Carbon Trace Analytics Determination of Elemental Carbon (EC) following Thermodesorption of Organic Carbon (OC)

Dr. Angela Gröbel, Product specialist, Analytik Jena AG, Konrad-Zuse-Str. 1, 07745 Jena, Germany

Reliable and rapid determination of EC and OC content - as parameters of relevance to the environment - is of major significance for air quality on account of the carcinogenic, environmentally damaging effects from particulates of incomplete combustion products; for example, this is especially relevant in production facilities, underground mines, in industrial urban areas or along congested inner city arterial roads. 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 multi EA® 3100 analysis system can be used without complex sample preparation, to determine the organic and elemental carbon content directly and quickly.

Introduction

In the combustion of fossil fuels (e.g. petroleum, coal, natural gas) and other organic substances in industry, transportation and in private households, the contained organic hydrocarbon compounds are oxidized to form mainly CO_2 and water. If this process does not proceed to completion, for example due to a lack of oxygen or if the temperature is too low, soot is also generated alongside the CO_2. The poorer the combustion, the higher the proportion of soot.

Soot is a mixture of elemental carbon and higher condensed organic hydrocarbons, usually having an unsaturated or aromatic structure. In air analytics it is considered to be the most important cause of lung carcinomas.

The analysis technique described here is suitable for the separate determination of EC and OC content. It was developed according to the guidelines of VDI 2465 Sheet 2.

Instrumentation

Sampling and sample preparation

A special fine dust sampling device was used for gathering samples. To obtain the samples, the ambient air under investigation is drawn over a previously conditioned quartz fiber filter at a rate of 2.3 m³/h for a defined period of time.

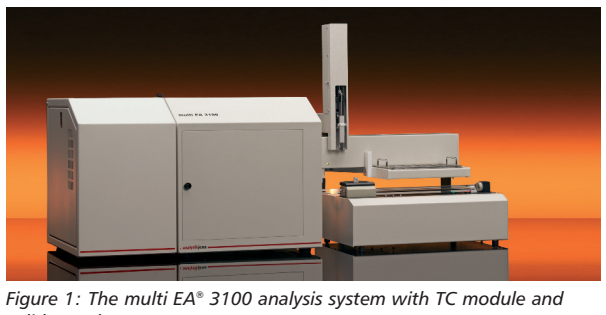


Figure 1: The multi EA® 3100 analysis system with TC module and solid sampler

Analysis system

All measurements were carried out with a multi EA® 3100 elemental analyzer *(see Fig. 1)* in the following configuration:

- multi EA® 3100 – basic instrument in horizontal operating mode with automatic sample boat drive
- TC module – NDIR detector for determining carbon content
- APG 3100 – automatic sampler for solids and liquids

Sample analysis

Determination of OC and EC content takes place in a two-phase process. Insertion of the sample and transfer of the filter samples into the combustion oven proceeds automatically in a user-friendly process using the solids sampler. Special sample boats are used to avoid loss of filter samples during transport. This guarantees stable positioning of the sample material inside the boat *(see Fig. 2)*. The first process phase serves to determine OC. The hydrocarbons on the partial filter are converted to the gaseous state by thermodesorption. For this purpose, the quartz fiber filter is rapidly heated to 650°C in an oxygen-free stream of argon. This is designed to avoid any pyrolysis of organic components that would otherwise give a falsely high EC content. The gaseous desorption products are then completely combusted to CO_2 and are detected.

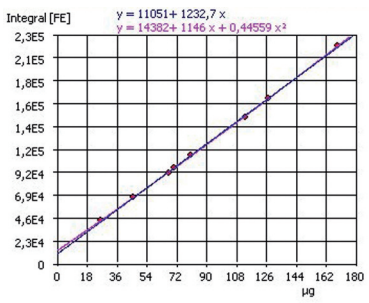
Figure 2: Special sample boat for optimal sample handling of filter samples

Once the first process phase is completed, the second begins immediately to determine the elemental carbon (EC). Here the sample is rapidly heated to 900°C in an oxygen rich atmosphere, which leads to complete conversion of the elemental carbon into CO_2.

The CO_2 formed by combustion is transferred to the TC detector after the drying of the measurement gas. The duration of a complete OC/EC determination, depending on the conditions selected for thermodesorption and the degree of coverage of the filter, is 600 - 1200 s.

Thanks to the excellent reproducibility of the technique, even the smallest elemental content is usually sufficient for a dual determination.

Calibration



Residual SD:	1279,6FE
Method SD:	103,8mg/kg
Method CV:	1,1913%
Qual. of rep.:	0,99957
Correl. coeff.:	0,99979

Figure 3, Example of a calibration curve for elemental carbon, acquired in EC mode

Calibration of the analysis system takes place in solid mode using a special soot standard. This standard was specially developed for this application and consists of highly pure quartz as the substrate material and elemental carbon generated from hydrocarbons in the combustion process. This allows optimal adaptation of the process to the sample matrix under investigation. A range of 0 - 175 µg absolute carbon was calibrated for the determinations performed. *Figure 3* shows the results of this calibration for the EC mode.

The state-of-the-art NDIR detection system used shows excellent linearity.

A detection limit of 4 µg C was ascertained for the calibration performed. Calculations followed from the calibration parameters according to DIN 32645 requirements.

Results and discussion

Sample 1 and 2 are real samples *(see Figure. 4)*. The values summarized in Table 1 are for the analysis results for measurements of partial filters with a diameter of 15 mm.

Sample 1 was selected as an example of a highly loaded filter. The sampling point was within an industrial area with serious air pollution.

The sampling point for the second sample *(see Fig. 5, Table 2)* with a lower load was near an inner city intersection.

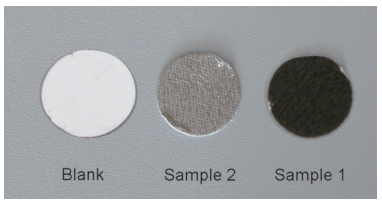


Figure 4: Filter samples for determining OC and EC content
Blank, unloaded quartz fiber filter,
Sample 2, low load quartz fiber filter,
Sample 1, high load quartz fiber filter

To assess the reproducibility of sampling and of the measurement technique, a soot standard of known EC concentration was also investigated *(see Fig. 6, Table 3)*.

Final review of the results shows that the separate determination of elemental and organic carbon using the multi EA® 3100 can be performed in a fast and uncomplicated manner, and with excellent precision thanks to its high degree of automation combined with the sensitive NDIR detection system.

Summary

A permanent effort is underway to continuously reduce the content of elemental carbon, a carcinogenic pollutant, in the air. In order to satisfy the elevated requirements for trace analytics, not only are reliable combustion systems required that can guarantee quantitative separation of the OC and EC content, but also highly sensitive detection techniques with long-term stability.

The multi EA® 3100 offers all this, and combines short measurement times with low maintenance and extremely simple handling. This guarantees straightforward implementation in shift operation that is required for modern contract laboratories and research institutions. The detection limits achieved by the system lie well below the stipulated carbon limit values.

Partial filter No.	OC in µg absolute	EC in µg absolute
1	59.18	121.1
2	51.28	118.3
3	47.30	116.9
4	53.30	118.3
Average value in µg	**53.31**	**118.7**
SD in µg	**4.22**	**2.16**
RSD in %	**7.91**	**1.82**

Table 1: EC and OC content of Sample 1

Partial filter No.	OC in µg absolute	EC in µg absolute
1	9.62	25.35
2	11.33	27.88
3	9.95	26.00
4	10.42	26.65
Average value in µg	**10.33**	**26.47**
SD in µg	**0.74**	**1.32**
RSD in %	**7.19**	**4.99**

Table 2: EC and OC content of Sample 2

Measurement	1	2	3	4	5	6	7	8	9	10
c_{EC} in µg/mg	6.22	6.20	6.24	6.25	6.20	6.29	6.30	6.26	6.25	6.13
Average value	**6.24 µg/mg**									
SD	**0.05 µg/mg**									
RSD	**0.81 %**									

Table 3: Reproducibility of the measurement technique for the example of an EC standard (c_{EC}: 6.22 µg/mg)

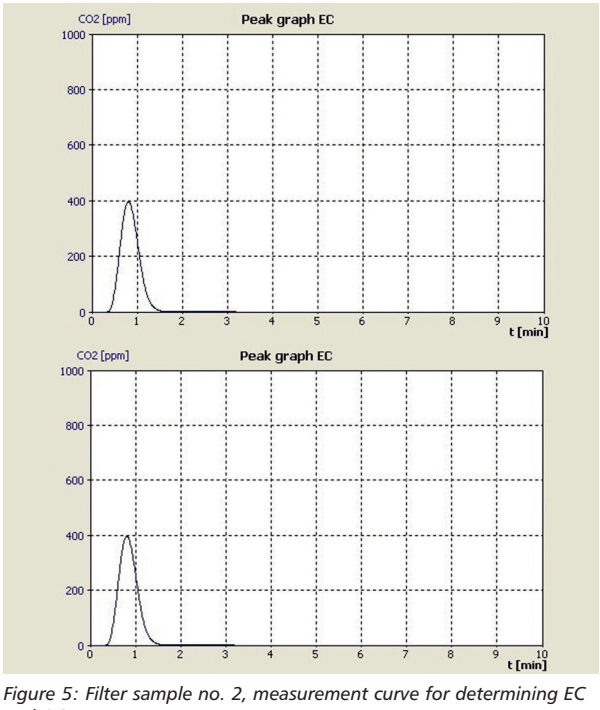


Figure 5: Filter sample no. 2, measurement curve for determining EC and OC content

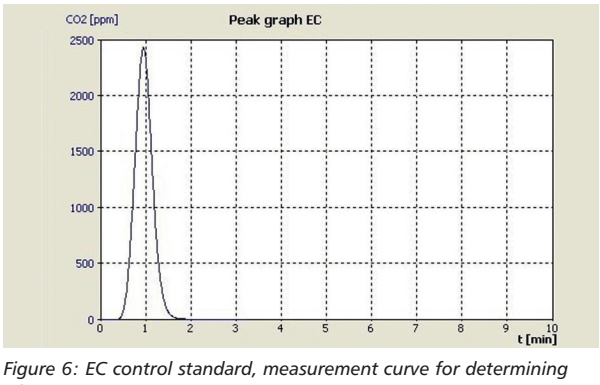


Figure 6: EC control standard, measurement curve for determining EC content