

SUB-COMMITTEE ON POLLUTION
PREVENTION AND RESPONSE
1st session
Agenda item 8

PPR 1/8/4
12 December 2013
Original: ENGLISH

**CONSIDERATION OF THE IMPACT ON THE ARCTIC OF EMISSIONS OF
BLACK CARBON FROM INTERNATIONAL SHIPPING**

**Proposed measurement method for Black Carbon:
Determination of Elemental Carbon from PM Filter Samples**

**Submitted by the European Association of Internal Combustion Engine Manufacturers
(EUROMOT)**

SUMMARY

Executive summary: This document presents further details of the involved method for elemental carbon (EC) determination from particulate matter (PM) filter samples in response to the correspondence group report. Owing to its technical nature the annex is provided in English only.

Strategic direction: 7.3

High-level action: 7.3.2

Planned output: 7.3.2.2

Action to be taken: Paragraph 3

Related documents: PPR 1/8 and PPR 1/8/3

1 This document is submitted in accordance with provisions of paragraph 6.12.5 of the Committees' Guidelines (MSC-MEPC.1/Circ.4/Rev.2) and comments on document PPR 1/8.

2 The examination method of particulate matter (PM) filter samples for its elemental carbon (EC) content by a multi-step thermal method with a thermal carbon analyzer according to VDI-2465 Part 2 (1999, note *VDI: The Association of German Engineers*) with an additional step from VDI-2465 Part 1 (1996) to minimize the effect of pyrolytic conversion of organic material (OM) into elemental carbon (EC) during the thermal treatment in the inert gas phase is set out in the annex. This information was kindly provided to EUROMOT by Germanischer Lloyd accredited laboratory "Analysetechnik". The described method minimizes pyrolytic conversion of OM into EC as commonly introduced by thermal analytic methods and has been adjusted to the PM contained in marine diesel engine exhaust.

Action requested of the Sub-Committee

3 The Sub-Committee is invited to note the information provided.

ANNEX

Version: 2.0; CKur; Date: 2013-11-29

Determination of Elemental Carbon from PM
Filter Samples



1. The analysis method described is suitable for the determination of elemental carbon (EC) embodied in particulate matter (PM) contained in the exhaust of marine Diesel engines. The measurement method is based on the German industrial standard VDI-2465 Part 2 (1999) including a process described in VDI-2465 Part 1 (1996).
2. The PM filter samples are to be examined for their EC content by a multi-step thermal method with a thermal carbon analyzer. This multi-step combustion method uses the thermal stability of EC which is higher than of organic carbon (OC) compounds. The complete analyzer set-up is shown in figure 1.

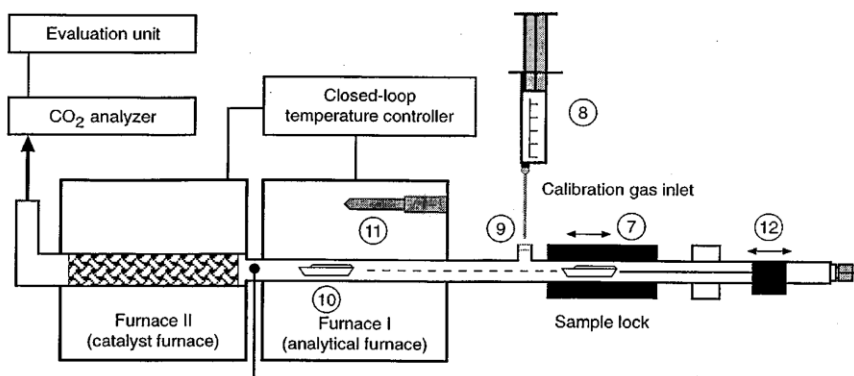


Figure 1: Analytical unit

3. The applied test program as given in table 1 is suitable for analysis of EC from marine Diesel engines running on DM-A or RM grade fuel. The temperature is the heating temperature to which the analyzer shall be adjusted. The gas stream, 100% helium or a mixture of 90% helium and 10% oxygen is introduced via mass flow rate regulator.

Gas	100% Helium									90% Helium / 10% Oxygen			
Step No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Time [sec.]	0	12	36	48	90	150	210	210	288	318	364	424	450
T-Level [°C]	<280	280	300	300	750	750	750	750	300	300	850	850	850
Function	Start	Organic Carbon (OC)								Elemental Carbon (EC)			

Table 1: Test program

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Determination of Elemental Carbon from PM Filter Samples



4. Figure 2 shows the time record of the analyzer test heating temperature and the corresponding gas mixture and a principal measurement response of the PM sample. During the process the organic compounds do vaporize in the helium stream at temperatures up to 750°C for approximately 300 seconds whereas the EC is remaining solid. Following, the EC is converted into the gas phase by combustion in the helium/oxygen stream, lasting for approximately further 150 seconds, forming the analyzer exhaust gas. An oxidation catalyst in the analyser exhaust gas stream converts the carbon compounds thereof into CO₂. The CO₂ concentration in the test gas is determined continuously using a non-dispersive infrared (NDIR) detector.

5. In order to minimize overestimation of EC due to pyrolytic conversion of organic material into EC during the evaporation of the organic compounds, a liquid extraction prior to the analysis of EC is necessary. The extractable organic carbon fraction must be removed in a soluble mixture of toluol and isopropanol at a ratio of 50:50.

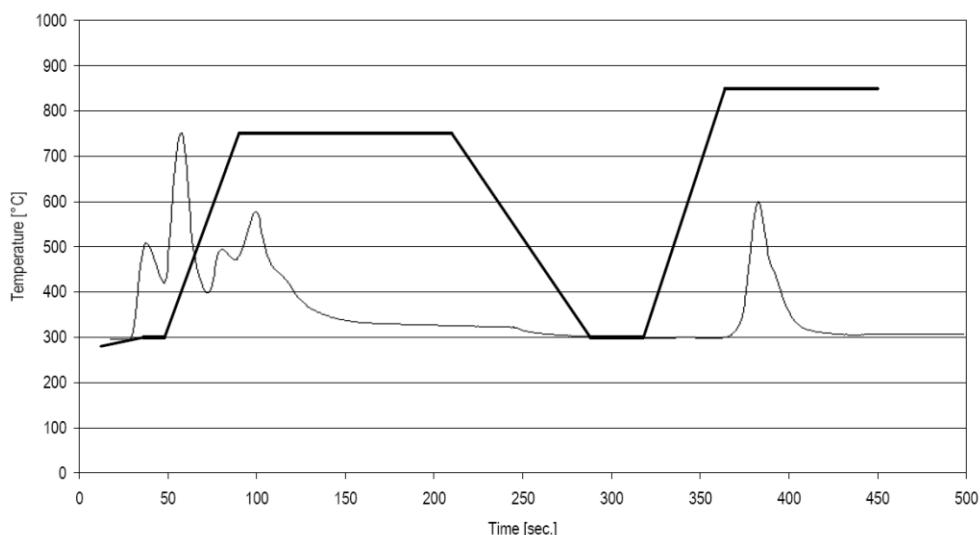


Figure 2: Temperature course and typical measurement signal

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Determination of Elemental Carbon from PM Filter Samples



References

VDI-2465 Part 1: Measurement of soot (immission) - Chemical analysis of elemental carbon by extraction and thermal desorption of the organic carbon, 1996

VDI-2465 Part 2: Measurement of soot (Ambient Air) - Thermographical determination of elemental carbon after thermal desorption of organic carbon, 1999

AAT 019: GL "Analysetechnik" In-house method - Thermographical determination of organic and elemental carbon, 2009

VDI: Verein Deutscher Ingenieure e.V., The Association of German Engineers

VDI Standards and their significance:

Today, approximately 200 VDI Standards based on the latest technical developments are produced by the VDI's technical divisions per year. That way the VDI has systematically built up a set of technical regulations, which today contains more than 2000 valid VDI Standards extensively covering the broad field of technology. VDI Standards play a very important role as pioneers for international standardization. Copyrights for VDI Standards are held exclusively by Verein Deutscher Ingenieure e.V.

Germanischer Lloyd „Analysetechnik“

Accredited according to DIN EN ISO 17020 as a notified inspection body

Accredited according to DIN EN ISO 17025 as a testing laboratory for exhaust gas emission measurements from combustion engines/plants (gaseous components and particulate matter) as well as chemical analysis of PM

Accredited as a testing laboratory according to Recreational Craft Directive (94/25/EC)

Notified Body and Technical Service acc. to River Rhine Vessel Inspection Regulations (CCNR)

Chemical analysis capabilities:

- Thermographic analysis of organic and elemental carbon
- Ion chromatographic analysis of sulphate and nitrate
- Determination of the soluble organic fraction (SOF)
- Analysis of fuel- and oil-derived hydrocarbons
- Analysis of the volatile and solid fraction

GL Laboratory 'Analysetechnik'

Laboratory for Exhaust Emission Measurement and Chemical Analyses

Accredited according to ISO 17020 and ISO 17025

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