Error Factors for Enforcing a 160 μg/m3 Total Carbon (EC+OC) Personal Exposure Limit

For purposes of enforcement, Total Carbon (TC) is defined as the sum of Elemental Carbon (EC) and Organic Carbon (OC). Both EC and OC are measured by NIOSH Method 5040.¹

MSHA will issue a noncompliance citation when a valid personal TC exposure measurement demonstrates noncompliance with the $160_{TC} \,\mu\text{g/m}^3$ PEL at a high level of confidence. To this end, MSHA will continue adjusting each measurement according to an unexposed control filter (i.e., field blank) corresponding to each exposed filter. As explained in more detail elsewhere, MSHA will further adjust the TC measurement, when necessary, to avoid interferences from extraneous sources of OC. These adjustments are intended to minimize uncertainty due to potential systematic errors.

Neither of these adjustments, however, addresses uncertainty due to potential sampling and analytical errors (SAE). Such errors, which reflect the imprecision inherent in any measurement process, cause individual measurements to deviate above or below the true value by a random but statistically quantifiable amount. Measurement imprecision is quantified by the total coefficient of variation for SAE, or CV_{total} .

As with all other single-sample M/NM noncompliance determinations, MSHA will address uncertainty due to SAE by allowing a margin of error before issuing a citation for exceeding the $160~\mu\text{g/m}^3$ TC limit. This margin of error is designed to ensure that a citation will be issued only when a sample measurement demonstrates noncompliance with at least 95-percent confidence. To achieve this 95-percent confidence level, the necessary margin of error is constructed by applying an error factor appropriate for the measurement being considered. The error factor is calculated as

$$EF = 1 + (1.645 \times CV_{total})$$
.

Each exposure measurement involves three components: the volume of air pumped through the filter that collects DPM, the deposit area of particles on the filter (cm²), and the laboratory analysis of EC and OC density within the deposit ($\mu g/cm^2$). CV_{total} consists of three corresponding independent components — denoted CV_P , CV_D , and CV_A — that respectively quantify the random variability associated with each of these factors. To determine CV_{total} for an individual EC or unadjusted TC measurement, the components of CV_{total} are estimated separately and then combined according to a standard propagation of errors formula:

$$CV_{total} = \sqrt{CV_P^2 + CV_D^2 + CV_A^2}$$

¹ NIOSH Manual of Analytical Methods, Fourth Edition, at www.cdc.gov/Niosh/nmam/pdfs/5040.pdf

 $^{^2}$ CV_{total} represents the magnitude of probable sampling and analytical errors. Sometimes called the relative standard deviation (RSD), CV_{total} is defined as the ratio of the standard deviation of sampling and analytical measurement errors to the true value of whatever quantity is being measured. It can be expressed either as a fraction (e.g., 0.1) or as a percent (e.g., 10 percent) of the true value.

Appendix 1 derives MSHA's best estimates of the three CV components, based on the most recent laboratory data available. Appendix 2, which has previously appeared on MSHA's website in connection with earlier DPM error factors, explains details of the method by which updated estimates of CV_A were calculated for EC and TC measurements. Based on these estimates, CV_{total} works out to be $CV_{total}[EC] = 5.7\%$ for an EC measurement³ and $CV_{total}[TC] = 11.7\%$ for an unadjusted TC measurement.⁴

In accordance with Program Policy Letter No. P08-IV-1, some personal TC measurements will be ratio-adjusted in order to avoid interferences from extraneous sources of OC. This will be done by multiplying the EC concentration measurement from the personal sample by the average (\overline{R}) of TC-to-EC ratios taken from some number (N) of area samples.⁵ For such a ratio-adjusted measurement,

$$CV_{total}[TC_{adi}] = \sqrt{CV_{total}^{2}[EC] + CV_{A}^{2}[\overline{R}]}$$

since (1) sampling and analytical measurement errors in the area samples are statistically independent of such errors in the personal sample and (2) airflow and deposit area errors cancel out when forming the ratio of TC to EC within each sample. The last section of Appendix 1 derives a formula for computing $CV_A[\overline{R}]$ for any given value of N. Using these values, along with the value of $CV_{total}[EC] = 5.7\%$ mentioned earlier, $CV_{total}[TC_{adj}]$ ranges from 15.7% for N=1 to 7.4% for N=10.6

In accordance with Program Policy Letter No. P08-IV-1, there are two situations in which MSHA will cite noncompliance:

1. The 8-hour equivalent EC concentration measured by a valid personal sample exceeds $160 \, \mu g/m^3$ multiplied by the EF for EC measurements. In this case,

$$EF_{EC} = 1.095$$

Therefore, in this case, a citation will be issued when the personal 8-hour equivalent EC concentration measurement equals or exceeds $176 \mu g/m^3$.

2. The 8-hour equivalent TC concentration (EC_{personal} + OC_{personal}) measured by a valid personal sample exceeds 160 μ g/m³ multiplied by the EF for such measurements,

AND

³ This measurement is based on the average EC from two punches of an exposed filter, reduced by the EC from a single punch of an unexposed control filter.

⁴ This refers to a TC measurement that has not been adjusted using the ratio of TC to EC in any area samples. However, like the EC measurement, it is based on the average TC from two punches of an exposed filter, reduced by the TC from a single punch of an unexposed control filter.

⁵ To be included in the average ratio, the measured EC content of an area sample must be at least 5 μg/cm².

⁶ Each area sample ratio is based on averaging TC and EC from two punches of an exposed filter, reduced by the corresponding results from a single punch of an unexposed control filter. As discussed in Appendix 2, CV_{total} for the ratio-adjusted TC measurements (and consequently the error factors derived from them) could be substantially reduced if MSHA based its blank filter correction for area TC measurements on the average TC density (μg/cm²) detected on two punches from the associated unexposed control filter.

the ratio-adjusted personal TC concentration exceeds $160~\mu g/m^3$ multiplied by the appropriate EF, which depends on N (i.e., the number of area samples used to form the adjustment).

In this case, $EF_{TC} = 1.192$ and $EF_{TC(adj)}$ ranges from 1.259 for N=1 to 1.121 for N=10. The general formula for $EF_{TC(adj)}$, for any given value of N, is:

$$EF_{TC(adj)} = 1 + 1.645\sqrt{0.05745^2 + \frac{0.03419^2 / 2}{2} + 0.1456^2}$$

Therefore, in this case, a citation will be issued when:

- (a) the personal 8-hour equivalent TC concentration measurement equals or exceeds 191 $\mu g/m^3$, and
- (b) the ratio-adjusted 8-hour equivalent TC concentration equals or exceeds the value tabulated below.

Number of Area Samples Included in Average Ratio [†]	Citation Threshold for TC _{adj}
1	202
2	192
3	187
4	185
5	183
6	182
7	182
8	181
9	180
10	180

[†]To be included in the average TC-to-EC ratio, the EC content of an area sample (i.e., the denominator of the ratio) must be at least 5 μg/cm².

We believe that our estimates of CV_{total} , and the error factors they produce, are based on the best scientific data currently available and adequately reflect current sampling and analytical errors. However, we recognize that future improvements in sampling and/or analytical technology may reduce the random variability associated with measuring carbon concentrations. Therefore, MSHA may update these error factors based on future experimental data.

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CV_P: Variability in volume of air pumped through the filter

Variability in air volume depends on three factors: (1) variability in the initial setting of the pump rotameter to a calibration mark when sampling begins, (2) pump calibration errors, and (3) variability in air flow during the sampling period. Based on Bowman et al. (1984)⁷, MSHA estimates that uncertainty due to the combined effects of calibration errors and flow rate variability is represented by a coefficient of variation (CV) no greater than 3%. Based on the experimental results described by Tomb (1994)⁸, MSHA estimates that the CV component associated with variability in setting the rotameter ball is approximately 3%. Since variability in the initial flow rate is independent of calibration of the pump rotameter and variability in flow rate during sampling, these two uncertainty components can be combined as follows to yield the CV representing uncertainty in total volume of air pumped:

$$CV_D = \sqrt{(0.03)^2 + (0.03)^2} = 0.042$$

or 4.2 percent.

CV_D : Variability in area of dust deposited on filter

Variability in SKC sampler performance is manifested as variability in the area and uniformity, or density, of the particulate matter deposited on the filter. Variability in the density of the deposit is included in the estimated value of CV_A and is discussed below. Variability in the deposit area is addressed by CV_D .

Since 2001, the manufacturer of the sampling device (SKC, Inc. Eighty Four, PA.) has made a number of improvements designed to reduce variability in the deposit area. MSHA's current estimate of CV_D is based on a 2005 study assessing the performance of the improved device. Using data collected on 94 improved SKC

⁷ Bowman et al. (1984), Precision of Coal Mine Dust Sampling, CDC (NIOSH); NTIS No. PB-85-220-721

⁸ Tomb (1994) Memorandum dated Sept. 1 to Chief, Division of Health, CMS&H, MSHA, Subject: Determination of the Precision of Setting the Rotameter Ball to a Calibration Mark on Personal Respirable Dust Sampling Pumps. (available from MSHA's CMS&H single-sample rulemaking record)

⁹ Noll, J.D., R.T. Timko, L. McWilliams, P. Hall, and R. Haney. "Sampling Results of the Improved SKC Diesel Particulate Matter Cassette," Journal of Occupational and Environmental Hygiene, 2:29-37, January 2005.

samplers, that study found the coefficient of variation in deposit area to be 0.005 (i.e., 0.5 percent). Therefore,

$$CV_D = 0.005$$

or 0.5 percent.

CV_A: Analytical measurement imprecision

Analytical measurement imprecision refers to the random variability of repeated measurements of an analyte, performed on different punches taken from the same filter, within the same or different laboratories. In addition to imprecision in the instrumentation, this encompasses random variability in the punch area and in the density of the deposit, but not in the deposit area. Variability in the deposit area (a form of sampling variability) is quantified separately as CV_D above.

To estimate CV_A, MSHA combined data obtained from two sources. *Inter*-laboratory variability was estimated, as in previous versions of the DPM error factor, based on the original "paired punch comparison" carried out as part of the "31-Mine Study." The estimate of *intra*-laboratory variability, however, was updated to reflect current performance within the MSHA laboratory that analyzes MSHA's DPM samples. This updated estimate of intra-laboratory variability was based on 364 paired punches (i.e., two punches from the same sample filter) analyzed from January 3, 2006 through April 3, 2008. The independent estimates of inter- and intra-laboratory measurement variability were then combined to form an estimate of overall CV_A. For both component estimates, a square-root transformation was applied to each TC_(OC+EC) and EC measurement to stabilize the variance in the statistical analysis. Appendix 2 contains a justification for using this transformation and explains how it can be used to estimate intra-laboratory CV_A as a function of the filter loading.

Inter-laboratory Variability

In the original paired punch comparison, 621 filters were analyzed using two standard punches taken from each filter. One punch (labeled "A") was always analyzed in MSHA's laboratory. The second punch from the same filter (labeled "B") was either analyzed in MSHA's laboratory or in one of three other laboratories.¹¹

A repeated measures, random effects Analysis of Variance (ANOVA) was performed to derive an estimates of the inter-laboratory components of analytic measurement imprecision, based on the available data from all four laboratories.

For reasons explained in Appendix 2, the model used in the ANOVA was:

$$\sqrt{X_{iA}} - \sqrt{X_{ijB}} = \Delta_i + \lambda_{ij} (i \neq \text{MSHA}) + \varepsilon_{ij}$$

where

.

¹⁰ MSHA's Report on Data Collected During a Joint MSHA/Industry Study of DPM Levels in Underground Metal and Nonmetal Mines (January 6, 2003), available in the M/NM DPM Rulemaking Record (RIN 1219-AB29). The report contains a full description of the paired punch comparison, along with all of the data collected in connection with the study. Although the study mainly addressed variability in TC measurements, EC was separately measured in the course of the laboratory analysis of each punch. Consequently, both the TC and the EC analytic results reported in connection with this study are in the DPM rulemaking record.

 $^{^{11}}$ Because of the particular experimental design employed, the results combine purely analytical imprecision with variability in the density of the particulate deposited on the filter and with variability in the way the two punches were handled prior to analysis. Therefore, the estimate of CV_A presented here covers all three of these uncertainty components.

X is the analytic result from punch A or B reported in μ g/cm²;

i indexes the laboratory analyzing Punch B;

j indexes a specific filter;

 Δ_i is a fixed effect, representing the systematic difference between MSHA's punch A results and the punch B results at laboratory i;

 λ_{ij} is a random, Normally distributed, inter-laboratory effect with mean = 0 and variance = σ_i^2 ;

 ε_{ij} is a random, Normally distributed, intra-laboratory error with mean = 0 and variance = σ_{ε}^2 .

Inter-laboratory imprecision in this model was quantified by σ_{λ}^2 and, based on the ANOVA, estimated to be $\hat{\sigma}_{\lambda}^2 = 0.01642$ for EC and $\hat{\sigma}_{\lambda}^2 = 0.07713$ for TC.

Intra-laboratory Variability

To estimate intra-laboratory imprecision, represented by σ_{ε}^2 , the method of Appendix 2 was applied to MSHA's new body of paired punch data, compiled from January 3, 2006 through April 3, 2008. Accordingly, σ_{ε}^2 was estimated by the squared sample standard deviation of $(\sqrt{X_1} - \sqrt{X_2})$, using the 364 available paired punches from that period. The resulting estimates are $\hat{\sigma}_{\varepsilon}^2 = 0.00768$ for EC and $\hat{\sigma}_{\varepsilon}^2 = 0.01412$ for TC.

Combined Analytical Uncertainty

The composite estimate of analytical measurement uncertainty, including both intra- and inter-laboratory imprecision, is represented by $\hat{\sigma}_T^2 = \hat{\sigma}_{\lambda}^2 + \hat{\sigma}_{\varepsilon}^2$. Therefore,

$$\hat{\sigma}_T = \sqrt{\hat{\sigma}_{\lambda}^2 + \hat{\sigma}_{\varepsilon}^2} = \begin{cases} 0.15524 \text{ for EC} \\ 0.30208 \text{ for TC} \end{cases}$$

Appendix 2 shows that for a carbon measurement (X) based on a single punch, the coefficient of variation in analytical error is

$$CV_{\mu}[X] = \sigma_T \sqrt{\frac{2}{\mu}}$$

where μ is the true carbon loading (μ g/cm²) on the filter. However, to reduce analytical measurement uncertainty, MSHA routinely averages the results (X_1 and X_2) from two punches taken from an exposed filter and then subtracts the corresponding result (B) from an unexposed control filter. The adjusted measurement based on averaging X_1 and X_2 can be expressed as

$$Y = \frac{X_1 + X_2}{2} - B \, .$$

To simplify the notation in what follows, σ will be used to represent σ_T . As shown in Appendix 2, $Var[X_i]$ (i.e., the variance of X_i) is $2\sigma^2\mu$. Similarly, $Var[B] = 2\sigma^2 E[B]$, where E[B] is the "expected" or mean density of carbon measured on a control filter. Therefore, assuming independent analytical measurement errors for X_1, X_2 , and B,

$$Var[Y] = \left(\frac{1}{2}\right)^{2} 2 Var[X] + Var[B]$$

$$= \sigma^{2} \mu + 2\sigma^{2} E[B]$$

$$= \sigma^{2} [\mu + 2E[B]]$$

$$= \sigma^{2} [(E[Y] + E[B]) + 2E[B]]$$
since $E[Y]$ is $\mu - E[B]$

$$= \sigma^{2} [E[Y] + 3E[B]]$$

It follows that:

$$CV_{A} = CV[Y]$$

$$= \frac{\sqrt{Var[Y]}}{E[Y]}$$

$$= \frac{\sigma\sqrt{E[Y] + 3E[B]}}{E[Y]}$$

Based on data compiled from MSHA's analysis of carbon measurements on available control filters between December 4, 2002 and April 3,2008,

$$E[B] = \begin{cases} 0.1 & \mu g/m^2 \text{ for EC} \\ 6.0 & \mu g/m^2 \text{ for TC} \end{cases}.$$

Furthermore, using an airflow rate of 1.7 L/min, a deposit area of 8.0425 cm², and a nominal sampling duration of 480 min:

$$E[Y] \ge 16.23 \text{ µg/cm}^2$$

for EC or TC 8-hour equivalent concentration levels at or above 160 μ g/m³. Therefore, substituting the respective EC and TC values of $\hat{\sigma}_T$ for σ in the formula for CV_A and noting that CV_A decreases as E[Y] increases, it is evident that:

$$CV_A \le \begin{cases} 0.0388841 \text{ or } 3.89 \text{ percent for EC} \\ 0.1088763 \text{ or } 10.89 \text{ percent for TC} \end{cases}$$

$CV_A[\overline{R}]$: Analytical measurement imprecision for an average ratio adjustment factor

Suppose N samples are used to determine the average ratio of TC to EC in a mine. The TC-to-EC ratio (R) exhibited by a single given sample is calculated as follows:

$$R = \frac{\frac{TC_1 + TC_2}{2} - B_{TC}}{\frac{EC_1 + EC_2}{2} - B_{EC}}$$

where the two analytical measurements shown for both EC and TC are all made on the same exposed filter. B_{EC} and B_{TC} are measurements made on the same unexposed control filter, applied as corrections for the EC and TC measurements respectively. \overline{R} , the ratio of TC to EC used to adjust a personal TC exposure measurement, is defined as the sample average of N such ratios.

Within each sample used to estimate $CV_A[\overline{R}]$, let $R_1 = \frac{TC_1}{EC_1}$ and $R_2 = \frac{TC_2}{EC_2}$. Let

 $W = \text{Log}_{e}\left(\frac{R_1}{R_2}\right)$. Then, assuming measurement errors in R_1 and R_2 are identically

distributed and statistically independent, $Var[W] \approx 2 \times CV^2[R_i]$ for i = 1 or 2. Utilizing this relationship, MSHA's most recent body of paired punch data (January 3, 2006 through April 3, 2008) was used to estimate $CV[R_i]$.

Figure 1 plots W against the average EC measurement from a single filter and shows that variability in W increases markedly for EC loadings less than 5 μ g/cm². ¹⁴ Therefore, the estimate of Var[W] presented here is restricted to samples for which the average EC \geq 5 μ g/cm². Based on the sample standard deviation calculated from the 326 (out of 364) measurement pairs meeting this criterion, the estimated value of Var[W] is $(0.03419)^2$. Therefore, the estimated value of CV²[R_i] is $(0.03419)^2/2$.

¹² Log_e denotes the natural logarithm (i.e., the logarithm to the base e).

¹³ This is because $Var[Log_e(R_i)] \approx Var[R_i] \div E^2[R_i]$. See Ku, H.H. "Notes on the Use of Propagation of Error Formulas", *Precision Measurement and Calibration*, NBS Special Publication 300, Vol. 1, 1969. pp. 331-341. Note also that $Log(R_1/R_2) = Log(R_1) - Log(R_2)$. Therefore, under the stated assumptions, $E[R_1] = E[R_2]$ and $Var[Log(R_1/R_2)] = 2 \times Var[Log(R_i)]$.

¹⁴ Since EC appears in the denominator of each ratio, even relatively small errors in the EC measurement can have a large impact on the ratio when EC < 5 μg/cm². The difference in Var[W] for EC above and below this threshold is statistically significant.

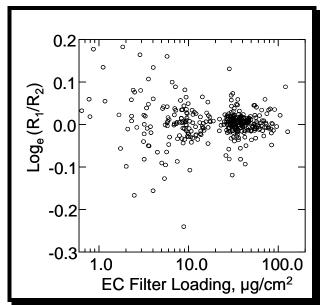


Figure 1. Natural logarithm of R1/R2, plotted against the average EC measurement from two punches of the same filter, based on 364 paired punches analyzed from January 3, 2006 through April 3, 2008.

As indicated above, $E[B_{EC}] = 0.1 \ \mu g/cm^2$ whereas $E[B_{TC}] = 6.0 \ \mu g/cm^2$. Therefore, for filters in which $EC \ge 5 \ \mu g/cm^2$, B_{EC} has a negligible effect on the calculation of R. Consequently, the contribution toward $CV_A[\overline{R}]$ of random error in the control filter adjustment can be considered to be based entirely on B_{TC} .

To obtain a conservative estimate of this contribution, the sample standard deviation of (R_1-R_2) was calculated for just those samples in which $TC \le 10 \ \mu g/cm^2$ and then divided by $\sqrt{2}$. ¹⁵ Based on the 15 samples (out of 364) for which $TC \le 10 \ \mu g/cm^2$, the contribution of error in a single control filter adjustment toward overall analytical variability in \overline{R} is conservatively estimated to be $\frac{0.20594}{\sqrt{2}}$, or 14.6 percent. ¹⁶

To construct an estimate of $CV_A[\overline{R}]$, the estimated value of $CV^2[R_i]$ is divided by two, to reflect the fact that each value of TC and EC used to form a ratio is based on the average of two independent punch measurements. The result is then combined, by means of a standard propagation of error formula, with the squared estimated contribution of the

¹⁵ The factor of $\sqrt{2}$ appears because Var[$R_1 - R_2$] = 2 σ_R^2 , where σ_R is the standard deviation of R_i . To calculate the CV component representing the actual contribution, σ_R must be divided by the ratio of TC to EC, which is unknown and anticipated to vary from mine to mine. However, since this ratio is always ≥ 1, the CV component is necessarily ≤ σ_R . In this sense, σ_R provides a conservative estimate.

¹⁶ If the average from two unexposed control filter punches were used to adjust each TC measurement, instead of from one punch, then σ_R would be reduced by an additional factor of $\sqrt{2}$. In this case, the conservatively estimated contribution to $CV_A[\overline{R}]$ would be reduced from no more than 14.6% down to no more than 10.3%.

control filter correction for TC. Since \overline{R} represents the average of N independently determined ratios, $CV_A^2[\overline{R}]$ is further reduced by a factor of N. This yields the following estimate, expressed as a decimal fraction:

$$CV_A[\overline{R}] = \sqrt{\frac{0.03419^2/2}{2} + 0.1456^2}$$
.

If the average TC from two unexposed control filter punches, instead of from one, were used to correct each TC measurement, then 0.1456 would be replaced by 0.1030 in this formula.

For reasons explained earlier, the estimated value of $CV_A[\overline{R}]$ is valid only when the samples used to calculate \overline{R} all exhibit average EC loadings $\geq 5 \, \mu \text{g/cm}^2$.

Appendix 2.

Use of Variance-Stabilizing Transformation for Analysis of TC_(OC+EC) and EC Measurement Variability

Let *i* index a specific filter, and let X_{il} and X_{i2} denote two carbon measurements ($\mu g/cm^2$) made using two punches from that filter. As noted in the documentation for NIOSH Method 5040, the variance of a carbon measurement made using this method ($Var[X_i]$) is roughly proportional to the carbon loading ($\mu g/cm^2$) on a filter. This relationship can be expressed as

$$Var[X_i] = \lambda^2 \mu_i \tag{Eq. 1}$$

where λ^2 is a constant and μ_i is the true loading on the i^{th} filter. Since μ varies but λ is constant, it follows that the coefficient of variation $(CV_{\mu}[X])$, which quantifies measurement variability relative to any given loading, decreases as μ increases:

$$CV_{\mu}[X] = \frac{\sqrt{Var[X]}}{\mu} = \frac{\lambda\sqrt{\mu}}{\mu} = \frac{\lambda}{\sqrt{\mu}}$$
 (Eq. 2)

To estimate λ , and thereby to calculate $CV_{\mu}[X]$ as a function of filter loading, a variance-stabilizing square-root transformation was applied to each measurement. Using the standard propagation of error formula applicable to Eq. 1,

$$Var\left[\sqrt{X_i}\right] \approx \frac{\lambda^2}{4}$$

for a carbon measurement at any filter loading. Based on this approximation, and assuming independent measurement errors in X_{i1} and X_{i2} ,

$$Var\left[\sqrt{X_{i1}} - \sqrt{X_{i2}}\right] = 2 \times Var\left[\sqrt{X_{i}}\right] = \frac{\lambda^{2}}{2}$$
 (Eq. 3)

Consequently,

$$\lambda = \left(2 \times Var \left[\sqrt{X_{i1}} - \sqrt{X_{i2}} \right] \right)^{1/2}$$

$$= \sigma \sqrt{2}$$
(Eq. 4)

where σ denotes the standard deviation of the differences $\sqrt{X_{i1}} - \sqrt{X_{i2}}$.

From Equations 1 and 4 it follows that $Var[X_i] = 2\sigma^2 \mu_i$, and combining Equations 2 and 4 yields the formula used to quantify EC or TC measurement variability at a given filter loading:

$$CV_{\mu}[X] = \sigma \sqrt{\frac{2}{\mu}}$$
 (Eq. 5)

¹⁷ NIOSH. *Manual of Analytical Methods (NMAM)*. *Chapter Q*, "Monitoring of Diesel Particulate Exhaust in the Workplace," Third Supplement to NMAM, 4th Edition (2003), p. 234.

¹⁸ Ku, H.H. "Notes on the Use of Propagation of Error Formulas", *Precision Measurement and Calibration*, NBS Special Publication 300, Vol. 1, 1969. pp. 331-341.