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Considerations in analysing elemental carbon from marine engine exhaust using residual, distillate and biofuels

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Abstract

Elemental carbon (EC) concentrations in the exhaust of a medium-speed marine engine was evaluated using thermal-optical analysis (TOA). Particulate matter (PM) samples were collected at 75% and 25% engine loads using residual and distillate fuels with sulphur contents of 2.5%, 0.5% and 0.1%, and a biofuel (30% of bio-component). The EC analysis of PM samples from a marine engine proved to be challenging. For example, transformations of structure of the sampled particles in the inert and the oxygen mode were observed for marine engine exhaust samples. The relationship between constituents present in the samples from the marine engine using different fuels, and phenomena observed in the thermograms are discussed. Temperature protocol selection and sample pre-treatment (extractions and drying) affected the reported EC mass. Modifications in the methodology were suggested to increase the accuracy of the analysis. Repeatability and reproducibility of the EC analysis was studied in the round-robin of three laboratories.

Keywords: Elemental carbon EC; thermal-optical analysis TOA; thermogram; marine engine; fuel; round-robin

1 Introduction

Black carbon (BC) is the second largest anthropogenic contributor to climate change, and is also associated with serious adverse health effects (Bond et al., 2013). Regulation for ship BC is anticipated, as ships are important emitters of BC particularly in Arctic areas (Quinn, Stohl, Arneth, & Berntsen, 2011). BC is optically measured carbon, which strongly absorbs visible light. Absorbing species are also coloured organic compounds called brown carbon (BrC), e.g., refractory high molecular-weight polymeric or polycyclic aromatic compounds and humic-like substances. In exhaust from marine engines, BrC is typically formed in combustion processes, but can also form, e.g., when sulphates react with organic compounds in low humidity (Andreae & Gelencser, 2006; Bond et al., 2013; Collaud Coen et al., 2010; Kupiainen & Klimont, 2007; Lim et al., 2014; Yang, Howell, Zhuang, & Huebert, 2009). Although not commensurable by definition, elemental carbon (EC) is often used synonymously with BC. EC is refractory, non-volatile material in particulate matter (PM) measured with thermal or thermal-optical analysis (TOA) methods based on the evolution of carbon species in different temperatures (Bauer, Yu, Cary, Laulainen, & Berkowitz, 2009; Birch & Cary, 1996; Turpin, Cary, & Huntzicker, 1990; Watson, Chow, & Chen,
2005). For both BC and EC, the change from refractory, black and graphitic structures to non-refractory and colourless organic compounds is gradual, and it is challenging to draw the line based on refractoriness or blackness (Long, Nascarella, & Valberg, 2013; Pöschl, 2003). The terminology of BC in relation to measurement methods is thoroughly discussed by Petzold, pointing out the complexity of this issue and recommending consistent reporting of data (Petzold et al., 2013). The existence of reliable and accepted analysis methods is a prerequisite for ship BC regulations, and thus the applicability of different methods to evaluate the ship emissions is sought for. Consideration is also given to the EC analysis method, which is widely used in atmospheric studies (Saarikoski et al., 2008; Viana et al., 2007; Viidanoja et al., 2002), and has also been utilised for diesel occupational exposure studies (Birch & Cary, 1996), vehicular emissions (Schauer, 2003), as well as for biomass-burning studies (Frey et al., 2009; Nuutinen et al., 2014). In addition, several review and intercomparison articles related to the TOA method of ambient samples have been previously published, e.g., (Cheng et al., 2011; Panteliadis et al., 2015; Watson et al., 2005). However, we note that PM from marine engines contain a low share of EC (Lappi & Ristimäki, 2017; O. Sippula et al., 2014), which is not the case for PM from land-transport applications (Schauer, 2003).

Previous studies have shown that the EC analysis can be challenging from a complex sample matrix containing substantial concentrations of other species than EC (Jung et al., 2011; Panteliadis et al., 2015). For example, the distinction of EC from organic carbon (OC) is difficult, e.g., for the ambient samples impacted with biomass burning (Kuhlbusch et al., 2009). PM from marine engines may contain constituents, such as asphaltenes (large aromatic molecules with nitrogen and metals), sulphur-containing species, water and metals (e.g. vanadium and nickel), potentially complicating the EC analysis and interpretation of results (Moldanová et al., 2013). This is particularly relevant when using fuel containing a kind of refinery residue (Mullins, 2010; Neste, 1987). Asphaltenes from refinery waste have shown the greatest tendency towards charring between 400 and 500 °C in inert atmosphere in a thermogravimetric study, although in the presence of oxygen, they oxidised rapidly at circa 400 °C (Barneto, Moltó, Ariza, & Conesa, 2014). Vanadium possesses a complex chemistry of absorbing coloured compounds: some of them are yellow, green, blue, black or grey (Shiju, 2004). Oxygen may be present in marine engine PM as sulphates, oxides and water. At thermal analysis, oxygen and catalytic metals may induce premature evolving of EC at high temperatures as early as the inert phase (Jung et al., 2011; Karanasiou et al., 2011; Panteliadis et al., 2015). Complex PM samples could be extracted with water and organic solvents prior to analysis to remove OC and other soluble constituents that may interfere with TOA (Karanasiou, Minguillón, Viana, Alastuey, & Putaud, 2015; Lappi & Ristimäki, 2017; Lauer, 2008). Besides PM composition and the presence of coloured or refractory material, as well as, e.g., loading of filter, laser stability or detection principle may affect the EC results. For example, larger EC to total carbon (TC) ratios have been observed in the instruments using the thermal-optical techniques and monitoring a laser signal with reflectance (TOR) compared to transmission (TOT) (Kuhlbusch et al., 2009). Chow et al. (2004) found a TOR monitoring method less sensitive towards different temperature programmes than a TOT method. The EC results were 30% to 80% lower when determined by TOT instead of TOR, depending on the protocol applied. TOT was sensitive to charring within the filter, whereas TOR was dominated by charring of the near-surface deposit that first evolve when oxygen is added (Chow et al., 2004).

This article focuses on the challenges and considerations related to the analysis of marine exhaust engine emissions using the TOA method. Additionally, the results of a round-robin test conducted in three different laboratories are presented.

2 Material and methods

2.1 Fuels, engine oil and engine
Four different fuels were used in the tests: low sulphur content (0.1%S) marine diesel oil (MDO DMB), an intermediate type of fuel oil with sulphur content of 0.5%S, heavy fuel oil (HFO) with sulphur content of 2.5%S and a biofuel (Bio30). Biofuel was a mixture of 30% of fatty-acid type biocomponent and 70% of diesel fuel (Bio30). Compositions of fuels are presented in Table 1 and fuel properties in the Supplementary Information (SI Section 1.1). Shortly, the 2.5%S and 0.5%S fuels contained heavy constituents with high distillation points, while 0.1%S and Bio30 were distillates with lighter fractions of crude oil. 0.1%S fuel still contained a substantial amount of sulphur, while Bio30 was practically "sulphur-free". A fatty-acid type of oxygenated biocomponent was not esterified. The Bio30 fuel contained a relatively high amount of oxygen, 3.9 %(m/m). Besides differences in sulphur contents, the 2.5%S fuel contained less hydrogen than the other fuels. Density, viscosity, nitrogen content, ash and metal contents of the fuels varied as well.

### Table 1. Carbon, hydrogen, sulphur, nitrogen, oxygen and ash contents of the test fuels.

<table>
<thead>
<tr>
<th></th>
<th>0.1%S</th>
<th>0.5%S</th>
<th>2.5%S</th>
<th>Bio30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>87.0</td>
<td>86.8</td>
<td>86.2</td>
<td>83.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>12.9</td>
<td>12.5</td>
<td>10.4</td>
<td>13.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.01</td>
<td>0.23</td>
<td>0.54</td>
<td>0.003</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>3.9</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.078</td>
<td>0.375</td>
<td>2.22</td>
<td>0.0004</td>
</tr>
<tr>
<td>Ash</td>
<td>0</td>
<td>0.038</td>
<td>0.094</td>
<td>0</td>
</tr>
</tbody>
</table>

In all experiments, the engine oil used was Shell Argina XL 40. Properties of engine oil are given in SI Section 1.1. The engine oil was aged for approximately 200 hours prior to the measurement campaign. The engine oil samples taken before and after the campaign, all fresh engine oil, demonstrated that oil was in good condition during the tests.

The PM samples were collected from VTT’s medium-speed engine (Wärtsilä Vasa 4R32 LN, modified configuration, see SI Section 1.1), which is in the size range of auxiliary power engines used in ships. The marine engine studied was equipped with a mechanical injection system, which is typically sensitive towards fuel properties. For example, viscosity and density of fuel affect the start of injection and spray formation (Nylund, Aakko, Mikkonen, & Niemi, 1997). Modern engines equipped with common rail systems are assumedly less sensitive towards fuel properties than the engines with mechanical injection systems.

Fuel temperatures were adjusted to reach manufacturer’s recommended viscosity for the tested engine (about 16 mm² s⁻¹): 100 °C for the 0.5%S fuel, 134 °C for the 2.5%S fuel and 28–34 °C for the 0.1%S and Bio30 fuels. The fuel supply pressures varied from 9.6 to 12 bar during the experiments.

The engine was warmed prior to the tests by running at 50% load for 10 minutes and at 75% load for 50 minutes. The engine was stabilised for 30 minutes after changing the engine load. Furthermore, the low-sulphur content fuel 0.1%S was used in the beginning and in the end of the measurement campaign to check the stability of the engine.

#### 1.1 PM sampling and filters

The PM samples were collected from diluted exhaust (temperature below 52 °C) according to the ISO 8178 (ISO, 2006) and from undiluted exhaust (hot 350-400 °C) using in-stack sampling according to EN 13284-1 (EN, 2002). In the ISO 8178 sampling, two partial flow dilution systems were used: an AVL SmartSampler SPC (with a dilution ratio of 8) and a Microtroll MT (with a
dilution ratio of 20-33). A partial flow from the raw exhaust from sampling point located 5.9 metres downstream of the engine was diluted with filtered and dried air, and flow was drawn through a filter material to collect the particles. Additional details are given in SI Section 1.2. In-stack (hot) sampling according to EN 13284-1 (EN, 2002) was conducted with a filter located inside of the exhaust duct under the prevailing conditions more than 6 metres downstream from the ISO 8178 sampling point. The filter, filter holder and nozzle arrangement was pre-heated at 430 °C, stabilised overnight in exsiccator and weighed. After sampling, the filter arrangement was after-heated to 160 °C, stabilised overnight in an exsiccator and weighed. A cyclone for removing large particles was not used.

For the EC, trace elements and oxygen analyses, the Munktell MK360 quartz microfibre filters were used, and for the PM mass, sulphate and polyaromatic hydrocarbons (PAH) analyses, the Pallflex TX40HI20-WW filters were used. The filter size in in-stack sampling was smaller (o.d. 47 mm) than in the ISO 8178 sampling (o.d. 70 mm). Prior to collections, the Munktell MK360 filters were pre-cleaned at 400 °C for in-stack sampling and for two hours at 850 °C for ISO 8178 sampling before being stabilised. The loaded filters were stored in the freezer before analyses.

The untreated loaded filters without pre-treatment (i.e., drying or extractions) were used in the tests. A separate study on pre-treatment (drying/extractions) of filter samples was conducted for the ISO 8178 samples obtained with the Microtroll MT dilution for the 2.5%S and 0.5%S fuels at 75% load. Drying of the loaded filters at 180 °C for 2 hours was studied, as well as two different washing procedures: a) toluene extraction followed by isopropanol (IPA)/water extraction and b) extraction with water only. The results of pre-treatment of loaded filters are presented in Section 3.4. Extractions or drying of filters were not applied to the round-robin samples in this study.

1.2 EC analysis

EC method and temperature programs

The thermal-optical techniques are based on the evolution of carbon species in different temperatures (Bauer et al., 2009; Birch & Cary, 1996; Watson et al., 2005). Temperature and gas atmosphere is adjusted while continuously monitoring a laser signal reflectance or transmission through the sample matrix. In the first phase, a sample is heated in steps up to 550–900 °C in inert Helium (He) atmosphere to remove OC. The organics may be pyrolysed to pyrolysed carbon (PC) during the inert phase, and this is observed by a decrease in the laser signal. In the second phase, oxygen is introduced and the temperature is elevated step-wise. Carbon is oxidised to CO₂, which is then converted to methane and detected by the Flame Ionisation Detector (FID). The PC formed during the temperature programme is compensated by determining the point (split) when the laser signal achieves its original value before pyrolysis. Methane is injected into the sample oven at the end of each analysis, introducing a known quantity of carbon for the internal calibration. Sucrose is typically used as an external standard solution for OC as it was used in this study. Carbonate carbon is not common for engine aerosols, even while it may be found in ambient aerosol samples (Kuhlbusch et al., 2009) and in biomass combustion-emitted aerosols (Olli Sippula, Hytönen, Tissari, Raunemaa, & Jokiniemi, 2007).

Applicability of three temperature protocols (NIOSH 5040/750°C, NIOSH5040/870°C and EUSAAR2) for the TOA of marine exhaust PM samples was explored. The NIOSH 5040 recommends lowering the peak temperature when EC loss is evident, and thus two peak temperatures in the inert mode of modified NIOSH 5040 / ASTM D6877 – 03 were studied, namely 750 and 870 °C. The EUSAAR2 protocol is designed for the ambient air samples while the NIOSH 5040 is designed for the diesel exhaust. However, EC content in ship exhaust is low, as is typically the case in ambient air samples (Aakko-Saksa, 2016; Ntziachristos et al., 2016; Park, Harrison, Pancras, & Ondov, 2005; Viiðanoja et al., 2002), while the EC content is high for samples from high-speed diesel engines using distillate fuels (Karjalainen et al., 2016; Murtonen et al., 2012; Saarikoski et al., 2017). The peak temperature (650 °C) in inert mode of the EUSAAR according to
prEN 16909 (EN, 2015) is lower and has a longer duration than those of the NIOSH programme (Table 2). The programme was prolonged by 60 seconds in the O₂/He-phase to ensure that the EC and calibration peak had clear baseline separation, as was also recommended by Kuhlbusch et al. (Kuhlbusch et al., 2009). Prolongation was needed as the EC peak for the 0.1%S and Bio30 fuels occurred late, close to the methane calibration peak. If true baseline level is not achieved between the EC and methane peaks, the area of the methane calibration peak is miscalculated.

The OC to EC split was estimated based on the TOT monitoring of the laser transmission through the sample and filter. In addition to this default procedure, concentrations of OC and EC with the round-robin samples were also calculated using constant split to test reproducibility of the carbon evolved after the split between replicate tests and different instruments and operators. The constant split point of 750 seconds was selected as it is close to the middle point of the first temperature step in O₂/He-phase in EUSAAR2 designed to oxidise PC in the presence of oxygen.

The EC results were obtained with the TOT method using three Carbon analysers manufactured by Sunset Laboratories Inc., Tigard, OR, USA. The EC results presented in Sections 3.1–3.4 were analysed at the Technical Research Centre of Finland Ltd (VTT), using a Carbon analyser model 4L (software Calc200). The same instrument was used at VTT for the round-robin test (Section 3.5). Two other laboratories, the Finnish Meteorological Institute (FMI) and the University of Eastern Finland (UEF) participated in the round-robin test. FMI used the Carbon analyser model 5L (software ECOC1029, calculation Cal359), and UEF used the Carbon analyser model 4L (software Inst231, Calc150, no temperature offset calibration). The different software versions used are not expected to affect the results, and thus they are not typically considered in the inter-laboratory comparisons of TOA (ACTRIS, 2017; Panteliadis et al., 2015). Automatic split point determination was used in FMI and UEF, while VTT used a manual split point (baseline) with methodology described by Lappi & Ristimäki (Lappi & Ristimäki, 2017), in which the decreased laser signal at the first temperature ramp in the inert phase for the baseline split was omitted.

Samples for the EC analysis met the recommendations from a manufacturer of instruments in almost all cases (see SI Section 1.3). For samples from undiluted exhaust (in-stack samples),

Table 2. Temperature programmes used in this study: modified NIOSH 5040 (870/750°C, left-hand side) and EUSAAR2 (prEN 16909) (right-hand side).

<table>
<thead>
<tr>
<th>NIOSH 5040 modified</th>
<th>EUSAAR2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Purge</strong> ****</td>
<td>Dura-</td>
</tr>
<tr>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>OC1 – He</td>
<td>10</td>
</tr>
<tr>
<td>OC2 – He</td>
<td>90</td>
</tr>
<tr>
<td>OC3 – He</td>
<td>60</td>
</tr>
<tr>
<td>OC4/CC – He</td>
<td>60</td>
</tr>
<tr>
<td>CO4/CC – He</td>
<td>90</td>
</tr>
<tr>
<td>He</td>
<td>50</td>
</tr>
<tr>
<td>He/O₂</td>
<td>45</td>
</tr>
<tr>
<td>EC1/PC – He/O₂</td>
<td>45</td>
</tr>
<tr>
<td>EC2 – He/O₂</td>
<td>45</td>
</tr>
<tr>
<td>EC3 – He/O₂</td>
<td>45</td>
</tr>
<tr>
<td>EC4 – He/O₂</td>
<td>45</td>
</tr>
<tr>
<td>EC5 – He/O₂</td>
<td>90</td>
</tr>
<tr>
<td>Cal &amp; cooling</td>
<td>110</td>
</tr>
</tbody>
</table>

* Prolongation of 60 s was used for the round-robin samples. ** Instrumental purge of 60 s with He before the start of temperature protocol.
loaded filters were easily overloaded with EC (dark) and the determination of the split point was not very repeatable. Hence, separate, short-sampling-time in-stack samples (light-coloured) were collected for the EC split determination. TC was analysed from the filters with longer sampling time and hence had a darker colour. Comparison of TC/PM results of the “dark” and “light” samples is presented in SI Section 1.3.

**Calculation of the EC results**

The EC concentrations (mg/m$^3$) were calculated based on the ratio of EC and PM loading on filter effective area, and on the PM concentration measured with standardised procedures (Equation 1). Concentrations were converted to the standard conditions (273.15 K, 101 323 Pa), and abbreviated as mass per Sm$^3$.

$$EC = \frac{EC_i \times A}{PM_{mass}} \times PM$$  \hspace{1cm} (1)

- EC = Elemental carbon (mg m$^{-3}$)
- EC$_L$ = EC loading on filter (mg cm$^{-2}$)
- A = Effective area of filter (cm$^2$)
- PM$_{mass}$ = Mass of PM sample on filter (mg)
- PM = PM concentration (mg m$^{-3}$)

1.3 PM composition

Compositional analyses were conducted from the PM samples collected directly from undiluted exhaust (in-stack) and from diluted exhaust (ISO 8178). The compositional results of PM are presented and discussed in order to understand the influence of sample composition to the EC results and to support the interpretation of the thermograms. Short description of each analysis is as follows:

- **Organic carbon (OC)** content of PM was analysed using the Sunset EC/OC-analyser. The OC fraction was divided in “Heavy OC”, associated in the in-stack samples (collected at 350-400 °C) and “Light OC”, which is achieved by subtracting “heavy OC” from the ISO 8178 SPC-diluted OC.
- Sulphates were analysed by electrophoresis from the water/isopropanol extracts of samples. No sulphuric acid was present in the in-stack samples due to the high sampling temperature, whereas non-volatile fraction of sulphate containing species, e.g., metal sulphates, “mSO$_4$”, were present. For the diluted ISO 8178 SPC samples, total sulphates included both sulphuric acid (H$_2$SO$_4$) and the “mSO$_4$” fraction. H$_2$SO$_4$ content was calculated by subtracting “mSO$_4$” from total sulphates. Water bound in H$_2$SO$_4$ depends on relative humidity of the weighting chamber, which was 50% in our measurements, meaning that 1.32 grams of water was bound in a gram of H$_2$SO$_4$, according to SAE J1936. Water bound in the metal and other sulphates does not follow the same equation and thus water is presented here only as a part of the “Rest” portion.
- **Oxygen** was analysed using a FLASH 2000 series analyser based on pyrolysis.
- **Trace elements** were analysed by using an inductively coupled plasma mass spectrometry (ICP–MS). Elements analysed included Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, Ti, U, V, Zn, Br, Cl, P, S, Si and Sn. Quartz filters were extracted in a micro oven using a solution of nitric acid and hydrofluoric acid (EN 14385). The Munktelll MK360 blank filters contained impurities, such as Al, Ca, Na and Fe.
- **Polyaromatic hydrocarbons (PAHs)** were analysed by using the gas chromatography – mass spectrometry (GC–MS) from toluene extracts from filters. The sum of seven heavy PAHs (benz[a]antracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene,
benzo[a]pyrene, indeno[1,2,3-cd]pyrene and dibenz(a,h)antracene) in PM was calculated
from the 24 PAHs analysed.

Results of PM compositional analyses are shown in SI Section 2.1.

3 Results and discussion

3.1 Composition of PM

General features of this measurement campaign have been presented previously in (Aakko-Saksa, 2016). Shortly, BC concentrations were studied with a variety of methods/instruments (Photo-Acoustic Spectrometer, Multi-angle absorption photometer, aethalometer and instruments measuring filter smoke number concentration) together with online chemical and physical characterisation of particulate emissions and concentrations of gaseous compounds.

For heavy residual-type fuels (2.5%S and 0.5%S) and for distillate fuels (0.1%S, Bio30), the PM concentrations ranged from 9 to 135 mg Sm⁻³ in the in-stack samples and from 18 to 153 mg Sm⁻³ in the ISO 8178 samples. The main chemical components in PM were organics, sulphuric acid, metal sulphates and oxides, water and EC. Measured PM mass concentrations and chemical composition for different fuels are shown in Figure 1. Large variation in both PM concentration and composition created an optimal sample matrix to study factors affecting the EC analysis and challenges related to it, which are discussed in this article focused on the EC from marine exhaust engine emissions. The following sections describe the interpretation of the thermograms (3.2), the temperature programme (3.3) and sample pre-treatment (3.4), as well as round-robin test results from three laboratories (3.5).

![Graph](image1.png)

**Fig 1.** Composition of diluted (ISO 8178) and hot in-stack PM samples using four fuels at 75% and 25% engine loads. We note that PM from diluted sampling contained sulphuric acid and semivolatile organics, which were not present in the hot in-stack samples.
1.4 Interpretation of thermograms

The EC/OC instrument produces a thermogram describing the amount of volatilised carbonaceous material and changes in the laser transmission through the filter as a function of time. EC is furthermore separated from OC and charred organic compounds based on laser transmission value. Several challenges were observed when interpreting the thermograms from marine engine exhaust samples (Figure 2), which are discussed in detail in this section taking into account PM composition. Here, we also present general view and special studies on the phenomena observed in the inert mode and in the oxygen phase of EUSAAR2.

The most complicated thermogram was observed for the 0.5 %S fuel at 75% engine load, particularly in the inert phase (Figure 2). Besides an early decrease (drop) in the laser signal, an increase in the laser intensity was observed during the second temperature ramp from 200 to 300 °C. This increase in the laser intensity was assumedly due to lightening of the colour of the sample as the coloured brownish organic compounds evaporated, or inorganic compounds transformed with their colour changes. A small peak in the third temperature step (450 °C) may relate to these same issues. For example, some of the bound crystal water may evaporate at relatively high temperatures. The last step of dehydration of many metal sulphates is known to take place at temperatures above 300 °C (Földvári, 2011). In the last temperature step of the inert phase, a gradual decrease in the laser signal (darkening) observed indicated the start of pyrolysis of OC. Step-wise reduction in laser signal was observed in the inert phase for the 2.5%S fuel assumedly caused by pyrolysis of OC combined with transformations of, e.g., vanadium compounds and related colour changes and other changes explained for the 0.5%S fuel. For the 2.5%S fuel, metals observed in PM may potentially act as catalysts leading to premature evolving EC, particularly when the PM also contains oxygen.

The samples for the distillate-type fuels (0.1%S and Bio30) contained mostly light organic compounds and EC, while sulphuric acid and metals were not substantially present. Thermograms were also relatively simple in the inert mode. However, for the 0.1%S fuel at 25% load, slight changes in the laser intensity led to misinterpretation of the split point when using the automatic programme. Samples for the Bio30 fuel contained fuel-originating oxygen, which was suspected to induce prematurely evolving EC in the inert phase.
Fig 2. Thermograms using the EUSAAR2 program for the samples obtained by diluted ISO 8178 sampling from marine engine exhaust at 75% and 25% engine loads using four fuels: 2.5%S, 0.5%S, 0.1%S and Bio30. Thermograms for undiluted (hot) in-stack samplings are presented in SI Section 5.1. Split ranges are attributed to similar samples in one laboratory. For a) and b) high-sulphur fuels, a laser drop at <200 °C (ca. 50 s), as well as other transformations and step-wise reduction in laser signal (pyrolysis of OC) were observed in the inert phase. For these fuels, punches remained yellow or pale yellow after analysis (75% engine load). In c), the 0.1%S fuel also showed a laser drop below 200 °C and pyrolysis of OC the inert phase. In the He/O2 phase, EC combusted clearly later and at a higher temperature for c) 0.1%S and d) Bio30 than for a) 2.5%S and b) 0.5%S.

In our study, an early drop in the laser signal in the inert phase was seen for the ISO 8178 diluted samples (sampling below 52 °C), particularly with the high-sulphur fuels and to lesser extent with the Bio30 and 0.1%S fuels. Early drop in the laser signal was not observed for the in-stack samples (sampling 350–400 °C), nor for the samples at 25% load. For high sulphur fuels (2.5%S and 0.5%S), the diluted ISO 8178 samples contained sulphuric acid, combined water and light organic compounds. These constituents were not present in the in-stack samples, as the sampling temperature was high. Sulphates in the in-stack samples are in another form than sulphuric acid, e.g., as metal sulphates ("mSO4" in Figure 1). For the 0.1%S and Bio30 fuels, an early drop in laser signal for the ISO 8178 diluted samples at 75% load may also be induced by the light organics. PM can also be hygroscopic when using an oxygenated biocomponent in diesel fuel (Happonen et al., 2013). At 25% engine load, only a low amount of sulphates was present, probably due to the insufficient combustion temperature for formation of the SO3 precursor.

An early drop in the intensity of the laser signal was also observed as early as the first temperature step of the inert phase by Lappi & Ristimäki (Lappi & Ristimäki, 2017), especially with high-sulphur fuels, assuming that volatile matter, probably sulphuric acid and bound water, will induce reactions on the filter at low temperatures. Lappi & Ristimäki (Lappi & Ristimäki, 2017) used the manual (baseline) split that omits the "early laser drop" when defining the initial laser signal. They achieved similar EC results with manual split as with water treatment of punches, but substantially higher than with the automatic split. In our study, interpretation of the thermograms proved to be even more complicated.

The split of OC and EC is based on the laser optical correction. When the laser signal returns to its initial value, it is understood as a split point. Thus it is important to understand, how "early laser drop" should be treated when defining the initial laser signal. Our tests with water-wetted filters (Figure 3a), vanadium salt (Figure 3b) and sulphuric acid with water (Figure 3c) showed that early laser drop is complicated phenomena associated with many issues. For water-wetted filters tested immediately after wetting, the laser signal is high in the beginning of the inert phase and decreases when the filter dries in pursuance of the temperature increase. This applies both to white and yellow punches (yellow punch obtained after the EUSAAR2 test run with the 2.5%S fuel). Drying of punches leads to changes in scattering and consequently decrease in the laser intensity. For yellow punches, decrease in the colour change from pale yellow (wet) to darker yellow (dry) during
Drying is also seen visually. It is noticeable that after drying of the water-wetted filters, the initial laser intensity was not recovered. Another test with the sucrose/water solution showed an early drop in the laser signal for the wet yellow punch, but not when the sucrose/water solution was added to the white filter punch (SI Section 3.1). Tests with sucrose started after drying until the laser signal was no longer decreasing.

As mentioned, vanadium possesses a complex chemistry of absorbing coloured compounds (Shiju, 2004). Knowing that the yellow filter punch after the EUSAAR2 run for the 2.5%S fuel contained vanadium (SI Section 2.5), we studied its effect on TOA by selecting vanadium oxide sulphate hydrate (VOSO₄·5H₂O) to mimic vanadium compounds present in exhaust from marine engines (Figure 3b). Surprisingly, VOSO₄·5H₂O led to substantial changes in laser intensity over EUSAAR2 including “early laser drop” and stepwise darkening in the inert phase, and also lightening and darkening in the oxygen phase of the EUSAAR2. These changes in laser intensity were not related to carbon as it was not present on punch. Instead, changes in the laser intensity were due to the colour changes of vanadium salts from initial pale blue to yellow in the end of EUSAAR2, through very dark compounds in the region where pyrolysis of OC is usually observed. Furthermore, we tested the 0.5%S fuel on yellow punch after analysing VOSO₄·5H₂O over EUSAAR2 (Figure 3d). Early drop in laser signal was seen in the inert phase, as well as stepwise darkening of sample that may indicate overlapping pyrolysis and transformations of vanadium salts. Overall, reliable distinction of OC and EC seems difficult in the presence of vanadium compounds.

The role of sulphuric acid was studied by doping the neat 0.5%S and 2.5%S fuels. Fuels doped with sulphuric acid led to a decrease in laser signal in inert phase of EUSAAR2 at below 200 °C, and also to other changes in laser intensity (Figure 3c). The share of EC in TC was 0.18% for the 0.5%S fuel and for H₂SO₄+H₂O doped fuel, 0.5%. The respective EC result for the 2.5%S fuel was 4.5%, and for doped fuel, 3.2%. For the 0.5%S fuel, sulphuric acid doping led to overestimated EC, while for the 2.5%S fuel, underestimated EC. This indicates overlapping scattering changes, pyrolysis, and EC oxidation. The manual split showed in both cases overestimated EC (1.2% and 6.3%).
Fig 3. Thermograms using the EUSAAR2 programme for a) wet and dry punches; b) vanadium oxide sulphate (VOSO$_4$ 5H$_2$O); c) sulphuric acid (H$_2$SO$_4$+H$_2$O) doped 0.5%S fuel; d) 0.5%S fuel on yellow punch after TOA of VOSO$_4$ 5H$_2$O; e) asphaltenes extracted from the 0.5%S and 2.5%S fuels and f) carbon black. Details of sample preparation procedures with additional information are given in SI Section 3. In case a), 60 s prolongation of the last temperature step of EUSAAR2 was not applied.

Oxygen is introduced in EUSAAR2 protocol at 670 seconds. PC artefact formed by charring of organic compounds is expected to rapidly oxidise at ca. 400 °C in the presence of oxygen (Barneto et al., 2014), which is a lower temperature than the first step of He/O$_2$ phase of EUSAAR2 (500 °C for 790 seconds). The split time is defined by detecting where the laser intensity in the oxygen phase reaches the same laser intensity as in the beginning of pyrolysis for compensation of PC artefact. When no charring takes place, the split point is defined at the point when the laser signal increases significantly above the initial value.

In the O$_2$/He-phase, the majority of EC combusted by 550 °C from the samples for the 2.5%S and 0.5%S fuels. However, a substantial carbon output in the O$_2$/He-phase was continuous almost until the end of the phase, possibly due to the simultaneous combustion of heavy BrC-type carbon originally present in the sample (the final boiling point of residual fuels can be well above the peak temperature of the inert phase (Mullins, 2010; Neste, 1987)), PC artefact, and finally, EC. When the split point was located in the region of substantial carbon output, small changes or noisiness in the laser signal caused differences in the split point and consequently, in the EC results. The potential role of asphaltenes present in the 0.5%S and 2.5%S fuels was demonstrated by analysis of almost black, solid asphaltene fraction from n-heptane extraction of fuels (Figure 3e, details in SI Section 4). From asphaltenes present in the 0.5%S fuel, 8% was classified as EC by TOA, and 12-19% for the 2.5%S fuel. The split point for asphaltenes in the 0.5%S fuel located at time when oven temperature was close to 850 °C and for the 2.5%S fuel close to 700 °C. The oxidation temperature of chemical grade carbon black (catalyst support) was also studied by TOA (Figure 3f, SI Section 3.3). A major portion of carbon black oxidised at 700 °C. Oxidation of exhaust soot is typically observed at temperatures above 600 °C, when no catalytic assistance for oxidation is used (Johansen, 2015).

For the distillate 0.1%S and Bio30 fuels, EC combusted at above 700 °C in the O$_2$/He phase, indicating the presence of refractory, graphitic-type EC. For these fuels, EC clearly combusted later than for the 2.5%S and 0.5%S fuels. Thus, determination of the split point should be easy. However, the deviation of the automatically determined split points was high particularly for samples obtained for 0.1%S fuel at 25% engine load. Minor deviations in the laser signal in the inert phase resulted in a wide spread in split times.

In summary, possible explanations for an early drop in the laser signal (reduced laser intensity) in the inert phase below 200 °C and other complex phenomena observed were a) drying of filters, e.g., change of filter punch colour from lighter (wet) to darker (dry) when volatile compounds evaporate b) transformations and catalytic effects of inorganic compounds (metals or sulphuric acid) and c) early pyrolysis. Artefacts were identified to be caused mainly by vanadium compounds and sulphuric acid and water present in samples from marine engine exhaust when using heavy fuels. Oxygen and catalytic metals in a sample may lead to premature evolving EC masked by
simultaneous pyrolysis of OC and other transformations of a sample. Defining a split time is challenging for samples undergoing complicated transformations, and redesign of temperature protocol may not be sufficient for reliable EC analysis. Thus we studied whether extractions and drying (see Section 3.4) could remove wetness and disturbing compounds of samples to alleviate challenges in the EC analysis of marine engine exhaust.

1.5 Comparison of three temperature protocols

The EC concentrations for 2.5%S, 0.5%S, 0.1%S and Bio30 fuels at 75% and 25% engine loads for ISO 8178 and in-stack samples obtained with three temperature programmes at peak temperatures of 870 °C, 750 °C and 650 °C in the inert mode are shown in Figure 3. The EC results were at the same level for the in-stack and ISO 8178-diluted samples when using the same temperature programme despite differences in the sampling principles.

On the contrary, differences in the EC results between different temperature programmes (EUSAAR2, NIOSH 5040) were observed. The EC concentrations were higher for the EUSAAR2 than for the NIOSH programs at high EC concentrations (above 5 mg Sm⁻³). The most substantial differences between the temperature programmes were observed for the 2.5%S and 0.5%S fuels containing substantial amounts of heavy organic compounds, sulphates and metals.

Fig 3. The EC results obtained using three programmes for samples collected with the ISO 8178 and in-stack sampling. Fitting is shown for ISO 8178 and in-stack samples using the EUSAAR2 protocol. The individual EC results (y-axis) from different temperature programmes are compared to EC average values (x-axis; calculated arithmetic average from the results of different temperature programmes (EUSAAR2, NIOSH 5040 /750°C, NIOSH 5040 /870°C)).

The pre-oxygen split indicates premature combustion of carbon in the inert phase in the presence of oxygen and catalysing species in sample, or in the case of instrumental oxygen leak. A pre-oxygen split was observed for many samples using the NIOSH 5040 programme at 870 °C peak temperature, particularly for the in-stack samples, while the pre-oxygen split was not observed when the peak temperature of the inert mode was lower (750 °C or 650 °C). Oxygen was present in the samples for residual fuels (e.g., as sulphates and metal oxides), and for the Bio30 fuel (unburned oxygenated fuel). We note that premature combustion of carbon suspected for these samples may be masked with simultaneous pyrolysis of OC and other reactions. Thus, a programme with a low peak temperature of inert phase and long temperature steps, namely
EUSAAR2, was selected to minimise the undesired reactions (Cavalli, Viana, Yttri, Genberg, & Putaud, 2010). With EUSAAR2, overestimated EC in the presence of heavy OC has been observed (Pantelidias et al., 2015). Further development of EUSAAR2 could be considered, for example, prolongation of the last step of the inert phase and the first temperature step in the O₂/He phase to oxidise PC and BrC more efficiently. The advantage of EUSAAR2 is also its capability to analyse higher TC concentrations than NIOSH 5040, as carbon evaporates in a wide time range and FID response peaks are lower. Also higher sucrose concentrations are useful for calibration (and thus a wider range can be achieved) with EUSAAR2 than with NIOSH 5040. Here we note that sucrose is designed exclusively for the calibration of OC, and no widely accepted commercial calibration material is available for the EC calibration. In this study, the EUSAAR2 temperature programme with 60 seconds’ prolongation of O₂/He phase was selected for the EC round-robin test (Section 3.5).

1.6 Sample pre-treatment

Many constituents, such as moisture, organic compounds including formed PC and inorganic cations disturb the distinction between EC and OC (Kuhlbusch et al., 2009). To avoid or minimise the influence of these constituents, samples can be dried or extracted prior to the analysis to minimise their effect (Lappi & Ristimäki, 2017; Lauer, 2008). In these experiments, drying of filters at 180 °C for one hour, as well as the extraction with only water or toluene followed, with the IPA/water being tested for samples obtained with the 2.5%S and 0.5%S fuels at 75% load.

Drying removed some constituents that were responsible for early laser drop, but did not prevent other changes that complicate interpretation of the laser signal, such as pyrolysis of OC or evaporation of coloured compounds (see SI Section 2.4). Toluene removed soluble organic compounds from PM, while IPA/water removed soluble inorganic compounds, including some metal compounds and sulphates. Drying is a more practical procedure than extractions, particularly if integrated in the instrumental protocol combined with continuous FID measurement of carbon.

For the 0.5%S fuel, the EC concentrations from the dried or extracted filters were lower than those from the untreated filters (Table 4). In the opposite, the EC concentrations for the 2.5%S fuel from the dried or extracted filters were higher than those from the untreated filters. In most cases, differences between untreated and extracted filters were below 0.5 mg/m³. Thermograms (see SI Section 2.4) revealed that the differences before and after extractions were seen in the most refractive EC appearing after 900 s (700 °C) in the EUSAAR2 programme. This could be explained for the 2.5%S fuel by prematurely evolving EC from untreated samples in the presence of catalytic species that are removed during the washing procedure. Instead, for the 0.5%S fuel, an explanation could be soluble material tightly attached to EC. Additionally, mechanical losses or movements of EC during the extraction procedure could be possible. As a conclusion supported by Section 3.2, water extraction is necessary when vanadium compounds and sulphuric acid are present in the marine engine exhaust samples. To allow analysis of both EC and OC from the same filter and to minimise risk of losing/moving PM mass on filter, we developed a fast extraction method (extraction time less than 10 minutes, see SI Section 2.4). The new extraction method showed mainly similar trends as those shown in Table 4 for samples obtained with 0.5%S and 2.5%S fuels.

The results of the limited sample pre-treatment tests showed systematic directions, indicating that these procedures could increase the accuracy of the EC analyses.
Table 4. Influence of pre-treatment (drying, extractions) on EC concentrations obtained from the filter samples with the 2.5%S and 0.5%S fuels at 75% load. The EC concentrations for untreated samples were 1-3 mg Sm$^{-3}$ (2.8-4.6 µg cm$^{-2}$). All EC results are based on an automatic split.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Change (µg cm$^{-2}$)</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%S, 75% load</td>
<td></td>
<td></td>
</tr>
<tr>
<td>drying at 180 °C, 1 h</td>
<td>+4.3</td>
<td>+98$^a$</td>
</tr>
<tr>
<td>toluene and water/IPA</td>
<td>+0.3$^a$; +0.8$^b$</td>
<td>+7$^a$; +18$^b$</td>
</tr>
<tr>
<td>water</td>
<td>+1.7$^a$; +0.4$^b$</td>
<td>+51$^a$; +10$^b$</td>
</tr>
<tr>
<td>0.5%S, 75% load</td>
<td></td>
<td></td>
</tr>
<tr>
<td>drying at 180 °C, 1 h</td>
<td>-0.3</td>
<td>-9$^a$</td>
</tr>
<tr>
<td>toluene and water/IPA</td>
<td>-0.5$^a$; -0.2$^b$</td>
<td>-21$^a$; -6$^b$</td>
</tr>
<tr>
<td>water</td>
<td>-0.6$^a$</td>
<td>-18$^a$</td>
</tr>
</tbody>
</table>

$^a$ NIOSH 5040 $^b$ EUSAAR2

1.7 Round-robin results

In the round-robin test, the same filter samples (EC1-EC10=exhaust samples, EC11=blank) were analysed in three laboratories using three instruments (see Section 2.3). Three punches were taken from each filter for each laboratory (3 x 3). Round-robin samples collected by the ISO 8178 SPC sampling represented different fuels and engine loads:

- 0.1 %S at 75% load (EC1, EC10) and at 25% load (EC2)
- 0.5 %S at 75% load (EC4) and at 25% load (EC3, EC5)
- 2.5 %S fuel at 75% load (EC6) and at 25% load (EC7)
- Bio30 fuel at 75% load (EC8) and at 25% load (EC9)

The EC concentrations from the round-robin of three laboratories are shown in Figure 4. Individual EC tests are shown in Figure 4a, and minimum, maximum and average EC results observed in three laboratories in Figure 4b. The EC concentrations at three laboratories indicated similar differences between engine loads and fuels. The EC concentrations were lower at 75% than at 25% engine load, and so were the differences between the EC concentrations obtained with different fuels. At 75% engine load, the highest difference in the EC concentrations between fuels was 2.3 mg/Sm$^3$ (3.6 mg/Sm$^3$ for 2.5%S fuel and 1.3 mg/Sm$^3$ for Bio30 fuel). At 25% engine load, the highest difference in the EC concentrations between fuels was 15.4 mg/Sm$^3$ (20.7 mg/Sm$^3$ for 0.5%S fuel and 5.3 mg/Sm$^3$ for Bio30 fuel). The highest EC concentration was observed for the 0.5%S fuel at 25% engine load.
Fig 4. The EC results from the round-robin of three laboratories a) Individual EC results as EC loadings (µg/cm²) in Lab a, Lab b and Lab c for three punches of each filter sample, one value per marker; and b) The minimum, maximum and average EC results as concentrations (mg/m³) of round-robin filter samples in three laboratories (n=9, outliers also included). Figure includes all three replicates of each sample. Recommended EC loadings (Figure 4a) were achieved by varying the PM mass collected on filters as shares of EC in PM depend on engine loads and fuels. Thus only calculated EC concentrations (Figure 4b, Equation 1) can be used for comparing the EC concentrations between different engine loads and fuels.

Differences in the EC concentrations between three laboratories were observed. Although the same temperature programme (EUSAAR2) was used in all three laboratories, some analysis procedures were different and may explain the differences observed. For instance, Lab b and Lab c used only automatic split in the EC analyses, while Lab a also used manual split for samples EC4, EC6 and EC7 (see SI Section 2.2). The EC results obtained with automatic split in Lab a for samples EC4, EC6 and EC7 are close to those obtained in Lab b. Further, the model year of instruments varied between laboratories, and so did the temperature offset calibrations. The TC concentrations were relatively similar in three laboratories, only Lab c observed slightly lower TC concentrations than Labs b and a (SI Section 2.2). Differences in the EC results between laboratories did not originate from the differences in the TC, as the carbon evolved after a constant split of 750 s was similar in all laboratories (Figure 4b, green markers). The constant split analysis here means that the EC results were additionally calculated using the constant split of 750 s to inspect whether the differences in the EC results were based on the differences in the thermograms, or in the optical determination of the split time. Indeed, the constant split method showed that the carbon that evolved after the same split was similar in different laboratories for all samples. As a conclusion, differences in the EC concentrations observed between laboratories were concluded to originate from the interpretation of the optical laser signal.

The anomalous EC concentrations were obtained for filter samples EC2 (0.1%S at 25% load) and EC5 (0.5%S at 25% load) in Lab c (see SI Section 5.4). In one of the three punches, an automatically determined split point occurred as early as the first temperature step of the inert phase, leading to the high EC concentrations. These concentrations were regarded as outliers in the calculation of the standard deviation of the EC results, although they are shown in Figure 4a and Figure 4b.

Differences between laboratories were also found for filter samples EC4 (0.5%S at 75% load) and EC6 (2.5%S at 75% load), for which higher EC concentrations were obtained in Lab a than in Lab b and Lab c. EC4 filter samples had the most complicated thermograms of the study (Figure 2b). The drop in laser signal in the first temperature step of the inert phase was interpreted as the start of pyrolysis in Lab b and Lab c using only an automatic split point leading to lower EC results than in Lab a, who used manual split to interpret this as a drying of filters. Laser signals for the filter
sample EC6 (Figure 2a) followed similar patterns as filter sample EC4, but with less pronounced changes.

Standard deviations of the EC concentrations using an EUSAAR2 temperature programme within each laboratory were in most cases below 0.5 mg/Sm^3 (outliers excluded), and below 1 mg/Sm^3 between three laboratories. The standard deviation within each laboratory was on average below 5%, however, up to 13% (0.5 µg cm^-2) in two laboratories, and up to 31% (3.5 µg cm^-2) in one laboratory. The standard deviation of EC between three laboratories was on average below 0.5 mg/Sm^3, and below 1 mg/Sm^3 between three laboratories. The standard deviation within each laboratory was on average below 5%, however, up to 13% (0.5 µg cm^-2) in two laboratories, and up to 31% (3.5 µg cm^-2) in one laboratory. The standard deviation of EC between three laboratories was on average 10%, ranging from 2% to 28%. The highest relative deviation of the results was observed for the 0.1% S fuel at 25% engine load (EC2). Round-robin results are shown in more detail in SI Section 2.2. For ambient filter samples, Panteliadis (Panteliadis et al., 2015) found the repeatability and reproducibility of EC to be 15 and 20% when using the EUSAAR2 temperature programme, and 20 and 26% for NIOSH 5040, respectively. Another inter-laboratory comparison of ambient samples (ACTRIS, 2017) reported repeatability from 3% to 12% for the EC/TC ratio, and reproducibility from 10% to 48%.

The results of this round-robin are not representative of repeatability of the TOA instrument in general. Rather, this exercise indicates deviation of the TOA results in different laboratories for challenging marine engine exhaust samples with routine procedures in a laboratory (including automatic and manual split). We note that water extraction (Sections 3.2 and 3.4) would increase the reliability of the EC results for some marine engine exhaust samples.

1.8 Considerations for the TOA

The relationship between the constituents of PM and phenomena observed in the thermograms for different samples are summarised in Table 5.

Table 5. The summary of PM composition and possible reactions in the EC analysis for different types of fuels. Indicated phenomena apply to different temperature protocols.

<table>
<thead>
<tr>
<th>PM composition (ISO 8178)</th>
<th>Residual fuels (2.5%S and 0.5%S)</th>
<th>Oxygenated fuel (Bio30)</th>
<th>Distillate fuel (0.1%S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert &lt;200 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂O, H₂SO₄, OC evaporation, OC pyrolysis (catalytic)</td>
<td>H₂O, OC evaporation</td>
<td>OC evaporation</td>
</tr>
<tr>
<td>Inert &gt;200 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OC (coloured) evaporation EC combustion (catalytic species &amp; oxygen in sample)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Crystal water &amp; changes in salts</td>
<td>OC pyrolysis</td>
<td>OC pyrolysis</td>
</tr>
<tr>
<td></td>
<td>PC oxidation</td>
<td>PC oxidation</td>
<td>PC oxidation</td>
</tr>
<tr>
<td></td>
<td>Heavy-OC oxidation</td>
<td>EC oxidation</td>
<td>EC oxidation</td>
</tr>
<tr>
<td></td>
<td>EC oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC indication</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Underestimated for 2.5%S</td>
<td>Underestimated</td>
<td>Low bias in principle</td>
</tr>
<tr>
<td></td>
<td>Overestimated for 0.5%S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the TOA method, a signal of a laser is monitored to eliminate pyrolysis artefact so that EC could be reliably analysed. When samples contain species causing decrease in initial laser signal that is
not related to pyrolysis, or colour changes in samples induced by, e.g., sulphuric acid and metal salts (particularly vanadium compounds), or premature evolving EC, reliable determination of EC with the TOA method is difficult regardless of the temperature protocol or parameter choices. Our study showed that exhaust from marine engines using heavy fuels contained species that disturbed the TOA.

For marine engine exhaust PM samples, many transformations during temperature protocol may interfere with the compensation procedure for pyrolysis. For example, a decrease in the laser signal below 200 °C may occur due to, e.g., the drying of filters or induced by sulphuric acid and bound water or vanadium compounds. Also in the inert phase, evaporation of coloured constituents and colour changes of inorganic species may mask possible premature evolving EC, which is a potential threat for samples containing oxygen and catalytic species. The defining split point is either automatically or manually challenging for samples undergoing complicated transformations.

To overcome these challenges, the following solutions are considered:

- Water extraction of samples containing vanadium or sulphuric acid to avoid changes in scattering due to the evaporation and colour changes related to transformations of inorganic species and their catalytic effects. Water extraction of samples simplified the thermograms, which indicates that disturbing species were generally water-soluble. We showed that a part of fuel asphaltenes are classified as EC using the TOA method, although they are soluble in, e.g., aromatic solvents. To avoid losses of this kind of EC which was originally present in the sample, extraction exclusively with water is considered prior to TOA instead of other solvents.

- Drying could be sufficient for samples that do not contain significantly sulphur or vanadium (or other disturbing species), but show decreases in laser signal below 200 °C. This procedure could be integrated in the instrumental protocol with continuous FID measurement.

- Using protocol that has sufficiently low peak temperature in the inert phase may alleviate some unintentional changes in the samples (e.g., EUSAAR2). However, in this case prolongation of the first temperature step in the He/O₂ phase could aid oxidation of heat-resistant heavy OC to avoid overestimated EC. Further, prolongation of the last step of EUSAAR2 is suggested to achieve baseline before the methane calibration peak when samples contain graphitic-type EC that is evolved late.

- An initial laser signal could be reconsidered for samples showing slight fluctuation of laser signal in the inert phase.

Conclusions

Regulation for ship BC is anticipated, particularly in the Arctic, where ships are important emitters. EC is often used synonymously with BC, although these are not commensurable by definition. Here, EC analysis was studied for samples emitted from a marine engine at 75% and 25% engine loads using fuels with different sulphur contents (2.5%S, 0.5%S and 0.1%S) and an oxygenated biofuel (Bio30). Samples with the 2.5%S and 0.5%S fuels contained a substantial amount of sulphates, water, heavy organic compounds and metals. Samples from 0.1%S and Bio30 fuels had mainly EC and semivolatile OC, while only minor amounts of sulphates and metals.

Thermal-optical analysis of complex samples from a marine engine exhaust was challenging. EUSAAR2 was deemed to be a more suitable temperature program than the NIOSH 5040 for the EC analyses of the untreated samples from a marine engine, as its relatively low peak temperature in the inert phase combined with slow temperature changes can alleviate prematurely evolving EC. In this study, EUSAAR2 was prolonged to avoid overlapping of the last EC peak and the methane
calibration peak. In addition, prolongation of the first step of the O₂/He phase could alleviate overestimated EC in the presence of heavy OC in-sample.

There was a relationship between PM constituents and behaviour observed in the thermograms. Interpretation of the changes in laser intensity in the inert phase below 200 °C affected the split time and consequently the EC results. This was deemed to be related to the sulphuric acid and combined water, and to the vanadium compounds leading to severe changes in the punch colour and scattering. At higher temperatures in the inert phase, premature evolving EC was suspected for samples containing catalytic species and oxygen. Many simultaneous transformations, including evaporation of coloured organics and colour changes of metal salts interfered with the analysis. Therefore, water extraction of samples containing sulphur and metal compounds is suggested prior to analysis with the TOA method. Variation in the split times between replicate tests was observed despite seemingly similar thermograms in the latter part of the EUSAAR2 programme. Even small changes in the split time led to substantial differences in the EC results when the split fell into the high carbon output region.

Round-robin tests showed deviation in the EC concentrations between the three laboratories. However, when two outliers were excluded, standard deviations of EC using the EUSAAR2 temperature programme were reasonable within each laboratory and between three laboratories. Improved accuracy of the EC analysis would require development of a calibration method or reference material for EC.

Our study discovered issues that deserve consideration when reliable EC results are desired from challenging marine engine exhaust samples. However, we also recognise the need for further fundamental studies to improve understanding of this complex issue. For example, particle chemical composition and physical properties vary depending on the engine, fuel and emission control technology used.

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Supplementary material

Supplementary material associated with this article can be found in the online version.

References


ACTRIS. (2017). Results of the inter-laboratory comparison exercise for TC and EC measurements (ref.:


ACCEPTED MANUSCRIPT


Highlights

- EC analysis was challenging for marine engine exhaust samples
- The behaviour observed in the thermograms changed depending on the fuel
- Temperature protocol used and sample extraction affected the EC results
- Interlaboratory round-robin of EC analysis showed differences between laboratories