

Uncertainty Associated with the Gravimetric Sampling of Particulate Matter

Jacqueline E. Price, Graduate Research Assistant

Texas A&M University, Department of Biological & Agricultural Engineering, College Station, TX,
jackie@tamu.edu

Ronald E. Lacey, Ph. D., P.E.

Associate Professor, Texas A&M University, Department of Biological & Agricultural Engineering,
College Station, TX, ron-lacey@tamu.edu

Written for presentation at the
2003 ASAE Annual International Meeting
Sponsored by ASAE
Riviera Hotel and Convention Center
Las Vegas, Nevada, USA
27- 30 July 2003

Abstract. *Gravimetric measurement of particulate matter (PM) concentration in ambient environments is the basis for regulation of PM fractions (i.e. PM_{10} and $PM_{2.5}$) under the Federal Clean Air Act. While the measurement is straight forward, there are numerous systematic errors that can enter the analysis that result in an unacceptably large error in the final concentration values. This paper discusses the importance of uncertainty approximation and analyzes the systematic errors inherent in a gravimetric measurement. Additionally, this paper explores a sensitivity analysis of the contributing errors in order to identify the most critical measurements and their implications on the calibration, operation, and design of PM samplers.*

Keywords. Uncertainty analysis, sensitivity analysis, air pollution, air quality, particulate matter, gravimetric sampling, systematic error, experimental uncertainty, emission abatement.

Introduction

Gravimetric measurement of particulate matter (PM) concentration in ambient environments is the basis for regulation of PM fractions (i.e. PM_{10} and $PM_{2.5}$) under the Federal Clean Air Act. The United States Environmental Protection Agency (USEPA) regulates particulate matter (PM) in the ambient air in the United States, and these regulations comprise what is known as the National Ambient Air Quality Standards (NAAQS) (USEPA, 1999). While the measurement is straight forward, there are numerous systematic errors that can enter the analysis, resulting in an unacceptably large error in the final concentration values. This discussion covers the incorporation of uncertainty analysis in gravimetric measurement of particulate matter (PM).

A measurement of a variable can only provide a deterministic estimate of the quantity being measured; thus, it can only be considered complete when supplemented by a quantitative statement of the inaccuracies surrounding the measurement. Therefore, proper experimental planning and design requires an understanding of the errors inherent in these measurements so that the experimenter can have some degree of certainty in the final measurements and calculations.

Uncertainty can be defined as the statistical representation of the reliability associated with a specific set of measurements (Yegnan et al., 2002). Uncertainty can also be described as the possible set of values on a given measurement and can be considered a statistical variable (Kline, 1985). The term *error* takes on a slightly different definition. The total error, δ , is the difference between the measured value and the true value of the quantity being measured. It can also be thought of as the sum of the *systematic error* and the *random error*, $\delta = \beta + \epsilon$, where β is the systematic error and ϵ is the random error (ANSI/ASME, 1998).

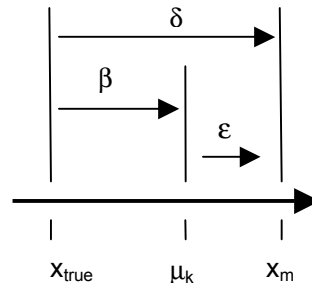


Figure 1. Illustration of Total Error, δ

Systematic error, β , also known as fixed error or bias, is defined as the constant element of the total error, δ ; therefore, this error value remains constant for each measurement. Random error, ϵ , also known as repeatability error or precision error, is the random error element of the total error, thus each measurement takes on a different value for this part of the total error measurement (ANSI/ASME, 1998). Thus, the term error refers to a fixed quantity, and it cannot be considered a statistical variable.

Many of the current methods of estimating the uncertainty surrounding experimental results are based upon an analysis by Kline and McClintock (1953). With the goal in mind of determining the effects of each potential measurement error, they proposed a process which considers the impact of these individual uncertainties, commonly referred to as the propagation of uncertainty (Kline and McClintock, 1953). This process involves a Taylor series approximation to estimate the uncertainty in various circumstances.

Objectives

The objectives of this uncertainty analysis are:

1. To determine the systematic uncertainty surrounding the gravimetric particulate matter (PM) concentration using a first-order Taylor series approximation method.
2. To identify the most critical measurements and their implications on the calibration, operation, and design of PM samplers using a sensitivity analysis.

Methodology

The impact of the individual uncertainties of each primary measurement in an experiment on the total systematic uncertainty of the experiment must be approximated. This idea is commonly referred to as the law of propagation of uncertainty (ISO, 1995). The uncertainties from the individual independent variables propagate through a data reduction equation into a resulting overall measurement of uncertainty (Coleman & Steele, 1999).

Primary Systematic Uncertainty Determination

Manufacturers specify the accuracy of their respective measurement instrument, and this information is used in this analysis as the value for the systematic uncertainty of the measuring device. This accuracy specification takes into account various factors such as linearity, gain, and zero errors (Coleman & Steele, 1999). All of the uncertainty values used in this discussion except for that of the pressure drop across the orifice meter (ΔP_a) were obtained from the specifications on the manufacturers' data sheets. The uncertainty value given by the manufacturer must include any sensor or transducer bias in the system. In the case of the ΔP_a reading from the Hobo instrument, the bias in both the pressure transducer and the Hobo data logger must be accounted for.

Uncertainty Propagation Calculation

With the individual systematic uncertainties now determined, the propagated systematic uncertainty can be calculated.

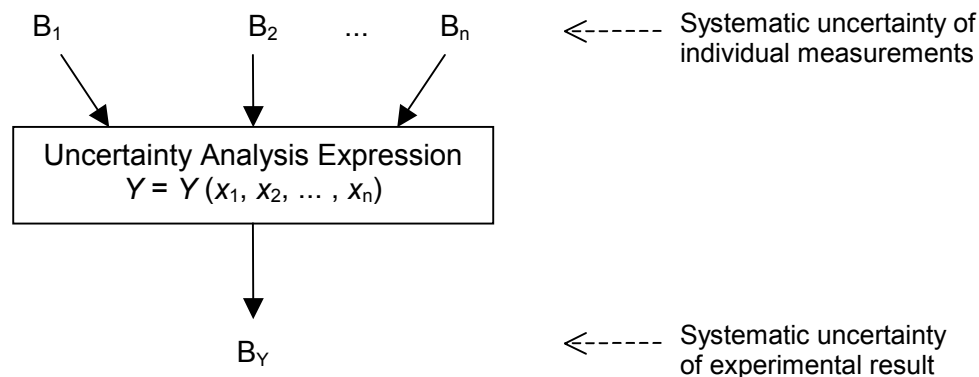


Figure 2. Determining the systematic uncertainty for an experiment (adapted from Coleman & Steele, 1999)

Assuming that all individual uncertainties are at the same confidence level (95% confidence interval or 20:1 odds in this instance), let Y be a function of independent variables $x_1, x_2, x_3, \dots, x_n$. Therefore, the data reduction equation for determining Y from each x_i is

$$Y = Y(x_1, x_2, \dots, x_n) \quad [1],$$

Furthermore, let ω be defined as the systematic uncertainty in the result and $\omega_1, \omega_2, \dots, \omega_n$ as the systematic uncertainties in each of the above independent variables. Given the same confidence interval on each of the independent (uncorrelated) variables, the resulting systematic uncertainty of Y , ω_y , can be calculated as the positive square root of the estimated variance, ω_y^2 , from the following equation (Holman, 2001)

$$\omega_y = +\sqrt{\omega_y^2} \quad [2],$$

where the variance, ω_y^2 , is calculated by

$$\omega_y^2 = \left(\frac{\delta Y}{\delta x_1} \omega_1 \right)^2 + \left(\frac{\delta Y}{\delta x_2} \omega_2 \right)^2 + \dots + \left(\frac{\delta Y}{\delta x_n} \omega_n \right)^2 \quad [3],$$

or

$$\omega_y^2 = (\theta_1 \omega_1)^2 + (\theta_2 \omega_2)^2 + \dots + (\theta_n \omega_n)^2 \quad [4],$$

where θ , the *sensitivity coefficient*, is defined as

$$\theta_i = \frac{\delta Y}{\delta x_i} \quad [5]$$

Gravimetric Sampling Governing Equations

The concentration of particulate matter (PM) in the air can be measure by gravimetric means, where the PM in the air is captured on a filter and then weighed. The particulate matter concentration is a function of the mass of PM collected in a known volume of air using the equation

$$C = \frac{W}{V} \quad [6],$$

where C is the concentration, W is the mass of PM collected on the filter, and V is the total volume of air through the system during the entire time of sampling. Both W and V are calculated quantities from other measurements. Therefore, these quantities must be reduced to basic measurements as seen in Figure 3 below.

$$C = \frac{W}{V} \quad (6)$$

$$\rightarrow W = W_f - W_i \quad (7)$$

$$\rightarrow V = Q * \theta \quad (8)$$

$$\rightarrow Q = 5.976 * k * (D_0)^2 * \sqrt{\frac{\Delta P_a}{\rho_a}} \quad (9)$$

$$\rightarrow \rho_a = \left[\frac{P_a - RH * P_s}{0.37 * (460 + T)} \right] + \left[\frac{RH * P_s}{0.596 * (460 + T)} \right] \quad (10)$$

$$\rightarrow k = \frac{Q_{LFE}}{5.976 * (D_0)^2 * \sqrt{\frac{\Delta P_c}{\rho_c}}} \quad (11)$$

$$\rightarrow \rho_c = \left[\frac{P_c - RH * P_s}{0.37 * (460 + T)} \right] + \left[\frac{RH * P_s}{0.596 * (460 + T)} \right] \quad (10)$$

Figure 3. Breakdown of Equations

First, the mass on the filter, W , is necessary. The mass of particulate matter on the filter is calculated by the equation

$$W = W_f - W_i \quad [7],$$

where W_f is the weight of the filter and PM after the sampling period and W_i is the weight of the bare filter before the sampling period. These filters are weighed three times before and after sampling under controlled environmental conditions (relative humidity and temperature has an impact on the accuracy), and the mean of each of these three measurements is used. Both W_f and W_i are primary measured quantities, so no further reduction is necessary.

The total volume of air in ft^3 , V , used during the sampling time is determined by

$$V = Q * \theta \quad [8],$$

where Q is the volumetric flow rate in cfm and θ is the elapsed time of the test in minutes. The elapsed time of the test, θ , is a measured quantity; however, Q is not. So, Q must be evaluated further. Each gravimetric sampler uses a fan or pump to draw air downward through the filter. The fan/pump setup includes an orifice meter in the line to the sampler in order to calculate the volumetric flow rate of air through the tube. The volumetric flow rate in cfm, Q , is calculated from the pressure drop across an orifice meter as in the following equation, which is derived from Bernoulli's equation (Sorenson and Parnell, 1991)

$$Q = 5.976 * k * (D_0)^2 * \sqrt{\frac{\Delta P_a}{\rho_a}} \quad [9],$$

where k is a calibration constant for the orifice meter, ΔP_a is the measured pressure drop across the orifice meter in inches of water using a transducer output to a data logger to record the instantaneous pressure drop across the orifice meter, ρ_a is the mean air density in $\text{lbs}\cdot\text{ft}^{-3}$, and D_0 is the diameter of the orifice in inches determined by the end mill specifications. For field sampling measurements, the gas used is air where the air density in $\text{lbs}\cdot\text{ft}^{-3}$ can be estimated by (Cooper and Alley, 1994)

$$\rho_a = \left[\frac{P_a - RH * P_s}{0.37 * (460 + T)} \right] + \left[\frac{RH * P_s}{0.596 * (460 + T)} \right] \quad [10],$$

where P_s is the saturated vapor pressure in $\text{lbs}\cdot\text{in}^{-2}$ at T (Engineering Toolbox, 2003), T is the dry bulb temperature of the air in degrees Fahrenheit, and RH is the relative humidity fraction of the air. In three of the four examples that follow, the value of k is determined against a laminar flow element (LFE) of greater precision and accuracy than the orifice meter, where the value of k is given by

$$k = \frac{Q_{LFE}}{5.976 * (D_0)^2 * \sqrt{\frac{\Delta P_c}{\rho_c}}} \quad [11],$$

where Q_{LFE} is the flow given by the LFE ($\text{ft}^3\cdot\text{min}^{-1}$), ρ_c is the density of the air during calibration ($\text{lbs}\cdot\text{ft}^{-3}$), and ΔP_c is the pressure drop across the orifice meter during calibration in inches of water. In the low volume example, the reading from a mass flow meter ($Q_{\text{massflowmeter}}$) is used in lieu of Q_{LFE} in equation 11 (to determine the k value). The density of the air during calibration, ρ_c , is calculated using the same equation as ρ_a , (equation 10).

Results and Discussion

Sensitivity Coefficient Determination

In order to evaluate the effect of each primary measurement on the final concentration measurement, the sensitivity must be calculated with respect to each of these primary measurements. The sensitivity coefficient for each element of gravimetric sampling system is based off of equation 5. In order to determine the sensitivity coefficients, the systematic uncertainty of each instrument is necessary. Table 1 specifies the instruments used for each measurement as well as the related systematic uncertainty as provided in the manufacturer's specifications. These uncertainty values are assumed to be at a 95% confidence interval (2 standard deviations from the mean, also referred to as 20:1 odds). Literature identifies this as a Type B analysis in which the evaluation of systematic uncertainty is based upon scientific judgment and manufacturers' specifications (NIST, 1994).

Table 1. Instrument Specification

Parameter	Instrument	Systematic Uncertainty
W_i, W_f	Sartorius SC2 (low volume) Mettler Toledo AG balance (high volume)	$1 * 10^{-7}$ g $2 * 10^{-4}$ g
Θ (Time)	HOBO data logger	0.20 min
ΔP_a	Omega PX274 Pressure Transducer + HOBO cord	0.075 0.1 mA + 3 %
D_o	End Mill Specs	0.025 in
T_a	HOBO Weather Station Temperature/RH Smart Sensor	0.8 °F
P_a	HOBO Weather Station Barometric Pressure Smart Sensor	1 %
RH_a	HOBO Weather Station Temperature/RH Smart Sensor	3 %
P_{sata}	Steam Tables	0.0001 psia
$Q_{\text{massflowmeter}}$	Aalborg GFC17 Mass Flowmeter	1.5 % FS
Q_{LFE}	Meriam Instruments Model 50MC2-2	0.344 cfm
ΔP_c	Digital Manometer - Dwyer Series 475 Mark III	0.5 % FS
T_c	Davis Perception II	1 °F
P_c	Davis Perception II	1 %
RH_c	Davis Perception II	5%
P_{satc}	Steam Tables	0.0001 psia

With this systematic uncertainty information, the sensitivity coefficient for each variable in equations 6-11 is determined using partial differential equations (as described by equation 5). The partial differentials used can be found in Appendix A.

Sensitivity & Uncertainty Analysis

To determine the most sensitive input parameters with respect to the output particulate matter concentration, a sensitivity analysis must be performed on the uncorrelated primary measurements (Yegnan et al, 2002). The information obtained from the sensitivity analysis is used to obtain the uncertainty in the particulate matter concentration calculation. Additionally, this information helps the experimenter identify the most influential sources of uncertainty. This proves to be important when the amount of uncertainty in the final computation needs to be reduced by identifying these influential sources of uncertainty. This analysis evaluates four situations: the high volume sampling technique ($Q \sim 50$ cfm, which is the midpoint of the USEPA defined appropriate operating flow rates) and low volume sampling technique ($Q \sim 0.6$ cfm ~ 1 m³/min) used by the Texas A&M Center for Agricultural Air Quality Engineering & Science as well as the upper and lower limit flow rates (39 – 60 cfm) as defined in USEPA (1999).

Each portion of Table 3 is a summary of the sensitivity of each independent parameter contributing to the final particulate matter concentration. This information is derived from a model in Microsoft Excel as developed by the authors. The standard type face values in the table represent the information provided by the user, while the bold type face values are those calculated by the Excel model.

Figures 4 through 7 are views of the Excel model and are provided in Appendix B. Using the process defined in the methods section, the sensitivities of each of the parameters are calculated based on equation 5. The uncertainty of each secondary measurement (the propagation of the primary measurements) is determined by the process as described in equations 3 and 4. These secondary uncertainties include not only the uncertainty in the

concentration measurement (ω_c) but also the uncertainty in the mass on the filter (ω_w), the volume of air (ω_v), the volumetric flow rate of air (ω_Q), the density of the air during the sampling period (ω_{pa}), the density of the air during the orifice meter calibration (ω_{pc}) and the k value across the orifice meter (ω_k). Ultimately, the model calculates the amount of impact of each parameter on the total uncertainty in the final concentration calculation. It is important to note that simply adding up the impact of each parameter on the final uncertainty will yield a value much larger than 100%. However, if the parameters representing the primary measurements are summed ($\Delta P_a, T_a, P_a, RH_a, P_{sata}, Q_{LFE}, D_0, \Delta P_c, T_c, P_c, RH_c, P_{satc}$), then the Percentage of Total Uncertainty results in 100% of the total uncertainty.

The following scenario evaluations are included in Tables 2 and 3 (with the calculations included in Appendix B):

- TAMU High Volume Gravimetric Sampling – Q ~ 50 cfm
- TAMU Low Volume Gravimetric Sampling – Q ~ 0.6 cfm
- USEPA Lower Limit Gravimetric Sampling – Q ~ 39 cfm
- USEPA Upper Limit Gravimetric Sampling – Q ~ 60 cfm

Table 2 displays the overall concentration uncertainty for each of the scenarios, while Table 3 breaks down the uncertainty into the contribution of each measurement to the total uncertainty.

In all four scenarios, it's important to note that the leading contributor to the uncertainty in the final concentration calculation is the pressure drop across the orifice meter. If we are to seek a higher degree of certainty in our final concentration calculation, then the optimal decision would be to decrease the uncertainty in the pressure drop across the orifice meter measurement.

Table 2. Total Uncertainty for Gravimetric Sampling Under Normal Conditions

	Concentration ($\mu\text{g}/\text{m}^3$)	Uncertainty ($\mu\text{g}/\text{m}^3$)	Uncertainty (%)
TAMU High Volume	333.53	28.92	8.67
TAMU Low Volume	333.21	39.48	11.85
USEPA Lower Limit – High Volume	427.60	51.22	11.98
USEPA Upper Limit – High Volume	277.94	20.14	7.25

Table 3. Gravimetric Sampler Sensitivity Analysis for Uncertainty Propagation

	Parameter	Units	TAMU High Volume			TAMU Low Volume			EPA Lower Limit High Volume			EPA Upper Limit High Volume		
			Nominal Value	Uncertainty	% of Total Uncertainty	Nominal Value	Uncertainty	% of Total Uncertainty	Nominal Value	Uncertainty	% of Total Uncertainty	Nominal Value	Uncertainty	% of Total Uncertainty
Mass	W _f	g	9.785	2.00E-04	0.07%	10.301	1.00E-07	0.00%	9.785	2.00E-04	0.04%	9.785	2.00E-04	0.11%
	W _i	g	9.7	2.00E-04	0.07%	10.3	1.00E-07	0.00%	9.7	2.00E-04	0.04%	9.7	2.00E-04	0.11%
Volume	Θ(Time)	min	180	0.20000	0.02%	180	0.20000	0.01%	180	0.20000	0.01%	180	0.20000	0.02%
	Q	cfm	50.00	4.33220	99.8%	0.589	0.06977	99.99%	39.00	4.66991	99.9%	60.00	4.34247	99.8%
Q	ΔP _a	in of H ₂ O	1.5493	0.2260	70.8%	1.074	0.2118	69.2%	0.9426	0.2078	84.7%	2.2310	0.2465	58.1%
	ρ _a	lbs/ft ³	0.07213	0.000736	0.35%	0.07213	0.000736	0.19%	0.07213	0.000736	0.18%	0.07213	0.000736	0.50%
	k		0.80235	0.037300	28.7%	0.72620	0.04761	30.6%	0.80235	0.03730	15.1%	0.80235	0.037300	41.2%
P _a	T _a	° F	85	0.8	0.01%	85	0.8	0.00%	85	0.8	0.00%	85	0.8	0.01%
	P _a	psia	14.676	0.14676	0.34%	14.676	0.14676	0.18%	14.676	0.14676	0.18%	14.676	0.14676	0.49%
	RH _a		0.58	0.0174	0.00%	0.58	0.0174	0.00%	0.58	0.0174	0.00%	0.58	0.0174	0.00%
	P _{sata}	psia	0.5961	0.0001	0.00%	0.5961	0.0001	0.00%	0.5961	0.0001	0.00%	0.5961	0.0001	0.00%
K	Q _{LFE} / Q _{massflow}	cfm	50	0.344	0.63%	0.5	0.00795	1.80%	50	0.344	0.33%	50	0.344	0.90%
	ΔP _c	in of H ₂ O	1.6	0.1	13.0%	0.8	0.1	27.8%	1.6	0.1	6.81%	1.6	0.1	18.6%
	D _o	inches	1.5	0.025	14.8%	0.1875	0.001	0.81%	1.5	0.025	7.74%	1.5	0.025	21.2%
	ρ _c	lbs/ft ³	0.07449	0.000762	0.35%	0.07449	0.000762	0.19%	0.07449	0.000762	0.18%	0.07449	0.000762	0.50%
P _c	T _c	° F	70	1	0.01%	70	1	0.01%	70	1	0.01%	70	1	0.02%
	P _c	psia	14.676	0.14676	0.34%	14.676	0.14676	0.18%	14.676	0.14676	0.18%	14.676	0.14676	0.48%
	RH _c		0.5	0.025	0.00%	0.5	0.025	0.00%	0.5	0.025	0.00%	0.5	0.025	0.00%
	P _{satc}	psia	0.36292	0.0001	0.00%	0.36292	0.0001	0.00%	0.36292	0.0001	0.00%	0.36292	0.0001	0.00%

Conclusion

Gravimetric measurement of particulate matter (PM) concentration in ambient environments is the basis for regulation of PM fractions (i.e. PM_{10} and $PM_{2.5}$) under the Federal Clean Air Act. A measurement of a variable can only provide a deterministic estimate of the quantity being measured; thus, it can only be considered complete when supplemented by a quantitative statement of the inaccuracies surrounding the measurement. Using a Taylor Series approximation, the total uncertainty surrounding the PM concentration is determined for four gravimetric sampling scenarios.

In addition to determining the total uncertainty, the most critical measurements in gravimetric sampling of PM are identified using a sensitivity analysis. In evaluating the uncertainty surrounding each measurement and the impact on the total uncertainty in the final calculation, it is notable that the pressure drop across the orifice meter during the test as well as during calibration accounts for approximately 60% - 80% of the total uncertainty in each of the four examples. With this knowledge, the experimenter has identified the optimal part of the measurement process to focus on to effectively reduce the total uncertainty in the experiment, if desired.

Thus, this analysis has provided a systematic method of determining which instruments in the process need to be improved on in terms of reducing overall uncertainty by using a Taylor Series approximation approach based on the pioneering research by Kline and McClintock in 1953. This concept of performing an uncertainty and sensitivity analysis on experimental measurements to determine the impact on the final calculation can and should be used in every experimental procedure.

References

- American National Standards Institute/American Society of Mechanical Engineers (ANSI/ASME). *Test Uncertainty*, Performance Test Code 19.1 – 1998. New York, NY: ASME.
- Coleman, Hugh W., and W. Glenn Steele. 1999. *Experimentation and Uncertainty Analysis for Engineers*. 2nd ed. New York, NY: John Wiley & Sons.
- Cooper, C. David, and Alley, F.C. 1994. *Air Pollution Control: A Design Approach*. 2nd ed. Prospect Heights, Illinois: Waveland Press, Inc.
- Devore, Jay L. 1995. *Probability and Statistics for Engineering and the Sciences*. 4th ed. Pacific Grove, CA: Brooks/Cole.
- The Engineering Toolbox. 2003. Saturated Steam Table in SI Units. <http://www.engineeringtoolbox.com/28_101.html>. Last accessed July 25, 2003.
- Holman, J.P. 2001. *Experimental Methods for Engineers*. 7th ed. Boston, MA: McGraw Hill.
- International Standards Organization (ISO). 1995. *Guide to the Expression of Uncertainty in Measurement*. Geneva: ISO.
- Kline, S.J., and McClintock, F.A. 1953. Describing Uncertainties in Single-Sample Experiments. *Mechanical Engineering*. 75: 3-8.
- Kline, S.J. 1985. The Purposes of Uncertainty Analysis. *Journal of Fluids Engineering*. 107: 153-161.
- National Institute of Standards and Technology (NIST). 1994. *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*. NIST Technical Note 1297. United States Department of Commerce. Washington, DC: US GPO.
- Sorenson, J.W., and Parnell, Calvin B. 1991. *Agricultural Processing Technology*. College Station, TX: Texas A&M University.
- USEPA. 1999. 40 CFR Part 50. National Ambient Air Quality Standards for Particulate Matter. *Federal Register*.
- Yegnan, A., D.G. Williamson, A.J. Graettinger. 2002. Uncertainty Analysis in Air Dispersion Modeling. *Environmental Modeling & Software*. 17: 639-649.

Appendix A Sensitivity Coefficient Determination

$$C = \frac{W}{V} \text{ (refer to equation 6)}$$

$$\frac{\delta C}{\delta W} = \frac{1}{V}$$

$$\frac{\delta C}{\delta V} = -\frac{W}{V^2}$$

$$W = W_f - W_i \text{ (refer to equation 7)}$$

$$\frac{\delta W}{\delta W_f} = 1$$

$$\frac{\delta W}{\delta W_i} = -1$$

$$V = Q * \Theta \text{ (refer to equation 8)}$$

$$\frac{\delta V}{\delta Q} = \Theta$$

$$\frac{\delta V}{\delta \Theta} = Q$$

$$Q = 5.976 * k * (D_0)^2 * \sqrt{\frac{\Delta P_a}{\rho_a}} \text{ (refer to equation 9)}$$

$$\frac{\delta Q}{\delta k} = 5.976 * (D_0)^2 * \sqrt{\frac{\Delta P_0}{\rho_a}}$$

$$\frac{\delta Q}{\delta D_0} = 11.952 * k * (D_0) * \sqrt{\frac{\Delta P_0}{\rho_a}}$$

$$\frac{\delta Q}{\delta \Delta P_0} = 2.988 * k * (D_0)^2 * \sqrt{\frac{1}{\Delta P_0 * \rho_a}}$$

$$\frac{\delta Q}{\delta \rho_a} = -2.988 * k * (D_0)^2 * \sqrt{\frac{\Delta P_0}{(\rho_a)^3}}$$

$$\rho_a = \left[\frac{P_a - RH * P_s}{0.37 * (460 + T)} \right] + \left[\frac{RH * P_s}{0.596 * (460 + T)} \right] \quad (\text{refer to equation 10})$$

$$\frac{\delta \rho_a}{\delta RH_a} = \frac{P_{sa}}{460 + T_a} * \left[\frac{1}{0.596} - \frac{1}{0.37} \right]$$

$$\frac{\delta \rho_a}{\delta P_{sa}} = \frac{RH_a}{460 + T_a} * \left[\frac{1}{0.596} - \frac{1}{0.37} \right]$$

$$\frac{\delta \rho_a}{\delta P_a} = \frac{1}{0.37 * (460 + T_a)}$$

$$\frac{\delta \rho_a}{\delta T_a} = \frac{1}{(460 + T_a)^2} * \left[\frac{-P_a}{0.37} + RH_a * P_{sa} * \left[\frac{1}{0.37} - \frac{1}{0.596} \right] \right]$$

$$k = \frac{Q_{LFE}}{5.976 * (D_0)^2 * \sqrt{\frac{\Delta P_c}{\rho_c}}} \quad (\text{refer to equation 11})$$

$$\frac{\delta k}{\delta Q_{LFE}} = \frac{1}{5.976 * (D_0)^2 * \sqrt{\frac{\Delta P_c}{\rho_c}}}$$

$$\frac{\delta k}{\delta D_0} = \frac{-2 * Q_{LFE}}{5.976 * (D_0)^3 * \sqrt{\frac{\Delta P_c}{\rho_c}}}$$

$$\frac{\delta k}{\delta \Delta P_c} = \frac{-\frac{1}{2} * Q_{LFE}}{5.976 * (D_0)^2 * \sqrt{\frac{\Delta P_c^3}{\rho_c}}}$$

$$\frac{\delta k}{\delta \Delta P_c} = \frac{\frac{1}{2} * Q_{LFE}}{5.976 * (D_0)^2 * \sqrt{\Delta P_c * \rho_c}}$$

Appendix B Excel Models – Determination of Overall Concentration Uncertainties

$C = W/V$	333.82752 $\mu\text{g}/\text{m}^3$	OVERALL CONCENTRATION UNCERTAINTY		
C_c	2.892E-05 g/m^3	28.92162888 $\mu\text{g}/\text{m}^3$	OR	8.67%
W	0.00028284 g	$\delta C/W$	0.00360285	0.1473%
V	22.0891655 m^3	$\delta C/V$	-1.3587E-06	99.8527%
% of TOTAL Uncertainty				
$W = W_1 - W_2$	0.005 g			
W_1	0.000282843 g			
W_2	2.00E-04 g	$\delta W/W_1$	1	50.0000%
W_3	2.00E-04 g	$\delta W/W_2$	-1	50.0000%
$V = Q \cdot t$	8909.998654 ft^3	254.8515 m^3		
Q	779.8598285 ft^3	22.08317 m^3		
t	0.2 min	$\delta W/Q$	49.9999825	0.0184%
Q	4.332197288 cfm	$\delta W/Q$	180	99.9836%
% of Partial Uncertain % of Total Uncertainty				
$Q = 5.878 \cdot k \cdot D_0^2 \cdot \sqrt{\Delta P_a / \rho_a}$	(Uncertainty in D_0 is already accounted for in the calibration of k) (assume $F_A = 1$)			
Q	49.99998 cfm			
D_0	4.302197 cfm			
D_0	0 (accounted for in k)	$\delta Q/\delta D_0$	66.6666	0.0000%
ΔP_a	0.22601105 in of H_2O	$\delta Q/\delta \Delta P_a$	16.139	70.8958%
k	0.03728956	$\delta Q/\delta k$	62.3173	28.7878%
ρ_a	0.00073572 lb/ft^3	$\delta Q/\delta \rho_a$	-348.599	0.3485%
% of Partial Uncertain % of Total Uncertainty				
$k = Q/t / (5.878 \cdot D_0^2 \cdot \sqrt{\Delta P_a / \rho_a})$	0.60234559			
k	0.03728956			
Q/t	0.344 cfm	$\delta k/\delta Q/t$	0.01605	2.1802%
D_0	0.025 in	$\delta k/\delta D_0$	-1.06979	51.4130%
ΔP_a	0.1 in of H_2O	$\delta k/\delta \Delta P_a$	-0.25073	45.1872%
ρ_a	0.00076168 lb/ft^3	$\delta k/\delta \rho_a$	5.3857	1.2095%
% of Partial Uncertain % of Total Uncertainty				
$\rho_t = ((P_t - (RH_t \cdot P_{sat})) / (0.37(460 + T_c))) + (RH_t \cdot P_{sat}) / (0.586(460 + T_c))$	0.07448848 lb/ft^3			
ρ_c	0.00076168 lb/ft^3			
ρ_c	0.025	$\delta \rho_c/\delta RH_t$	-0.0007	0.0531%
ρ_c	0.0001 psia	$\delta \rho_c/\delta P_{sat}$	-0.00097	0.0000%
ρ_c	0.14678 psia	$\delta \rho_c/\delta P_c$	0.0061	86.5422%
ρ_c	1 °F	$\delta \rho_c/\delta T_c$	-0.00014	3.4047%
% of Partial Uncertainty % of Total U				
$\rho_a = ((P_a - (RH_a \cdot P_{sat})) / (0.37(460 + T_a))) + ((RH_a \cdot P_{sat}) / (0.586(460 + T_a)))$	0.07212842 lb/ft^3			
ρ_a	0.00073572 lb/ft^3			
ρ_a	0.0174	$\delta \rho_a/\delta RH_a$	-0.00112	0.0703%
ρ_a	0.0001 psia	$\delta \rho_a/\delta P_{sat}$	-0.00109	0.0000%
ρ_a	0.14678 psia	$\delta \rho_a/\delta P_a$	0.00496	97.8587%
ρ_a	8.8 °F	$\delta \rho_a/\delta T_a$	-0.00013	2.0711%
% of Partial Uncertain % of Total Uncertainty				

Figure 4. TAMU High Volume Uncertainty Analysis

$C = WV$	333.20577 $\mu\text{g}/\text{m}^3$	OVERALL CONCENTRATION UNCERTAINTY			
c_c	3.948E-05 g/m^3	33.45206515 $\mu\text{g}/\text{m}^3$	OR	11.85%	
W	1.4142E-07 g	$\delta C/\delta W$	0.33320577	0.0001%	
V	0.35581045 m^3	$\delta C/\delta V$	-0.00011103	98.9998%	
% of TOTAL Uncertainty					
$W = W_f - W_i$	0.001 g				
W	1.41421E-07 g				
% of Partial Uncertain % of Total Uncertainty					
W_f	1.00E-07 g	$\delta W/\delta W_f$	1	50.0000%	0.0001%
W_i	1.00E-07 g	$\delta W/\delta W_i$	-1	50.0000%	0.0001%
$V = QB$	105.9945585 ft^3	3.00115 m^3			
V	12.5582648 ft^3	0.35581 m^3			
% of Partial Uncertain % of Total Uncertainty					
Q	0.2 min	$\delta V/\delta Q$	0.5895031	0.0088%	0.0088%
B	0.080785 cfm	$\delta V/\delta B$	180	99.9912%	99.9911%
$Q = 5.978 * k * D_o^{-2} * \text{sqrt}(\Delta P/\rho_a)$ (uncertainty in D_o is already accounted for in the calibration of k)					
	0.5888 cfm	(assume $F_A = 1$)			
Q	0.08977 cfm				
% of Partial Uncertal % of Total Uncertainty					
D_o	0 (accounted for in k)	$\delta Q/\delta D_o$	5.28057	0.0000%	0.0000%
ΔP_a	0.21179235 in of H_2O	$\delta Q/\delta \Delta P_a$	0.27405	69.1930%	69.1999%
ρ_a	0.04761448	$\delta Q/\delta \rho_a$	0.8108	30.6217%	30.6190%
p_a	0.00073572 lbs/ft^2	$\delta Q/\delta p_a$	-4.0016	0.1853%	0.1853%
$k = Q_{\text{mass flow rate}} / (5.978 * D_o^{-2} * \text{sqrt}(\Delta P/\rho_a))$					
	0.73820033				
k	0.04761448				
% of Partial Uncertal % of Total Uncertainty					
$Q_{\text{mass flow}}$	0.00705 cfm	$\delta k/\delta Q_{\text{mass}}$	1.4524	5.8907%	1.8006%
D_o	0.001 in	$\delta k/\delta D_o$	-7.7461	2.6499%	0.8104%
ΔP_a	0.1 in of H_2O	$\delta k/\delta \Delta P_a$	-0.4538	90.8540%	27.8218%
p_a	0.00078188 lbs/ft^2	$\delta k/\delta p_a$	4.87458	0.6081%	0.1862%
$p_c = ((P_c - (RH_c * P_{\text{sat}})) / (0.37 * (460 + T_c))) + (RH_c * P_{\text{sat}}) / (0.598 * (460 + T_c))$					
	0.07449348 lbs/ft^2				
p_c	0.00078188 lbs/ft^2				
% of Partial Uncertal % of Total Uncertainty					
RH_c	0.025	$\delta p_c/\delta RH_c$	-0.0007	0.0531%	0.0001%
P_{sat}	0.0001 psia	$\delta p_c/\delta P_{\text{sat}}$	-0.00087	0.0000%	0.0000%
P_c	0.14676 psia	$\delta p_c/\delta P_c$	0.0051	96.5422%	0.1707%
T_c	1 * F	$\delta p_c/\delta T_c$	-0.00014	3.4047%	0.0063%
$p_a = ((P_a - (RH_a * P_{\text{sat}})) / (0.37 * (460 + T_a))) + (RH_a * P_{\text{sat}}) / (0.598 * (460 + T_a))$					
	0.07212942 lbs/ft^2				
p_a	0.00073572 lbs/ft^2				
% of Total Uncertainty					
% of Partial Uncertal % of Total Uncertainty					
RH_a	0.0174	$\delta p_a/\delta RH_a$	-0.0011	0.0703%	0.0001%
P_{sat}	0.0001 psia	$\delta p_a/\delta P_{\text{sat}}$	-0.0011	0.0000%	0.0000%
P_a	0.14676 psia	$\delta p_a/\delta P_a$	0.00496	97.8687%	0.1813%
T_a	0.8 * F	$\delta p_a/\delta T_a$	-0.0001	2.0711%	0.0028%

Figure 5. TAMU Low Volume Uncertainty Analysis

C = WV		427.59892 $\mu\text{g}/\text{m}^3$		OVERALL CONCENTRATION UNCERTAINTY	
σ_c	5.122E-05 g/m^3	51.22319747 $\mu\text{g}/\text{m}^3$	OR	11.98%	
% of TOTAL Uncertainty					
σ_W	0.00026284 g	$\delta C/\delta W$	0.00500058	0.0772%	
σ_V	23.8037135 m^3	$\delta C/\delta V$	-2.1511E-06	98.8228%	
$W = W_f - W_i$ 0.085 g					
σ_W	0.000282843 g	% of Partial Uncertain % of Total Uncertainty			
σ_{w_f}	2.00E-04 g	$\delta W/\delta W_f$	1	50.0000%	0.0388%
σ_{w_i}	2.00E-04 g	$\delta W/\delta W_i$	-1	50.0000%	0.0388%
$V = QB$ 7020.005311 ft^3 198.794 m^3					
σ_V	840.6202073 ft^3 23.8037 m^3	% of Partial Uncertain % of Total Uncertainty			
σ_Q	0.2 min	$\delta V/\delta Q$	39.0000295	0.0080%	0.0080%
σ_B	4.669911 cfm	$\delta V/\delta B$	180	99.9914%	99.9142%
$Q = 5.876 * k * D_o^{-2} * \text{sqrt}(\Delta P_c/\rho_a)$ (uncertainty in D_o is already accounted for in the calibration of k) 39 cfm (assume $F_A = 1$)					
σ_Q	4.66991 cfm	% of Partial Uncertain % of Total Uncertainty			
σ_{k_c}	0 (accounted for in k)	$\delta Q/\delta k_c$	52	0.0000%	0.0000%
$\sigma_{\Delta P_c}$	0.2076082 in of H_2O	$\delta Q/\delta \Delta P_c$	20.6672	84.7457%	84.8730%
σ_{ρ_a}	0.03728666	$\delta Q/\delta \rho_a$	48.6075	15.0729%	15.0600%
σ_{P_a}	0.00073572 lb/ft^2	$\delta Q/\delta P_a$	-270.35	0.1814%	0.1812%
$k = Q/B * (5.876 * D_o^{-2} * \text{sqrt}(\Delta P_c/\rho_a))$ 0.80234569					
σ_k	0.03728666	% of Partial Uncertain % of Total Uncertainty			
$\sigma_{Q_{cal}}$	0.344 cfm	$\delta k/\delta Q_{cal}$	0.01905	2.1902%	0.3299%
σ_{D_o}	0.025 in	$\delta k/\delta D_o$	-1.0098	51.4130%	7.7428%
$\sigma_{\Delta P_c}$	0.1 in of H_2O	$\delta k/\delta \Delta P_c$	-0.2507	45.1872%	6.8652%
σ_{P_c}	0.00076188 lb/ft^2	$\delta k/\delta P_c$	5.3957	1.2665%	0.1822%
$P_c = ((P_c - (RH_c * P_{sat})) / (0.37(460 + T_c))) + ((RH_c * P_{sat})) / (0.586(460 + T_c))$ 0.07493948 lb/ft^2					
σ_{P_c}	0.00076188 lb/ft^2	% of Partial Uncertain % of Total Uncertainty			
σ_{RH_c}	0.025	$\delta P_c/\delta RH_c$	-0.0007	0.0531%	0.0001%
$\sigma_{P_{sat}}$	0.0001 psia	$\delta P_c/\delta P_{sat}$	-0.001	0.0000%	0.0000%
σ_{T_c}	0.14676 psia	$\delta P_c/\delta T_c$	0.0051	66.5422%	0.1756%
σ_{T_c}	1 ° F	$\delta P_c/\delta T_c$	-0.0001	3.4047%	0.0002%
$P_a = (P_a - (RH_a * P_{sat})) / (0.37(460 + T_a)) + ((RH_a * P_{sat})) / (0.586(460 + T_a))$ 0.07212942 lb/ft^2					
σ_{P_a}	0.00073572 lb/ft^2	% of Total Uncertainty			
σ_{RH_a}	0.0174	$\delta P_a/\delta RH_a$	-0.0011	0.0703%	0.0001%
$\sigma_{P_{sat}}$	0.0001 psia	$\delta P_a/\delta P_{sat}$	-0.0011	0.0000%	0.0000%
σ_{P_a}	0.14676 psia	$\delta P_a/\delta P_a$	0.00498	67.9587%	0.1774%
σ_{T_a}	0.8 ° F	$\delta P_a/\delta T_a$	-0.0001	2.0711%	0.0039%

Figure 6. USEPA Lower Limit – High Volume Uncertainty Analysis

C = WV	277.93853 $\mu\text{g}/\text{m}^3$	OVERALL CONCENTRATION UNCERTAINTY			
ρ_c	2.014E-05 g/m^3	20.13634863 $\mu\text{g}/\text{m}^3$	CR	7.25%	
% of TOTAL Uncertainty					
ρ_W	0.00028284 g	$\delta C/\delta W$	0.00326889	0.2103%	
ρ_V	22.1363121 m^3	$\delta C/\delta V$	-9.0883E-07	89.7891%	
W = $W_f - W_i$ 0.085 g					
ρ_W	0.000282843 g				
% of Partial Uncertain % of Total Uncertainty					
ρ_{wf}	2.00E-04 g	$\delta W/\delta W_f$	1	50.0000%	0.1054%
ρ_{wi}	2.00E-04 g	$\delta W/\delta W_i$	-1	50.0000%	0.1054%
V = QB 10799.99901 ft^3 305.822 m^3					
ρ_V	781.7364849 ft^3	22.1363 m^3			
% of Partial Uncertain % of Total Uncertainty					
ρ_B	0.2 min	$\delta W/\delta B$	59.9999945	0.0238%	0.0235%
ρ_Q	4.342488 cfm	$\delta W/\delta Q$	100	99.9764%	99.7856%
Q = $5.978 \cdot k \cdot D_p^2 \cdot \sqrt{\rho \Delta P}$ (uncertainty in D_p is already accounted for in the calibration of k) 60 cfm (assume $F_A = 1$)					
ρ_Q	4.34247 cfm				
% of Partial Uncertain % of Total Uncertainty					
ρ_{Dp}	0 (accounted for in k)	$\delta Q/\delta Dp$	80	0.0000%	0.0000%
$\rho_{\Delta Pa}$	0.2484622 in of H_2O	$\delta Q/\delta \Delta Pa$	13.4467	58.2449%	59.1094%
ρ_k	0.03728668	$\delta Q/\delta k$	34.7807	41.2585%	41.1618%
$\rho_{\rho a}$	0.00073572 lbs/ft^3	$\delta Q/\delta \rho a$	-415.93	0.4889%	0.4954%
k = $Q_{std} / (5.978 \cdot D_p^2 \cdot \sqrt{\rho_c \Delta P_c})$ 0.80234558 0.10729958					
% of Partial Uncertain % of Total Uncertainty					
ρ_{Qstd}	0.344 cfm	$\delta k/\delta Q_{std}$	0.01605	2.1902%	0.8015%
ρ_{Dp}	0.025 in	$\delta k/\delta Dp$	-1.0698	51.4130%	21.1625%
$\rho_{\Delta Pc}$	0.1 in of H_2O	$\delta k/\delta \Delta Pc$	-0.2507	45.1872%	18.5999%
$\rho_{\rho c}$	0.00076108 lbs/ft^3	$\delta k/\delta \rho c$	5.2857	1.2093%	0.4879%
$\rho_c = (P_c - (RH_c \cdot P_{sat})) / (0.37 (460 + T_c)) + (RH_c \cdot P_{sat}) / (0.598 (460 + T_c))$ 0.07448848 lbs/ft^3 0.00076108 lbs/ft^3					
% of Partial Uncertain % of Total Uncertainty					
ρ_{RHc}	0.025	$\delta \rho_c/\delta RHc$	-0.0037	0.0531%	0.0033%
$\rho_{P_{satc}}$	0.0001 psia	$\delta \rho_c/\delta P_{satc}$	-0.001	0.0000%	0.0000%
ρ_{P_c}	0.14676 psia	$\delta \rho_c/\delta P_c$	0.0051	98.5422%	0.4937%
ρ_{Tc}	1 ° F	$\delta \rho_c/\delta Tc$	-0.0001	3.4047%	0.0170%
$\rho_a = (P_a - (RH_a \cdot P_{sat})) / (0.37 (460 + T_a)) + (RH_a \cdot P_{sat}) / (0.598 (460 + T_a))$ 0.07212942 lbs/ft^3 0.00073572 lbs/ft^3					
ρ_{RHa}	0.0174	$\delta \rho_a/\delta RHa$	-0.0011	0.0703%	0.0003%
$\rho_{P_{sata}}$	0.0001 psia	$\delta \rho_a/\delta P_{sata}$	-0.0011	0.0000%	0.0000%
ρ_{P_a}	0.14676 psia	$\delta \rho_a/\delta P_a$	0.00498	87.8587%	0.4848%
ρ_{T_a}	0.8 ° F	$\delta \rho_a/\delta T_a$	-0.0001	2.0711%	0.0103%

Figure 7. USEPA Upper Limit – High Volume Uncertainty Analysis