Comparison of two carbon analysis methods for monitoring diesel particulate levels in mines

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Two carbon analysis methods are currently being applied to the occupational monitoring of diesel particulate matter. Both methods are based on thermal techniques for the determination of organic and elemental carbon. In Germany, method ZH 1/120.44 has been published. This method, or a variation of it, is being used for compliance measurements in several European countries, and a Comité Européen de Normalization Working Group was formed recently to address the establishment of a European measurement standard. In the USA, a 'thermal–optical' method has been published as Method 5040 by the National Institute for Occupational Safety and Health. As with ZH 1/120.44, organic and elemental carbon are determined through temperature and atmosphere control, but different instrumentation and analysis conditions are used. Although the two methods are similar in principle, they gave statistically different results in a previous interlaboratory comparison. Because different instruments and operating conditions are used, between-method differences can be expected in some cases. Reasonable agreement is expected when the sample contains no other (*i.e.*, non-diesel) sources of carbonaceous particulate and the organic fraction is essentially removed below about 500 °C. Airborne particulate samples from some mines may meet these criteria. Comparison data on samples from mines are important because the methods are being applied in this workplace for occupational monitoring and epidemiological studies. In this paper, results of a recent comparison on samples collected in a Canadian mine are reported. As seen in a previous comparison, there was good agreement between the total carbon results found by the two methods, with ZH 1/120.44 giving about 6% less carbon than Method 5040. Differences in the organic and elemental carbon results were again seen, but they were much smaller than those obtained in the previous comparison. The relatively small differences in the split between organic and elemental carbon are attributed to the different thermal programs used.

Introduction

Diesel-powered equipment is used in many occupational settings (*e.g.*, trucking, transit, mining, railroads, agriculture), exposing millions of workers to diesel exhaust. Such exposures are of concern because diesel exhaust has been classified as a probable human carcinogen.[1,2] Exposures in the mining industry are of particular concern because diesel particulate levels in mines are often high (sometimes 1000 times environmental levels).

Diesel exhaust is a complex aerosol containing thousands of compounds. For this reason, a surrogate measure of exposure must be used. Because animal studies link tumor induction to the particulate fraction of the exhaust, monitoring methods for diesel particulate matter have been developed. Methods for the determination of the particulate mass have been used previously, but these are inadequate for low-level measurements. More recently, methods based on carbon analysis have been applied to the assessment of workers' exposures to diesel particulate matter. Carbon is a logical analyte choice because diesel soot is composed primarily of carbon, but there are many possible sources of airborne organic carbon. In contrast, elemental carbon (EC) is a specific marker of occupational exposure to diesel particulate matter. The rationale for the selection of an EC marker has been detailed elsewhere.[3] Currently, EC is accepted internationally as a surrogate measure of exposure to this industrial pollutant.

Two carbon analysis techniques are currently being applied to the occupational monitoring of diesel particulate matter. The techniques are similar in that they both entail thermal removal of carbon (organic and elemental) in inert and oxidizing atmospheres. Organic carbon (OC) is removed first in an inert gas as the temperature is increased to a pre-set maximum. After volatilization of OC, oxygen is introduced to effect combustion of the remaining material. The carbon quantified during this second stage of the analysis is considered 'elemental' (*i.e.*, carbon in the diesel particle core). All evolved carbon is catalytically oxidized to carbon dioxide, which is then determined directly or reduced to methane (CH_4) and quantified by flame ionization detection (FID). The total carbon (TC) in the sample is simply the sum of OC and EC.

In Europe, carbon determination is achieved by coulometric titration of CO_2. An official method (ZH 1/120.44), sometimes called the 'coulometric' method after the mode of detection, has been published in Germany[4] and has been applied there since the early 1990s.[5] ZH 1/120.44, or a variation of it, is being used for threshold limit compliance measurements in Austria, Germany and Switzerland, and a Comité Européen de Normalization (CEN) Working Group is currently addressing the establishment of a European standard for measurement of diesel particulate matter. Results of a recent interlaboratory (European laboratories) comparison[6] indicate reasonable between-laboratory agreement, but poor precision was seen in some cases. Additional comparison work has been conducted recently to identify the potential causes of

Table 1 OC, EC and TC results for filter samples of diesel particulate analyzed by two different thermal methods: ZH 1/120.44 (IGF) and NIOSH Method 5040. All results reported as µg carbon per cm^2 filter

	OC[a]			EC[a]			TC[a]		
Sample No.	IGF	NIOSH	RPD[b]	IGF	NIOSH	RPD	IGF	NIOSH	RPD
1	1.90	(1.42)	29	0.80	(0.79)	1	2.70	(2.21)	20
2	2.50	(3.10)	−21	4.40	3.66	18	6.90	6.76	2
3	1.40	(1.26)	11	0.30	(0.41)	−31	1.70	(1.67)	2
4	5.00	6.77	−30	14.10	13.66	3	19.19	20.43	−7
5	1.30	(1.49)	−14	1.8	2.17	−19	3.10	(3.66)	−16
6	7.40	9.49	−25	15.10	13.37	12	22.50	22.86	−2
7	1.30	(1.43)	−10	1.20	(1.03)	15	2.50	(2.46)	2
8	4.70	6.51	−32	13.30	11.53	14	18.00	18.04	0
9	1.30	(1.83)	−34	1.10	(1.49)	−30	2.40	(3.32)	−32
10	4.00	7.04	−55	14.20	12.41	13	18.20	19.45	−7
11	5.20	6.76	−26	2.90	2.54	13	8.10	9.30	−14
12	7.70	11.09	−36	17.40	14.90	15	25.10	25.99	−3
13	1.20	(1.74)	−37	0.30	(0.07)	–	1.50	(1.81)	−19
14	5.10	7.35	−36	12.60	10.85	15	17.70	18.20	−3
15	1.50	(1.62)	−8	0.43	(0.28)	–	1.90	(1.90)	0
16	2.30	(2.00)	14	1.10	1.66	−41	3.40	(3.66)	−7
17	1.50	(1.45)	3	0.43	(0.73)	−52	1.93	(2.18)	−12
18	5.40	9.40	−54	11.90	9.60	21	17.30	19.00	−9
19	1.50	(2.09)	−33	1.10	(0.51)	73	2.60	(2.60)	0
20	5.60	10.22	−58	13.60	10.24	28	19.20	20.46	−6
21	1.40	(1.89)	−30	1.00	(0.61)	48	2.40	(2.50)	−4
22	13.70	21.04	−42	14.00	10.21	31	27.80	31.25	−12

[a] Results below limit of quantification (LOQ) for Method 5040 are listed in parentheses. [b] RPD = relative percentage difference calculated as 100(IGF − NIOSH)/average. RPD not reported for results below limit of detection (LOD). LOQ for OC and TC is about 4 µg cm^{-2}; LOQ for EC is about 1.5 µg cm^{-2}. LOQs based on media blanks.

imprecision. Results of the latest comparison have not yet been published.

In the USA, a 'thermal–optical' method for diesel particulate matter was published as Method 5040 by the National Institute for Occupational Safety and Health (NIOSH). An updated version of Method 5040 (initially published in 1996) was recently published in the *NIOSH Manual of Analytical Methods*.[7] The analytical technique on which Method 5040 is based is being applied to the determination of particulate carbon in both workplace and environmental settings. The analysis is currently offered by five commercial laboratories (four in the USA and one in Canada), and the instrument is commercially available. As with method ZH 1/120.44, the OC and EC in a quartz-fiber filter sample are determined through temperature and atmosphere control, but a different gas (helium instead of nitrogen) and thermal program are employed. In addition, the instrument has an optical feature that corrects for the char that sometimes forms on the filter during the first part (in inert gas) of the analysis. This feature also corrects for any loss of EC during the first part of the analysis. Losses are uncommon and relatively small, but do occur on occasion, depending on the sample matrix.

Although the two methods are similar in principle, the European (*e.g.*, ZH 1/120.44) and NIOSH methods gave statistically different results in a previous interlaboratory comparison.[8] Because different thermal programs are used and a char correction is made in thermal–optical analysis, differences between methods can be expected, particularly with some types of samples. Reasonable agreement is expected when the sample contains no other (*i.e.*, non-diesel) sources of carbonaceous particulate and the organic fraction is essentially removed below about 500 °C. Airborne particulate samples from some mines may meet these criteria. Comparison data on samples from mines are important because the methods are being applied in this workplace for occupational monitoring and epidemiological studies. In this paper, results of a recent comparison on samples collected in a Canadian mine are reported.

Experimental

The filter samples used for this comparison were collected as part of a research project sponsored by the Diesel Emission Evaluation Program (DEEP) of Canada. The project goal was to determine the impact of a blended 'biodiesel' fuel and oxidation catalyst on exhaust emissions and mine air quality. Biodiesel fuels with high oxygen content are produced from vegetable oils. Oxygen groups in the fuel promote combustion, which decreases soot emissions. The oxidation catalyst lowers aldehyde emissions and the organic fraction of the particulate. A 50 : 50 blend of biodiesel (soybean methyl ester) and low sulfur winter diesel (D2) fuels was tested relative to standard (D2) diesel fuel. The tests were conducted at International Nickel's (INCO Limited) Creighton mine in Sudbury, Ontario, Canada.

At the request of INCO, all samples collected during the biodiesel study were analyzed by Method 5040 at NIOSH (Cincinnati, OH, USA). Over 150 filter samples of diesel particulate matter were collected as part of the biodiesel study. In addition, a separate set of 22 samples was collected for a comparison between NIOSH Method 5040 and ZH 1/120.44. After analysis at NIOSH, these samples were shipped to the Institut für Gefahrstoff-Forschung der Bergbau-Berufsgenossenschaft (IGF) (Bochum, Germany), where they were analyzed according to ZH 1/120.44. Each filter in the set of 22 was analyzed once at both laboratories. Results of this comparison are reported here. Details on the biodiesel project itself are available electronically at www.deep.org.

Results

EC, OC and TC results (in µg cm^{-2}) for the 22 samples of diesel particulate are listed in Table 1. Bar graphs illustrating the comparison of results obtained by each laboratory are shown in Figs. 1–3. The correlation between the results from the two laboratories was examined through least squares regression of the data; regression results are given in Table 2.

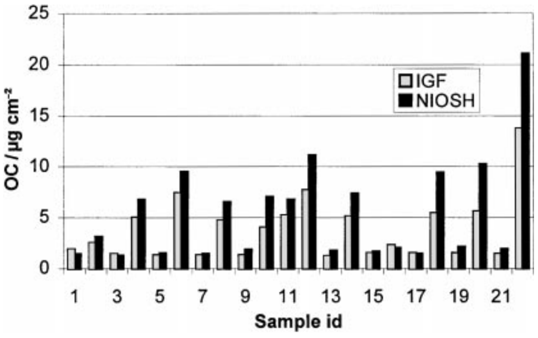

Fig. 1 OC results obtained by IGF and NIOSH laboratories. Samples analyzed by Method ZH 1/120.44 (IGF) and NIOSH Method 5040.

Discussion

In general, lower EC (higher OC) results will be obtained by NIOSH Method 5040 relative to ZH 1/120.44 whenever a sample contains carbonaceous materials (*e.g.*, combustion aerosols such as cigarette and wood smokes, condensation aerosols, plant debris) that require high temperatures (*e.g.*, above 500 °C) for removal in a non-oxidizing atmosphere. This result is to be expected because a higher maximum temperature is used during the first part of the analysis (Method 5040) and a correction is made for deposited char. Higher OC results are also expected with Method 5040 when analyzing samples from some types of mines because, unlike ZH 1/120.44, samples are not acidified unless this is requested by the client. In the case of EC, acidification is unnecessary with Method 5040 because carbonates ordinarily do not pose an interference problem. If present, carbonates contribute to the OC fraction, but a carbonate-subtracted result will be provided by the laboratory if a client requests it.

When the diesel particulate sample contains no other (*i.e.*, non-diesel) sources of carbonaceous particulate and the OC fraction of the particulate is essentially removed at temperatures below about 500 °C, better agreement between the two methods is expected. Airborne particulate samples from underground, non-coal mines in Germany may meet these criteria,[9] so reasonable between-method agreement might be found in this workplace. Between-method agreement would be advantageous because it would permit direct comparison of recently acquired data on EC levels in mines. In-mine levels have been determined in a number of countries through use of the coulometric (Germany) and thermal–optical (USA, Canada, Australia) methods.

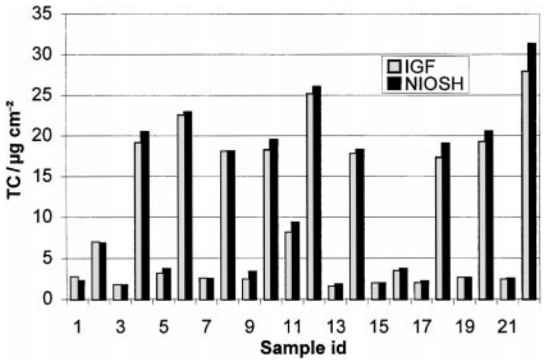

Fig. 3 TC results obtained by IGF and NIOSH laboratories. Samples analyzed by Method ZH 1/120.44 (IGF) and NIOSH Method 5040.

Table 2 Regression results (IGF *vs.* NIOSH) for OC, EC and TC data

Analyte	Regression equation	r^2
OC	IGF = 0.62(NIOSH) + 0.48	0.97
EC	IGF = 1.17(NIOSH) − 0.05	0.98
TC	IGF = 0.94(NIOSH) + 0.06	0.99

Good correlation between the results obtained by the two laboratories was seen in this comparison. The methods gave essentially equivalent results for TC, with IGF finding about 6% less carbon than NIOSH. Relative percentage differences (RPD) given in Table 1 were ⩽20% for all samples except sample 9, where the RPD was 32%. These results compare fairly favorably given that 11 of 22 results (including sample 9) were below the limit of quantification (LOQ) for TC (about 4 µg cm^{-2}). The small differences between the TC results obtained by the two methods, even after shipping and handling by three laboratories, indicates that TC measurement by both methods is accurate. Based on a previous comparison,[8] this result was expected.

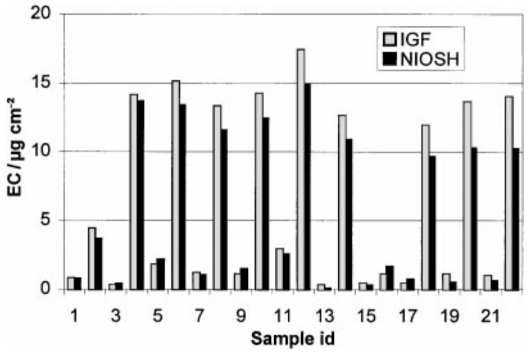

Fig. 2 EC results obtained by IGF and NIOSH laboratories. Samples analyzed by Method ZH 1/120.44 (IGF) and NIOSH Method 5040.

Differences in the EC and OC values reported by the two laboratories were again seen, but were much smaller than those obtained in the previous comparison.[8] As indicated by the regression results (Table 2), higher (by about 17%) EC results (and, consequently, lower OC results) were obtained with method ZH 1/120.44. The mean EC fractions (*i.e.*, EC/TC) found with ZH 1/120.44 and Method 5040 were 0.53 ($\sigma = 0.19$) and 0.46 ($\sigma = 0.15$), respectively, which is typical of diesel particulate emissions in mines. The difference in the 'split' between the organic and elemental carbon is small relative to those seen in a previous comparison.[8] The relatively minor difference reported here is attributed to the different thermal programs used. Neither charring nor loss of a significant amount of carbon above 500 °C (and up to 850 °C in helium) was noted in the thermograms (*i.e.*, output signal of the thermal–optical instrument), which was not the case in the previous comparison.[8]

The previous comparison[8] included diesel samples collected in workplace settings in addition to other types of carbonaceous particulate. In contrast, the 22 samples used for this comparison were collected in a simulated mining environment that was relatively interference free. The diesel equipment was well maintained and the engines were tuned prior to the tests so changes in particulate carbon levels could be attributed solely to the fuel type. Because diesel particulate from well maintained, tuned equipment was the only major sample component, the results of this comparison probably represent a best-case scenario. Additional comparison data for a variety of mines (non-coal) are needed to determine whether the two methods (ZH 1/120.44 and Method 5040) give equivalent results in this workplace.

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Mention of a company name or product does not constitute endorsement by the Centers for Disease Control and Prevention.

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