Atmospheric Environment 175 (2018) 145–153

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Light attenuation versus evolved carbon (AVEC) – A new way to look at elemental and organic carbon analysis

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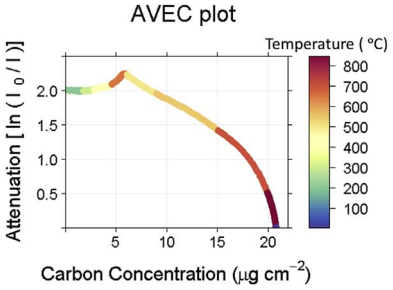
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
OCEC analysis
Thermal desorption
Optical attenuation
Air quality
Particulate matter

ABSTRACT

The Attenuation Versus Evolved Carbon (AVEC) plot is a new way to represent thermal-optical organic carbon/elemental carbon (OC/EC) analysis data. The accumulated carbon concentration is plotted against the attenuation (ln (I_0/I)). Unlike the thermogram, it provides information about the sample properties rather than the instantaneous instrument sensor status.

The plot can be used to refine the determination of OC and EC split point, either from consideration of laser instability or transit time within the instrument; to investigate the optical properties of the particles; and to spot the early evolution of pyrolysed carbon (PC) and/or EC during the inert phase.

168 samples from three sites were studied. The gradient of the AVEC plot curve in the oxygenated phase provides information about the mass absorption cross section (σ) of the particles leaving the filter. The σ of the PC generated in the higher temperature Quartz protocol was greater than the PC generated in the lower temperature EUSAAR_2 protocol. Also, in both cases the PC evolved at a lower temperature in the oxygenated phase than the native EC.

To minimise the shadowing effect, σ was also measured for the particles leaving the filter at the end of the analysis. These σ values, which are expected to be a combination of inherent σ together with fixed instrumental factors, were consistent between the different sites ($45 \pm 10\,m^2\,g^{-1}$ in rural samples, $42 \pm 8\,m^2\,g^{-1}$ in urban samples and $35 \pm 14\,m^2\,g^{-1}$ in roadside samples).

The AVEC plot can be generated from the data routinely produced by the analytical instrument using the R-code supplied in the supplementary material.

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https://doi.org/10.1016/j.atmosenv.2017.12.011
Received 17 March 2017; Received in revised form 27 November 2017; Accepted 11 December 2017
Available online 12 December 2017

1. Introduction

Elemental Carbon (EC) is an important component of our air pollution. Air pollution consists of a complex combination of gases and particulate matter (PM), the term for the mixture of solid particles and liquid droplets found in the air.

PM profoundly impacts human health (Kim et al., 2015), visibility, natural ecosystems, the weather, and the climate (IPCC, 2013). These PM effects are dependent on the aerosol properties, including the number concentration, size, and chemical composition. PM is emitted directly into the atmosphere (primary) or formed in the atmosphere through gas-to-particle conversion (secondary) (Zhang et al., 2015). Furthermore, primary and secondary PM undergoes chemical and physical transformations and is subjected to transport, cloud processing, and removal from the atmosphere.

Carbon in PM falls broadly into three categories that are defined operationally: EC, organic carbon (OC), and carbonate carbon (CC). Recently, more attention has been drawn to EC, due to its linkage to adverse health (Janssen et al., 2011, 2012; Samoli et al., 2016) and climate effects (Ramanathan and Carmichael, 2008; Jacobson, 2010). Several studies suggest that EC is a valid indicator for traffic emissions and include its analysis during monitoring campaigns (Lena et al., 2002; Schauer et al., 2003; Chiappini et al., 2014; Atkinson et al., 2015; Qadir et al., 2013). A number of EC measurement techniques exists (Cachier et al., 1989; Watson et al., 2005; Hitzenberger et al., 2006) with the thermal-optical method being broadly used in Europe and the USA. Usually this follows one of three common protocols: NIOSH5040 (Birch and Cary, 1996), IMPROVE_A (Chow et al., 2007) and EUSAAR_2 (Cavalli et al., 2010).

Measurements of the OC and EC content of particulate samples collected on quartz filters are commonly made and feature in legislation such as the European Air Quality Directive [Directive 2008/50/EC]. Details of the analytical technique are given in the Methods section.

While the determination of the total amount of carbon (TC = OC + EC) in the sample is relatively well defined, it is important to realise that the split of the TC into OC and EC is a useful but ultimately convention-based process with no precisely correct values. EC is generally expected to be comparable with eBC, a measure of light-absorbing material loosely termed “soot” (Petzold et al., 2013). By convention, the OC is the carbonaceous material that is removed from the filter by heating to a defined temperature in an inert atmosphere (He), plus any carbonaceous material determined to have been pyrolysed (PC) during this phase. Optical information is used to assess the pyrolysis using a laser that measures the transmittance through the filter. EC is the remaining carbonaceous material removed during the heating of the sample in the later, oxidising atmosphere (He/O_2), phase of the measurement. The system is complicated by the presence of carbonaceous material in the form of carbonate (Karanasiou et al., 2015), and by interactions with other chemical components of the material (Fung et al., 2002).

The main aim of this paper is to present a new method of visualising the sample analysis data from thermal-optical measurements. This new method has two main advantages: it provides a more intuitive and useful visual summary of the analysis than the thermogram, which is commonly used; and it provides information about the optical properties of the material evolving from the sample during the oxidising phase of the analysis. This opens up the possibility of improved discrimination between OC and EC, using the data that are available from routine analysis. We call the new presentation of the analytical data the Attenuation Versus Carbon Evolved (AVEC) plot.

2. Methods

2.1. Sampling

Two sets of samples were analyzed in this study. First, a set was collected during the Intensive Observational Periods of the NERC-funded Clean Air for London (ClearfLo) Project (www.clearflo.ac.uk); a large, multi-institutional collaborative scientific project based in the UK. Those comprised a winter (January–February) and a summer (July–August) campaign in 2012. The sample locations were Harwell (a rural site in Oxfordshire, 85 km west of London); London North Kensington (an urban background site located in a school playground in a residential area); and London Marylebone Road (a roadside site located within 1 m of the kerbside of a busy main arterial route in central London with traffic flows of ~90,000 vehicles per day). The locations were also part of the Defra Particles Network (Butterfield et al., 2013). These samples were collected on quartz filters using a Partisol Plus 2025 operating at a flow rate of 16.7 L min^{-1}.

The Centre for Research into Atmospheric Chemistry, University College Cork, supplied the samples of coal burning emissions that constitute the second set of samples analysed.

2.2. OC/EC analysis

OC and EC were measured by an OCEC Sunset laboratory thermal/optical analyser (Birch and Cary, 1996) using the EUSAAR_2 protocol (Cavalli et al., 2010) and a modified version of the NIOSH protocol, Quartz. The parameters of the two protocols can be found in the supplementary material, Table 1.

The analysis procedure was the following: after the sample was placed in the main oven, the temperature was increased from the laboratory temperature to the one stated in the chosen protocol. At the same time helium (He) was supplied into the sample chamber. The inert atmosphere and the increasing temperature allowed OC to leave the filter and move towards the manganese dioxide (oxidising) oven. This consisted of a manganese dioxide catalyst that converted OC to carbon dioxide (CO_2) at 840 °C. CO_2 was then reduced to methane (CH_4) by a heated nickel catalyst. The CH_4 passed through a flame ionisation detector (FID), which quantified the carbon concentration. After the last temperature ramp in the inert atmosphere a He/O_2 (10%) mixture was introduced into the main oven. In these conditions, additional carbonaceous material was desorbed from the filter and measured through the same process as the OC. To correct for OC pyrolysis, the darkening of the filter was monitored during the analysis by measuring the intensity of light (λ = 660 nm) transmitted through it (Huntzicker et al., 1982). The light transmittance was then used to determine the split point between the PC formed from the OC and the native EC by determining when the transmittance returned to its original value (Turpin et al., 1990; Birch and Cary, 1996).

A machine blank analysis to check for contamination, and analysis of a standard solution (potassium phthalate) to check the accuracy of the system for TC, were performed daily. The blank analysis upper limit was 0.2 µg. The standard solution analysis was not allowed to deviate more than 5% from the expected value.

2.3. Basics of attenuation versus evolved carbon (AVEC) plots

An AVEC plot relates the attenuation through the filter due to the PM collected on the filter at each second of the analysis to the cumulative carbon evolved during the analysis. Here, attenuation is defined as $ln\ (I_0/I)$ where I_0 is the laser transmittance measured at the end of the analysis when all the carbonaceous compounds were desorbed and I is the transmittance measured at each second of analysis (Haessler, 1965; Ahlquist and Charlson, 1967; Petzold et al., 1997). The cumulative evolved carbon at each second of analysis was calculated from the calibrated, integrated FID signal expressed as mass of carbon per unit area of filter.

Due to the use of I_0, the AVEC plot can only be created once the analysis is complete. The R package ggplot2 (Ginestet, 2011) was used to create the AVEC plots from the Rawdata.txt file, as given in the supplement.