

DETERMINING ORGANIC CARBON ADSORPTION ON QUARTZ FIBER FILTERS BY SAMPLE SPLITTING AND THERMAL/OPTICAL ANALYSIS

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ABSTRACT

A filter-slicing device was fabricated to separate the particulate (top) portion of quartz filter from the bottom portion. Gravimetric analysis showed that the slices were produced with a relative precision of better than 10%. Thermal optical analysis of the each portion showed that: 1) Organic and elemental carbon of the top slice were similar to the original filters, indicating that the particulate concentration was not disturbed by the slicing; 2) The bottom portion charred, indicating that the charring was not due to the presence of particles; and 3) The OC-1 and most OC-2 fractions under the IMPROVE protocol were likely from gaseous organic compounds adsorbed by the quartz-fiber filter.

INTRODUCTION

Particulate organic carbon is routinely determined by collection of the particulate matter onto quartz fiber filters for analysis using thermal techniques. As the filter is known to adsorb organic gases, the organic and elemental carbon (OC and EC) measured will be distorted unless appropriate blank correction is made. The effects are inflating the particulate OC and changing the OC/EC split in thermal optical analysis techniques that use transmittance for pyrolysis correction. This internal darkening due to charring of adsorbed organic vapor can result in an over-correction when the light absorption of pyrolytic carbon of particulate OC differs from that of the gases.

Traditional correction of this positive artifact relies on determining the organic carbon of the back filter of a tandem pair of either quartz-quartz, or Teflon-quartz filters used for the sampling. This approach, while can be successfully applied, requires using quartz fiber filters from the same manufacturing lot. This tandem filter approach has also been found to under-correcting for the positive artifact when the sampling duration is short [1]. These problems are attributed to the varying adsorption capacity of quartz fiber. Also, the collection of such dynamic blanks increases the complexity of sampling logistics and costs.

Microscopic examination of filter cross section revealed that particles do not penetrate into much beyond one third the thickness of a quartz filter even under heavy loading situations, as in 24-hour collection. Thus, if a sample filter is sliced into two halves, the top half should contain all the particles and the back half can serve as its own dynamic blank. This approach is equivalent to sampling with a tandem quartz filter arrangement except that the filters are only half as thick as normal. To accomplish this objective, a filter-slicing device was designed and fabricated. The resulting filter sample slices were analyzed for OC and EC to assess the artifact and how it can affect the OC/EC split in thermal optical methods.

EXPERIMENTAL

To demonstrate particle penetration, microscopic examination of the filter cross section was performed on a 24-hour heavily loaded PM_{2.5} roadside filter. For the filter slicing, a prototype device was fabricated from milling a channel 9.5 mm wide and 0.25 mm deep onto an approximately 15 cm square, 1.3 cm thick piece of aluminum plate. A filter disc 9.5 mm in diameter was placed deposit-side down onto the channel and held in place by a plane of glass. The portion of the filter that was above the aluminum plate was sliced off with a sharp razor. The filter slices were weighed to assess the variability of the split.

A 24-hour roadside sample with heavy deposit from the Central West site in Hong Kong was used to demonstrate particle penetration. The original filters, the particulate, and the bottom halves were analyzed by a DRI Model 2001 thermal/optical carbon analyzer following the IMPROVE protocol [2]. Thus, each filter resulted in three analyses. The Model 2001 provides concurrent reflectance and transmittance measurements during the analysis. Thus both pyrolysis correction approaches can be evaluated under identical conditions.

In the IMPROVE protocol, a 0.5 cm² filter disk is analyzed, producing four OC fractions at 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C (OC4) in a pure He atmosphere, and three EC fractions at 550°C (EC1), 700°C (EC2), and 800°C (EC3) in a 2% O₂/98% He oxidizing atmosphere. One ml of a 5% methane in He standard is injected at the end of the analysis for calibration. The filter's optical properties are monitored by the reflectance of a He/Neon (Ne) laser beam (632.8 nm) for pyrolysis correction. The split between OC and EC is defined by the point when the laser signal returns to its initial level. Total OC is the sum of the OC fractions evolved during the various temperature steps plus any optically detected pyrolytic carbon (OP, from charring correction), and EC is the sum of all the EC fractions minus OP. Total carbon is the sum of all the species. The IMPROVE protocol is event-driven—the program will stay at a temperature step until the evolving peak has reached the designated slope value before advancing to the next step. Thus, analysis time varies. Typically, it is approximately 25 minutes.

RESULTS AND DISCUSSION

Figure 1 shows the cross section of a filter loaded with soot. It is apparent that particles do not penetrate much beyond one-third of the filter thickness despite the heavy loading. Particles should reside mostly on the surface under normal loading conditions. Thus, the device used in the current experiment should clearly separate the particulate from the non-particulate portion of the filter. This fact is further verified by the results of subsequent carbon analysis of the sliced samples. All the filter samples analyzed showed the same trend in that EC from the deposit slice agreed with the original intact filter, and the bottom slice showed no EC after pyrolysis correction.

Gravimetric analysis of the filter slices indicated that for a 70:30 split, the top and bottom slices had a coefficient of variation (CV) of 6.1% and 11.9% respectively. The CV for even split slices would be under 10%. Since a typical Whatman QMA quartz-fiber filter is approximately 0.5 mm thick, the slicing resulted in an approximately even split, but could vary up to a 60:40 split depending on the force applied to hold the disc in place during the sectioning. Pall QAO tissue quartz-fiber filters were found to be more difficult to slice evenly because the substrate is not as rigid as QMA. However, the split was deemed adequate for the

purpose of the experiment, as the particles do not penetrate deeply into the filter matrix. The carbon measured can be normalized using the weight fraction of the slice to the original disc.

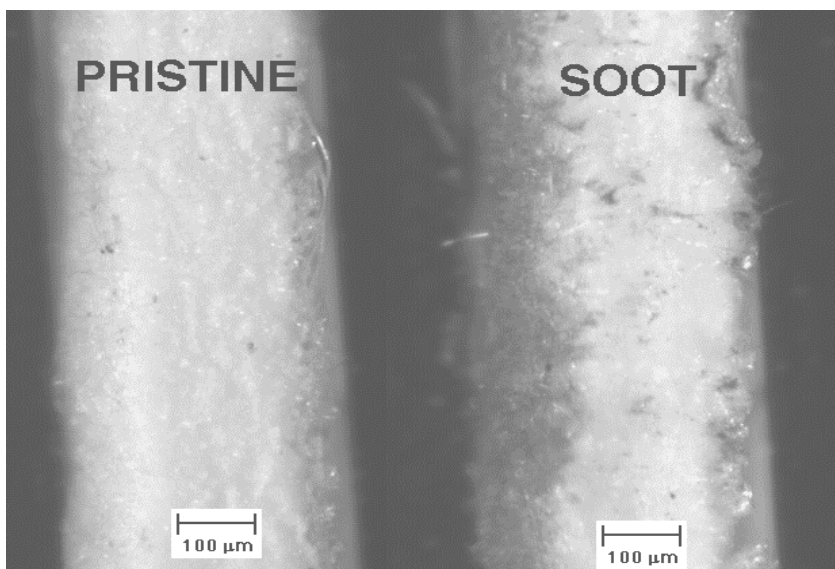


Figure 1. Quartz fiber filter cross sections of a blank and a sample loaded with soot. Particle penetration into the filter matrix is approximately one-third of thickness.

The thermograms of the top and bottom slices of the Hong Kong roadside intact sample are shown in Figures 2-4. The large OC1-OC4 fractions and EC are evidence of the heavy deposit. The laser reflectance (R) and transmittance (T) signals were highly depressed by the particulate loading, resulting in larger uncertainties in pyrolysis correction [3]. The bottom slice contained essentially no deposit, as indicated by the lack of EC after pyrolysis correction. But charring was clearly present, as shown by the depressed laser R and T signals during analysis. In all cases, as analysis progressed, the laser R signal returned to the original value before the T signal, indicating that the charring correction terminated earlier according to the R. Consequently, the pyrolyzed OC (OP) fraction is smaller using the R than T.

These observations are consistent with the fact that reflectance monitors the optical properties of the filter surface, while transmittance monitors changes throughout the filter. Thus, when there is darkening within the filter matrix, the pyrolytic carbon must be combusted before the T signal returns to the original level. With an intact filter (i.e., unsliced), it is impossible to determine if the darkening is due to the vapor of the particles that diffused downward during volatilization. When the intact filter is sliced and the deposits (top half of filter) have been separated, the charring seen in the bottom slice can be due only to organic compounds that are already present prior to the analysis. That the slicing process had not disturbed the deposit was evidenced by the agreement of EC mass of the intact and the top slice shown by the composite thermogram in Figure 5. Hence, the absence of EC in the bottom slice suggested that no particles were present. Then the corollary is that this OC must have been gaseous in nature.

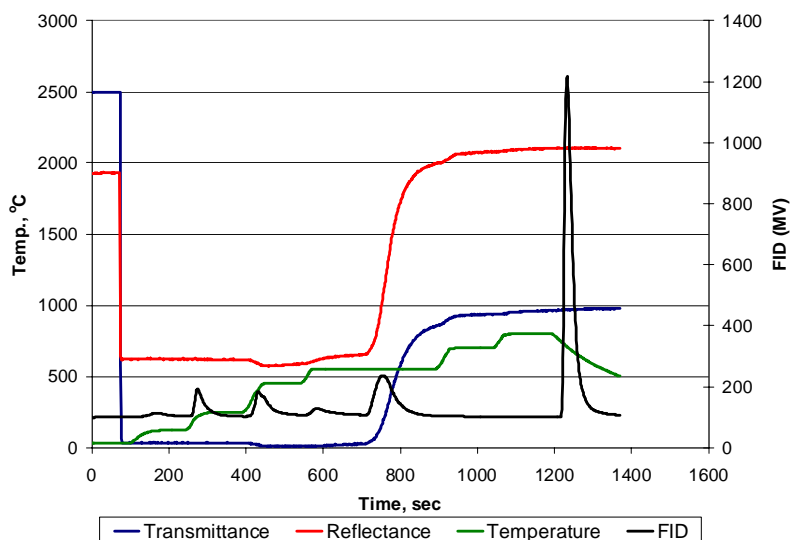


Figure 2. Thermogram of intact particulate filter from the Hong Kong Central West station using the IMPROVE protocol. From left to right, the five peaks are OC1, OC2, OC3, OC4, and EC1. The large peak at the end is the methane standard. The sample is heavily loaded with a large amount of EC. The laser reflectance (R) and transmittance (T) signals are significantly attenuated. Laser R returns to the original level earlier than laser T.

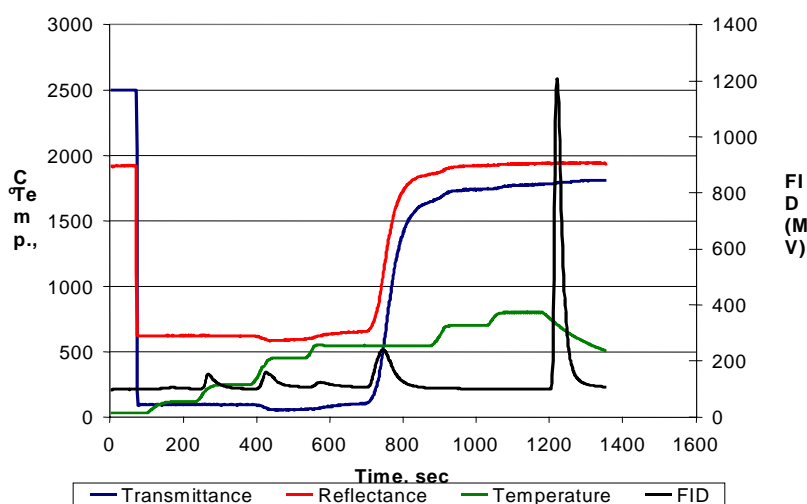


Figure 3. Thermogram of top deposit slice of a particulate filter from the Hong Kong Central West station using the IMPROVE protocol. EC is identical to Figure 2. The laser reflectance (R) and transmittance (T) signals remain highly attenuated. Laser R returns to the original level earlier than laser T.

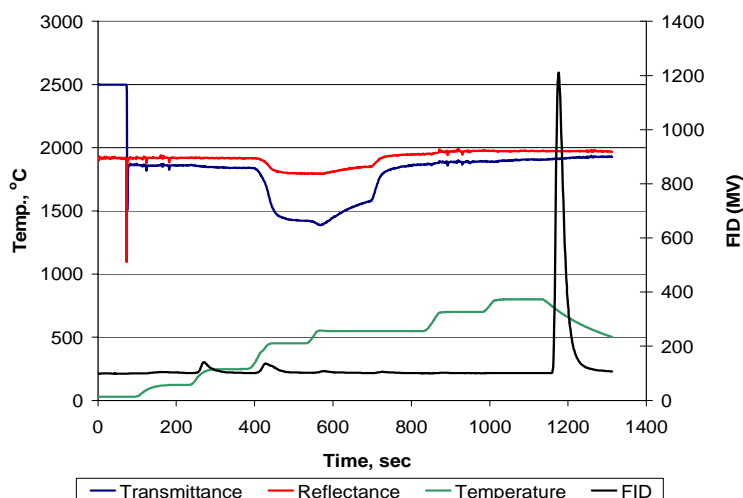


Figure 4. Thermogram of bottom slice of a particulate filter from the Hong Kong Central West station using the IMPROVE protocol. There is an abundance of the OC fractions, but EC is lacking after pyrolysis correction. Charring is evident by the attenuation of laser reflectance (R) and transmittance (T) signals. Even in this thinner filter slice, the T signal returns to the initial value later than R.

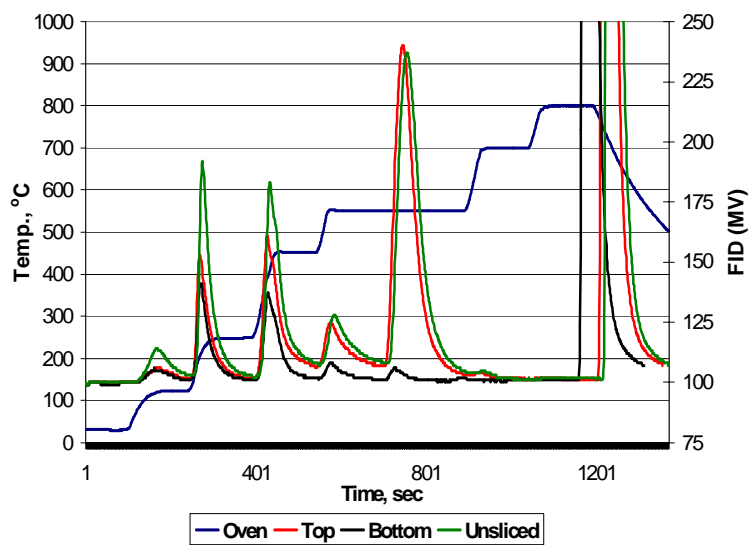


Figure 5. Composite thermogram of a particulate filter from the Hong Kong Central West station using the IMPROVE protocol. EC from the deposit slice is identical to the intact filter, indicating that slicing has not affected the deposit.

The nature of the compounds present in the bottom slice may be deduced from studying the thermograms and the mass of the OC fractions. When the mass of OC1 and OC2 from the bottom slice are normalized, they accounted for all the OC1 and OC2 in the intact filter. In other words, OC1 and OC2 are compounds that are distributed evenly throughout the filter, and these could only be due to adsorbed gaseous organic compounds. The intact filter showed slightly larger OC3 to suggest that 1) OC-3 in the bottom slice also represents adsorbed organic compounds, and the deposit contains additional non-volatile particles, or 2) the compounds might be semi-volatile, with the particulate phase present as part of the deposit, but mostly as adsorbed vapor on the bottom slice. As shown in Figure 4, charring in the bottom slice began with OC2, but was most prominent during OC3. Either hypothesis suggests that charring of the bottom slice is due to adsorbed organic vapor, and not particles. At present, there is no way to indicate which (or either) hypothesis is correct. Future chemical analysis of the bottom slice should provide a more definitive answer.

A small amount of OC4 was also present in the bottom slice. The exact nature is not clear. However, that the laser signals started to climb during this phase of the analysis suggests that the carbon detected could have been an artifact, such as the presence of an oxidant causing the combustion of some of the sample carbon.

CONCLUSIONS

The filter slicing technique is useful in determining filter artifacts. The experimental data support the fact that charring within the filter matrix is due to adsorbed gaseous organic compounds. Since light absorption of the char from adsorbed OC may be different from that of the particles, pyrolysis correction using transmittance would be affected by this internal charring.

REFERENCES

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