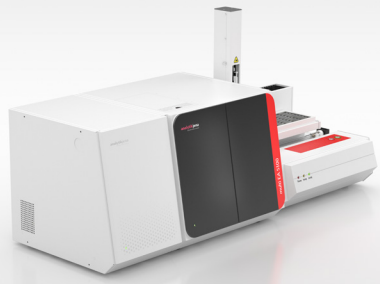

Measurement of Soot in Ambient Air – Determination of Elemental Carbon (EC) after Thermal Desorption of Organic Carbon (OC) Based on VDI 2465-2

Challenge

Separation and quantitative determination of EC/OC in a wide concentration range. Reliable matrix-related calibration and optimized processing times.

Solution

Pretreatment-free, separate EC/OC determination by elemental analysis. Fully automated, fast processing. Calibration by special elemental carbon standards.

Introduction

Elemental carbon (EC) and organic carbon (OC) are two important parameters for environmental protection, health and safety at work. Their reliable and rapid determination is essential for sufficient air quality, as EC-/OC-containing particles of incomplete combustion products have carcinogenic, environmentally harmful effects. In the combustion process of fossil fuels (e.g., petroleum, coal, natural gas) and other organic substances in industry, transportation and in private households, the contained organic hydrocarbons are mainly oxidized to CO_2 and water. If this process is not completed, e.g., due to a lack of oxygen or too low temperatures, soot is formed in addition to the CO_2. The poorer the combustion quality, the higher the amount of generated soot. This substance consists of elemental carbon and many other higher condensed organic hydrocarbons, adsorbed on the surface of the soot particles. As elemental carbon is considered to be the most important cause of lung carcinomas, this parameter is limited and must therefore be strictly controlled.

Adherence to these limits is especially relevant in production facilities with diesel engine-driven vehicles operating in closed rooms, underground mines, in industrial urban areas or along congested inner city arterial roads.

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The EC parameter is also of major interest in engine and catalytic converter research, for monitoring the effectiveness of combustion, exhaust filters and the activity of catalyst materials.

The combustion-based elemental analyzer multi EA 5100 offers an automated, quick and reliable alternative to time-consuming competing techniques. The process utilized is mainly based on the recommendations of the VDI 2465 sheet 2, with improvements in matters of processing time and calibration.

Materials and Methods

Samples and Reagents

Different round filter plates (particulate emission - including elemental and organic carbon, on the surface of quartz fiber filters) have been analyzed. The color of the filter plates was ranging from white (blank) over light grey (traffic reduced zone) to dark black (industrial zone). The color is an indicator for either the degree of pollution or the time and duration of sampling.

- Specially prepared soot standards (with 1.01 g/kg and 9.96 g/kg elemental carbon absolute)

Figure 1: Filter samples, uncontaminated (a.) blank filter, (b.) slight contamination, (c) heavily contaminated filter

Sample Preparation

Before analysis the round filters (d = 15 mm) were cut into four pieces using a scalpel. This was done to provide a better and faster desorption of the organic and combustion of the elemental carbon. All filter quarters were analyzed together in one sample run. Alternatively the entire filter can be folded or wrapped and put in the sample boat, the boat's downholder ensures that the filter resp. its aliquots remain in the proper position during the entire process.

Calibration / Recovery Check

A specially prepared soot standard based on a known content of elemental carbon on quartz powder as a carrier was used to calibrate and check the system performance and recovery. This allows optimal adaptation of the process to the sample matrix under investigation. To cover a range as wide as 0 to 900 µg carbon absolute, different quantities (5–100 mg) of the EC standards were used.

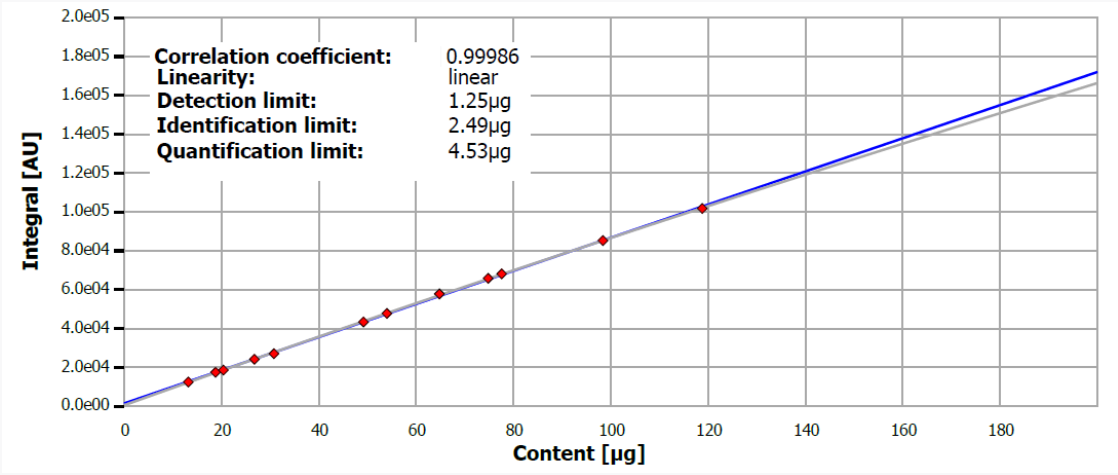

Figure 2: Example of an EC calibration for the trace range, curve including statistics

Instrumentation

The measurements were performed using a horizontally configured multi EA 5100, equipped with the HiPerSens NDIR detector for carbon determination. Sample introduction was carried out fully automatically using the MMS multi matrix sampler in solids mode with boat sensor, in combination with the ABD – automatic boat drive. This ensures a high sample throughput and allows unattended operation of the analyzer.

The analyses have been run in horizontal operation mode. Therefore the samples were put in special sample boats with a downholder, located at the 35 positions sample tray of the MMS sampler. Insertion of the filled boats and transfer into the furnace happens automatically. Thereby the special shape of the boats avoids loss of filter samples during transport.

Determination of the OC and EC content takes place in a two-phase process. The first process phase is intended to determine the complete OC content. Therefore the sample boat is quickly pushed to a defined temperature plateau of the desorption/evaporation zone, while it is surrounded only by the inert gas argon. The hydrocarbons adsorbed on the surface of the filter are now released by the increased temperature. Due to the lack of oxygen combustion of the EC does not take place. The volatized organic compounds are purged to the combustion chamber by the argon stream. In presence of an excess of oxygen they are converted to CO_2. After drying, then reaction gas is purged to the detector, where the carbon is quantified by means of non-dispersive infrared spectrometry (NDIR). After the OC determination is finished, the second process phase starts. The system is now purged by pure oxygen. The boat is quickly moved to the combustion zone, were the remaining EC is immediately converted to CO_2. The detection process is the same as before. The processing time is between 600 s and 1200 s, strongly depending on the degree of polution.

Figure 2: multi EA 5100 with MMS in horizontal operation mode

Method Parameters

The methods *ECOC_content* and *ECOC_concentration* from the method library were used for sample analysis resp. calibration and system check.

Both differ only in the calculation algorithm of the final results. The first indicates the absolute carbon contents, the second the concentration of the carbon. The following table summarizes the parameter settings for the combustion process.

Table 1: Process parameters multi EA 5100 in horizontal mode

Parameter	Specification
Furnace temperature	1,000 °C
Thermodesorption	750 °C
Purge time	60 s
Ar flow (first phase)	200 mL/min
O_2 main flow	200 mL/min
O_2 flow (second phase)	200 mL/min

Evaluation Parameters

Standard method settings were applied. The parameter settings are summarized in the following table.

Table 2: Detection parameters for the EC/OC determination with NDIR

Parameter	Specification OC	Specification EC
Max. integration time	600 s	180 s
Start	0.12 ppm	0.12 ppm
Stability	3	3
Threshold	5 ppm	0 ppm

Results and Discussion

The results of the filter samples and standards are given in Table 3 and 4. They are single analyses.

Table 3: Results of the EC/OC determination of the filter samples and the EC determination of the standard

Measurement	EC	OC
Filter 1	875 µg	656 µg
Filter 2	124 µg	118 µg
Filter 3	32.8 µg	112.1 µg
Test standard EC = 1.01 g/kg	1.0 g/kg	-

Figures 4 – 8 show typical measuring curves for selected filter samples (EC and OC) resp. the standard (EC).

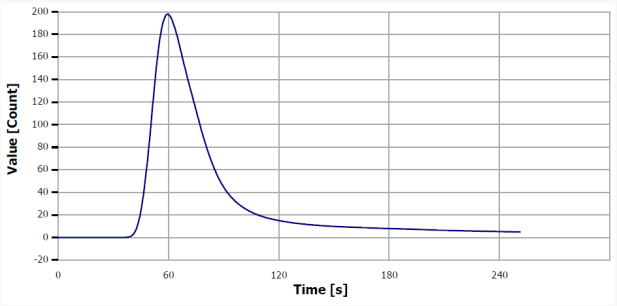

Figure 4: OC analysis curve of "filter 1"

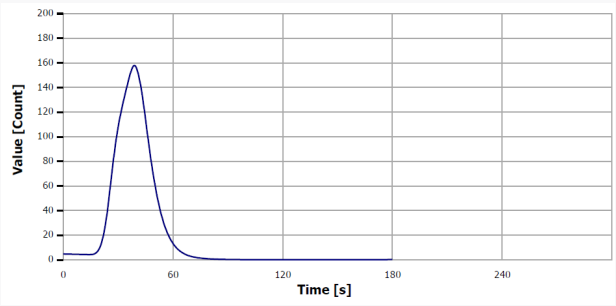

Figure 5: EC analysis curve of "filter 1"

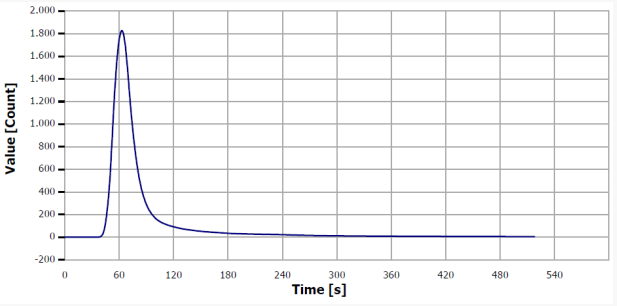

Figure 6: OC analysis curve of "filter 2"

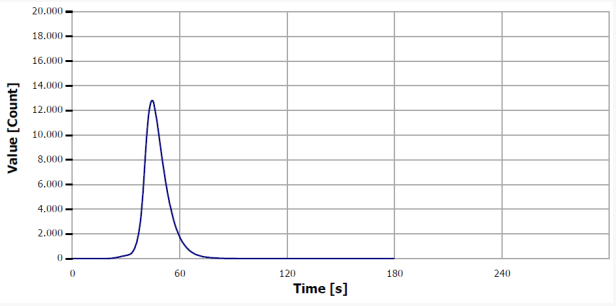

Figure 7: EC analysis curve of "filter 2"

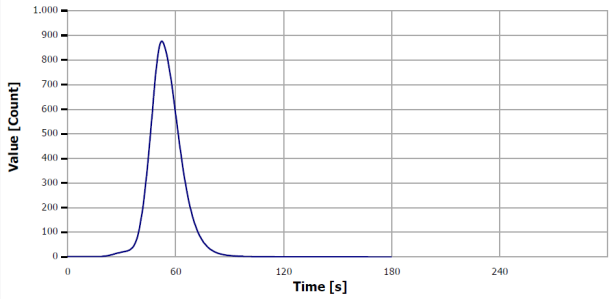

Figure 8: EC analysis curve of "EC standad 1.01 g/kg"

Due to the matrix-optimized quantitative combustion, the EC calibration can also be used for quantification of the OC contents. This makes a second calibration for the OC redundant and saves additional time. The analysis results received for the 5-fold-repeated EC standard test prove the performance of the digestion process, results are given in Table 4.

Table 4: Repeatability and performance check, for the standard EC=1.01 g/kg

Measurement	1	2	3	4	5
EC content in g/kg	0.99	1.00	1.00	1.01	1.02
Average value EC	1.01 g/kg				
SD	± 0.01 g/kg				
RSD	± 0.1%				

Conclusion

The multi EA 5100 analysis system provides a fast and reliable solution for the separate determination of the environmental sum parameters EC and OC.

Both parameters can be measured sequentially in a fully automated process. Without the necessity of a time-consuming sample treatment step (e.g., removal of organic carbon by extraction) information about organically bound as well as elemental carbon is available for each sample. Thus and the fact that reliable matrix-related calibrations can be generated by just one easy-to-prepare material, simplifies daily routine work and helps to remarkably increase sample throughput while reducing operation and maintenance effort.

If needed, the analysis system can be extended for the analysis of other matrix types like gases and liquids, or the determination of additional elements and parameters (e.g., nitrogen, sulfur, chlorine, TOC, AOX, EOX) by just adding the suited sampling or detection system.

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

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