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DETERMINATION OF ORGANIC CARBON IN ATMOSPHERIC PARTICULATE MATTER BY  
SOLUTION OXIDATION WITH PEROXYDISULFATE

The University of Arizona

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DETERMINATION OF ORGANIC CARBON  
IN ATMOSPHERIC PARTICULATE MATTER  
BY SOLUTION OXIDATION WITH PEROXYDISULFATE

by

Suporn Promyarat

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A Thesis Submitted to the Faculty of the  
DEPARTMENT OF CHEMISTRY  
In partial Fulfillment of the Requirements  
For the Degree of  
MASTER OF ART  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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## ABSTRACT

The concentration of carbon in atmospheric particulate matter collected on both quartz and Teflon filters is determined by a solution oxidation method. Carbon is oxidized in a sealed container at 120°C using peroxydisulfate and the evolved CO<sub>2</sub> is detected by a nondispersive infrared analyzer. For oxidation to take place, a small amount of NH<sub>4</sub>Cl must also be present to "wet" the Teflon material. Studies show that 80%-100% of the total carbon collected on quartz is oxidizable by peroxydisulfate. A high correlation is seen between oxidizable carbon on both quartz and Teflon filter samples collected simultaneously. Despite the good correlation, a lower amount of oxidizable carbon is found on Teflon compared to that obtained from quartz filters. These lower results, however, can probably be accounted for by problems associated with sample collections. Experiments indicate that the adsorption of gaseous organic compounds by quartz fiber filters could account for as much as 7% of the total collected carbon. Additionally, there is evidence that the Teflon filters will not collect and retain large particles as efficiently as quartz filters will.

From these studies, it is concluded that the determination of organic carbon using solution oxidation with peroxydisulfate can provide reliable and useful information about atmospheric particulate matter.

## INTRODUCTION

In the past decade, many studies have been conducted to understand various pollutants in the atmosphere. Suspended particulate matter (aerosols) is known to cause various adverse effects such as decreasing visibility and increasing human health hazard (Williamson 1973). Many techniques of analyzing atmospheric particulate matter have been developed with the ultimate goal of understanding the aerosol formation processes and their behavior in the atmosphere. Recent studies have indicated that the light elements, C, N, O and S, account for a majority of the mass in particulates whose size is less than 3  $\mu\text{m}$  aerodynamic diameter (AD). It is the less than 3  $\mu\text{m}$  particles (i.e., fine particles) which are the most effective light scattering centers and which penetrate to the deeper sections of the respiratory tract. Thus, they are of primary concern in air pollution related work. While a great deal of information about sulfate and nitrogen species ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ) in the particulate matter has been obtained in recent years, information about carbon and various organic compounds is at best incomplete.

During the past five years, low volume aerosol collection systems using a Teflon membrane as a sample collection matrix have become increasingly popular in air pollution research programs. Teflon filters are essentially chemically inert and are well suited for the multi-element analysis technique of x-ray fluorescence. Obviously, the determination of carbon containing species on the low volume Teflon filters is

complicated by carbon matrix and the small amount of collected sample (typically 0.5-1.0 mg).

At the present, a convenient, fast and inexpensive method for the determination of carbon or total organic matter is high temperature combustion in an oxygen atmosphere (Patterson 1973). A temperature of approximately 950°C is sufficient to convert all carbon present in a sample to CO<sub>2</sub>. Because of the high temperature, this technique can be used only with inorganic collection substrates such as glass and quartz filters which contain only traces of carbon. Deuteron activation analysis has also been used to determine total carbon in atmospheric aerosols (Clemson et al. 1980). This is a nondestructive method which can be used for detection of other light elements as well as carbon. However, carbon-containing collection substrates such as those made of Teflon are unsuitable for sample collection. Macias and coworkers (1978) determined C, N and S composition in aerosol samples collected on quartz fiber filters using proton induced  $\gamma$ -ray analysis. Their results for carbon on fine particle filters were obtained with a precision of 5%. However, an average difference of about 16% was found between the combustion and proton induced  $\gamma$ -ray method. The determination of carbon by the  $\gamma$ -ray method also requires the use of non-carbon matrix collection substrates.

In addition to the techniques used for total carbon analysis, light absorption measurements have been used to estimate the elemental carbon (or "soot") present in aerosol samples (McLaine 1980). However, this procedure presents problems since it is generally based on the assumption that carbon is the only photon absorbing species in the samples.

Additionally, the mass absorption coefficient of "soot" is not known precisely, and the effective pathlength through a generally reflective and highly scattering substrate is uncertain and difficult to measure. Various extraction methods have also been used to determine organic carbon present in atmospheric particulate matter. Twenty-six solvents and 24 binary mixtures were studied for their abilities to extract organic components in aerosol samples (Grosjean 1975). This study indicated that binary mixtures or successive extraction, using a polar and nonpolar solvent, extracted the maximum amount of organic material. Only 50% of the total extractable organic carbon was obtained by the commonly used benzene extraction procedure. Cadle and Groblicki (1980) used solvent extraction, nitric acid digestion and pyrolysis to remove organic carbon in aerosol samples. This study showed that nitric acid digestion and heating in air at 350°C removed about 70% of the carbon while 55% carbon removal was obtained by the most effective solvent (4:1 benzene-ethanol).

Another method, wet oxidation with peroxydisulfate, is used for the determination of organic carbon. This technique is based on the measurement of CO<sub>2</sub> released from the oxidation of carbon by potassium peroxydisulfate at an elevated temperature. A nondispersive infrared analyzer is used for detection of CO<sub>2</sub> released from the oxidation process. This technique has been routinely applied to oceanographic studies of dissolved organic material and particulate matter in seawater (Menzel and Vaccaro 1964, Mills and Quinn 1979). Hoffman and Duce (1974) used this method to study the organic carbon content of marine aerosols from the Bermuda coast.

In this paper, the determination of carbon by the wet oxidation method for urban aerosol samples is discussed. The purpose of this study is to develop an easy, sensitive method for the analysis of organic carbon contents in aerosol samples. Additionally, this paper focuses on the organic carbon determination of aerosol samples collected on inert Teflon filters since present carbon measurement methods prohibit Teflon filter use because of matrix interference. Slight modifications of the wet oxidation procedures described in the literature are made to measure organic material in aerosol samples collected on the hydrophobic Teflon filters. It is demonstrated that such measurement when applied to aerosol samples collected with Teflon filters can obtain useful and reproducible information about the organic carbon content of suspended particulate matter. It should be pointed out that although this method is widely used for the analysis of dissolved organic carbon, the oxidation efficiency of peroxydisulfate is controversial. Some workers have reported that the oxidation efficiency of peroxydisulfate may be as low as 50% for certain types of samples and compounds. The study by Menzel and Vaccaro (1964) indicated that 100% recovery was found for a series of organic compounds (primarily aliphatic acids, amino acids and sugars) dissolved in seawater. Since the carbonaceous species present in atmospheric particulate matter are very complicated (ranging from low molecular weight species to large, perhaps polymeric compounds to a graphite type material), this method (wet oxidation) may not necessarily be a measure of the total organic carbon. This work is undertaken with the hypothesis that operationally, one can define the carbon measured by this method as "reactive or oxidizable carbon".

## EXPERIMENTAL

### Apparatus

A commercial total carbon analyzer (Oceanography International Corporation, College Station, Texas) was employed for carbon analysis in this work. The apparatus consists of two individual units: the ampule purging-sealing system and the analyzing system. In the purging-sealing unit,  $O_2$  is used following sample acidification to remove atmospheric  $CO_2$ ,  $HCO_3^-$  and  $CO_3^{=}$  present in the samples. An oxy-propane microburner attached to this unit provides for fast ampule sealings immediately after purging. The analyzing unit consists of a device for breaking the ampules, a nondispersive infrared analyzer and a digital integrator. A  $N_2$  carrier gas is swept through the breaking assembly. Drying tubes (containing magnesium perchlorate) are used to remove water before the sample stream enters the nondispersive IR analyzer where the  $CO_2$  is measured.

Total carbon is measured by high temperature combustion using a modified Perkin-Elmer Model 240 elemental analyzer. A strip of quartz fiber filter was combusted in the oxygen atmosphere at  $950^\circ C$  and carbon was converted to  $CO_2$ .

Doubly distilled-deionized water and reagent grade chemicals were used throughout this work.

### Sample Collection

In order to investigate the peroxydisulfate oxidation efficiency for actual particulate matter, a series of samples was collected on quartz fiber filters using a standard high volume sampler filled with an Anderson Size Selective Inlet (SSI). The SSI collects particulate matter on 20 cm by 25 cm quartz fiber filters and theoretically limits collected particle size to less than 15  $\mu\text{m}$  AD. The sampler was operated at a flow rate of 50-70  $\text{m}^3/\text{hour}$  for a period of 24 hours. Sample collection was done on the roof of a one-story building of the University of Arizona Campus, Tucson, Arizona.

In addition to the above-mentioned system, special sampling systems were set up to collect total suspended particulates simultaneously on a Teflon membrane filter and a quartz fiber filter. The filters were circular with an approximate diameter of 37 mm. The 37 mm filter holders were hung upside-down about 2 feet above the roof and the pumps, and were connected to low volume sampling pumps ( $\sim 1\text{m}^3/\text{hour}$ ) with gum rubber hoses. These samples were collected for a period of 12-24 hours.

### Sample Preparation

The 20 cm by 25 cm quartz filter samples were folded in half and the sample section was cut with a cork borer of 5 mm diameter. This particular size was selected because the cut sections fit conveniently into ampules used in the procedure. For the low volume samples, a 1.22 cm (diameter) borer was used and the cut pieces were carefully folded and inserted in the ampules containing 0.4 g  $\text{K}_2\text{S}_2\text{O}_8$ , followed by the addition of 0.5 ml of 10%  $\text{H}_3\text{PO}_4$  and 5 ml distilled-deionized water. The ampules

were purged with  $O_2$  for three minutes to eliminate atmospheric  $CO_2$  and the  $CO_2$  that evolved from acidification of  $HCO_3^-$  and  $CO_3^{2-}$  in the sample. After purging, the ampule was capped with aluminum foil and sealed immediately with the microburner.

In order to cut a section from a Teflon filter, the Teflon filter was placed on top of a piece of glass fiber filter. Then both filters were cut by applying pressure with a cork borer. The Teflon section was gently peeled from the glass filter and inserted into the ampule. In a given ampule, 0.5 ml of 0.5 M  $NH_4Cl$  and 0.5 ml of 10%  $H_3PO_4$  were added. Approximately 0.4 g of  $K_2S_2O_8$  was placed into each ampule. Finally, 4.5 ml water was added. The ampule was purged with  $O_2$  for 3 minutes, capped with aluminum foil, and immediately sealed with the microburner.

The ampules containing the prepared samples were heated in a pressure vessel at  $120^\circ C$  for 3 hours to oxidize the organic material in the sample to  $CO_2$ . After the pressure vessel was cool, the ampules were removed and placed into the breaking assembly of the analyzing unit. The ampules were then broken and a flow of  $N_2$  was used to sweep the generated  $CO_2$  to the detector cell. The signal was monitored by a digital integrator.

For preparation of standard calibration curves, sodium carbonate was acidified with  $H_3PO_4$  to generate known quantities of  $CO_2$ . Sucrose of known concentration was run with each set of filters to provide checks of the oxidation efficiency.

## RESULTS AND DISCUSSION

### Oxidation Efficiencies

The oxidation efficiency of organic compounds by  $K_2S_2O_8$  depends on the rigidity of the organic compounds. In past work, sugars and organic acids were shown to be completely oxidized by this technique (Menzel and Vaccaro 1964). The oxidation of those compounds was successfully reproduced in this work. However, by using a more extensive set of test compounds, it was shown that some organic compounds could not be totally oxidized, and some could not be oxidized at all with this procedure. Table 1 lists the percent recovery obtained for various test compounds. For the non-polymeric substances tested in this work, complete oxidation was achieved using the described procedure. Polystyrene and polyaromatic-ether-ketone sulfone are polymeric substances which could not be oxidized by this method. Graphite was also found to be resistant to oxidation. For the National Bureau of Standard (NBS) reference samples such as urban particulate matter and orchard leaves, it was found that the efficiency of wet oxidation ranged from 60% to 70% of that measured by combustion. Only 2% of inorganic carbon ( $HCO_3^-$ ,  $CO_3^{=}$ ) was seen upon acidification of the urban particulate standards with  $H_3PO_4$ .

From Table 1, it is clear that the efficiencies of organic substances fell in a wide range depending on the type of compounds undergoing oxidation by this procedure. The carbon measured from readily oxidizable compounds such as sugars and organic acids yielded about 100%.

Table 1. Organic Carbon Oxidation Efficiencies for Several Organic Compounds and Reference Samples.

Sample	% Recovery
Benzoic acid	101.4±0.2
Malic acid	99.4±0.3
Oxalic acid	97.9±8.2
Carminic acid	100.7±5.9
Brucine	100.6±4.2
Sucrose	104.4±2.2
KHP (on quartz filters)	96.4±1.6
Graphite	<2.0
Polystyrene	<2.0
Polyaromatic ether-ketone-sulfone	<2.0
NBS Urban Particulate (SRM No. 1648)	73.1±3.5
NBS Urban Particulate (SRM No. 1649)	58.9±0.3
NBS Orchard Leaves (SRM No. 1571)	58.3±4.7

Further, less than 2% of the carbon in polymers and graphite is oxidizable by this procedure. Based on these trends, it was decided that a useful measurement of oxidizable organic carbon on Teflon filters should be possible.

#### Wet Oxidation of Particulate Carbon Collected on Quartz Filters

The results obtained for oxidizable carbon aerosol samples collected on quartz fiber filters are presented in Table 2. The measured carbon content ranged from 80% to 100% of the corresponding total carbon measured by high temperature combustion on a duplicate sample. These data indicate that the organic carbon present in these particulate matter samples is largely oxidizable. The relationship between total carbon and oxidized carbon is shown in Figure 1. Explicitly, a high correlation coefficient ( $r=0.92$ ) was obtained and a slope of 0.86 implies that on the average, approximately 86% of the total carbon in the aerosols is oxidizable organic material. Thus, for these described samples the aerosol carbon measured by this method represents the majority of organic carbon present.

Since the total carbon measurement by combustion also measures inorganic carbon (wet oxidation eliminates  $\text{CO}_3^{=}$ ,  $\text{HCO}_3^-$  in the preparation step), estimates of this carbon component were made by measuring the  $\text{CO}_2$  evolved upon acidification of several aerosol samples on quartz filters. These experiments showed that the inorganic carbon of the samples employed in this study ranged from 5% to 10% of the total and to be on average of 7%. These data then imply that the wet oxidation procedure will oxidize approximately 90% of the non-carbonate carbon associated with the atmospheric aerosols investigated in this study.

Table 2. Oxidizable and Total Carbon Determined in Aerosols Collected on Quartz Filters.

Sample Number	Total Carbon ( $\mu\text{g}/\text{cm}^2$ )	Oxidizable Carbon ( $\mu\text{g}/\text{cm}^2$ )	Ratio $\frac{\text{(oxidizable)}}{\text{(total)}}$
539A	29.7	25.3	0.85
540A	22.9	22.2	0.97
541A	23.9	19.5	0.82
542A	29.5	29.7	1.01
543A	41.6	31.3	0.75
544A	39.2	36.6	0.93
545A	41.1	37.1	0.90
546A	36.1	33.7	0.93
547A	30.1	25.7	0.85
1	50.8	50.3	0.99
2	43.9	46.2	1.05
3	45.1	37.0	0.82
4	43.0	39.9	0.93
5	30.2	29.5	0.98
6	53.9	46.7	0.87
7	25.6	22.1	0.86
8	29.5	28.0	0.95
9	38.0	31.3	0.82
10	28.0	29.6	1.06
11	8.6	10.0	1.16
12	52.6	42.1	0.80
13	22.2	24.2	1.09
14	20.8	19.3	0.93
15	29.1	19.7	0.68
16	20.3	20.4	1.00
17	20.8	17.9	0.86

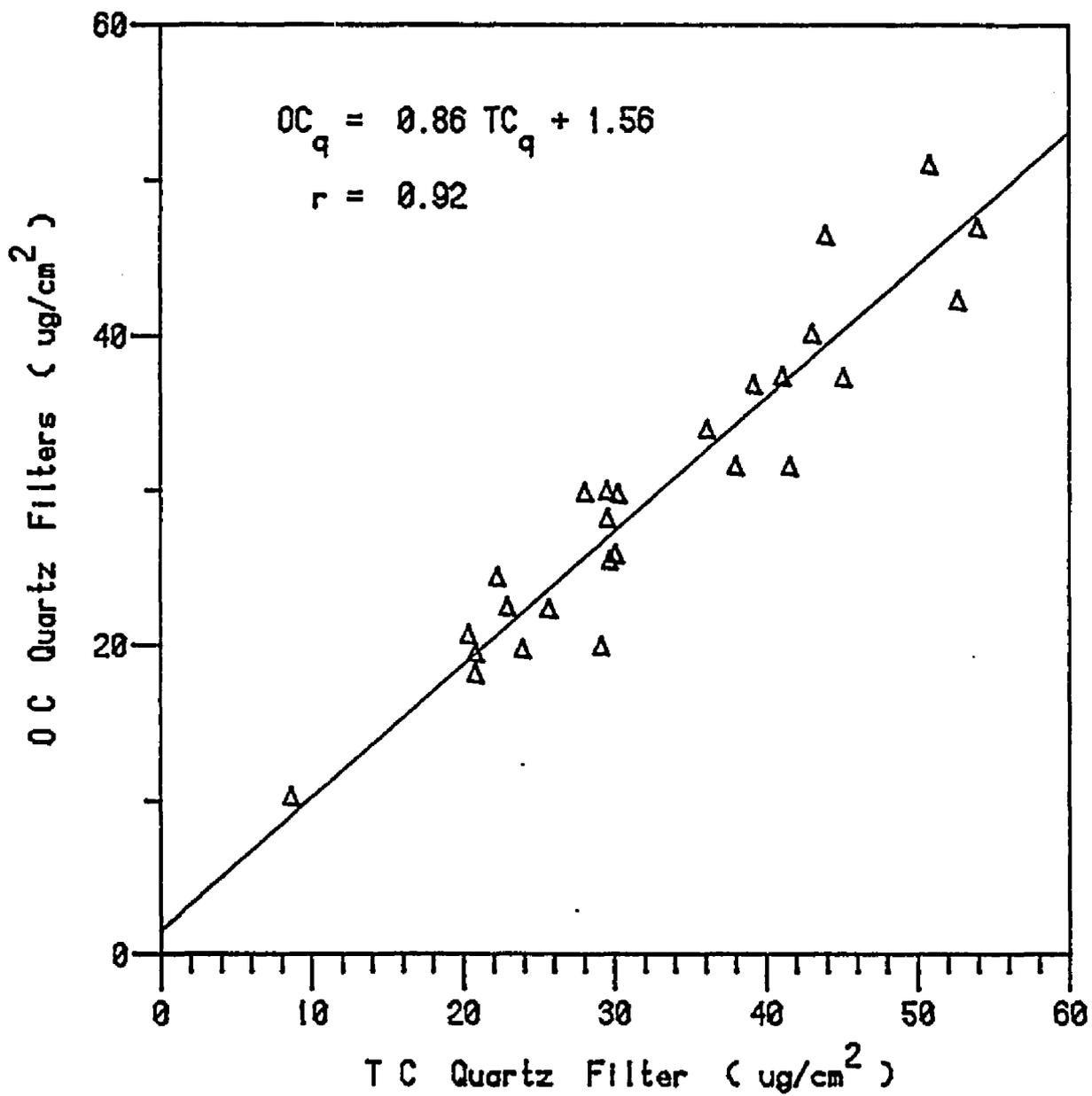


Figure 1. Total Carbon Versus Oxidizable Carbon for Samples Collected on Quartz Filters.

Many currently used procedures for measuring carbon in atmospheric particulate matter attempt to classify this carbon as "organic" and "soot" (this is also often referred to as "elemental" or "graphitic" carbon). The methods employed for this classification included differential thermal technique (Cadle and Groblicki 1980), combustion resulting in differences before and after extraction (Pierson and Russell 1979, Pimenta and Wood 1980), and light absorption measurements (Rosen et al. 1978). It was originally anticipated that the wet oxidation procedure discussed here would provide this same type of distinction. However, it was observed that the filters (which are grey to black from the "soot") was highly discolored after peroxydisulfate oxidation. This indicated that the dark soot-like material in these samples is much more susceptible to oxidation than is graphite. This finding has important atmospheric science implications since it has been suggested that "soot", because of its resistance to oxidation, may accumulate in the stratosphere or at the poles. Since its optical properties may possibly influence the earth's radiation balance, the "soot" may have an effect on global climate. The oxidation of "soot" in the atmosphere may proceed at a rate fast enough to influence its average atmospheric residence time. The more efficient than expected oxidation by peroxydisulfate probably results from a combination of surface area (soot particles are reported to be 50-100 Å in diameter) and chemical structure effects.

Additional evaluation of this procedure was performed by participating in a carbon measurement method intercomparison study conducted by General Motors Research Laboratories (Cadle and Groblicki 1982).

Wet oxidation was used for the determination of "organic" carbon while high temperature combustion provided total carbon measurements for High Volume filter samples collected in Warren, Michigan. A KHP standard (on quartz filter) and a National Bureau of Standard Urban Particulate (SRM No. 1648) were also analyzed by the participants in this program. Table 3 contains the results obtained from wet oxidation and combustion of such samples. The average of "organic" carbon (total carbon less soot as previously defined) determined by 10 laboratories is shown. Differential thermal analysis techniques were used by most participants while one of the participants used toluene-n-propanol and oxygen-saturated o-dichlorobenzene to extract organic components. In this study, it was found that oxidation by peroxydisulfate gave higher results for "organic" carbon than did the various other methods. The carbon oxidized by peroxydisulfate on filter samples was 29% higher than the average results obtained from the alternative methods for determining "organic" carbon. The peroxydisulfate procedure gave about 15% higher results for organic carbon in the NBS Urban Particulate compared to other methods. Wet oxidation of the KHP standard which contained only organic carbon, yielded essentially the same results by all methods used in this intermethod comparison. These data and the previously discussed observation on "soot" discoloration suggest that the wet oxidation technique can operationally be defined as a procedure for measuring "oxidizable organics" in atmospheric particulate matter.

Several sets of quartz filter samples were analyzed in replicate over several weeks. Results from these experiments showed the sample to sample variation to be about 5%. The day to day relative standard

Table 3. Comparison of Peroxydisulfate Oxidation Results with Total Carbon, and Organic Carbon Determinations in the General Motors Intermethod Comparison of Aerosol Carbon Measurement Techniques.

	Hi-Vol 1 ( g/cm )	Hi-Vol 2 ( g/cm )	Hi-Vol 3 ( g/cm )	KHP ( g )	NBS Particulate No. 1648 ( g )
Oxidizable Organic Carbon (wet oxidation)	19.7±3.4	46.7±3.2	68.5± 2.8	28.1±0.5	9.5±1.3
Organic Carbon (average from 10 labs)	17.8±4.9	34.0±6.5	49.3±11.6	30.4±3.8	8.4±2.1
Total Carbon (combustion)	25.7±0.3	54.1±2.8	87.8± 0.6	29.2±1.2	14.3±0.1
Total Carbon (average from 11 labs)	27.0±8.0	53.4±3.9	79.8±13.8	32.4±5.9	14.1±1.2
<u>Oxidizable Organic Carbon</u> Organic Carbon	1.11	1.37	1.38	0.92	1.13

deviation for this technique was found to be 10%. An average blank value of  $7.4 \pm 1.4 \mu\text{g}/\text{cm}^2$  was found in wet oxidation of quartz filters. If the detection limit is defined to be twice that of the standard deviation of the blank value, this technique gives a detection limit of  $3.0 \mu\text{g}/\text{cm}^2$  for quartz fiber filters. For a typical high volume filter samples, this corresponds to an atmospheric particulate carbon concentration of about  $0.5 \mu\text{g}/\text{m}^3$ .

#### Wet Oxidation of Teflon Filter Samples

Due to the hydrophobic behavior of Teflon filters, wet oxidation is not successful when such filters are treated in the same manner as described for the quartz filters. The nonreactivity was indicated by negligible  $\text{CO}_2$  production and no visible change in the color of the sample on the filter. Various approaches were attempted to solve the flotation problem associated with Teflon-water interactions. Organic solvents are known to lower the surface tension between Teflon and water. However, an organic liquid may not be used to wet Teflon samples since carbon is being determined. Stevens et al. (1978) indicated that dilute perchloric acid improved the extraction of inorganic ions from Teflon filters over that obtained with distilled water. Perchlorate and several other inorganic ions were studied to determine if the water-Teflon interfacial tension could be lowered to allow better contact between the sample and the oxidizing solution. In these experiments, it was found that when  $0.5 \text{ M NH}_4\text{Cl}$  was added to the oxidizing solution, samples oxidized with  $\text{NH}_4\text{Cl}$  showed sample discoloration and increased  $\text{CO}_2$  production compared to that obtained when  $\text{NH}_4\text{Cl}$  was not in the

solution. The samples, however, would still float which indicated that there was still a relatively high interfacial tension between the solution and the filter. Apparently, interfacial tension between the Teflon filter and the oxidation solution containing  $\text{NH}_4\text{Cl}$  is low enough to allow the solution of  $\text{K}_2\text{S}_2\text{O}_8$  to permeate to the particles. Consequently, wet oxidation can take place while Teflon samples are still floating on the solution surface if the particle layer is in contact with the  $\text{K}_2\text{S}_2\text{O}_8$  solution. Additionally, it was found that the process was most efficient when 0.5 M  $\text{NH}_4\text{Cl}$  was added to the Teflon filter prior to the addition of the oxidizing components ( $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{O}$ ).

Table 4 presents data from the wet oxidation of both quartz and Teflon filters collected in parallel (a subset of the previously described samples). Apparently, less carbon was oxidized on the Teflon filters than on the corresponding quartz filters. The relationship between oxidizable carbon found on Teflon filters versus quartz filters is shown in Figure 2. The least square regression fit line for these sample pairs gives a slope of 0.51. Initially, this suggests that oxidizable carbon found on Teflon filters is only about half of the oxidizable carbon determined on quartz filters. Despite this discrepancy, there is a very good correlation ( $r=0.93$ ) between oxidizable carbon on both quartz and Teflon filters. There are at least two factors associated with sample collection that may contribute to the discrepancy between the results obtained for the two types of filters. The special systems set up for the simultaneous collection of particles on both quartz and Teflon filters were sampling systems with 37 mm filter holders placed in an inverted position. Since the filters were hanging up-side down, it is

Table 4. Solution Oxidation with Peroxydisulfate of Aerosol Samples Collected Simultaneously on Quartz and Teflon Filters

Sample	Oxidation	
	Quartz ( $\mu\text{g}/\text{cm}^2$ )	Teflon ( $\mu\text{g}/\text{cm}^2$ )
1	50.3	28.7
2	46.2	21.1
3	37.0	25.6
4	39.9	22.8
5	29.5	16.9
6	46.7	27.8
7	22.1	18.4
8	28.0	15.6
9	31.3	18.7
10	29.6	15.8
11	10.0	4.2
12	42.1	26.0
13	24.2	15.5
14	19.3	12.5
15	19.7	17.0
16	20.4	17.5
17	17.9	13.5

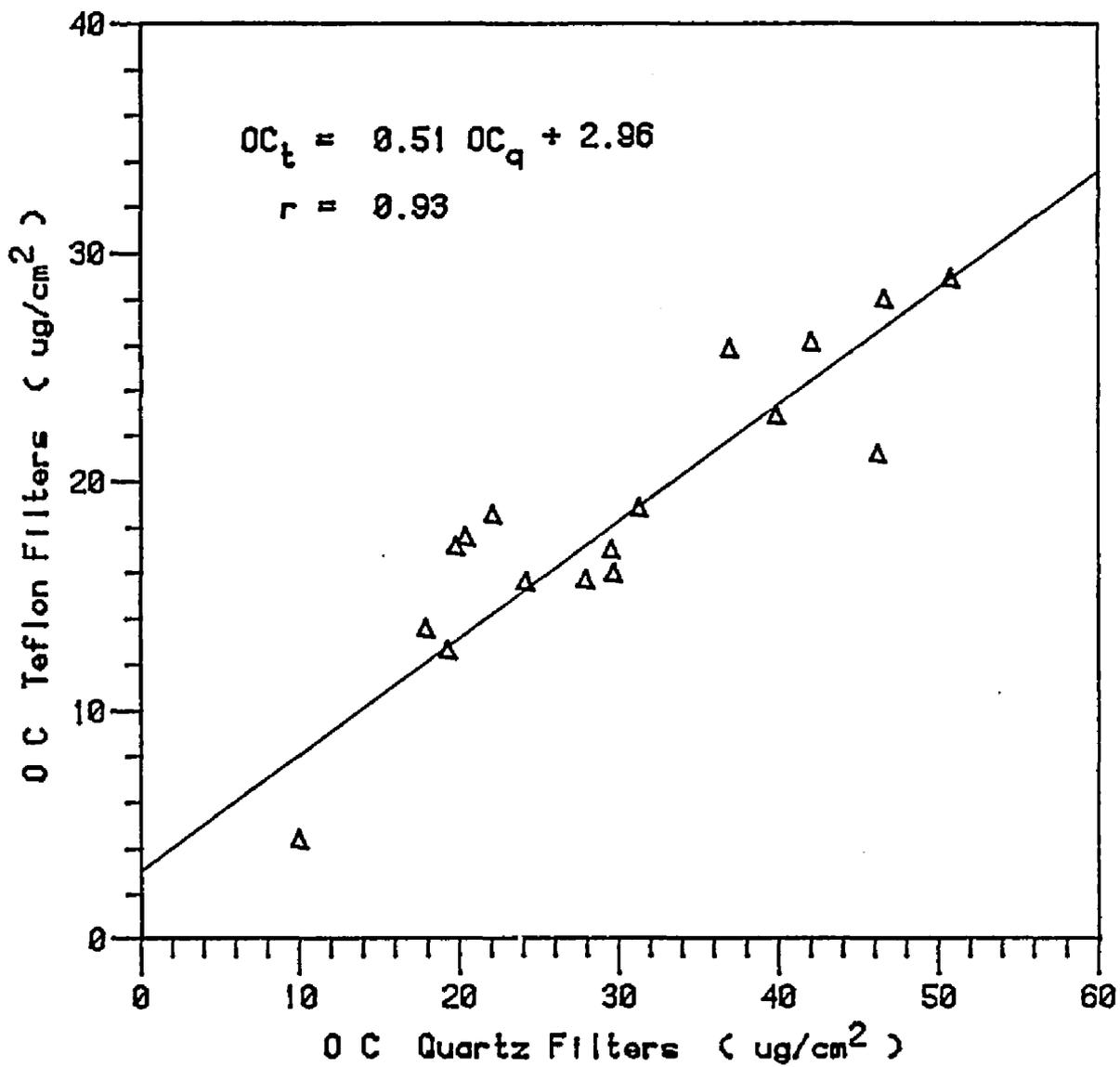


Figure 2. Oxidizable Particulate Carbon on Quartz Versus Oxidizable Particulate Carbon on Teflon Filters.

suspected that large particles may not be collected with equal efficiencies on the two types of filters. Large particles may penetrate the fibrous quartz and be trapped while they bounce off or not adhere to the smooth Teflon membrane filters. Teflon filters were designed primarily for collection of small particles (less than 10  $\mu\text{m AD}$ ). Therefore, they may not efficiently collect large particles. For this reason, there may be less organic particles collected on Teflon filters. The second factor is due to the adsorption of gas-phase organic compounds on quartz fiber filters during sample collections. A special test was performed by collecting series of samples with 2 quartz filters in series. These samples showed that 5%-10% of total carbon collected on the quartz filter was apparently artifact carbon from the adsorption of gas-phase organic compounds by the filter surface.

Replicate analysis of Teflon filter samples gives a relative precision of 10%. Teflon blank filters were analyzed for carbon and the average of  $3.5 \pm 1.1 \mu\text{g/cm}^2$  was found. The detection limit for Teflon filters by this technique is estimated to be  $2.2 \mu\text{g/cm}^2$  when twice the standard deviation of Teflon blank filters is used as a definition of the detection limit. For a standard dichotomous filter sample ( $\sim 1 \text{ m}^3/\text{hr}$  for 24 hours), this corresponds to the atmospheric particulate carbon concentration of  $0.5 \mu\text{g/m}^3$  or about the same as can be achieved with high volume samples collected on quartz filters.

Due to the sampling-related problems, it is difficult to compare the results obtained for samples collected on the two types of filters. A more meaningful comparison of the results would have been possible by using two dichotomous samplers and by analyzing only the fine particle

fraction (particle adhesion is not a problem for particles of less than  $3 \mu\text{m AD}$ ). Such equipment, however, was not available for this work. Despite the remaining uncertainties about the oxidation efficiency of samples collected on Teflon filters, it is suggested that these data demonstrate the utility of this technique for atmospheric chemistry studies. Clearly, the majority of the organic material on such samples is oxidizable by this technique. The high correlation between simultaneously collected samples on different types of filters and the reproducibility of replicate samples on Teflon filters suggest a systematic bias. This is probably not related to sample exposure to the oxidizing solutions. If this is the case, one would expect more of a random error problem. Thus, it is suggested that meaningful information about carbon in the atmospheric particulate matter collected on Teflon filters can be obtained with this technique.

## CONCLUSION

Since the carbon measured by peroxydisulfate oxidation of aerosol samples on quartz filter yields 80%-100% of the corresponding total carbon obtained from the high temperature combustion method, this demonstrates that this method will provide reliable and useful information about carbon in the atmospheric particulate matter. Additionally, low detection limits make solution oxidation with peroxydisulfate an attractive method for the determination of aerosol organic carbon collected with low volume sampling systems. Experiments show discoloration of particulate layers on filter samples. This implies that the "soot" in aerosols is oxidizable. Some polymeric components, if present in collected samples, are probably resistant to solution oxidation. The analysis of a set of Teflon filters which yield lower apparent carbon results, correlates very well with the results obtained from quartz filters run simultaneously. The discrepancy in lower amounts of measured carbon is accounted for by differences in particle collection efficiencies for the two filter types and the adsorption of gas-phase organic compounds on quartz filters. Solution oxidation is a sensitive technique for organic carbon determination of Teflon filters as well as for quartz filters.

This technique should find wide acceptance in studies concerned with the composition and distribution of atmospheric particulate matter.

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