# UPDATE ON THE FIELD EVALUATION OF EPA METHOD CTM-039 (PM2.5 STACK SAMPLING METHOD) Michael D. Buser USDA-ARS Cotton Production and Processing Research Unit Lubbock, TX Derek P. Whitelock USDA-ARS, Southwestern Cotton Ginning Research Laboratory

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### <u>Abstract</u>

Agricultural operations are encountering difficulties complying with current air pollution regulations for particulate matter (PM). These regulations are based on the National Ambient Air Quality Standards, which set maximum concentration limits for ambient air PM. Source sampling for compliance purposes require the use of U.S. Environmental Protection Agency (EPA) approved samplers. Ideally, these samplers would produce accurate measures of the pollutant; for instance, PM2.5 samplers would produce accurate measures of PM less than or equal to 2.5µm (true PM2.5). However, samplers are not perfect and errors are introduced due to established tolerances for sampler performance characteristics and the interaction of particle size and sampler performance characteristics. A performance evaluation of the stack sampler referenced in EPA Method CTM-039 was conducted at a commercial roller cotton gin. EPA Methods CTM-039 and 5 were used to sample the PM emissions being emitted from the gin's No. 1 stick machine system, the overflow and seed-cotton carryover reclaimer system, and the feeder dust system. Total suspended particulate (TSP), PM10, and PM2.5 concentrations were obtained according to EPA defined methodology. A particle size analysis was conducted on the filter and wash from the Method 5 sampler. These particle size distributions and the TSP concentrations were used to determine the true PM10 and PM2.5 concentrations for comparison with the Method CTM-039 concentrations. Based on a preliminary data analysis, the CTM-039 PM10 concentrations were similar to the true PM10 concentrations. However, the CTM-039 PM2.5 concentrations were 5.8, 11, and 13 times greater than the true PM2.5 concentrations for the stick machine, feeder, and overflow systems, respectively.

### **Introduction**

The original EPA method for determining PM stack emission rates was Method 5 (*Federal Register*, 1977). This method was used to determine TSP emission rates through isokinetic stack sampling (USEPA, 1996a). In response to the 1987 National Ambient Air Quality Standards (NAAQS) changes, EPA approved Method 201a. Method 201a is a constant sampling rate procedure (isokinetic) that utilizes a stainless steel cyclone to determine PM<sub>10</sub> emission rates from exhaust stacks. EPA has developed a new method (titled CTM-039) that uses a cyclone with a nominal cutpoint of 2.5  $\mu$ m in series with the Method 201a cyclone. This sampling system consists of a nozzle (matched with the air velocity in the stack to provide isokinetic sampling), PM<sub>10</sub> cyclone with a grit pot, PM<sub>2.5</sub> cyclone with a grit pot, and a filter holder that attaches to the Method 5 sampling train. A picture of the combination PM<sub>10</sub> and PM<sub>2.5</sub> stack sampler is shown in Figure 1.

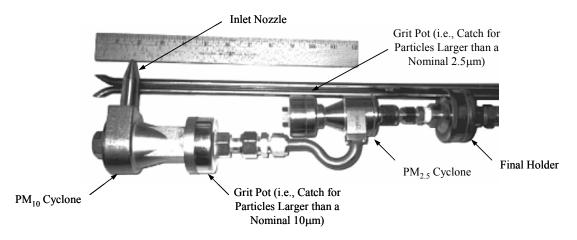


Figure 1. PM<sub>10</sub> and PM<sub>2.5</sub> cyclone combination sampler.

USEPA (2002) describes the validation methods and procedures and the criteria of acceptance for in-stack  $PM_{10}$  samplers. The operating principle of this in-stack sampler requires that isokinetic sampling be maintained within the well-defined limits, as deviations in the sampling flow rate can distort the flow pattern in the stack resulting in  $PM_{10}$  measurement errors. The validation methods call for the in-stack sampler to be tested in a wind tunnel at target gas velocities of 7 +/- 1.0, 15 +/- 1.5, and 25 +/- 2.5 m/s. The sampler's collection efficiency is evaluated by exposing the sampler to dispersed concentrations of mono-disperse particles. The various mono-disperse particle sizes used in the wind tunnel validation studies include: 5, 7, 10, 14, and 20  $\mu$ m. A smooth curve is drawn through the reported collection efficiencies, associated with the various mono-disperse particle sizes, and compared to the curves shown in Figure 2. According to the USEPA (2002), the in-stack sampler's performance is acceptable if the reported fraction efficiency curve falls within the banded region for all particle sizes tested and the sampler's cutpoint is 10.0 +/- 1.0  $\mu$ m AED.

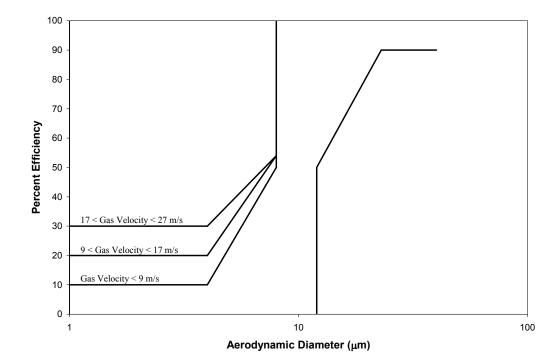


Figure 2. Efficiency envelope for the PM<sub>10</sub> cyclone (USEPA, 2002).

The cutpoint ( $d_{50}$ ) of the PM<sub>10</sub> stack sampler is explicitly defined as 10.0 +/-1.0 µm AED. Using the following equation with *a* equal to infinity, slopes were determined for  $d_{50}$ 's of 9.0, 10.0, and 11.0 µm that fall within the EPA acceptable Method 201a PM<sub>10</sub> cyclone efficiency envelope.

$$P_{m}(a, d_{50}, slope) = 1 - \int_{0}^{a} \left[ \frac{1}{d_{p} \ln(slope)\sqrt{2\pi}} exp \left[ \frac{-\left[ ln(d_{p}) - ln(d_{50}) \right]^{2}}{2(ln(slope))^{2}} \right] \right] dd_{p}$$
(1)

where  $P_m(a, d_{50}, slope)$  is the sampler penetration efficiency for particles having diameters less than *a*. The resulting collection efficiency curves are shown in Figure 3 along with the EPA collection efficiency envelope. It was determined that collection efficiency curve of PM<sub>10</sub> stack sampling cyclone could be described by a d<sub>50</sub> of 9 µm and a slope of 1.87, a d<sub>50</sub> of 10 µm and a slope of 1.90, or a d<sub>50</sub> of 11 µm and a slope of 1.76 and still meet the EPA performance requirements.

Using the methodology described by Buser et al. (2007), theoretical simulations of the errors associated with EPA approved PM10 stack samplers were conducted to determine the expected range of errors associated with these samplers. Using the EPA defined performance criteria, it was theoretically determined that concentrations from the Method 201a stack samplers could be 87 to 100%, 91 to 108%, and 100 to 160% of the true PM10 concentration when the samplers are exposed to particulate matter characterized by a mass median diameters (MMD) of 5.7, 10, and 20 microns, respectively with a geometric standard deviation (GSD) of 2.0, as shown in Figure 4. These ranges of uncertainty increase as the GSD decreases. For example, the theoretical Method 201a stack samplers are exposed to a MMD of 5.7, 10, and 100 to 457% of the true concentration when the samplers are exposed to a MMD of 5.7, 10, and 20 microns, respectively with a GSD of 1.5, as shown in Figure 5. Due to the extremely limited information describing the performance characteristics of the PM2.5 stack sampler, similar simulations could not be performed for the EPA approved PM2.5 stack sampler.

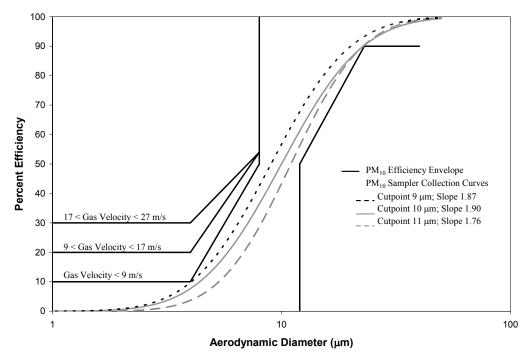


Figure 3. Method 201a  $PM_{10}$  cyclone efficiency envelope and theoretical  $PM_{10}$  cyclone collection efficiency curves.

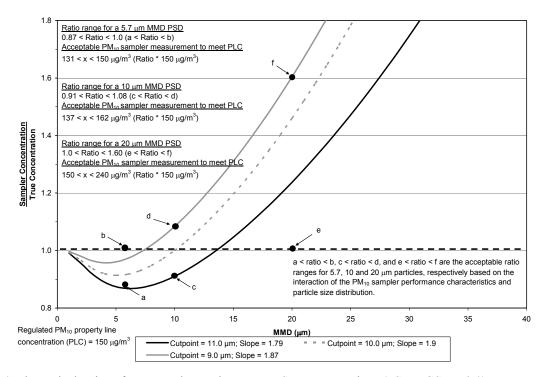


Figure 4. Theoretical ratios of  $PM_{10}$  stack sampler to true PSD concentrations (PSD – GSD = 2.0).

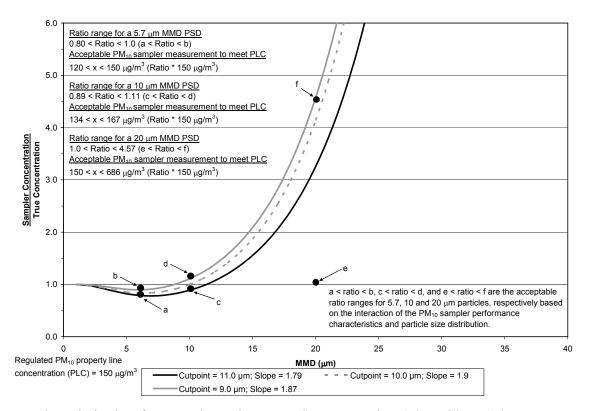


Figure 5. Theoretical ratios of  $PM_{10}$  stack sampler to true PSD concentrations (PSD – GSD = 1.5).

In 2006, laboratory tests were conducted to determine the actual errors associated with EPA's Method 201a and CTM-039. The first experimental test consisted of exposing the samplers to particulate matter with known characteristics, conducting isokinetic sampling, maintaining a constant loading rate, and evaluating only Method 201a. The test dusts were Micro Alumina #3 characterized by a MMD of 10.0 microns and a GSD of 1.5 and a starch characterized by a MMD of 19.4 microns and a GSD of 1.34 (should resulting in over-sampling). Based on the results of the study the Method 201a stack sampler under-sampled the true PM10 concentration by 17% when exposed to the Micro Alumina #3 and over-sampled the true PM10 concentration by 143% when exposed to the starch. A second round of testing focused on two test dusts, two loading rates, and Method 201a and CTM-039 sampling methods. Results for the Method 201 and CTM-039 tests are shown in Table 1 and Table 2, respectively.

These results indicate that the sampler performance characteristics can vary beyond the EPA defined tolerances; therefore, predicting over or under-sampling based simply on the characteristics of the particulate matter being sampled becomes complicated as it is dependent on the large shifts in the sampler performance characteristics.

	$True \ PM_{10}$	Sampler PM <sub>10</sub>	Sampler PM <sub>10</sub> /True PM <sub>10</sub>
Limestone {MMD = 14.8; GSD	= 1.8}		
Rate = 32 g/m <sup>3</sup>	27%	23%	86%
Rate = 148 g/m <sup>3</sup>	27%	31%	113%
Starch {MMD = 19.5; GSD = 1.3	5}		
Rate = 32 g/m <sup>3</sup>	5%	12%	250%
Rate = 148 g/m <sup>3</sup>	5%	11%	228%

Table 1. 2006 experimental test results for EPA's Method 201a.

Table 2. 2006 experimental test results for EPA's Method CTM-039.

	PM <sub>10</sub>			<u>PM25</u>			
	True	Sampler	Sampler/True	True	Sampler	Sampler/True	
Limestone {MMD = 14.8; GSD = 1.8}							
Rate = 32 g/m <sup>3</sup>	27%	33%	123%	1%	9%	700%	
Rate = $148 \text{ g/m}^3$		36%	133%	1%	8%	606%	
Starch {MMD = 19.5; GSD = 1.3}							
Rate = 32 g/m <sup>3</sup>		22%	477%	0.02%	6%	30000%	
Rate = 148 g/m <sup>3</sup>	5%	21%	444%	0.02%	5%	25316%	

## **Methods**

The field evaluation was conducted at a California roller gin. The sampling was conducted on December 12 & 13, 2006. The gin's No. 1 stick machine, feeder dust, and the overflow/seed reclaimer systems were evaluated. Both the No. 1 stick machine and feed dust system exhausts were equipped with two 38 inch 1D-3D cyclones. The overflow/seed reclaimer system was equipped with four 38 inch 1D-3D cyclones. The gin's production data (bales of cotton ginned per hour) was collected from the gin's management by the Environmental Services and Testing company and was provided to the USDA-ARS through the source testing companies official report.

The CTM-039 and Method 5 stack sampling performed by the USDA-ARS was conducted in conjunction with Method 201a and Method 202 stack sampling that was performed by Environmental Services and Testing. Method 5 sampling was conducted to quantify the total suspended particulate (TSP) being emitted from the stacks. Method 201a was used to quantify the solid PM10 being emitted from the stacks. Method 202 is an analytical procedure that was used to quantify the organic and water soluble PM10 that penetrated the filter and condensed in the impingement train. Method CTM-039 was used to quantify both the PM10 and PM2.5 solid particulates being emitted for the stacks. The sampling ports used in the tests were positioned in accordance with EPA Method 1 to accommodate a 12-point traverse. The volumetric airflow was determined in accordance with EPA Methods 2 through 4. Stack gas  $O_2$  and  $CO_2$  levels were ambient ( $O_2 = 20.9\%$ ,  $CO_2 = 0.1\%$ ) and were not measured. All

volumetric airflow rates were corrected to dry standard conditions (T = 68 °F, P = 29.92 in. Hg). All airflow rate measurements were conducted by Environmental Services and Testing and were provided to the USDA-ARS.

Three replications of each test method were performed on one of the cyclone exhausts from each of the systems. A candy cane equipped with two ports was attached to the cyclone exhaust. Each Method 201a run lasted approximately 60 minutes and were performed in accordance to EPA's defined protocol. The protocols used for Methods 5 and CTM-039 were modified versions of EPA's defined protocol. Each of the Method 5 and CTM-039 runs lasted 30 minutes. No Method 5 or CTM-039 traverse sampling was conducted, as only center point measurements were collected. These modifications were made so that the Method 5 and CTM-039 sampling could be conducted in conjunction with the Method 201a sampling without interfering with Method 201a sampling protocol. Therefore, the results from the Method 5 and Method CTM-039 tests should only be used to compare the various methods and should not be used to quantify the total PM emissions being emitted from the exhausts.

Sampler preparation, operation, and wash and filter sample collections were conducted in accordance to EPA's defined protocols. All Method 201a washes and filter media collections and gravimetric analysis of these samples were conducted by Environmental Services and Testing personnel. Arrangements were established for the samples to be shipped to the USDA-ARS Cotton Production and Processing Research Unit's Air Quality Laboratory for particle size analyses to be conducted on the wash and filter samples. All Method 5 and CTM-039 washes and filter media collections and gravimetric and particle size analysis of these samples were conducted by USDA-ARS personnel. Particle size analysis is above and beyond the scoped defined by the various EPA protocols. The particle size procedures defined by Buser (2004) were used to generate all the particle size distributions for the PM wash and filter samples.

#### **Results and Discussion**

To date, all the gravimetric analyses have been completed. The USDA-ARS has received Environmental Services and Testing's official source sampling report but have not included the results in this discussion. The Method 201a wash and filter samples have not been received by the USDA-ARS and therefore, the subsequent particle size analysis has not been completed. The particle size analyses for the Method 5 samples have been completed; however, the particle size analyses for the CTM-039 samples have not been completed. The comparative results reported in this manuscript are based on the gravimetric analyses of the Method 5 and CTM-039 samples and the particle size analyses of the Method 5 samples.

The particle size distributions for the No. 1 Stick Machine, Overflow/Seed Reclaimer, and Feeder Dust systems are shown in Figures 6, 7, and 8, respectively. The PM captured on the Method 5 filters from the No. 1 Stick Machine and the Feeder Dust systems were similar size. The MMD, GSD, percent PM10, and percent PM2.5 for the No. 1 Stick Machine was 6.4  $\mu$ m, 1.8, 78.3%, and 4.89%, respectively. The MMD, GSD, percent PM10, and percent PM10, and percent PM2.5 for the Feeder Dust system was 6.0  $\mu$ m, 1.6, 86.3%, and 3.29%, respectively. The particle size distribution of the PM captured on the Method 5 filters from the Overflow/Seed Reclaimer system was shifted slightly to the right resulting in a larger MMD and smaller PM10 and PM2.5 percentages. The MMD, GSD, percent PM10, and percent PM2.5 for the Overflow/Seed Reclaimer system was 8.0  $\mu$ m, 1.7, 66.9%, and 1.26%, respectively.

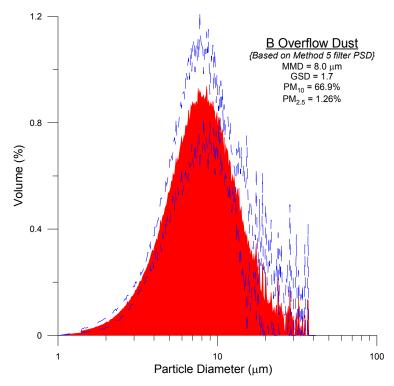


Figure 6. Average particle size distribution for the Overflow/Seed Reclaimer system as determined from the Method 5 filter.

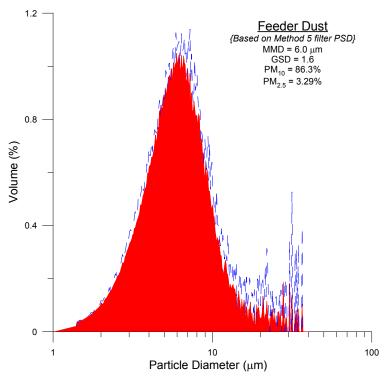


Figure 7. Average particle size distribution for the Feeder Dust system as determined from the Method 5 filter.

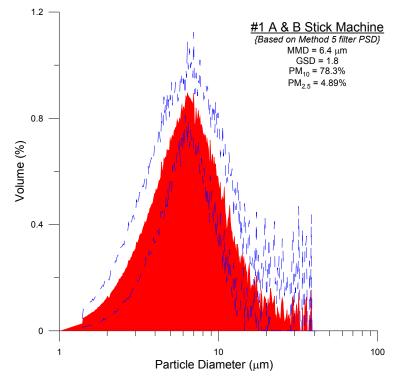


Figure 8. Average particle size distribution for the No. 1 Stick Machine as determined from the Method 5 filter.

The percent PM10 and PM2.5 based on the CTM-039 gravimetric analyses and the ratios of the sampler (CTM-039 sampler) to the true (based on particle size distribution analyses of the Method 5 filters), also referred to as the overor under-sampling rate, are shown in Table 3. The PM10 percentages as determine by the CTM-039 method and Method 5/particle size analyses method produced similar results. For the PM10 analyses, the CTM-039 concentrations were 93% to 100% (exactly matching) of the true concentrations. For the PM2.5 percentages, the CTM-039 method produced PM2.5 concentrations higher than the true PM2.5 concentrations. The percent PM2.5 for the No. 1 Stick Machine was 28.3 and 4.9% based on the CTM-039 and Method 5/particle size analyses methods, respectively. In other words, the CTM-039 concentration estimates were 5.79 times higher than the true concentrations. The percent PM2.5 for the Overflow/Seed Reclaimer system was 16.8 and 1.30% based on the CTM-039 concentration estimates were 13.35 times higher than the true concentrations. The percent PM2.5 for the Feeder Dust system was 36.0 and 3.30% based on the CTM-039 and Method 5/particle size analyses methods. Based on these results the CTM-039 concentration estimates were 10.95 times higher than the true concentrations.

Table 3. 2007 Field evaluation results for the CTM-039 stack samp
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CTM-039 Results		PSD Analysis of	f Method 5 Filter	Sampler/True		
Exhaust	% < 10µm	% < 2.5µm	% < 10µm	% < 2.5μm	% < 10μm	% < 2.5µm
Stick Machine	73%	28.3%	78%	4.90%	93%	579%
Overflow	67%	16.8%	67%	1.30%	100%	1335%
Feeder	81%	36.0%	86%	3.30%	93%	1095%

### **Conclusion**

These types of samplers are beginning to be used to monitor and/or evaluate emissions emitted by agricultural point source exhausts. Theoretical estimates indicate that the PM10 stack samplers could be producing concentrations that are in excess of 4.5 times higher than the true PM10 concentrations for certain PM. The experimental data collected to date also indicates that the sampler's performance characteristics could be shifting beyond the EPA defined criteria even when the sampler is operated in accordance to EPA protocol. The experimental data on EPA CTM-039 method (PM2.5 stack sampling) indicates dramatic over-sampling when used to sample certain PM.

Why should regulatory and agricultural industries care about these sampler errors?

- 1) Creating standards based on data containing sampler errors creates a huge demand for resources (time, money, and other resources) with no direct benefit or reduction of health effect risks.
- 2) By not accounting for these errors, regulatory agencies will end up focusing on the truly smaller PM2.5 emitters as opposed to the larger emitters (the regulatory agencies should be looking to get the biggest bang for your buck).
- 3) If regulatory agencies do not account for these sampler errors, agricultural sources are going to have a tough time complying with EPA's PM2.5 standards.

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# **Disclaimer**

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