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Four methods are used to quantify diesel particulate matter (DPM) in the mine environment: respirable combustible dust sampling (RCD), size selective sampling with gravimetric analysis (SSG), respirable dust sampling with elemental carbon (EC) analysis, and respirable dust sampling with total carbon (TC) analysis. The authors assembled data from three underground mine studies to statistically compare these methods. The sampling protocol used in each study was similar. For all the four methods, samples were collected in triplicate at three locations—upwind and downwind of the diesel scoop and on the scoop. The methods were compared with respect to their precision, selectivity, sensitivity, and LOD, as well as their limitations in measuring DPM concentrations. This constitutes a meta-analysis of the available data and provides information over a broader range of mining conditions and DPM concentrations than any of the individual studies. The weighing imprecision for the SSG method is almost twice that for the RCD technique. The imprecision of the EC and TC methods are a function of the mass loading, and EC has a lower imprecision than TC. The EC method was used as the reference "gold standard" against which the other methods were evaluated. The RCD, SSG, and TC methods exhibited substantial levels of interference, leading to much higher minimum concentrations that can be measured by these methods. Of the three, the SSG method has the highest level of interference, primarily from nondiesel material that is collected in the <0.8 μm size range.

Keywords: diesel particulate matter, interference, limit of detection, precision, sensitivity

In recent years attention has focused on the potential carcinogenicity of diesel particulate matter (DPM) and its human health impact. In 1988 the National Institute for Occupational Safety and Health (NIOSH) recommended that whole diesel exhaust be regarded as a "potential occupational carcinogen," and stated that reductions in workplace exposure would reduce cancer risks.[1, p. 1] In 1989 the International Agency for Research on Cancer declared "diesel engine exhaust is probably carcinogenic to humans."[2, p. 41]

There is a considerable difference in recommended or established allowable concentrations for DPM in the workplace. In 1995 the American Conference of Governmental Industrial Hygienists (ACGIH) added DPM to the Notice of Intended Changes for 1995–96 with a threshold limit value (TLV®) recommendation of 0.15 mg/m³.[3] DPM <1.0 μm in size remained on the ACGIH Notice of Intended Changes in 1999, but with a reduction in the proposed TLV to 0.05 mg/m³.[4] The notice of Intended Changes for 2001 further modifies the DPM recommendation.[5] ACGIH has included diesel exhaust particulate as elemental carbon (EC) with a time-weighted average TLV of 20 μg/m³.

DPM limits are also in place in Canada and Europe. British Columbia, New Brunswick, Quebec, and Ontario have adopted a 1.5-mg/m³ level for respirable combustible dust (RCD).[6] The Federal Republic of Germany has adopted technical exposure limits (TRK) for the general workplace, tunneling, and mining.[7] For the general workplace the TRK is 0.1 mg/m³ EC or 0.15 mg/m³ total carbon (TC) when the sample contains $>50\%$ organic material. For mining and tunneling the TRK is 0.3 mg/m³.

The standard for mining is being revised. In Switzerland the standard is 0.1 mg/m³ of TC.[8]

The U.S. Mine Safety and Health Administration (MSHA) promulgated a DPM permissible exposure limit for noncoal mines based on TC.[9,10] An interim standard of 0.4 mg/m³ TC takes effect 18 months after the publication of the final rule. Five years later the DPM standard will be lowered to 0.16 mg/m³ of TC. TC would be determined using NIOSH *Manual for Analytical Methods* NMAM 5040.[11]

Several sampling and analytical methods are used to determine DPM concentrations in the workplace. Four methods in particular, described later, are used in mining environments. Each of these methods measures a different portion of diesel particulate matter. Replicated simultaneous samples of DPM aerosols, using these different methods, have been gathered as part of several research projects. Although these data were not always obtained explicitly to compare methods, this body of data makes such comparison possible over a broad range of DPM concentrations and under a variety of different mining conditions.

In the analysis presented in this article, the authors assembled the available field measurements using all four methods from three studies in Canadian mining environments. They then compared the methods with respect to their precision, selectivity, sensitivity, and limit of detection (LOD), and their limitations in measuring DPM concentrations. The authors also recommend appropriate conditions for and uses of each method.

MEASUREMENT METHODS

Measuring diesel aerosol in the workplace is challenging due to the physical characteristics and chemical complexity of the aerosol. DPM has a mass median diameter of 0.2 μm, with 90% of the particles being <1.0 μm in diameter. It is composed primarily of OC, EC, and sulfate.[2,12] The proportion of OC to EC varies depending on a number of factors, such as fuel, engine type, duty cycle, engine maintenance, operator habits, use of emission control devices, and lube oil consumption. Four methods to sample and analyze DPM are used in underground mines: (1) RCD, (2) size selective sampling with gravimetric analysis or SSG, (3) respirable dust sampling with EC, and (4) respirable dust sampling with TC analysis.[13,14] Each of these is described briefly in following paragraphs.

RCD

The RCD method was developed in Canada to estimate DPM concentrations in noncoal mines.[15] RCD is composed of all combustible materials collected on a filter, including drill oil mist, the soluble organic fraction of DPM, EC, and other combustible material collected on the filter such as carbonaceous material found in the ore dust. Thus, only a portion of RCD is attributable to diesel exhaust aerosol.

In the RCD method, respirable dust is collected on a 25 or 37 mm, 0.8 μm silver membrane or precombusted, glass fiber filter after passing air through a 10 mm Dorr-Oliver (Orilla, Ontario, Canada) cyclone at a flow rate of 1.7 L/min. Flow is controlled using a personal sampling pump. The cyclone is a respirable dust preclassifier with a 50% cut point of 4.0 μm. Respirable dust is determined gravimetrically by weighing the silver membrane or glass fiber filter before and after the sample is collected. RCD is determined gravimetrically from the amount of material removed from the silver membrane by controlled combustion at 400°C (500°C for the glass fiber filter) for 1 to 2 hours. A correction is made for the loss of mass on both the glass fiber and silver membrane filters due to combustion. Blank glass or silver membrane filters are equilibrated and then preweighed on a microbalance. The filters are then ashed, 3 hours at 500°C for the glass fiber filters and no less than 1.5 hours at 400°C for the silver membranes. After ashing the filters are again equilibrated and reweighed with the average difference being used for the correction factor.

SSG

The SSG method is based on a body of literature developed by the University of Minnesota and the U.S. Bureau of Mines.[15–18] These studies showed that submicron aerosols found in coal mines were primarily diesel in origin. The difference in the aerodynamic diameter of combustion and mechanically generated aerosols can be used to separate diesel aerosol from noncombustion aerosols.

Respirable aerosol sampling at 1.7 L/min has a 50% cut point at 4.0 μm and collects particles having diameters up to 10 μm in size. The first stage of the sampler is a 10 mm Dorr-Oliver cyclone. A four-nozzle inertial impactor with a 0.8 μm cut point follows the cyclone. The impaction surface consists of a 37-mm oiled, aluminum substrate that is used to collect respirable dust larger than 0.8 μm. Air is drawn through the sampler at 1.7 L/min using a personal sampling pump. DPM, which is primarily smaller than 0.8 μm, passes through the central exit of the impaction surface and is collected on a polyvinyl chloride filter mounted within a filter cassette. The amount of DPM is determined gravimetrically from the filter. The mass of respirable dust is determined gravimetrically from the combined mass of material collected on the filter and the aluminum substrate.

The collection efficiencies of the impactors used in the samplers were measured as a function of aerosol size using monodispersed polystyrene latex particles ranging in size from 0.56 to 1.10 μm. Details of the test protocol are available elsewhere.[17] The 50% collection efficiency point (E_{50}) for the Bureau of Mines impactor was 0.79 ± 0.01 μm with a geometric standard deviation (GSD) of 1.18 ± 0.05, indicating a sharp cut. The GSD is defined as the square root of the ratio of the particle diameter corresponding to the 84.1% collection efficiency to the diameter at an efficiency of 15.9%. The University of Minnesota impactor had an E_{50} cut point of 0.77 ± 0.03 μm and a GSD of 1.07 ± 0.04.

EC

DPM is chemically complex. It is composed of soluble organic hydrocarbons, sulfate, EC, and traces of other compounds. In general, EC accounts for about 50% of the mass of DPM, but this percentage varies depending on engine duty cycle, fuel quality, after-treatment device, and other factors.[13]

NIOSH[11,19] refined the thermal-optical method that was originally adopted for atmospheric aerosols.[20–22] This technique (NMAM 5040) is a sensitive measure of the EC portion of DPM. It has a working range of 6–630 μg/m³ with a LOD of about 2.0 μg/m³ for a 960-L air sample collected on a 37-mm filter with a 1.5-cm² punch from the filter. If a lower LOD is desired, a larger sample volume and/or a 25-mm filter may be used. If a 1920-L sample is collected on a 25-mm filter then the lower LOD is 0.4 μg/m³.[11]

The method also determines OC; TC is determined by summation (EC + OC). Diesel soot particles contain EC and are composed of aciniform carbon. EC is a product of combustion, and it is a specific marker of diesel exhaust aerosol in many occupational settings where other combustion aerosols are not present. The

method also has selectivity in the presence of some combustion aerosols (e.g., cigarette and wood smokes). EC is not a measure of total DPM exposure, because the OC portion is excluded. However, the OC portion of the collected aerosol is subject to interference from other organic aerosols not associated with diesel exhaust, such as drill oil mist, hydraulic fluids, coal dust, cigarette smoke, and other organic material. Despite this, TC has been used as a measure of DPM exposure.[9,10,23] The NIOSH method allows the identification of some nondiesel sources of OC, thus allowing the TC estimate to be corrected for these contributions.

METHODS

Samples for EC were collected using a sampling train consisting of a 10 mm Dorr-Oliver cyclone followed by a 37-mm precombusted ultra-pure quartz fiber filter mounted in a 37-mm plastic cassette. A disadvantage of the quartz fiber filter is the tendency to adsorb organic vapor, thus increasing the mass on the filter and the amount of OC. Dynamic blanks must be used to correct for this sampling artifact.[24] Dynamic blanks are samples that are collected to determine the amount of adsorbed organic material collected by the quartz filter. Dynamic blanks can consist of multiple quartz filters in the same cassette or of a nonadsorbing material, such as a filter made of Teflon® in front of a quartz filter. If two quartz filters are used, they should be from the same manufacturer's batch. The top filter removes the particulate matter and the bottom filter collects adsorb organic material.

IN-MINE FIELD STUDIES

Recent underground mine studies have collected data that can be used to compare the RCD, SSG, EC, and TC methods to determine advantages, disadvantages, and limitations.[23,25,26] A brief review is included for each study to serve as background for the ensuing statistical analysis.

1996 Creighton Mine Study

In 1996 University of Minnesota, INCO, Ltd., and NIOSH collaborated to evaluate the four measurement methods.[24] The study was carried out in a nonproducing section of INCO's Creighton mine, Sudbury, Canada. Sampling was performed on a mucking operation employing two diesel scoops. One vehicle was operated, while the other served as a backup in case the operating scoop malfunctioned. The scoop moved muck between two drifts where ventilation airflow was carefully regulated. Samples were collected in triplicate at three locations upwind and downwind of scoop activity and on the scoop, over 8 days for a total of 216 samples (3 samples $\times$ 3 sample types $\times$ 3 sample locations $\times$ 8 days = 216 samples).

All samplers and pumps were mounted in baskets, one sampler for each method (SSG, RCD, EC, and TC) in each basket, and three baskets per site. Pumps were calibrated underground to a flow rate of 1.7 L/min $\pm$2% using a Gilibrator (Gilian Instruments, Clearwater, Fla.) at the beginning, middle, and end of each week. The average of the pre- and postcalibration was used to determine the sample flow rate. The difference between the postweight and preweight mass was the mass collected during sampling. This mass was used to calculate sample concentrations. RCD analysis was performed by INCO. The EC samples were collected without the 0.8 μm impactor and analyzed by American Industrial Hygiene Association-accredited laboratories using NIOSH method 5040.

1997 Creighton Mine Study

The goal of this investigation was to determine the impact of a blended biodiesel fuel and oxidation catalyst on exhaust emissions and air quality.[25] Data were collected in such a way as to allow comparison of the four measurement methods, but the comparison was not within the scope of the research program.

Arrays of SSG, RCD, and EC/TC samplers were co-located in baskets upwind (air intake), downwind (air exhaust), and on the diesel scoop, one sampler for each method in each basket, three baskets per site. All samples were collected in triplicate over 10 days for a total of 270 samples (3 samples $\times$ 3 sample types $\times$ 3 sample locations $\times$ 10 days = 270 samples). Twenty-two additional EC samples were used to assess aerosol stratification at the downwind location. NIOSH analyzed all samples for EC, and a German laboratory also analyzed the subset of samples collected to assess aerosol stratification. The German laboratory used the Coulometric method to determine EC. A comparison of the methods was published by Birch et al.[27]

SSG, RCD, and EC/TC samplers were operated at a flow rate of 1.7 L/min. Pumps (MSA, Pittsburgh, Pa.) were calibrated in the test section's underground refuge shelter at the beginning, middle, and end of each week. Gilibrators were used for pump calibration.

1997 Brunswick Mine Study

This study was conducted to determine the impact of high sulfide ore dust on the four sampling methods.[26] The first goal of the project was to investigate the impact of the presence of respirable sulfides on the RCD method. The second goal was to compare the three methods in high DPM and mixed sulfide mineral dust conditions. Sampling was conducted in a similar fashion as the studies previously described for intake, vehicle, and exhaust sampling locations.

A total of 525 DPM samples were collected (315 RCD, 105 SSG, and 105 EC/OC samples). The samples were equally divided between the three sampling locations and between the 2 weeks. Further details on this study are available elsewhere.[26]

Field Measurements Available for Statistical Analysis

For each of the four measures of DPM (RCD, SSG, EC, and TC), for each sampling day, measurements were made in triplicate at three locations: upwind and downwind of the scoop activity and on the scoop vehicle. For each set of three measurements at a location, the authors calculated the average mass gain, flow rate, and calculated concentration, and the corresponding coefficients of variance.

Table I presents summary statistics for each of the measurement methods combining data from all three studies. The number of samples (N) shown in the table differs for each of the measurements because portions of data sets were excluded. For instance, if a mass measurement was handled inappropriately causing an erroneous mass to be measured, only the mass was excluded, as the pump flow rate would not have been affected.

STATISTICAL ANALYSIS OF FIELD MEASUREMENTS

The main objective was to assemble the available field data in a format conducive to appropriate statistical analyses, perform

TABLE I. Summary Statistics for Each Measurement Type for All Three Studies Combined

	Mass (μg)	CV of Mass Gain (%)	Flow Rate (L/min)	CV of Flow Rate (%)	Conc. (μg/m³)	CV of Conc. (%)	Sampling Time (min)
Respirable combustible dust							
No. of cases	73	72	76	76	73	78	78
Minimum	13.34	0.00	1.62	0.00	21.89	0.00	134.0
Maximum	606.67	50.00	1.73	9.27	1228.38	50.00	442.67
Mean	207.70	12.88	1.70	1.27	398.21	14.14	318.06
Standard Deviation	117.60	13.09	0.02	1.80	258.43	14.68	59.85
Size selective sampling							
No. of cases	79	80	53	51	79	78	90
Maximum	753.00	70.33	1.82	10.09	1468.93	70.33	442.67
Mean	225.65	17.10	1.71	2.25	421.42	15.67	315.10
Standard Deviation	129.42	16.99	0.04	2.44	237.48	15.71	63.55
Elemental carbon							
No. of cases	90	86	90	86	90	86	90
Maximum	315.07	62.34	1.79	14.18	617.78	97.91	444.00
Mean	79.18	17.08	1.69	3.46	148.50	17.55	314.56
Standard Deviation	59.60	16.73	0.05	3.82	112.23	18.33	64.02
Total carbon							
No. of cases	90	86	90	86	90	86	90
Maximum	460.72	60.78	1.79	14.18	903.38	91.37	444.00
Mean	137.79	15.89	1.69	3.46	264.17	16.40	314.56
Standard Deviation	97.44	14.94	0.05	3.82	181.99	16.75	64.02

these analyses in as consistent a manner as the various data sets permit, and use the results to compare the methods (SSG, RCD, EC, and TC) with respect to their (a) precision, (b) selectivity, (c) sensitivity, and (d) detection limits. In essence, this constitutes a meta-analysis of the available data and provides information over a broader range of mining conditions and DPM concentrations than any of the individual studies.

(a) Measurement precision is expressed as the coefficient of variance (standard deviation divided by the mean) of repeated measurements of the same aerosol.

(b) Selectivity refers to the extent to which DPM can be measured by a particular method without interference due to the presence of other substances. In the presence of an interferant thought to affect one measurement method but not another, the average effect of all the interferants was modeled as the intercept of the calibration curve relating the two measurement methods.

(c) Sensitivity refers to the smallest change in DPM concentration that can be measured by a particular method at a specified confidence level. To determine sensitivity, the slopes of the calibration curves relating measurement methods, along with their associated standard errors, were used. The EC method was selected as the reference measurement method.

(d) The LOD for the method was derived by multiplying a confidence coefficient (reflecting the level of confidence desired for establishing that a minimum level of DPM is actually present) by the ratio of the method's imprecision (as expressed by the standard deviation of repeated measurements of the same aerosol) to its sensitivity.

Systematic differences in DPM measurements were used to evaluate relative biases in the methods, including those attributable to known interferences. These systematic differences were combined with the variability of replicated measurements to assess the accuracy of each method under various conditions. Confidence intervals were calculated for all differences observed between methods, and any such differences were tested for statistical significance.

Modeling of Imprecision

Variability or imprecision of diesel exhaust concentration measurements is caused by analytical errors and variability in the flow rate. The concentration is calculated as:

$$C = \frac{M}{Q \times t} \quad (1)$$

where M is the mass collected on the filter (which is measured either by gravimetry or by an analytical method such as for EC); Q is the flow rate of the pump; and t is the sampling time. The precision of a measurement is defined as the standard deviation of repeated measurements of the same aerosol. The precision in the concentration C_i is related to the precision in the measurement of M_i and Q_i (assuming that the errors in determining sampling time t are negligible) by the following relationship:

$$\left(\frac{\sigma_C}{\bar{C}_i}\right)^2 = \left(\frac{\sigma_M}{\bar{M}_i}\right)^2 + \left(\frac{\sigma_Q}{\bar{Q}_i}\right)^2 \quad (2)$$

where $\bar{C}_i$, $\bar{M}_i$, $\bar{Q}_i$ are the arithmetic averages of the i^{th} set of replicates. This expression is an approximation and assumes that the errors made in the determination of M and Q are independent, and σ_Q is small. Thus, the coefficient of variation (standard deviation of repeated measurements divided by the mean value of those measurements) of the concentration is given by

$$CV_C^2 = CV_M^2 + CV_Q^2 = \left(\frac{\sigma_M}{\bar{M}_i}\right)^2 + \left(\frac{\sigma_Q}{\bar{Q}_i}\right)^2 \quad (3)$$

Equations 2 and 3 are true for RCD and SSG measurements. For EC and TC measurements, it has been reported that

$$CV_M^2 = \frac{K^2}{M} \quad (4)$$

that is, the coefficient of variation is inversely proportional to the square root of the carbon loading, and $K = \sigma_M/\sqrt{M}$.[11] Therefore, for EC and TC, Equation 2 needs to be modified by using Equation 4 for the first term on the right-hand side.

The approach developed by Kogut et al.[29] to estimate CV_C directly from multiple simultaneous measurements of the same aerosol was used in this analysis. As indicated by the summary statistics in Table I, roughly 70 to 90 sets of measurements (for each of the methods) were made over a broad range of aerosol concentrations. The complete data set is available at www.deep.org/reports/watts_final.pdf. Each set of measurements for each of the methods consists of information regarding the study and sampler location (upwind, downwind, or near the vehicle), as well as the following statistics on the three to six replicates available for each measurements set: along with average mass collected, the CV of the mass gain, the average flow rate, the CV of the flow rate, the average concentration and the CV of the concentration.

Imprecision of an aerosol concentration measurement refers to the variability of measurements as they deviate from the average time-weighted concentration within a set of replicates. These were evaluated for the four measurement methods. The estimates of CV_C are based on at most three to six replicates, and thus they are not reliable estimates of the true CV_C. Because the aerosol concentrations varied considerably between measurement sets, CV_C can be estimated as a function of filter loading and flow rate. Although σ_M^2 and σ_Q^2 can be estimated from Equation 2, using linear regression using $(1/\bar{M}_i)^2$ and $(1/\bar{Q}_i)^2$ as the independent variables, Kogut et al.[29] point out that, in practice, more stable estimates can be obtained through nonlinear regression. Thus, σ_M^2 and σ_Q^2 were estimated by nonlinear regression using $(\bar{M}_i)^2$ and $(\bar{Q}_i)^2$ as the independent variables and an estimate of CV_C as the dependent variable in the following model:

$$CV_{c_i} = \left[\left(\frac{\sigma_M}{M_i}\right)^2 + \left(\frac{\sigma_Q}{Q_i}\right)^2\right]^{1/2} + \epsilon_i \qquad (5)$$

where CV_{ci} is the sample coefficient of variation observed in the i^{th} set of measurements and ϵ_i is the residual regression error (the difference between estimated and true values of CV_c for the i^{th} set. It should be kept in mind that Equation 5 is applicable for RCD and SSG measurements. For EC and TC measurements, the following should be used:

$$CV_{c_i} = \left[\left(\frac{K^2}{M_i}\right) + \left(\frac{\sigma_Q}{Q_i}\right)^2\right]^{1/2} + \epsilon_i \qquad (6)$$

where, as before, $\sigma_M = K\sqrt{M}$. To obtain a sense of the relative contributions of CV_M^2 and CV_Q^2, the authors plotted these against $\bar{M}_i$ and $\bar{Q}_i$, respectively, for the four types of measurement methods. Figure 1 shows the plot of CV_M versus $\bar{M}_i$ using the EC method as an example. The other measurement methods show similar trends. Imprecision in determination of the mass of EC is the major contributor to total variability (as much as 50–60%), and the imprecision in flow rate measurements is minor in comparison (with most measurements less than 6%). The plots of CV (filter loading) versus filter loading show a decrease in the CV with increase in filter loading. This is because the filter loading is calculated by subtracting preexposure filter loads from postexposure filter loads. Because the mass gain is a very small percentage of the total mass being analyzed, filter loading errors can be assumed to be independent of sampling time and quantity of dust collected, leading to a decrease in the CV of filter loading with increase in filter loading. There is no trend in the variability of the CV (flow rate) with flow rate. This is because flow rate is supposed to be set to a fixed value of 1.7 L/min, and the variability in flow rate is distributed randomly around this central value.

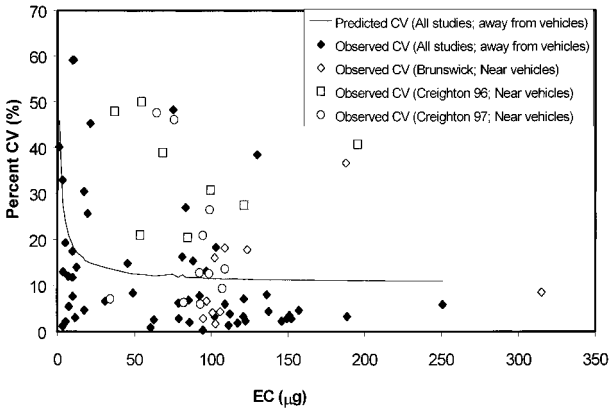

FIGURE 1. Coefficient of variance (CV) as a function of weight gain for EC measurements. Measurements are grouped by study and whether they were made in the proximity of a scoop vehicle or not. The figure also shows the predicted coefficient of variance.

In Figure 1, measurements are grouped by study and also according to whether they were made in the vicinity of the diesel scoop. All these plots show a higher CV for measurements made in the vicinity of the scoop compared with measurements made upwind or downwind of the scoop. Diesel exhaust exits the tailpipe in a hot gas stream. Over time and distance the aerosol is mixed in the ventilation airstream. Aerosol stratification occurs if the aerosol is not thoroughly mixed. This results in different concentrations of aerosol being measured at different locations within the same vertical plane. Thus, it is expected that the aerosol concentration measured on the scoop vehicle would be more variable than far upstream or downstream of the scoop, because the aerosol would have less time to become completely mixed near the vehicle. This was the case for all four types of measurements.

To account for this contribution to total variability, the regression model was modified by including the effect of location of sampling (near the vehicle or away from the vehicle) for each of the three studies. The revised model (for RCD and SSG measurements) is now given as:

$$CV_{c_i} = \left[\left(\frac{\sigma_M}{M_i}\right)^2 + \left(\frac{\sigma_Q}{Q_i}\right)^2 + \text{vehicle} \times (\text{Creighton1996} \times \text{Veh1} + \text{Creighton1997} \times \text{Veh2} + \text{Brunswick} \times \text{Veh3})\right]^{1/2} + \epsilon_i \qquad (7)$$

where *vehicle* is a categorical variable that takes a value of 1 when the measurement location is near a vehicle and 0 otherwise, *Creighton1996, Creighton1997,* and *Brunswick* are categorical variables denoting each study (taking values of 0 or 1), and *Veh1, Veh2,* and *Veh3* are regression coefficients that describe the effect of sampling location in each study. A similar model for EC and TC measurements is given as:

TABLE II. Results of Regression Analysis for All Four Types of Measurements

Parameter	Least Squares Estimate	Asymptotic Standard Error	Wald 95% Confidence Interval
RCD Measurements ($R^2_{adj} = 0.5$)			
σ_M (μg)	6.96	0.80	(5.35, 8.56)
σ_Q(L/min)	0.10	0.04	(0.02, 0.17)
Veh 1 (%)	4.38	7.98	(−11.57, 20.32)
Veh 2 (%)	17.59	3.45	(10.70, 24.49)
Veh 3 (%)	11.91	3.92	(4.08, 19.74)
σ_ϵ (%)	10.39	NA	NA
SSG measurements ($R^2_{adj} = 0.29$)			
σ_M (μg)	13.05	0.12	(12.81, 13.29)
σ_Q(L/min)	0.17	0.003	(0.16, 0.18)
Veh 1 (%)	10.13	0.91	(8.35, 11.91)
Veh 2 (%)	2.22	1.64	(−0.99, 5.43)
Veh 3 (%)	5.47	0.75	(3.99, 6.94)
σ_ϵ (%)	14.38	NA	NA
EC measurements ($R^2_{adj} = 0.2$)			
σ_M (μg)	$0.49 \times \sqrt{\text{EC loading}}$	$0.006 \times \sqrt{\text{EC loading}}$	$(0.47 \times \sqrt{\text{EC loading}}, 0.50 \times \sqrt{\text{EC loading}})$
σ_Q(L/min)	0.18	0.003	(0.17, 0.185)
Veh 1 (%)	32.35	0.38	(31.59, 33.10)
Veh 2 (%)	14.91	0.40	(14.12, 15.69)
Veh 3 (%)	2.94	1.42	(0.16, 5.72)
σ_ϵ (%)	16.8	NA	NA
TC measurements ($R^2_{adj} = 0.2$)			
σ_M (μg)	$0.40 \times \sqrt{\text{TC loading}}$	$0.014 \times \sqrt{\text{TC loading}}$	$(0.37 \times \sqrt{\text{TC loading}}, 0.42 \times \sqrt{\text{TC loading}})$
σ_Q(L/min)	0.22	0.003	(0.211, 0.222)
Veh 1 (%)	29.12	0.47	(28.19, 30.05)
Veh 2 (%)	10.65	0.50	(9.66, 11.63)
Veh 3 (%)	2.95	1.61	(−0.21, 6.12)
σ_ϵ (%)	14.8	NA	NA

$$CV_{c_i} = \left[\left(\frac{K^2}{M_i}\right) + \left(\frac{\sigma_Q}{Q_i}\right)^2 + \text{vehicle} \times (\text{Creighton1996} \times \text{Veh1} + \text{Creighton1997} \times \text{Veh2} + \text{Brunswick} \times \text{Veh3})\right]^{1/2} + \epsilon_i \quad (8)$$

Results of nonlinear regression analyses for the four methods are shown in Table II. This table contains estimates of σ_M and σ_Q, the percentage contribution of the sampling location to total variability, along with the standard error of the regression estimate, σ_ϵ. The table also shows the symmetric Wald 95% confidence intervals for the estimates of the parameters. From Table II we can see that the weighing imprecision for the SSG method is almost twice that for the RCD technique. The imprecisions of the EC and TC methods are a function of the loading, and EC has a lower imprecision than TC.

In Figure 1 the values of CV_C predicted by the regression equations and the observed values of CV_C are plotted against the filter loading for the EC method. The other methods had similar trends. The effect of sampling location on measurement imprecision is clearly seen in Figure 1 and corresponding data for the other methods. Figure 2 shows the corresponding residual plot as a function of filter loading. The residuals are the differences between predicted and observed values of CV_C.

Sensitivity, Selectivity, and Limits of Detection

Although NMAM 5040 quantifies both OC and EC, the method recommends use of EC as an exposure index because it is a more selective measure of exposure. Linear regressions were performed of the simultaneous RCD, SSG, and TC measurements against the EC measurements.

Ordinary least squares regression overestimates the intercepts,

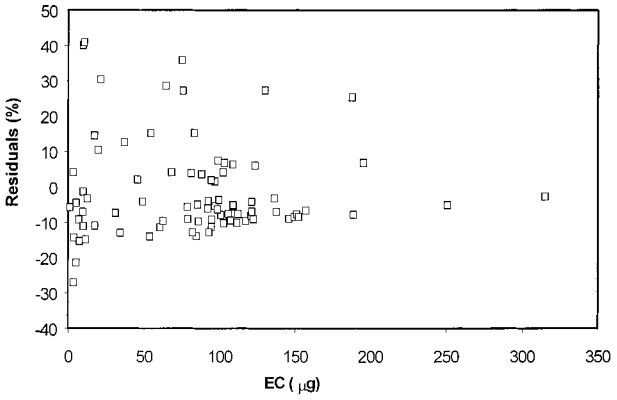

FIGURE 2. Residuals between predicted as observed CV for EC measurements as a function of weight gain

TABLE III. Slopes and Intercepts of the Regression Lines for the Three Calibration Curves, with the Associated Standard Errors

Calibration	Slope, *m* ± Standard error	Intercept, *b* (μg/m³) ± Standard error	R_{adj}^2
RCD vs. EC	2.06 ± 0.17	25.5 ± 3.6	0.68
SSG vs. EC	1.68 ± 0.15	96.6 ± 1.04	0.62
TC vs. EC	1.59 ± 0.10	14.8 ± 0.49	0.72

and hence a weighted least squares procedure was adopted. For example, in the model comparing RCD measurements with EC measurements,

$$RCD_i = \beta_0 + \beta_1 \times EC_i + \epsilon_i \quad (9)$$

it is assumed that the errors ϵ_i are independent with constant variance. However, the variability of the errors is smaller for small values of EC than it is for large values of EC. The same is true for SSG and TC measurements. Thus, it might be appropriate to give higher weights to observations with small EC values. Therefore, the authors chose the weights to be equal to variances of the ϵ_i. Thus, the weighted least squares procedure minimizes the expression

$$\sum_i \frac{1}{EC^2}(RCD_i - \beta_0 - \beta_1 \times EC_i)^2. \quad (10)$$

Table III shows the slopes and intercepts of the regression lines for the three calibration curves, along with their associated standard errors. Figure 3 shows an example of one such calibration curve of the SSG method versus the EC method. The intercepts can be interpreted as the selectivity of the measurement method. For instance, in the case of RCD versus EC, the intercept of 25.5 (μg/m³) means that the RCD method gives this reading when the EC method reads zero. EC and RCD measure different components of the exhaust. EC is more specific than RCD.

Such regressions assume that the X variable (in this case, the EC measurement) is error-free. However, in the presence of measurement error, the classical error model predicts that the estimated slope is attenuated by a factor c, where $c = var(EC)/(var(EC) + (CV_{EC})^2)$. For this data set, c = 0.95; that is, the attenuation was less than 5% and thus less than the reported standard error in the slope estimates calculated using ordinary least squares regression. Under an alternate Berkson error model, there is no attenuation in the estimated slope.[29]

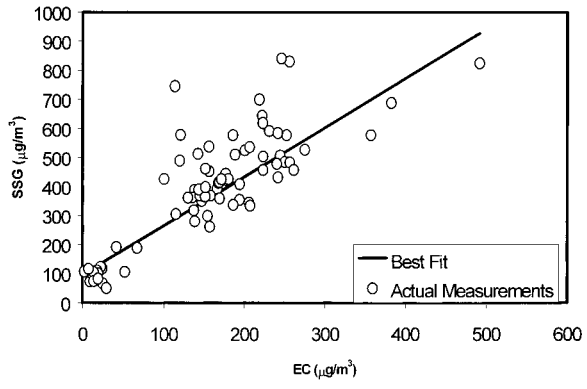

FIGURE 3. Calibration curve of SSG measurements versus EC measurements

TABLE IV. Comparison of Method Interferences

Analytical Method	Interferences	Source Range (μg/m³)
SSG	atmosphere	1–30
	coal/ore	3–80
RCD	oil mist	0–50
	ore	0–10
EC	atmosphere	0.5–2
	coal/ore	5–15

Table IV provides estimates of the interferences to which RCD, SSG, and EC are susceptible as presented by Cantrell and summarized by Watts.[31] Such interferences pertain to both the selectivity and precision of the methods, but the statistical methods used to obtain these estimates have not been published in detail. The estimates shown in Table III suggest that except for SSG, they are in the range proposed by Cantrell.[31]

The slopes of the calibration curves shown in Table III can be interpreted as the sensitivity of the method in relation to the EC method. It refers to the smallest change in DPM concentration that can be measured by a particular method at a specified confidence level.

The LOD is defined as the lowest mass or concentration level that can be determined to be statistically different from a blank. Assume that the measurements are distributed approximately normally. Let S_t represent the total value measured for the sample, S_b the value for the blank, and σ the standard deviation for the measurements. The analyte signal is the difference $(S_t - S_b)$. It can be shown that for normal distributions, $(S_t - S_b) > 0$ at the 99% confidence level when that difference $(S_t - S_b) > 3\sigma$. Because the authors chose for the EC measurements to be the reference measurements, all other measurement methods need to be converted to this reference. This is done using the calculated sensitivity of the method. The LOD for the method is thus derived by multiplying a confidence coefficient (reflecting the level of confidence desired for establishing that a minimum level of DPM is actually present) by the ratio of the method's imprecision (as expressed by the standard deviation of repeated measurements of the same aerosol) to its sensitivity. Thus,

$$LOD = 3.0 \times \left(\frac{\sigma_M}{m}\right) \quad (11)$$

Table V presents LODs for RCD, SSG, and TC derived from field measurements.

This analysis treats the EC method (NMAM 5040) as the reference method against which the other three methods are compared. The EC method itself has an estimated LOD in the laboratory of 0.15 μg of elemental carbon per square centimeter of filter, which translates to a concentration of 2 μg/m³ for a 37-mm filter, assuming sampling at 2 L/min for 8 hours.[19] If it is assumed that the LOD for OC is similar to that for EC, then the

TABLE V. Limits of Detection for RCD, SSG, and TC Methods from Field Data

Method	LOD (μg)	LOD (μg/m³)
RCD	10.14	10.56
SSG	23.3	24.3
TC (at 23 μg/m³)	4.4	4.6

LOD for TC calculated from field data is remarkably close to the laboratory values.

It has been proposed that for the SSG method, if the sampling flow rate is 2 L/min and gravimetric analysis is to within 0.005 mg (5 μg), then for an 8-hour sampling time the aerosol concentration for the fraction of aerosol less than 0.8 μm should have a theoretical LOD of 15 μg/m³ ±50% with a confidence level of 95%.[31] The results of this analysis based on field data yields a higher number for the LOD of the SSG method (24.3 μg/m³).

Similarly, the RCD method is a gravimetric method with a reported detection limit of 0.02 mg (20 μg), which corresponds to a concentration of roughly 21 μg/m³.[32] This again is higher than the value of 10.56 μg/m³ that was obtained in this study.

DISCUSSION

The EC, RCD, and SSG methods measure different portions of the mine aerosol, and comparisons between the methods must take this into account. The EC method (NMAM 5040) measures EC, OC, and TC. EC is produced under the conditions of high temperature combustion and is a sensitive and specific marker of diesel exhaust, but it does not measure total DPM exposure unless an estimate of the OC is included. Unfortunately, there are sources of OC other than diesel exhaust such as oil mist, blasting fumes, and cigarette smoke. The RCD method measures TC and is subject to similar interferences plus carbon and sulfide in the ore.[27] The SSG method is subject to interferences due to coal and ore (Table IV) and to misclassification by particle size. Some diesel aerosol may be excluded because it is larger than the 0.8 μm and nondiesel aerosol <0.8 μm may be collected. Of the four measures of DPM, only the EC result is not affected by adsorbed organic vapors.

As mentioned previously, the level of interference determined in this analysis is within the range of that reported by Cantrell as shown in Table IV for RCD. According to Table IV the total interference expected for the RCD method ranges from 0–60 μg/m³. In the present study the interference varied between 21.9–29.1 μg/m³, as shown in Table III. Part of this difference can be accounted for by the vehicle data, which shows more spatial variability. Some of the differences are mine-dependent, with some mines having higher levels of respirable combustible dust.

During the 1996 and 1997 studies, there was a hydraulic oil leak on the scoop that sprayed an oil mist onto the deck near the sampling baskets. After a day of sampling the baskets and samplers located on the scoop were frequently covered with hydraulic oil. The investigators believe that oil droplets formed under this condition were generally large nonrespirable particles that were removed by the cyclones on the samplers. However, gaseous volatile material and a few small oil droplets may have passed through the cyclone. The gaseous material may have adsorbed to the particulate matter collected on the filter and the small oil droplets may have collected on the filter. No correction was made (or possible) for this potential contamination.

During the 1997 study at Creighton there was also a period of time when excess diesel fuel from the fuel tank overflowed onto the hot surface of the diesel oxidation catalyst. This created very high concentrations of smoke for short periods of time that would have affected the SSG, TC, and RCD measurements collected on the scoop, because there was little opportunity for dilution. Again no attempt was made by the investigators to correct for this problem. These possible interferences help explain the least squares estimates shown in Table III and point out the need for careful assessment of potential sources of interference so that estimates of exposure can be corrected. Table IV shows that the level of interference for the SSG method would be expected to vary from 4–110 μg/m³.[31] This compares with 96 μg/m³ shown in Table III. There is no direct comparison between Tables III and IV for EC, but about twice as much interference is reported for TC as Cantrell reported for EC. However, unlike EC, TC interference can be expected to be quite variable, depending on the workplace.

CONCLUSIONS

Based on this analysis, the following lower concentrations are recommended for each method: RCD =100 μg/m³, SSG = 200 μg/m³, and TC = 100 μg/m³. This is determined by adding the maximum interference (Table III) + the LOD (Table V) + a 25% error factor and rounding upward to the nearest 100 μg. Thus, for the SSG method the calculation is as follows (96.6 + 1.04 + 24.3) = 121.9; 121.9 + (0.25)*(121.9) = 152.4 μg/m³ that rounds upward to 200 μg/m³.

The most sensitive measure of diesel exhaust is EC. Regulations for DPM are reducing allowable levels of DPM in mines. Mines are reducing concentrations of DPM underground through the use of improved engine technology, higher quality diesel fuel, better aftertreatment devices, increased ventilation, and other methods. As allowable levels decrease, the need to use EC as the measure of exposure increases because the other methods lack the necessary sensitivity to determine exposure. Although TC targets a larger and less variable fraction of DPM, TC measurements are interference prone. Unless care is taken to correct the OC measurement for nondiesel sources and to include dynamic blanks to correct for OC adsorbed by the ultra-pure quartz fiber filter, the OC carbon and subsequent TC measurements will be inflated.

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