TECHNOLOGY FOR BUSINESS

Analysing Elemental Carbon from Ship Particulate Matter: Artefacts and Possible Solutions

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Introduction

International Maritime Organisation (IMO) is evaluating needs for control of Black Carbon (BC) from ships. Elemental carbon (EC) is not a commensurable definition with BC, but it is often discussed with the BC results. The EC determination using thermal-optical principle is challenging, particularly when samples contain minerals, organics or sulphates and bound water substantially. In this work, pathways to alleviate artefacts in the EC analysis from ship PM were studied. The PM samples were collected from a 1.6-MW ship engine (Wärtsilä Vasa 4R32) at 75% and 25% engine loads using four fuels with different sulphur contents (2.5%S, 0.5%S and 0.1%S) and a biofuel (Bio30). The EC round-robin was conducted by three laboratories using three different instruments.

EUSAAR2 suited for ship samples

In this work, the EUSAAR2 (prEN 16909) and NIOSH 5040 with two peak temperatures (870 °C and 750 °C) were studied. The EUSAAR2 protocol suited best for the ship PM samples as its peak temperature in the inert mode is sufficiently low and temperature rise is sufficiently slow to avoid pre-oxygen split. Smooth temperature program also minimises unintentional transformations in the sample. Prolongation of the last temperature step of EUSAAR2 was needed for distillate fuels to avoid overlapping of the last sample peak and the methane calibration peak.

Manual split point needed for ship PM

PM may contain a large amount of organic carbon (OC) prone to pyrolysis, and thus the laser signal is recorded to detect the split point when the laser intensity reaches the pre-pyrolysis value. For some ship PM samples, particularly those obtained with residual fuels, complicated changes in the laser throughput are observed (Fig. 1). Filters are drying, OC is pyrolysed and EC is prematurely evolving due to minerals or oxygen containing compounds in PM. Furthermore, the punch may remain yellow after analysis. All these factors may bias the optical split point. One option to alleviate these artefacts would be extractions of the PM samples with water, alcohols or organic solvents prior to the EC analysis to remove solubles. However, our pre-tests showed irregular changes in the EC results from the extracted PM samples. Moreover, OC cannot be determined after the washing procedure. Instead, manual split point was used for the most difficult samples.

Constant split point for quality assurance

The round-robin EC results depended on a laboratory, personnel and generation of the instrument when using the optical split point determination (Fig. 2). However, we observed that the EC part of thermograms was similar in all three laboratories, and so were the EC results when using the constant split time. The automatic split point determination failed for the challenging ship PM samples, which was reflected in the EC results. The constant split method seemed feasible as the quality control method for the EC analysis.

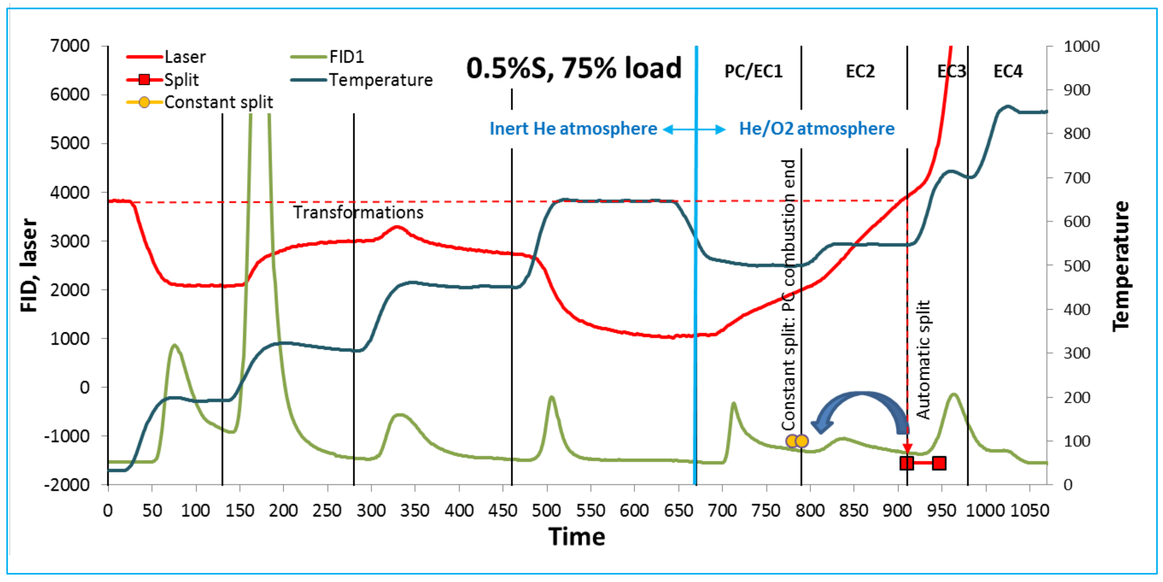

Figure 1. Changes in the laser throughput were complicated for some ship PM samples. EUSAAR2, 0.5%S fuel, 75% engine load.

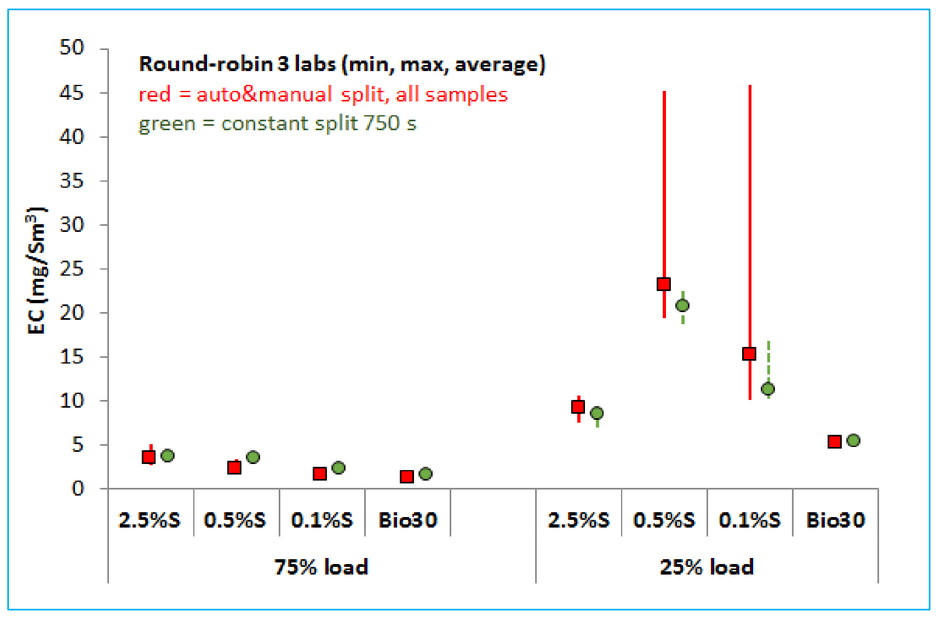

Figure 2. In the round-robin of three laboratories, spread in the EC results was higher for the optical split time than for the constant split time.

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Conclusions

The EUSAAR2 protocol suited best for the ship PM samples as its peak temperature in the inert mode is sufficiently low and temperature rise is sufficiently slow to avoid premature evolving of EC. Manual split point determination was needed for the challenging ship PM samples that could not be analysed reliably using the automatic optical split point. Futhermore, the constant split method is suggested as the quality control method of the EC analyses from ship PM.

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Reference

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