

DRI STANDARD OPERATING PROCEDURE

**Thermal/Optical Reflectance Carbon Analysis
of Aerosol Filter Samples**

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Title: Thermal/Optical Reflectance Carbon
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1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This standard operating procedure is intended to:

- provide a basic understanding of the principles of carbon analysis and carbon analyzer operation;
- describe routine determination of organic, elemental, and carbonate carbon from ambient and source filter samples using the DRI thermal/optical reflectance carbon analyzer;
- detail the concerns and procedures that will insure a state-of-the-art carbon analysis measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility of the Division of Atmospheric Sciences at the Desert Research Institute.

1.2 Measurement Principle

The DRI thermal/optical carbon analyzer is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch (normally 0.536 cm²) taken from a quartz fiber filter; 2) converting these compounds to carbon dioxide (CO₂) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO₂); 3) reduction of CO₂ to methane (CH₄) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH₄ equivalents by a flame ionization detector (FID).

The principal function of the optical (laser reflectance) component of the analyzer is correction for pyrolysis of organic carbon compounds to elemental carbon. Without this correction, the organic carbon fraction of the sample would be underestimated and the elemental carbon fraction would be overestimated by including some pyrolyzed organic carbon. The correction for pyrolysis is made by continuously monitoring the filter reflectance (via a helium-neon laser and a photodetector) throughout an analysis cycle. This reflectance, largely dominated by the presence of light absorbing elemental carbon, decreases as pyrolysis takes place and increases as light absorbing carbon is liberated during the latter part of the analysis. By monitoring the reflectance, the portion of the elemental carbon peak corresponding to pyrolyzed organic carbon can be accurately assigned to the organic fraction. The correction for pyrolytic conversion of organic to elemental carbon is essential for an unbiased measurement of both carbon fractions, as discussed in Johnson et al. (1981).

Carbonate carbon can be determined by measuring the CO₂ evolved upon acidification of the sample punch before the normal carbon analysis procedure.

Seven temperature fractions as well as the pyrolysis correction are individually determined and can be reported. Values routinely reported include total organic carbon, organic carbon evolved at temperatures greater than 120°C (high-temperature organic carbon), total elemental carbon, elemental carbon evolved at temperatures greater than 550°C (high-temperature elemental carbon), total carbon, and carbonate.

1.3 Measurement Interferences and Their Minimization

- Carbonate carbon presents significant interference in carbon analysis if it constitutes more than 5% of total carbon in the ambient or source sample, as it is measured as both organic and elemental carbon during thermal/optical carbon analysis. Acid pretreatment of the filter samples can eliminate the carbonate interference.
- The presence of certain minerals in some soils can affect the laser correction for pyrolysis. These minerals change color as the sample punch is heated, generally resulting in a sample which is darker. For samples which contain large fractions of resuspended soils, the split between organic and elemental carbon should be examined manually.
- Some minerals, again predominantly in soil samples or soil dominated samples, may affect the laser reflectance by temporarily changing color or changing the surface texture of the deposit residue. Unlike the effect described above, these changes are reversible and highly temperature dependent.
- Some colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed. This effect is readily ascertained by examining the laser response during the organic portion of the analysis. The split between organic and elemental carbon should be examined manually if the effect is large.
- The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr), existing either as contaminants on the filters (e.g., glass fiber filters) or as part of the deposit material, has been shown to catalyze the removal of elemental carbon at lower temperatures (Lin and Friedlander, 1988). Such catalysis would affect the distribution of carbon peaks during the analysis.
- Water vapor, either contained in the deposit or remaining after acidification of the sample punch, can shift the FID baseline. Allowing the sample punch to dry in the analyzer by passing carrier gases over it will eliminate this effect.

1.4 Ranges and Typical Values of Measurements

A wide range of aerosol concentrations can be measured with this method, the limiting factor being the concentration of the carbon compounds on a µg/filter basis. Heavily polluted environments, which would normally have carbon concentrations above the working range of the carbon analyzer,

may be sampled and analyzed within the range of the carbon analyzer by increasing the filter deposit area or by decreasing the sampling flow rate and/or sampling time.

The carbon analyzer can effectively measure between 0.05 and 750 $\mu\text{g carbon/cm}^2$. The upper range is somewhat arbitrary, depending on the particular compounds on the filter and the temperatures at which they evolve. This upper range may be extended by taking special precautions, such as reducing the punch size or by special temperature programming, to avoid an over-range FID signal.

Typical carbon values range between 10 and 100 $\mu\text{g carbon/cm}^2$ for ambient samples. The distribution between organic and elemental carbon depends on the particulate source types, and range from no elemental carbon (e.g., hot gasoline exhaust) to 80% or more elemental carbon (e.g., woodsmoke and diesel exhaust).

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The lower quantifiable limits (LQLs) of carbon combustion methods depend upon the variable carbon content of the blank quartz filters as well as the analysis method. For better LQLs, the unexposed filters should be pre-fired in an oven at high temperatures for several hours to remove any residual carbon contamination (Fung, 1986; Huntzicker, 1986; Rau, 1986). All quartz filters originating from DRI are pre-fired for a minimum of four hours at 900°C and are acceptance-tested for blank levels before use. Any filters that fail to pass the preset acceptance levels (1.5 $\mu\text{g/cm}^2$ organic carbon, 0.5 μg elemental carbon, and 2.0 μg total carbon) are discarded and not used for sample collection. Average pre-fired blank levels are 0.41 ± 0.2 $\mu\text{g organic carbon/cm}^2$, 0.03 ± 0.2 $\mu\text{g elemental carbon/cm}^2$, and 0.44 ± 0.2 $\mu\text{g total carbon/cm}^2$. Because even pre-fired filters can absorb organic vapors during shipping and storage, the LQL of analysis on a particular set filters depends on the number of field blanks analyzed and the variability in the results from those blanks.

The minimum detection limit (MDL) of the DRI carbon analyzers based on the analyses of 693 individual quartz-fiber filters and defined as three times the standard deviation of their measured results. They are:

total organic carbon	0.82 $\mu\text{g/cm}^2$
high-temperature organic carbon	0.81 $\mu\text{g/cm}^2$
total elemental carbon	0.19 $\mu\text{g/cm}^2$
high-temperature elemental carbon	0.12 $\mu\text{g/cm}^2$
total carbon	0.93 $\mu\text{g/cm}^2$

Acid-evolved carbonate levels in pre-fired quartz filters have been shown to be quite variable (0.0-1.0 $\mu\text{g/cm}^2$) over time. The reaction of ambient CO_2 with alkaline sites on the quartz fibers may be the cause of such variable blank levels. Acceptance testing for carbonate is not routinely performed at DRI, as carbonate analysis is performed only upon special request by the client.

The precision of this analysis has been reported to range from 2 to 4% (Johnson, 1981). For analysis of actual ambient and source filters, homogeneity of the deposit is most important for reproducible results. For homogeneous deposits containing >10 $\mu\text{g/filter}$ of total carbon, precision

is generally 5% or less; for inhomogeneous deposits replicates may deviate by as much as 30%. The precision of carbonate analysis results is approximately 10%.

The precision of the laser-dependent split between organic and elemental carbon fractions depends upon how rapidly the laser is increasing at the time of the split and whether the split falls in the middle of a large carbon peak or not. Typically, relative laser split times are reproducible within 10 seconds and deviations in calculated splits are less than 5% of the total measured carbon.

The accuracy of the thermal/optical reflectance method for total carbon determined by analyzing a known amount of carbon is between 2 to 6% (Rau, 1986). Accuracy of the organic/elemental carbon split is between 5 and 10%.

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing carbon analysis, which includes routine system calibration, actual analysis, and immediate review of the data as it is produced to correct system problems.

It is the responsibility of the laboratory manager or supervisor to ensure the carbon analyses procedures are properly followed, to examine and document all replicate, standard, and blank performance test data, to designate samples for reanalysis, to arrange for maintenance and repair, to maintain the supplies and gases necessary to insure uninterrupted analysis, and to deliver the analysis results in database format to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Division of Atmospheric Sciences is responsible to determine the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

The following terms are used in this document:

Calibration Injection: The injection of calibration gases (methane in helium [CH₄/He] or carbon dioxide in helium [CO₂/He]) into the sample stream to check instrument performance.

Calibration Peak: The FID peak resulting from the automatic injection of methane calibration gas (CH₄/He) at the end of each analysis run (each sample). All integrated peak areas are divided by the calibration peak area and multiplied by an instrument-specific calibration factor to obtain µg carbon.

FID Split Time: The time at which the laser split occurs plus the time required for carbon compounds to travel from the sample punch to the FID.

High Temperature

Elemental Carbon: Carbon evolved from the filter punch in an oxygen/helium (O₂/He) atmosphere at 700 and 800°C minus any pyrolyzed organic carbon present in these two peaks.

High Temperature

Organic Carbon: Carbon evolved from the filter punch in a He-only atmosphere at 250, 450, and 550°C plus pyrolyzed organic carbon. This is the same as regular OC without the first organic carbon peak (VOC).

Laser Split:

The demarcation between organic and elemental carbon, at which the laser-measured reflectance of the filter punch reaches its initial value. At this point all pyrolyzed organic carbon has been removed and original elemental carbon is beginning to evolve.

Lower Split Time:

The time at which the laser-measured reflectance of the filter punch reaches its initial value minus the precision of the laser signal (currently defined as 10 counts).

Pyrolysis:

The conversion of organic carbon compounds to elemental carbon due to incomplete combustion/oxidation; may be envisioned as "charring" during the organic portion of the analysis.

Pyrolyzed Carbon:

The carbon evolved from the time that the carrier gas flow is changed from He to He/O₂ at 550°C to the time that the laser-measured filter reflectance reaches its initial value.

**Regular Elemental
Carbon (EC):**

Carbon evolved from the filter punch in a helium/ oxygen (He/O₂) atmosphere at 550, 700, and 800°C minus pyrolyzed organic carbon.

**Regular Organic
Carbon (OC):**

Carbon evolved from the filter punch in a He atmosphere at 120, 250, 450, and 550°C plus pyrolyzed organic carbon. This is the same as VOC plus high temperature OC.

Regular Split Time:

The time at which the laser-measured reflectance of the filter punch reaches its initial value.

Total Carbon (TC):

All carbon evolved from the filter punch between ambient and 800°C under He and O₂/He atmospheres.

Upper Split Time:

The time at which the laser-measured reflectance of the filter punch reaches its initial value plus the precision of the laser signal (currently defined as 10 counts).

Volatile Organic
Carbon (VOC):

Organic carbon evolved from the filter punch in a He-only atmosphere between ambient and 120°C (the first organic carbon peak).

1.8 Related Procedures

SOP's related to carbon analysis activities and other manuals which should be reviewed in conjunction with this document are:

- DRI SOP #6-001.1 Shipping and Mailing Procedures.
- DRI SOP #6-009.1 Field and Laboratory Safety Procedures.
- DRI SOP #4-001.1 Creation, Revision, Distribution, and Archiving of Standard Operating Procedures.
- DRI SOP #2-106.3 Pre-Firing of Quartz Filters for Carbon Analysis

The DRI Carbon Analyzer Model 3000 Owner's Manual, revised 6/90.

The DRI Carbon Analyzer Model 3000 Maintenance and Troubleshooting Manual, revised 7/94.

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The components of the DRI thermal/optical carbon analyzer are depicted in Figures 2-1 and 2-2; the complete gas flow schematic is shown in Figure 2-3. The programmable combustion oven is the heart of the carbon analyzer and includes loading, combustion, and oxidation zones in a single quartz "oven" as depicted in Figure 2-4.

In addition to the DRI thermal/optical analyzer connected to a Pentium compatible computer, the following items are needed for routine carbon analysis:

- Stainless steel punching tool: 0.516 cm² area for removing small sample punches from quartz filters. This punching tool must be kept clean and sharp. If the punching tool is sharpened, the punch area must be reverified.