DEVELOPMENT AND EVALUATION OF A THERMAL/OPTICAL METHOD FOR THE ANALYSIS OF CARBONACEOUS AEROSOL

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DEDICATION

This thesis is dedicated to Shirley O'Brien whose love and patience allowed me to complete it, and to my parents, who have given me more than I can express.

ACKNOWLEDGEMENTS

This thesis represents the efforts of many people. Foremost among these is James J. Huntzicker whose timely advice and confidence in me allowed us to take the sometimes major steps necessary to develop the carbon analyzer. No less valuable was the help of Jitu Shah, whose countless hours of work and discussion were critical to our success. The microprocessor hardware and software developed by Bob Cary added new dimensions of flexibility and ease of operation to the work reported here. Joel Johnson suggested the clever optical design that was the key to the pyrolysis correction method. Emily Heyerdahl tirelessly performed thousands of analyses and logged hundreds of hours on the computer. It has become hard to imagine the whole process working without Emily. The carbon analyzer would not exist as it does today without the support of the Oregon State Department of Environmental Quality, the National Science Foundation (Grant No. PFR-7824554), and the Environmental Protection Agency (Cooperative Agreement CR806274). The confidence of people like John Core, John Kowalczyk, Carol Cummings, and Thomas Ellestad are gratefully acknowledged.

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ABSTRACT

A thermal-optical method has been developed for the analysis of organic and elemental carbonaceous aerosol on glass or quartz fiber filters. Organic carbon is volatilized in two steps: at 350°C in an O_2(2%)-He mixture and at 600°C in He. The volatilized organic carbon is oxidized to CO_2, reduced to CH_4, and measured by a flame ionization detector. Elemental carbon is combusted to CO_2 in O_2(2%)-He at 400, 500, and 600°C, and the CO_2 is measured as above. The reflectance of the filter segment, which is continuously measured with a He-Ne laser system, decreases during the organic analysis because of pyrolytic conversion of organic to elemental carbon and increases during the combustion of elemental carbon. Correction for pyrolytic production of elemental carbon is accomplished by measuring the amount of elemental carbon oxidation necessary to return the filter reflectance to the value it had before pyrolysis occurred. This is facilitated by the slow, three-step elemental carbon combustion process. All switching of gas flows, timing, temperature control, pyrolysis correction, analog to digital conversion electronics, electrometer functions, signal integration, data storage and data outputs are controlled by a microprocessor system built around a Motorola 6802 microprocessor.

The method has been compared to organic and elemental carbon analyses by the integrating plate method (IPM) and solvent extraction. Good agreement between the thermal-optical method and IPM was found.

The solvent extraction method, however, suffered from incomplete extraction of organic carbon. The instrument was used to measure organic and elemental carbon concentrations at a variety of urban and rural sites in the United States, and representative examples are given. Both organic and elemental carbon were found to be important components of the ambient aerosol in all samples.

I. INTRODUCTION

I.A. The Need for Carbon Analysis

Identification of the sources of atmospheric particulate matter remains a major goal in air pollution research. The ability to assess the relative contribution of sources in an airshed is important for the maximum effectiveness of control strategies at a minimum of economic and social expense. Such an assessment can be made with source-receptor models (such as the Chemical Element Balance (CEB) method) (Friedlander, 1973), which are based on the chemical relationships between aerosol samples collected at pollution sources and ambient sites. The presence of tracer elements in both source and ambient samples as well as correlation between changes in elemental concentrations in a time series can lead to the identification of sources and a quantitative estimation of their contribution. This kind of approach has worked well for sources emitting trace metals, both because of excellent analytical procedures available and because the variety of elements often provides a "fingerprint" for the sources. It has also worked for sulfur and nitrogen compounds, which often comprise a major fraction of the aerosol and occur predominantly as $SO_4^=$, NO_3^-, or NH_4^+. Methods have been developed for the analysis of these ions, and their sources and impact have been well studied. Carbon, on the other hand, is found as a complex mixture of compounds falling into three broad classes: organic, elemental, and carbonate carbon. Each of these arises from a variety of sources and differs widely in its impact on man and the environment.

In principle, the analysis of specific organic compounds in source and ambient samples should fit directly into the source-receptor model methodology. In practice, because of very low concentrations and the complexity of the organic aerosol, this is not only very time-consuming and labor-intensive but is often beyond the reach of current analytical techniques. It has been demonstrated (Watson, 1979; Heisler et al., 1980; and Shah, 1981) that by combining the bulk analysis of organic and elemental carbon in ambient and source filters with trace metal analysis and other data the sources of much of the organic and elemental carbon in an airshed can be identified. The purpose of this work was to develop an instrumental method which yields an accurate measure of the organic and elemental carbon aerosol content in ambient air for application to the identification of the sources of pollutant aerosols.

I.B. The Sources of Carbon

The organic fraction of the aerosol consists of both biological and non-biological materials. Biological carbon includes a wide range of complex organic molecules usually associated with animal or vegetable materials and is found primarily in large particles. Non-biological organic aerosols can be classified as either primary or secondary. The former are emitted to the atmosphere either directly as particles or as vapors which condense immediately after emission. The latter are formed from atmospheric chemical reactions which produce condensable substances. (Some naturally emitted gaseous compounds may also undergo atmospheric reactions leading to condensed species.) Much work has been done both to determine the relative importance of primary and secondary carbon and to catalog the organic compounds found in each type (Schuetzle et al., 1975; Cronn et al., 1977; Grosjean, 1979; Appel et al., 1979).

Elemental carbon is present in the atmosphere primarily as soot particles resulting from the incomplete combustion of carbonaceous fuels. Soot particles are emitted as chain agglomerates of 10-50nm diameter spheres and contain approximately 1% hydrogen by weight (i.e., C_8H) (Palmer and Cullis, 1965). Soot can provide condensation sites for both organic and inorganic molecules and, in particular, is believed to be a carrier of polynuclear aromatic compounds. In addition soot has been shown to absorb significant amounts of visible radiation in urban atmospheres (Weiss et al., 1979) and might be capable of influencing the albedo of an urban area.

Carbonates are present in the atmosphere as soil minerals (e.g., calcite-$CaCO_3$ or dolomite-$CaCO_3$ $MgCO_3$) and as industrial process emissions (e.g., K_2CO_3 and Na_2CO_3 from kraft mills). In general, carbonates usually comprise a minor fraction of total aerosol carbon (Mueller et al., 1972; Appel et al., 1976; Shah, 1981).

I.C. Methods of Carbon Analysis.

A wide range of physical properties has been exploited in the analysis of organic and/or elemental carbon. The most common methods for carbon analysis involve combustion or oxidation of the carbon to CO_2 and measurement of the CO_2 by conductimetric, infrared, or flame ionization methods. Most carbonate analysis of ambient samples is modeled after the method reported by Mueller et al. (1971). They measured carbonate and non-carbonate (total) carbon on glass fiber filters by first acidifying the sample and measuring the CO_2 evolved from the carbonates with a thermal conductivity detector. This was followed by combustion in oxygen of both organic and elemental carbon and measurement of the total carbon as CO_2. Combustion methods for organic carbon have been reported by Van Hall et al. (1963), Dobbs et al. (1967), and Grosjean (1975). Methods for organic and elemental carbon have been reported by Cadle et al. (1980), Grosjean et al. (1979), Johnson et al. (1979a, 1979b, 1980), and Huntzicker et al. (1980).

Optical absorption methods (Hansen et al., 1979; Rosen et al., 1980) and reflectance methods (Macias et al., 1978) have also been used to measure elemental carbon. In order to relate optical properties of elemental carbon to its concentration on the filter, two important assumptions must be satisfied, namely: 1) that elemental carbon is the only important absorber of visible radiation in the aerosol, and 2) that the size distribution of elemental carbon lies in the range for which absorption is a constant function of the carbon mass. The validity of these for atmospheric aerosols has not been adequately demonstrated. In addition, the specific absorption of elemental carbon must be determined experimentally by some other means.

Edwards (1980) compared reflectance and transmission measurements on the same filter samples for a variety of sampling media and found them to be highly correlated. Edwards also compared absorption properties of identical aerosol on several filter media using an optical transmission system. He found that aerosol on glass fiber filters absorbed 2.86 times that for the same aerosol on Nuclepore filters. Lin et al. (1973) showed that adsorption measured on Nuclepore filters agreed well with *in situ* absorption measurements. Thus, filter media-dependent correction factors must also be determined if elemental carbon is to be estimated by absorption.

Grosjean (1975), Appel et al. (1976, 1979), and others measured aerosol organic carbon by solvent extraction of the filters and carbon analysis of the extracts after evaporation of the solvent. Historically, benzene extraction followed by gravimetric analysis of the extract has been used for measuring organic carbon expressed as "benzene soluble organics". As Grosjean (1975) pointed out, however, benzene is not a good choice of solvent because of its poor extraction efficiency for organic carbon. Also, carbon analysis of the extract, rather than a gravimetric determination, is important in this type of analysis because of the high and variable non-carbon content of the extract (particularly when more polar solvents are used). Following the procedure of Appel et al. (1976), Gundel et al. (1979) analyzed both the extract and the filter after extraction in an attempt to evaluate the extraction process as a method of determining primary and secondary carbon. Appel et al. (1976, 1979) and Daisey et al. (1979) estimated the upper limit of elemental carbon as the difference between total carbon (minus carbonates) and solvent extractable carbon. Pierson and Russel (1979) reported a method using oxygen-saturated o-dichlorobenzene extraction followed by carbon analysis to estimate organic and elemental carbon.

Wet chemical methods for elemental carbon have also been reported. They involve the digestion of an aerosol loaded filter in hot, concentrated HNO_3 for the purpose of removing organic carbon (McCarthy and Moore, 1952; Kukreja and Bove, 1976; Pimenta and Wood, 1980). Weighing of the residue before and after combustion in air provided a measure of the elemental carbon. This method, however, has not been well characterized with respect to types of organic compounds typically found in ambient aerosols.

Macias et al. (1978) reported a nuclear method for total aerosol carbon in which aerosol samples on quartz fiber filters were irradiated in a cyclotron with 7MeV protons and the intensity of the induced gamma rays from the carbon measured. Clemenson et al. (1980) reported another activation technique in which deuterons instead of protons were used. This technique requires much shorter irradiation times than proton activation and could be used to measure both carbon and nitrogen on collected air samples. Because these methods are nondestructive, the samples can be run to measure total carbon; then the organic and/or carbonate carbon can be removed and the sample re-analyzed to give a measure of the various carbon classes on the filter.

In developing an analytical method for organic and elemental carbon analysis, several criteria should ideally be satisfied: 1) it should be rapid, automated, and able to analyze a large number of samples at a low cost per analysis; 2) it should provide information compatible with receptor type air pollution models; 3) it should have sufficient sensitivity to allow the analysis of time resolved or lightly loaded samples; 4) it should have enough dynamic range to allow analysis of heavily loaded samples (e.g., source test samples); 5) it must be free from interference by other components of the aerosol; and 6) it must be free from "operational" definitions of organic and elemental carbon (i.e., the separation of organic and elemental carbon must be complete).

The work reported here describes the development of a thermal/optical carbon analyzer. The method requires no sample pretreatment, has a sensitivity limited by the response of blank filters, requires approximately 23 minutes per analysis, and yields an accurate measure of the organic and elemental carbon content of aerosols collected on glass or quartz fiber filters.

II. THE THERMAL/OPTICAL METHOD

The thermal analysis system, consisting of a temperature-programmable oven and a flame ionization detector (FID), is used to measure the carbon evolved from the filter under a variety of gas flow and temperature conditions and to separate organic and elemental carbon. The optical system was found to be necessary because in the early stages of the research it was observed that organic carbon was pyrolytically converted to elemental carbon during the organic analysis. This was first suspected when samples were removed from the oven combustion zone after heating to 600°C in He but before oxidation of elemental carbon had begun. Filter segments were visibly blacker. Elemental carbon produced during the analysis was confirmed as the source of increased light absorption when source samples originally containing no elemental carbon were analyzed in the system. In this instance carbon analysis showed elemental carbon to be present and the filters were quite black if they were removed from the oven before the elemental carbon oxidation step. This pyrolytic conversion of organic to elemental carbon became the principal obstacle to overcome in determining organic and elemental carbon by thermal analysis. By optimizing gas composition and oven temperature, organic to elemental carbon conversion during analysis was minimized but could not be eliminated, and a method for its correction was developed. The procedure by which the correction is made is explained more fully both in the following sections on system operation and in the section on instrument evaluation (Sec. III).

II.A. The Thermal Analysis System

The basic process of the thermal system is to convert separately organic and elemental carbon to CO_2, reduce the CO_2 to CH_4, and measure the CH_4 in a flame ionization detector. Speciation between organic and elemental carbon relies on the fact that most organic compounds can be volatilized from the filter under conditions where elemental carbon is not oxidized. (This is, of course, complicated by the pyrolytic conversion which occurs during the source of analysis.)

The initial approach (Johnson and Huntzicker, 1979) was to heat the filter sample first at 600°C in a helium atmosphere to volatilize organic carbon. This carbon was oxidized to CO_2 in a MnO_2 bed at 900°C and the CO_2 measured as above. Elemental carbon was then measured by combusting the sample in oxygen and measuring the CO_2 evolved. The principal difficulty with this approach, however, was that during the organic carbon analysis some organic material was converted to elemental carbon. The degree of conversion was variable and could not be related in any simple manner to measurable properties of the sample (e.g., total carbon, etc.). To monitor the increase in elemental carbon during the analysis, an optical system which continuously monitors the filter reflectance was developed.

The current instrumental design is shown in block form in Figure II.A.1 and the complete gas flow system in Figure II.A.2. The heart of the system is the sample oven which contains loading, combustion, and oxidation zones in a single quartz tube (Figure II.A.3).

A sample consisting usually of four glass or quartz fiber filter disks, each 0.25 cm^2 in area, is placed into a quartz boat located in

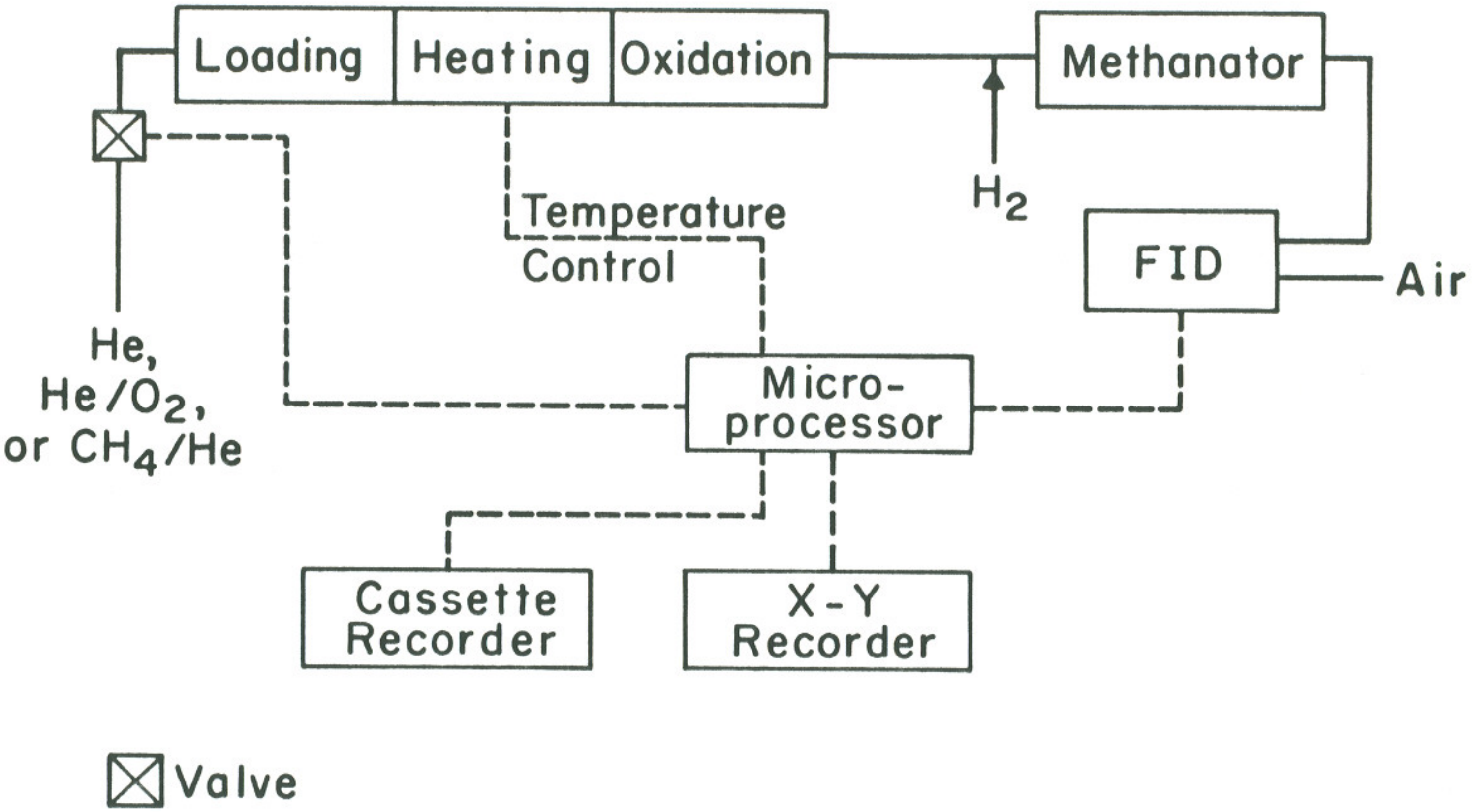


Figure II.A.1. Carbon analyzer block diagram.

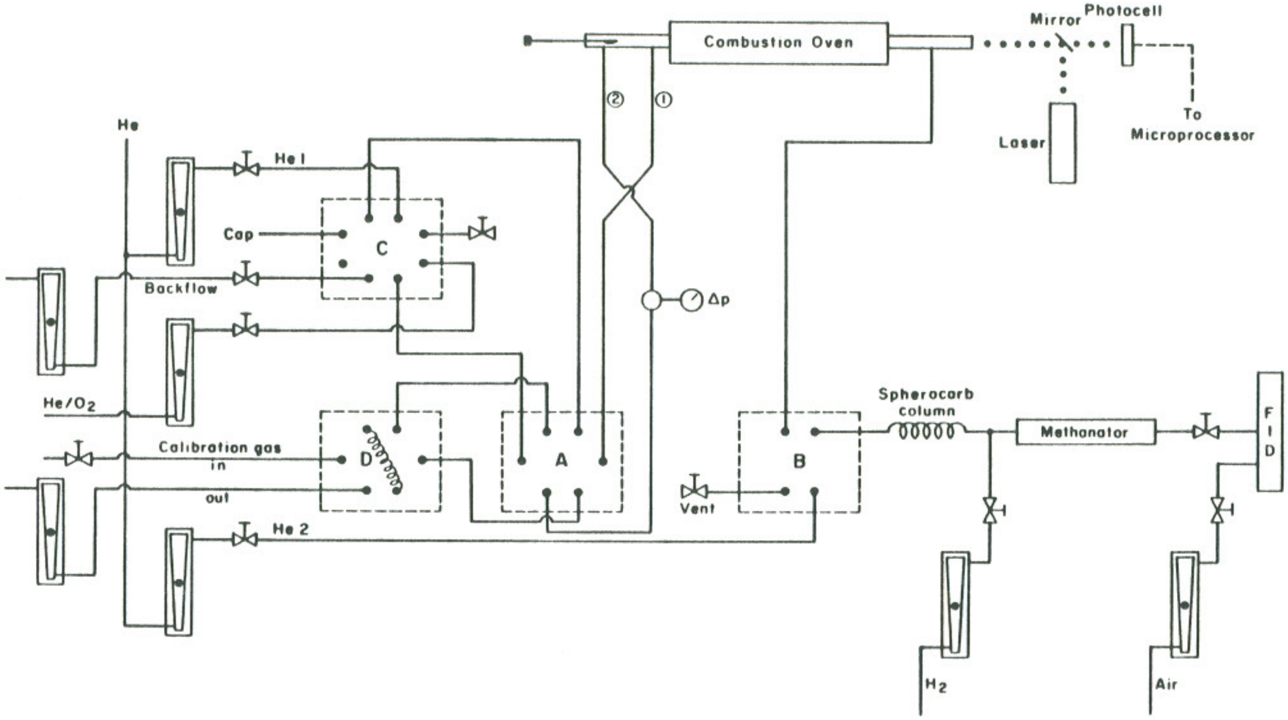


Figure II.A.2. Carbon analyzer gas flow diagram.

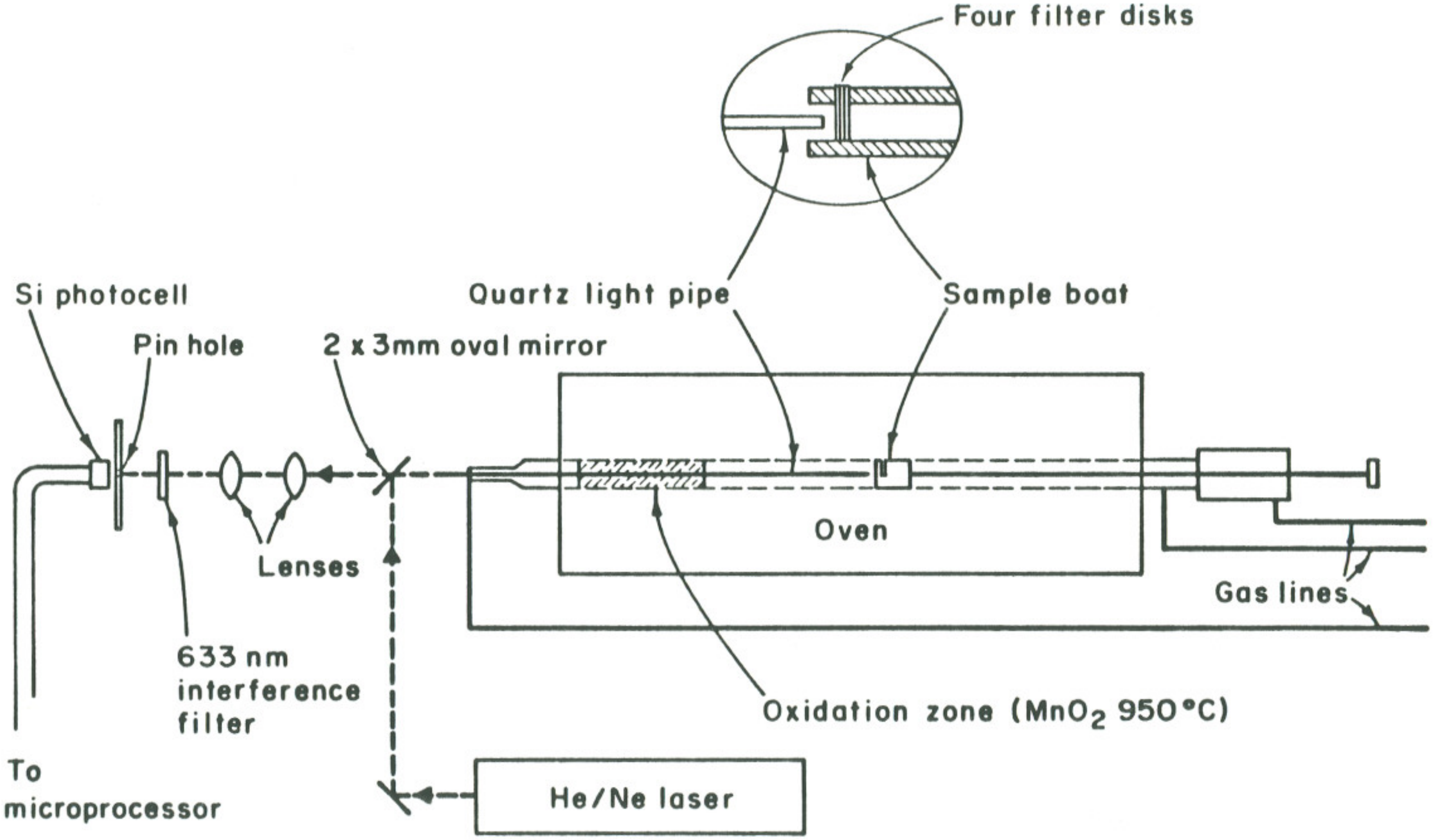


Figure II.A.3. Carbon analyzer combustion oven.

the room temperature loading zone. No pretreatment of these disks is necessary prior to analysis although acidification of the filter can be carried out if $CO_3^{=}$ is anticipated to be in large concentration on the filter. After loading, the oven is purged with an O_2(2%)-He(98%) mixture and the temperature of the combustion zone is set at 350°C. The boat is then inserted into the combustion zone in which oxidation and volatilization of organic carbon into the flowing O_2-He stream occur. The flow moves through the oxidation zone (MnO_2 at 950°C) where all volatilized carbon is converted to CO_2. The CO_2 is reduced to CH_4 in the methanator and measured by the FID-microprocessor system. This step typically removes about two-thirds of the organic carbon. On the basis of optical measurements of the "blackness" of the filter no net oxidation of elemental carbon occurs during this step. In addition, pyrolytic conversion of organic to elemental carbon appears to be inhibited by the oxygen in the carrier gas. The sample oven is then purged with helium such that all oxygen is removed from the oven. During this process the sample remains in the oven, and the oven temperature is maintained at 350°C. When purging is complete, the combustion zone temperature is raised to 600°C, and the remaining organic carbon is volatilized into the helium carrier gas. This carbon is measured as above.

Elemental carbon is determined by changing the carrier gas back to the O_2-He mixture and combusting the carbon to CO_2 which is measured in the usual manner. Before oxidation begins, the temperature of the combustion oven is dropped to 400°C. Oxygen is re-introduced into the flow stream and the temperature is increased in a series of steps (400, 500, 600°C). This is done to promote slow oxidation of the elemental carbon on the filter and to facilitate the correction for pyrolytically generated elemental carbon. (This is discussed in the section on pyrolysis correction.) In preparation for the next run the temperature of the combustion zone is lowered to 350°C. The complete cycle takes about 23 minutes.

Calibration of the system is carried out using a gas sampling loop that allows a known amount of CH_4 (26.8 or 6.5 μg) to be injected into the analyzer and the response measured. This is usually accomplished as the temperature is decreasing at the end of a run. It can, however, be carried out at any point during the run to determine if FID response remains constant throughout the run. These calibration injections can also be used as a diagnostic tool to evaluate the performance of the oven oxidation zone and the methanator. The timing and valve change sequence is summarized in Table II.A.1.

Flame ionization detectors (FID) are insensitive to the CO_2 generated in the oxidation process. In order to measure the carbon evolved, the CO_2 must be reduced to CH_4. This is accomplished in an oven filled with a nickel reducing catalyst (Smith et al., 1972) in a reducing atmosphere (50% H_2). A FID is preferable to other methods of CO_2 detection (such as infrared or thermal conductivity methods) because of its much greater sensitivity (allowing smaller samples to be analyzed), its excellent linearity over a wide dynamic range, and its freedom from interference.

TABLE II.A.1

Timing sequence for carbon analyzer program

Time (sec)	Event
0	Initialize valve position and temperature; begin run (350°C, He/O_2).
8	Switch oven on line with detector; insert sample into heating zone.
60	Begin integrating peak 1.
156	Switch from He/O_2 to He.
286	Raise temperature to 600°C.
360	Stop integrating peak 1 and begin integrating peak 2.
520	Drop oven temperature to 400°C.
700	Begin examining photocell output (used in pyrolysis correction.
720	Switch from He to He/O_2 and begin oxidation.
780	Stop integrating peak 2; begin peak 3.
840	Raise oven temperature to 500°C.
980	Raise oven temperature to 600°C.
1240	Drop oven temperature to 350°C; inject calibration gas.
1280	Stop integrating peak 3; begin integrating calibration peak.
1420	Return valves to initial configuration.
1430	End of run.

A typical FID carbon output is seen in Figure II.A.4c. Each analysis can be divided into four sections. The first peak evolves from the filter while it sits in the 350°C, He/O_2 environment and corresponds to the volatile organic carbon in the sample. The second peak results from the heating of the sample to 600°C in a helium atmosphere. This might be designated non-volatile organic carbon. To this point no elemental carbon has been oxidized. After the elution of the second organic peak, the temperature of the oven is dropped to 400°C. When oxygen is re-introduced, the third peak, which corresponds to elemental carbon, begins. The fourth and final peak is the routine calibration that accompanies every run. Correction for pyrolysis removes some of the carbon associated with the elemental carbon (3rd peak) and adds it back into the non-volatile organic carbon (2nd peak).

II.B. The Optical System

The schematic for the optical system is shown in Figure II.A.3. Light from a He/Ne laser (Hughes model 3225) is reflected off a 2x3 mm oval mirror and down the quartz optical rod to the filter sample. The sample is mounted vertically with the aerosol deposit toward the rod. Light which is reflected off the filter is transmitted back down the rod. Because the returning light has been diffusely reflected from the filter, much of it misses the oval mirror and is collected by the lens system. This light is focused onto a photocell (United Detector Technology Model PIN5D) which generates the signal measured. Some of the light incident on the quartz rod is specularly reflected from the ends

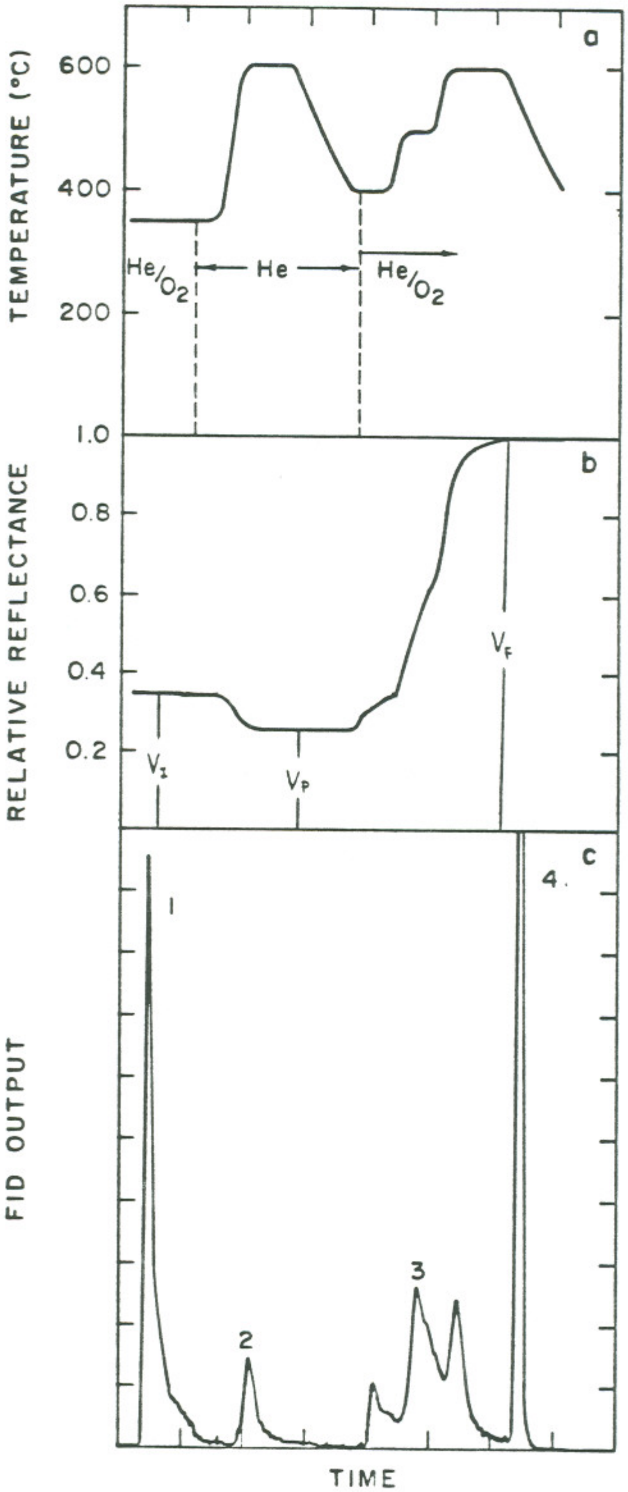


Figure II.A.4. Carbon analyzer output. a) temperature profile and carrier gas composition; b) filter reflectance output; c) FID output.

of the rod and remains collimated. This light is deflected away from the photocell by the oval mirror. This is the principal function of the oval mirror: to eliminate essentially all of the unwanted signal in the system resulting from reflections within the optical system (i.e., the light remaining collimated) while transmitting to the photocell the light reflected from the filter. Measurements of filter reflectance are made continuously throughout the run. With this information the optical system in concert with the thermal analysis is able to determine the extent of the pyrolytic conversion of organic to elemental carbon. (See Section II.C.)

In Figure II.A.4 a full output of an analysis is seen. As the sample is introduced into the 350°C He-O_2 atmosphere oven, the reflectance rises to its initial value, V_i. After the carrier gas is switched to He and as the temperature is raised to 600°C, a decrease in reflectance (an increase in "blackness") corresponding to pyrolysis is observed. The optical output stabilizes at some new lower voltage, V_p. The temperature is dropped to 400°C, and when oxygen is re-introduced into the oven, elemental carbon oxidation begins. The filter reflectance rises until it reaches some final voltage, V_f, corresponding to the complete oxidation of elemental carbon. Because of the presence on the filter of absorbing, non-carbonaceous aerosol, this value is almost always lower than the reflectance of a blank filter.

Because of the way in which the thermal and optical systems are combined, it is possible to plot filter reflectance at any point in time vs. the total elemental carbon remaining on the filter (TECR) at that point. This process is depicted graphically in Figure II.B.1. This suggested that a general relationship between TECR and reflectance could be developed which could then be applied to individual filters for the determination of the fractions of the total elemental carbon corresponding to original and pyrolysis-generated elemental carbon.

Two relationships between TECR and reflectance were explored for this purpose. The first was essentially a Beer's law type of equation:

$$\mathrm{TECR(I)} = -k \ln[\mathrm{V(I)}/\mathrm{V_f}]$$

where V(I) is the photocell output at time I, V_f is the photocell output at the end of the run, and "k" is a proportionality constant. The second is derived from Kubelka-Munk reflectance theory (Kortüm, 1979):

$$\mathrm{TECR(I)} = k[1-(\mathrm{V(I)}/\mathrm{V_f})]^2/[2\mathrm{x}\mathrm{V(I)}/\mathrm{V_f}]$$

The analysis of a number of sources and ambient samples showed that the results were not well fitted by either of these relationships. Therefore, two alternate methods of correction were developed. First, because the data from each analysis are stored on the Oregon Graduate Center (OGC) Prime 350 computer, values of $V(I)/V_f$ and TECR(I), obtained as in Figure II.B.1., can be fitted with an nth order polynomial regression equation. Once such a function is obtained, it can be solved for the value corresponding to the initial filter reflectance. This gives the mass of elemental carbon originally on the filter (OEC). The principal difficulty with this method is that it can occur only

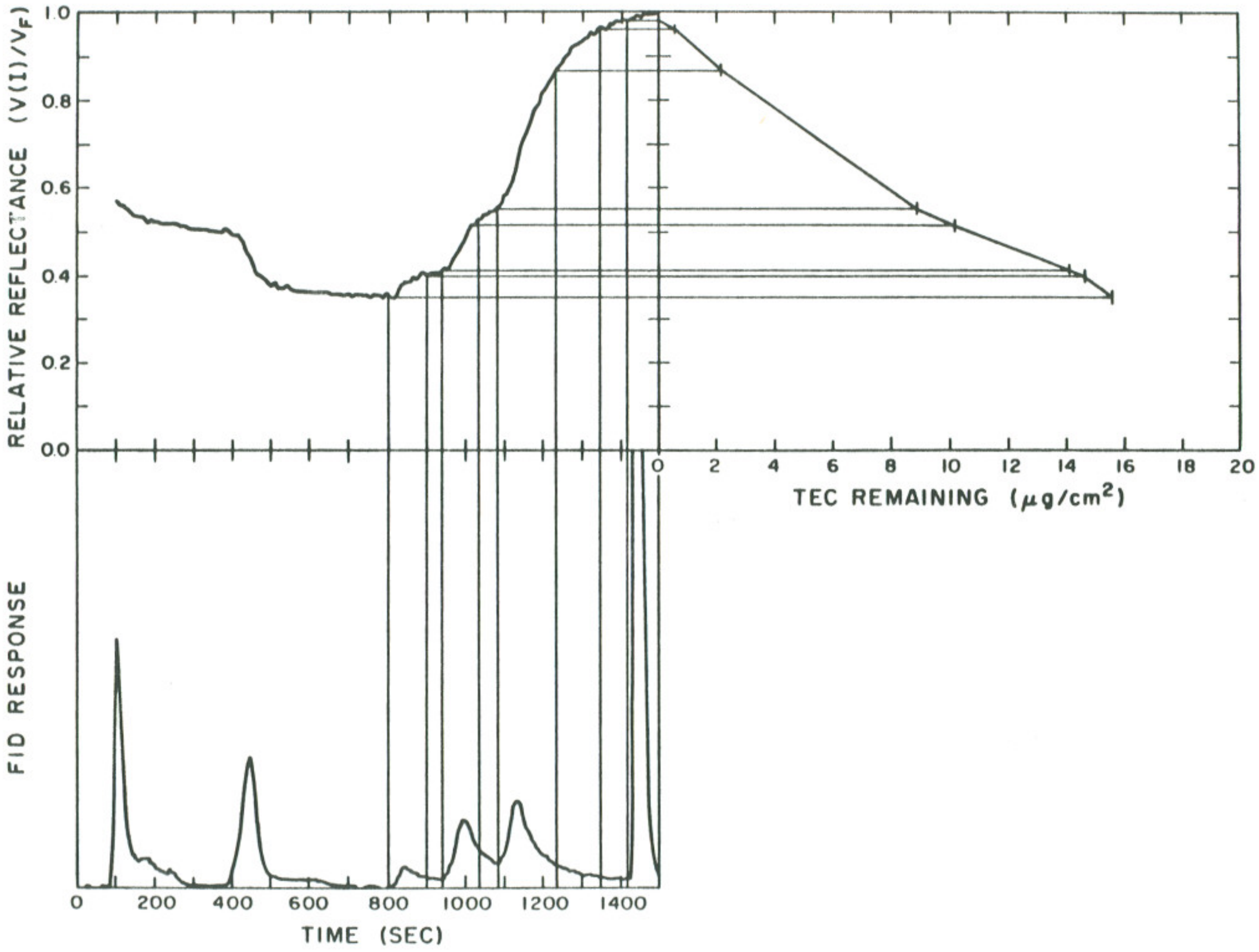


Figure II.B.1. Filter reflectance vs. total elemental carbon remaining on the filter.

after the data have been transferred to the Prime computer and reduced. It was desired to have a method by which the microprocessor system could determine the amount of "original" elemental carbon (OEC) at the time of the analysis. At present the microprocessor is not capable of carrying out the non-linear regression necessary to make the calculation as above. As a result the following correction procedure was developed and is currently in use in the microprocessor system.

II.C. The Pyrolysis Correction Procedure

As previously discussed, the second phase of thermal analysis (He, 600°C) produces a decrease in reflectance resulting from the pyrolytic generation of elemental carbon followed by an increase in reflectance in the elemental carbon combustion step. As seen in Figure II.C.1, the correction for the pyrolytic production of elemental carbon is determined by measuring the amount of elemental carbon oxidation necessary to return the filter reflectance to its initial value. The amount of elemental carbon evolved before that equivalence (peak 3a) is added to the non-volatile organic carbon (peak 2). The rest of the elemental carbon (peak 3b) is taken to be the same mass of elemental carbon as was originally on the filter. It is not presumed that the remaining elemental carbon is the same elemental carbon as was on the filter originally -- only that the mass is the same.

The pyrolysis correction procedure requires an accurate knowledge of the relationship between filter reflectance and flame ioniza-

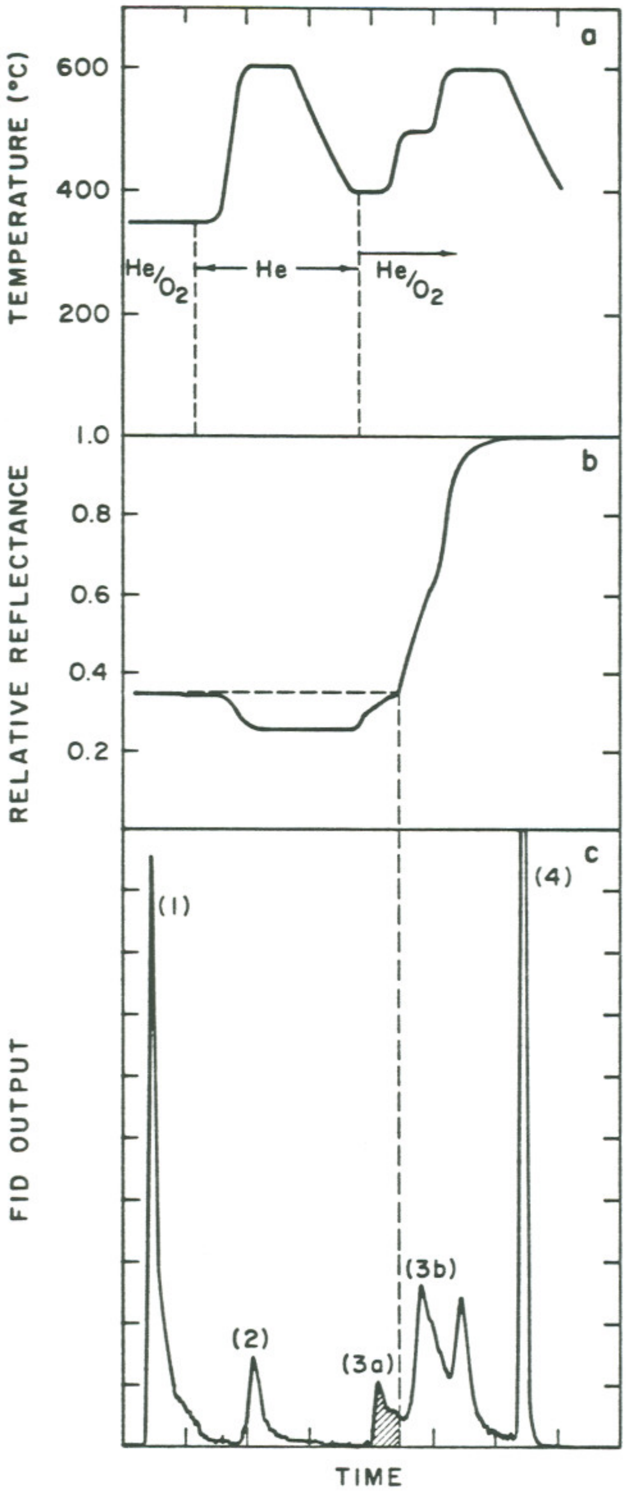


Figure II.C.1. The pyrolysis correction procedure. The shaded portion (3a) corresponds to the pyrolytically produced elemental carbon and is added to peaks 1 and 2 to give organic carbon. Peak 3b corresponds to the amount of elemental carbon originally on the filter, and peak 4 is the calibration peak.

tion detector (FID) output with respect to time. (The photocell response is immediate; the FID response is delayed by the gas flow system.) The program currently in operation in the carbon analyzer uses a 90-second delay between the two measurements. This delay was determined experimentally by removing the sample from the carbon analysis oven when filter reflectance returned to its original value but allowing the analysis to go to completion (as if the sample were still in the oven). This resulted in a dramatic drop in FID output at the time corresponding to the filter removal. For the conditions employed in the usual analytical cycle, delay times between the FID and the optical response were in the range 90-96 seconds. Because integration takes place over several hundred seconds, timing differences of the order of a few seconds do not pose a significant problem. Variation in the elution time can be oserved during the course of routine analysis, and problems can be corrected by adjusting carrier gas flows.

II.D. System Hardware

The carbon analyzer is under the control of a Motorola 6802 microprocessor. As seen in block form in Figure II.D.1, all switching of gas flows, timing, temperature control, error detection, analog to digital (A/D) conversion electronics, electrometer functions, integration, data storage and output are controlled by the computer system. A brief discussion of the important components of the system follows.

THE CPU BOARD. The central processor, input/output control, random access memory (RAM), read-only memory (ROM), timer, and operat-

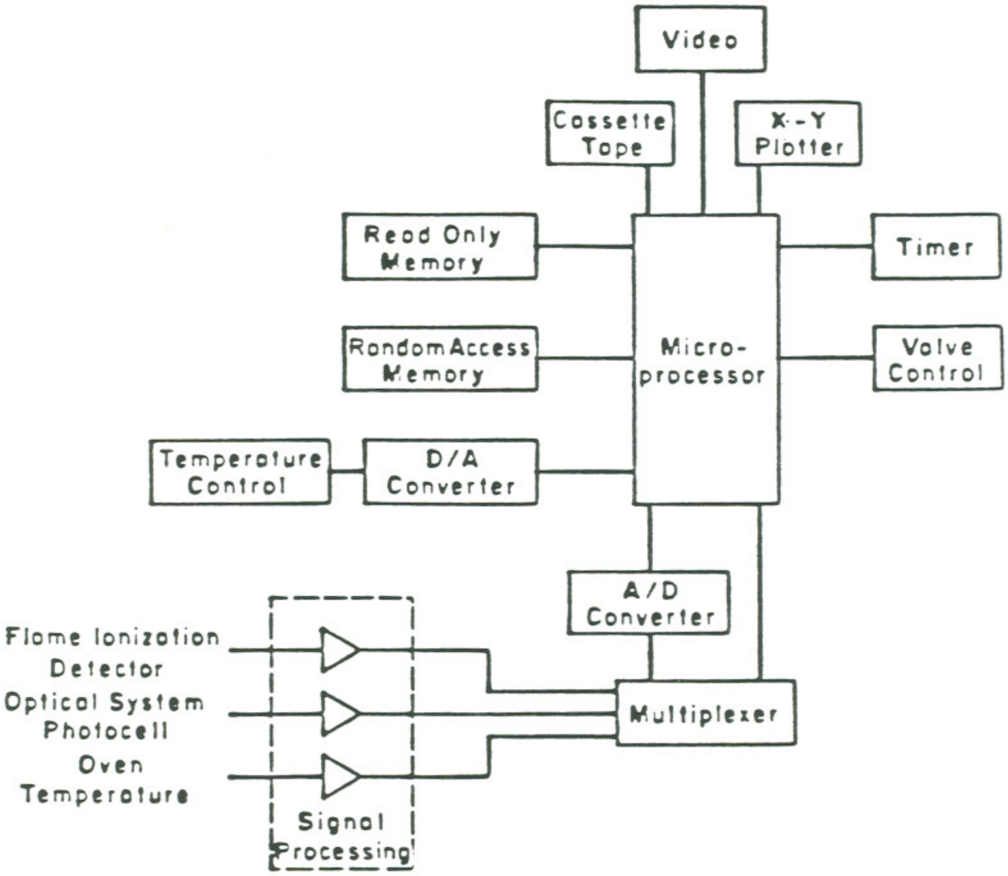


Figure II.D.1. Microprocessor organization.

ing system are contained on this board. Programs operate out of read-only memory, and data are stored temporarily in RAM before being transferred to magnetic tape for permanent storage.

THE A/D CONVERSION BOARD. A 12-bit A/D chip multiplexed to any of four input lines is the heart of this board. Analog signals from the FID, optical system photocell, and temperature thermocouples are brought to the A/D board where they are amplified to 0-5 V signals before being digitized.

FLOW SYSTEM CONTROL. Carle multi-port valves with electronic actuators are controlled by relays. The relays are controlled by relay driver circuitry which is in turn controlled by an output port of the microprocessor CPU.

OVEN TEMPERATURE CONTROL. Omega (Model 49) temperature controllers were modified to accept an external voltage used to determine the desired combustion oven temperature. The external voltage is specified by the CPU and is provided by circuitry on the A/D board.

THE FLAME IONIZATION DETECTOR. A GOW-MAC FID with its own 160 V biasing supply was used. As mentioned previously, the detector signal is amplified on the A/D card before digitization.

DATA STORAGE. A Techtran Model 815 data cassette system was interfaced to the microprocessor system through an RS-232 port on the CPU card. The information stored on tape is transferred to the main computer system (PRIME 350) at OGC for subsequent data processing.

RECORDER PRESENTATION. A hard copy of the responses of the FID, optical system, and oxidation oven thermocouple for each run is made on an X-Y digital plotter (Houston Instruments HiPlot Plotter) on which a record is also made of the analysis number, the filter identification, appropriate optical signals, and integrated peak areas.

II.E. System Software

System sofrware can be broken into two categories: microprocessor software and Fortran software written for the Prime 350 computer system. Microprocessor software can be divided into 5 sections: 1) timing, temperature, and valve control, 2) data storage (temporary and permanent), 3) analog to digital (A/D) conversion and optical measurements, 4) integration and mathematical manipulations, and 5) input/output (I/O) presentation (recorder and video terminal). Each of these is discussed briefly below.

TIMING. A series of times important to the analysis and the changes associated with them are located in a data array near the end of the program. Selection of one set from the array determines the particular valving and temperature sequence which the computer will follow. Timing is controlled by the M6846 chip of the CPU board. The basic timing interval used in this system was 1/2 second.

A/D CONVERSION AND MATH OPERATIONS. A/D conversion of each of the input signals is made every one-half second. Values of the reflected laser light and temperature are averaged and stored every eight seconds and the FID value every four seconds. The A/D conversion is 12-bit; however, the photocell and temperature voltages are set such that only the lower 8 bits need be used. This is done to conserve RAM space since 1 in 256 resolution is sufficient for both of those functions. The full 12-bit conversion is used for FID digitization for maximum resolution and over-ranging.

FID INTEGRATION. For peaks 1, 2, and 4 (see Figure II.C.1), digitized FID signals are summed over prespecified time intervals as the run progresses. These sums are stored in RAM until the end of the run when they are transmitted to the plotter and magnetic tape. Peak 3, because of the need for pyrolysis correction, is handled differently. Integration of peak 3a begins at a prespecified time. When the optical reflectance system has determined the point where reflectance has returned to its original value, integration of peak 3a stops, and all subsequent A/D conversions are summed into peak 3b. Integration of peak 3b ends at a prespecified time.

DATA STORAGE. Four-second averages of the FID data, as well as 8-second averages of the photocell output data are stored on magnetic tape as the run progresses. In addition, the filter identification number and the analysis number are stored on tape at the beginning of the run, and photocell output and peak integration data are stored on tape at the end of analysis. Eight-second averages of photocell output and temperature are stored in RAM for graphic plotter output at the end of the run.

RECORDER PRESENTATION. All movements of the X-Y plotter are controlled by the microprocessor. A record of the position of the pen must be maintained by the system to allow repositioning during the display process. Pen movement sequences used to form alphanumeric characters all reside in system ROM.

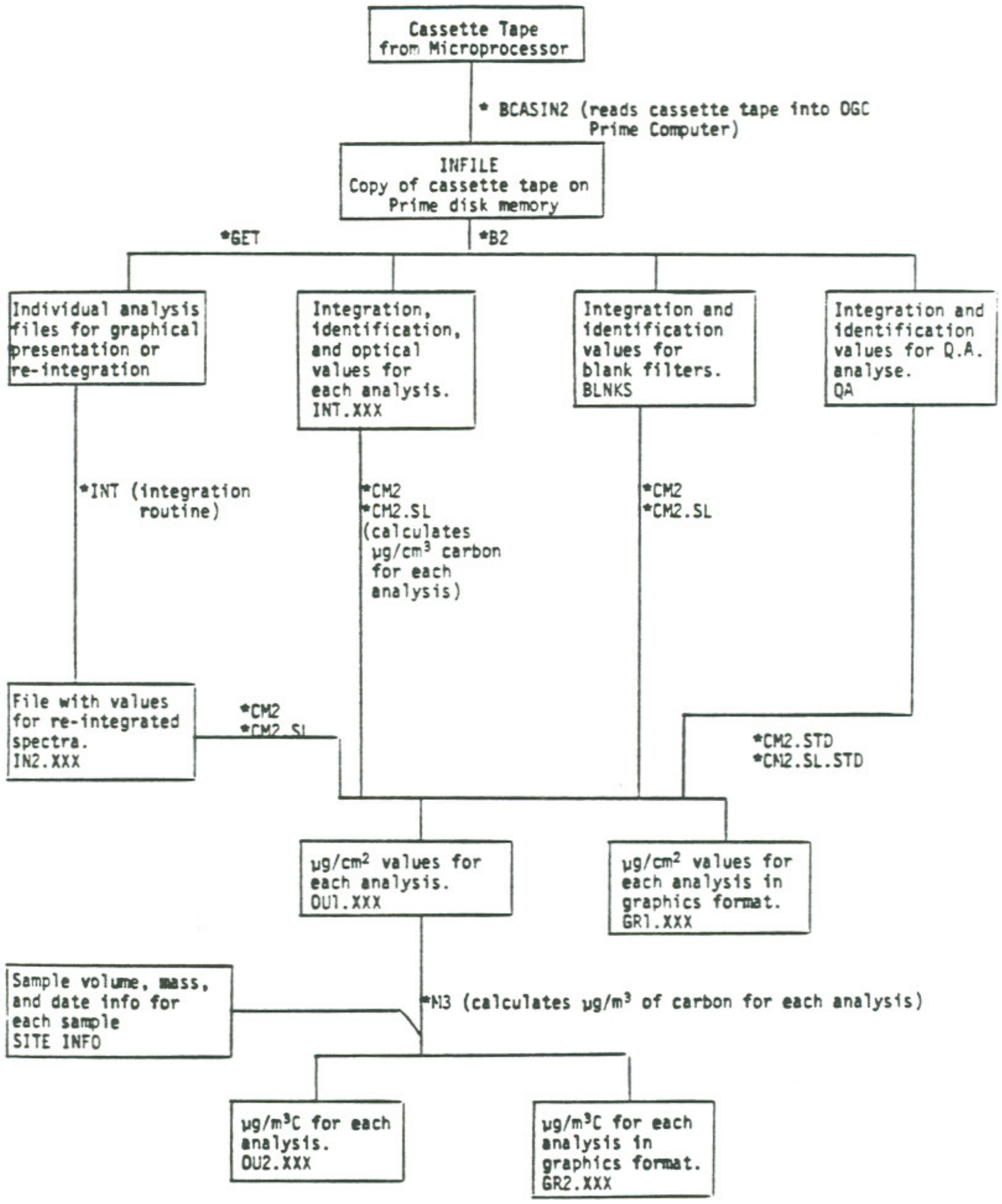
II.F. Fortran Software

The data stored on cassette magnetic tape by the microprocessor (filter and analysis numbers, FID and photocell outputs, and integration data) are transferred to permanent storage on 9-track magnetic tape via the Prime 350 computer. While stored in the Prime, the data are re-organized and can be re-analyzed using the programs listed below. As seen in Figure II.F.1, Fortran programs have been written to perform six major functions in data reduction: 1) data transfer from cassette to disc storage (program BCASIN2); 2) compilation of integration, optical system, and sample identification information (program B2); 3) separation of the data into files containing digitized spectra for individual analyses (program GET); 4) integration of the stored spectral data (program INT; this program is used if there was a problem in the integration carried out at the time of the analysis); 5) calculation of the concentrations of carbon on the filter ($\mu g/cm^2$) (program CM2; this program includes blank and background subtractions); 6) calculation of volumetric concentrations of the carbon classes ($\mu g/m^3$) (program M3). Analytical uncertainties are propagated through the calculations; a discussion of the uncertainties is found in the sections on error analysis (Section III.F. and Appendix C).

FIGURE II.F.1

Fortran Software

Programs (*'s) and Outputs (Boxes) of Fortran Software



III. INSTRUMENT EVALUATION

III.A. FID Calibration

The purpose of the method is to make a quantitative measure of the organic, elemental, and carbonate carbon present on filters of collected aerosol. These data are subsequently used to determine the fractions of the collected aerosol corresponding to organic and elemental carbon. As such it is desired to have an accuracy and precision of analysis similar to those associated with the collection of the sample. To accomplish this, the response per atom of carbon must be known, i.e., the detector system must be calibrated. Steps in this process are discussed below.

To simplify FID calibration, all carbon compounds on the filter are converted to CH_4. This is necessary because not all carbon-containing molecules respond equally in the FID. As previously mentioned, reduction to CH_4 is a two-step process: carbon is first oxidized to CO_2 which is then reduced to CH_4. To insure that these processes remain quantitative, the conversion efficiency of the system is monitored routinely. Evaluation of the oxidation efficiency of the MnO_2 bed in the absence of oxygen is conducted on a daily basis as part of the start-up procedure by methane injection. Methane is used for two reasons: 1) it is more difficult to oxidize than most organic compounds, and 2) it allows evaluation of both oxidation and methanation processes with the same calibration gas. Methanation efficiency is monitored every run with the routine calibration injection. Any decrease in efficiency is manifested as a smaller calibration peak. (The potential problem of not being able to detect a simultaneous failure of oxidation and methanation processes (which would lead to unoxidized methane reaching the detector) is avoided because of a Spherocarb (Analabs, Inc.) chromatographic column in the gas flow system. It separates CH_4 and CO_2 and gives a shorter elution time for any CH_4 not oxidized to CO_2. In the case of simultaneous failure, this results in two "calibration" peaks.) In addition, known amounts of organic compounds are combusted as a check on the routine calibration procedure.

To insure accurate calibration injections, the volume of the calibration loop was determined by several methods including: 1) injection via calibrated syringe of known volumes of calibration gas and comparison of the response to that from a loop injection; 2) measurement of the volume of the calibration gas sample injection loop by measuring both its physical dimensions and the change in weight of the loop before and after filling with water; and 3) combustion of known amounts of carbonaceous compounds to compare the mass of carbon combusted to that recovered as CH_4.

III.B. Inter-Laboratory Comparisons

In addition to the primary calibration methods, interlaboratory studies were carried out on a set of 10 ambient samples. The results are given in Tables III.B.1 and 2. The good agreement in total carbon

Table III.B.1.

Carbon Analysis Interlaboratory Comparison Results.

	OGC			GM			DEQ
Sample	OC	EC	TC	OC	EC	TC	TC
C71017	26.8	13.9	40.6	30.2	9.2	39.4	42.5
C71021	21.7	14.8	36.5	24.9	9.3	34.2	32.3
C80216	19.8	12.8	32.6	20.9	10.0	30.9	34.4
C80217	17.9	17.5	35.4	19.9	11.4	31.3	33.4
C80316	31.2	21.1	52.2	41.7	20.6	62.3	53.6
C80317	42.4	36.8	79.2	57.1	25.0	82.1	83.7
C80321	29.4	16.3	45.6	35.9	9.2	45.1	45.2
C80323	8.9	4.7	13.5	8.1	2.7	10.8	13.5
C80415	19.0	13.4	32.5	24.9	7.2	32.1	33.9

OGC: Oregon Graduate Center. GM: General Motors Research Laboratories.

DEQ: Oregon Department of Environmental Quality.

TABLE III.B.2.

CARBON RATIOS FROM INTERLABORATORY COMPARISON

$$OC_{GM}/OC_{OGC}{}^{*} = 1.17 \pm 0.14$$

$$EC_{GM}/EC_{OGC} = 0.67 \pm 0.13$$

$$TC_{GM}/TC_{OGC} = 0.97 \pm 0.10$$

$$TC_{DEQ}/TC_{OGC} = 1.00 \pm 0.06$$

* OGC: OREGON GRADUATE CENTER
GM: GENERAL MOTORS RESEARCH LABORATORIES
DEQ: OREGON DEPARTMENT OF ENVIRONMENTAL QUALITY

measurements indicates the relative ease with which this method can be calibrated. The systematic differences in organic and elemental carbon point to the problem of "operational" definitions even between combustion methods.

III.C. Model Compound Analysis

The analysis of model compounds served several important functions in the instrument development. These include: 1) calibration; 2) evaluation of the behavior of elemental carbon in the system; 3) evaluation of the behavior of compounds known to be in ambient aerosols; and 4) analysis of polymeric materials and compounds that tend to pyrolyze. Table III.C.1 gives a listing of the materials which have been evaluated. For each compound a known mass of material was deposited on a filter which was placed in the instrument and analyzed. This simultaneously gave the behavior in the instrument of the compound of interest as well as verifying system calibration. Items one through four were compounds known to be present in ambient aerosols. Mannitol, a sugar, was also tested because it seemed a likely candidate to undergo conversion to elemental carbon during the organic analysis. Lampblack samples, because they are almost totally elemental carbon, were analyzed to detect any premature oxidation of elemental carbon and to evaluate the completeness of oxidation. Clean filters were also analyzed to determine the blank correction. The results indicate that for all compounds, the response occurs primarily in the expected mode (organic or elemental). With the exception of mannitol and humic ma-

Table III.C.1.

Model Compound Analysis Results

COMPOUND	% RECOVERED AS ORGANIC CARBON	% RECOVERED AS ELEMENTAL CARBON	% TOTAL CARBON RECOVERED
Tetracosane	103	0	103
Tetradecane	102	0	102
Tetratriacontane	106	0	106
Coronene	92	0	92
Perylene	103	1	104
Glutaric Acid	103	2	105
Oleic Acid	92	0	92
Stearic Acid	90	1	91
Humic Acid	72	9	81
DOP	95	1	96
Mannitol	92	6	98
Lampblack	1	97	98
PSL **	98	2	*

* Original mass of material not measured. These values are the relative response.

** Polystyrene latex spheres (1.0 µm diameter).

terial, the small amount of crossover between the organic and elemental modes is within the uncertainty of the blank subtraction and does not represent any pyrolytic conversion of organic to elemental carbon. The sums of the organic and elemental carbon are tabulated in the column labelled "total" and indicate quantitative recovery within reasonable limits of uncertainty for all the compounds tested. The low apparent recovery of humic acid is probably a result of the uncertain elemental characterization of the material.

Table III.C.2 lists the fractional response in each mode of a series of carbonaceous materials found in ambient particulate matter. All are expected to be difficult to analyze in the carbon analyzer because they contain a wide variety of large organic molecules which are susceptible to pyrolysis. The samples of auto and diesel exhaust and street dust were deposited on quartz fiber filters, and thus pyrolytic conversion could be observed directly with the optical system. Leaf material and wood dust contain no elemental carbon; thus, all of the carbon measured in the final mode corresponds to pyrolytically produced elemental carbon. Pyrolysis in the tire rubber sample has not been estimated. The wide range of pyrolytic conversion seen in the model compounds and materials analysis points to the need for the optical system to monitor and correct it on a filter-by-filter basis.

III.D. Comparison of Predicted Elemental Carbon from Thermal/Optical Carbon Analysis (CA) and the Integrating Plate Method (IPM)

The first step in comparing the thermal/optical carbon analyzer

Table III.C.2.

Model Materials Analysis Results

	Without Pyrolysis Correction		With Pyrolysis Correction	
Material	% Organic	% Elemental	% Organic	% Elemental
Auto Exhaust (leaded)	85	15	94	6
Auto Exhaust (unleaded)	64	36	71	29
Diesel Truck Exhaust	27	73	27	73
Distillate Oil Soot	29	71	45	55
Residual Oil Soot	60	40	82	18
Wood Fiber	55	45	96	4
Plant Leaf Material	36	64	*	
Pollen (ragweed)	82	18	*	
Tire Rubber	81	19	*	

* Because these samples were not aerosol deposits, no pyrolysis correction could be made.

and the IPM was the calibration of the IPM. As previously mentioned, estimation of elemental carbon on glass filters using absorption methods requires calibration via some absolute measurement of elemental carbon (e.g., combustion). To accomplish this, a set of special diesel samples were analyzed which were: 1) almost exclusively elemental carbon, 2) showed little or no pyrolysis, and 3) should be composed of small (<0.3 µm) particles (Kittelson and Dolan, 1979). The results of carbon and IPM analysis are shown in Figure III.D.1. It is important to note that the curve is not linear. As filter loadings increase, the "effective" absorption/mass of the aerosol decreases. (This non-linearity results because the assumptions underlying Beer's Law are not satisfied at heavy filter loadings.) This curve was used both as a basis for comparing the absorption/mass of the original elemental carbon with that of the pyrolysis elemental carbon and to estimate the elemental carbon originally on ambient filters.

Elemental carbon results from thermal/optical carbon analysis and IPM analysis were compared for ambient aerosol samples from several sample sites. The results are shown graphically in Figures III.D.2-6, and are summarized in Table III.D.1. The average ratio of elemental carbon (CA)/elemental carbon (IPM) for all the sets is 0.88 ± 0.06.

III.E. Solvent Extraction of Aerosol Samples

The principal goal of solvent extraction was to compare the elemental carbon values obtained from carbon analysis to estimated values

Figure III.D.1. Absorption vs. elemental carbon for diesel exhaust samples.

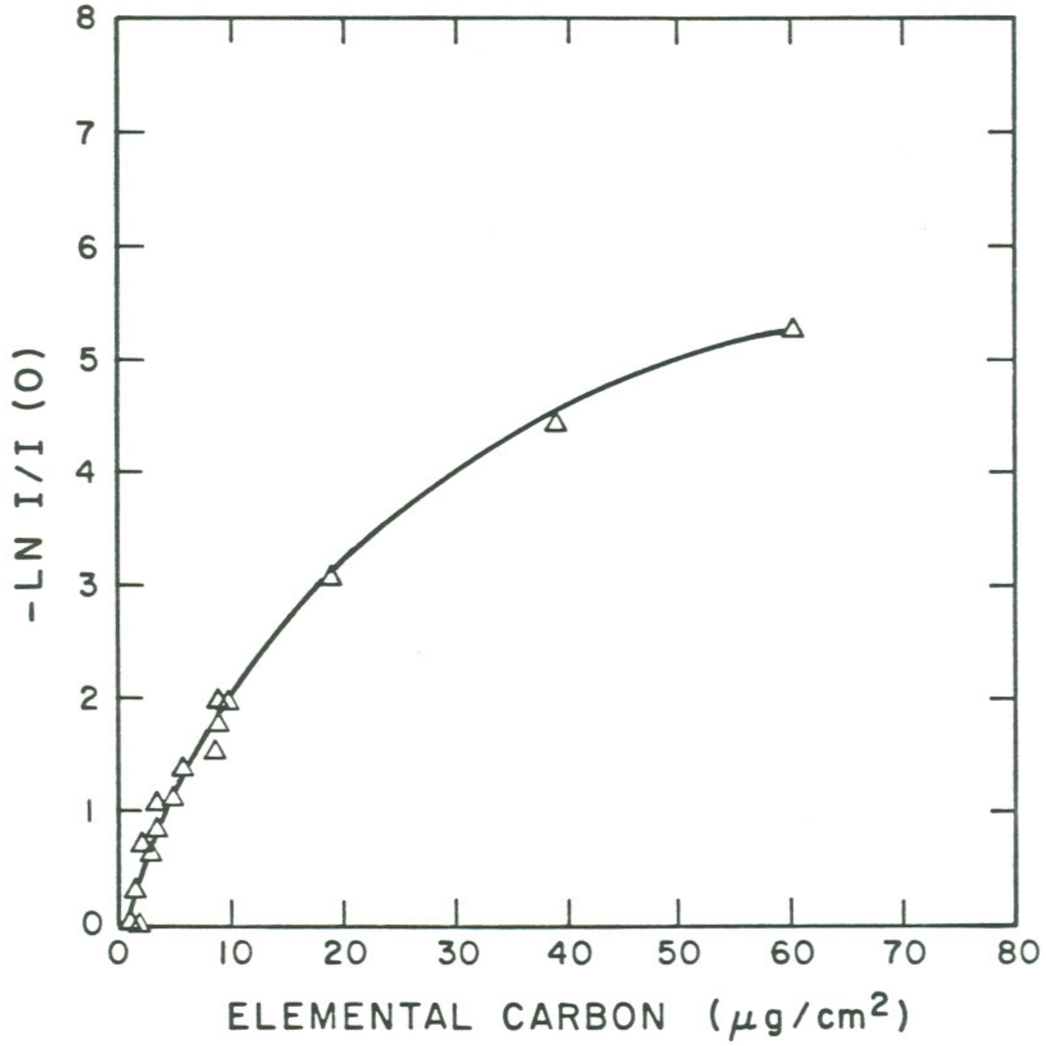


Figure III.D.2. Samples from Portland, Oregon (downtown, low-volume).

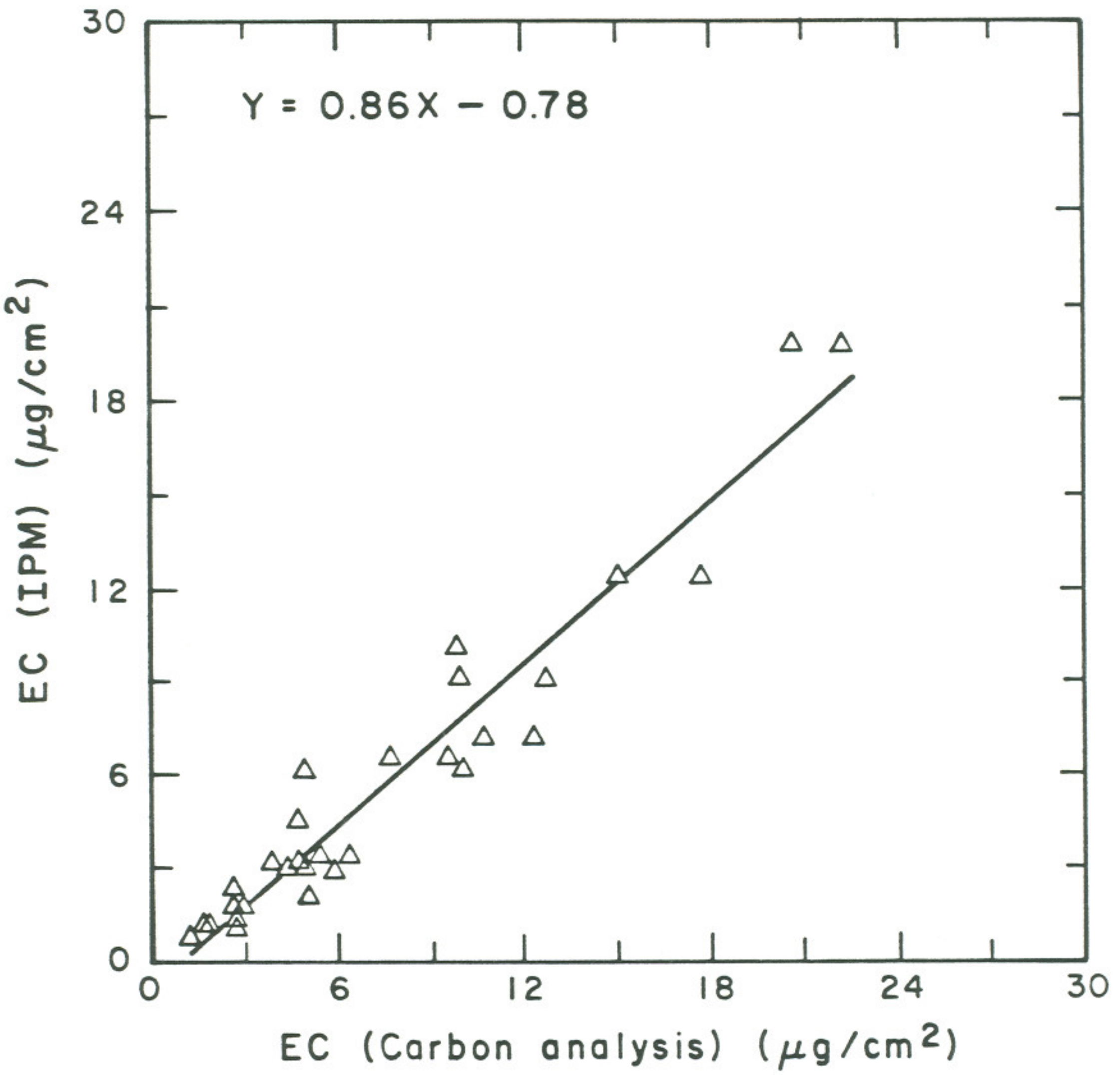


Figure III.D.3. Samples from Portland, Oregon (downtown, high-volume).

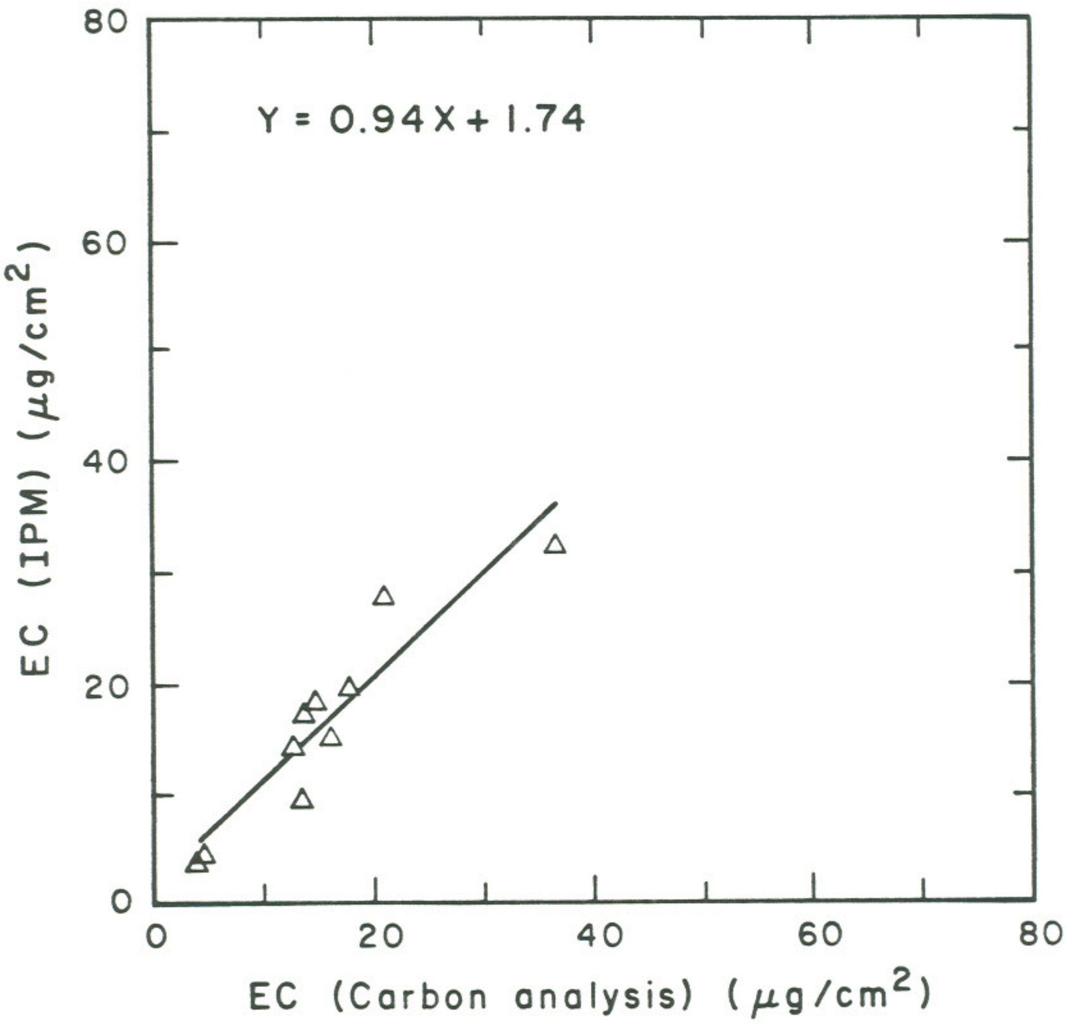


Figure III.D.4. Samples from Seattle, Washington (UW).

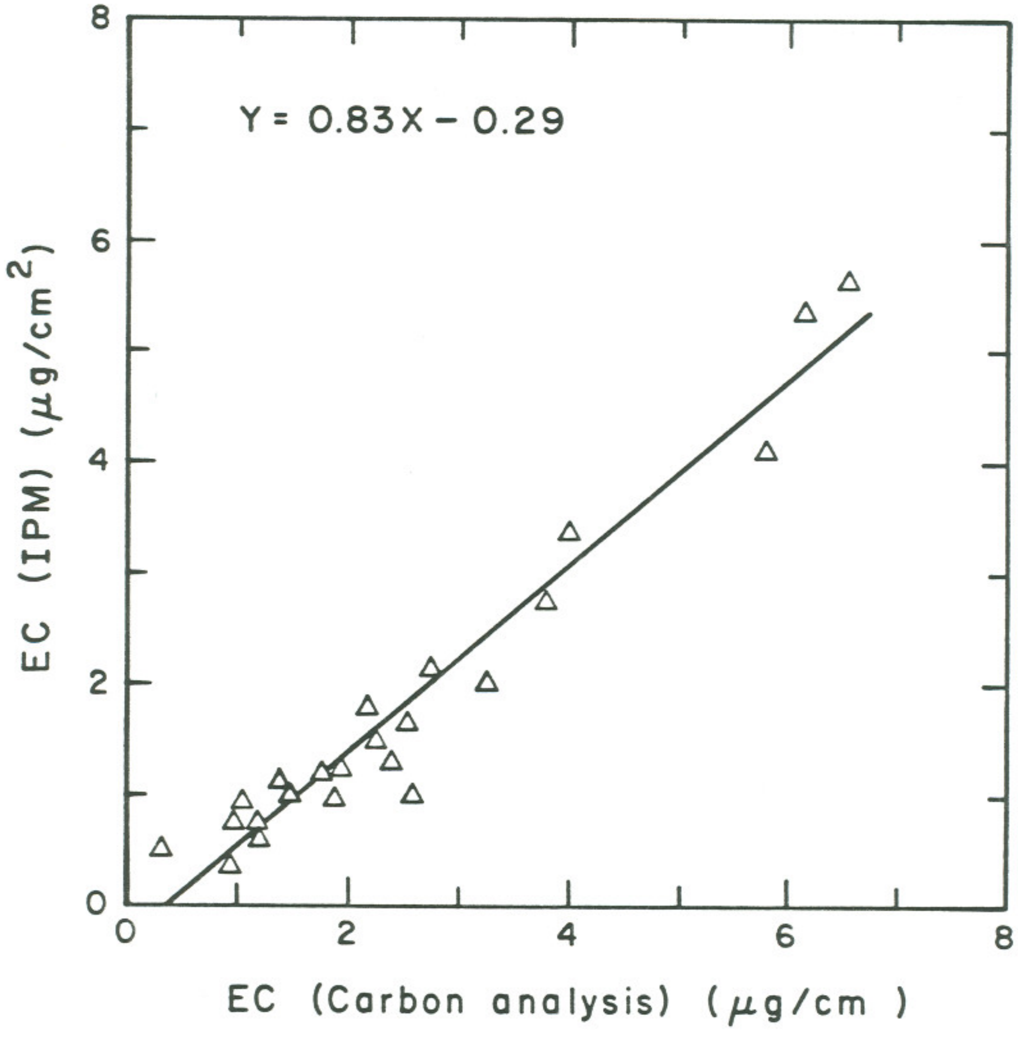


Figure III.D.5. Samples from Berkeley, California.

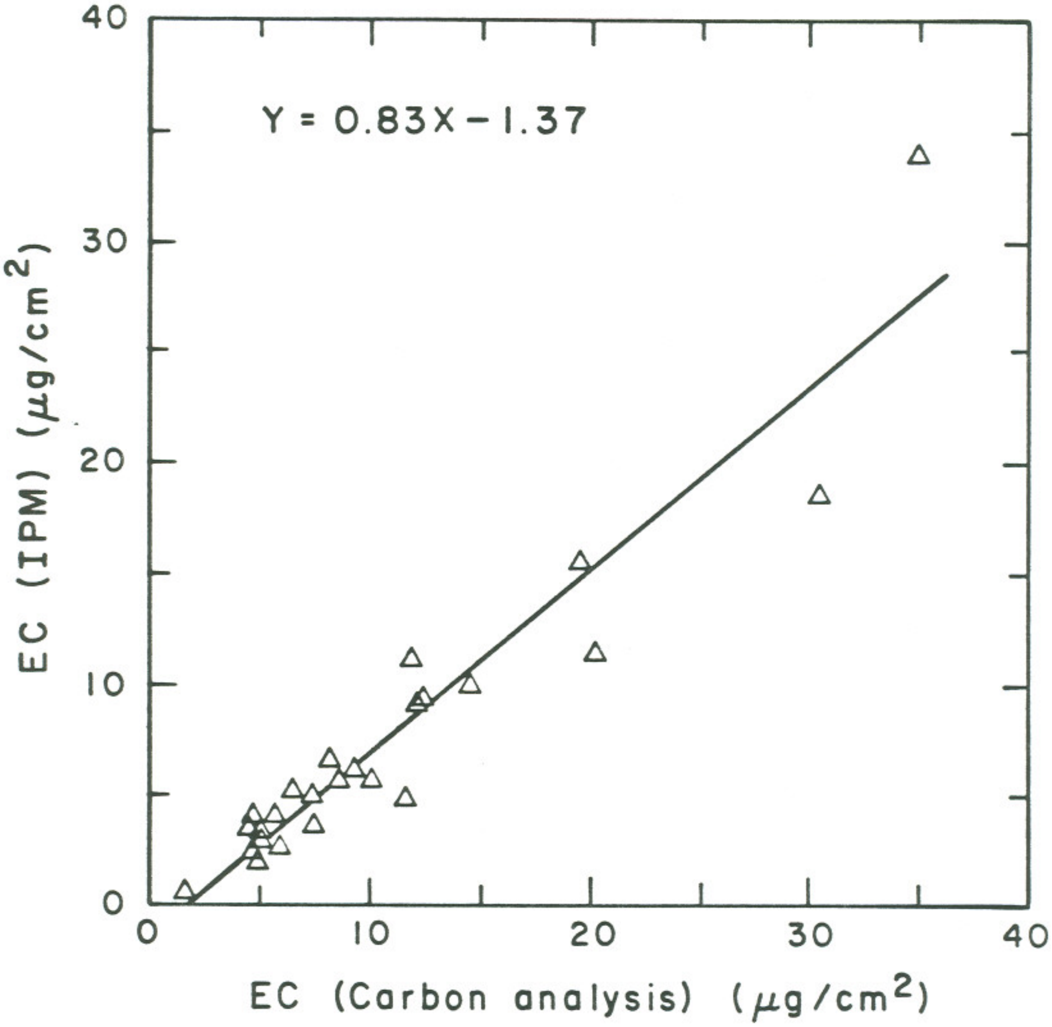


Figure III.D.6. Samples from Portland, Oregon.
(S.W. Portland, low-volume).

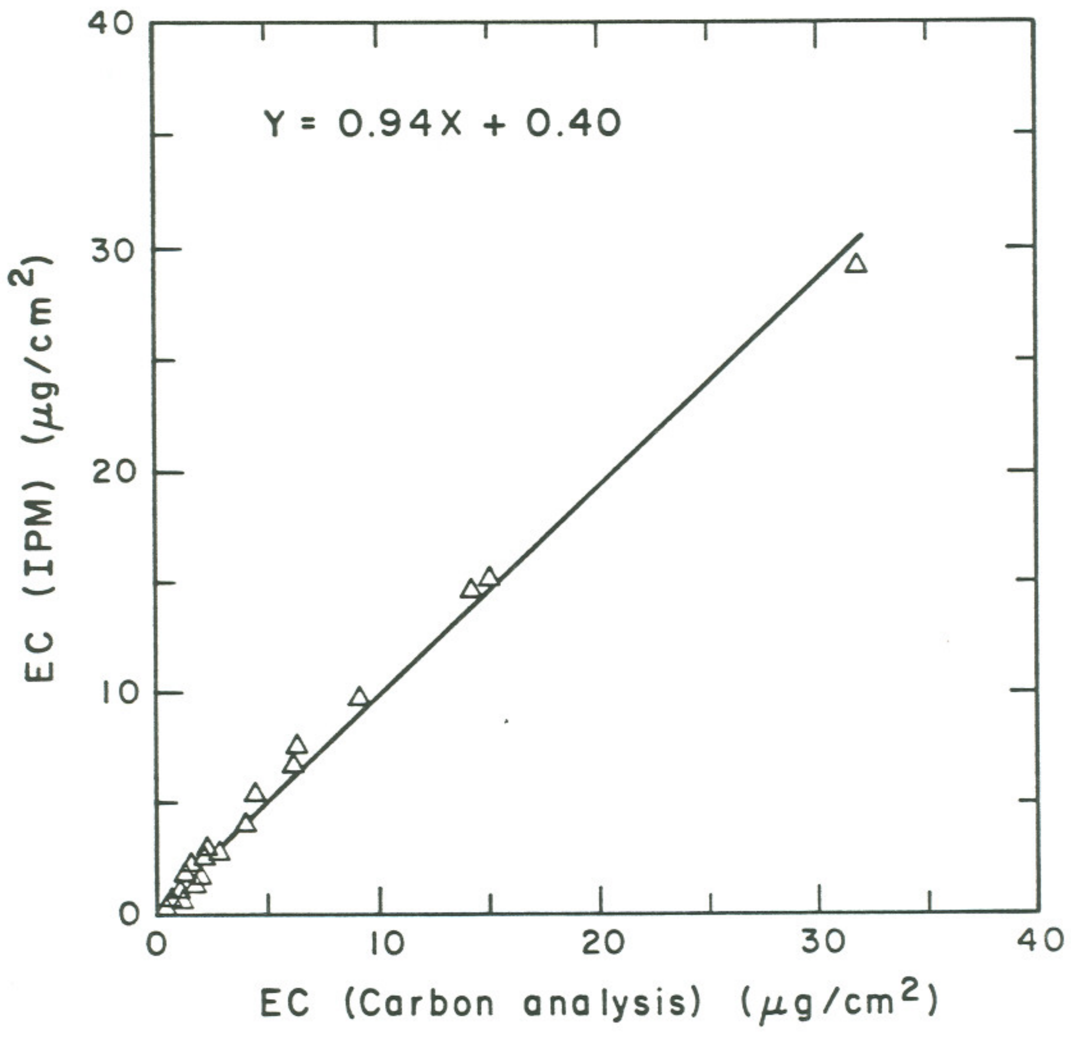


Table III.D.1.

Elemental Carbon Comparison - Carbon Analyzer vs. IPM

Sample Site	Slope of plot EC_{CA} vs. EC_{IPM}
Portland (downtown, high-volume)	0.94
Portland (downtown, low-volume)	0.86
Berkeley (NASN)	0.83
Seattle (UW)	0.83
OGC (Rocket)	0.94
	0.88 ± 0.06

of elemental carbon from solvent extraction. Historically, estimation of elemental carbon using solvent extraction involves total carbon analysis on both the extract residue and the original filter (see for example Appel, 1976, 1979). Extracted carbon is labeled organic and the difference between total carbon on the original filter and extract is taken to be the upper limit to elemental carbon. In this work both the original and extracted filters were analyzed for organic and elemental carbon, and the extract was analyzed for total carbon. This allowed not only a comparison between elemental carbon values from carbon analysis and solvent extraction, but also: 1) a measure of how much of the carbon remaining on the filter is really organic carbon that was not extracted, and 2) an opportunity to obtain a mass balance between filter and extract.

Two extraction procedures were used to prepare samples for carbon analysis. One is a modification of the traditional Soxhlet extractor; the other uses a syringe pump to move a volume of solvent slowly through the filter sample. Both methods are described in Appendix A.

The methods have been designed to remove organic carbon from the filter while minimizing the wash-off of elemental carbon and other insoluble material. Filters from Portland, Oregon, were analyzed using both procedures, and the data are summarized in Tables III.E.1 and 2. These results indicate that the syringe pump extractor is less efficient than the Soxhlet at removing organic carbon but, as will be shown next, appears to disrupt the aerosol deposit less.

TABLE III.E.1

METHANOL/BENZENE EXTRACTION WITH THE SOXHLET EXTRACTOR

ID	EC_{CA} *	EC_{EXT}	% EC Remaining (Uncorr.)	% EC Remaining (Corrected)	% PEC Remaining	% Absorbing Material Remaining	% OC Remaining (Corrected)	Original EC/PEC
C70818	4.09	3.52	0.86	0.97	17	89	34	1.12
C71017	13.88	10.09	0.73	0.85	23	86	27	1.98
C71021	14.81	9.38	0.63	0.75	18	84	46	2.80
C80216	12.77	9.29	0.73	0.90	0	81	10	1.80
C80217	17.45	11.46	0.66	0.75	26	87	34	4.97
C80316	21.05	17.10	0.81	1.13	49	73	46	1.94
C80321	16.28	10.56	0.65	0.75	35	87	32	2.05
C80323	4.69	2.79	0.59	0.63	6	94	14	2.25
C80715	12.67	7.28	0.57	0.77	18	75	24	3.21
				84±15	21±15	84±7	30±12	2.4±1.1

* EC_{CA} ≡ elemental carbon measured by standard analysis.

EC_{EXT} ≡ elemental carbon measured by standard analysis after extraction.

PEC ≡ pyrolysis-generated elemental carbon.

OC ≡ organic carbon measured by standard analysis.

TABLE III.E.2

METHANOL/BENZENE EXTRACTION WITH THE SYRINGE PUMP

ID	EC_{CA} *	EC_{EXT}	% EC Remaining (Uncorr.)	% EC Remaining (Corrected)	% PEC Remaining	% Absorbing Material Remaining	% OC Remaining (Corrected)	Original EC/PEC
C70818	4.09	3.75	0.92	1.00	0.42	0.92	0.43	1.12
C71017	13.88	12.86	0.93	1.09	0.46	0.85	0.41	1.98
C71021	14.81	10.81	0.73	0.89	0.63	0.82	0.49	2.80
C80216	12.77	12.58	0.99	1.05	0.10	0.94	0.20	1.80
C80217	17.48	13.03	0.75	0.96	0.25	0.78	0.26	4.97
C80316	21.05	21.28	1.01	1.15	0.20	0.95	0.32	1.94
C80321	16.28	13.70	0.84	0.88	0.50	0.96	0.45	2.05
C80323	4.69	3.62	0.77	0.76	0.56	1.01	0.39	2.25
C80415	13.43	9.94	0.74	0.80	0.64	0.92	0.42	3.21
				95±13	42±19	0.91±0.07	37±9	

* EC_{CA} ≡ elemental carbon measured by standard analysis.

EC_{EXT} ≡ elemental carbon measured by standard analysis after extraction.

PEC ≡ pyrolysis-generated elemental carbon.

OC ≡ organic carbon measured by standard analysis.

The amount of insoluble carbonaceous aerosol dislodged from the filter during extraction can be estimated using the integrating plate method. If the filter transmittance is measured before and after extraction, the loss of insoluble organic and elemental carbon from the extracted filter can be corrected by scaling with the ratio.

$$f(I/I(0))(\text{unextracted})/f(I/I(0))(\text{extracted})$$

where "$f(I/I(0))$" is a function empirically determined from the calibration of the IPM (Figure III.D.1). (This assumes that elemental carbon is the dominant light absorber on the filter.) Tables III.E.1 and 2 indicate for the Soxhlet and syringe pump extractors 84% and 91%, respectively, of the elemental carbon remained after extraction.

Three measures of elemental carbon were determined from the solvent extraction data. First, elemental carbon was estimated as the difference between total carbon on the filter and the total carbon content of the extract. Second, the Soxhlet-extracted filters were analyzed for organic and elemental carbon (and corrected for loss of material off the filter). Third, the syringe pump-extracted filters were analyzed for organic and elemental carbon and corrected as above. The results are summarized in Table III.E.3 and are shown graphically in Figure III.E.1. Several points are immediately apparent: 1) the traditional solvent extraction method of estimating organic and elemental carbon (i.e., equating unextracted carbon as an upper limit to elemen-

TABLE III.E.3

COMPARISON OF ELEMENTAL CARBON ANALYSIS BY VARIOUS METHODS

($\mu g/cm^2$)

Sample	EC_{CA}*	EC_{SE}	$EC_{SE/CA}$	$EC_{SP/CA}$
C70818	4.09	11.94	4.00	4.08
C71017	13.88	19.24	11.80	15.13
C71021	14.81	23.64	11.11	13.18
C80216	12.77	21.91	11.50	13.38
C80217	17.48	19.90	13.28	16.71
C80316	21.05	33.68	23.37	22.40
C80321	16.28	22.71	12.21	14.27
C80323	4.69	5.62	2.97	3.61
C80415	13.43		9.71	10.80

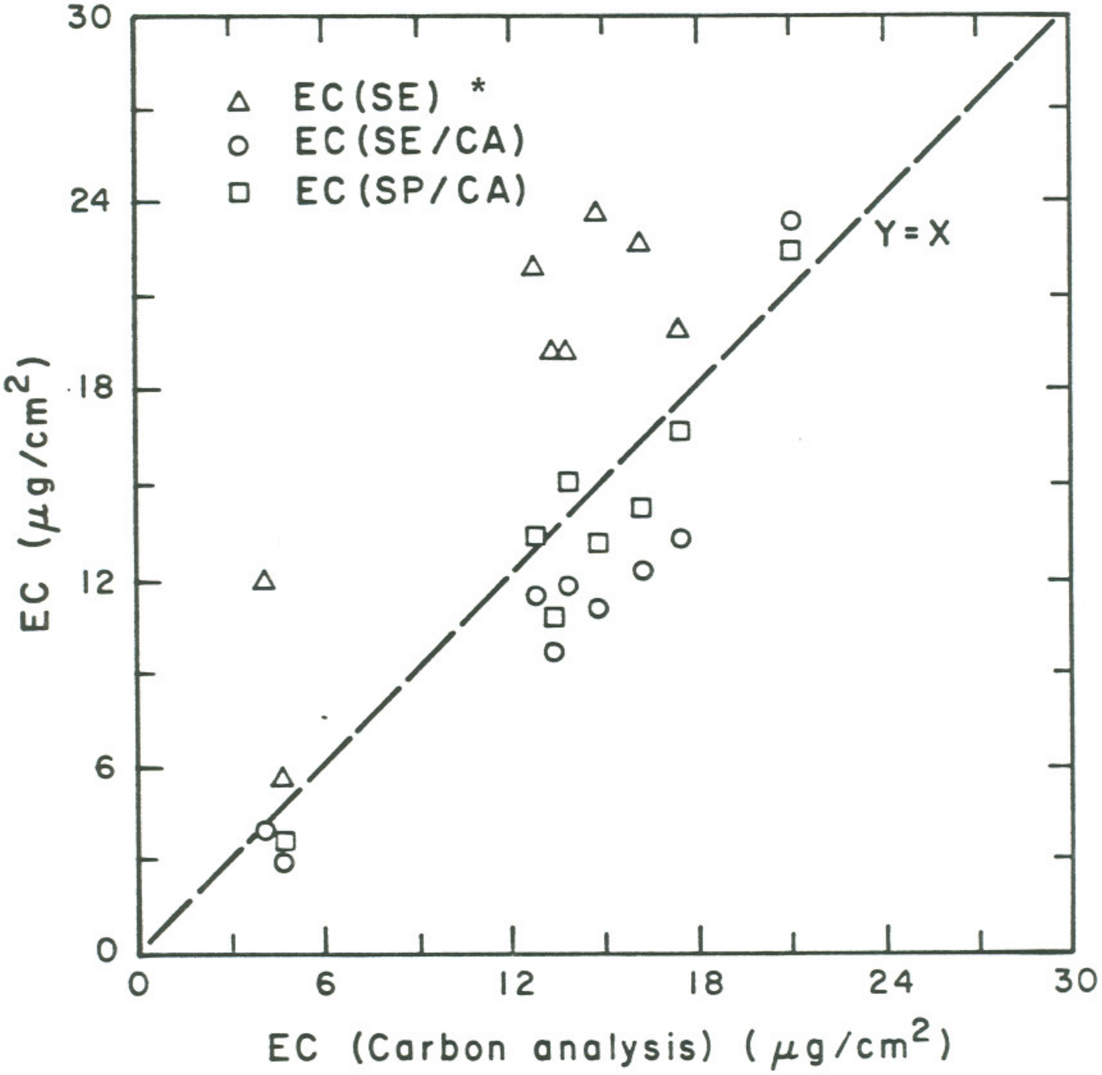
* EC_{CA} ≡ elemental carbon measured by the standard method.

EC_{SE} ≡ elemental carbon estimated as the difference between total carbon and extractable carbon.

$EC_{SE/CA}$ ≡ elemental carbon measured by the standard method after Soxhlet extraction.

$EC_{SP/CA}$ ≡ elemental carbon measured by the standard method after syringe pump extraction.

Figure III.E.1. Elemental carbon comparison - carbon analyzer vs. solvent extraction.



* EC(SE) ≡ elemental carbon estimated as the difference between total carbon and extractable carbon.

EC(SE/CA) ≡ elemental carbon measured by the standard method after Soxhlet extraction.

EC(SP/CA) ≡ elemental carbon measured by the standard method after syringe pump extraction.

tal carbon) seriously over-estimates elemental carbon with respect to the thermal/optical carbon analysis method; 2) from thermal/optical analysis of the extracted filter, it is clear that this over-estimation is the result of organic carbon left on the filter after extraction; and 3) thermal/optical analysis of the filters extracted with both methods shows a decrease in estimated elemental carbon even after correction using the IPM. The decrease in the syringe pump samples is, however, on the order of the uncertainty of the analysis (< ±10%), and 4) from Tables III.E.1 and 2 it is seen that the amounts of pyrolytically produced elemental carbon are significantly reduced using both extraction procedures (i.e., by 58% for the syringe pump procedure and 79% for the Soxhlet method).

Measured elemental carbon concentrations on the filters typically decrease after solvent extraction. In samples where the pyrolysis elemental carbon is a large fraction of the total elemental carbon (33% in these samples) this decrease might be the result of an error in the pyrolysis correction procedure on the unextracted filters. As a worst case, if it is assumed that all of the decrease in elemental carbon measured on extracted filters (after correcting for wash-off) is the result of errors in pyrolysis correction and that the rest of the pyrolyzable material would result in the same error per mass of pyrolyzed material, an upper limit to the uncertainty of the pyrolysis correction for these samples can be estimated by calculating:

(% elemental carbon missing/% PEC removed) x 100

For the Soxhlet extractor results, the maximum error in elemental carbon is approximately 20%. For the syringe pump extractor results, it is 8.6%.

To ensure that there were no major problems in the extraction procedure, a mass balance for carbon on the filter was carried out. Table III.E.4 compares the original total carbon to the sums of total carbon on the extracted filter (i.e., unextracted carbon) and in the extract and shows that the average recovery for the methanol-benzene extraction was 85 ± 9%. The 15% loss can probably be explained in terms of non-quantitative transfer and volatilization losses during solvent removal (Gundel et al., 1979). The latter should occur only for organic carbon; any decrease in elemental carbon must result from handling losses or errors in analysis.

III.F. Error Analysis

An important limitation to the determination of ambient concentrations of organic and elemental carbon is the analytical uncertainty, which consists of both precision and accuracy components. Sources of error in the accuracy of the measurement include: 1) loss of carbon off the filter prior to analysis; 2) error in sampling volume calibration; 3) error in the measurement of the collection area of the filter; 4) error in the measurement of the area of the filter segment analyzed; 5) error in the measurement of the volume of the calibration loop; 6) leaks in the gas flow system; 7) non-quantitative oxidation or metha-

TABLE III.E.4

MASS BALANCE FOR SOLVENT EXTRACTION

Sample	* TC (orig.) ($\mu g/cm^2$)	TC Extracted Filter ($\mu g/cm^2$)	TC Extract ($\mu g/cm^2$ filter)	$\frac{TC_{extract} + TC_{extracted\ filter}}{TC_{(orig.)}}$
C70818	16.16	6.87	4.22	0.69
C71017	40.64	16.36	21.40	0.93
C71021	36.49	17.86	12.85	0.84
C80216	32.55	10.81	10.64	0.66
C80217	35.41	16.81	15.51	0.91
C80316	52.22	29.21	18.54	0.91
C80317	79.19	30.43	33.11	0.80
C80321	45.63	18.72	22.92	0.91
C80323	13.54	4.22	7.92	0.90
				0.85±0.09

* TC ≡ total carbon

nation; and 8) systematic errors in the separation of organic and elemental carbon resulting from such processes as incomplete removal of organic carbon during the first phases of the analysis and incorrect correction for the pyrolytic production of elemental carbon. Items 1-3 are often not within the analyst's control, and will be assumed to be less than 10%. Items 4 and 5 are less than 5% (based on the measurement of dimensions of both the filter cutter and the calibration loop). Items 6 and 7 are difficult to estimate; however, diagnostic tests have been developed that allow these to be routinely monitored and eliminated. Systematic errors, as discussed earlier, have been minimized whenever possible. The corrections for them occur as multiplicative terms in the calculation of the mass of carbon and have uncertainties associated with them which can be propagated as random errors.

In discussing the precision of the method the propagation of error through the analytical procedure will be examined. Errors in precision have been divided into two categories: sampling errors and analytical errors. Sampling errors result from: 1) uncertainty in the volume of air samples; 2) the non-uniformity of the sample deposited on the filter; and 3) uncertainty in the amount of filter taken for the analysis. Of the sources of analytical errors in each analysis, the following are considered most significant: 1) integration, 2) calibration of the detector response, 3) reproducibility of the temperature program, and 4) variation in pyrolytic conversion due to variation in oxygen contamination. Many of these are variable and difficult to estimate. Whenever possible, experiments designed to estimate uncertainties have been carried out and are discussed in the section dealing with that uncertainty. Table III.F.1 lists estimates of the uncertainties associated with the analysis; each of the estimates is discussed below.

Uncertainty values of 10% for the measurement of sampled air volume and for non-uniform sample deposition have been assumed. These are probably realistic values, and it is these values which will ultimately limit the precision of the analytical method.

Integration uncertainty results from several sources: 1) approximations involved in analog to digital (A/D) conversion; 2) variation in peak shape and elution time because of gas flow changes. (An unusual peak shape or gas flow could result in some of the peak to be integrated falling outside of the integration interval); 3) noise in the detector (FID) signal; and 4) uncertainty in baseline subtraction. The noise in the FID signal introduced by items 1 and 3 causes digital values for FID output to differ from the average FID value by one unit approximately 25% of the time and by two about 10% of the time. This results in an uncertainty of approximately ±0.07 μg/peak based on the following estimations: a) the peaks to be integrated are divided into roughly 100 A/D conversions, b) the detector response is approximately 0.0019 μg carbon per A/D unit. Thus, the uncertainty in baseline is approximated by:

$$(0.25 \times 100 \times 0.0019) + (0.1 \times 2 \times 100 \times 0.0019) = \pm 0.07\ \mu\text{gC}$$

TABLE III.F.1.

SOURCES OF UNCERTAINTY FOR ORGANIC AND ELEMENTAL CARBON

Source of Uncertainty	Uncertainty	Method of Estimating Uncertainty
Sampling Errors	±10%	Estimation
Analytical errors:		
Integration	±0.07 µg/peak	Observed in analysis.
Baseline subtraction	±0.15 µg/peak	Observed in analysis.
Calibration and detector response	±8%	Observation of detector response.
Blanks	±0.25 µg/peak	Estimated from repeat analysis.
Uncertainty in splitting peak 3	for OC $0.05 \times \frac{3a+3b}{3a}$	Estimated from repeat analysis.
	for EC $0.05 \times \frac{3a+3b}{3b}$	
Uncertainty in the accuracy of the pyrolysis correction method	±10%	Estimation

In the early portion of the analysis before any sample has reached the detector, a measure of the detector background current is made. This value is used throughout the rest of the run as the baseline value. The uncertainty in baseline subtraction stems from the probability that the calculated value for the baseline is not representative of the actual baseline for that analysis. (This may result from changes in detector background current caused by changes in gas flow rate or composition, or by changes in signal amplification.) An uncertainty of approximately ±0.15 μg C/peak results from the estimation that in 40% of the analyses the value used in baseline subtraction differs by one unit from the "correct" value, and in 20% of the analyses it differs by 2. If 100 A/D conversions are again integrated, the result is:

$$(0.40 \times 100 \times 0.0019) + (0.2 \times 2 \times 100 \times 0.0019) = 0.15\ \mu gC$$

Calibration uncertainty results from changes in FID response. Systematic, long-term changes (e.g., flow changes or changes in burner characteristics) are corrected with the routine calibration procedure. FID response changes within a run result because of changes in flame characteristics caused by: 1) changes in the composition of the carrier gas (from He/O_2 to He to He/O_2), and 2) variation in the ratio of carrier gas, hydrogen, and air. Methane injections can be made during the run when either carrier gas is flowing through the detector. The results indicate detector response is independent of carrier gas type.

Figure III.F.1 shows the effect of changing the relative flows of carrier gas, hydrogen, and air. The range of expected variation of the gas flows within a run for each gas is shown by a vertical slash through the plot for that gas, and indicates that a variation in FID response of less than 8% for each gas can be expected.

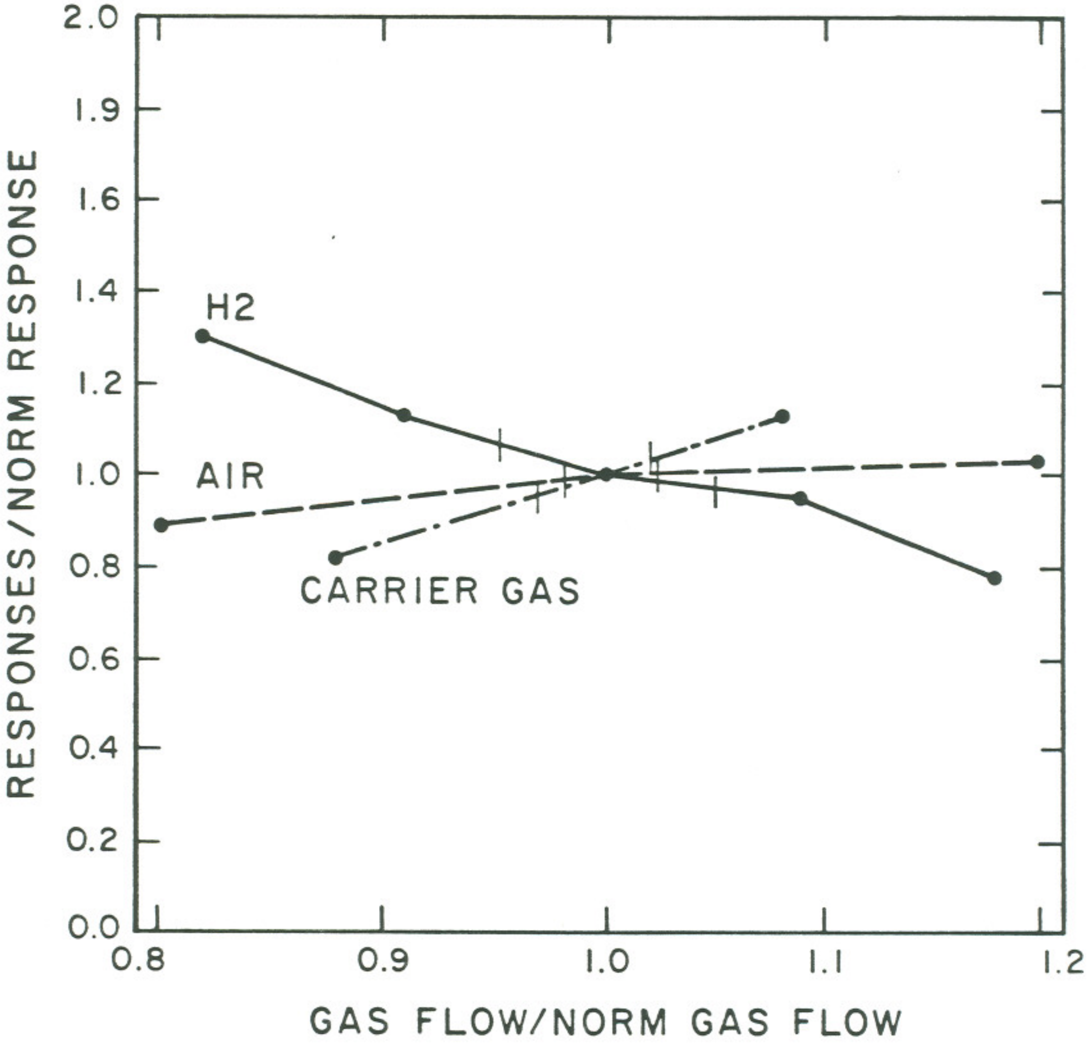
Uncertainties resulting from leaks in the gas flow system and incomplete oxidation or methanation will not be considered here. Routine system evaluation and calibration are capable of detecting all of these problems, and corrective action can be taken to eliminate them.

The uncertainty in splitting peak 3 comes from two principal sources: 1) variation in the actual time the FID lags behind the optical system; and 2) noise in the optical system that leads to incorrect determination of the reflectance-equivalence point.

The uncertainty in the accuracy of the pyrolysis correction procedure is estimated to be ±10% from the solvent extraction and IPM results. As noted earlier, the possibility of a systematic error as large as 10% also exists. This, however, has not been considered in the error analysis. Further inter-method comparisons are needed to resolve this problem, however. The uncertainty in blank values is estimated from repeat analysis of blank filters. Values for the various components of the uncertainty can be substituted into the error propagation equations found in Appendix C to determine overall analytical uncertainties.

As part of the quality assurance procedure, a reference filter is analyzed each day and provides a day to day evaluation of instrument

Figure III.F.1. Gas flow vs. detector response.



operation. These data can be used to estimate the actual uncertainties in repeat analysis. Measured and predicted uncertainties for organic, elemental, and total carbon values for a standard filter are given in Table III.F.2, and indicate that all important sources of uncertainty have probably been taken into account (and in some cases over-estimated).

As a result of the preceding error analysis, a conservative estimation of the minimum detectable concentration can be set at approximately 1 $\mu g/cm^2$ for organic and elemental carbon on quartz fiber filters. To satisfy the needs of ambient air sampling, the method should have a sensitivity on the order of 1 $\mu g/m^3$ for each type of carbon. This means that the recommended minimum sampling volume for ambient air samples is on the order of 1 m^3 of air per cm^2 of filter area. This is well within the range of even time resolved sampling. (For example, the standard 24-hour high volume sampler collects approximately 5 m^3/cm^2.) For typical urban high volume ambient samples error analysis gives an analytical uncertainty of approximately ±15% for organic and elemental carbon and ±10% for total carbon.

III.G. Conclusions from Instrument Evaluation

The important conclusions from instrument evaluation include: 1) the method is well calibrated as a measure of total carbon on aerosol loaded filters; 2) model compounds tested were correctly separated into organic and elemental carbon by the method; 3) some important sources of aerosol show a large tendency to pyrolyze; thus a procedure

Table III.F.2.

ANALYSIS UNCERTAINTY FOR THE REPEAT ANALYSIS

OF SAMPLE AG12F

	Carbon μg/cm^2	1σ Uncertainty from the Analysis	1σ Uncertainty (calculated)
OC	68.01	4.15	8.23
EC	32.57	2.79	4.71
TC	100.58	6.03	7.29

is needed to correct for pyrolysis; 4) the thermal/optical method agrees to within about 10% with both optical absorption and solvent extraction methods; and 5) the thermal/optical carbon analyzer is able to measure organic and elemental carbon on quartz fiber filters down to 1 μg/cm^2 with a typical analytic uncertainty of ±15% for each carbon type.

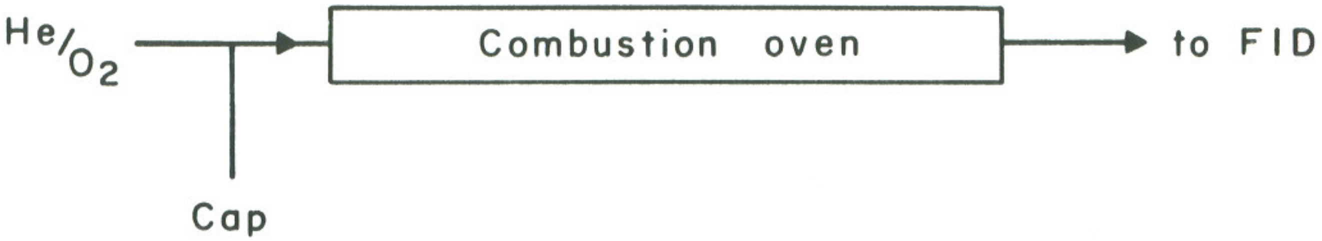
IV. DETAILED INVESTIGATION OF THE OXIDATIVE AND PYROLYTIC PROCESSES IN THE THERMAL/OPTICAL CARBON ANALYZER

In order to gain a more complete understanding of the thermal/optical separation in the carbon analyzer, several experiments were performed. Their purpose was to evaluate potential problems arising from: 1) the premature oxidation of elemental carbon in the organic carbon cycle; 2) the incomplete removal of organic carbon before elemental carbon analysis was initiated; 3) the accuracy of the optical monitoring system; and 4) differences in optical properties of original (OEC) and pyrolysis-generated (PEC) elemental carbon.

IV.A. The Premature Oxidation of Elemental Carbon

In the current analysis procedure the sample is heated in a He(98%)-Oxygen(2%) carrier gas to remove volatile organic carbon. Two potential problems arise in this procedure. First, it has been reported that elemental carbon in ambient samples begins to oxidize below 400°C in oxygen (Dod et al., 1979) and thus 350°C might be too hot to avoid some elemental carbon oxidation. Second, in order to keep analysis times reasonable, all of the oxygen must be purged from the oven in less than 3-5 minutes before the oven temperature is raised to 600°C. Experimentation with thousands of ambient filters from more than 70 sites around the world has shown measurable oxidation of elemental carbon at 350°C in only two samples using the current gas flow system (as evidenced by no increase in filter reflectance during the organic carbon removal steps).

The problem of incomplete purging prior to the 600°C He step proved more difficult to overcome. Although the helium carrier gas was free of oxygen before entering the oven system, purge times of as long as 45 minutes were necessary to remove traces of oxygen left in the front end of the oven during the first step of the procedure. The solution to this problem was found by changing the flow system such that when the carrier gas was changed to He, it was introduced into the oven part way down its length. Simultaneously the front of the oven was opened to vent (see Figure IV.A.1). The result is that the carrier gas flow was split with the bulk of the gas proceeding through the oven to carry the oxidized and volatilized sample to the detector while a small portion of the helium was used to backflush the front of the oven. The outcome was essentially complete elimination of oxygen from the oven within 3 minutes, allowing the temperature to be raised and the analysis to proceed quickly to the next stages. The effectiveness of this approach was evidenced by the absence of a reflectance increase during the 600°C-He step. In fact, as previously seen, a decrease in reflectance corresponding to pyrolytic conversion was observed.



(a) Normal flow mode

(b) "Backflow" mode

Figure IV.A.1. Combustion oven gas flow patterns.

IV.B. Incomplete Removal of Organic Carbon

To investigate incomplete removal of organic carbon from the filter before elemental carbon analysis, aerosol samples collected on quartz fiber filters were analyzed in the usual manner. The analysis program was then modified to raise the temperature during the second phase of the analysis (600°C, He) to 750°C to remove any residual carbon from the filter. If any additional organic carbon were removed from the filter, it would result in a decreased value for elemental carbon. The results are given in Table IV.B.1 and indicate that the mass of carbon reported as elemental carbon is not reduced by this process. Cadle et al. (1980) have performed similar experiments, using temperatures up to 800°C without an appreciable change in elemental carbon concentration.

IV.C. Non-Representative Monitoring of Oxidation

Four filter disks are typically used in carbon analysis. Only one of the disks is monitored by the reflectance system. In order to ensure that the monitored disk is representative of the others (and as a result that the pyrolysis splitting of peak 3 is at the proper point), the disks were removed from the oven at the reflectance equivalence point and IPM measurements made on each of the disks. Results given in Table IV.C.1 (determined by estimating elemental carbon on each disk from the IPM calibration curve) indicate that the forward filter

TABLE IV.B.1

ELEMENTAL CARBON REMAINING AFTER HEATING TO 750°C

Sample	EC *	EC_{750} **	$\frac{EC_{750}}{EC}$
Ind.04	11.37	11.36	1.00
Ind.38	10.17	9.13	0.91
Ken.31	10.23	10.77	1.05
Ken.32	15.30	18.74	1.20
			1.04 ± 0.13

* Measured by the standard analysis procedure.

** Measured after heating to 750°C.

TABLE IV.C.1

COMPARISON OF ELEMENTAL CARBON PREDICTED USING THE IPM MEASUREMENTS OF THE MONITORED FILTER DISK (DISK 1) AND THE AVERAGE OF ALL DISKS

Sample	EC (disk 1)	EC (Average)	$\frac{EC_{disk\ 1}}{EC_{average}}$
C71017I	20.17	20.97	0.96
C71021I	30.55	36.71	0.83
C80216I	20.17	23.93	0.84
C80217I	36.71	41.34	0.88
C80316I	61.59	68.04	0.88
C80317I	25.13	30.55	0.83
C80321I	28.32	30.55	0.93
C80323I	5.95	5.68	1.05
C80415I	28.32	30.55	0.93
			0.91 ± 0.07

(i.e., the one for which the reflectance is monitored) oxidizes slightly faster than the others. This could result in an approximately 9% overestimation of elemental carbon. As indicated below, however, this overestimation is offset by other effects.

IV.D. Evaluation of the Assumption of Constant Specific Absorption

The basic assumption underlying all pyrolysis correction procesures investigated here is that the specific absorptions of the pyrolysis-generated elemental carbon and the elemental carbon oxidized from the filter in peak 3a (the pyrolysis correction) are the same. Differences in specific absorption might result in systematic errors in the pyrolysis correction procedure. The evaluation of the absorption/mass relies on the comparison of optical absorption (as measured by the integrating plate method (IPM) and carbon analysis of a series of specially selected filters. These range from samples composed almost exclusively of elemental carbon and which showed no pyrolysis to samples which originally contained no elemental carbon but pyrolyzed extensively. Also included are sets of ambient samples which consisted of identical aerosol at different filter loadings to evaluate the effects of filter loading on pyrolysis correction. Finally, sets of samples which show pyrolysis were interrupted in mid-analysis for the measurement of optical absorption. That value divided by the total elemental carbon on the filter gives the specific absorption for the total elemental carbon.

Filter samples from source tests on veneer dryers and wood sanding operations -- both of which have no original elemental carbon but which show pyrolysis -- were analyzed in the carbon analyzer system. To measure the absorption/mass of the pyrolytically generated elemental carbon, these samples were removed from the oven after pyrolysis had occurred but before oxidation was initiated, and analyzed with the IPM system. These samples give an absorption/mass relative to the diesel exhaust samples of 0.98 and 1.14, respectively, for the pyrolytically generated elemental carbon. Different results were found, however, when two other source samples from forest slash and field burns were analyzed in a similar manner. Both of these contained elemental carbon originally and both showed a large degree of pyrolysis. (Original (OEC) and pyrolysis-generated (PEC) elemental carbon were of approximately equal mass.) The absorption/mass for the total elemental carbon (OEC + PEC) was 1.44 times the value expected (from the diesel exhaust calibration curve). This suggests the possibility of under-estimating the mass of original elemental carbon using the optical absorption correction method. (If original elemental carbon (OEC) and pyrolysis elemental carbon (PEC) oxidized at the same rate, and PEC had a higher specific absorption than OEC, it would be necessary to oxidize more OEC than the PEC actually produced to return filter reflectance to its original value.)

To estimate the importance of differences between the specific absorption of original elemental carbon and pyrolysis elemental carbon for ambient samples, a group of 10 filters from Portland, Oregon, were analyzed using 3 different timing and flow sequences in the carbon analyzer. These sequences were: 1) the normal procedure; 2) removal of filters from the oven for IPM analysis after pyrolysis had occurred but before oxidation of elemental carbon; and 3) removal of the samples from the analyzer at the point in the analysis where the filter reflectance had returned to its original value.

The specific absorption of the original elemental carbon was calculated for the filters using the IPM absorption values from the original filter and the mass of original elemental carbon from the carbon analyses. These are compared to the values estimated from the IPM calibration curve (Figure III.D.). Table IV.D.1. indicates that the absorption/mass for the ambient samples are slightly higher (1.04) than that for diesel exhaust.

To estimate the specific absorption of the pyrolysis-generated elemental carbon, the same samples were removed from the carbon analyzer before oxidation and analyzed using the integrating plate method. The absorption/mass for the total elemental carbon (i.e., OEC + PEC) was calculated to be much higher (1.83X) than expected from the diesel exhaust calibration curve (Figure III.D.1). This means that the absorption/mass for the pyrolyzed material is significantly higher than the "effective" specific absorption originally measured on the filter. The consequence is that the mass of elemental carbon attributable to pyrolysis elemental carbon might be over-estimated and elemental carbon under-estimated.

One possible explanation for this is seen in the results of IPM analysis of Portland samples which were removed from the carbon analysis when their reflectance had returned to its original value (at the

TABLE IV.D.1

OBSERVED AND PREDICTED ABSORPTIONS FOR AMBIENT SAMPLES

Sample	EC_{CA} **	$\left[-\ln {}^{I}/_{I(o)}{}^{*}_{meas}/EC_{CA}\right]$ $\left(\text{meters}^2/\text{gram}\right)$	$\left[\dfrac{-\ln {}^{I}/_{I(o)}{}^{*}_{\text{predicted from III.D.1}}}{EC_{CA}}\right]$ $\left(\text{meters}^2/\text{gram}\right)$	$\left[\dfrac{\ln {}^{I}/_{I(o)}{}_{meas}}{\ln {}^{I}/_{I(o)}{}_{predict.}}\right]$
C70818	4.09	10.35	9.2	1.12
C71017	13.88	6.78	6.62	1.02
C71021	14.81	6.78	6.44	1.05
C80216	12.77	7.02	6.84	1.03
C80217	17.48	6.63	6.00	1.11
C80316	21.05	6.65	5.50	1.20
C80321	16.28	6.00	6.19	0.97
C80323	4.69	9.10	8.98	1.01
C80415	13.43	5.67	6.71	0.85
		7.22 ∓ 1.5	6.94 ± 1.3	1.04 ± 0.07

---

* Corrected by multiplying by 0.35 (Edwards, 1980).

** EC_{CA} ≡ elemental carbon measured by the standard thermal/optical method.

point used for the pyrolysis correction procedure). From Table IV.D.2 it is clear that even though the reflectance had returned to its original value, the optical transmission had not. This is believed to result because elemental carbon produced by pyrolysis is distributed throughout the filter, rather than near the surface with the original aerosol deposit. The result is that the pyrolysis-generated elemental carbon found deep within the filter has a smaller effect on the reflectance than the original elemental carbon. This lessens the effect of the higher specific absorption for PEC.

Another set of ambient filters was collected. All were from the same aerosol and collected for the same length of time but at different flow rates and hence different loadings on the filters. These were analyzed to observe both the effect of filter loading on the organic/elemental speciation and, as before, to compare the specific absorption of the samples to that of diesel exhaust.

Figure IV.D.1 shows the volumetric concentrations of organic, elemental, and total carbon as a function of face velocity. Clearly elemental carbon concentration remains constant within a few percent over the nearly eight-fold variation in filter loading. Organic carbon, however, shows a systematic decrease in concentration as face velocity is increased. This is not thought to be an analytical problem; rather it is an artifact of volatilization losses or the effect of adsorption of gas-phase organics on the filter substrate during sampling. For carbon analyzer evaluation the important conclusion from these samples is

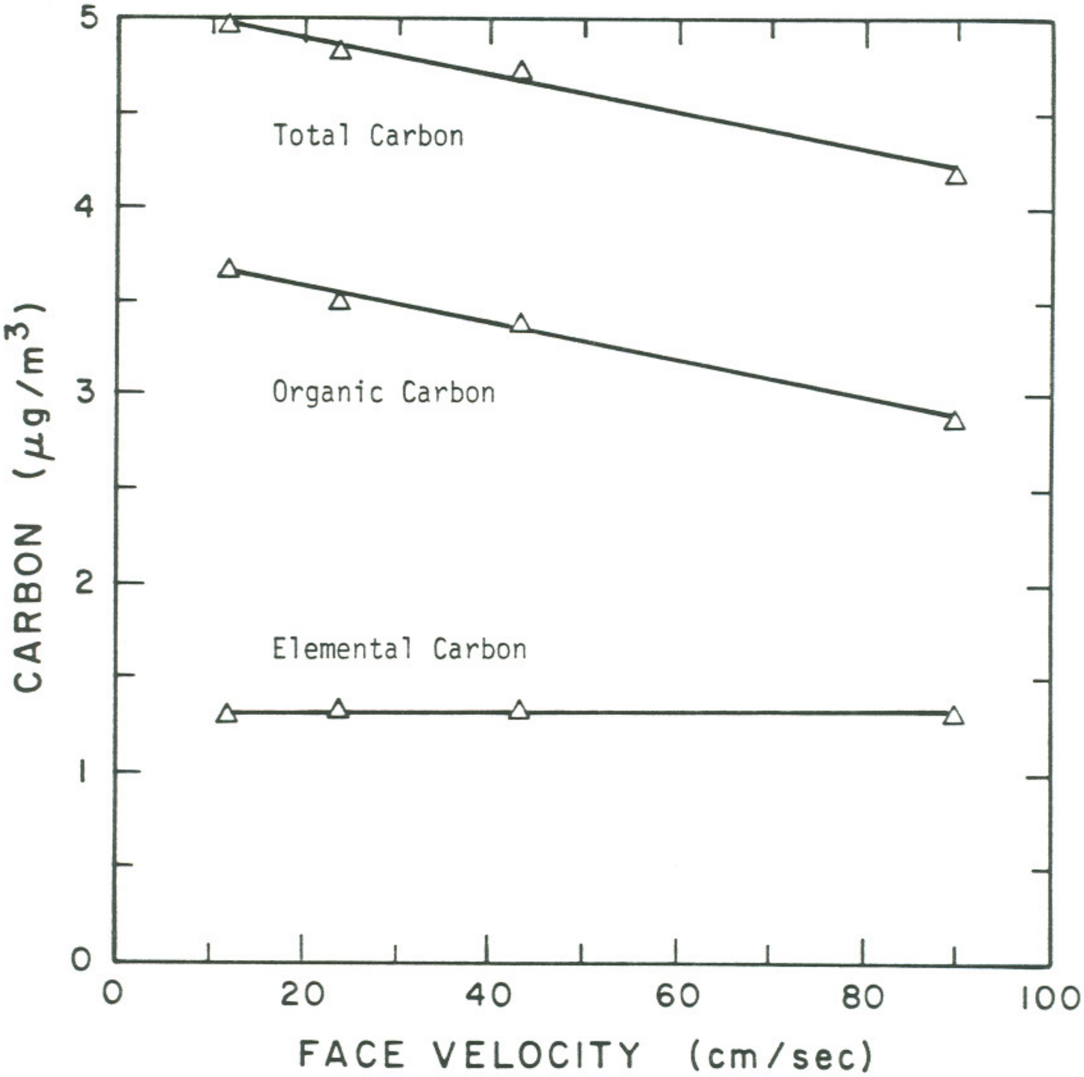
TABLE IV.D.2

ABSORPTION AT REFLECTANCE EQUIVALENCE POINT

Sample	$-\ln {}^{I}/_{I(o)_{orig.}}$	$-\ln {}^{I}/_{I(o)_{REP}}$ *	$\dfrac{\ln {}^{I}/_{I(o)_{orig}}}{\ln {}^{I}/_{I(o)_{REP}}}$
C70818	1.21	2.22	0.55
C71017	2.69	3.45	0.78
C71021	2.87	4.48	0.64
C80216	2.56	3.69	0.69
C80217	3.31	4.70	0.70
C80316	4.00	5.68	0.70
C80317	3.89	4.14	0.94
C80321	2.79	4.14	0.67
C80323	1.22	1.53	0.80
C80415	2.17	4.14	0.52
			0.70 ± 0.12

* $-\ln {}^{I}/_{I(o)_{REP}} \equiv$ absorption at the reflectance equivalence point.

Figure IV.D.1. Carbon concentration as a function of face velocity. Sample from Portland, Oregon.



that elemental carbon concentration does not appear to be affected by loading on the filter.

For these samples of identical aerosol, seen in Figure III.D.2., IPM and thermal/optical elemental carbon analyses correlate well, with carbon analysis giving consistently higher results. As discussed in Section III the difference between methods might result from systematic overestimation of elemental carbon by the thermal/optical system or by differences in specific absorption between the elemental carbon on ambient samples and the elemental carbon on the diesel exhaust samples used to calibrate the IPM system.

IV.E. Oxidation Rates of Original and Pyrolysis-Generated Elemental Carbon

Another effect which must be considered is the possibility of a difference in oxidation rates of the original (OEC) and pyrolysis-generated (PEC) elemental carbon. To investigate this effect, two experiments were conducted. In the first experiment filters were placed in the carbon analyzer with the aerosol deposit away from the light source (backward). In this configuration the aerosol deposit had only a small effect on filter reflectance. As analysis proceeded, a large decrease in reflectance was seen when pyrolysis occurred. This confirmed that the pyrolytically produced elemental carbon was deposited throughout the filter. During a normal analysis with the aerosol deposit toward the light source, absorption would be dominated by the original deposit and would result in a lower than expected absorption/mass for the PEC in the reflectance system. With the filter in backward the reflectance system primarily monitors the PEC (rather than OEC). If OEC and PEC oxidize at the same rate, nearly all elemental carbon (OEC and PEC) should be oxidized from the filter when the PEC is completely oxidized. If not, it is evidence that the PEC oxidizes more rapidly than the OEC. Table IV.E.1 indicates that a significant fraction of the total elemental carbon (TEC) remains on the filter when reflectance has returned to its original value. Thus, PEC oxidizes faster than OEC.

In the second experiment, it was observed in the analysis of solvent-extracted filters that the mass of elemental carbon oxidized at 400 and 500°C was greatly reduced with respect to the unextracted filter while the 600°C peak was only slightly changed. A typical example of this is seen in Figure IV.E.1, and results from several filters are given in Table IV.E.2. Most of the decrease in mass of the total elemental carbon (OEC + PEC) after the solvent extraction results from a decrease in pyrolysis (PEC). Thus most of the PEC is oxidized at 400-500°C whereas the OEC requires the higher temperature (600°C) for oxidation. This again implies a faster oxidation rate for PEC than OEC.

These results indicate that the elemental carbon which is oxidized in peak 3a (the pyrolysis correction peak, see Figure II.C.1) is primarily PEC and that which is oxidized in peak 3b primarily OEC.

TABLE IV.E.1.

Elemental Carbon Remaining on Filter after PEC Removal.

Sample	% TEC remaining after 100% of the PEC had been removed	$\frac{\text{OEC}}{\text{TEC}}$ x 100	% of OEC remaining
C70818	39%	57%	68%
C80321	34%	52%	65%
C71017	26%	68%	38%
	33%	61%	57%

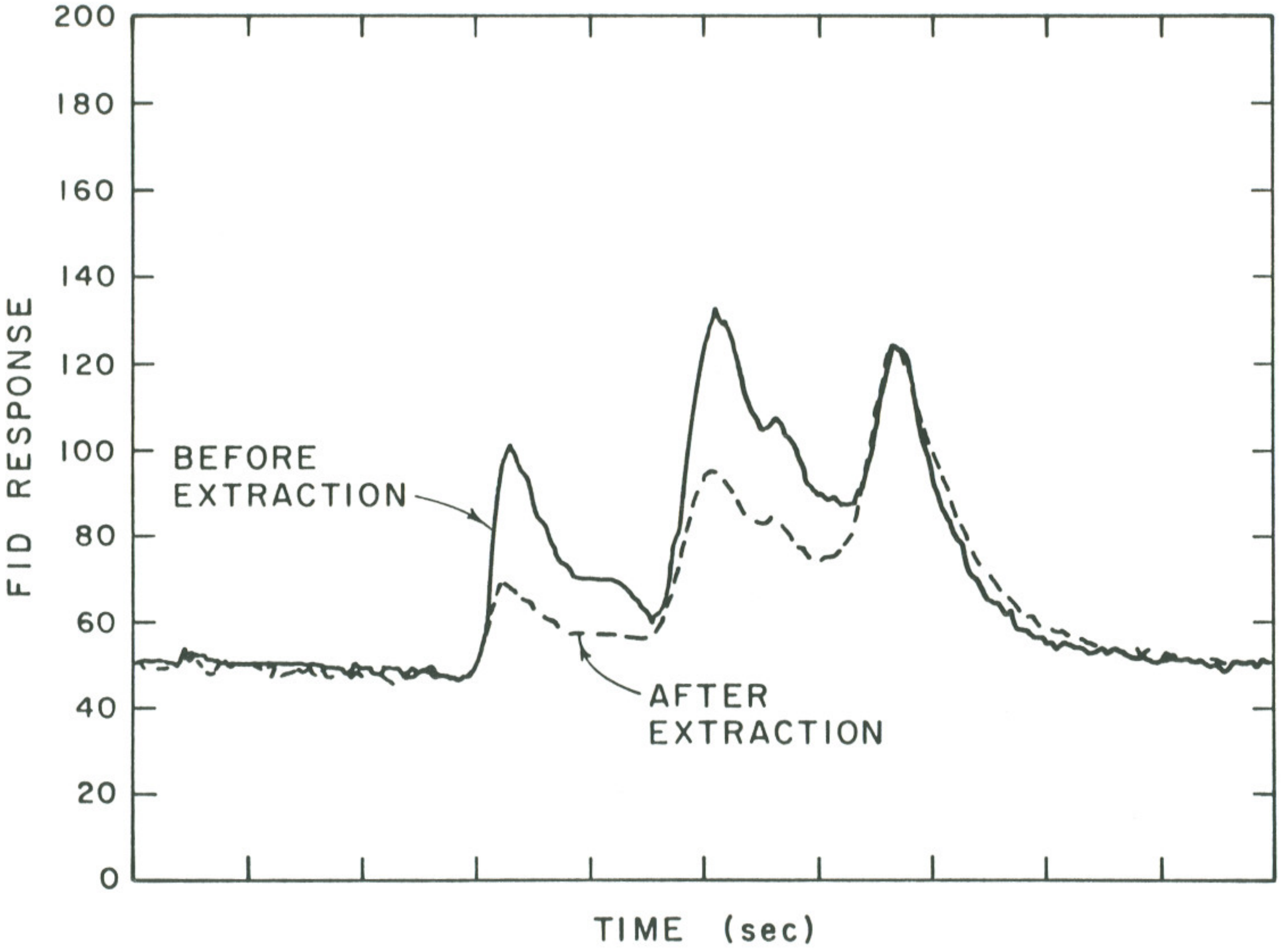


Figure IV.E.1. Peak 3 (elemental carbon) before and after solvent extraction.

TABLE IV.E.2

Fractions of Elemental Carbon Peaks Remaining After Solvent Extraction

Sample	$\frac{\text{peak 1 (extracted)}}{\text{peak 1 (unextracted)}}$	$\frac{\text{peak 2 (extracted)}}{\text{peak 2 (unextracted)}}$	$\frac{\text{peak 3 (extracted)}}{\text{peak 3 (unextracted)}}$
C71017	0.24	0.44	0.85
C80321	0.27	0.47	0.90
C80317	0.20	0.42	0.84
C80415	0.32	0.50	1.01
D41016	0.35	0.34	0.82
Average	0.28	0.43	0.88

IV.F. Conclusions

In conclusion, the greatest potential source of systematic error in the carbon analysis is the problem of determining the "correct" mass of pyrolysis elemental carbon. Differences in specific absorption of the original and pyrolysis-generated elemental carbon and the complex relationship between pyrolysis elemental carbon and filter reflectance are potentially the most important sources of this error although it is unclear if these factors over- or under-estimate elemental carbon in the instrument. Incomplete removal of organic carbon and preferential oxidation of the monitored filter are both expected to over-estimate elemental carbon although the former was shown to be a small effect. The higher specific absorption of the pyrolysis-generated carbon produces the opposite effect, however. Results from the comparison of the thermal/optical carbon analysis with solvent extraction and integrating plate methods indicate agreement between the three methods within about 10% and suggest that systematic problems in the thermal/optical method cancel to a large extent.

V. CARBONATE ANALYSIS

The method of carbonate analysis is a modification of that used by Mueller et al. (1971). The basis of the technique is the acidification of a segment of air filter with 20 µl of 1% phosphoric acid which results in the conversion of carbonate to gaseous CO_2. The CO_2 is detected as CH_4 as previously described in the section on carbon analysis. The filter segment is heated to 50°C during acidification to promote rapid and complete decomposition. The method has been modified to increase sensitivity by the use of a flame ionization detector (FID). A block diagram of the system is seen in Figure V.1.

Carbonate analysis serves two functions. First it allows any carbonate incorrectly measured as organic or elemental carbon in carbon analysis to be subtracted out of the measured filter concentration. Second, as with carbon analysis, it finds application in receptor type air pollution models as a potential tracer of both soil-derived material (principally $CaCO_3$ and $MgCO_3$) and anthropogenic activity (commonly Na_2CO_3). All of these carbonate types respond equally in the acidification system.

When carbonate is present on a filter, it can be thermally decomposed during organic and/or elemental carbon analysis, causing a positive interference. In Figure V.2 the responses of several carbonates to thermal analysis are shown. K_2CO_3, Na_2CO_3, and $MgCO_3$ respond

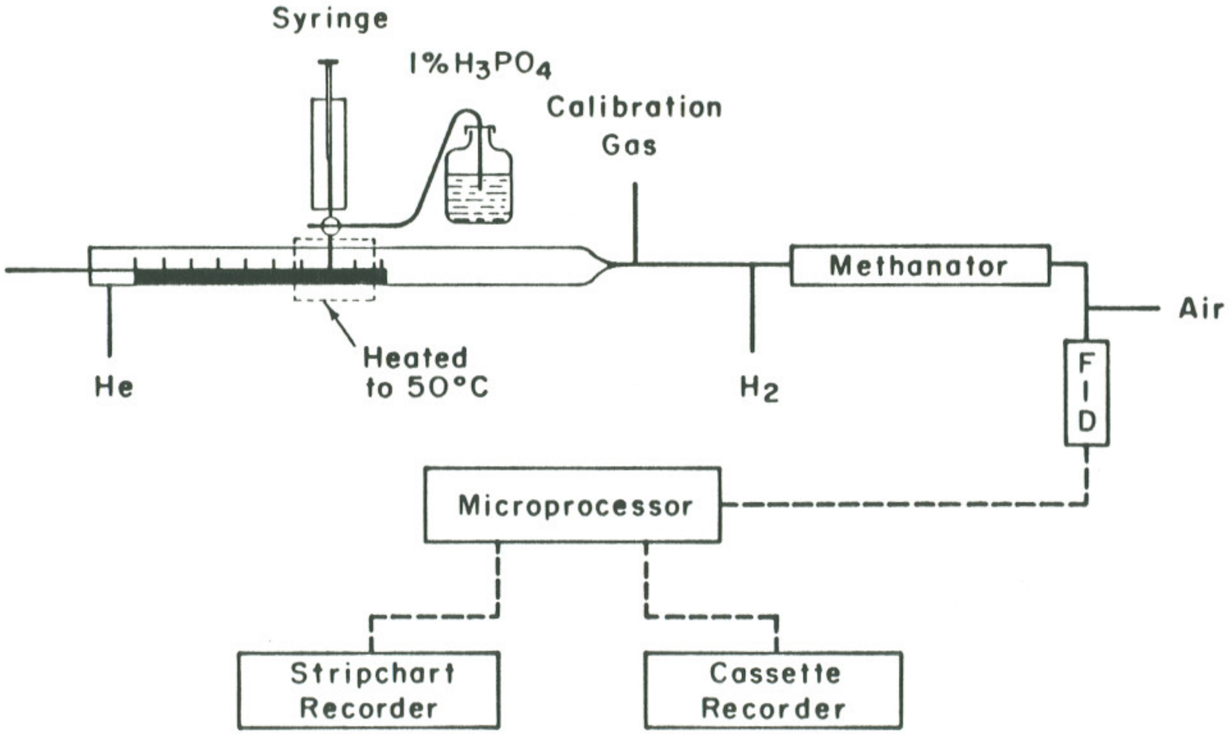


Figure V.1. Carbonate analyzer system.

solely in the organic carbon peaks. $CaCO_3$ responds partially both as organic and as elemental carbon.

Initial attempts to eliminate the carbonate interference involved carbonate analysis by acidification to remove carbonates with subsequent organic and elemental carbon analysis of the acidified filter segments. This, however, results in analysis errors in the determination of organic and elemental carbon. (Organic and elemental carbon were removed from the filter during acidification.) As a result the following correction procedure was developed.

1. When carbonate carbon is a significant fraction (e.g., >5%) of the organic or elemental carbon, a correction is made.
2. Carbonate carbon concentrations are determined on
    a. the original filter;
    b. a filter segment after organic and elemental carbon analysis; and
    c. a filter segment removed from the carbon analyzer in mid-run (e.g., after heating to 600°C in He but before elemental carbon analysis).
3. Differences in carbonate carbon concentration between the three filter segments are then used to correct organic and/or elemental carbon concentrations (i.e., original carbonate carbon concentration, from segment a, minus the value from segment c gives the organic carbon interference.

> The difference between segments a and b less the organic carbon interference is the elemental carbon interference).

This procedure is somewhat cumbersome, and it is fortunate that carbonate carbon typically represents less than 5% of the carbon on an air sample (Appel et al., 1976; Mueller et al., 1972; Shah, 1981). In our experience correction has been necessary only in samples which were clearly impacted by local carbonate sources.

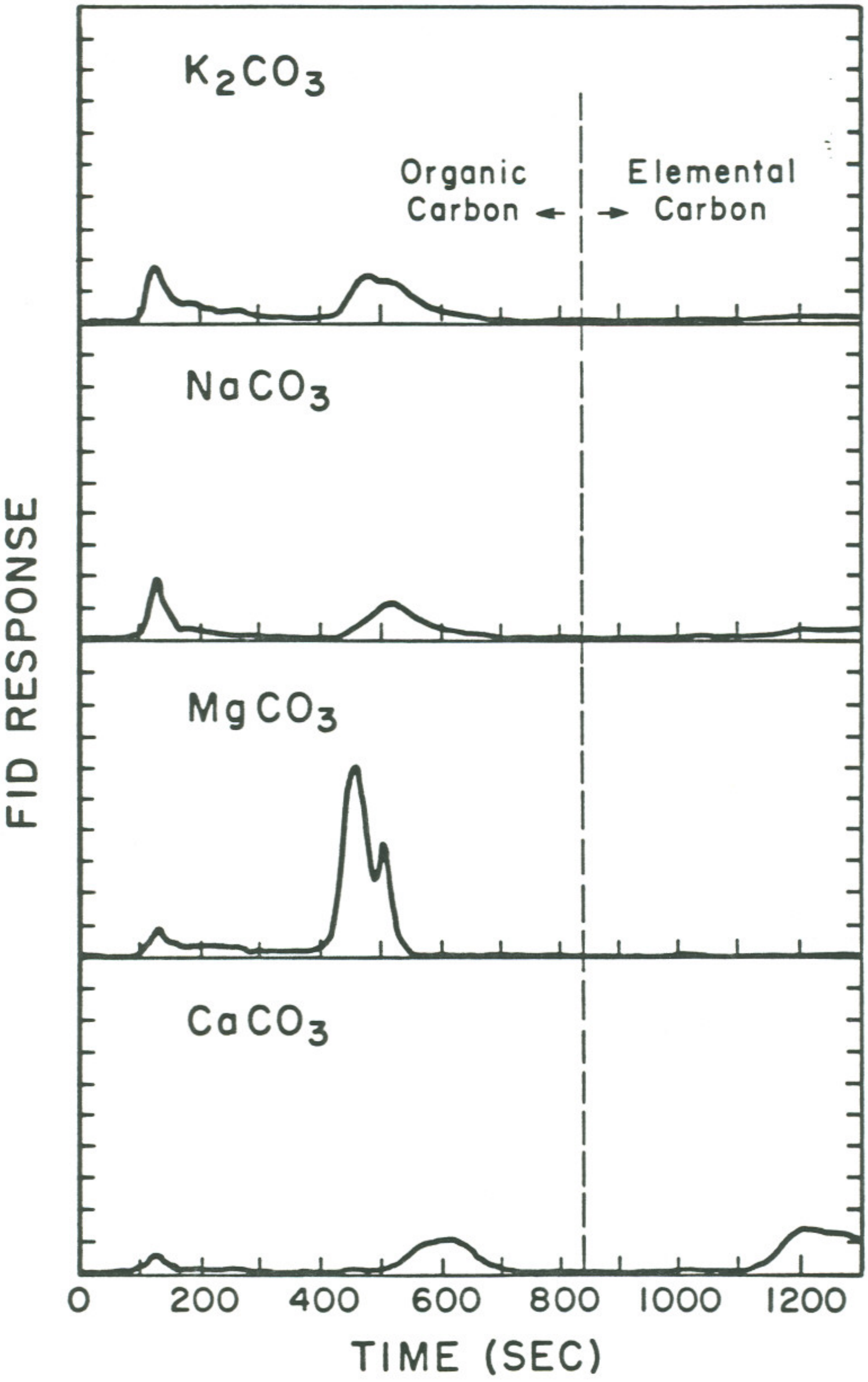


Figure V.2. Response of carbonates in the thermal/optical carbon analyzer

VI. THE ANALYSIS OF AMBIENT AIR SAMPLES

The goal of thermal/optical carbon analysis is the quantitative measure of organic and elemental carbon content of ambient aerosol collected on filters to determine the sources and impact of carbonaceous aerosol. While this kind of interpretation is not the goal of this thesis, it is instructive to report some of the results from ambient samples analyzed with this method to demonstrate the utility of the analyses.

The analysis of a wide range of ambient samples has been carried out, and Table VI.1 lists the average results obtained for several sample sites. In all cases elemental carbon (EC) represents a large fraction of the total carbon, and both the organic (OC) and elemental carbon represent a significant fraction of the total aerosol loading (TSP).

Figure VI.1 shows plots of organic vs. elemental carbon for several U.S. cities. Correlation coefficients range from 0.65 to 0.97. Some of the correlation between organic and elemental carbon results from common atmospheric dispersion. Henry (1977) has shown that much of the dispersion-related inter-correlation can be removed by dividing the chemical species concentration by the total aerosol mass concentration (TSP). Table IV.2 lists the correlations (r) between organic and elemental carbon and organic carbon/TSP and elemental carbon/TSP. Some correlations remain nearly unchanged by this process while others show

TABLE VI.1

AMBIENT CARBON AND AVERAGES OF RATIOS FOR AMBIENT AIR SAMPLES

(in $\mu g/m^3$)

SITE	OC	EC	TC	OC/TSP	EC/TSP
Berkeley	2.35 ±2.32	2.37 ±2.65	5.73	0.080	0.056
Los Angeles	8.73 ±4.95	5.45 ±4.34	14.18	0.075	0.047
Chicago	7.85 ±3.77	5.48 ±2.33	13.33	0.063	0.044
Pasadena	8.43 ±3.74	4.22 ±1.80	12.65	0.099	0.050
Philadelphia	5.31 ±1.75	4.49 ±1.57	9.80	0.077	0.065
East Chicago	6.42 ±2.63	5.67 ±2.77	12.09	0.054	0.048
Denver	7.61 ±8.31	4.12 ±3.40	11.74	0.070	0.038
Portland, Oregon	4.13 ±1.80	3.10 ±1.54	7.23	0.084	0.063
Elizabeth, N. J.	6.32 ±2.34	3.70 ±1.45	10.02	0.097	0.057

OC: organic carbon. EC: elemental carbon. TC: total (i.e., organic + elemental) carbon. TSP: total suspended aerosol.

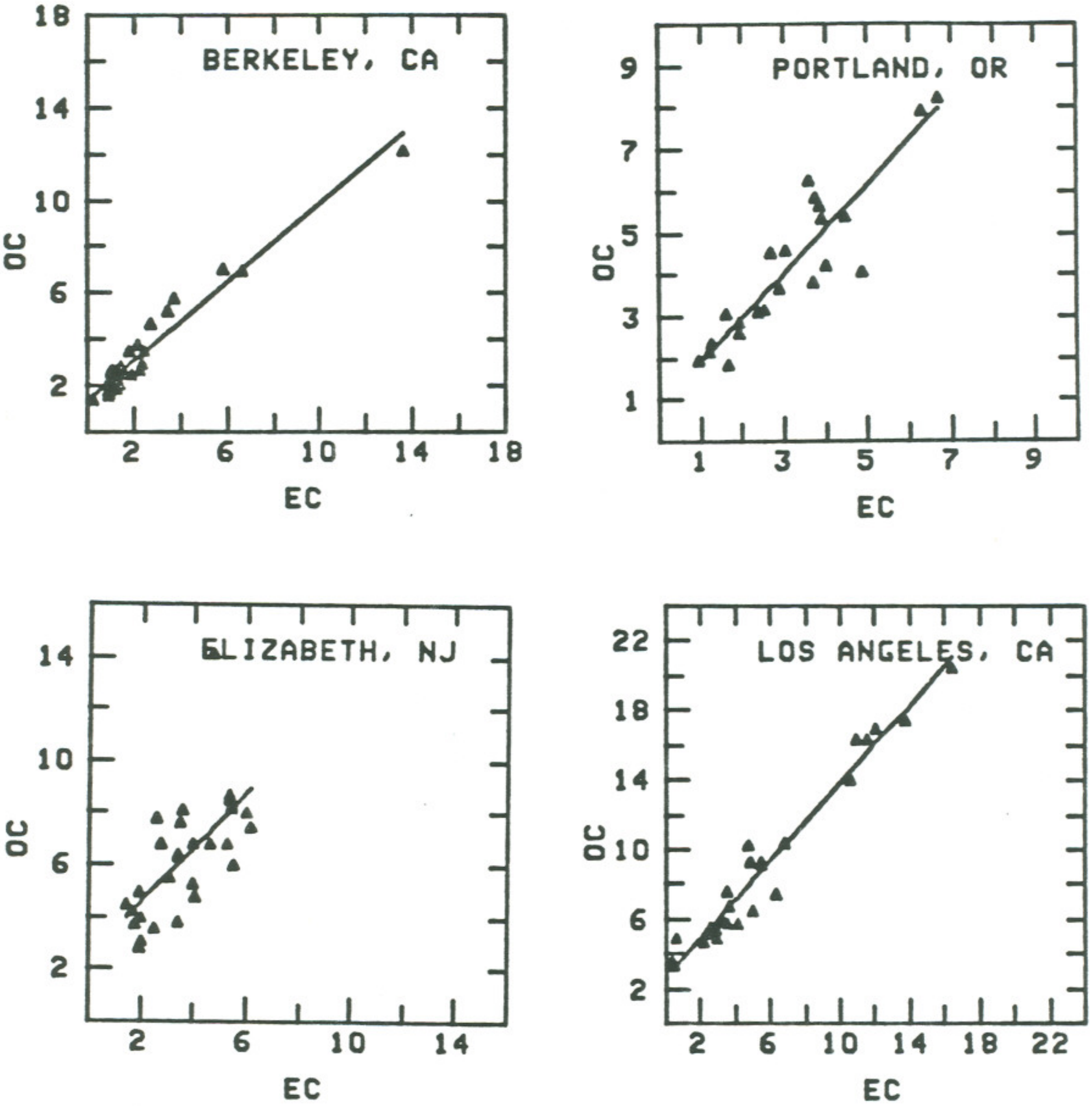


Figure VI.1.
Elemental carbon ($\mu g/m^3$) vs. organic carbon ($\mu g/m^3$).

TABLE VI.2

CORRELATIONS OF ORGANIC AND ELEMENTAL CARBON FOR SEVERAL AMBIENT SITES

CITY	r(OC vs. EC)	r(OC/TSP vs. EC/TSP)
Berkeley	0.97	0.78
Los Angeles	0.98	0.84
Chicago	0.84	0.61
Pasadena	0.73	0.39
Philadelphia	0.77	0.48
East Chicago	0.73	0.41
Denver	0.95	0.36
Portland, Oregon	0.91	0.82
Elizabeth, N. J.	0.65	0.72

a marked decrease. This kind of information will be useful in evaluating the sources of air pollution within each sampling area but is beyond the scope of this thesis.

When values for organic and elemental carbon (collected in 1975) for several U.S. cities are plotted in a time series (Figures VI.2-5), it is immediately apparent that little, if any, seasonal variation in carbon is seen. Instead, the variation is dominated by sample to sample differences, again perhaps the result of meteorological variations. If the values are divided by the TSP, the sample to sample variation decreases but strong seasonal variations are still not apparent (Figures VI.2-5). These results will be discussed in detail elsewhere (Shah, 1981).

The pyrolysis correction procedure plays an important role in the carbon analysis of ambient samples. Table VI.3 gives the ratios of pyrolytically produced elemental carbon (PEC) to the corrected organic and elemental carbon analysis of several urban sites. Three points are immediately apparent: 1) PEC is a significant fraction of the elemental carbon originally on the filter, 2) the degree of pyrolytic conversion varies greatly from site to site, and 3) the variability of pyrolytic conversion from sample to sample at many of the sites is very large; thus, the correction must be made on a filter by filter basis.

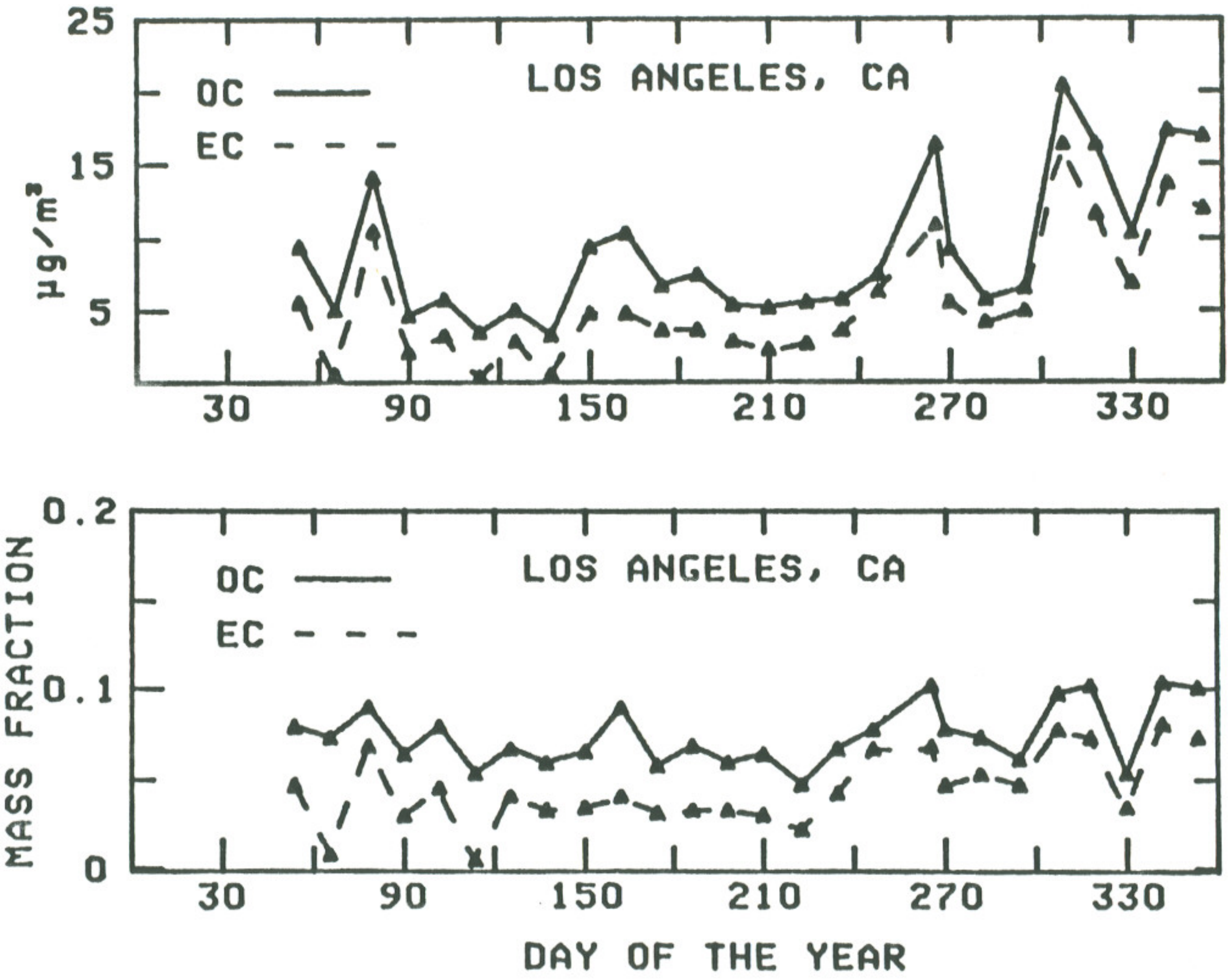


Figure VI.2. Carbon concentration vs. day of the year for Los Angeles (1975).

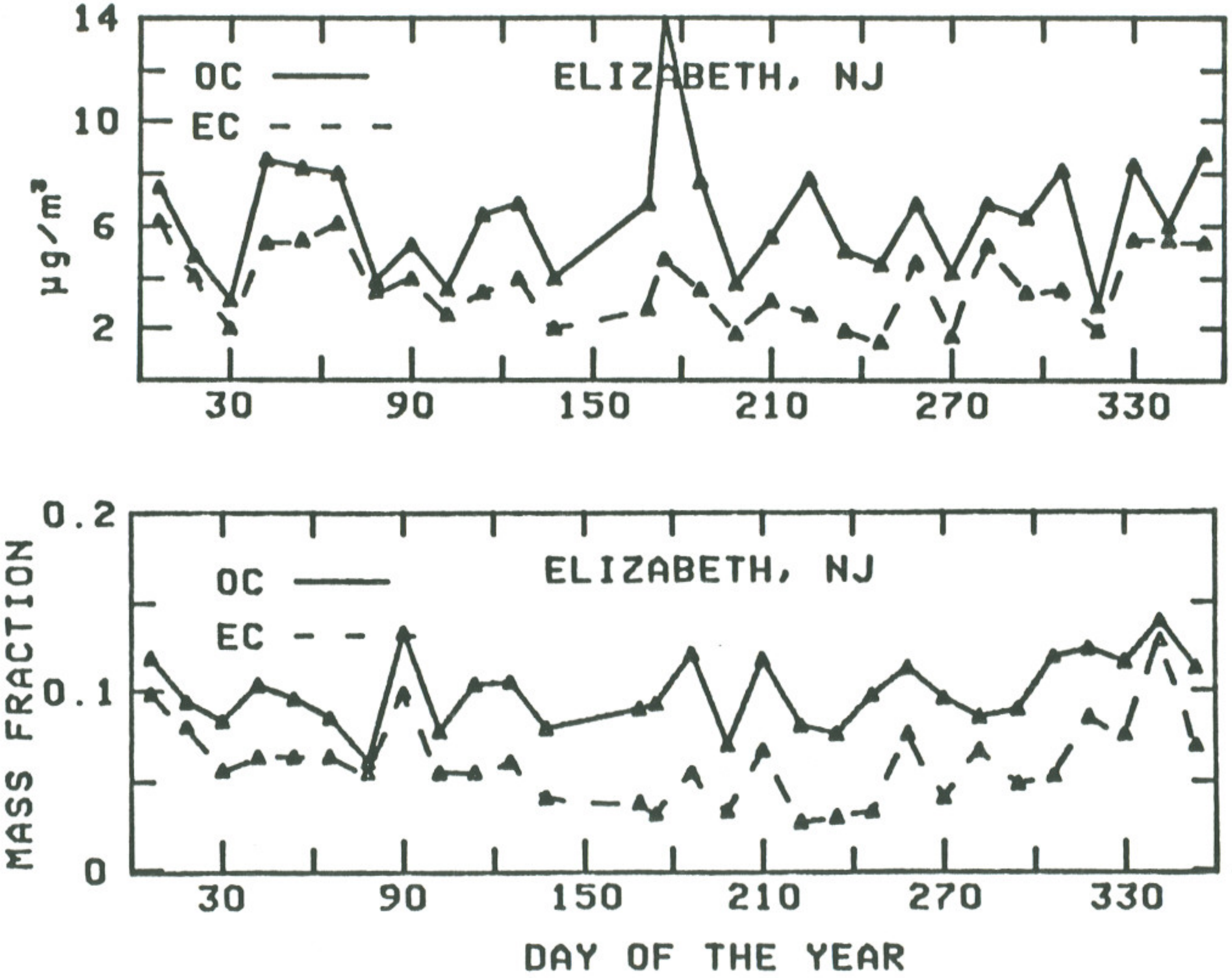


Figure VI.3. Carbon concentration vs. day of the year for Elizabeth, N.J. (1975).

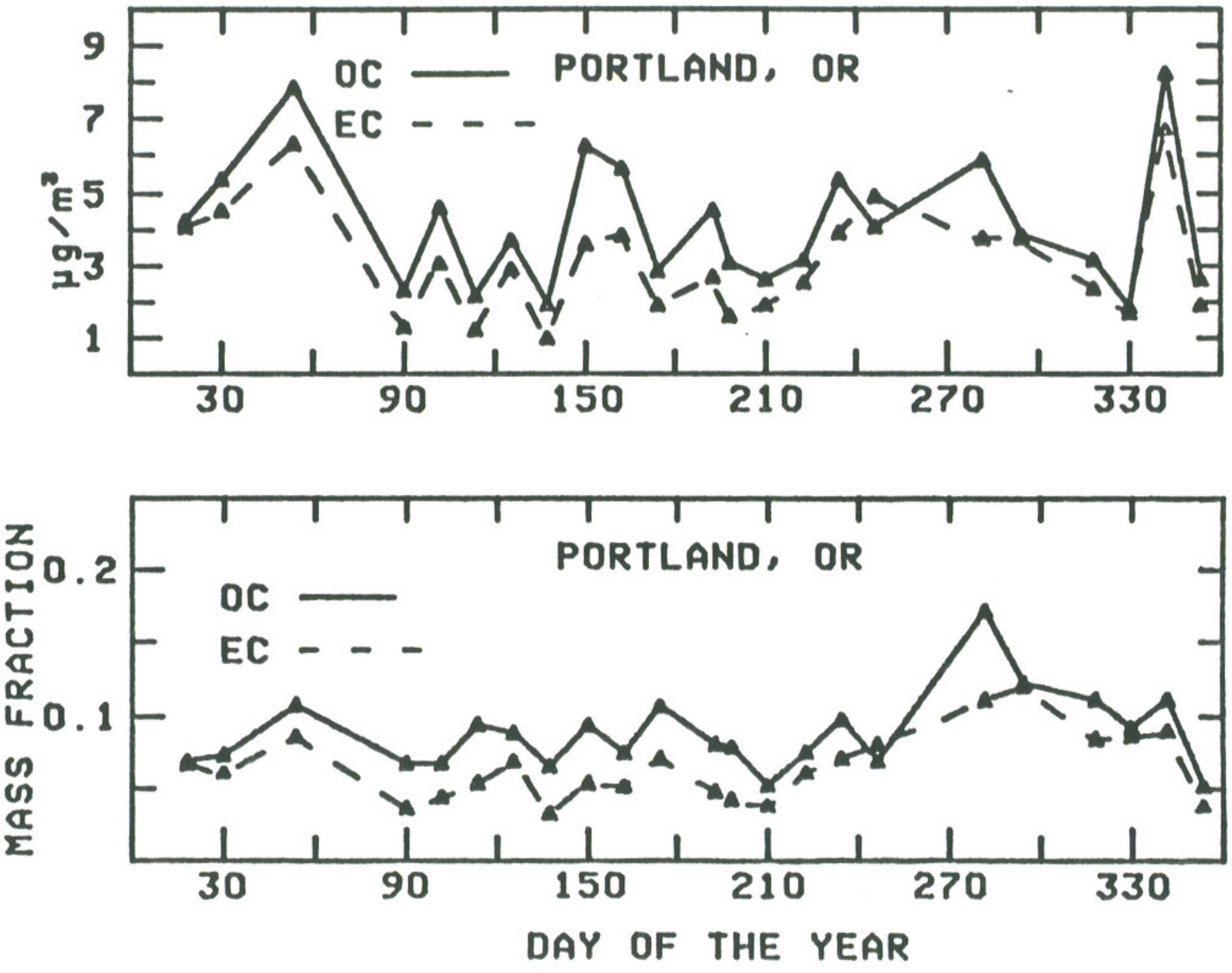


Figure VI.4. Carbon concentration vs. day of the year for Portland, Oregon (1975).

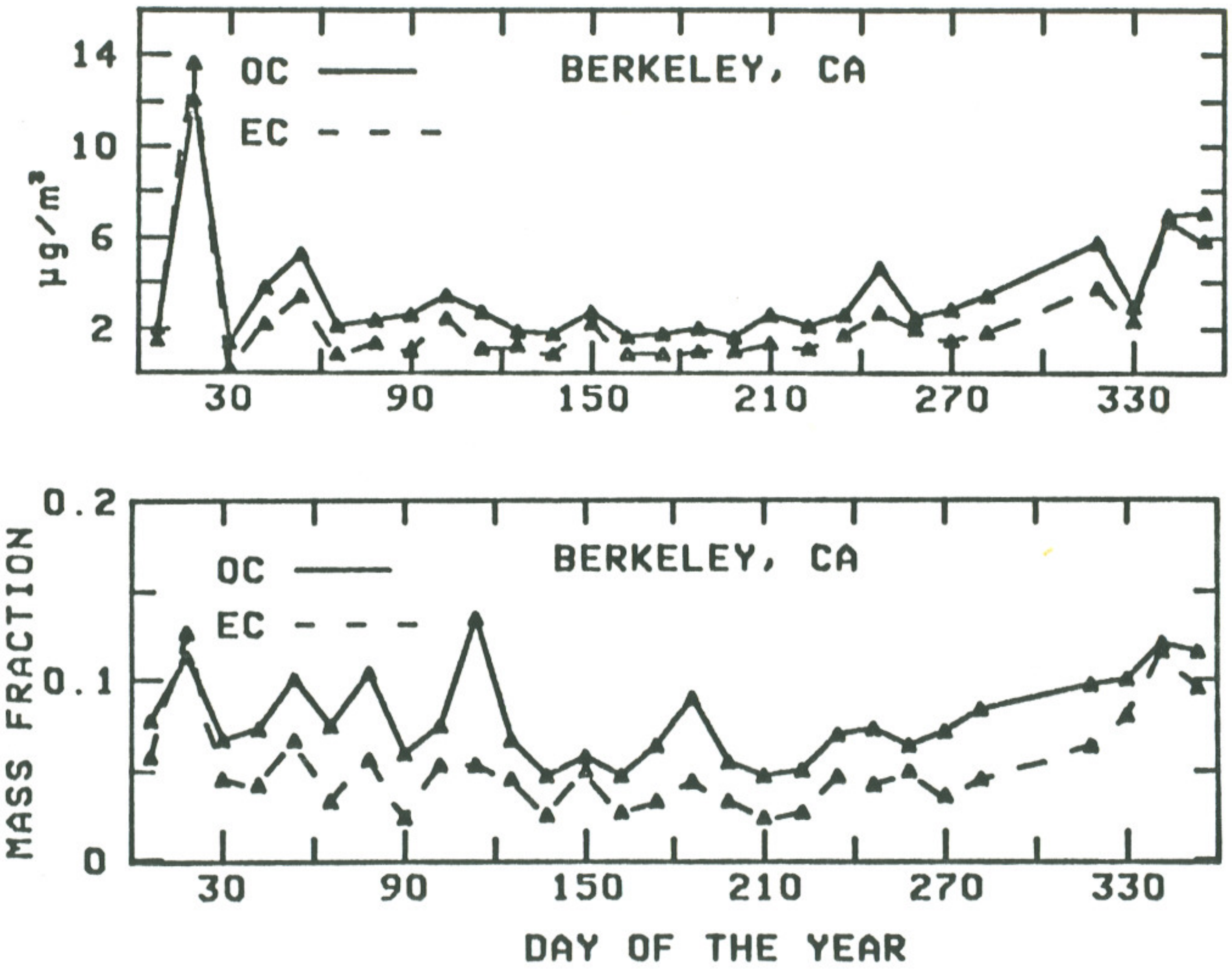


Figure VI.5. Carbon concentration vs. day of the year for Berkeley, Cal. (1975).

Table VI.3.

Ratios of Pyrolytically Produced Elemental Carbon (PEC) to Corrected Organic Carbon (OC) and to Corrected Elemental Carbon (EC)

SITE	PEC/OC	PEC/EC
Elizabeth (N.J.)	0.26 ± 0.15	0.21 ± 0.17
Berkeley (Calif.)	0.21 ± 0.15	0.36 ± 0.30
Los Angeles	0.21 ± 0.20	0.28 ± 0.29
Chicago	0.30 ± 0.14	0.35 ± 0.24
Pasadena	0.19 ± 0.15	0.33 ± 0.26
Philadelphia	0.28 ± 0.13	0.28 ± 0.17
East Chicago	0.34 ± 0.19	0.28 ± 0.20
Denver	0.42 ± 0.18	0.58 ± 0.41
Portland (Ore.)	0.29 ± 0.12	0.34 ± 0.19

Average ± one standard deviation about the mean.

VII. CONCLUSIONS

The purpose of this work has been to develop an instrument and analytical method for the measurement of organic, elemental, and carbonate carbon in filter-collected aerosol. The technique is designed to satisfy several analytical needs which arose out of studies attempting to characterize regional aerosol systems. Principal among these needs is a method which: 1) is rapid, automated, and labor-non-intensive, allowing a large number of samples to be analyzed, 2) provides information compatible in complexity with receptor type air pollution models (i.e., more detailed than the single measurement of total carbon but less complex and labor-intensive than individual compound or compound class analysis); 3) possesses sufficient sensitivity to allow the analysis of samples in the low microgram per cubic meter range for filters on which 1 m^3 of air per cm^2 filter area has been collected; 4) has the ability to analyze samples with large variations in organic and elemental carbon, including samples in which the organic/elemental carbon ratio may vary over a wide range; 5) has the ability to analyze source samples, some of which can contain non-carbonaceous, absorbing material with variable size distribution of the absorbing material. All of these criteria are well satisfied by the thermal/optical method.

The principal innovation of the method is the coupling of thermal and optical techniques in a quantitative manner to allow analysis of a broad range of ambient samples. The synthesis of methods has proved essential in performing this type of thermal carbon analysis because of the pyrolytic conversion of organic to elemental carbon which occurs when carbonaceous aerosol is heated in an inert atmosphere. The optical system continuously monitors the filter reflectance to assess the magnitude of analysis induced changes and to facilitate their correction.

Separation of organic and elemental carbon using the thermal/optical carbon analyzer was compared to elemental carbon analysis using the integrating plate method (IPM) and solvent extraction. Important conclusions are: 1) the thermal/optical and integrating plate methods correlate well over the range 0-30 $\mu g/cm^2$, with the IPM measurements of elemental carbon about 10% lower than the carbon analyzer measurements; 2) measurement of organic and elemental carbon using solvent extraction followed by total carbon analysis (where organic carbon is defined as extractable carbon and elemental carbon as the difference between total carbon on the filter and extractable carbon) seriously over-estimates the mass of elemental carbon and under-estimates the organic carbon; and 3) solvent extraction removes much of the organic carbon which pyrolyzes to elemental carbon during carbon analysis. Comparison of elemental carbon measured on extracted and unextracted filters indicates that the carbon analyzer results are higher than the combined solvent extraction/carbon analyzer results by 10 ± 10%.

The analysis of aerosol samples collected at several sites around the U.S. demonstrates several points pertinent to this work:

1) that elemental carbon represents a large fraction of the total carbon (in some cases more than half of the carbon on the filter), 2) that carbon represents a large fraction of the total aerosol (in some cases more than 25%), and 3) that elemental carbon can or cannot be highly correlated with organic carbon. All samples demonstrate the pyrolysis of organic to elemental carbon during thermal analysis; thus some method of correction (e.g., the optical one used here) is necessary for an accurate separation of organic and elemental carbon.

The goal of this research has been to develop an analysis technique whose measurement of organic and elemental carbon is free from "operational" definitions of organic and elemental carbon. Because of the complexity of the carbonaceous aerosol, this goal has not been fully realized. It has been demonstrated, however, that the method does agree well with other methods of organic and elemental carbon analysis and has the advantages that it is rapid, automated, sensitive, accurate, and able to analyze samples over a wide dynamic range.

Appendix A

SOLVENT EXTRACTION

As previously discussed, the role of solvent extraction in carbon analysis was two-fold. First, because it is a commonly used method of organic and elemental carbon analysis, it was important to compare its analysis to that of the thermal/optical carbon analyzer. Second, in many cases solvent extraction removes a significant fraction of the organic carbon which pyrolyzes during thermal analysis. As a result the organic-elemental speciation becomes more certain because the need for pyrolysis correction has been reduced or in some cases eliminated.

In order to allow analysis of the filter after extraction, it is necessary to preserve the integrity of the aerosol deposit during the extraction. Two procedures were developed for this purpose. All results reported here used an extraction cocktail of 60% benzene-40% methanol (which is essentially the azeotropic mixture). In both procedures a 25 mm diameter filter holder has been used.

A.A. The Modified Soxhlet Procedure

Figure A.1 represents the continuous extractor used in this work. In the traditional Soxhlet extractor solvent is moved from reservoir 2 (where the filter is located) directly to reservoir 1 by siphon action when 2 has filled. In the modified design the filter to be extracted has been moved out of solvent reservoir 2 and placed in the filter holder below reservoir 3. In the modified design solvent

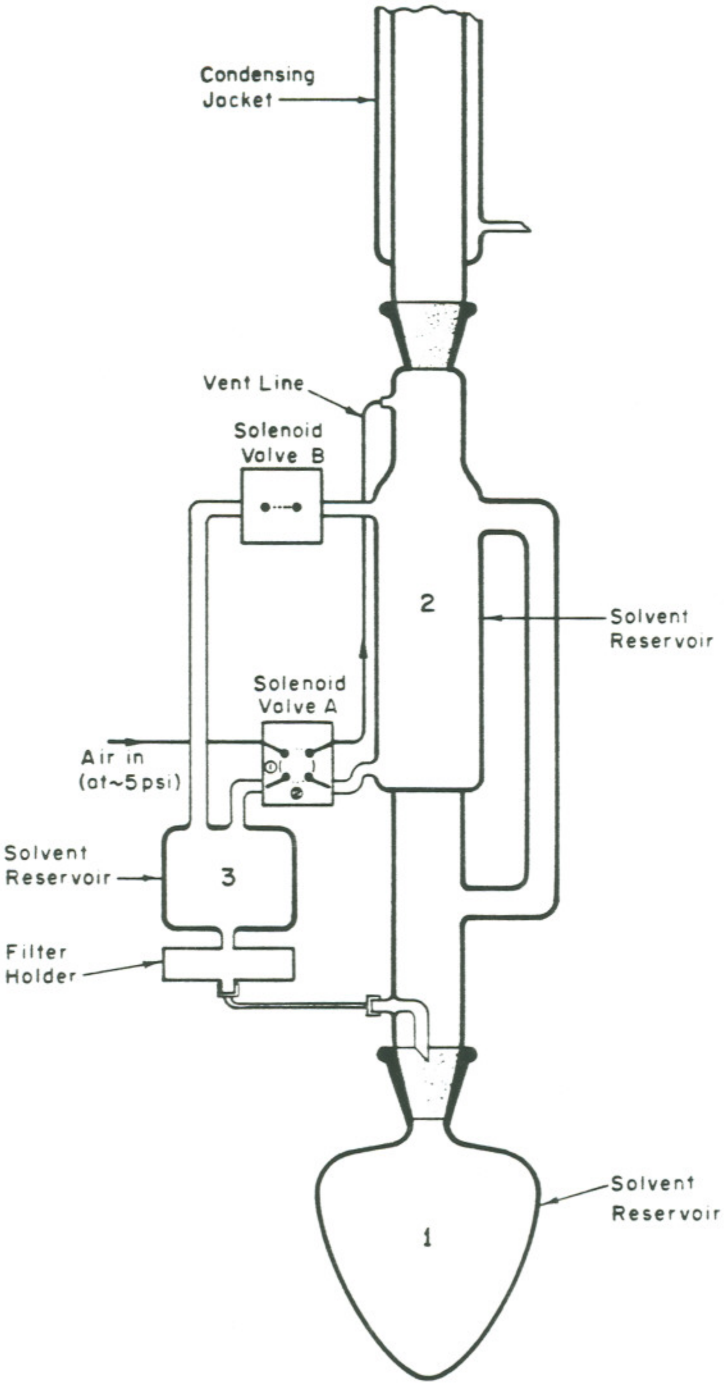


Figure A.1. The modified Soxhlet Extractor.

would not flow back to reservoir 1 because of the resistance posed by the filter. As a result reservoir 3 had to be pressurized with compressed nitrogen with respect to the rest of the system in order to force solvent through the filter.

There are two cycles in the extractor operation: 1) valve B is closed and solvent distills into reservoir 2, and 2) valves A and B are opened and solvent flows from 2 to 3. Upon returning to configuration 1), reservoir 3 is pressurized and solvent is forced through the filter. The current design allows 14 minutes for distilling solvent into reservoir 2 and pushing solvent through the filter and 1 minute for draining 2 into 3. A total of 30 mL of solvent is used in the extractor.

A.B. The Syringe Pump Extractor

As seen in Figure A.2, in the syringe pump procedure the filter to be extracted is mounted on a syringe placed vertically in a constant flow syringe pump (Harvard Apparatus, Inc.). 40 mL of solvent cocktail are forced through at the rate of 0.75 mL/minute. The solvent as well as the filter can be collected and analyzed.

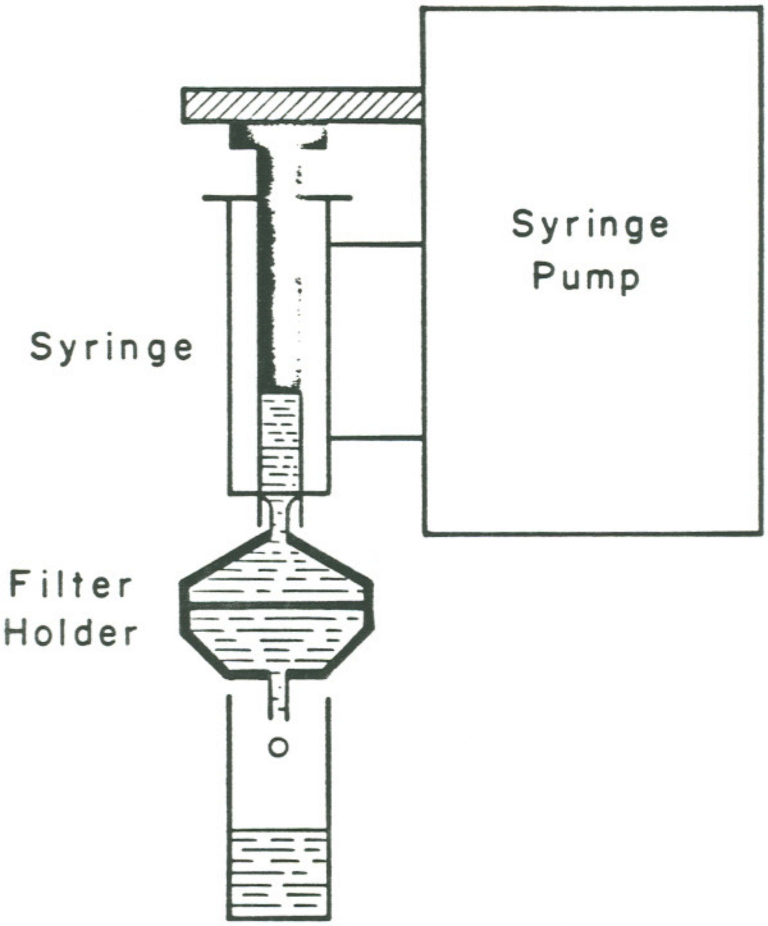


Figure A.2. Syringe pump extractor.

Appendix B

THE INTEGRATING PLATE METHOD

The apparatus designed for making optical absorption measurements on filters is a modification of the procedure first proposed by Lin et al. (1973). As seen in Figure B.1, a 5-mw He-Ne laser is used as the light source and a silicon photocell as the detector. As was originally reported by Lin, the filter was placed deposit-side towards the photocell.

Results from transmission measurements of a series of ambient samples have been compared with an IPM system at the University of Washington, and, as seen in Figure B.2, the agreement between the two is excellent.

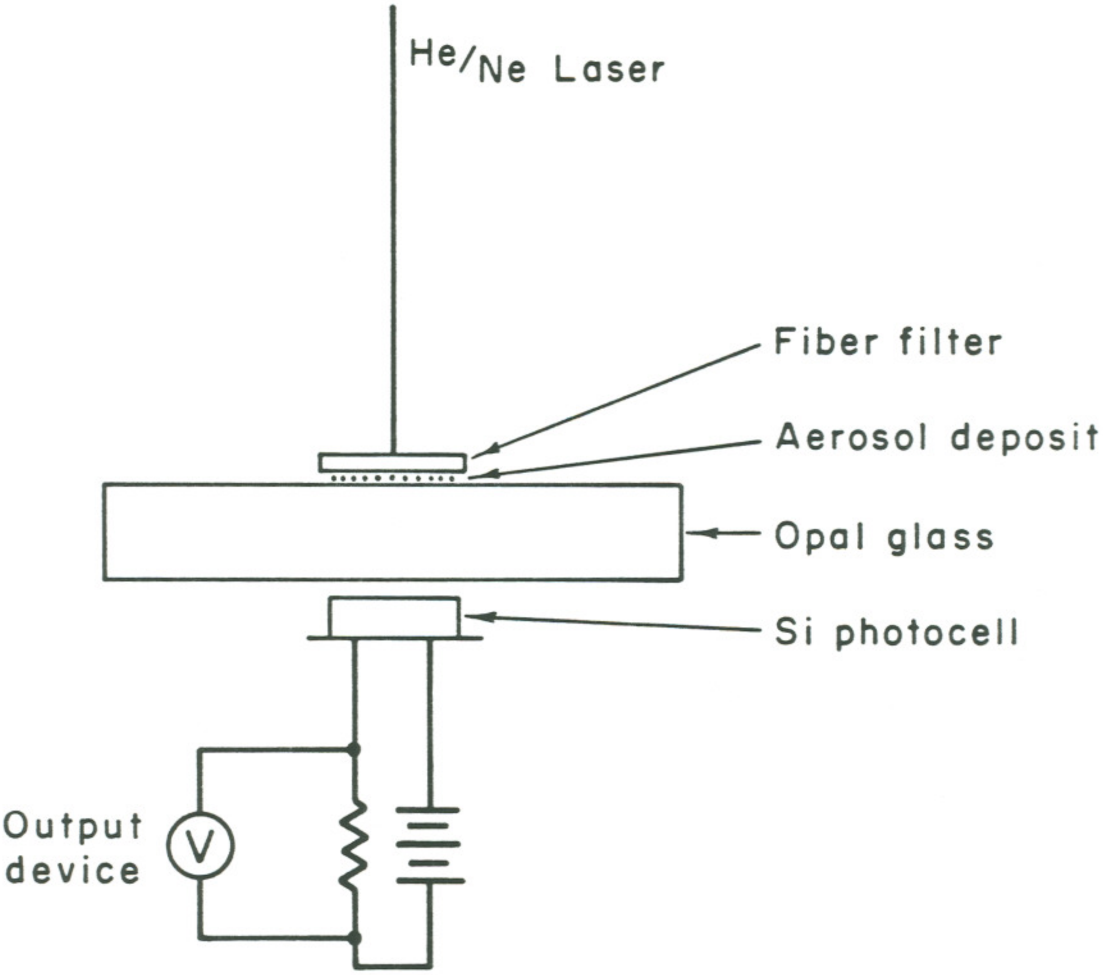


Figure B.1. Integrating plate absorption measurement system.

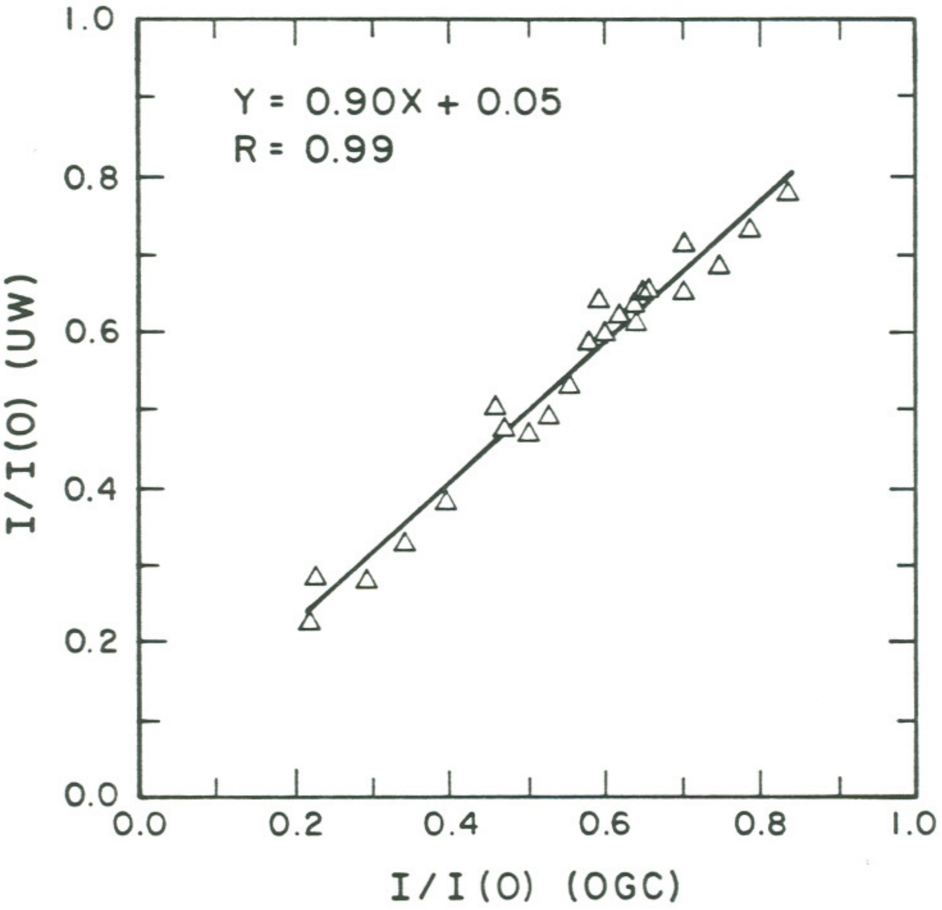


Figure B.2. Absorption measurement comparison: OGC vs. the University of Washington.

Appendix C

ERROR PROPAGATION

The uncertainties for organic, elemental, and total carbon can be estimated with the uncertainty values estimated in Section III.F. This Appendix develops the equations necessary to estimate how uncertainties are propagated through the analysis.

For each peak in a spectrum, the carbon concentration (C) ($\mu g/cm^2$) on the filter is calculated using the equation:

$$C = (\text{integrated area} \times \text{calibration} \times F) - \text{blank subtraction} \qquad (C.1)$$

where calibration is in units of μg C (A/D conversion unit), and F is a correction factor (usually equal to 1.0) which takes into account errors in sample size (the filter cutter taking more or less than 1 cm^2) and non-uniform aerosol deposition on the filter.

The integrated area is the difference of two terms, the total integrated area and the baseline integrated area

$$\text{integrated area} = \text{total integrated area} - \text{baseline integrated area} \qquad (C.2)$$

but the baseline integrated area is independent of the deposit and area ratios. Equation C.1 can be rewritten:

$$C = (TIA \times Cal \times F) - (BIA \times Cal) - Blank \qquad (C.3)$$

where TIA = total integrated area, and BIA = baseline integrated area.

The separation of organic and elemental carbon can be made after the mass of carbon for each peak in the spectrum is calculated.

$$C(OEC) = C3b \times CF$$

where C(OEC) is the mass of elemental carbon originally on the filter, and C3b is the carbon mass associated with peak 3b.

$$C(OC) = (C1 + C2 + C3a) + (1 - CF) \times C(OEC)$$

where C(OC) is the mass of organic carbon and where C1, C2, and C3a are the masses of carbon in peaks 1, 2, and 3a, respectively. CF is the correction factor results from systematic errors in the accuracy of the correction process. From this the uncertainties can be calculated.

Uncertainties for the multiplicative terms can be calculated first. Thus, if the mass of carbon in a peak is

$$C = TA - BA - BL$$

where

$$TA = TIA \times Cal \times F$$

and

$$BA = BIA \times Cal$$

then

$$\sigma_{TA} = (\mathrm{TIA} \times \mathrm{Cal} \times F)\sqrt{\left(\frac{\sigma_{TIA}}{\mathrm{TIA}}\right)^2 + \left(\frac{\sigma_{Cal}}{\mathrm{Cal}}\right)^2 + \left(\frac{\sigma_F}{F}\right)^2}$$

and

$$\sigma_{BA} = (\mathrm{BIA} \times \mathrm{Cal})\sqrt{\left(\frac{\sigma_{BIA}}{\mathrm{BIA}}\right)^2 + \left(\frac{\sigma_{Cal}}{\mathrm{Cal}}\right)^2}$$

The uncertainty in C can now be written

$$\sigma_C = \sqrt{\sigma_{TA}{}^2 + \sigma_{BA}{}^2 + \sigma_{BL}{}^2}$$

(where σ_{BL} is determined experimentally).

In calculating the mass of elemental carbon originally on the filter, C(OEC), the carbon value of peak 3b (C3b) is multiplied by the pyrolysis method correction factor. The uncertainty in C(OEC) can now be written:

$$\sigma_{OEC} = (\mathrm{CF} \times \mathrm{C3b})\sqrt{\left(\frac{\sigma_{CF}}{\mathrm{CF}}\right)^2 + \left(\frac{\sigma_{C3b}}{\mathrm{C3b}}\right)^2 + \left(\frac{\sigma_{EPCF}}{\mathrm{EPCF}}\right)^2}$$

or

$$\sigma_{C(OEC)} = \mathrm{C3b}\sqrt{(0.1)^2 + \left(\frac{\sigma_{C3b}}{\mathrm{C3b}}\right)^2 + \left\{\frac{0.05 \times (\mathrm{C3a} + \mathrm{Ceb})}{\mathrm{C3b}}\right\}^2}$$

where EPCF is the correction factor for random errors in the splitting of peak 3. (It is normally equal to 1.0.)

Uncertainty in the estimation of the mass of organic carbon, C(OC), is based on the equation:

$$C(OC) = C1 + C2 + C3a \times EPCF + (1-CF) \times C(OEC)$$

The uncertainty in the first product term is

$$\sigma_{(C3axEPCF)} = C3a \times \sqrt{\left(\frac{\sigma_{C3a}}{C3a}\right)^2 + \left\{0.05 \times \frac{(C3a + C3b)}{C3a}\right\}^2}$$

If the uncertainty in the term (1-CF) * C(OEC) is set to be $\sigma(C(OEC))$, the uncertainty in organic carbon can be calculated by the equation:

$$\sigma_{C(OC)} = \sqrt{\sigma_{C1}^2 + \sigma_{C2}^2 + \sigma_{C3a}^2 + \left\{0.05 \times (C3a + C3b)\right\}^2 + \sigma_{C(OEC)}^2}$$

The uncertainty in the TC is simply

$$\sigma_{TC} = \sqrt{\sigma_{C1}^2 + \sigma_{C2}^2 + \sigma_{C3a}^2 + \sigma_{C3b}^2}$$

Sampling uncertainty has been assumed to be 10% of the measured quantity. The overall uncertainty is calculated based on the equation:

$$C'(OC) = C(OC) \times SCF$$

$$C'(OEC) = C(OEC) \times SCF$$

$$C'(TC) = C(TC) \times SCF$$

where SCF is the sampling error correction factor (usually 1 ± 0.1). The equations for total uncertainty are thus:

$$\sigma'_{C(OC)} = (C(OC) \times SCF)\sqrt{\left(\frac{\sigma_{C(OC)}}{C(OC)}\right)^2 + \left(\frac{\sigma_{SCF}}{SCF}\right)^2}$$

$$\sigma'_{C(OEC)} = (C(OEC) \times SCF)\sqrt{\left(\frac{\sigma_{C(OEC)}}{C(OEC)}\right)^2 + \left(\frac{\sigma_{SCF}}{SCF}\right)^2}$$

$$\sigma'_{C(TC)} = (C(TC) \times SCF)\sqrt{\left(\frac{\sigma_{C(TC)}}{C(TC)}\right)^2 + \left(\frac{\sigma_{SCF}}{SCF}\right)^2}$$

As part of the quality assurance procedure, a reference filter is analyzed each day and provides a day to day evaluation of instrument operation. These data can be used to estimate the actual uncertainties in the analysis. The uncertainties in repeat analysis should not include sampling error uncertainties or uncertainty in the accuracy in the pyrolysis correction. The equations for uncertainty in repeat analysis are:

$$\sigma''_{C(OEC)} = C3b \times \sqrt{\sigma_{EPCF}^2 + \left(\frac{\sigma_{C3b}}{C3b}\right)^2}$$

and

$$\sigma''_{C(OC)} = (C1 + C2 + C3a) \times \sqrt{\left\{ (\sigma_{C1}^2 + \sigma_{C2}^2 + \sigma_{C3a}^2 + \left[C3a \times 0.05 \times \frac{(C3a+C3b)}{(C1+C2+C3)} \right] \right\}^2}$$

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2. Analysis of Volatilizable and Elemental Carbon in Ambient Aerosols.
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