Semi-continuous measurement of elemental carbon (EC) and organic carbon (OC)

Intro:

The text describes the practice of measuring particulate OC and EC using the semi-continuous field analyser from Sunset Laboratory Inc. (USA). The analyser itself is characterized by Bauer et al. (2009) and is depicted in Fig. 1. However, the analyser has been continuously improved since 2009, e.g. by enhancing the detection limits or by setting up a dual-laser optical correction and thus brown carbon (BrC) detection (Bao et al., 2021; Vodička et al., 2020). In Europe, long-term semi-continuous measurements of EC and OC using the EUSAAR2 protocol have been evaluated for both urban and rural stations in several papers (e.g., Karanasiou et al., 2020; Mbengue et al., 2018; Vodička et al., 2013). The instrument was also evaluated for semi-continuous measurements by the US EPA project (Brown et al., 2019).

Sampling:

Sampling is carried out on quartz fibre filters. Before sampling, two filters in series are inserted into the instrument and heated directly in the instrument oven by a temperature protocol that reaches 850°C. Then filters are ready for sampling.

No filter pre-treatment (as in the case of sampling for off-line analysis) is necessary before inserting the filter into the instruments. Obviously, there are also no rules for transport and storage of filters as in the case of off-line analysis.

Sampling may be biased by negative and positive artefacts. The negative artefact occurs when semi-volatile substances evaporate from filter collected aerosol particles. The negative artefact is minimized by using two filters, placed in series, to increase the adsorption capacity for the most volatile particulate OC components during sampling. The negative effect is also minimised by the shorter sampling time and the immediate analysis of the sample after sampling. A positive artefact, on the other hand, results from the adsorption of gaseous organic compounds from the air onto the filter or the collected aerosol particles. The positive artefact is minimized by placing a diffusion denuder in the sampling line (see Fig. 1). The diffusion denuder is supplied by Sunset Lab together with the analyser and the filters in it have to be changed depending on the sampling location, season etc. (usually in 2 month intervals). Despite the use of a denuder, there may remain a positive artefact, whose magnitude can be determined by measuring so-called dynamic blank (i.e. sampling as under normal conditions, but with HEPA filter on the inlet, so to determine the amount of gaseous OC absorbed on the sampling filters).

During sampling, air is suck into the analyser at a flow rate of 8 lpm through an cyclone inlet (cyclones are available for PM_1, $PM_{2.5}$ and PM_{10} size fractions). The operator may select the sampling time (and therefore the time resolution) based on the type of site to keep the minimum concentrations as far as possible over the detection limit of the instrument. Usually it is possible to measure with higher time resolution at an urban station (e.g., 1-2 h, Rattigan et al. (2010)) than at a rural (4-h, Mbengue et al. (2018)) or even sub-arctic (8-h, Vodička et al. (2020)) sites. To compare urban and rural stations then a compromise (e.g. 3-h time resolution) is applicable (Aurela et al., 2011).

The sampling filters cannot be used indefinitely. During repeated sampling and analysis, the filter gradually darkens due to the gradual accumulation of e.g. mineral oxides on the filter. This phenomenon is more pronounced at higher aerosol concentrations and for the coarse aerosol fraction. As a result, it affects the determination of the split point between OC and EC for older filters (Jung et al., 2011; Karanasiou et al., 2020). For this reason, sampling filters must be replaced periodically. The frequency depends mainly on the darkening and sampling of the mineral material on the filter. In a city with higher concentrations, for example, weekly replacement can be needed. At a rural site, filters replacement can be planned every 2-3 weeks. The analyser offers filter darkening detection based on which the operator can decide when to change the filter.

Analysis:

Any temperature protocol can be selected for analysis. For European stations, the EUSAAR2 protocol is used (Cavalli et al., 2010). During on-line measurements in short periods (e.g. 2 h), it is a good idea to extend the sampling time as much as possible in order to obtain a sample content that is above the detection limit of the instrument, while minimizing the time without sampling. For these reasons, it can be chosen to use a shortened versions of the protocols - e.g. shortened EUSAAR2 protocol: step [gas] temperature [°C]/duration [s] (fraction) He 200/90 (OC1), He 300/90 (OC2), He 450/90 (OC3), He 650/135 (OC4), He–Ox. 500/60 (EC1), He–Ox. 550/60 (EC2), He–Ox. 700/60 (EC3), and He–Ox. 850/100 (EC4). If we measure in 2-h time resolution, this means that in this case we sample for approx. 1h 40min and the analysis takes 20 min. Then the cycle is repeated.

Blank measurements are taken to verify the quality of the instrument and they are usually taken once a day.

The raw data from the analysis shall be processed. Sunstet Lab provides the RTCalc software, which is continuously updated. It is recommended to use the updated software (on request from manufacturer) as different versions of the software may differ in the interpretation of the measured data (Vodička et al., 2020; Zheng et al., 2014). The data are evaluated automatically after each measurement in newer versions of the RTCalc software and saved as csv files. However, they can also be downloaded and manually checked by the operator, which is strongly recommended. As additional information, concentrations of OC and EC fractions as well as black carbon (BC) concentrations can be obtained from the raw data.

Quality control:

Control measurements are made using a sucrose solution (usually 10 µl with concentration of 10 g/l) at regular intervals (e.g. 1 month) and whenever one of the analytical gases is changed. If the control measurement is not correct, it is necessary to take measurements with different sucrose concentrations, find the calibration curve and update the calibration constant in the evaluation software.

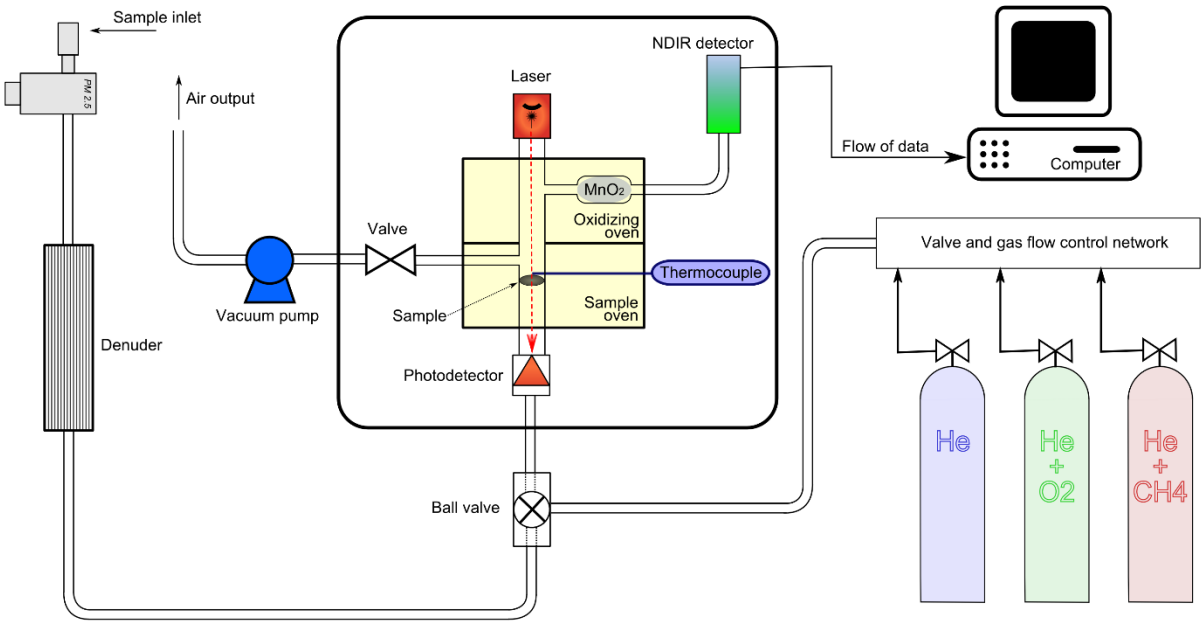

Fig. 1: Scheme of the instrument for semi-continuous analysis of EC and OC in aerosols.

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