappa is valuable for any experiment that has to do with aerosols or mixtures of different types of aerosols since it encapsulates the chemical component effect on cloud droplet activation into a single parameter. Table 1 shows that Kappa values range from 0.0 for insoluble soot to 1.0 for soluble salts.

Table 1: Table showing Kappa values for different chemical compounds of aerosols (Petters and Kreidenweis 2008) and (D. Rose et, al. 2010).

Compound	Soot	Ammonium Sulfate ((NH ₄) ₂ SO ₄)	3:7 Organic: Inorganic Material	Sulfuric Acid (H ₂ SO ₄)	Sodium Chloride (NaCl)
Kappa	0.00	0.61	0.62	0.90	1.28

When fresh biomass (fresh leaves, pine needles, and plants) is burned, it mixes externally and the instruments used to measure Kappa values have issues eliminating multiply charged particles, which causes inaccurate size distribution measurements and Kappa calculations. From what was able to be determined, the Kappa values for multiple types of smokes ranges from 0.06 to 0.7 (Petters et. al. 2009). Also, fresh biomass has a complex chemistry where smaller particles are less

hygroscopic than large particles. Liquid smoke has the potential to reduce these issues and become a standard for biomass burning research.

Liquid smoke is a manufactured food flavor enhancer and preservative (Simon et al. 2005) made by condensing smoke produced by burning wood chips in a limited oxygen environment. The smoke condenses to the sides of the burn chamber and is collected and refined (Montazeri et. al. 2013). Different types of woods are burned at certain temperatures to produce the different kinds of liquid smokes. Liquid smoke can be mixed with ultra-purified water to form a solution which can be aerosolized and sampled with many types of aerosol instruments without complication. To determine if liquid smoke is a good proxy for biomass burning, lab measurements of the aerosol size distribution and Kappa values are necessary. These parameters should be similar to biomass burning smoke values if liquid smoke is used as a laboratory proxy.

2. Methodology

a. Apparatus and Instruments

To determine the particle size distribution of liquid smoke and Kappa values, a variety of instruments are used. The TSI Aerosol Generator (Model 3076) generates polydisperse aerosols from a solution of liquid smoke and ultra-pure water. The aerosols are dried using a diffusional dryer containing Alfa Aesar molecular sieve 13X beads. A dilution system consisting of a filter and metering valve sets the concentration within the range where the instruments can accurately count. A TSI Scanning Mobility Particle Sizer (SMPS) Model 3080, made up of a TSI Differential Mobility Analyzer (DMA) Model 3081 and TSI Condensation Particle Counter (CPC) Model 3772, measures the particle size distribution. The SMPS utilizes a bipolar charger to produce an aerosol sample with a known charge distribution so counting the number of single charged particles gives the total number of particles. The DMA separates particles by size using their electric mobility, which is inversely proportional to the size of the particle and proportional to the number of charges on the particle. The DMA allows particles of the selected size to exit the column for counting by the CPC. The CPC pulls the aerosol sample into a heated saturator where butanol vapor saturates the sample stream. A condenser cools the sample stream to create a supersaturated environment with respect to the butanol vapor. The vapor condenses onto particles and grows large enough to be counted by an optical particle counter system, which enables the model 3772 CPC to count all particles larger than 10 nm in diameter (Agarwal, 1980). Figure 1 shows the setup of these instruments that were used to get the particle size distribution of liquid smoke.

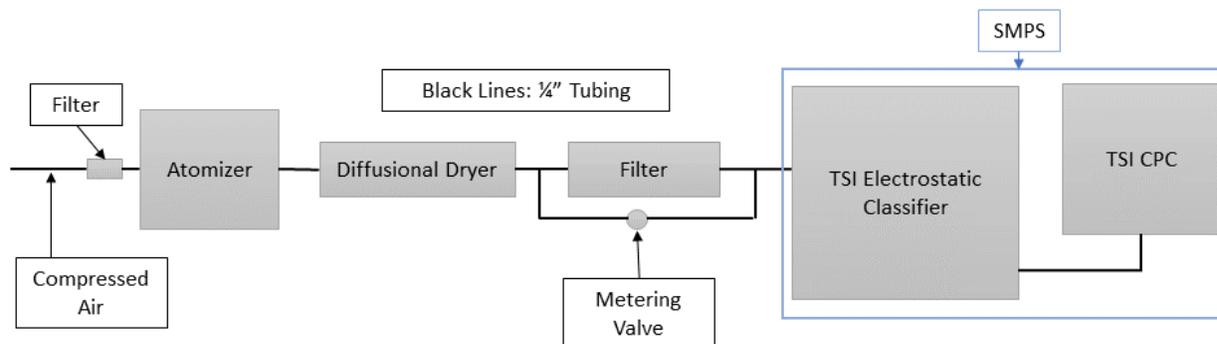


Figure 1: Lab apparatus used to measure the particle size distribution. The Spectral Mobility Particle Sizer (SMPS) is made up of the Electrostatic Classifier and a model 3772 Condensation Particle Counter (CPC).

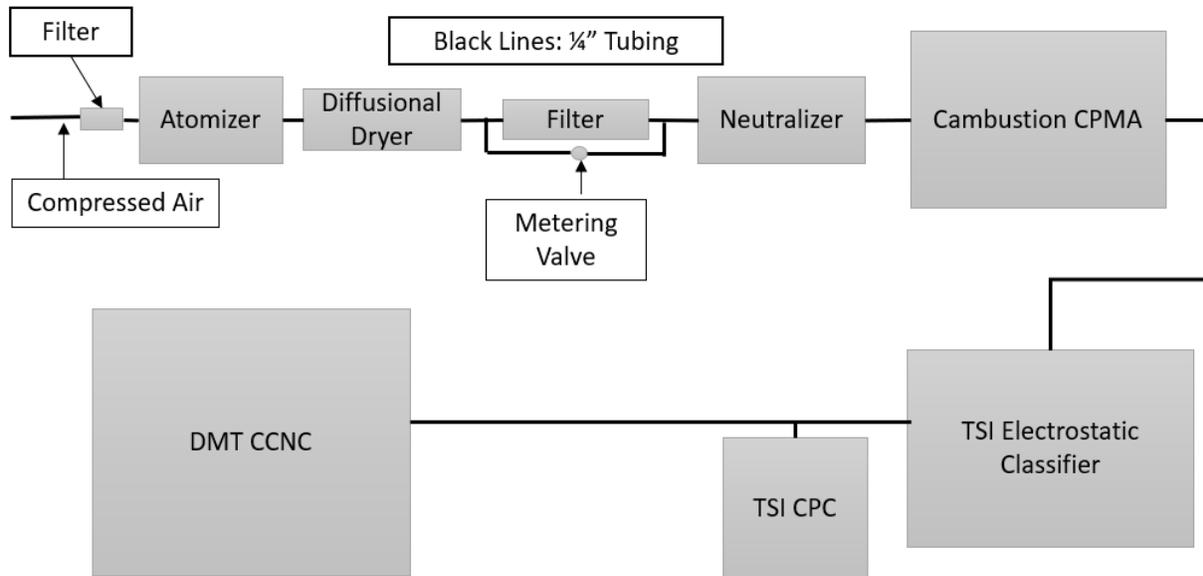
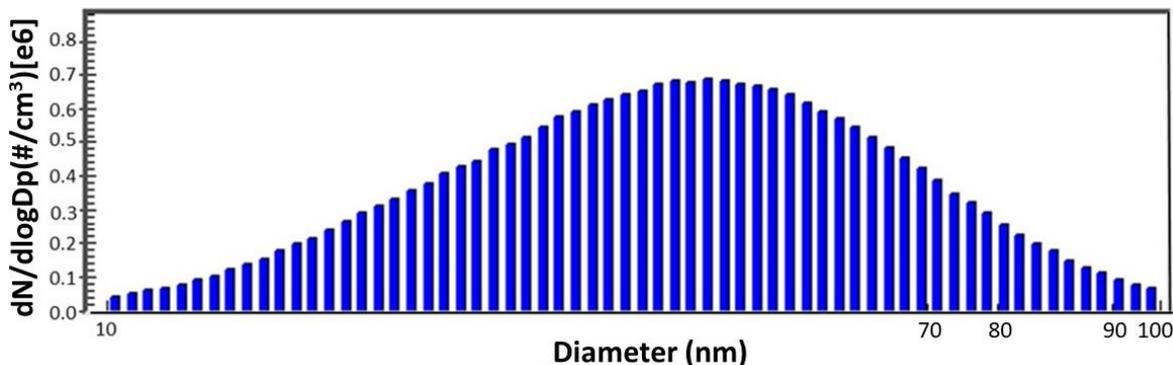


Figure 2: Diagram showing the lab apparatus that is used to obtain data to determine the activation ratios. The Centrifugal Particle Mass Analyzer (CPMA) is used to eliminate the issue with multiple charge particles in the electrostatic classifier. Size selected stream of particles are concurrent measurements with Condensation Particles Counter (CPC) and Cloud Condensation Nuclei Counter (CCNC).

In addition to a TSI Aerosol Generator, diffusional dryer, and TSI SMPS, a Combustion Centrifugal Particle Mass Analyzer (CPMA) and a Droplet Measurement Technology (DMT) Cloud Condensation Nuclei (CCN) Counter are used to determine the Kappa values (Figure 2). The DMT CCNC is an instrument that can measure CCN concentration by creating a supersaturated environment using a temperature gradient in a vertical column. The column's maximum supersaturation can be set from 0.1 % to 3.0 % supersaturation (Roberts and Nenes 2005). The aerosols flow into the CCN counter, enter the supersaturated environment, grow by the condensation of water vapor, and are detected at the column exit using an optical particle counter system. (Roberts and Nenes 2005). The CPMA is similar to the DMA in selecting certain particles; however, the CPMA classifies particles by their mass to charge ratio instead of electric charge to aerosol drag ratio. Electric charge and aerosol drag depends on particle morphology, which require empirical factors to account for the varying particle morphology. The CPMA allows the particle to be classified based on mass and overcome the issues with morphology. The CPMA utilizes opposite electrical and centrifugal fields to classify aerosols. To select different masses, the electrical field and rotation speed can be varied (Olfert and Collings 2005).

b. Particle Size Distribution of Liquid Smoke

To determine the size distribution of liquid smoke, a solution must be made consisting of liquid smoke (Wright's Mesquite Liquid Smoke) and ultra-pure water. A solution of 0.21 ml of liquid



smoke to 700 ml pure water (a ratio of 3/10,000) is mixed for use by the Aerosol Generator. The generated aerosols are dried and the SMPS used to measure the particle size distribution (Figure 3). The SMPS voltage range is set to measure particles from 10 to 100 nm. The size distribution of a solution of 0.03 % liquid smoke and ultra-pure water has a peak diameter of 45 nm.

Figure 3: The particle size distribution of solution (0.03%) of liquid smoke and ultra-pure water measured using the setup in **Error! Reference source not found.**

c. Activation Curves of Liquid Smoke

Cloud Condensation Nuclei (CCN) supersaturation spectrum measurements are combined with the SMPS measured particle size distribution to determine the Kappa values of liquid smoke. Activation curves of the CCN to CPC ratio are used to determine the critical supersaturation for a specific particle size. To obtain CCN to CPC ratios, the liquid smoke solution is used in the aerosol generator to produce particles that are drier, neutralizer, and size selected by the CPMA (Figure 2). Five particle sizes (40.0 nm, 55.2 nm, 71.0 nm, 85.0 nm, and 98.2 nm) on the right-hand side of the particles size distribution are used for determining Kappa. The liquid smoke solution of 0.03 % is used so that all particles sizes are on the right-hand side of the distribution, so effects of double charged particles are minimized. When size selecting particles with the Electrostatic Classifier, particles can be singly, doubly and triply charged. A particle that has a single charge has almost the same electric mobility as a particle twice the diameter with two charges. Selecting particles on the right-hand side of the particle size distribution gives fewer particles with diameters larger than what is selected so there are fewer particles with the same electric mobility but doubly charged. Additionally, the CPMA is used before the Electrostatic Classifier to greatly reduce the issue with multiple charged particles.

Size selected particles are concurrently measured by the CPC, which pulls 1.0 lpm and the CCN counter, which pulls 0.5 lpm of air. Before each laboratory experiment, the CPC and CCN counter data acquisition systems are time synced manually. The CCN counter is operated over a range of supersaturations (Table 2). After each change in supersaturation, the temperature is allowed to stabilize for 4 min before 1 min of data is collected. A rough estimate of the CCN concentration

and CPC concentration is manually calculated and noted in the experiment's log book, and an estimate of the activated ratio is determined at the end each supersaturation run.

Table 2: Table of percentage of supersaturation set points (SS% Set Points) for the Cloud Condensation Nuclei (CCN) counter used for determining the activation curves of liquid smoke for the different diameter particles.

Diameter	SS% Set Points
40.0 nm	0.10, 0.15, 0.24, 0.30, 0.34, 0.37, 0.45, 0.50, 0.52, 0.55, 0.57, 0.60, 0.70, 0.80, 0.90, 1.0
55.2 nm	0.10, 0.15, 0.19, 0.24, 0.30, 0.34, 0.37, 0.40, 0.45, 0.50, 0.60, 0.70, 0.80, 0.90
71.0 nm	0.10, 0.15, 0.19, 0.24, 0.30, 0.34, 0.37, 0.40, 0.45, 0.50, 0.60, 0.70, 0.80, 0.90
85.0 nm	0.11, 0.15, 0.17, 0.18, 0.19, 0.24, 0.30, 0.34, 0.37, 0.40, 0.45, 0.50, 0.60
98.2 nm	0.10, 0.13, 0.14, 0.15, 0.16, 0.18, 0.19, 0.24, 0.30, 0.40, 0.45, 0.50, 0.60, 0.70

3. Results

a. Data Processing for Activation Curves

The sigmoid fit uses Equation 1:

$$Y = D / (1 + ae^{(-b(X-c))}) \quad (\text{Eq. 1})$$

where Y represents the ratio of CCN concentration to CPC concentration, X represents the corresponding supersaturation, and a, b, c, and Dare constants calculated based on the best fit that minimizes the sum of absolute errors. Creating these activation curves is done for several particle diameters (Table 2). To calculate Kappa value for a specific size of aerosol, the critical supersaturation has to be determined by finding the point where the activated ratio is fifty percent of the difference between the maximum and minimum values. The critical supersaturation is converted into a saturation ratio. For example, a supersaturation of 0.8% has a saturation ratio of 1.008. The critical supersaturation ratios for varying diameters are listed in Table 3.

Table 3: Saturation Ratios corresponding to varying diameters of liquid smoke

Diameter	40.0 nm	55.2 nm	71.0 nm	85.0 nm	98.2 nm
Saturation Ratio	1.0055	1.0034	1.0024	1.0018	1.0015

Since the critical saturation ratio can be found, the Critical Saturation Ratio Equation (Rose et. al, 2008) (Eq. 2) can be manipulated to determine the Kappa values.

$$Sc = e^{\sqrt{((4A^3) \div (27 \kappa Ds^3))}} \quad (\text{Eq. 2})$$

$$A = (0.66 \times 10^{-6} Km) \div T \quad (\text{Eq. 3})$$

Equations 2 and 3 calculate the critical saturation ratio for a selected dry diameter (Ds) and the temperature (T) in Kelvin. Since the critical saturation ratio is already known the equation can be manipulated (Eq. 4) to calculate the Kappa value (κ).

$$\kappa = (4A^3) \div (27Ds^3(\ln(Sc))^2) \quad (\text{Eq. 4})$$

Using these equations with the calculated critical supersaturation ratios (Sc) listed above and the Temperature (T) in Kelvin, the Kappa values can be calculated. The Kappa values that were calculated for this experiment are listed in **Error! Reference source not found.** Figure 4 is an example of the activation curve. The activation curves for 55, 71, 85, and 100 nm diameter particles are shown in Figure 5. As the particle size increase the critical supersaturation decrease.

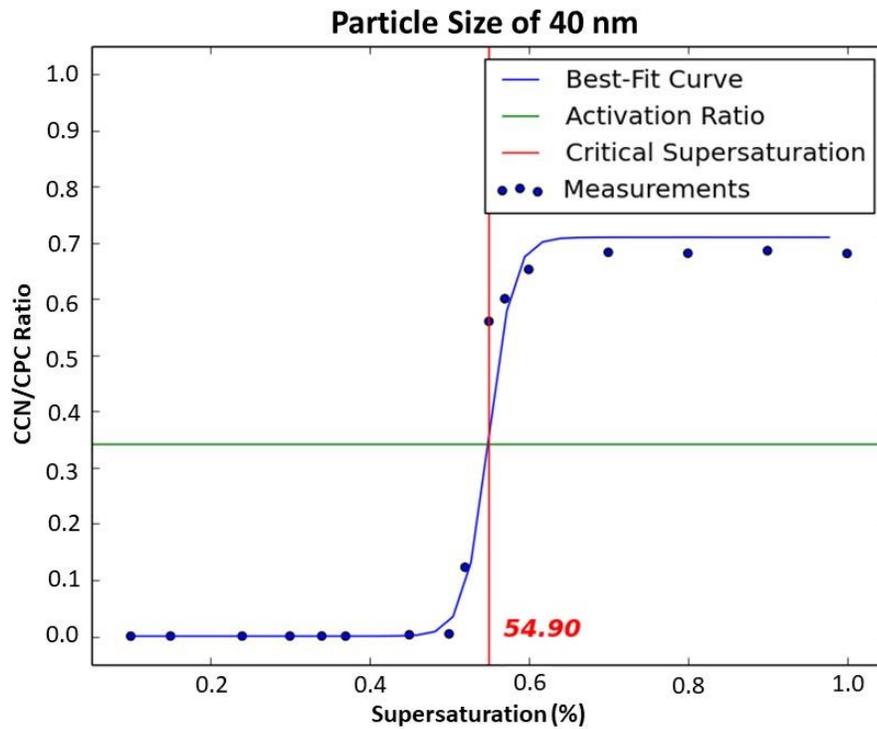


Figure 4: Image Displaying the Activation Curve used to find the Critical Supersaturation of Liquid Smoke at 40.0 nm. The critical supersaturation for each diameter is represented in red.

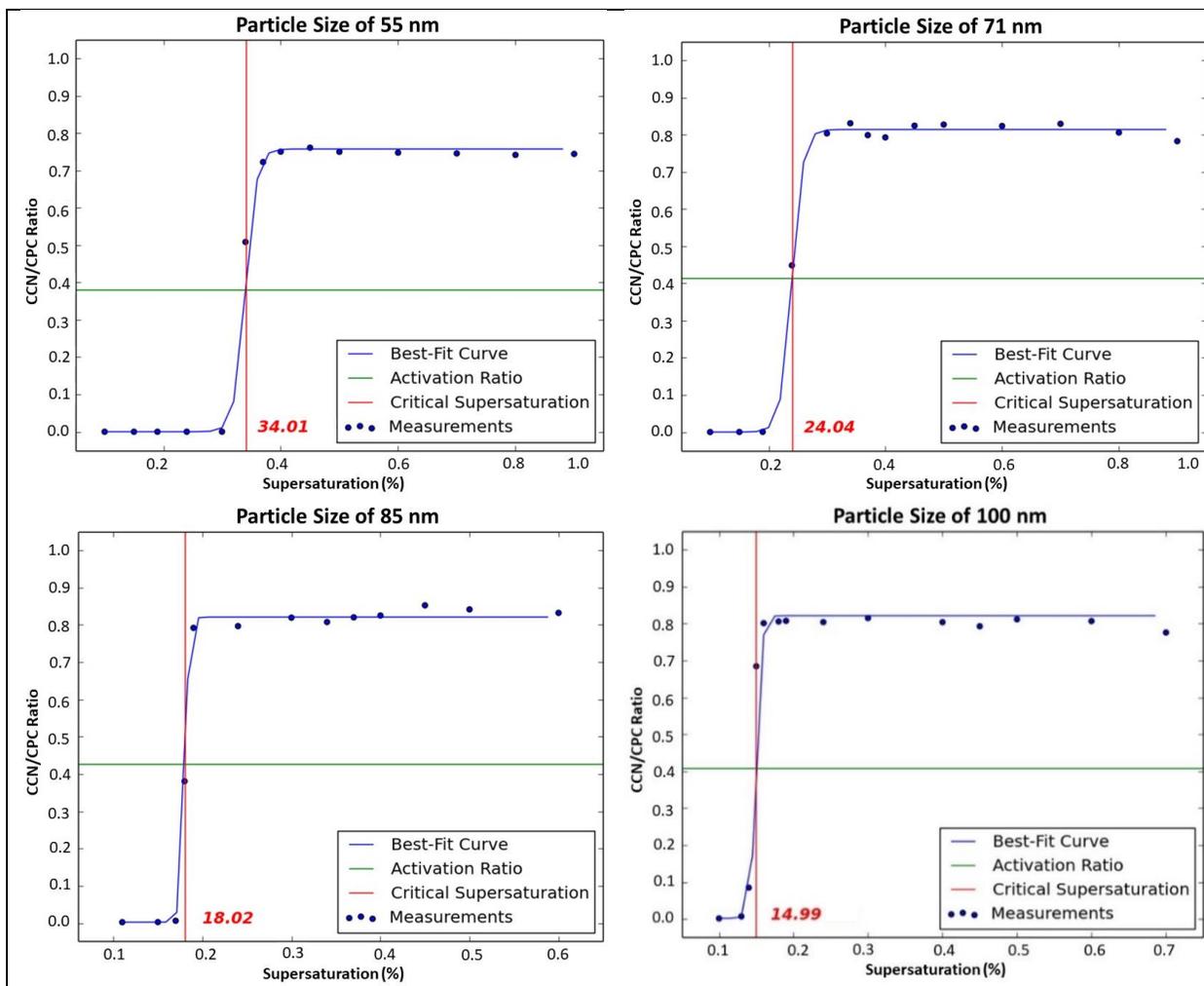


Figure 5: Figures of activation curves for Liquid Smoke of diameters 55 nm, 71 nm, 85 nm, and 100 nm. The critical supersaturation for each diameter is represented in red.

Table 4: Table of Kappa values for Liquid Smoke at varying diameters.

Diameter	40.0 nm	55.2 nm	71.0 nm	85.0 nm	98.2 nm
Kappa	0.87	0.84	0.78	0.81	0.76

4. Conclusions

The size distribution and Kappa values have been calculated for commercial gradeliquid smoke. The Kappa values for liquid smoke are very similar across varying diameters between 40.0 m and 100.0 nm. The Kappa values range from 0.76 to 0.87 and the average Kappa value for liquid smoke is 0.81 +/- 0.04. The kappa values seem to be slightly higher than the expected value of 0.60 as the Organic and Inorganic material mix is closer to 0.60. Since liquid smoke is manufactured, most liquid smokes should have the similar characteristics, although this should be tested further.

Additional work is required to determine if liquid smoke could be a proxy for biomass burning. Chemical analysis of the liquid smoke used is needed to determine what type of biomass burning it simulates. In addition, testing in the PI cloud chamber at Michigan Technological University would give helpful information on how liquid smoke reacts in a simulated atmosphere and if it is similar to biomass burning.

5. References

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Model 3772/3771 Condensation Particle Counter Operation and Service Manual. 127.

Appendix (A)

Data and Code Files

The data collected during the activation curve experiment is processed using the Airborne Data Processing and Analysis (ADPAA) software package. This software is a collection of many different scripts to analyze and process in-situ data that is collected on airborne platforms but can be utilized on the ground as well (Delene 2011). Using this package, the CPC files are converted from text files that are exported from the AIMS program with a comma delimiter to NASA format in an ASCII file to be used in other programs. The command to convert the CPC files is named `convert_cpc3771tonasa`. The CCNC data files are converted to NASA format and raw files created using the `process_day_dmtccnc` command. After the CPC and CCNC data is processed, Interval files are made following the ADPAA format and converting the start and stop times that the data was collected during from hours, minutes and seconds to seconds from midnight. Once the interval files are created, the script `CCNCactivationsize.py` is run utilizing the interval files, CPC files and the CCNC serialh and serialc files that are created from the `process_day_dmtccnc` command. This script outputs a raw file with the ratio of CCNC count to CPC concentration. Next, the script `sigmoid_fit.py` is run using the ratio raw file that is created from the `CCNCactivationsize.py` command to create a sigmoid fit in equation 1.

Project Folder on UND Network:

```
/nas/und/NorthDakota/2018/Liquid_Smoke_Senior_Project
```

Data Files in Folder:

```
Liquid_Smoke_Senior_Project/20180710_00000
```

```
/CPC_Data
```

```
/DMT (CCNC data)
```

```
/Intervals (Time intervals for data processing)
```

```
/PostProcessing (Processed DMT CCNC files into NASA format)
```

```
/18_07_10_00_00_00.ccncpratio.raw
```

```
/18_07_00_00_00.raw
```

```
/18_07_11_55.raw (55nm raw file for graphing)
```

```
Liquid_Smoke_Senior_Project/20180711_00000
```

```
/CPC_Data
```

```
/DMT (CCNC data)
```

```
/Intervals (Time intervals for data processing)
```

```
/PostProcessing (Processed DMT CCNC files into NASA format)
```

```
/18_07_11_00_00_00.ccncpratio.raw
```

/18_07_11_71.raw
/18_07_11_71_00_00.raw
18_07_11_85.raw (85 nm raw file for graphing)
/18_07_11_100.raw (100 nm raw file for graphing)

Liquid_Smoke_Senior_Project/20180712_00000

/CPC_Data
/DMT (CCNC data)
/Intervals (Time intervals for data processing)
/PostProcessing (Processed DMT CCNC files into NASA format)
/18_07_12_00_00_00.ccncpratio.raw
/18_07_12_40.raw
/18_07_12_100.raw

Liquid_Smoke_Senior_Project/Plots
/CS1001.png (100 nm Critical SS)
/CS_401.png (40.0 nm Critical SS)
/CS_55.png (55.0 nm Critical SS)
/CS_711.png (71.0 nm Critical SS)
/CS_851.png (85.0 nm Critical SS)
/Liquid_Smoke_Lab_apparatus_20181115.jpg (Size Distribution Set Up)
/Liquid_Smoke_Lab_Apparatus_20181115(1).jpg (Kappa Value Set Up)
/Size_Distribution.png (Size Distribution)
/Size_Distribution_12nm_to_100nm.png (Size Distribution between 12nm to 100nm)

Processing Code:

<https://sourceforge.net/projects/adpaa>

convert_cpc3771tonasa
process_day_dmtccnc

/scripts_python/CCNCactivationsize.py
/scripts_python/sigmoid_fit.py