Development of a method to measure the $\delta^{13}C$ for OC and EC in PM

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Information on the atmospheric composition, from the local to the global scale, is of strategic value in particular for climate and air quality related studies. Stable isotope research for both compounds specific and bulk analysis finds its applications in various fields (Hoefs, 1987; Flanagan et al 2005). One of its applications is the source identification since the $^{13}C/^{12}C$ is highly dependent on its origin. This has been done by the study of the stable carbon isotopic composition ($^{13}C/^{12}C$) (Cachier et al 1989; Widory et al 2004; Ceburnis et al 2011).

In the literature, the simultaneous characterization of OC/EC and $\delta^{13}C$ is made with two different analyses (Huang et al 2006). Our objective is to develop a method to obtain in one single analysis the OC and EC concentrations and their isotopic ratios.

Methodology

The original reference method (EA-IRMS) has been modified by replacing the elemental analyser by a sunset lab. instrument. An extra reducing oven was installed in order to convert the NO_2 produced by the PM samples while heating the filter. In the following, the experimental set-up is designated as S-RT-IRMS.

The calibration of OC and EC is performed with known amount of sucrose, as usually used. For the isotopic ratio, since the standard VPDB is in very limited quantity, we used methionine to calibrate the analysis.

Two different temperature protocols have been used. The first one (Huang2006.par) has been adapted from Huang et al (2006). The second one (eusaar2.par) has been developed within the EUSAAR project (Cavalli et al 2010).

Results

Table 1. Mean $\delta^{13}C_{VPDB}$ (‰) and standard deviation of sucrose, methionine and graphite.

	EA-IRMS		S-RT-IRMS	
	powder	solution	Huang2006	Eusaar2
Sucr.	-25.67 ± 0.46	-25.82 ± 0.06	-25.08 ± 0.09	-25.02 ± 0.40
Meth.	-27.99*	-27.99 ± 0.10	-27.76 ± 0.17	-27.66 ± 0.25
Grap.	-16.34 ± 0.05		-16.25 ± 0.21	

* reference value

The isotopic ratios of pure compounds were measured with both reference method and the S-RT-IRMS (Table 1). There is a good agreement with both methods.

Some repeatability tests have been done. It appeared that the inhomogeneity of the filter creates a higher variability than the one due to the S-RT-IRMS.

Last, the analysis of real PM filters showed a good agreement (Table 2) between the reference method and our development.

Table 2. $\delta^{13}C$ of filters (eusaar2.par). The uncertainty is ± 0.27; value obtained from the repeatability tests.

	EA-IRMS	S-RT-IRMS
02/02/2012	-25.34 ‰	-25.55 ‰
23/01/2012	-26.60 ‰	-26.61 ‰
09/01/2012	-25.85‰	-25.93 ‰
27/01/2012	-26.35 ‰	-26.00 ‰
19/03/2012	-25.78 ‰	-25.85‰

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