



Project Summary

Techniques for the Measurement of Aerosol Carbon Content

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In this summary, two techniques for total and elemental carbon analysis are described. Both methods are totally instrumented, automated, and nondestructive. Total carbon is determined using the gamma-ray analysis of light elements (GRALE) technique. Elemental carbon is determined by a light reflectance method. The extension of the methods to Teflon filters is also described.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Ambient aerosols, particularly those with diameters of less than $3\ \mu\text{m}$ are a serious pollution problem. Carbonaceous material is a major component of the fine particle concentration and has undergone extensive study in the past few years, in large part due to concern that these particles play an important role in urban haze and community health.

Particulate carbon in the atmosphere exists predominantly in three forms: elemental carbon (soot) with attached hydrocarbons, organic compounds, and carbonates. Carbonaceous urban fine particles are composed mainly of elemental and organic carbon. These

particles can be emitted into the air directly in the particulate state or condense rapidly after introduction into the atmosphere by chemical reactions involving gaseous pollutant precursors (secondary aerosol).

In this report, the development of two techniques for total and elemental carbon analysis is described. Both methods are totally instrumented, automated and nondestructive. Total carbon is determined using the gamma-ray analysis of light elements (GRALE) technique. This method involves the in-beam measurement of γ rays emitted during the inelastic scattering of protons accelerated in a cyclotron. In the second method, elemental carbon is determined by a light reflectance method. Much of the analysis has been of aerosols deposited on low carbon glass and quartz filters. Extension of the methods to Teflon filters is also described.

Total Carbon Analysis by the GRALE Technique

The GRALE method is a non-destructive technique based on the measurement of gamma-ray emission induced by proton bombardment of aerosol samples. The γ -ray energy is unique to a particular nuclide and thus can be used as a signature for the element. Elemental concentrations are obtained in units of $\mu\text{g cm}^{-2}$ and are not affected by the chemical form of the elements. The GRALE technique has been used for

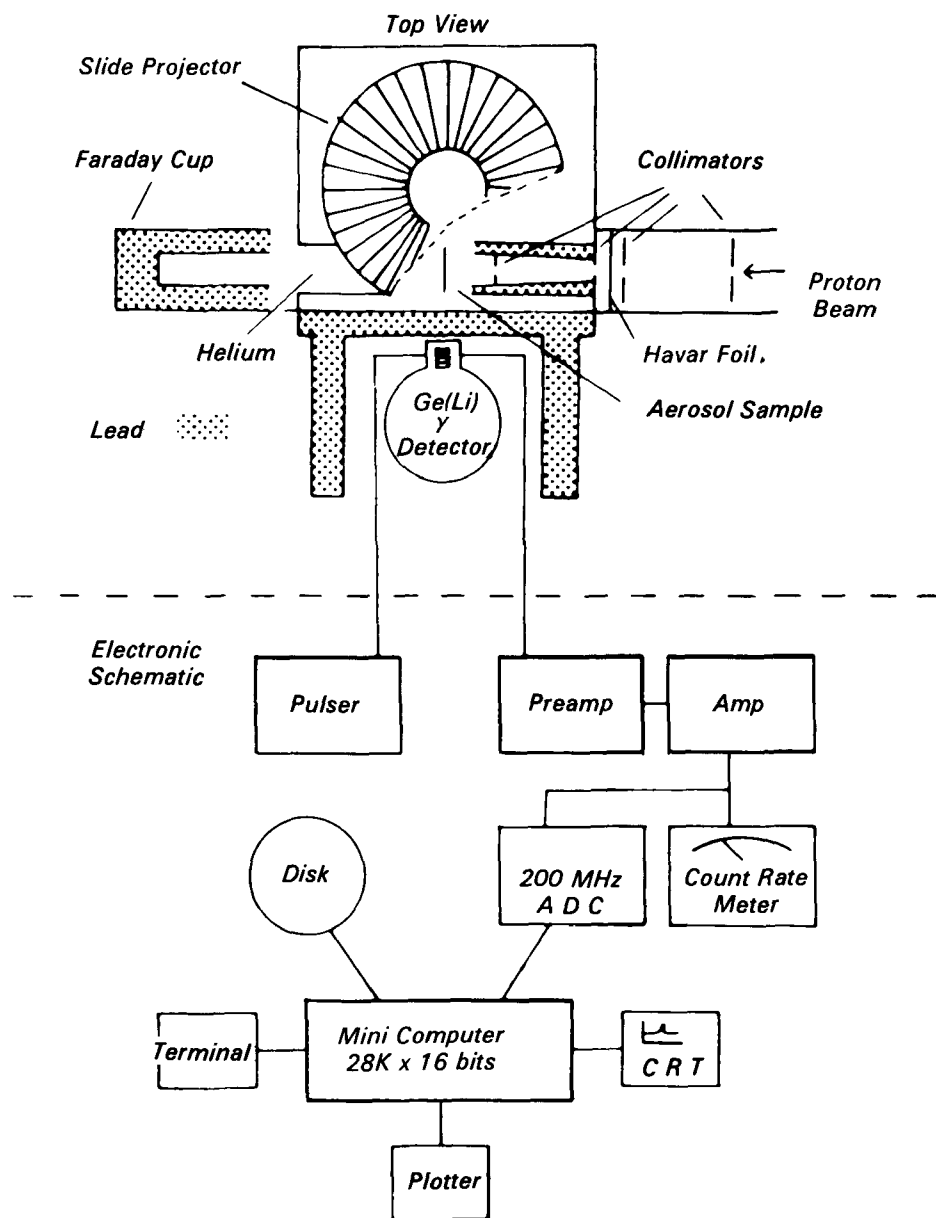


Figure 1. Schematic diagram of the sample irradiation chamber and electronics used for carbon, sulfur, and nitrogen analysis.

total carbon analysis here but the method can also be used to determine the concentration of other elements such as sulfur, nitrogen, and oxygen.

Filter samples are collected and mounted in 5 x 5 slide mounts after removal of the cellulose backing. The samples are irradiated with a collimated beam of 7 MeV protons in the external beam facility of the Washington University, St. Louis, 135-cm sector focused cyclotron with an automated sample changing chamber maintained

in 1 atm of helium. The experimental setup is shown schematically in Figure 1.

Gamma rays produced in the proton bombardment are detected with a 60 cm³ lithium drifted germanium Ge(Li) detector. The γ -ray data are stored and processed in an on-line minicomputer. The spectra are analyzed immediately after each irradiation with the on-line computer. The intensity of each peak is determined from the integrated peak area after subtracting the background

and correcting for system dead-time losses (typically 20 percent). These data are normalized to the proton beam intensity, and intensities of the filter blanks are subtracted from the aerosol results.

Carbon peak intensity is converted into carbon mass by calibrating with standard methionine aerosol (C₅H₁₁O₂SN) deposited on the same type of filter. The mass of methionine deposited on the filter is determined using a beta attenuation mass monitor. Filter blanks, atmospheric, laboratory, and methionine standard aerosol samples are run under nearly identical conditions which yield nearly equal detector count rates. All samples are analyzed similarly.

The GRALE total carbon technique has been extensively compared to the Dohrmann DC-50 carbon analyzer and the Perkin-Elmer Model 240 Elemental Analyser. The latter two methods are based on the high temperature combustion of carbon compounds with subsequent detection of CH₄ and CO₂, respectively. This intercomparison indicates that, to within 5 percent, no systematic discrepancies exist in any of the methods investigated. The GRALE technique is non-destructive and unaffected by the chemical form of the aerosol, two advantages over combustion methods.

Elemental Carbon Analysis by Reflectance

A laboratory reflectometer, shown schematically in Figure 2, has been constructed for use with fine particle filter samples. This light-tight system consists of two blackened aluminum tubes (5.5-cm dia.) each mounted at 45° to an aluminum sample chamber which holds standard 5 x 5 cm slide mounts. A 12-V Tungsten filament lamp powered by a stabilized 12-V supply is used as a light source. Plano-convex lenses are used to focus the incident light onto the sample (0.3 cm²) and reflected light onto a solid state photodetector. The photodetector output is monitored with a digital voltmeter. Unexposed filter, taken from the same filter roll as the samples, is used to determine the initial, or blank, intensity (I₀).

Elemental carbon (soot) standards were prepared by the combustion of polystyrene, paraffin, and butane. The aerosol generated was aspirated into a 5-L container, mixed with filtered air and drawn through a sampler equipped

Elemental Carbon Analyzer

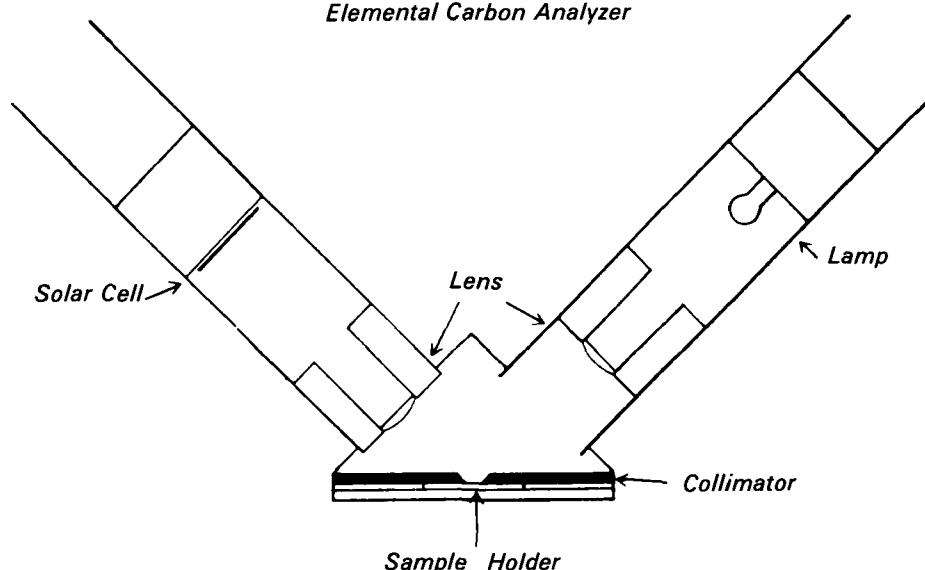


Figure 2. Reflectance photometer.

with the on-line reflectometer. The mass of the deposit was determined by beta attenuation. The reflectance of the spot before and after loading was also measured. Since the aerosol could contain appreciable nonelemental carbon (organic) compounds, a method for their removal was developed. A set of butane-generated samples was mounted over a 1.3-cm dia. hole in 5 x 5 cm aluminum plates and total carbon was determined via the GRALE technique. The samples were then placed in the oven of a conventional gas chromatograph equipped with a programmable temperature ramp. Samples were heated at $20^{\circ}\text{C min}^{-1}$ to a fixed temperature and left at that temperature for 20 min. The reflectance of the sample was measured after cooling to room temperature; the procedure was then repeated at a higher temperature. The reflectance of the sample was nearly constant up to 350°C . Above 350°C , the reflectance relative to 25°C increased, indicating loss of elemental carbon. Therefore, a temperature of 300°C was used to remove organic compounds from the soot samples with minimal loss of elemental carbon.

Analysis of butane-generated samples for total carbon content by GRALE after heating to 300° shows $\sim 25\%$ carbon loss upon heating without appreciable change in reflectance. The

after-heating GRALE carbon mass was taken to be the actual elemental carbon content of the samples which were then considered elemental carbon standards.

A calibration curve was prepared by plotting the log of the ratio of the final to initial reflectance of the elemental carbon standards versus the carbon mass determined by GRALE analysis after heating to 300°C . Alternately, the total mass of the soot standard after heating to 300°C determined by beta attenuation can be used in place of the GRALE carbon mass.

Measurements with Atmospheric Samples

Atmospheric fine particle aerosol samples were collected on the roof of the six-story Chemistry Building of Washington University, located six miles west of downtown St. Louis. The immediate area is primarily residential with a major expressway one mile away which is usually upwind from the sampling site. Samples were collected on an automated TWOMASS sampler equipped with the on-line reflectometer and beta-attenuation system for soot carbon and mass analysis. The samples were analyzed via the GRALE technique for total carbon content. After the samples were heated, the carbon content and reflectance were

remeasured. Figure 3 shows the average decrease in total and elemental carbon content versus the temperature of two samples collected on preashed Pallflex TissueQuartz (2500 QAO) filters. A significant amount of carbon is lost at temperatures up to 300°C without an appreciable loss of elemental carbon. It may be assumed that this carbon loss at or below 300°C is due to volatile organic compounds. However, it is not certain that all organic compounds have been removed at this temperature. The amount of organic carbon loss below 300°C is dependent on the composition of the aerosol. Between 300 and 450°C , the carbon content continues to decrease with a corresponding decrease in reflectance due primarily to the loss of elemental carbon.

It is instructive to compare the amount of total and elemental carbon determined after heating atmospheric aerosol samples to 300°C to estimate the amount of nonelemental carbon remaining at that temperature. The data show a high correlation ($r = 0.96$) indicating a linear relationship between elemental carbon and total mass. The least squares fit to the data has a slope of nearly unity (0.9 ± 0.2) indicating good agreement between total and elemental carbon. The y intercept is $3 \pm 4 \mu\text{g cm}^{-2}$, and indicates there may be a small amount of nonelemental carbon remaining at 300°C in the ambient samples.

Total and Elemental Carbon Analysis on Teflon Filters

The work described above employed glass or quartz filters. Teflon filters present a different problem because this material is 25 percent carbon $[(\text{C}_2\text{F}_4)_n]$. Previously, no carbon analysis method has been shown to be applicable with this high carbon filter. However, if the carbon to fluorine mass ratio is constant in Teflon filters, the fluorine γ -ray can be used as an internal standard in GRALE analysis to indicate the thickness of the filter blanks and to determine the carbon filter blank value. In this section, the successful extension of the GRALE and reflectance analysis techniques for total and elemental carbon for use with Teflon filters is described.

Teflon filters with $1 \mu\text{m}$ pore size and a nominal areal density of 1mg/cm^2 mounted on a 37-mm polyolefin ring,

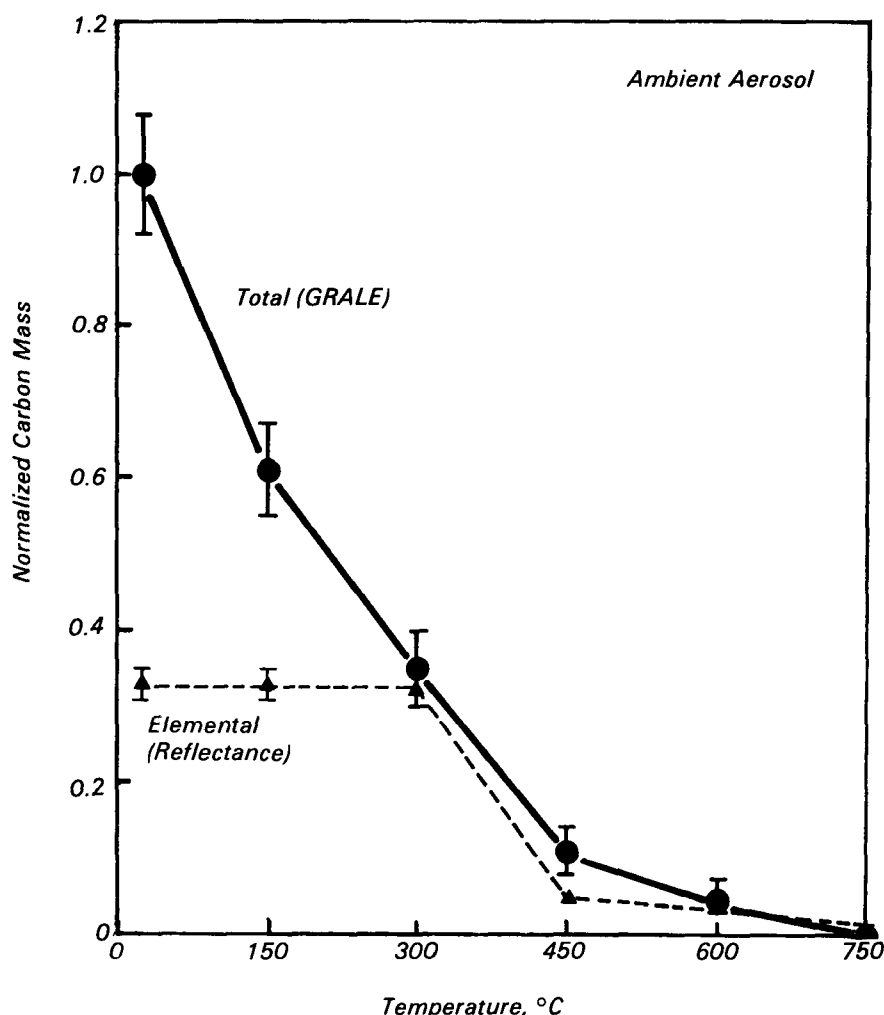


Figure 3. Average decrease in total and elemental carbon in atmospheric aerosol samples versus increasing temperature.

and Pallflex E-70 glass fiber filter tape with a detachable cellulose backing, were used as filter media.

Ambient aerosols were collected with a manual dichotomous virtual impactor sampler and a TWOMASS automated sequential tape sampler from the same aerosol manifold simultaneously. Both samplers fractionated the aerosol into two size classes; the fine fraction consisting of particles with aerodynamic diameters of less than 3 μm were examined.

The dichotomous sampler employed Teflon filters; the TWOMASS sampler used glass fiber as a filter medium. The dichotomous sampler operated at a flow rate of 14 L min^{-1} was used to collect 6-, 12-, and 24-h samples. Six-h samples were collected with the TWOMASS sampler at a flow rate of 12 L min^{-1} .

Both samplers were equipped with automatic flow controllers.

GRALE analysis of blank Teflon filters yielded a linear relationship between fluorine counts and carbon counts ($r = 0.99$), an indication that fluorine can be used for subtraction of carbon background from Teflon filters. Teflon blanks gave a C/F count ratio of 0.128 ± 0.004 . The large variation in carbon counts on blank filters shows that reliable calibration can be achieved only when a correction for carbon variations in the Teflon filters is made by using the fluorine peak intensity as an indicator.

The average intensity of the 1.35-MeV fluorine peak from the blank filters was chosen as the standard reference peak for fluorine. The 4.43-MeV carbon peak intensity associated only with the

deposited carbon was obtained using the following equation:

$$C_D = [C_S - (\overline{C/F})_B F_S] * N_{\text{Beam}}$$

where C_D is the carbon intensity from the deposit, C_S is the total carbon intensity from the sample, $(\overline{C/F})_B$ is the average C/F ratio for blank filters, F_S is the total fluorine intensity from the sample, and N_{Beam} is a normalization factor which corrects for variations in the proton beam intensity. Using this method, a calibration curve for carbon obtained from methionine standards was constructed. The proportionality between the measured γ -ray counts and deposited carbon was excellent ($r=0.99$).

A calibration curve for elemental carbon, using butane soot deposited on Teflon filters was prepared by plotting the log of the ratio of reflectance of the blank filter (I_0) to the reflectance after addition of the soot (I) versus carbon mass determined by the GRALE technique. The deposited soot mass on these calibration samples was also determined gravimetrically. The comparison of these two methods of calibration gave an excellent linear correlation with a slope of 1.02 ± 0.02 and a correlation coefficient of 0.99.

The total carbon detection limit is estimated from the irradiation conditions and counting statistics. The minimum sensitivity (1σ) with Teflon filters is $10 \mu\text{g}/\text{cm}^2$ which corresponds to $1.5 \mu\text{g}/\text{m}^3$ for 6-h sampling at 14 L min^{-1} with a 10-mm diameter sample deposit. This finding compares to $4.5 \mu\text{g}/\text{cm}^2$ on glass fiber filters or $0.7 \mu\text{g}/\text{m}^3$ for 6-h sampling under the same conditions as above.

The reflectance analysis of elemental carbon on Teflon filters has a minimum detectable limit of $1.8 \mu\text{g}/\text{cm}^2$ or $0.3 \mu\text{g}/\text{m}^3$ for 6-h sampling as given above. The upper detection limit of the reflectance method due to saturation of the surface is $\sim 70 \mu\text{g}/\text{cm}^2$.

Comparison of Carbon Analysis on Teflon and Glass Fiber Filters

Fine ambient aerosols were collected on both Teflon and glass fiber filters during the period of February 16-March 8, 1980, in St. Louis. Comparison of the results on Teflon and glass fiber filters for total carbon analyses by the GRALE technique and for elemental carbon by reflectance analysis was made during

this period. The results from both filters agree (total carbon slope = 0.99 ± 0.09 , $r = 0.95$; elemental carbon slope = 1.18 ± 0.26 , $r = 0.93$).

Conclusions and Recommendations

Through a detailed series of intercomparisons, two new methods for the measurement of total and elemental aerosol carbon concentrations have been established. The methods have since been extensively used for studies in Charleston, WV, St. Louis, MO, the southwestern United States, Los Angeles, CA, and China Lake, CA, and are recommended for future usage.

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Charles W. Lewis is the EPA Project Officer (see below).

The complete report, entitled "Techniques for the Measurement of Aerosol Carbon Content," (Order No. PB 82-249 152; Cost: \$7.50, subject to change) will be available only from:

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