AEROSOL
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The Magee Scientific

Real-Time Total Carbon Aerosol Analyzer

Model TCA-08

Discussion Topics concerning the use of the Model TCA-08 Total Carbon Analyzer to deduce the “EC / OC” content of aerosols

Berkeley, Ljubljana August 2017

EXECUTIVE SUMMARY

The Magee Scientific
Real-Time Total Carbon Aerosol Analyzer
Model TCA-08

The Magee Scientific Real-Time Total Carbon Aerosol Analyzer, Model TCA-08, is a revolutionary scientific instrument that measures the Total Carbon Content ("TC") of suspended aerosol particles in near-Real Time.

Carbonaceous (OC + EC) matter is usually the largest contributor to PM2.5 mass. Conventional thermal analysis for the 'EC/OC' content of aerosols gives data that is highly dependent on the thermal analysis protocol that is used: 'NIOSH' vs. 'IMPROVE' vs. 'EUSAAR'. The Magee Scientific TC-BC Method yields data that is in the 'center' of this range, but which can be related to primary reference standards.

The mathematical principle is simple:
Total Carbon (TC) = Black (or Elemental) Carbon (BC, EC) + Organic Carbon (OC).

Measure TC with the TCA-08;
Measure BC with the AE33 Aethalometer;
Derive OC immediately in near-Real Time.

The AE33 Aethalometer also identifies 'Brown Carbon' (BrC) by multi-wavelength optical analysis, to separate Biomass Smoke from Diesel Emissions.

The combination of {AE33 Aethalometer} plus {TCA-08 Total Carbon Analyzer} provides a complete identification and quantitation of the carbonaceous component of ambient aerosols in near-Real Time:

BC ("EC") ; BrC ; OC : TC

in a rugged instrument package suitable for laboratory and Air Quality monitoring applications. The equipment contains "No Glass", and requires "No Gas".

Carbonaceous Aerosols

Carbonaceous aerosols are extremely diverse and are frequently the largest and most important fraction of fine particulate matter mass (PM2.5) (Turpin, 2001;

Solomon, 2008). They impact air quality, visibility, climate forcing, cloud nucleation, the planetary radiation balance, and public health.

The carbonaceous fractions are frequently separated into organic carbon (OC) and elemental carbon (EC) based on their volatility using thermal-optical methods. Although the combined measurement of total carbon (TC) concentration is usually reliable, (Karanasiou, 2015), the results for the separation of OC and especially EC fractions vary significantly for different thermal analysis methods (Schmid, 2001; tenBrink, 2004; Bae, 2009).

Colorless 'organic' (OC) compounds usually comprise the largest carbon-containing fraction of ambient aerosols: often more than 50% of the PM2.5 mass. A smaller fraction is categorized as Light-Absorbing Carbon ("LAC"), often described in terms of Black ("BC") and Brown ("BrC") Carbon (Petzold, 2013); or 'Elemental' Carbon ('EC') which is defined instrumentally by thermal analysis methods..

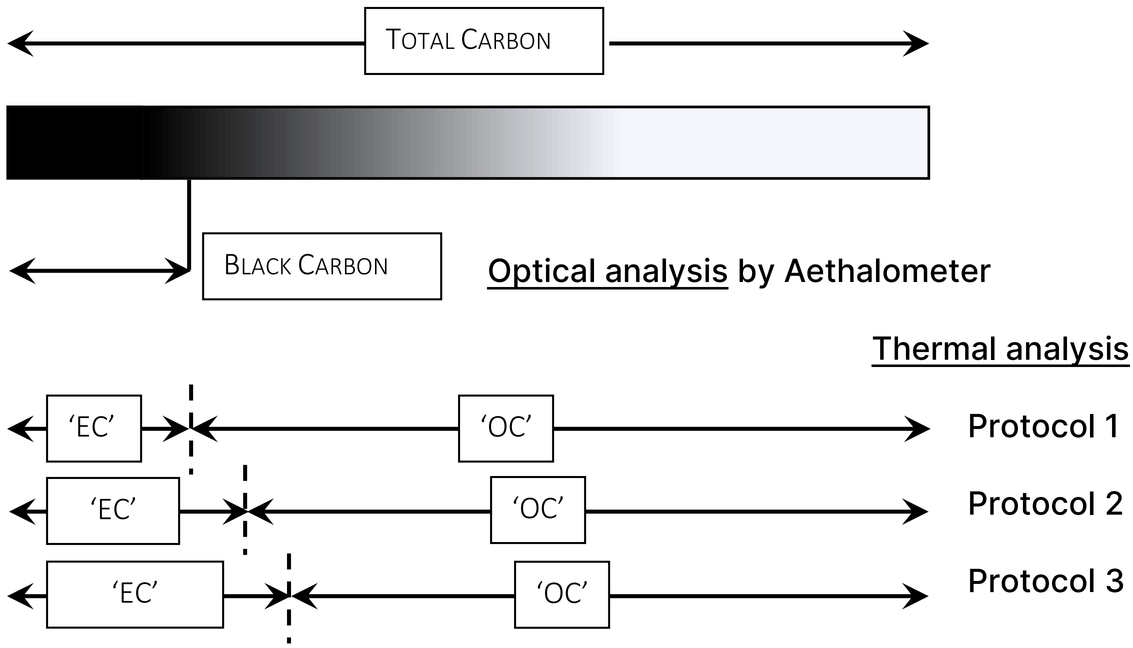
The measurement of Black Carbon (BC) is based upon the absorption of light by carbon in a micro-crystalline graphitic structure (Rosen and Hansen, 1978). This fraction of the total carbon has a very clearly identifiable physical-chemical structure. The measurement of Optical Attenuation can be related to primary photometric standards, (e.g., NIST SRM 8785) and the measurement method may be validated in the field by means of traceable optical test elements (e.g., the Magee Scientific "Neutral Density Optical Filter Kit").

Black Carbon is the major portion of the less-thermally-volatile material. When subjected to thermal analysis, this material is generally denoted as 'Elemental Carbon', even though no definition of 'elementarity' exists. This fraction is defined by its decomposition in either inert or oxygen-containing atmospheres, but these definitions are dependent on the programming of the analytical instrument in terms of time, temperature and atmosphere. At present, three analytical protocols are commonly used: "IMPROVE-A"; "NIOSH"; and "EUSAAR".

Each of these thermal programs attempts (in different ways) to correct for the pyrolysis ("charring") of carbonaceous material, which can convert 'original organic material' into 'apparent elemental material'.

For many reasons, the "EC/OC" separation from the analysis of the same samples; using different thermal protocols; can differ by more than 50%, depending on other aspects of the aerosol sample's composition.

These methods and their differences may be summarized in the following diagram:



Thermal analysis methods usually agree quite well with each other for the determination of the Total Carbon content of the sample: but there may be substantial differences in the "EC/OC" partitioning, depending on the nature of the sample and the thermal protocol which is used for analysis.

Relationship between 'BC' and 'EC'

The Magee Scientific Model AE33 Aethalometer® measures the Black Carbon component of the ambient aerosol. This measurement is calibrated by comparison of Aethalometer Optical Attenuation versus NIST-traceable photometric standards; and may be validated in the field by the use of the Neutral Density Optical Filter Kit.

Original work by Harvard University (Figure 2, Babich et al., 2000) showed that the 'EC' analysis of ambient aerosol samples using the "IMPROVE" thermal protocol was related to the Aethalometer measurement of BC by a multiplicative factor of 1.3. In other words, the reported values of "elemental" carbon were larger than the data for Black Carbon, by a factor which could represent the effects of pyrolysis ('charring'). Other published work has reported ratios between 1.05 and 1.64 for "IMPROVE" analyses.

A large amount of published work has studied the relationship between Aethalometer BC and “elemental” EC, when thermal analysis was done using the “NIOSH” thermal protocol. These results show a ratio ranging from 0.52 to 0.81, with an average of 0.68. This implies that the EC value reported by “NIOSH” thermal analysis would be approximately only one-half of the EC value reported by “IMPROVE” analysis.

The published results from these analyses are summarized in Table 1.

Finally, the paper by Bae et al. (2009) shows that the comparative difference between ‘NIOSH’ and ‘IMPROVE’ analytical results for co-located sampling, may depend on aerosol composition, season, sources, and aging.

The split between ‘EC’ and ‘OC’ in conventional thermal analysis is not well defined, and depends on the settings and protocol of the thermal analysis instrument that is used. There is no absolute definition nor standard for ‘elementarity’ that is not linked to the thermal protocol settings: whereas the measurement of Black Carbon by the Aethalometer is always related to primary photometric standards of “blackness”.

Table 1: Published Work on relationship of ‘BC’ and ‘EC’

EC/BC ratio	Thermal protocol	Location	Reference
0.52	NIOSH	Fresno, CA, USA	Chow Watson (2009): AR 93:874
0.57	NIOSH	Columbus, OH, USA	EPA ETV report 2014
0.63	NIOSH	Korea	Bae (2007): AE 41:2791 "Instrument NIER"
0.68	NIOSH	Boston, MA, USA	Kang (2010): JAWMA 60:1327 : impactor inlet
0.71	NIOSH	Boston, MA, USA	Kang (2010): JAWMA 60:1327
0.73	NIOSH	Korea	Bae: (2007): AE 41:2791 "Instrument UT"
0.74	NIOSH	Fresno, CA, USA	Park Chow (2006): JAWMA 56:474
0.76	NIOSH	Helsinki	Timonen (2014): Boreal Environ. Res. 19:71
0.81	NIOSH	Atlanta, GA, USA	Turpin Lim (2002): JGR-A "Atlanta Supersite":
1.05	IMPROVE	Uniontown, PA, USA	Allen (1999): AE 33:817
1.23	IMPROVE	Fresno, CA, USA	Park Chow (2006): JAWMA 56:474 : summer
1.25	IMPROVE	Pittsburgh, PA, USA	EPA ETV report 2001
1.31	IMPROVE	7 cities in US	Babich (2000): JAWMA 50:1095.
1.37	IMPROVE	Fresno, CA, USA	Chow Watson (2009): AR 93:874
1.39	IMPROVE	Fresno, CA, USA	EPA ETV report 2001
1.64	IMPROVE	Fresno, CA, USA	Park Chow (2006): JAWMA 56:474 : winter

Any comparison of Black Carbon with a particular method for ‘EC’, must necessarily specify the ‘EC/OC’ thermal protocol, and acknowledge that the results will be different if a different thermal protocol had been used.

Extensive research by Magee Scientific / Aerosol Co. has studied this relationship for a range of aerosols, in comparison to thermal analysis using ‘IMPROVE’, ‘NIOSH’ and ‘EUSAAR’ protocols.

Calculation of 'OC'

If

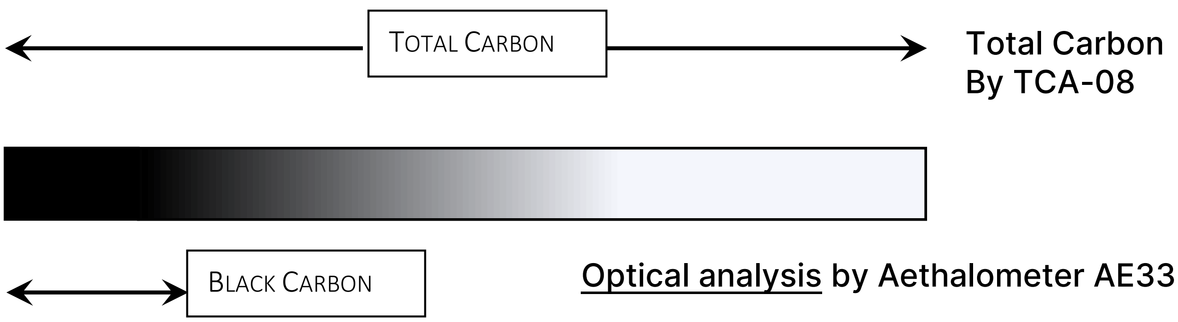
Total Carbon (TC) = Black (or Elemental) Carbon (BC, EC) + Organic Carbon (OC);

Then

Organic Carbon (OC) = Total Carbon (TC) - Black (or Elemental) Carbon (BC, EC).

Table 1 (above) shows that parallel analysis of ambient aerosols by co-located thermal analyzers; but using different analytical protocols; shows radically different relationship between 'EC' and 'BC'. Consequently, the definition of 'OC' is not absolute: instead, it depends on the thermal protocol which was used.

If a certain proportionality is used for the relation between Black Carbon and 'EC';
for example, '(IMPROVE) EC' = 1.3 x BC (Babich et al., 2000);
then this value may be used to calculate what the 'reported' value of OC would have been, if the sample had been analyzed thermally using the 'IMPROVE' protocol.



Multiply BC by 1.3 to estimate "IMPROVE EC": subtract from TC to derive 'OC'.

Fortunately, the 'OC' fraction of ambient aerosols is almost always much larger than the 'EC' fraction. Consequently, the relative uncertainty in an 'OC' determination is reduced. The following two examples illustrate the effect of the mathematics:

Reference	Protocol	EC	TC	Deduced OC
Kang	NIOSH	0.4	3.7	3.3
	IMPROVE	*0.8*		*2.9*
	Aethalometer BC	0.6		3.1
Park	IMPROVE	3.0	13.0	10.0
	NIOSH	*1.5*		*11.5*
	Aethalometer BC	2.2		10.8

The first row of data (in black font) is the actual reported data using the specified thermal protocol.

The second row (in *ITALIC BLUE* font) is the result that “would” have been calculated, if the alternative thermal protocol had been used.

The third row (in RED font) show an estimate of what the Aethalometer BC data might have been; together with the deduced result for ‘OC’ if that Aethalometer BC value had been used directly for subtraction.

The results for the calculation of OC show that if the direct Aethalometer ‘BC’ value is used, the resulting calculated ‘OC’ value is midway between the values that would have been obtained using either of the thermal protocols.

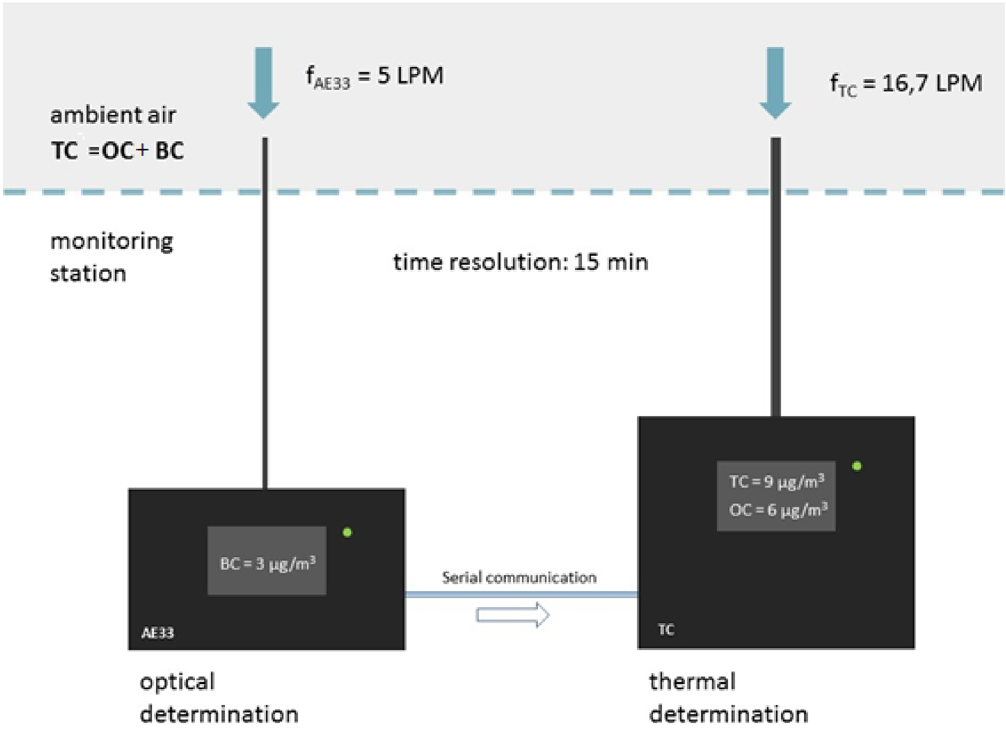
The Magee Scientific TC-BC Method

The principle of the Magee Scientific TC-BC Method is simple:

[1] to robustly measure the Total Carbon (TC) content of the ambient aerosol;
[2] to robustly measure the Black Carbon (BC) content of the aerosol;
[3] to calculate the Organic Carbon (OC) content by simple subtraction, after choosing the definition of ‘EC’ by choosing its proportion to BC.

Simple Equipment Setup

The instrumental setup is simple: a Model AE33 Aethalometer is coupled to the Model TCA-08 Total Carbon Analyzer. Each instrument is rugged, reliable, and suitable for field operations:



The TC and BC data are combined to yield the OC result by simple subtraction.

Applications and Utility of the TCA-08 Total Carbon Analyzer

The TCA-08 Real-Time Total Carbon Analyzer is designed for routine, unattended analysis of ambient aerosols.

The combination of {AE33 Aethalometer} plus {TCA-08 Total Carbon Analyzer} provides a complete speciation and quantitation of the carbonaceous component of ambient aerosols in near-Real Time: BC ("EC") ; BrC ; OC : TC

This equipment package is designed for operation at routine Air-Quality monitoring stations; at scientific research project sites, even at the most remote locations; and in laboratory studies. The unique advantages of the TCA-08 Real-Time Total Carbon Analyzer may be summarized very simply:

No Gas

No Glass

Rugged, Reliable

High Time Resolution

Designed for Routine, Unattended Field Operation

The Model TCA-08 Real-Time Total Carbon Analyzer has been extensively field-tested at leading research institutes in Europe, to prove not only its scientific analytical performance but also its reliable and automatic operation. The TCA-08 is made with the same quality and reliability as the Model AE33 Aethalometer, and is supported by our worldwide network of representatives.

For further information, detailed specifications, price quotations or to request a demonstration: please contact us as shown on the end-pages of this report.

References

(copies available on request)

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