

**The effect of
water-soluble
compounds**

A. Piazzalunga et al.

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

On the effect of water-soluble compounds removal on EC quantification by TOT analysis in aerosol samples

A. Piazzalunga^{1,*}, V. Bernardoni², P. Fermo¹, G. Valli², and R. Vecchi²

¹Department of Inorganic, Metallorganic and Analytical Chemistry, Università degli Studi di Milano, Via Venezian 22, 20133 Milan, Italy

²Department of Physics, Università degli Studi di Milano, Via Celoria 16, 20133 Milan, Italy

*now at: Department of Environmental and Territorial Sciences, Università di Milano-Bicocca, Piazza della Scienza 1, 20126 Milan, Italy

Received: 16 May 2011 – Accepted: 5 July 2011 – Published: 12 July 2011

Correspondence to: A. Piazzalunga (andrea.piazzalunga@unimib.it)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

In this work, three different thermal protocols were tested on untreated and water-washed aerosol samples to study the influence of soluble organic and inorganic compounds on EC measurements. Moreover, analyses on the water soluble extracts were carried out. The aim was to find out the most suitable protocol to analyse samples collected in a heavily polluted area. Indeed, the tests were performed on real samples collected at an urban background station in the Po Valley, which is one of the main pollution hot-spots in Europe.

The main differences among the tested protocols were the maximum temperature of the He step (i.e. 870 °C, 650 °C, and 580 °C) and the duration of the plateaus during the heating procedure. Our measurements evidenced the presence of a significant amount of weakly light-absorbing aerosol evolving during the highest temperature step in He (i.e. 870 °C), which makes lower temperature protocols not suitable for EC determination in samples collected in heavily polluted areas like Milan.

1 Introduction

At the state of the art the identification of organic (OC) and elemental (EC) carbon in aerosol samples using thermal protocols is ambiguous; therefore, they are operationally defined. Indeed, part of the EC thermally evolves in oxidising atmosphere and part of the OC can char especially in an oxygen-poor atmosphere giving origin to a refractory component (pyrolytic carbon, PyC) similar to EC (Watson et al., 2005 and therein cited literature). The presence of organic compounds prone to pyrolysis (e.g. water soluble compounds) and of tar-like organic compounds (produced to a great extent by wood burning) can interfere with EC determination. The presence of inorganic catalytic compounds in the samples further complicates the understanding of the thermal behaviour of aerosol carbonaceous samples.

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



suitable for aerosol samples collected in different environments.

In this work, tests were carried out with the aim of identifying the most suitable protocol for OC/EC measurements on samples collected at an urban area in the Po Valley, which is one of the major pollution hot-spots in Europe. Three protocols mainly differing for the highest temperature in the inert atmosphere (i.e. 870 °C, 650 °C, and 580 °C) were tested. The novelty of this work is that the tests were performed both on untreated and water-washed samples. In addition, water-soluble organic compounds (WSOC) extracted from our samples were also analysed to study their thermal behaviour and gain further information on the different carbonaceous aerosol components.

2 Experimental methods

2.1 Samplings

The sampling campaigns were carried out at an urban background station in the Milan university campus at about 10 m above ground level. PM₁₀ was sampled on two parallel quartz fibre filters (2500 QAO-UP, Pall Corporation, 47 mm diameter) pre-fired at 700 °C for 1 h (Vecchi et al., 2009) using low volume samplers (flow rate 2.3 m³ h⁻¹).

28 parallel samplings were carried out from 17 January to 9 February 2010. The sampling strategy was to perform 9-h samplings (from 09:00 to 18:00 and from 21:00 to 06:00) in order to limit the filter loading and to operate the carbon analyses in optimal conditions (see Sect. 3.2).

During the sampling period the weather was cloudy or foggy (snow was registered on 5 February 2010 and no other precipitations occurred in the period). Temperature ranged from -1 °C to 10 °C. PM₁₀ mass was on average 74 µg m⁻³ (range 35–111 µg m⁻³) and TC accounted for about 25 % of the PM₁₀ mass on average.

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.2 Thermal-optical transmittance analysis

In this work, a thermal-optical transmittance (TOT) analyser by the Sunset Laboratory Inc. was used to quantify EC, OC, and TC in aerosol samples. The carbonatic carbon component was not considered in this work as previous studies reported that in PM₁₀ carbonate is negligible in most European areas except for coastal sites in south Europe (ten Brink et al., 2004; Sillanpää et al., 2005; Perrone et al., 2011).

Briefly, in the first part of the TOT analysis the sample is heated in an inert atmosphere (He) using different thermal ramps depending on the protocol in use. Then, the second part of the analysis is carried out in an oxidising atmosphere (He/O₂ mixture, 90/10 %) (Birch and Cary, 1996). The carbon evolving during heating is completely oxidised to CO₂ by a MnO₂ catalyst and then reduced to CH₄ to be quantified by a flame ionisation detector (FID).

To account for PyC formation, the transmission of a laser beam through the sample is constantly monitored during the analysis. Transmittance usually decreases throughout the He-step, indicating the formation of light-absorbing PyC. In the the He/O₂ phase, an increase of the laser signal is registered and the PyC evolution is conventionally assumed completed when the transmittance reaches its initial value. Carbon evolving after this point (called split-point) is then considered as EC.

In this work, three thermal protocols mainly differing for the highest temperature in the He atmosphere were tested (see Table 1 for details). The protocol called He-870 is very similar to NIOSH2 (Maenhaut and Claves, 2007) and ACE-Asia base (Schauer et al., 2003). The He-580 is a low temperature and time variable protocol which is a proxy of the Desert Research Institute IMPROVE_A protocol (Chow et al., 2007) implemented on a thermal-optical transmittance instrument. The third protocol is EUSAAR_2 (Cavalli et al., 2010), which has been recently proposed as a standard for carbon analysis on samples collected at European regional background sites. It is noteworthy that few samples analysed by EUSAAR_2 required the last step in oxidising atmosphere to be prolonged in order to obtain a complete carbon evolution, as previously reported by

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



other authors (Kuhlbusch et al., 2009; Gilardoni et al., 2011).

The protocols differ for temperature and duration of the heating steps. It is important to point out that the plateau temperatures and step time-lengths in He-870 and EUSAAR_2 are fixed. As for He-580, the plateau temperatures are fixed but the step time-lengths are variable; indeed, this protocol allows the complete evolution of the carbon at each step (i.e. each plateau lasts till the FID signal approaches to zero).

Of the two quartz filters sampled in parallel, one was analysed as-is (in the following named untreated sample) and the other was water-washed to remove water soluble compounds, as explained in Sect. 2.3. The protocols were tested on a 1 cm² punch taken from the untreated and the water washed samples.

2.3 Washing procedure

To set up the filter washing procedure, PM₁₀ samples were collected at the previously described location (see Sect. 2.1) using a high-volume sampler (flow-rate: 30 m³ h⁻¹) on 150 mm diameter quartz fibre filters (QAT-UP, Pall Corporation), which allowed multiple tests on the same material.

Water soluble compounds were removed washing portions of the high volume sampled filters using MilliQ (Millipore) water (TOC <5 ppb). Each portion of the filter was placed in a filtration assembly – similar to the one reported by Yttri et al. (2009) – suitably designed for this application. The washed area was 37 mm diameter wide (i.e. smaller than the total deposit area) to avoid the possible loss of sampled particles from the filter edge.

Tests were carried out to determine the minimum amount of water needed for a complete water soluble compounds removal so that different punches of the same sampled filter were washed using increasing water quantities. Residual total carbon (TC) concentrations measured by TOT were used to check the washing efficiency with different water quantities. It was noticed that the residual TC on the filter decreased when the water used for the washing increased, until a minimum TC quantity (TC_w) was reached. The water quantity (V_{H₂O}) necessary to reach TC_w was different for each

19856

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



filter and depended on the initial TC load. A linear relationship ($R^2=0.99$) was found between the TC load of the sample (in the range 20–100 $\mu\text{g cm}^{-2}$) and $V_{\text{H}_2\text{O}}$:

$$V_{\text{H}_2\text{O}}(\text{mL}) = \frac{\text{TC} \left(\frac{\mu\text{g}}{\text{cm}^2} \right)}{7.5 \left(\frac{\mu\text{g}}{\text{mL}} \right)} \cdot \text{washed area} (\text{cm}^2).$$

This relation was used to estimate the water quantity to be used for the washing of the LV samples collected for testing different protocols. It is noteworthy that the minimum water quantity used corresponded to the amount necessary for washing a 20 $\mu\text{g cm}^{-2}$ TC loaded sample. After washing, filters were placed in open but dust-protected sievetrays and air dried at room temperature for 24 h.

The uniformity of the washed filter was tested measuring the TC concentration on three different punches (area: 1 cm^2) taken from the same filter and washed with $V_{\text{H}_2\text{O}}$. Differences among the three values were lower than 10 %.

3 Results

3.1 TC measurements

TC was measured on untreated and water washed samples using the three protocols. In Fig. 1 the comparison between TC measured by the protocols is shown. As expected, a good agreement was found among the different protocols; indeed TC quantification is not dependent on the thermal treatment as previously found in different inter-comparison exercises (Schmid et al., 2001; Watson et al. 2005; and therein cited literature).

The TC results variability on each sample was evaluated as the ratio between the standard deviation of the three TC measurements and the average concentration value.

In the untreated samples, a 4% variability was detected on average (range of TC concentration: 17.6–57.0 $\mu\text{g cm}^{-2}$). This estimate is consistent with the $\pm 5\%$

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



measurement precision on TC values and $0.2 \mu\text{g cm}^{-2}$ as minimum uncertainty reported for this instrument (Subramanian et al., 2006). Nine field blanks were also analysed. The TC content in untreated field blanks was in the range $0.4\text{--}3.5 \mu\text{g cm}^{-2}$.

The average TC variability in the washed samples was 9%. Four field blanks were also washed and their TC content was in the range $0.7\text{--}3.2 \mu\text{g cm}^{-2}$. These values are comparable to those measured on untreated field blanks; therefore, our washing procedure did not introduce any systematic filter contamination. Moreover, the comparison between the TC variability on untreated and washed samples indicates that our washing procedure did not significantly affect the filter uniformity (i.e. no more than 5%).

3.2 EC measurements

EC results obtained by the three protocols were compared for both the untreated and washed samples. There was one outlier in the dataset with an EC concentration exceeding $15 \mu\text{g cm}^{-2}$. Previous works evidenced that the transmittance variation through heavily loaded filters (i.e. samples with $\text{EC} > 15 \mu\text{g cm}^{-2}$) cannot be correctly monitored because the initial laser signal is too low (Subramanian et al., 2006; Wallén et al., 2010), thus the outlier was excluded from the database. It is noteworthy that EC concentration was higher than $5.5 \mu\text{g cm}^{-2}$ in about half of the 9-h samples collected at our station. Therefore, if 24-h instead of 9-h samplings were carried out, EC concentration would have been higher than $15 \mu\text{g cm}^{-2}$ in one half of the samples, preventing the detection of transmittance variations during the He step. This observation is of particular interest because it evidences that traditional 24-h samplings in heavily polluted areas can limit the possibility to obtain reliable EC concentrations by the TOT method.

EC results obtained by the three protocols on both untreated and washed samples showed a good correlation ($R^2 > 0.87$). However, significant differences (slope > 1.48) in absolute EC concentrations were detected on untreated filters when comparing the results obtained by the He-870 protocol to those by other protocols (Fig. 2). These

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



differences were lower in the results obtained on water-washed filters. As expected, these results show that the removal of water soluble compounds from the filter is effective in reducing the differences among the EC values measured by different protocols. However, washing filters is not enough to obtain a full agreement among protocols as EC quantification depends also on other parameters, as it will be shown later in the text.

An unexpected finding was that EC concentrations were generally (in 83 %, 67 % and 79 % of the cases for He-870, EUSAAR_2 and He-580, respectively) higher in the washed than in the untreated samples; the increases were up to 54 % (with He-870), 24 % (with EUSAAR_2), and 43 % (with He-580) of the EC measured on untreated filters. This result suggests that measurements on untreated filters can lead to an EC underestimation.

The role of the carbon fraction evolving in He at high temperature (see Sect. 3.3) and PyC formation (see Sect. 3.5) were explored to better understand differences among protocols and between washed and untreated samples, in order to choose the most suitable thermal treatment for our samples.

3.3 Matching the different protocols: the nature of carbon evolving at high temperature in the inert atmosphere

As mentioned before, EC results were protocol-dependent in both untreated and washed samples. One of the main differences among the tested protocols is the highest temperature in the He step. Subramanian et al. (2006) identified the carbon evolving at high temperature (about 850 °C) in the He atmosphere as responsible for the disagreement observed in EC results.

In our tests, a good agreement was found comparing the sum of EC and the carbon fraction evolving in the He₄ step in the He-870 protocol (in the following called C_He_{4,870}) to the EC values obtained by EUSAAR_2 and He-580 for both untreated and washed samples (Fig. 3). This result suggests that to obtain the most reliable EC estimate, it is mandatory to understand the chemical nature of the C_He_{4,870} fraction

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(i.e. whether it is OC or EC) in the samples collected in the area of investigation (in our case a heavily polluted urban area in the Po Valley). It is useful to point out that the concentration of this fraction in the sample is comparable to the EC content, thus its wrong attribution can strongly affect EC determination.

5 Opposite to what reported in the literature (Chow et al., 2004; Subramanian et al., 2006), no significant increase in the laser signal was registered during the He4₈₇₀ step (see Fig.4), especially in the case of washed filters. The laser attenuation by the sample was calculated at the starting point of the analysis, at the maximum attenuation point, and at the end of the He step as $ATN = -100 \ln(I_j/I_0)$ (I_j , with $j = 1 \dots 3$ is the laser transmission measured at the three points of interest and I_0 is the laser signal at the end of the analysis, see Fig.4a). The increase in the laser signal registered during the He4₈₇₀ step corresponded on average to a 4% (range 2%–7%) variation of the initial attenuation on the washed samples and a 6% (range 3%–12%) on the untreated ones. The slight difference between washed and untreated samples is probably due to soluble compounds (e.g. sulphates or other salts) which can alter the thermal behaviour of the light-absorbing carbonaceous species and are removed by the washing procedure (Novakov and Corrigan, 1995; Yu et al., 2002; Hitzengerger and Rosati, 2010; Wang et al., 2010; and therein cited literature).

20 The apparent average attenuation coefficient related to the C_He4₈₇₀ (defined as the ratio between the ATN variation and the carbon evolved during the He4₈₇₀ step) was calculated. It was about $2.6 \text{ m}^2 \text{ g}^{-1}$ and about $3 \text{ m}^2 \text{ g}^{-1}$ for washed and untreated samples, respectively. These values are much lower than those reported in the literature for EC (about $20 \text{ m}^2 \text{ g}^{-1}$) and PyC (about $40\text{--}50 \text{ m}^2 \text{ g}^{-1}$) on filters (Chow et al., 2004; Subramanian et al., 2006; Boparai et al., 2008) indicating that most of the C_He4₈₇₀ in our samples is not strongly light-absorbing. Therefore, the C_He4₈₇₀ in this kind of samples is likely composed mainly by organic compounds showing a weak light attenuation and only a slight evolution of the light-absorbing material is registered (i.e. about 10% of the C_He4₈₇₀ is estimated to be light-absorbing). Moreover, assuming $20 \text{ m}^2 \text{ g}^{-1}$ as the EC attenuation coefficient a rough estimate of the EC evolved in He4₈₇₀ step was carried

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



out. Comparing this value to the measured EC concentration – and considering that also PyC can contribute to light-absorbing carbon evolution during He₄₈₇₀ – an upper limit for EC pre-combustion was calculated (12 % and 5 % for untreated and washed samples, respectively).

5 With the aim of understanding the higher EC values measured by the lower temperature protocols compared to He-870, EUSAAR_2 temperatures at the split point were analysed. As the split-point in EUSAAR_2 occurred in all cases at temperatures in the 560–710 °C range, it is possible that the organic compounds evolving in He₄₈₇₀ burn together with the EC fraction when EUSAAR_2 is applied, thus leading to an EC
10 overestimation when analysing our samples by the EUSAAR_2 protocol. However, it should be taken into account that this hypothesis needs further investigations because the thermal evolution occurs in different atmospheres (He and He/O₂) and the organic compounds might behave differently. Similar results were found using He-580, where the split points were always detected during the oxygen step at 580 °C.

15 It is noteworthy that the C_{He4870} value was lower (–28 % on average) on washed than on untreated samples. The presence of soluble compounds in the C_{He4870} is another indication of the role of organic compounds evolving at high temperatures in He; these organics can increase PyC and EC measured concentrations when using low temperature protocols.

20 The reduction of this organic fraction, which contributes to the protocols disagreement (Andreae and Gelencsér, 2006), can further explain the slight improvement in protocols comparability reported in Sect. 3.2.

3.4 WSOC analysis

25 For a better comprehension of the differences between the results obtained on untreated and washed samples, filter extracts were also analysed to determine the thermal behaviour of WSOC. To analyse water soluble compounds the water extracts obtained by all samples were joined together, vacuum-dried, and rinsed with methanol (Piazzalunga et al., 2010a). A drop of this solution was then deposited on 1 cm²

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



punches of a pre-fired quartz fibre filter. The punches were placed in open but dust-protected sieve-trays, air dried (2 h at room temperature), and analysed using the three protocols.

In Fig. 5 thermograms of WSOC obtained by He-870, EUSAAR_2, and He-580 protocols are shown.

As already found in previous works (Andreae and Gelencsér, 2006; Wallén et al., 2010), the He1 and He4 carbon fractions gave the highest signal when WSOC were analysed by He-870.

It is noteworthy that a substantially higher carbon quantity (about + 77 %) evolved in the He/O₂ phase with the low-temperature protocols than with the He-870 protocol, indicating that the He4₈₇₀ step was important to allow the WSOC evolution in the He phase.

The WSOC laser signal increases in the He4₈₇₀ step. The apparent attenuation coefficient for the C_He4₈₇₀ was about 5 m² g⁻¹, indicating again that most of this carbon fraction was weakly light-absorbing. Moreover, the few light-absorbing carbon evolving in He4₈₇₀ is PyC in this case, as no EC is expected in WSOC due to the extraction procedure. This is a further confirmation that the EC pre-combustion estimates given in Sect. 3.3 have to be considered as upper limits.

Results on water extracts obtained by the three protocols (see Table 2) showed that no EC was measured during the analysis by the He-870 protocol, while about 1 µgC cm⁻² was observed using the low-temperature protocols.

This observation further suggests that in the Milan urban atmosphere organic compounds exist, which evolve in the He step at a temperature in the 650–870 °C range (about 20 % of WSOC) and are weakly light-absorbing. In this work, these compounds have been demonstrated to interfere with EC determination when low-temperature protocols are used for the analysis, leading to a possible EC overestimation.

Part of these compounds can be ascribed to HULIS (HUMic-Like Substances), which are weakly absorbing materials with a biogenic origin or generated during biomass burning (Andreae and Crutzen, 1997; Andreae and Gelencsér, 2006; Iinuma et al.,

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2007; Schmidl et al., 2008). HULIS mainly evolve at temperatures higher than 600 °C in oxygen atmosphere.

It should be noted that wood burning is a not-negligible emission source in the Milan urban area during wintertime. Its primary component was estimated to account for about 14 % of the PM₁₀ mass in Milan during a winter period (Bernardoni et al., 2011). Following Varga et al. (2001) preliminary HULIS measurements had been carried out by our group (Fermo et al., 2009); the results showed that HULIS can account for the 30–50 % of the OC in the Milan urban area during wintertime.

In the same samples analysed by the three protocols also levoglucosan – a marker for biomass burning (Simoneit and Elias, 2001) – was measured using the methodology reported in detail in Piazzalunga et al. (2010b). The presence of levoglucosan (concentration range: 0.6–4.0 µg cm⁻² and levoglucosan carbon/TC = 3 % on average) in our samples indicated a not negligible contribution by wood burning during the investigated period, which can explain the presence of an important refractory, not strongly light-absorbing fraction.

It is noteworthy that the significant contributions due to biomass burning products makes low-temperature protocols not suitable for a correct assessment of the EC content in our samples because low-temperature TOT protocols can strongly overestimate it.

3.5 Pyrolytic carbon formation

It is well-known that PyC formation is another important source of troubles for OC/EC quantification. Indeed, literature studies (Yang and Yu, 2002) showed that neither of the following statements – necessary for a correct EC quantification – is respected in thermal-optical analysis: (a) pyrolytic carbon evolves before EC during the analysis, (b) pyrolytic carbon and OC have the same light absorption coefficient.

Therefore, if PyC formation is minimised, the analysis results are more reliable.

Figure 6 shows the comparison between the thermal evolution of one untreated and one washed sample with the EUSAAR.2 and the He-870 protocols. Strong reductions

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in the carbon evolving in the washed filter can be noticed both in the He and He/O₂ phase. A reduction of the carbon signal in the He/O₂ phase was found also for the He-580 protocol, but no thermogram superimposition is possible due to the variable time lengths in the analysis performed by this protocol.

The carbon evolving in the He/O₂ step was compared among the tested protocols to gain information on PyC formation. It was assumed that carbon evolving in oxygen with the EUSAAR_2 and He-580 protocols is comparable to that evolved in the He-870 but only with the addition of the C_He4₈₇₀ contribution (in the following all these quantities will be called He/O₂ carbon), according to the considerations reported in Sect. 3.3. He/O₂ carbon represents the sum of native EC, the refractory fraction of OC, and PyC formed during the thermal treatment. The He/O₂ carbon concentrations are represented in Fig. 7 separately for untreated and washed samples. Since the native EC on the filter does not depend on the chosen protocol, differences in He/O₂ measurements among protocols can be ascribed only to differences in PyC formation in the first part of the analysis.

Few differences are registered between He-870 and EUSAAR_2 He/O₂ carbon (on average 7% in the untreated samples and 12% in the washed samples), while the He-580 data are much lower (on average about -32% in both cases). Thus, the He-870 and EUSAAR_2 protocols seem to produce comparable PyC quantities in samples collected in a polluted urban area while PyC formed by He-580 is much lower. This finding is opposite to what reported by Cavalli et al. (2010) for the EUSAAR_2 protocol but they referred to samples collected at regional background stations in Europe and likely characterised by a very different chemical composition.

The observed differences on the He/O₂ carbon could be due to the time duration of the He steps in the different protocols. In the He-580 protocol the steps are variable; the duration of each temperature plateau is such to allow the evolution of carbon at a specific temperature step until the peak approaches to zero. In the other two protocols, time steps are fixed.

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Previous works (Yu et al., 2002) showed the importance of allowing a complete carbon evolution at each step to limit PyC formation. Figure 8 shows that when the He step duration in EUSAAR_2 is comparable to the He-580 one, differences between these protocols approach to zero. On the contrary, the shorter is the step time in EUSAAR_2 compared to the He-580 one the higher is the He/O₂ carbon (i.e. PyC) formed using EUSAAR_2.

Focusing on the differences between untreated and washed samples, reduction of the He/O₂ carbon is registered after washing (−40 % for He-870 and EUSAAR_2 and −30 % for He-580). The missing fraction in the washed samples is therefore either soluble or produced by the thermal treatment of soluble compounds. Thus, the washing procedure applied to our samples reduces possible interferences in the measurements (e.g. presence of refractory organic carbon and of inorganic compounds which modify the carbon thermal behaviour, as well as PyC formation), improving the protocols agreement on EC measurements as shown in Sect. 3.2. The lower reduction in the He-580 protocol can be justified considering that this protocol is less prone to pyrolysis even in untreated samples, therefore limiting the possibility of reduction of the pyrolysing carbon component.

4 Conclusions

This work aimed at the evaluation of the best approach to analyse EC and OC by TOT in real aerosol samples collected in a polluted urban area. Tests were carried out on both washed and untreated samples collected during a winter period in Milan (Po valley, Italy). Results obtained by TOT analysis using three different thermal protocols were discussed.

As expected, EC values measured by the three tested protocols were different. The main difference was ascribed to the carbon fraction evolving during the He step at 870 °C (C_He₈₇₀), which was demonstrated to evolve in He/O₂ atmosphere with the two lower-temperature protocols. The evolution of this fraction before or after the split-point

can differently affect the EC measured by the lower temperature protocols. It was also demonstrated that the C_{He4870} is mainly not light-absorbing in our samples, thus it has to be considered mainly OC. Therefore, the He-870 protocol prevents EC overestimation when analysing samples collected in polluted urban environments like Milan.

WSOC were also analysed as they are significant contributors to PyC. The washing procedure used to remove WSOC from our samples resulted in a more reliable EC estimation as the PyC formation was limited. Moreover, as WSOC contribute to part of the C_{He4870} their removal allowed also a slight improvement in the protocols comparability.

In summary, our tests on real samples – characterised by a chemical composition typical of an area affected by a complex mixture of pollution sources – suggest that protocols reaching high temperatures in He atmosphere are preferable to low-temperature ones to get rid of typical interferences which affect EC results. Moreover, our results indicate that the best approach to analyse carbon in urban aerosol samples should consider steps long enough for complete carbon evolution in order to reduce pyrolysis formation.

Acknowledgements. The authors are grateful to Chiara Abate and Chiara Paganelli for their contribution to the experiment both in the laboratory and on the field.

References

- Andreae, M. O. and Crutzen, P. J.: Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry, *Science*, 276, 1052–1058, 1997.
- Andreae, M. O. and Gelencér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmos. Chem. Phys.*, 6, 3131–3148, 2006, <http://www.atmos-chem-phys.net/6/3131/2006/>.
- Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., and Fermo, P.: PM₁₀ source apportionment in Milan (Italy) using time- and size-resolved data, *Sci. Total Environ.*, in review, 2011.
- Birch, M. E. and Cary, R. A.: Elemental Carbon–Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust, *Aerosol Sci. Tech.*, 25, 221–241, 1996.

19866

ACPD

11, 19851–19880, 2011

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The effect of
water-soluble
compounds**

A. Piazzalunga et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- Boparai, P., Lee, J., and Bond, T. C.: Revisiting Thermal-Optical Analyses of Carbonaceous Aerosol Using a Physical Model, *Aerosol Sci. Tech.*, 42, 930–948, 2008.
- Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EU-SAAR protocol, *Atmos. Meas. Techn.*, 3, 79–89, doi:10.5194/amt-3-79-2010, 2010.
- Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, Evaluation, and Applications in U.S. Air Quality Studies, *Atmos. Environ. A-Gen.*, 27A, 1185–1201, 1993.
- Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IMPROVE and NIOSH Carbon Measurements, *Aerosol Sci. Technol.*, 34, 23–34, 2001.
- Chow, J. C., Watson, J. G., Chen, L.-W. A., Arnott, W. P., and Moosmüller, H.: Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols, *Environ. Sci. Technol.*, 38, 4414–4122, 2004.
- Chow, J. C., Watson, J. G., Chen, L. W., Chang, M. C., Robinson, N. F., Trimble, D., and Kohl, S.: The IMPROVE_A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database, *J. Air Waste Manage.*, 57, 1014–1023, 2007.
- Conny, J. M., Klinedinst, D. B., Wight, S. A., and Paulsen, J. L.: Optimizing Thermal-Optical Methods for Measuring Atmospheric Elemental (Black) Carbon: A Response Surface Study, *Aerosol Sci. Tech.*, 37, 703–723, 2003.
- Fermo, P., Piazzalunga, A., Tuccillo, F., Brambilla, L., Cazzuli, O., Vecchi, R., and Valli, G.: Analytical methods for quantification and characterization of HULIS (HUmic Like Substances) in atmospheric aerosol, European Aerosol Conference, Karlsruhe, Germany, 6–11 September 2009, T022A18, 2009.
- Gilardoni, S., Vignati, E., Marmer, E., Cavalli, F., Belis, C., Pianelle, V., Loureiro, A., and Artaxo, P.: Sources of carbonaceous aerosol in the Amazon basin, *Atmos. Chem. Phys.*, 11, 2747–2764, doi:10.5194/acp-11-2747-2011, 2011.
- Hitzenberger, R. and Rosati, B.: Laboratory investigation of interferences in thermal and optical carbon analysis, International Aerosol Conference, Helsinki, Finland, 29 August–3 September 2010, 3A3, 2010.
- Iinuma, Y., Brüggemann, E., Gnauk, T., Andreae, M. O., Helas, G., Müller, K., Parmar, R., and Herrmann, H.: Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savannah grass, German peat and Indonesian peat, *J. Geophys. Res.*, 112, D08209, doi:10.1029/2006JD007120, 2007.

The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Kuhlbusch, T. A. J., Borowiak, A., Gelenscer, A., Genberg, J., Gladtko, D., Maenhaut, W., Pio, C., Popovicheva, O., Putaud, J.-P., Quincy, P., Sciare, J., ten Brink, H., Viana, M., and Yttri, K. E.: Measurement of Elemental and Organic carbon in Europe. JRC Scientific and Technical Reports (EUR collection), EUR23992 EN, available online at: <http://publications.jrc.ec.europa.eu/repository/handle/111111111/7803/>, 2009.

Maenhaut, W. and Claves, M.: Characterisation and sources of carbonaceous atmospheric aerosol, in: Scientific support plan for a sustainable development policy (SPSD II), Belgian Science Policy, Bruxelles, Belgium, 2007.

Novakov, T. and Corrigan, C. E.: Thermal Characterization of Biomass Smoke Particles, *Mikrochim. Acta*, 119, 157–166, 1995.

Perrone, M.R., Piazzalunga, A., Prato, M., and Carofalo, I.: Composition of Fine and Coarse Particles in a coastal site of the Central Mediterranean: carbonaceous specie contributions, *Atmos. Environ.*, doi:10.1016/j.atmosenv.2011.04.030, in press, 2011.

Piazzalunga, A., Abate, C., Bernardoni, V., Bianchi, F., Fermo, P., Paganelli, C., Valli, G., and Vecchi, R.: BC/EC assessment on real samples by optical/thermal methods with and without WSOC removal and using different protocols, International Aerosol Conference, Helsinki, Finland, 29 August–3 September 2010, 11, D4, 2010a.

Piazzalunga, A., Fermo, P., Bernardoni, V., Vecchi, R., Valli, G., and De Gregorio, M. A.: A simplified method for levoglucosan quantification in wintertime atmospheric particulate matter by high performance anion-exchange chromatography coupled with pulsed amperometric detection, *Int. J. Environ. An. Ch.*, 90, 934–947, 2010b.

Schauer, J. J., Mader, B. T., Deminter, J. T., Heidmann, G., Bae, M. S., Seinfeld, J. H., Flagan, R. C., Cary, R. A., Smith, D., Huebert, B. J., Bertram, T., Howell, S., Kline, J. T., Quinn, P., Bates, T., Turpin, B., Lim, H. J., Yu, J. Z., Yang, H., and Keywood, M. D.: ACE-Asia Intercomparison of a Thermal-Optical Method for the Determination of Particle-Phase Organic and Elemental Carbon, *Environ. Sci. Technol.*, 37, 993–1001, 2003.

Schmid, H., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H. M., Giesen, K.-P., Hitzinger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., and Puxbaum H.: Results of the “carbon conference” international aerosol carbon round robin test stage I, *Atmos. Environ.*, 35, 2111–2121, 2001.

Schmidl, C., Bauer, H., Dattler, A., Hitzinger, R., Weissenboeck, G., Marr, I. L., and Puxbaum, H.: Chemical characterisation of particle emissions from burning leaves, *Atmos.*

**The effect of
water-soluble
compounds**A. Piazzalunga et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Environ., 42, 9070–9079, 2008.

Simoneit, B. R. T. and Elias, V. O.: Detecting organic tracers from biomass burning in the atmosphere, *Mar. Pollut. Bull.*, 42, 805–810, 2001.

5 Sillampää, M., Frey, A., Hillamo, R., Pennanen, A. S., and Salonen, R. O.: Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe, *Atmos. Chem. Phys.*, 5, 2869–2879, 2005, <http://www.atmos-chem-phys.net/5/2869/2005/>.

10 Subramanian, R., Khlystov, A. Y., and Robinson, A. L.: Effect of Peak Inert-Mode Temperature on Elemental Carbon Measured Using Thermal-Optical Analysis, *Aerosol Sci. Tech.*, 40, 763–780, 2006.

ten Brink, H., Maenhaut, W., Hitzengerger, R., Gnauk, T., Spindler, G., Even, A., Chi, H., Bauer, H., Puxbaum, H., Putaud, J.-P., Tursic, T., and Berner, A.: INTERCOMP2000: the comparability of methods in use in Europe for measuring the carbon content of aerosol, *Atmos. Environ.*, 38, 6507–6519, 2004.

15 Varga, B., Kiss, G., Ganszky, I., Gelencsér, A., and Krivácsy, Z.: Isolation of water-soluble organic matter in atmospheric aerosol, *Talanta*, 55, 561–572, 2001.

Vecchi, R., Valli, G., Fermo, P., D'Alessandro, A., Piazzalunga, A., and Bernardoni, V.: Organic and inorganic sampling artefacts assessment, *Atmos. Environ.*, 43, 1713–1720, 2009.

20 Wallén, A., Lidén, G., and Hansson, H.-C.: Measured Elemental Carbon by Thermo-Optical Transmittance Analysis in Water-Soluble Extracts from Diesel Exhaust, Woodsmoke, and Ambient Particulate Samples, *J. Occup. Environ. Hyg.*, 7, 35–45, 2010.

Wang, Y., Chung, A., and Paulson, S. E.: The effect of metal salts on quantification of elemental and organic carbon in diesel exhaust particles using thermal-optical evolved gas analysis, *Atmos. Chem. Phys.*, 10, 11447–11457, doi:10.5194/acp-10-11447-2010, 2010.

25 Watson, J. G., Chow, J. C., and Chen, L.-W. A.: Summary of Organic and Elemental carbon/Black Carbon Analysis Methods and Intercomparisons, *Aerosol Air Qual. Res.*, 5, 65–102, 2005.

Yang, H. and Yu, J. Z.: Uncertainties in Charring Correction in the Analysis of Elemental and Organic Carbon in Atmospheric Particles by Thermal/Optical Methods, *Environ. Sci. Technol.*, 36, 5199–5204, 2002.

30 Yttri, K. E., Dye, C., Braathen, O.-A., Simpson, D., and Steinnes, E.: Carbonaceous aerosols in Norwegian urban areas, *Atmos. Chem. Phys.*, 9, 2007–2020, doi:10.5194/acp-9-2007-2009, 2009.

Yu, J. Z., Xu, J. H., and Yang, H.: Charring Characteristics of Atmospheric Organic Particulate Matter in Thermal Analysis, Environ. Sci. Technol., 36, 754–761, 2002.

- 5 Zhi, G., Chen, Y., Sheng, G., and Fu, J.: Effects of temperature parameters on thermal-optical analysis of organic and elemental carbon in aerosol, Environ. Monit. Assess., 154, 253–261, 2009.

**The effect of
water-soluble
compounds**

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The effect of water-soluble compounds

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Thermal protocols tested in this work.

Atmosphere	He-870		He-580		EUSAAR_2	
	Temp. (°C)	Duration (s)	Temp. (°C)	Temp. (°C)	Duration (s)	Duration (s)
He 1	310	60	140	200	120	
He 2	475	60	280	300	150	
He 3	615	60	480	450	180	
He 4	870	105	580	650	180	
He	–	80	No	–	30	
He/O ₂ 1	550	45	580	500	120	
He/O ₂ 2	625	45	740	550	120	
He/O ₂ 3	700	45	840	700	80	
He/O ₂ 4	775	45		850	80	
He/O ₂ 5	850	45				
He/O ₂ 6	870	120				

**The effect of
water-soluble
compounds**

A. Piazzalunga et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Table 2.** WSOC results obtained by different protocols in $\mu\text{g cm}^{-2}$.

Protocol	OC	EC	TC	He1	He2	He3	He4	PyC
He-870	49.9	0.0	50.0	19.2	7.6	2.6	9.8	10.7
He-580	45.0	1.1	46.1	7.5	9.2	9.4	2.0	17.0
EUSAAR_2	47.6	1.0	48.6	11.7	6.9	6.8	4.2	17.9

The effect of water-soluble compounds

A. Piazzalunga et al.

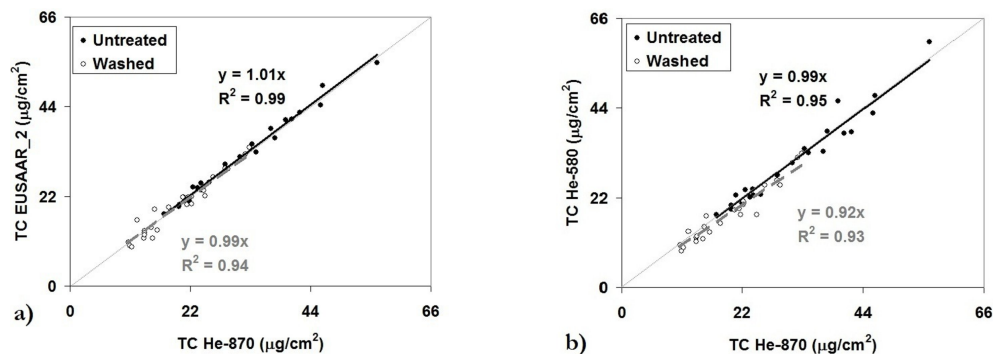


Fig. 1. Comparison between the TC results obtained by EUSAAR_2 and He-870 (a), and He-580 and He-870 (b) on untreated and washed filters

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The effect of water-soluble compounds

A. Piazzalunga et al.

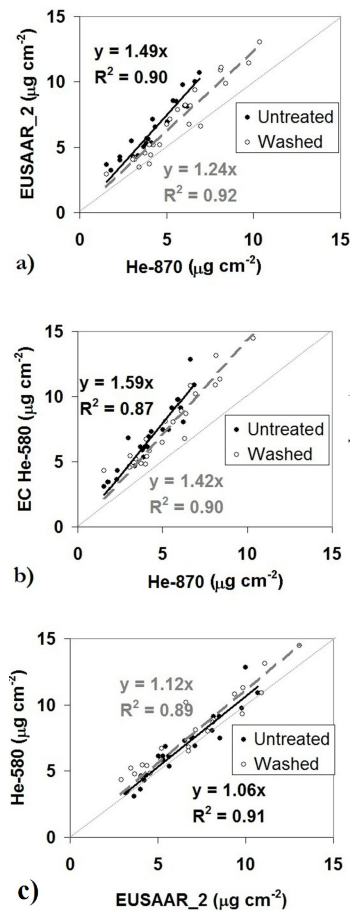


Fig. 2. Comparison between the EC results obtained by EUSAAR.2 and He-870 **(a)**, He-580 and He-870 **(b)**, and He-580 and EUSAAR.2 **(c)** on untreated and washed samples.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The effect of
water-soluble
compounds**

A. Piazzalunga et al.

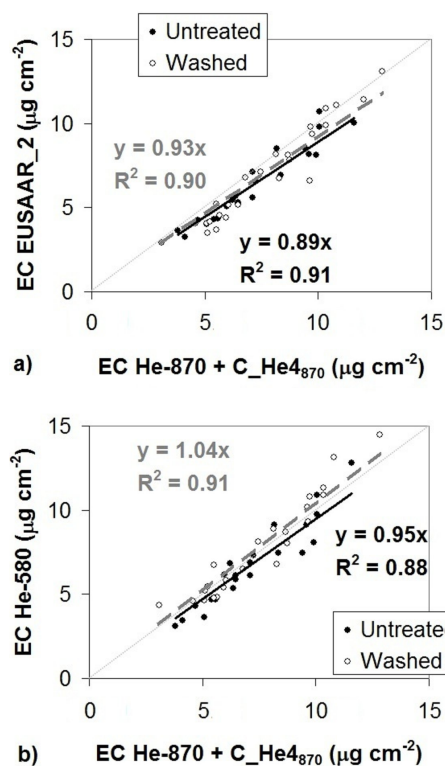


Fig. 3. EC measured by EUSAAR_2 (a) and He-580 (b) vs. EC concentration obtained by the He-870 protocol summed to the carbon fraction evolving in the He₄₈₇₀ (i.e. EC He-870 + C_He₄₈₇₀).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The effect of water-soluble compounds

A. Piazzalunga et al.

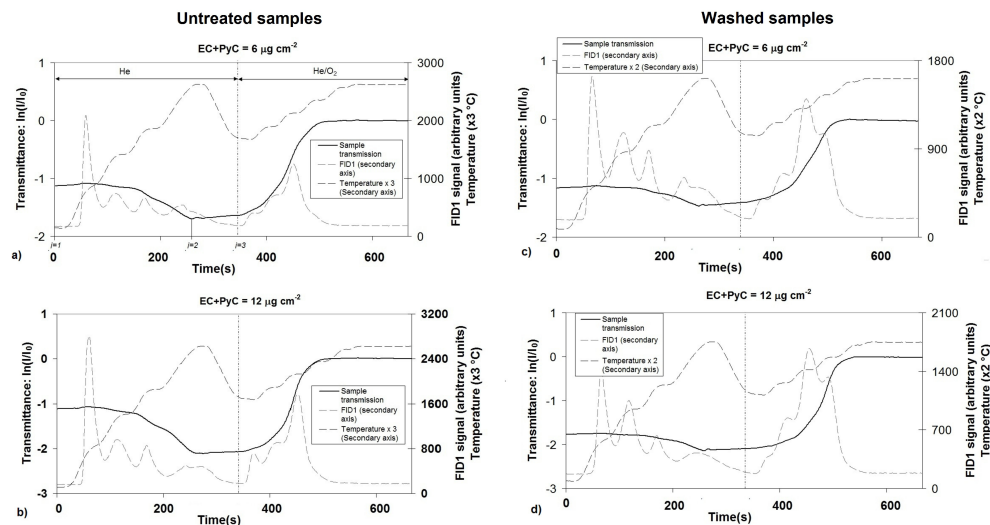


Fig. 4. Thermograms of untreated and washed sample for low (**a** and **c**) and high (**b** and **d**) loaded samples. In (**a**), the beginning of the analysis ($j = 1$), the point of minimum laser signal ($j = 2$) and the switching point ($j = 3$ and dashed vertical line) between the He and He/O₂ atmosphere are also reported.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The effect of water-soluble compounds

A. Piazzalunga et al.

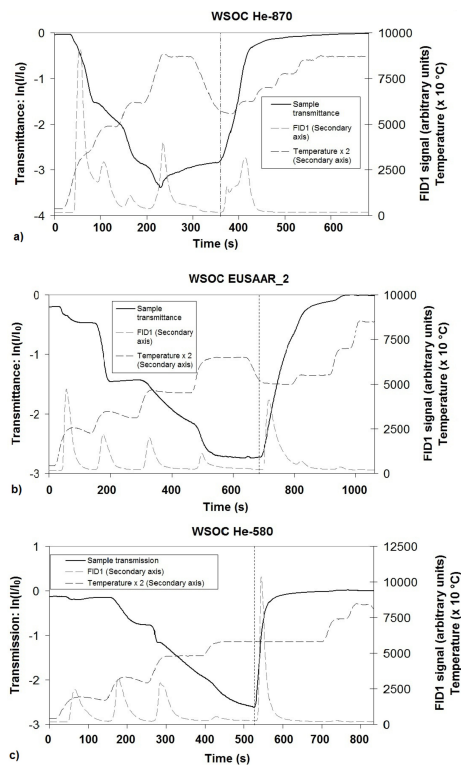


Fig. 5. WSOC thermograms obtained by the He-870 (a), EUSAAR.2 (b), and He-580 (c) protocols. The vertical line indicates the switch between He and He/O₂ atmosphere.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The effect of water-soluble compounds

A. Piazzalunga et al.

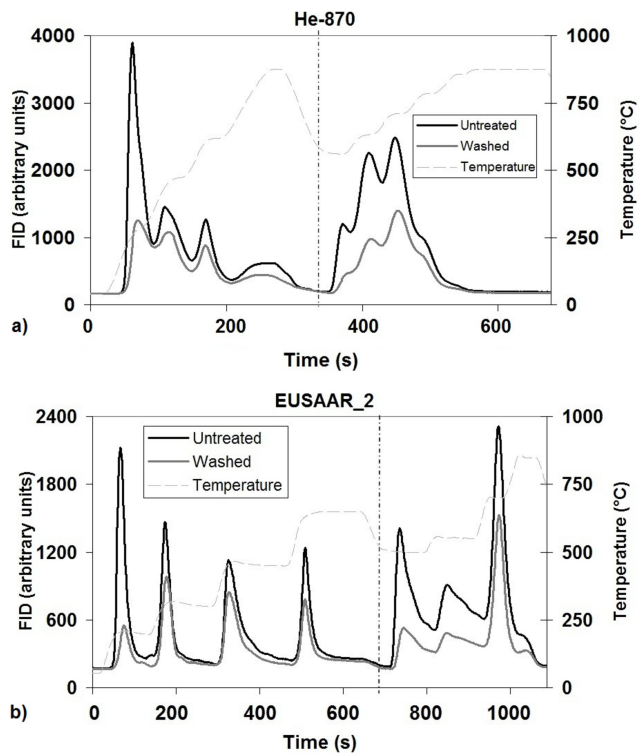


Fig. 6. Comparison between thermograms obtained analysing untreated and washed samples with the He-870 (a) and EUSAAR_2 (b) protocols.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The effect of water-soluble compounds

A. Piazzalunga et al.

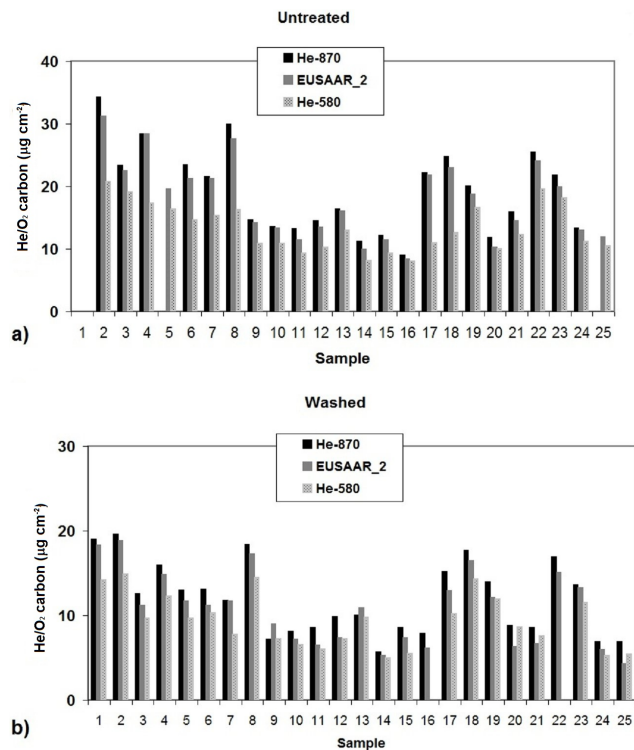


Fig. 7. He/O₂ carbon in untreated (a) and washed (b) samples.

