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Thermal Separation of Soot Carbon

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We present here a simple and versatile variant of the thermal analysis of soot carbon, and a discussion on the encountered analytical artifacts. The method is based on a two-step combustion procedure; the removal of the organic material that does not absorb visible light is optimized during a precombustion step at 340°C during 2 hours under a pure oxygen flow, and the remaining carbon is then determined by coulometric titration of the CO₂ evolved from the combustion of the samples. These analytical conditions minimize the crossover between the different components of the aerosol, but better to a clear-cut division between organics and soot carbon, the quantitative evaluation of their thermal evolution is ob-

tained. Artifacts have been tested thoroughly with various standards and replicates of ambient air samples collected. The method gives reliable soot carbon determination at the microgram level in samples from a wide variety of environments. Combined H/C atomic ratio measurements and investigations of the problems associated with the thermal determination of soot carbon permit gaining some insight on the nature of carbonaceous aerosols. They reinforce the indication that soot carbon is not composed primarily of elemental carbon. Also, it is suggested that highly polymerized natural organic aerosols though different in nature could behave thermally and optically like soot.

1. INTRODUCTION

There is increasing evidence that soot carbon is widespread in the global atmosphere. It can be found in detectable amounts even in remote areas (Andreae et al., 1984; Hansen and Rosen, 1984; Heintzenberg, 1985). Consequently, an enhancement of the concentration of soot aerosols is of potential importance for climatic change (Clarke et al., 1984). Though necessary, a comprehensive study of the global atmospheric cycle of soot carbon has not yet been carried out. One of the reasons for the sparse data is the difficulty in assessing reliable soot concentration values for ambient aerosol samples. This difficulty is related to the nature itself of soot carbon. Effectively, soot carbon, which is referred to as the dark, optically absorptive component of the carbonaceous aerosols, can be a very complex mixture of polymerized organic matter along with elemental carbon (Goldberg, 1985). The chemical composition and the physical properties of this mixture are very variable.

All the techniques developed to date suffer limitations due to: (a) the difficulty for providing representative standards and (b) the variable crossover between the different components of the aerosol (Wolff and Klimisch, 1982). Among them, thermal analyses are based on a pretreatment of the sample which allows the volatilization of the organic matter. They aim to set up a cut between the nonabsorptive organic matter and the soot carbon and this is to a certain extent arbitrary (Tanner et al., 1982). Furthermore, these thermal procedures have to deal with two counteracting phenomena that take place during the preheating step: the charring of the organics and the untimely loss of the soot. To address this important problem, thermo-optical methods are probably the most efficient techniques, since optical measurements allow evaluation of the artifacts during the volatilization step of the thermal treatment (Dod et al., 1978; Huntzicker et al., 1982; Ellis et al., 1984); however, the accuracy of these methods is

very sensitive to the variability of the load deposited on the collection surfaces.

In this work, we investigate the thermal behavior of the carbonaceous components of the aerosol. The parameter "duration of the precombustion" is introduced in the experimental protocols. It is shown that this approach allows to optimize a simple and versatile thermal method for soot carbon determination. Combined with atomic ratio measurements (H/C), it provides some indications on the nature of soot carbon.

2. EXPERIMENTAL

2.1 Samples and Standards

Air filtration was performed at the CNRS campus, Gif sur Yvette, a semirural area, at different seasons and during field experiments conducted in the Landes pine forest (France) and in tropical regions in Africa. The aerosol samples were collected on pre-cleaned glass fiber filters (Cachier et al., 1986). Sampling duration was adapted in order to obtain a carbon concentration in the range 10–80 $\mu\text{g}/\text{cm}^2$ on the collection surface.

The optimization of the method required the analysis of other samples: standards that were prepared by dissolution of pure organic compounds and impregnation of filters, size-fractionated plant samples burnt directly on combustion boats, and graphite samples obtained by filtration of either $< 20 \mu\text{m}$ commercial artificial graphite powder (Carbone-Lorraine, France) or black carbon produced in the laboratory by the combustion of toluene.

2.2 Analytical

The samples are systematically subjected to HCl fumes for decarbonation. (Cachier et al., 1986, 1987). The remaining carbon is referred to as atmospheric particulate carbon and is composed of primary and secondary organic carbon and of soot carbon. The collection surfaces are homogeneous enough to allow analysis of aliquots.

2.2.1 Thermal Analysis. The samples are placed in combustion boats and burnt in a furnace. In our procedure, for the first step of the thermal process, the "precombustion step," the temperature is found to be very critical and thus carefully regulated in a 1°C range in a 2-cm diameter insulated-tubular furnace, by the means of a PID type alimination. For the second step, the combustion boat is placed in the furnace of a carbon analyzer (Ströhlein Coulomat 702C) and the remaining thermally refractory carbon (soot carbon) completely oxidized at 1100°C . At this point, the CO_2 that has evolved is detected by coulometric titration. A first aliquot is directly oxidized in the carbon analyzer and leads to the total carbon content (C_T). Other aliquots may undergo the two-step thermal procedure, and the amount of carbon detected with the analyzer is referred to as their refractory carbon content (C_R). The accuracy of the analyzer ($< 1 \mu\text{g}$ of C) and the reproducibility of the load of blank filter (~ 0.5 of μg of C/ cm^2) allow the determination of very low carbon contents (down to 10 μg of C per sample). For average samples, the precision is found better than 5%. This system does not require any calibration, and thus offers the advantage over optical methods to avoid the problem of soot standards.

2.2.2 Atomic Ratio Measurements (H/C). Only the surface of the filter is submitted to the analysis. Samples are carefully kept dry until analysed. Concentrations of the two elements are determined in a C-H analyzer performing separate coulometric titration of H (converted in H_2O and then CO_2) and C. High blanks are obtained for hydrogen loads, but the reproducibility of all the analyses allows H/C measurements.

3. RESULTS AND DISCUSSION

3.1 Thermal Pretreatment

The adjustment of the precombustion aims to find the experimental conditions where soot determinations are optimized and where there is a simple relation between C_R and

the initial soot content. Pure oxygen is chosen in order to minimize charring of the organic compounds. Also, the samples are heated rapidly to favor the desorption of organics relative to chemical reactions leading to polycondensation and charring (Cadle et al., 1980, Cadle and Groblicki, 1982).

3.1.1 Loss of Soot Carbon. Previous works on the thermal analysis of carbonaceous aerosols, although conducted in other conditions (Ellis et al., 1984; Ohta and Okita, 1984) have given indication that the optimized precombustion temperature is around 300°C. Figure 1 presents the typical evolution of the remaining carbon content when several fractions of a given aerosol sample are submitted to different precombustion durations. In the temperature range 260–350°C, all the precombusted samples display the same pattern whatever the sampling location or the chosen temperature for the precombustion process. During the first minutes of the precombustion there is a drastic change in the carbon content whereas later in the experiments (after 1 hour of treatment) the loss of carbonaceous material is considerably less significant. Simultaneously, it was observed visually that collection surfaces gradually lose their color during this precombustion step. Thus, the material which evolves slowly and holds the color of the sample could be primarily the soot component of the aerosol sample if soot is defined as its dark absorptive fraction. Also, the organic matter which has pyrolyzed during the precombustion treatment is likely to evolve in these conditions. Our results indicate that within a precombustion duration range of 120–150 mn the decomposition rate of this remaining refractory component is quasi-constant. It has been estimated for different samples and is found to vary with the precombustion temperature. The values are reported in Table 1 and give evidence that beyond 340°C there is an acceleration of the decomposition process. It is also found that at a given temperature, the decomposition rates of the refractory component of aerosols

FIGURE 1. Typical evolution pattern during the precombustion treatment at different temperatures of the carbon content of an ambient aerosol from Gif sur Yvette (France).

originating from different environments are similar. This could indicate that, in our method, the thermal behavior of soot carbon is not directly related to its origin and hence to its physical and chemical characteristics. Furthermore, it can also be deduced that pyrolysed organic matter behaves thermally like soot. In contrast, artificial samples obtained from pure graphite powder (graphite from Carbone-Lorraine, France < 20- μ m mesh) deposited on a filter do not show any alteration at temperature less than 340°C.

TABLE 1. Decomposition Rate of the Refractory Component of Carbonaceous Aerosols During the Precombustion Step (Ambient Samples from Temperate Areas)

Precombustion temperature (°C)	$K \pm s^a$ (%/min)
260	0.03
280	0.05
300	0.12
320	0.14 ± 0.03
330	0.17 ± 0.02
340	0.22 ± 0.02
350	0.37 ± 0.04

^a K : percentage of lost refractory carbon per minute referred to total refractory carbon (soot carbon and pyrolysed organic matter).

This result suggests that ambient atmospheric soot carbon is not primarily composed of pure elemental carbon. A similar conclusion was obtained by other authors (Chang et al., 1982; Tanner et al., 1982; Goldberg, 1985; Castillo, 1986) and this will be discussed elsewhere.

3.1.2 Charring. Various experiments were undertaken with samples in which the carbonaceous material is soot-free. The percentage of charring for the tested materials has been evaluated and is reported in Table 2. This phenomenon appears to take place readily during the first minutes of the precombustion and in the temperature range which we have investigated, the duration of the precombustion does not affect significantly the carbon content whereas the temperature is one of the major determinants. Charring is depending on the concentration of the organic matter in the sample and as found by other authors (Cadle et al., 1980) is an important complication of the treatment of refractory natural compounds (i.e., plant debris or pollens). In these cases, we find that the effectiveness of the method is very dependent upon particle size. According to Table 2, for particles smaller than 20 μm (which is the case for average aerosols), pyrolysis during the precombustion would affect 10% or less of the initial organic matter

TABLE 2. Charring Tests

Pure organic compounds		
	Total carbon on the filter ($\mu\text{g}/\text{cm}^2$)	Remaining carbon (%)
	9	0
Glucose	15	6.9 ± 0.6
	20 – 40	10.0 ± 3.0
Pyrogallol	88	3.2 ± 0.2
Natural mixture (powders)		
	Carbon percentage in the mixture	Remaining carbon (%)
Humic acids (from marine sediment)	55 ± 5	37 ± 3
Fulvic acids (polysaccharides)	49 ± 3	29 ± 2
Dry leaf		
< 160 μm	45 ± 1	26 ± 1
< 50 μm	45 ± 1	20 ± 2
< 20 μm	45 ± 1	10 ± 1
Green leaf		
< 20 μm	45 ± 2	15 ± 1
Marine sediment	3.2 ± 0.2	17 ± 3
Fluvial sediment	4.3 ± 0.1	16 ± 1
Soil (humus)		
< 20 μm	9.7 ± 0.6	11 ± 1

$T = 340^\circ\text{C}$; $t = 120$ minutes

content. Among the set of tested materials, only pure humic acids char significantly more than 30%. Their thermal behavior compare with that of soot carbon. Although this could be a problem in the determination of ambient soot carbon contents, their contribution to the dark to black color of carbonaceous aerosols has still to be assessed. This important question has to be addressed. The results obtained here indicate that charring rates are systematically lower than what has been previously reported using other thermal procedures. Considering the average pyrolysis rate found for aerosol particles in these works ($\sim 20\%$) it may be assumed that in most of the aerosol samples, this rate would be of the order of 10% or less by using our method.

3.1.3 Optimized Precombustion Conditions. The relative importance of pyrolysis of the organics and loss of the soot carbon depends on both the temperature (T) and the duration (t) of the treatment. The choice of the temperature is based on the following considerations. Pyrolysis varies with the chemical nature of the sample and displays a slow decrease with increasing temperature. In the 300–350°C temperature range, it can be assessed to affect commonly less than 20% of the total particulate carbon load. Within the same temperature range, soot carbon undergoes increasing oxidation with temperature; this process has been evaluated previously (Table 1) and, 340°C appears to be the highest acceptable temperature for an accurate determination of the loss of the soot component. Consequently, 340°C has been chosen as the optimized precombustion temperature.

The loss of soot carbon is minimized by a short precombustion step. However, the duration of the thermal treatment must be sufficient to allow the maximum release of the volatile organic matter. Glucose spiked filters have shown that the precombustion necessitates a duration of 2 hours at least to evolve the maximum organic content. Furthermore at 340°C, for our whole set of aerosol samples (Figure 1) this process appears to be achieved at least after 120 mn. Consequently, this duration value has been adopted for the precombustion.

If the precombustion is controlled in the mentioned conditions, it is possible to evaluate the uncertainty of the method for the measurement of the soot carbon load of ambient aerosol samples. Effectively, we have estimations for both the rate of the loss of the refractory soot carbon (K') and for the pyrolysis rate of the organic matter (Q):

$$K' = 0.22 \times 120 = 26.4\% \quad (\text{Table 1})$$

$$Q \sim 10\% \quad (\text{Section 3.1.2})$$

If x = the initial soot carbon content of the aerosol sample and $1 - x$ = its organic carbon content, then $(1 - x) \cdot Q$ represents the

charring of the organic carbon and $x \cdot K'$ represents the loss of refractory carbon.

The method artifact can be defined as the difference between charring and loss:

$$A = (1 - x) \cdot Q - x \cdot K'.$$

Figure 2 represents $y = x + A$ as a function of x . The charring and the loss of carbon balance each other ($y = x$) when, in carbonaceous aerosols, the relative abundance of soot is 27% of the total carbon content. Assuming that the initial soot carbon content is equal to the load of refractory carbon that remains in the sample after the precombustion process, leads to an overestimate if soot carbon is less abundant than 27%. On the contrary, if the initial soot carbon content is higher than this value, the method causes an underestimation of this content. If the relative accuracy of the determinations of the atmospheric soot carbon concentrations is acceptable up to 10%, carbonaceous aerosols with soot carbon contents from 21% to 38% could be analyzed directly. According to previous works, this would be the range of the soot carbon content of most ambient aerosol samples from various environments (Wolff and Klimisch, 1982; Goldberg, 1985; Japar et al., 1986). In other situations, it is possible to determine the soot concentrations using a correction.

FIGURE 2. Atmospheric soot carbon determinations with an accuracy of 10%.

TABLE 3. Results for Ambient Aerosol

Location	Date (number of samples)	Volume (m ³)	C _{total} (μg/m ³)	C _{soot} (measured) (μg/m ³)	C _{soot} /C _{total} (initial) (%)	H/C	
						C _{total}	C _{soot}
Temperate (France)							
Urban							
Paris	Fall 1984	67.2	5.8	1.6	28	—	—
	(1)						
	Winter 1985	2.8	20.5	5.9	30	0.38	0.24
	(1)						
Gif/Yvette	Winter 1986	73.6	3.4	1.0	31	—	—
	(3)	83.8	19.0	5.4	28	—	—
		329.5	4.8	0.9	14	—	—
	Spring 1986–87	130.4	7.7	1.5	14	—	—
	(5)	276.0	6.3	1.4	20	—	—
		585.0	3.7	0.9	22	—	—
		78.9	20.2	4.6	20	—	—
		109.5	4.0	1.0	22	—	—
	Summer 1984–87	1924.0	9.5	2.3	22	0.33	0.28
	(3)	189.0	4.6	1.1	20	—	—
		104.0	4.9	1.0	17	—	—
	Fall 1985	973.0	13.3	2.5	14	0.20	—
	(3)	6.4	33.7	4.5	5	—	—
		2809.0	21.6	5.1	22	1.20	0.09
	Near fire	27.7	75.9	10.3	6	—	—
	(5)	97.2	29.7	4.8	9	—	—
		60.0	18.1	4.1	20	—	—
		357.2	7.4	1.3	13	—	—
		95.7	—	—	—	0.29	0.22
	Fall 1985 ^a	1973.0	12.0	2.0	11	0.27	0.17
	(1)						
Rural							
Landes	Fall 1984	3970.0	1.8	0.3	9	0.50	0.22
Coastal							
Corsica	Spring 1986	59.7	3.6	0.8	19	—	—
	(13)	90.1	1.3	0.4	36	—	—
		88.4	1.0	0.2	9	—	—
		86.6	1.5	0.2	5	—	—
		88.2	1.9	0.3	9	—	—
		44.0	2.2	0.6	25	—	—
		80.6	2.5	0.6	20	—	—
		82.7	2.3	0.5	17	—	—
		83.0	2.2	0.3	9	—	—
		84.4	1.6	0.1	0	—	—
		164.8	1.1	0.3	25	—	—
		156.0	1.6	0.3	13	—	—
	Near fire	37.3	1.8	0.7	47	—	—
Tropical (Africa)							
Savannah							
Ivory Coast	Spring 1981 ^a	6500.0	2.4	0.4	11	0.25	—
	(1)						
	Winter 1981–82 ^a	2460.0	6.3	0.9	6	0.22	0.12
	(3)	1070.0	12.1	1.6	5	0.45	0.45
	Near fire	1300.0	20.9	3.1	8	0.23	0.04
	Fall 1982 ^a	1400.0	1.2	0.2	6	1.10	0.46
	(1)						
Forest							
Congo	Spring 1983	53.0	6.7	1.1	6	—	—
	(1)						
	Spring 1983–84 ^a	760.0	5.4	1.2	17	1.50	0.90
	(3)	769.0	5.4	1.1	17	1.00	1.00
		1314.0	3.6	0.7	16	1.20	1.00
	Fall 1982 ^a	614.0	—	—	—	0.95	—

Bulk samples or ^abackup filter of cascade impactor samples

3.2 Ambient Sample Data

We have performed measurements of the carbon content of various ambient aerosol samples (Table 3). In continental aerosols, in spite of the variability of the carbon concentration, the relative amount of soot is rather constant. Even very close to the combustion sources, the major part of the atmospheric particulate carbon is in the organic mode. Preliminary results for samples from the Mediterranean Sea (Corsica), show that soot is always present in detectable amounts. The percentage of soot varies in a wider range (from 3% to 40%) due to the variability of the mixture of sources prevailing in that area.

The H/C atomic ratio measurements of the carbonaceous material deposited on the filters give some further insights on the nature of the aerosols. This ratio varies from 1.50 to 0.20 for the total aerosol, thus indicating that they are made up primarily of highly polymerized organic matter. Soot carbon has an average H/C ratio of 0.15 ± 0.05 . It is different from pure elemental carbon but this value confirms its very polymeric nature.

In aerosols sampled in the equatorial forest of the Congo when combustion contributions can be excluded and where only strong natural emissions from the biomass are prevailing, there is a dark refractory component. This natural "black carbon" is likely originating from the oxidative gas-to-particle conversion of volatile organic species emitted by the vegetation. In our thermal analysis, it behaves thermally like soot but it can be differentiated by its higher H/C atomic ratio (~ 0.80).

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