Evaluation of self-developed separation methods for OC-EC analysis in aerosol particles against a standard method in dependence of sampling frequency and with regard to $^{14}$C analysis


$^1$Centre for Isotope Research (CIO), University of Groningen, Groningen, 9747 AG, The Netherlands
$^2$Department of Chemistry and Biochemistry & Oeschger Centre for Climate Change Research, University of Bern, Bern, 3012, Switzerland
$^3$Department of Physics and Astronomy, University of Florence & INFN, Sesto Fiorentino, 50019, Italy
$^4$Department of Physics, Università degli Studi di Milano & INFN, Milan, 20133, Italy
$^5$TNO, Netherlands Organization for Applied Scientific Research, Utrecht, 3584 CB, The Netherlands

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Presenting author email: k.zenker@rug.nl

The analysis of $^{14}$C in carbonaceous constituents of aerosol particle is a useful tool for source apportionment. For $^{14}$C analysis it is essential to clearly separate the organic (OC) and the elemental (EC) part of the carbon, which is especially challenging for EC. Currently, there is no standard protocol to achieve this. The aim of this study is therefore to systematically compare several recently developed separation methods among each other and with a well-characterized standard method for OC-EC quantification. As the standard method the EUSAAR (EUSAAR2) thermal-optical protocol (Cavalli et al., 2010), which is commonly used in Europe, was chosen. For $^{14}$C analysis, higher carbon concentrations are often preferred to increase the measurement precision. That means the common practice is to collect particles for longer than a day. On the other hand OC-EC concentrations are routinely analysed on 24-hour filters. A second objective is to investigate if longer sampling times have an influence on quantification and separation of OC and EC.

High volume filter samples have been collected at a rural site in the Netherlands with different sampling frequencies (2 to 5 days) and in parallel on a 24-hour basis. The samples were analysed for OC-EC concentrations using a Sunset analyser and different measurement protocols. The EUSAAR2 protocol is used to quantify OC and EC. This is compared to a three-step heating protocol in pure O$_2$ (pureO2 WE), which is used for OC-EC separation at the CIO laboratory for subsequent $^{14}$C analysis (Dusek et al., 2014). Prior to the separation of EC it is necessary to water-extract the filter samples to prevent charring. To allow a better comparison the water-extracted samples were also analysed with the EUSAAR protocol (EUSAAR2 WE).

First results show no essential differences in OC and total carbon (TC) concentrations between the different protocols for water-extracted samples. OC and TC concentrations on long-term filters and the sum of the corresponding 24-hour filter samples are also similar. However, as shown in figure 1 the EC concentrations show significant differences. For the sum of the 24-hour filters (red), EC shows lower values on the water-extracted filters and is lowest for the pure O$_2$ protocol. This can be expected, because there is a slight loss of EC during water extraction and the pure O$_2$ protocol is designed to exclude a fraction of the EC. For the long-term filters (blue) EC concentrations are higher after water extraction, which might indicate that the EUSAAR protocol underestimates EC for highly loaded samples. The disagreement between EC concentrations is stronger for the highly particle-loaded 5-day filter samples.

This study will be extended to a larger data set of filters with different sampling times and aerosol particle loadings. For further investigation of the influence of the separation method on the $^{14}$C content of EC, results of an intercomparison of different OC-EC separation protocols developed by different laboratories will be shown.

Figure 1. Comparison of the EC concentration on 2-day, 5-day filter samples and the corresponding sum of the 24-hour filter values in dependence of different measurement protocols.