

Metal and Nonmetal Diesel Particulate Matter (DPM) Standard Error Factors for 350 µg/m³ Total Carbon Exposure Limit

Error Factor

As with all other exposure-based M/NM compliance determinations, MSHA will address uncontrollable sampling and analytical errors (SAE) by allowing a margin of error before issuing a citation for exceeding the total carbon (TC) limit. In addition to using the sum of organic carbon (OC) and elemental carbon (EC) as a measure of total carbon (i.e. TC_(OC+EC)) MSHA will employ an enforcement policy for the personal exposure limit that will use elemental carbon as a measure of TC (i.e. TC_(ECx1.3)). This policy will assure that a citation based on the 350 microgram per cubic meter of air (µg/m³) limit of TC is valid and not the result of interferences. MSHA has developed appropriate error factors to account for variability in sampling and analysis from such things as pump flow rate, filters, and the NIOSH 5040 method. If the TC_(OC+EC) measurement is equal to or below 350 (µg/m³) times the error factor, MSHA will not issue a citation.

If the TC_(OC+EC) measurement is above the error factor level of 396 µg/m³ (350 µg/m³ times 1.13), MSHA will look at the EC measurement from the sample and apply a factor of 1.3 to produce a statistical estimate of TC without interferences. As a matter of enforcement discretion, MSHA will use the TC_(ECx1.3) measurement as a check to validate that an overexposure is not the result of interferences.

The Agency will issue a citation only if the personal exposure measurement demonstrates noncompliance with at least 95-percent confidence. We will achieve this 95-percent confidence level by comparing each TC and EC measurement to the concentration limit multiplied by the appropriate error factor. The error factor (EF) is calculated as $EF = 1 + (1.645 \times CV_{total})$ where CV_{total} is the coefficient of variation of the combined sampling and analytical method.^{1,2}

The error factor accounts for three uncontrollable variance components represented by CV_{total} and then applied to the eight-hour equivalent full-shift measurement of TC_(OC+EC) or TC_(ECx1.3) using Method 5040. The three components address: (1) pump performance relative to the nominal airflow of 1.7 L/min, (2) variability of the deposit area

¹ The constant 1.645 is a 95-percent 1-tailed confidence coefficient.

of particles on the filter, and (3) laboratory analysis of carbon within the deposit area on the filter. These individual variance components are denoted as CV_P , CV_D , and CV_A respectively. To determine CV_{total} , the individual components were estimated separately and then combined according to a standard propagation of errors formula:

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

Appendix 1 presents MSHA's estimates of the three CV components. Because CV_A varies according to the amount of carbon deposited on a filter,² the error factor will be different for different personal exposure limits. Based on the estimates shown in the following section and the filter loadings corresponding to $TC_{(OC+EC)}$ and $TC_{(ECx1.3)}$ at the exposure limit, the error factors we will use for the final personal exposure limit of $350 \mu\text{g}/\text{m}^3$ total carbon effective January 20, 2007 are:

- $EF = 1.13$ for $TC_{(OC+EC)}$; and
- $EF = 1.11$ for $TC_{(ECx1.3)}$.

This means MSHA will issue a citation for noncompliance with the $350 \mu\text{g}/\text{m}^3$ total carbon exposure limit if we obtain eight-hour equivalent full shift concentration measurements of TC that are:

- $396 \mu\text{g}/\text{m}^3$ $TC_{(OC+EC)}$ or greater and are also
- $389 \mu\text{g}/\text{m}^3$ $TC_{(ECx1.3)}$ or greater.

We believe that our estimates of CV_{total} are based on the best scientific data currently available and reflects current sampling and analytical errors. However, MSHA recognizes 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.

² As explained in the appendix, CV_A (the analytical component of CV_{total}) increases as the filter loading (i.e., density of deposited carbon) decreases. Therefore, since the loading will generally be lower at lower carbon concentrations, CV_A (and hence CV_{total}) will increase as carbon concentration levels decrease.

Appendix 1. Determination of the Error Factor

The error factor (EF) is defined as

$EF = 1 + (1.645 \times CV_{total})$, where $CV_{total} = \sqrt{CV_P^2 + CV_D^2 + CV_A^2}$. In this appendix, we will present and explain MSHA's current estimate for each of the three components contributing to CV_{total} . These estimates are used to determine the EF for $TC_{(OC+EC)}$ and $TC_{(ECx1.3)}$.

CV_P : Variability in volume of air pumped through the filter

Variability in the 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)³, 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)⁴, 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:

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

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. The variability in the total deposit area is addressed using CV_D .

³ Bowman et al. (1984), Precision of Coal Mine Dust Sampling, CDC (NIOSH); NTIS No. PB-85-220-721

⁴ 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 CMS&H single-sample rulemaking record)

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. The CV_D is based on a recent study assessing the performance of the improved SKC sampler.⁵ The increased precision of the deposit area was determined to be 0.005 using the data collected on 94 improved SKC samplers, therefore the CV_D is 0.5 (i.e. 0.005 times 100).

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 used data obtained from the "paired punch comparison" carried out as part of the Joint MSHA/Industry Study: Determination of DPM Levels in Underground Metal and Nonmetal Mines (Report on the 31-Mine Study, January 6, 2003). A full description of the paired punch comparison is presented in that report, which has, along with all of the data collected in connection with the study, been placed into the public record for the Diesel Particulate Matter Exposure of Underground Metal and Nonmetal Mines rule (RIN 1219-AB29). 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 TC and EC analytic results are in the DPM rulemaking record.

In the 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.⁶

⁵Noll, 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.

⁶ 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

A repeated measures, random effects Analysis of Variance (ANOVA) was performed to derive composite estimates of the intra- and inter-laboratory components of analytic measurement imprecision, based on the available data from all four laboratories. To stabilize the variance in this analysis, a square-root transformation was first applied to each $TC_{(OC+EC)}$ and EC measurement. Appendix 2 contains further justification for using this transformation and explains how it can be used to estimate CV_A as a function of the filter loading.

The model used in the ANOVA was:

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

where

X is the analytic result from punch A or B reported in $\mu\text{g}/\text{cm}^2$;

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_λ^2 ;

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

Since MSHA was the only laboratory to have analyzed more than one punch from the same filter, it was necessary to assume that intra-laboratory imprecision, represented by σ_ϵ^2 , was the same in all four laboratories.

Although Δ_i is a necessary part of the ANOVA model, it represents bias that equally affects all results in the same laboratory. Therefore, MSHA expects Δ_i to be canceled out when control filters are used to adjust the calculated concentrations. Consequently, for exposure measurements that are appropriately corrected by means of control filters, the composite estimate of analytical measurement uncertainty, including both intra- and inter-laboratory imprecision, is represented by $\hat{\sigma}_T^2 = \hat{\sigma}_\lambda^2 + \hat{\sigma}_\epsilon^2$. The estimates of

way the two punches were handled prior to analysis. Therefore, the estimate of CV_A presented here covers all three of these uncertainty components.

σ_λ^2 , σ_ε^2 , and σ_T^2 for $TC_{(ECx1.3)}$ or $TC_{(OC+EC)}$ based on this ANOVA are shown in the following two tables.⁷

Estimated analytical imprecision of EC measurements.

	σ_λ^2	σ_ε^2	σ_T^2	σ_T
Estimate	0.01642	0.04917	0.06559	0.256
Standard Error	0.00751	0.00624	0.00418	N/A
95% UCL	0.02877	0.05943	0.07246	0.269

Estimated analytical imprecision of $TC_{(OC+EC)}$ measurements.

	σ_λ^2	σ_ε^2	σ_T^2	σ_T
Estimate	0.07713	0.03746	0.11459	0.339
Standard Error	0.00872	0.00476	0.01196	N/A
95% UCL	0.09147	0.04529	0.13426	0.366

As shown in Appendix 2, for a carbon measurement (X , expressed in $\mu\text{g}/\text{cm}^2$) 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 ($\mu\text{g}/\text{cm}^2$) on the filter. However, to reduce analytical measurement uncertainty, MSHA will average the results (X_1 and X_2) from two punches taken from each exposed filter and then subtract the corresponding result (B) from the 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, $\text{Var}[X_i]$, the variance of X_i , is $2\sigma^2\mu$. Similarly, $\text{Var}[B] = 2\sigma^2E[B]$, 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 ,

⁷ Restricted Maximum Likelihood Estimates (REML) of the parameters were obtained using Module 3V of the BMDP statistical software package. The REML restriction is to the class of unbiased estimators.

$$\begin{aligned}
\text{Var}[Y] &= \left(\frac{1}{2}\right)^2 2 \text{Var}[X] + \text{Var}[B] \\
&= \sigma^2 \mu + 2\sigma^2 E[B] \\
&= \sigma^2 [\mu + 2E[B]] \\
&= \sigma^2 [(E[Y] + E[B]) + 2E[B]] \\
&\quad \text{since } E[Y] \text{ is } \mu - E[B] \\
&= \sigma^2 [E[Y] + 3E[B]]
\end{aligned}$$

It follows that:

$$\begin{aligned}
CV_A &= CV[Y] \\
&= \frac{\sqrt{\text{Var}[Y]}}{E[Y]} \\
&= \frac{\sigma \sqrt{E[Y] + 3E[B]}}{E[Y]}
\end{aligned}$$

Based on data compiled from MSHA's analysis of carbon measurements on available control filters between 12/04/2002 and 10/11/06, the $E[B]$ is $0.1 \mu\text{g}/\text{cm}^2$ for EC and $6.0 \mu\text{g}/\text{cm}^2$ for $\text{TC}_{(\text{OC}+\text{EC})}$. Furthermore, using an airflow rate of 1.7 L/min, a deposit area of 8.0425 cm^2 , and a nominal sampling duration of 480 min:

$E[Y] \geq 27.39 \mu\text{g}/\text{cm}^2$ for EC filter concentration levels at or above the exposure limit of $350 \mu\text{g}/\text{m}^3$ total carbon;

$E[Y] \geq 35.51 \mu\text{g}/\text{cm}^2$ for $\text{TC}_{(\text{OC}+\text{EC})}$ filter concentration levels at or above the exposure limit of $350 \mu\text{g}/\text{m}^3$ total carbon.

Therefore, substituting the estimated value of σ_T for σ in the formula for CV_A and noting that CV_A decreases as $E[Y]$ increases, it is evident that:

$$CV_A \leq 0.049 \text{ for } EC \geq 270 \mu\text{g}/\text{m}^3;$$

$$CV_A \leq 0.070 \text{ for } \text{TC}_{(\text{OC}+\text{EC})} \geq 350 \mu\text{g}/\text{m}^3.$$

The net effect of including revised values for $E[B]$ and CV_D results in an increase in overall precision (CV_{Total}) of 0.01 when applying $\text{TC}_{(\text{OC}+\text{EC})}$ and $\text{TC}_{(\text{EC} \times 1.3)}$ as measures of total carbon.

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_{i1} and X_{i2} denote the two carbon measurements ($\mu\text{g}/\text{cm}^2$) made using the two punches from that filter. As noted in the documentation for Method 5040, the variance of a carbon measurement made using this method ($\text{Var}[X_i]$) is roughly proportional to the carbon loading ($\mu\text{g}/\text{cm}^2$) on a filter.⁸ This relationship can be expressed as

$$\text{Var}[X_i] = \lambda^2 \mu_i \quad (\text{Eq. 1})$$

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 ($\text{CV}_\mu[X]$), which quantifies measurement variability relative to any given loading, decreases as μ increases:

$$\text{CV}_\mu[X] = \frac{\sqrt{\text{Var}[X]}}{\mu} = \frac{\lambda\sqrt{\mu}}{\mu} = \frac{\lambda}{\sqrt{\mu}} \quad (\text{Eq. 2})$$

To estimate λ , and thereby to calculate $\text{CV}_\mu[X]$ 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,

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

for a carbon measurement at any filter loading.⁹ Based on this approximation, and assuming independent measurement errors in X_{i1} and X_{i2} ,

$$\text{Var}[\sqrt{X_{i1}} - \sqrt{X_{i2}}] = 2 \times \text{Var}[\sqrt{X_i}] = \frac{\lambda^2}{2} \quad (\text{Eq. 3})$$

Consequently,

$$\begin{aligned} \lambda &= \left(2 \times \text{Var}[\sqrt{X_{i1}} - \sqrt{X_{i2}}]\right)^{1/2} \\ &= \sigma\sqrt{2} \end{aligned} \quad (\text{Eq. 4})$$

⁸ NIOSH Method of Analytical Methods, Fourth Edition. Method 5040, Issue 3 (interim), Sept. 30, 1999. p. 4.

⁹ 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.

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 TC measurement variability at a given filter loading:

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