(7) DIESEL EXHAUST AEROSOL, REVIEW OF MEASUREMENT TECHNOLOGY

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INTRODUCTION

The U.S. Bureau of Mines and others have conducted a number of occupational exposure surveys since the publication of the International Agency for Research on Cancer report of 1989[1], which labeled diesel exhaust as a probable human carcinogen. These surveys have assessed diesel exhaust exposure using measurement of diesel aerosol and/or specific polycyclic aromatic hydrocarbons as indicators of exposure. This report reviews, available diesel exhaust aerosol and gas measurement techniques.

Measurement of human exposure to toxic agents is the first step in determining the exposure-dose-response relationship. It is a fundamental step in risk assessment. Measuring exposure to diesel exhaust pollutants is particularly challenging due to the complexity and variability of exhaust components. This paper reviews current occupational health standards for diesel emissions and available diesel exhaust gas and aerosol measurement techniques. Although surveys in mines have primarily assessed diesel exhaust exposure using diesel particulate matter (DPM) some exhaust gas measurements have been used as indicators of exposure. DPM is emphasized because it is a major component of diesel exhaust, is suspected to make a major contribution to the health hazard, and is measurable.

OCCUPATIONAL HEALTH STANDARDS

Occupational exposure surveys of diesel exhaust frequently measure regulated pollutants, or pollutants that are suspected carcinogens, even if no permissible exposure limits (PELs) have been established. In the United States, various organizations recommend a range of allowable values for diesel exhaust gaseous constituents, including carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitric oxide (NO), and formaldehyde (HCHO). Table I summarizes these recommended levels, showing 8-hour or 10-hour time-weighted-average values where available; where these are not available, 15-minute short-term

Table I: Range[a] of Allowable Gaseous Exposure Limits for 8-hr-Time-Weighted-Average Occupational Exposures[b].

Pollutant	Range, ppm
CH_2O[c]	0.016-2.0
CO	25-50
CO_2	5,000-10,000
NO	25
NO_2[d]	1.0-5.0
SO_2	2.0-5.0

[a] ACGIH, MSHA, NIOSH, OSHA; [b]NIOSH has a 10-hr-time-weighted average value
[c] Suspect carcinogen, MSHA has only a 15-min short-term value
[d] NIOSH and OSHA have 15-min short-term values exposure values are included.

The Mine Safety and Health Administration (MSHA) has proposed revised air quality regulations, but these are not shown.[2]

There is no specific U.S. permissible exposure limit (PEL) for DPM at this time. Diesel aerosol is of respirable size and thus is limited under a variety of PELs for respirable dust, including MSHA's 2.0 mg/m^3 respirable coal mine dust standard. MSHA has announced that it will consider regulating DPM.[3] Recently, the American Conference of Governmental Industrial Hygienists (ACGIH) added diesel exhaust to the list of Notice of Intended Changes for 1995-1996 with a recommended threshold limit value (TLV) of 0.15 mg/m^3 and a designation of suspected human carcinogen.[4]

Respirable combustible dust (RCD) is used to estimate DPM concentrations in Canadian non-coal mines. This is determined from the amount of combustible dust in a respirable dust sample by determining the mass that is removed from the sample by combustion at 500 °C.[5, 6] An estimate of the DPM concentration is made by multiplying the respirable combustible dust measurement by an empirical correction factor of 0.67. This adjusts for the contribution of unburnt fuel, evaporated lube oil, and other carbonaceous material to the DPM estimate. For aerosol samples collected in a coal mine or other environments where non-diesel carbonaceous aerosol is present, respirable combustible dust analysis is not appropriate to estimate DPM levels.

Based on RCD measurements, British Columbia has established a respirable combustible dust standard of 1.5-mg/m^3 for underground non-coal mines.[7] The Canada Centre for Mineral and Energy Technology recommends that this standard be reduced eventually to 0.75 mg/m^3.[8]

In the Federal Republic of Germany, DPM is defined by the coulometric determination of total carbon content in fine dust particulate.[9] Based on this analytical procedure, the following technical exposure limits were established: 0.6 mg/m^3 for DPM in underground non-coal mines and construction sites; and 0.2 mg/m^3 for other occupational environments. Coal mines are not regulated. The technical exposure limit of a hazardous material is the minimum concentration possible with current technology and serves as a guidance mechanism for implementing necessary protective measures and monitoring policies in the workplace.[10] This standard is currently being revised. The proposed standard based on elemental carbon is given in Table II.

Table II: Current and proposed German PEL for diesel exhaust.

INDUSTRY	PEL (mg/m^3)
Curent PEL - based on Total Carbon	
General Industry	0.2
Non-coal mining	0.6
Proposed PEL - based on Elemental Carbon	
General Industry	0.1
Mining	0.3
General Industry (where >50% of total carbon is organic)	0.15

As with RCD, the current method of measurement is also not appropriate for coal mines or other areas where substantial amounts of carbonaceous material from non-diesel sources are present. The new standard promises to be more widely applicable.

Of the diesel associated PAHs, only chrysene (0.2 mg/m^3) and those connected with coal tar pitch volatiles, 0.2 mg/m^3 as benzene solubles, have Occupational Safety and Health Administration (OSHA) PELs.[11] The OSHA PEL for coal tar pitch volatiles specifically includes anthracene, benzo[a]pyrene, phenanthrene, acridine, chrysene, and pyrene.

No PELs are established for other gas-phase or particle-bound PAHs. The ACGIH designates diesel exhaust components benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, and chrysene as "suspected human carcinogens"; but recommends no TLVs.

The benzene-extractable portion of coal tar pitch volatiles is designated as a "confirmed human carcinogen" by the ACGIH, with a TLV of 0.2 mg/m^3.[12]

DPM SAMPLING AND ANALYTICAL METHODS

DPM, depicted in Figure 1, is small in size (0.2μm mass mean size) and is composed of organic and elemental carbon, adsorbed and condensed hydrocarbons, and sulfate. The proportion of organic to inorganic carbon varies depending upon a number of factors, which include fuel, engine type, duty cycle, engine maintenance, operator habits, use of emission control devices, and lube oil consumption. In general, non-extractable elemental carbon accounts for a greater fraction of DPM mass than extractable organics.[13]

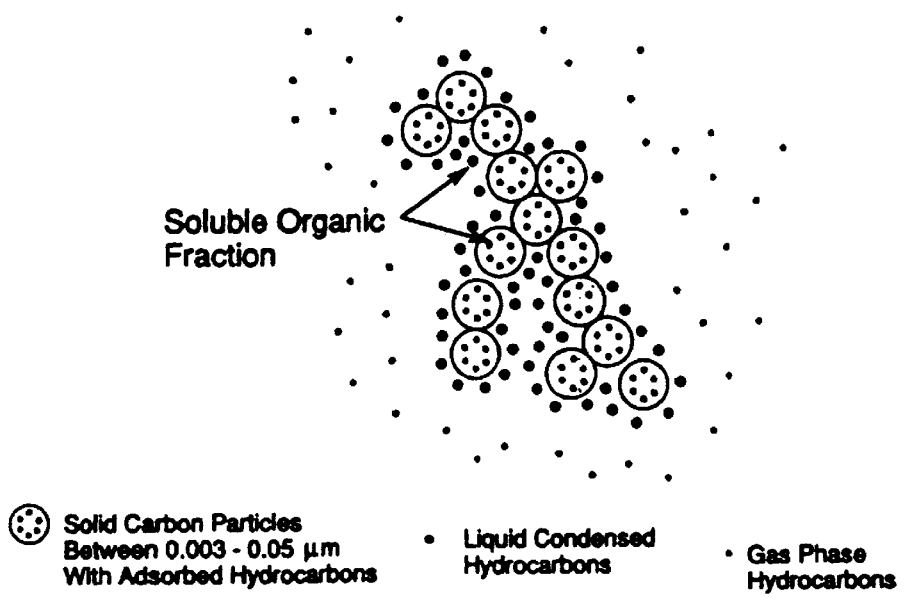

Figure 1: Summary schematic of a typical diesel exhaust aerosol.

In addition to RCD measurements, two other techniques have been used in the subject surveys to measure exposure to diesel aerosol in the workplace. These are size-selective sampling with gravimetric analysis and elemental carbon analysis.

1. Size-selective Sampling

Figure 2 depicts the trimodal size distribution that arises from different mechanisms of aerosol generation.[14] Primary combustion aerosols, including diesel exhaust aerosol, are formed as very small particles in the 0.001 to 0.08 μm range, but physical mechanisms such as condensation and coagulation quickly transfer the aerosol mass from the nuclei mode to the accumulation mode. These processes result in an approximately 0.2 μm mass median diameter for diesel aerosol, with 90% of the particles less than 1.0 μm in size. Mechanically generated aerosols, on the other hand, typically contain particles greater than a micron in diameter, with only a small portion of the mass under a micron in size.

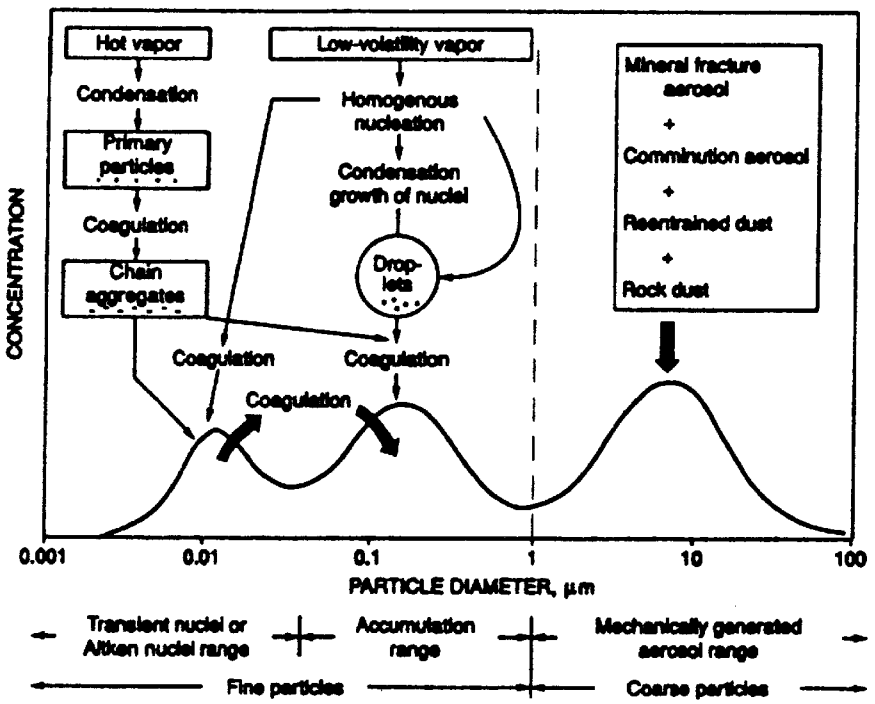

Figure 2: Schematic of the distribution of aerosol size from a combination of combustion and mechanical sources.

The difference in the aerodynamic diameter particle size between combustion and mechanically generated aerosols can be used to separate diesel aerosol from noncombustion aerosols in the collecting process. This is done using inertial impaction, which removes large non-diesel particles and a small percentage of large diesel particles. The submicrometer aerosol, predominantly diesel in origin, is collected on a filter downstream of the impaction substrate. Gravimetric analysis is used to determine the mass concentration in each of these size fractions. The respirable dust mass concentration can be calculated from the concentrations of the two measured fractions.

Size-selective sampling has been used extensively in mining to evaluate the performance of emission control devices and to determine the concentrations of respirable dust and DPM in the mine atmosphere.[15-20] One such sampler, a personal diesel exhaust aerosol sampler (PDEAS), pictured in Figure 3, is based upon the principles of size-selective sampling and has been used extensively by the Bureau.[21] The sampler operates at a flow rate of 2 L/min, which is compatible with commercial personal sampler pumps. The final sample of material less than 0.8 μm aerodynamic diameter contains most of the DPM present in the mine air plus a small amount of mineral dust contamination, usually less than 10%.

This technique, coupled with gravimetric analysis, has limitations. In environments where submicrometer aerosol sources are well-defined and have relatively high concentration, this method is effective. If a sample flow rate of 2 L/min is used and gravimetric analysis is to within 0.1 mg, the aerosol concentration for the fraction of aerosol less than 0.8 μm should have a theoretical limit of detection of 0.3 mg/m^3 $\pm$ 50% with a confidence level of 95%.[20] This lower limit of detection is a worst-case estimate based on MSHA's current gravimetric analysis practice, mine aerosol interferences, and tolerances in sampler manufacture. With gravimetric analysis to within 0.005 mg, the lower limit of detection would be 0.2 mg/m^3. Measurements have shown that the PDEAS is capable of a precision of 0.015 mg/m^3. When other forms of submicrometer aerosol are present or concentrations are low, other analysis methods with greater specificity and sensitivity are required to quantify the diesel aerosol fraction.

2. Elemental Carbon Analysis

Size selective sampling can collect a sample of submicron particulate matter that can be analyzed gravimetrically and by other analytical methods.

These methods are frequently more specific and sensitive than the gravimetric method. Recent research has focused on analyzing the submicron or respirable fraction for elemental carbon. Elemental carbon accounts for a significant fraction of DPM emissions, acts as a carrier of suspected mutagens and carcinogens, and is readily detectable by thermal-optical analysis. The association between particle exposure and health effects, discussed elsewhere, further strengthens the use of elemental carbon as a surrogate for DPM exposure. Elemental carbon has an analytical definition which is operationally defined by the method of analysis.[22]

It has been claimed that elemental carbon is the most reliable overall measure of exposure to diesel exhaust because selecting an extractable organic compound or class of compounds as a reliable surrogate of exposure is difficult.[23] The soluble organic fraction (SOF) associated with diesel exhaust aerosol is highly variable in composition, is chemically complex, and uncertainty exists about the compounds responsible for mutagenic and carcinogenic activity. Also, low concentrations and the presence of interfering chemical compounds make analysis difficult. These factors makes SOF an unreliable measure of diesel exposure.

The use of a temperature-based thermal-optical method for speciation of organic (volatile and nonvolatile) and inorganic (carbonate) compounds, and elemental carbon is being investigated.[24] Aerosol samples are collected by inertial impaction to classify particles by

size. As noted previously, particles less than 1.0 μm in size are predominately from combustion sources. Thermal-optical analysis is used to detect and quantify different types of carbon. Volatilized carbon is oxidized to CO_2 and subsequently reduced to methane, which is quantified by flame-ionization detection. The second stage of analysis begins by reducing the combustion chamber temperature, introducing oxygen, and reheating to 750 °C. During this stage, elemental carbon and char content are determined. The estimated limit of detection in the laboratory is 2 μg of either elemental or organic carbon per filter, which translates to a concentration of about 1 $\mu g/m^3$, assuming 2 m^3 of sample air volume.[25]

An experiment to investigate possible environmental tobacco smoke interference with elemental carbon measurements was conducted.[26] Tobacco aerosol was generated in a controlled environment by three men smoking a total of eight cigarettes per hour. Respirable particulate was on the order of 1,100 $\mu g/m^3$. The total carbon from tobacco smoke was found to average 1.8% elemental carbon and 98.2% organic carbon.

As part of the same study, an experiment was conducted to investigate the precision and reproducibility of the thermal-optical method to determine elemental carbon in diesel exhaust. Diesel aerosol was generated under four load-and-speed conditions and diluted in a dilution tube at Ford Motor Company's Research and Engineering Facility in Dearborn, Michigan. Elemental carbon constituted an average of 62% of the total particulate mass on the filters and 64% of the total carbon loading. Total carbon constituted 91% of the total mass on the filters. The mean coefficient of variation of the method for elemental carbon determination was 7.3%.

As a consequence of these results, a proposal for the use of elemental carbon as a surrogate measure of diesel exhaust exposure determined with the thermal-optical method of analysis has been advanced.[27] The arguments for this are: (1) most diesel exhaust aerosol mutagenicity appears associated with the particulate phase, and lung tumor induction in laboratory rats is primarily associated with the particulate phase; (2) clearance in animals is adversely affected by particulate deposition, and "inert" substances deposited in the lung may also induce lung cancer; (3) submicrometer elemental carbon detection by thermal-optical analysis has sensitivity 100-fold greater than the gravimetric method, and the diesel particulate fraction is mostly carbon; and (4) nearly all the elemental carbon from vehicular traffic is attributable to diesel exhaust.

SUMMARY

Diesel exhaust is chemically complex, containing literally hundreds of different substances. This complexity makes it impossible to monitor all exhaust pollutants to determine exposure. Exposure assessments generally monitor regulated pollutants or select a surrogate measure(s) of exposure. The surrogate measure should be representative of diesel exhaust as a whole, have some relationship to adverse health effects, and, if possible, be unique to diesel exhaust. Unfortunately, many of the compounds found in diesel exhaust are also emitted from other combustion sources and are thus not unique to diesel exhaust.

A limited number of exhaust constituents have PELs. These include the gases CO, CO_2, NO, NO_2, SO_2, HCHO, and some PAHs. Canada has recommended a limit for respirable combustible dust of 1.5 mg/m^3 in non-coal mines. Germany has established technical

exposure limits of 0.6 mg/m^3 for the total carbon content in fine dust particulate in underground non-coal mines and construction sites; and a 0.2 mg/m^3 limit for other occupational environments. The U.S. has no PEL for DPM at this time.

DPM is formed during combustion and as a result the aerosol is small in size with a mass median aerodynamic diameter of 0.2 μm. DPM is composed of organic and elemental carbon, adsorbed and condensed hydrocarbons, and sulfate. The proportion of organic to inorganic carbon varies, depending upon a number of factors: fuel, engine type, duty cycle, engine maintenance, operator habits, use of emission control devices, and lube oil consumption. In general, non-extractable elemental carbon accounts for a greater fraction of DPM mass than extractable organics.

The aerodynamic diameter particle size difference between combustion and mechanically generated aerosols is used to separate diesel aerosol from non-combustion aerosols by inertial impaction. Submicrometer DPM is collected on a filter downstream of the impaction substrate. Gravimetric analysis determines the mass fraction in each size range. Also, the filter containing the submicrometer material can be analyzed by other methods to increase the sensitivity and specificity for DPM. This is an advantage over other aerosol measurement techniques, which either do not collect a sample or destroy the sample during analyses. However, size-selective sampling collects all DPM meeting specific aerosol sampling criteria but may not be representative of the amount of DPM deposited in human lung airways. Hence, reliance on measurements of total DPM as the indicator of exposure may overestimate the actual deposited dose of DPM in lung tissue and lead to inaccurate health effects assessments.

At the present time, the best surrogate measure of DPM in the occupational environment appears to be elemental carbon. Elemental carbon generally accounts for about 40 to 60 % of DPM mass, and is detectable at relatively low levels using size-selective sampling and thermal-optical analysis. Elemental carbon is detectable apart from the organic carbon found in cigarette smoke and diesel exhaust. Additionally, data summarized in other sections of this report suggest that carbon particles can cause cancer in laboratory rats. As pointed out earlier, the percentage of elemental carbon in total DPM fluctuates. The fluctuation in the ratio of elemental to organic carbon can cause an inaccurate estimate of the total DPM present. The estimate will improve if both organic and elemental carbon are measured and an adjustment is made for the presence of non-diesel carbon sources. Consideration should also be given to the measurement of a few specific PAHs which are known carcinogens. Unfortunately, these compounds are typically found at very low levels and are not unique to diesel exhaust.

REFERENCES

1. IARC Monographs on the Evaluation of Carcinogenic Risks To Humans - Diesel and Gasoline Engine Exhausts and Some Nitroarenes, vol. 46, 458 pp. International Agency for Research on Cancer, Lyon, France (1989).
2. Mine Safety and Health Administration, U.S. Department of Labor: Air Quality, Chemical Substances, and Respiratory Protection Standards; Proposed Rule. 30 CFR Part 56 et al. Fed. Reg. 54 (166}:35769-35852 (Aug. 29, 1989).

3. Mine Safety and Health Administration, U.S. Department of Labor: Permissible Exposure Limit for Diesel Particulate. Fed. Reg. 57(3):500-503 (Jan. 6, 1992).
4. American Conference of Governmental Industrial Hygienists: Annual Reports of the Committees on Threshold Limit Values and Biological Exposure Indices. Notice of Intended Changes for 1995-1996. ACGIH Today 3(2):1 (1995).
5. Gangal, M.; Ebersole, J.; Vallieres, J.; et al.: Laboratory Study of Current (1990/91) SOOT/RCD Sampling Methodology for the Mine Environment. Mining Research Laboratory, Canada Centre for Mineral and Energy Technology (CANMET), Ottawa, Canada (1990).
6. Gangal, M.K.; Dainty E.D.: Ambient Measurement of Diesel Particulate Matter and Respirable Combustible Dust in Canadian Mines. In: Proceedings of the 6th US Mine Ventilation Symposium, Salt Lake City, UT, 1993, pp. 83-89. R. Bhaskar, Ed., Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO (1993).
7. Ministry of Energy, Mines and Petroleum Resources, Resource Management Branch: Health, Safety and Reclamation Code for Mines in British Columbia: Part 6, Mine Design and Procedures, Victoria, British Columbia, Canada, pg. 6-21 (1992).
8. I.W. French and Associates, Ltd.: Addendum to Health Implications of Exposure of Underground Mine Workers to Diesel Exhaust Emissions. Energy, Mines & Resources, Canada, Contract No. 09SQ.23440-7-9042, 152 pp (1990).
9. Bauer, H.; Dahmann, D.; Fricke, H.: Coulometric Determination of Diesel-engine-emissions in Non-coal Mines. Staub-Reinhaltung der Luft, 51:319-325 (1991).
10. Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area: MAK-and BAT-Values 1993: Maximum Concentrations at the Workplace and Biological Tolerance Values for Working Materials, Report No. 29, pp. 98-102, VCH Verlagsgesellschaft, Weinheim (Federal Republic of Germany) (1993).
11. American Conference of Governmental Industrial Hygienists: Guide to Occupational Exposure Values-1992. Amer. Conf. Gov. Ind. Hyg. Cincinnati, OH, 137 pp (1992).
12. American Conference of Governmental Industrial Hygienists: 1994-1995 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Amer. Conf. Gov. Ind. Hyg. Cincinnati, OH, 119 pp (1994).
13. Perez, J.M.; Williams, R.L.: A Study of Particulate Extracts from 1980s Heavy Duty Diesel Engines Run on Steady-State and Transient Cycles. Soc. Auto. Eng. Tech. Paper 892491, 11 pp (1989).
14. Cantrell, B.K.; Rubow, K.L.: Measurement of Diesel Exhaust Aerosol in Underground Coal Mines. Bureau of Mines IC 9324, pp. 11-17 (1992).
15. McCawley, M.; Cocalis, J.: Diesel Particulate Measurement Techniques for Use With Ventilation Control Strategies in Underground Coal Mines. Ann. Amer. Conf. Gov. Ind. Hyg., v. 14:271-279 (1986).
16. Marple, V.A.; Kittelson, D.B.; Rubow, K.L.; et al.: Methods for the Selective Sampling of Diesel Particulates in Mine Dust Aerosols. Bureau of Mines OFR 44-87, NITS PB 88-130810, 94 pp (1986).
17. Rubow, K.L.; Cantrell, B.K.; Marple, V.A.: Measurement of Coal Dust and Diesel Exhaust Aerosols in Underground Mines. In: Proceedings of the 7th International Conference on the Pneumoconiosis, Pittsburgh, PA, August 23-26, 1988. NIOSH Publication No. 90-108, pp. 645-650. U.S. Department of Health and Human Services, Atlanta, GA (1990).
18. Cantrell, B.K.; Zeller, H.W.; Williams, K.L.; et al.: Monitoring and Measurement of In-Mine Aerosol: Diesel Emissions, Bureau of Mines IC 9141, pp 41-51 (1987).

19. Cantrell, B.K.; Rubow, K.L.: Mineral Dust and Diesel Aerosol Measurements in Underground Metal and Nonmetal Mines. In: Proceedings of the 7th International Conference on the Pneumoconiosis, Pittsburgh, PA, August 23-26, 1988. NIOSH Publication No. 90-108, pp. 651-655. U.S. Department of Health and Human Services, Atlanta, GA (1990).
20. Cantrell, B.K.; Rubow, K.L.: Development of Personal Diesel Aerosol Sampler Design and Performance Criteria. SME Preprint No. 90-74, 5 pp. Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO (1990).
21. Rubow, K.L.; Marple, V.A.; Tao, Y.; et al.: Design and Evaluation of a Personal Diesel Aerosol Sampler for Underground Coal Mines. SME Preprint No. 90-132, 5 pp. Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO (1990).
22. Cadle, S.H.; Groblicki, P.J.: An Evaluation of Methods for Determination of Organic and Elemental Carbon in Particulate Samples. In: Particulate Carbon: Atmospheric Life, pp. 89-109. GT Wolff and RL Klimisch, Ed's, Plenum Press, NY, NY (1982).
23. Fowler, D.P.: Industrial Hygiene/Environmental Sampling Program to Develop Qualitative and Quantitative Data on Diesel Exhaust Emission Exposure. Final Report on CRC-APRAC Project No. CAPM-24-78. SRI International, Menlo Park, CA (1985).
24. Birch, M.E.; Cary, R.A.: An Elemental Carbon Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust. Aerosol Sci. and Tech., In-Press (1996).
25. Johnson, R.L.; Shaw, J.J.; Cary, R.A.; et al.: An Automated Thermal-Optical Method for the Analysis of Carbonaceous Aerosols, Atmospheric Aerosol: Source/Air Quality Relationships. In: Amer. Chem. Soc. Symp. Ser. No. 167, pp. 223-233. Macias ES, Hopke PK eds., Amer. Chem. Soc., Washinton, DC (1981).
26. Zaebst, D.D.; Clapp, D.E.; Bade, L.M.; etal.: Quantitative Determination of Trucking Industry Workers' Exposure to Diesel Exhaust Particles. Am. Ind. Hyg. Assoc. J., 52(12):529-541 (1991).