OP – DRAFT -

MEASUREMENT AND CHEMICAL ANALYSIS OF PARTICLE NUMBER SIZE DISTRIBUTIONS IN AMBIENT AIR USING RSMS-3

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1. SCOPE AND APPLICABILITY

This OP contains the protocol for performing measurements of particle number size distribution (10 nm - 1500 nm in diameter) in outdoor air for the Baltimore PM supersite study. The instrument consists of a Rapid Single-particle Mass Spectrometer, version 3 (RSMS-3). This is an evaluation version of an anticipated standard operating procedure (SOP), which will result from experiences with this OP. Consequently, this OP is subject to change. Every addition to this OP will be added as an Appendix during this study. This instrument will be operated by on-site personnel after training my the RSMS group.

2. SUMMARY OF METHOD

It has been known for a number of years that passing an aerosol through a sharp or conical orifice where the flow is choked (that is, sonic) focuses certain particles (Dahneke, 1982; Fernandez de la Mora and Riesco-Chueca, 1988 and references therein). The focussed particles have a Stokes number value around one, the exact value depending on the nozzle geometry and the distance from the nozzle to the focal point. We employ this principle in the current single particle instrument, a second generation version that we call RSMS-II (Rapid Single-particle Mass Spectrometry -II). The instrument focuses only a narrow range of particles sizes to the source region of the mass spectrometer, but this size range can be selected by adjusting the pressure upstream of the nozzle. If we consider a given nozzle geometry, let us term the Stokes number that is focused by Stk_f. Thus we can write

$$Stk_f = (Dp^2 \rho_p u_o / 18 \mu Dn) Cc \qquad 1$$

where Dp is the particle diameter that is focussed, ρ_p is its density, u_o is the velocity through the orifice (which is sonic since the flow is choked), μ is the viscosity of air, Dn is the orifice diameter and Cc is the Cunningham non-slip correction factor. All the terms except Dp and Cc can be combined into an effective diameter, $Dp,max = (18 \mu Dn\ Stk_f / \rho_p u_o)^{1/2}$ giving $(Dp/Dp,max)^2 = 1/Cc$. Since the maximum value of Cc is 1, Dp,max is the maximum particle aerodynamic diameter than the nozzle can focus.

Cc is a function of the particle diameter and pressure. The usual function for the Cunningham correction factor is difficult to manipulate analytically (Seinfeld and Pandis, 1998), but a simple linear approximation, $Cc = 1 + 1.66\ (2\lambda/Dp)$, is close to the more precise equation and has a maximum error of only 10% at Kn=1. Using this approximation for Cc gives a quadratic in Dp whose solution is

$$Dp = ((3.32\lambda)^2 + Dp,max^2)^{1/2} - 3.32\lambda \qquad 2$$

where λ, the mean free path, is a function of pressure via $\lambda = \lambda_o p_o/p$, where p_o and λ_o are the pressure and mean free path at standard conditions. Since the mean free path is a function of pressure, the particle size focussed in the mass spectrometer can selected by adjusting the pressure as long as this size is smaller than Dp,max.

The maximum size that can be focussed, Dp,max, is a function of properties of air (μ, u_o) and the particle (ρ_p) which are not adjustable. The only adjustable parameter is the nozzle diameter, Dn, and geometric considerations such as the cone angle and distance from the orifice to the focal point, which are incorporated in Stk_f.

It is best to run the orifice choked because this focuses the smallest particles, but this requirement places limits on the orifice diameter in that the vacuum pump driving the orifice must be large enough to choke the flow. A 3 mm orifice can be choked with two modest vacuum pumps. The result is that for unit density particles, Dp,max is about 2 micron. At low pressures, the focused diameter is a linear function of pressure but this sensitivity reduces as the focused diameter approaches Dp,max. By scanning the pressure from about 300 torr to about 1 torr, the nozzle is able to focus particles ranging from 1 micron to 10 nm in aerodynamic diameter -- selecting the pressure is the next step.

One challenge to the design of the instrument is controlling the pressure upstream of the nozzle over a wide dynamic range while efficiently transmitting particles. We use a bank of 10 critical orifices whose flow is controlled by a rotary valve (Valco Instruments http://www.vici.com). The area of each orifice is selected to evenly distribute the 10 particle diameters logarithmically over the 10 nm to 2 micron size range. Each flow-control orifice is a sharp hole minimizing particle deposition and associated clogging. After the orifice bank is a section of straight tube where the flow straightens and becomes laminar before it enters the focusing orifice, giving more reliable focussing characteristics. The transmission efficiency of the inlet and the instrument's ability to size and analyze atmospheric particles has been submitted for publication (Mallina et al., 1999).

Particle Detection

Particles that are focused to the source region of the mass spectrometer are detected in one of two ways. Larger particles are detected by light scattering. A CW doubled Nd-YAG laser passes through the particle beam just upstream of the center of the source region. Two PMTs in the source region detect forward scattered radiation at angles of +/-30 degrees and signal coincidence from these two PMTs is used to trigger the ablation laser (Ohigashi et al., 1994). Tests show that light scattering is effective down to about 200 nm.

For smaller particles, light scattering is not effective so the ablation laser is free fired (Reents et al., 1994; Carson et al., 1997; Ge et al., 1998). We use a GAM EX10 laser, which fires up to 100 Hz. To maintain single particle analysis, it is important to operate the instrument such that most laser shots miss a particle. For instance, if one in 100 shots result is a hit, then 1 out of 100 hits is a double hit, that is, two particles were in the source region. Here the nozzle flow rate characteristics become useful. Generally, the atmosphere contains a great many ultrafine particles and relatively fewer fines. This is somewhat counterbalanced by the flow rate through the nozzle. Larger particles are focused at higher pressures where the sampling flow rate is higher whereas smaller particles are focused at lower pressures where the sampling flow rate is lower. Nevertheless, if the hit rate is too high, dilution of particle stream is necessary to maintain single particle analysis. Particles are "detected" by the presence of a spectrum. The technique has been used in the laboratory to analyze particles down to 10 nm (Carson et al., 1997) and we have used it to demonstrate sensitivity to 0.1 mass percent impurities in 50 nm particles (Ge et al., 1998).

Particle Analysis

The source region of the mass spectrometer is specially designed to maximize the probability of a particle hit when the laser is free-fired. First, the excimer laser beam propagates collinear to and in the opposite direction from the particle beam. In most designs these two beams are normal to each other so the overlap region is only a few hundred microns. With collinear beams, the overlap is very large and the source region size is governed by the ion optics in the mass spectrometer. In RSMS-II the ion optics have been designed to allow a 4 cm source region (Carson et al., 1997). The excimer laser beam is focused to the center of the source region where it has a waist about 0.6 mm in diameter. This widens to about 2mm at the top and bottom of the source region. The particle beam passes through a 1 mm skimmer before it enters the source region of the mass spectrometer. In the center of the source region, 18 cm from the primary orifice, the beam is very well defined and about 4mm across (measured by impacting oleic acid particles on a glass slide). It is the overlap between the hour-glass-shaped laser beam and the conical particle beam, which determines the particle hit-rate probability. The overall particle hit rate is the product of this probability and the volume flow rate sampled.

Data System

The data system consists of a 500 MHz 8-bit A/D converter mounted in a PC (vendor will be GAGE or Acqiris). A LabView code collects data from the A/D board and determines if it is valid. Valid spectra are stored on the PC disk and archived on writeable CD-ROM. The LabView code also controls the particle size to be sampled, via the rotary valve. The ART-2a algorithm is built into the code so that the particle spectra are classified in real time. Sufficient time is spent sampling at each particle size so that a significant number of particles are sampled in each composition class at each size. The LabView code also controls the laser firing rate and frequency, records the laser pulse energy, and powers the laser down between sampling periods.

3. DATA QUALITY OBJECTIVES

RSMS-3 is a research instrument. There is inherent variability in the mass spectra due to the desorption/ionization process. In addition, these instruments are custom made and still in their infancy.

Currently it is not feasible to determine the accuracy and precision of the absolute values of the m/e intensities of the mass spectra with respect to the actual composition of each individual particle. For the kind of data analyses being conducted, the relative precision of the m/e intensities is of the order of 25%, while the absolute intensities can vary by up to a factor of 2. The relative precision is sufficient for the assignment of each particle to appropriate particle class types.

The estimate aerodynamic diameter of each particle, d, will be within the range of $d/1.5 < d(true) < d*1.5$. The nominal diameter, d(true), can be obtained from the inlet pressure which is recorded with each spectrum. Drifts in the inlet pressure from nominal preset values indicate clogging of the inlet orifices. If drifts in the pressure are observed, the orifices will be replaced.

With these caveats, our objectives are

3a. Collect data from particles sizes ranging from 30 nm to 1000 nm.
3b. Sample a statistically significant number of particles in each size and composition class.
3c. Attain unit mass resolution to 150 amu.
3d. Collect a complete size scan once per hour.
3e. Collect data for one third of the hours for the sampling period.

4. HEALTH AND SAFETY WARNINGS

5a. Laser light. Although the laser light path is completely enclosed, there is some small change that the light can escape especially during maintenance. Goggles should be employed in the room with the instrument

5b.Excimer gas. We will have a tank of excimer gas, which contains a very small fraction of fluorine. A leak will not be hazardous but it has an unpleasant smell. If a strong odor of fluorine is present (like a heavily chlorinated pool), please contact UCD to fix the leak.

5. CAUTIONS

None known.

6. INTERFERENCES

None known.

7. PERSONNEL QUALIFICATIONS

Not applicable.

8. APPARATUS AND MATERIALS

See section 2.

9. INSTRUMENT OR METHOD CALIBRATION AND QUALITY ASSURANCE

See section 11.

10. SAMPLE COLLECTION AND HANDLING

Not applicable.

11. PROCEDURES

ALL MAINTANCE PROCEDURES MUST BE RECORDED IN THE OFF-SITE OR ON-SITE LABORATORY BOOKS

11.1 Daily maintenance of RSMS-3

a) Check (remotely) laser power and gas consumption to make sure that the laser is working properly.
b) Check (remotely) inlet pressures to make sure the clogging is not significantly altering performance.
c) Check (remotely) mass spectrometer performance by confirming that time to mass conversions place peaks on reasonable integer values and that peak widths are near one at 100 mass units.
d) Change the DVD both remotely and on-site.

e)

RSMS-3 DAILY CHECK LIST								
		Check:					Remarks:	Signature
							<---nominal values, only to be changed by primary operator	
Day	**Date**	**Laser Power**	**Laser Gas Usage**	**Inlet Press.**	**Mass Spec Calib**	**Change DVD**	**e.g. laser adjustment, call to UCD**	
Mon								
Tues								
Wed								
Thurs								
Fri								
Sat								
Sun								

11.2 Weekly maintenance of RSMS-3

a) Run a complete size scan on nebulized oleic acid particles to ensure consistent mass calibration, size distribution, and hit rate.
b) Compare (remotely) SMPS and RSMS-3 size distributions to ensure consistent transmission efficiency.

RSMS-3 WEEKLY CHECK LIST					
		Check:		Remarks:	Signature
				<---nominal values, only to be changed by primary operator	
Week	**Date**	**Oleic Acid Scan**	**SMPS comp.**	**e.g. laser adjustment, call to UCD**	
1					
2					
3					
4					
5					
6					
7					
8					
9					

11.3 Monthly maintenance of RSMS-3

a) Remove laser path cover and measure laser pulse energy out of laser and after steering mirror.
b) Break vacuum using a nitrogen purge on the mass spectrometers to protect them from ambient humidity. Measure laser pulse energy in the source region.
c) Compare these three pulse energy measurements and replace mirror or lens as needed to restore source region pulse energy.
d) Check excimer gas level and replace cylinder if low.

RSMS-3 MONTHLY CHECK LIST							
		Check:				Remarks:	Signature
						<---nominal values, only to be changed by primary operator	
Month	**Date**	**Energy from Laser**	**Energy after Mirror**	**Energy in Source**	**Excimer Gas Level**	**e.g. replaced mirror, replaced lens, replaced cylinder, etc.**	
1							
2							
3							
4							
5							
6							
7							
8							

12. TROUBLESHOOTING

12a. Laser power. The laser pulse will drop as the laser is used. We continuously monitor laser pulse energy. The remedies in order of application are

i. Increase the cavity voltage to compensate (can be done under software control)
ii. Refill the cavity with excimer gas (can be done under software control)
iii. Change the laser's output coupler (requires us to be on-site)
iv. Swap in a spare laser and return original to the factory for refurbishment (requires us to be on-site)

12b. Optics Damage. The excimer laser path has a mirror and lens that will be destroyed by the laser over the course of the project. We will replace these components as necessary. CMU on-site personnel can replace both with phone instruction from UC Davis.

13. DATA ACQUISITION, CALCULATIONS & DATA REDUCTION

The mass spectra along with header data describing the particle size, date and time, and other pertinent information will be stored together. NARSTO has specified the format for storage of single particle mass spectra and we will adhere to that format.

14. DATA MANAGEMENT & RECORDS MANAGEMENT

All data will be recorded in real time. Data will be streamed over the internet from the instrument to UC Davis. Once per day, the data will be copied to DVD on site. A copy of the data will be stored in UC Davis on disk and on DVD.

Logbooks will be maintained on site and at UC Davis.

15. CONTACTS

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16. REFERENCES

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