A Review of NIOSH Manual of Analytical Methods *Chapter DL – Monitoring Diesel Particulate Exhaust in the Workplace*

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Overview

- One of the functions of the National Institute of Occupational Safety and Health (NIOSH) is the development of sampling and analytical methodology for occupational exposures to airborne toxic substances.
- Research methodology is validated, compiled and published in the NIOSH Manual of Analytical Methods (NMAM).
- In April 2016, NIOSH released the 5th Edition of NMAM.
- The preface to the compilation of methods includes sections referred to as 'Chapters', which provide detail as to the purpose and scope of NMAM, as well as detailed discussions on specific areas of information.

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Overview

- NMAM 5th Edition Chapters include:
  - PL – Purpose and scope
  - AE – Factors affecting aerosol sampling
  - DL – Monitoring diesel particulate exhaust in the workplace
  - FI – Measurement of fibres
  - FP – Filter pore size and aerosol sample collection
  - GL – Glossary
  - ME- Development and evaluation of methods
  - SA – General considerations for sampling airborne contaminants
  - SM – Sampling and analysis of soluble metals
  - UA – Measurement uncertainty and NIOSH method accuracy range

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Overview

- Chapter Q (predecessor to Chapter DL, in NMAM 4th Edition; 2003) was published to provide supplemental information to support NIOSH methodology for the sampling and analysis of elemental carbon (NIOSH Method 5040) as a surrogate measure of exposure to diesel particulate matter.
- Chapter Q contents included:
  - Composition and health effects of diesel exhaust particulate
  - Numerous aspects of NIOSH 5040 analytical methodology
  - Interlaboratory comparisons
  - Occupational exposure criteria

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Overview

- Chapter DL (NMAM 5th Ed.) provides updated references and information on the following topics:
  - Classification of diesel exhaust as a human carcinogen
  - A study of miners exposed to diesel exhaust
  - Results of round robin laboratory studies by NIOSH investigators
  - Application, operation and performance issues associated with NIOSH 5040
- This presentation provides a selective review of the contents of Chapter DL, with specific focus on the application of NIOSH 5040 to the mine environment.

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Health Effects

- In 2012, IARC reclassified diesel exhaust as carcinogenic to humans (Group 1).
- Reference to the joint NIOSH/NCI diesel exhaust in miners study; a cohort mortality study which established an increased risk of death from lung cancer for exposed miners.
- Evidence supporting diesel exhaust particles as a nonspecific airway irritant (higher concentrations) and promoter of allergenic and inflammatory responses (such as asthma).

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EC as Surrogate DPM Exposure Measure

- Surrogate measures have historically been used for the assessment of exposure to diesel particulate matter (DPM).
- Specifically, DPM assessment techniques have moved from size-selective enhanced gravimetric analyses, to carbon based methodology, since DPM is typically greater than 80% carbon.
- NIOSH recommends the use of elemental carbon (EC) fraction of diesel emissions as the preferred surrogate measure, as opposed to organic carbon (OC) or total carbon (TC).

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NIOSH Method 5040

- *NIOSH Method 5040 – Diesel Particulate Matter (as Elemental Carbon)* entails the collection of airborne particulates (with an optional size device) onto quartz fibre filters followed by thermal optical analytical technique.
- NIOSH 5040 offers greater selectivity and flexibility than previous methods.
- Thermal-optical analysis of EC-OC have historical application in environmental monitoring of particulate carbon air pollution.

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Thermal-Optical Analyzer

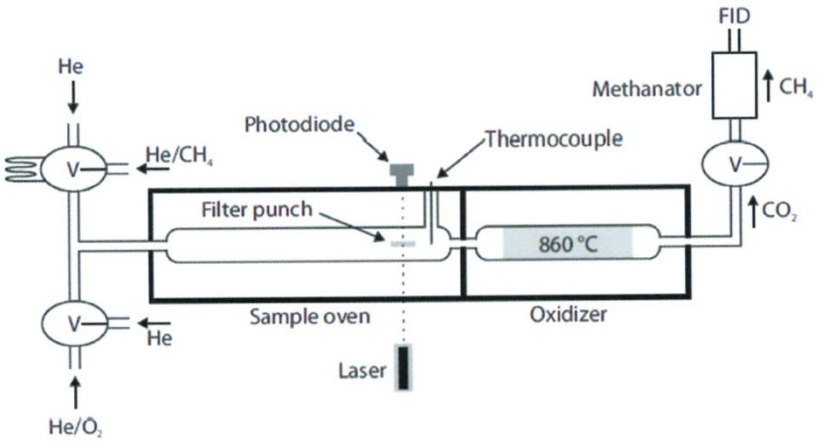

Figure 1. Schematic of thermal-optical transmittance instrument (V = valve) for determining OC and EC in carbonaceous aerosols.

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Thermogram

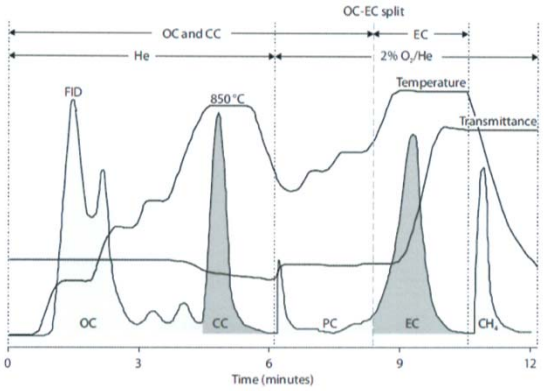

Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or "char." Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and DPM.

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Method Sensitivity

- NIOSH Method 5040 was developed for monitoring workplace exposure to DPM, especially in mines, where EC concentrations are relatively high.
- Present working range is approx. 6 to 630 µg/m^3 EC, with a limit of detection of 2 µg/m^3 for a 960-L air sample collected on a 37 mm diameter filter with a 1.5 cm^2 punch.
- Recommendations have been included in NIOSH 5040 (i.e. smaller 25 mm diameter filter, higher flow rate, changes to pyrolysis/oxidation thermogram) to achieve lower detection limits for other applications, such as carbon nanomaterials.

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Interferences – Char Formation

- High bias can occur during analysis through char formation - the pyrolysis of predominantly organic sources of carbon when heated under a helium environment.
- Char is a strong absorber of light, which results in a decrease in filter transmittance/absorbance.
- NIOSH 5040 allows for optical correction for char with a pulsed diode laser and photodetector that continuously monitor the transmittance/reflectance of the filter punch, which is then used to effect changes in the instrument thermogram settings.

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Interferences – OC Vapour

- Adsorbed OC in the form of organic vapour is a potential source of positive bias in NIOSH 5040.
- Correction is not achieved through the traditional use of blanks, which collect vapour passively.
- A more representative correction for adsorbed organic vapour is achieved through the use of two filters in tandem (i.e. Teflon or quartz upper filter and quartz bottom filter).
- Bottom filter is used to correct for presence of adsorbed vapour on upper filter, which contains particulate matter.

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Standards and Reference Materials

- Calibration of thermal-optical transmittance analyzer is achieved by direct methane injection as external standard.
- However, a suitable reference material for EC/OC is not available to characterize the effects of sample interferences, such as char correction.
- National Institute of Standards and Technology (NIST) provides an urban dust standard (SRM 1649a) which has a certified TC mass fraction, but only an Information Value (non-certified) is provided for EC content.
- Assessment of EC fraction of SRM 1649a as determined by 13 methods yielded too broad of a range to use it as an analytical standard.

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Standards and Reference Materials

- SRM 1649a is provided in powder form, which is an obstacle for the filter-based thermal-optical analyzer.
- Need for filter-based EC reference materials (e.g. char correction validation, interlaboratory comparison and proficiency testing programs).
- Current developmental work into the use of soot with alginic acid, sucrose, cellulose, etc. incorporated into standard reference materials for purposes of char correction.

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Additional Considerations

- Air sampling considerations
  - Face velocity effects
  - Use of size-selective devices
  - Filter deposition effects
  - Interference effects of carbonates
- Interlaboratory comparisons with other techniques
- U.S. occupational exposure criteria

https://www.cdc.gov/niosh/docs/2014-151/pdfs/chapters/chapter-dl.pdf

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Additional Considerations

QUESTIONS?

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