

Interactive comment on “On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols” by A. Karanasiou et al.

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In the paper “On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols” by Karanasiou et al., the analytical performance of different thermal-optical protocols, among which also the EUSAAR_2 protocol, is investigated based on carbonate carbon (CC) loaded samples. In Figure 6, the authors show that applying the EUSAAR_2 protocol a large fraction of CC evolves in the He/O₂ -mode of the analysis, potentially leading to a significant overestimation of EC content of ambient aerosol samples rich in CC. In the definition of the EUSAAR_2 protocol, as described in the paper Cavalli et al. 2010, tests were also performed to address the issue of CC possible interferences (Par. 3.1.4), and the results obtained contradict those presented in

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the paper currently under discussion. I will summarise the main evidences and conclusions of our work. Analyses of filters spiked with a CaCO₃ suspension were performed using the EUSAAR_2 thermal-optical protocol (Cavalli et al, 2010). The thermogram obtained from the analysis of 15.1 $\mu\text{g cm}^{-2}$ of CC indicates that 96% of CC evolves in the OC4 step of the analysis at 650 °C and the remaining 4% in the EC3 at 700 °C (Figure 1). These results were confirmed by analyses of natural calcite from Spain (grain dimension $\leq 300 \mu\text{m}$). Figure 2 shows the thermograms obtained from the analysis of two different types of natural calcite with CC concentrations of 15.6 $\mu\text{g cm}^{-2}$ and 16.2 $\mu\text{g cm}^{-2}$, respectively. In both cases, CC completely evolves in the He-mode of the analysis; and, in particular 5-10 % of CC evolves in the OC3 step at 450°C and the remaining 95%-90% in the OC4. The concentrations of CC we investigated (about 15 $\mu\text{g cm}^{-2}$) correspond, for a 24h sampling with a face velocity of 20 cm s⁻¹, to a CaCO₃ atmospheric mass concentration of ca. 60 $\mu\text{g m}^{-3}$ and to a dust mass concentration of ca. 200 $\mu\text{g m}^{-3}$ assuming a carbonate contribution to dust composition of 30%, as reported by Querol et al. (2009) for the most calcareous African dust particles measured in Cyprus. In other words, the CC concentrations we investigated well exceeded (by a factor 2 or 3) the maximum CaCO₃ concentrations measured in European urban environments, i.e. 30 $\mu\text{g m}^{-3}$ in Athens during the summer 2003 (Sillanpää et al., 2005) and the highest PM10 dust load observed in Eastern Mediterranean basin, i.e. 70 $\mu\text{g m}^{-3}$ in Ayia Marina during the winter 2006 (Querol et al., 2009). These results undoubtedly indicate that the EUSAAR_2 protocol allows the complete evolution of CC in the He-mode of the analysis without any “slip” of carbon into the He/O₂-mode when amounts of CC in the range of what can be obtained from atmospheric samples are used. Therefore, the use of EUSAAR_2 does not lead to any erroneous overestimation of EC due to CC interferences, even for the high CC loadings that can occur during important African dust event. We stated that when a suspiciously high OC4 peak is observed in thermograms, or the presence of CC is suspected in aerosol samples (e.g. from Ca content), a separated analysis should be envisaged to quantify CC and, then, subtract CC’s contribution to the OC signal.

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Figure 1: Thermogram obtained from the analysis of CaCO_3 suspension spiked filter.

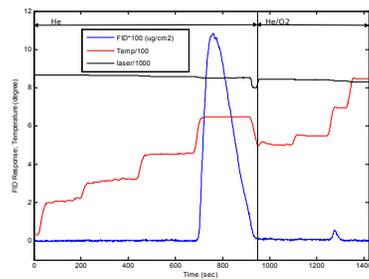


Fig. 1. Thermogram obtained from the analysis of CaCO_3 suspension spiked filter.

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Figure 2: Thermograms obtained from the analysis of two types of natural calcite loaded filters.

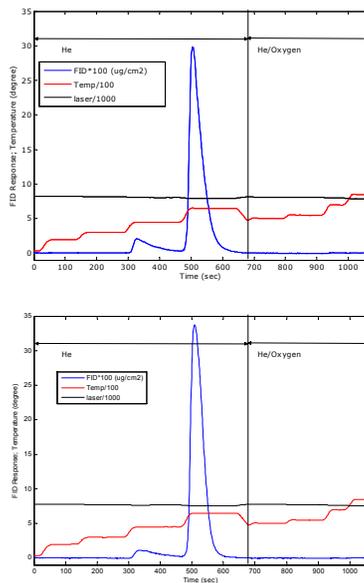


Fig. 2. Thermograms obtained from the analysis of two types of natural calcite loaded filters.