Metal and Nonmetal Diesel Particulate Matter (Dpm)
Standard Error Factor for TC Analysis

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. MSHA will employ an enforcement policy for the interim concentration limit that will use elemental carbon (EC) as an analyte to ensure that a citation based on the 400 microgram per cubic meter of air limit of TC is valid and not the result of interferences. MSHA has developed an appropriate error factor to account for variability in sampling and analysis from such things as pump flow rate, filters, and the NIOSH 5040 method. If the TC measurement is below 400 micrograms per cubic meter of air times the error factor, MSHA will not issue a citation.

If the TC measurement is above the error factor level, MSHA will look at the EC measurement from the sample, and multiply EC by a factor of 1.3 to produce a statistical estimate of what TC should be without interferences. If the TC measurement is above this estimate, as a matter of enforcement discretion, MSHA will not issue a citation when the EC measurement times the multiplier is below the error factor level.

The Agency will issue a citation only if a measurement demonstrated noncompliance with at least 95-percent confidence. We will achieve this 95-percent confidence level by comparing each EC measurement to the EC concentration limit multiplied by an appropriate "error factor." The error factor (EF) would be calculated as $EF = 1 + (1.645 \times CV_{total})$.[1,2]

There are three factors involved in an eight-hour equivalent full-shift measurement of EC concentration using Method 5040: air volume (i.e., pump performance relative to the nominal airflow of 1.7 L/min), deposit area of particles on the filter (cm^2), and laboratory analysis of EC density within the deposit ($\mu g/cm^2$). CV_{total} consists of three 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}, its components can be estimated separately and then

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

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 EC deposited on a filter,[2] the error factor will be different for different concentration limits. Based on the estimates shown in Appendix 1 for EC filter loadings corresponding to the proposed interim and final limits, the error factor we propose to use is:

- EF = 1.12 for the interim EC concentration limit of 308_{EC} µg/m^3 in effect until January 19, 2006;
- EF = 1.15 for the EC concentration limit of 123_{EC} µg/m^3 in effect after January 19, 2006.

This means we will issue a citation for noncompliance with the exposure limit if we obtain an eight-hour equivalent full shift EC concentration measurement that is:

- 345_{EC} µg/m^3 or greater until January 19, 2006 (i.e., 1.12×308);
- 142_{EC} µg/m^3 or greater after January 19, 2006 (i.e., 1.15×123).

If a measurement exceeds the concentration limit, but not the limit multiplied by the error factor, we will interpret this as evidence of noncompliance —— but not strong enough evidence to warrant a citation.

We believe that our estimate of CV_{total} is based on the best scientific data currently available and accurately 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 EC concentrations. Therefore, MSHA may update the error factor, if appropriate, based on future experimental data.

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

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, discussed below.

To estimate CV_D, MSHA measured the diameter of the deposit on a random selection of 75 exposed filters and calculated the corresponding deposit areas. The mean

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[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)

measured deposit area was 9.12 cm^2, and the standard deviation was 0.283 cm^2. Based on these data:

$$CV_D = \frac{0.283}{9.12} = 0.031$$

It should be noted that since the time these data were obtained (in 2001), the manufacturer of the sampling device (SKC) has made a number of improvements designed to reduce variability in the deposit area. SKC's specification for the deposit area is now 8.0425 ± 0.0383 cm^2. Although these specifications correspond to a value of CV_D substantially lower than 0.031, experimental data supporting a lower value are not yet available.

CV_A: Analytical measurement imprecision

Analytical measurement imprecision refers to the random variability of repeated EC measurements, performed on different punches taken from the same filter, within the same or different laboratories. In addition to imprecision in the laboratory analysis itself, 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 (2002). 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 this proposed rule. Although the report dealt exclusively with TC measurements, EC was separately measured in the course of the laboratory analysis of each punch, so the EC data used here to estimate CV_A are already in the public record.

In the paired punch comparison, 621 filters were analyzed twice for EC content. To do this, two standard punches were 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.[5]

[5] 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 ANOVA was performed to derive composite estimates of the intra- and inter-laboratory components of EC 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 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:

$$\sqrt{EC_{jA}} - \sqrt{EC_{ijB}} = \Delta_i + \lambda_{ij}\,(i \neq \mathrm{MSHA}) + \varepsilon_{ij}$$

where

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 unexposed control filters are used to adjust the calculated EC 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 $\hat{\sigma}_T^2 = \hat{\sigma}_\lambda^2 + \hat{\sigma}_\varepsilon^2$. The estimates of σ_λ^2, σ_ε^2, and σ_T^2 based on this ANOVA are shown in the following table.[6]

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

[6] 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.

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

As shown in Appendix 2, for an EC measurement (X, expressed in µg/cm^2) based on a single punch, the coefficient of variation in analytical error is

$$CV_\mu[X] = \sigma_{\mathrm{T}}\sqrt{\frac{2}{\mu}}$$

where μ is the true EC loading (µg/cm^2) on the filter. However, to reduce analytical measurement uncertainty, MSHA will average the EC results (X_1 and X_2) from two punches taken from each exposed filter and then subtract the EC result (B) from an associated, unexposed (blank) filter. The blank-adjusted EC 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], 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 EC measured on an unexposed filter. Therefore, assuming independent analytical measurement errors for X_1, X_2, and B,

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

It follows that:

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

Based on data compiled for the Joint MSHA/Industry Study (op. cit.), E[B] = 0.2 μg/cm^2. 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] ≥ 31.22 μg/cm^2 for EC concentration levels at or above the proposed interim standard of 308_{EC} μg/m^3;

E[Y] ≥ 12.49 μg/cm^2 for EC concentration levels at or above the proposed final standard of 123_{EC} μg/m^3.

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 ≤ 0.046 for EC ≥ 308 μg/m^3;

CV_A ≤ 0.074 for EC ≥ 123 μg/m^3.

Appendix 2. Use of Variance-Stabilizing Transformation for Analysis of EC Measurement Variability

Let i index a specific filter, and let X_{i1} and X_{i2} denote the two EC measurements (µg/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 (Var[X_i]) is roughly proportional to the carbon loading (µg/cm^2) on a filter.[7] This relationship can be expressed as

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

where λ^2 is a constant and μ_i is the true loading on the $i^{\underline{th}}$ 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:

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

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 an EC measurement at any filter loading.[8] Based on this approximation, and assuming independent measurement errors in X_{i1} and X_{i2},

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

Consequently,

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

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

[8] 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:

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