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TECHNICAL NOTE

Optimisation of analytical procedures for the quantification of ionic and carbonaceous fractions in the atmospheric aerosol and applications to ambient samples

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Abstract In the last decade, our research group set up and optimised analytical techniques for the characterisation of the major components of atmospheric aerosol (i.e. secondary inorganic ions and carbonaceous material) and source markers (e.g. levoglucosan, carbonates). In this study, we present a complete overview on the most problematic aspects that can be encountered during the quantification of the two main components of aerosol, i.e. the ionic and carbonaceous fractions. More in detail, different liquid chromatographic approaches were set up for main ions and anhydrosugars determination. Quality assurance procedures (i.e. ~~test~~ on data reliability) were applied during the set-up phase and they are presented in this work. As regards the carbonaceous component characterisation, two evolved gas analysis techniques were set up and applied: the thermogravimetric technique coupled to the Fourier transformed infrared spectroscopy (TGA/FTIR) and the thermal–optical transmittance method (TOT). A suitable protocol for organic and elemental carbon separation was set up for the TGA/FTIR system and a comparison with the results obtained by the TOT method was carried out. Studies on the impact of filter load, field blanks, and sample composition on OC/EC quantification by the TOT method were performed. Moreover, approaches for carbonate carbon quantification on different kinds of filters were developed. It was demonstrated that this approach allows to reach the ionic balance in samples impacted by carbonate compounds. The optimised methods have been applied for the analysis of thousands of PM filters allowing the obtainment of reliable results.

Keywords Aerosol characterisation · Liquid chromatographic techniques · Thermal-optical transmittance method · Thermogravimetric analysis · Carbonate quantification

Introduction

The characterisation of atmospheric aerosol is important because of its negative effects on human health, air quality, visibility and cultural heritage degradation as well as for its impact on the Earth's radiation balance ([1–5], among many others).

In this context, a detailed chemical characterisation is mandatory for both assessing the aerosol effects and for source identification.

Secondary inorganic ions and carbonaceous material are among the main contributors to the aerosol mass [6]. Their measurement is thus important for a rough assessment of aerosol composition.

Secondary inorganic ions (nitrate, sulphate and ammonium) are formed in the atmosphere by gas-to-particle conversion [7].

Total carbon (TC) in the atmospheric aerosol consists mainly of two fractions: organic (OC) and elemental (EC) carbon. OC is either directly released in the atmosphere in

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the particulate form (primary origin) or it is formed in the atmosphere by gas-to-particle conversion of anthropogenic or biogenic precursor gases (secondary origin) [8]. EC has only primary origin and it is produced by the incomplete combustion of fossil and biomass fuels in an oxygen-poor environment. Moreover, it is the main light absorber material in atmosphere [8].

Currently, the definition of OC and EC is operative (therefore depending on the technique used) and a unique reference methodology does not exist. Problems concerning thermal analyses of OC and EC are the possible conversion of OC into EC-like material during the heating (OC charring or pyrolysis), and the possible incomplete OC evolution or EC pre-combustion during the first part of the analysis. Results of round-robin tests carried out on atmospheric aerosol samples showed good agreement (better than 10 %) for TC concentrations obtained by different instruments and techniques, whereas discrepancies up to a factor 2 are commonly found in EC measurements carried out using different methodologies (e.g. [9, 10] and literature therein). Further problems have to be ascribed to the absence of commonly accepted reference materials that can be used to quantify EC as it appears in the atmosphere and work on this topic is ongoing [11–13].

Also, carbonate carbon (CC) can contribute to TC. It is generally negligible in PM10 in most European areas, but it can become an important component at specific sites (e.g. coastal sites in south Europe or peculiar situations [14–17]).

In these cases, several inter-comparison studies showed that the CC could be one of the reasons for the large discrepancies among EC values determined by different thermal–optical protocols [18, 19]. Nevertheless, a standard methodology for carbonate quantification does not exist, and the methods commonly used present some drawbacks (see 'Methodologies for carbonate determination' section).

Besides the main aerosol components, minor species can be of interest for toxicological purposes (e.g. PAH) or as source markers (e.g. levoglucosan). Levoglucosan (1,6-anhydro-β-D-glucopyranose) is an anhydrosugar emitted by the cellulose pyrolysis at T >300 °C [20] and it is commonly used as a tracer for primary wood burning contribution to PM emissions. Wood burning has been identified as a major aerosol source especially during wintertime throughout Europe, and many studies have been recently carried out to study the impact of wood smoke on atmospheric pollution (e.g. [21, 22]). As an example, primary wood burning was estimated to account for about 17.5 % to TC [23] and for about 15 % to PM10 [24, 25] in a hot-spot pollution area in Italy (i.e. the urban area of Milan).

In this work, we present an overview of the analytical techniques set up by our group in the last decade for the quantification of the different constituents previously mentioned.

One of the main goals of our laboratory was the set-up and optimisation of liquid chromatographic techniques for the measurement of inorganic ions (ion chromatography) and levoglucosan (high performance anion-exchange chromatography coupled with pulsed amperometric detection, HPAEC–PAD) in aerosol samples. Compared to our previous works, we present here more in detail the approach followed for the data quality assurance (QA, i.e. an evaluation of the reliability of our data). Indeed, especially for what concerns ion chromatography, many procedures have been reported in the literature up to now, but the issue of the method validation has been often neglected.

Our group devoted also great attention to the set-up of evolved gas analysis techniques: TGA/FTIR (thermogravimetric analysis coupled to Fourier transformed infrared spectroscopy) and TOT (thermal–optical transmittance method); an insight into the open debate on OC/EC separation is carried out and methodologies for estimating the contribution of CC are presented and validated in this work.

Advantages and limits of the techniques applied to quantify aerosol main components (ions, levoglucosan as tracer of wood combustion and the carbonaceous fraction—i.e. OC, EC and CC) are explored and highlighted.

Moreover, the samples dataset has been extended and a complete overview of the results obtained analysing thousands of filters is shown. This huge number of results has allowed inter-comparisons between different approaches and the assessment of the reliability of the presented methods.

Experimental methodologies

Liquid chromatographic techniques

Ion chromatography

In our laboratory, an ICS-1000 Ion Chromatograph (Dionex) was set up for the water-soluble inorganic determination. Anions analysis was carried out by means of a Ion Pac AS14A (Dionex) column using 8 mM Na_2CO_3/1 mM $NaHCO_3$ as eluent at 1 mL min^{-1} flow rate and, for the detection, a conductivity system equipped with a ASRS-ULTRA suppression mode (Dionex). Cations determination was performed by means of a CS12A (Dionex) column using 20 mM MSA as eluent at 1 mL min^{-1} flow rate and, for the detection, a conductivity system equipped with a CSRS-ULTRA suppression mode (Dionex).

The set-up of the extraction procedure is described in detail in Fermo et al. [26]. Briefly, we chose to perform three subsequent extractions of about one fourth of filter by 20-min sonication using 2 mL Millipore-MilliQ water with the renewal of the water at each step to ensure the complete

Q1

deposit recovery. For the ions extraction from PTFE filters, the portion of filter to be analysed was previously wetted with 50 µL methanol because of its hygroscopicity as it is suggested in the literature [27]. For the final choice of the number of extractions needed for complete recovery, multiple extractions of the same filter were carried out and the percentage recovery was evaluated for the main ionic species (see Table 1). It must be highlighted that three subsequent extractions are needed to ensure good and reproducible Cl^- recovery.

MSA extraction was also applied to test the effectiveness of our water extraction procedure in CO_3^{2-} solubilisation (see 'Efficiency of the extraction procedure for carbonate solubilisation' section) as acidic extractions ensure the complete CO_3^{2-} decomposition [18]. More details on this procedure can be found in [16].

Major ionic species (NO_3^-, SO_4^{2-}, F^-, Cl^-, NO_2^-, Br^-, NH_4^+, Na^+, K^+ and Ca^{2+}) were determined. Estimates of the technique uncertainties and minimum detection limits (see Table 2) were carried out as described in detail in Fermo et al. [26]. The instrument was daily calibrated with standard solutions. Solutions obtained after sample extraction, solutions prepared extracting blank filters and blank solutions of MilliQ water were analysed.

High performance anion-exchange chromatography coupled with pulsed amperometric detection

In our laboratory, levoglucosan and its isomers analysis was carried out by HPAEC–PAD using an ion chromatograph (Dionex ICS1000) equipped with an isocratic pump and a sample injection valve with a 100-µL sample loop. Different anhydrosugars (levoglucosan, mannosan and galactosan) were separated using a Carbopac PA-10 guard column (50 mm×4 mm) and a Carbopac PA-10 anion exchange analytical column (250 mm×4 mm). As eluent, NaOH 18 mM was used. The analytical system comprised an amperometric detector (Dionex ED50) equipped with an electrochemical cell. The detector cell had a disposable gold electrode and a pH electrode as reference (both from Dionex) and was operated in the pulsed amperometric detection (PAD) mode. The extraction procedure is the same used for inorganic ions. Technique uncertainty and levoglucosan limit of detection are reported in Table 2. Further details can be found in Piazzalunga et al. [28].

It is noteworthy that levoglucosan detection by HPAEC–PAD can be affected by interference by arabitol, a polyoil. However, we demonstrated that this interference is negligible for winter samples collected in Northern Italy [28] (see 'Quality assurance in levoglucosan analysis' section).

Thermal methods for the carbonaceous fraction characterisation

Aerosol carbonaceous fractions (OC and EC) were quantified by means of a TGA/FTIR system and a TOT instrument. These techniques are based on the analysis of the gas thermally evolved from a portion of the sample (about 1.5 cm^2) placed into a chamber and heated in the presence of one or more carrier gases.

TGA/FTIR consists of a simple home-made apparatus obtained by coupling a JASCO-FTIR spectrophotometer Model 360 to a DuPont Thermogravimetric analyser model 951. More information on the system set-up is given in Fermo et al. [29]. A suitably optimised two-step heating in oxygen atmosphere is performed using this instrumentation (see 'Optimisation of a TGA–FTIR system' section). By monitoring the CO_2 infrared absorbance at 2,361 cm^{-1}, it is possible to obtain CO_2 evolution curves where OC and EC are detectable as separated peaks.

Table 1 Recovery percentages (%) for major ions obtained analysing quartz and PTFE filters

		1st extraction average	std. dev.	2nd extraction average	std. dev.	3rd extraction average	std. dev.
PTFE filter	Cl^-	29	15	55	15	16	5
	NO_3^-	95	1	3	1	2	1
	SO_4^{2-}	93	4	4	3	3	1
	NH_4^+	91	6	9	5	-	-
Quartz fibre filter	Cl^-	49	15	36	27	14	12
	NO_3^-	85	3	11	3	4	2
	SO_4^{2-}	83	4	13	2	5	2
	NH_4^+	80	6	15	4	5	3

Table 2 Uncertainties (%) and limits of detection (in nanograms per cubic meter, evaluated for a 24-h sampling at 2.3 m^3/h) of liquid chromatographic techniques considering blank values for water only and water+field blanks

	Uncertainty (%)	Limit of detection Water only	Limit of detection Quartz filter	Limit of detection PTFE filter
F^-	0.4	0.4	0.7	0.8
Cl^-	7.0	7.6	25.3	6.0
NO_2^-	1.9	16.0	8.0	8.6
NO_3^-	1.7	6.6	60.8	14.5
SO_4^{2-}	0.8	1.8	28.3	14.5
Na^+	2.0	22.8	89.3	47.4
NH_4^+	1.3	4.3	7.7	3.4
K^+	4.3	13.5	39.9	24.5
Mg^+	1.0	1.1	1.5	1.4
Ca^{2+}	3.5	12.3	27.1	14.9
Levoglucosan	4.8	1.6	1.6	1.6

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The TOT instrument is a carbon analyser by Sunset Laboratory. 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/O_2 mixture, 90/10 %) [30]. The carbon evolving during heating is completely oxidised to CO_2 by a MnO_2 catalyst and then reduced to CH_4 to be quantified by a flame ionisation detector (FID).

The two systems use different approaches to limit the influence of pyrolytic carbon (PyC) on EC determination. As for the TGA–FTIR, a flash heating in pure oxygen is used to minimise PyC formation [31, 32]. As for the TOT method, the laser transmission through the sample is monitored during the analysis. Sample transmittance usually decreases throughout the He step, indicating the formation of light-absorbing PyC. In the He/O_2 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.

It is noteworthy that both methods are based on temperature ramps for carbon fractions separation; therefore, the verification of the correct sample temperature is mandatory [33].

FTIR analysis for carbonate determination

FTIR analysis was performed by a Thermo-Nicolet 380 instrument on PTFE filters [16]. The spectra were acquired in transmission mode using 64 scans and a resolution of 4 cm^{-1}. Quantification of carbonate on ambient samples was performed by a commercial chemometric software (Thermo TQ Analyst 8.0) using the partial least squares algorithm after suitable calibration. Further details on the technique can be found in Cuccia et al. [16].

Sampling

In this work, results from samples collected at different sites are presented. Samples are generally collected using low-volume CEN- or EPA-equivalent samplers, on PTFE or quartz fibre filters, depending on the analytical technique to be applied. More details or references on sampling site and duration are given in each paragraph of section 'Results and discussion'.

Results and discussion

Quality assurance of ion chromatographic analysis (IC)

Inter-comparisons and ionic balance

One of the goals of this step was to allow the quality assurance (QA) of IC, i.e. to ensure the reliability of laboratory results. Our extraction procedure and IC analysis were applied to thousands of samples mainly collected on PTFE or quartz fibre filters. Lots of inter-comparisons for Ca^{2+} and sulphate measurements were carried out with the energy-dispersion X-ray fluorescence technique (ED-XRF) [34]. To perform the IC versus XRF inter-comparison, we assumed that all the sulphur measured by ED-XRF is present as soluble sulphate in the measured aerosol (an estimate of SO_4^{2-} by ED-XRF measurements was therefore carried out as $SO_4^{2-}{}_{XRF}=S_{XRF}\cdot 3$). An example of inter-comparison between IC and ED-XRF for Ca^{2+} and sulphate is presented in Fig. 1a and b, respectively, for ambient samples collected in a monitoring campaign described in Marenco et al. [35]. The good agreement (usually within analytical uncertainties) found between the techniques ensures that our assumption—i.e. sulphur is mainly present in the SO_4^{2-} form—is generally verified in atmospheric aerosol samples.

It is also noteworthy that a good ionic balance is generally found in the analysed samples. As already mentioned,

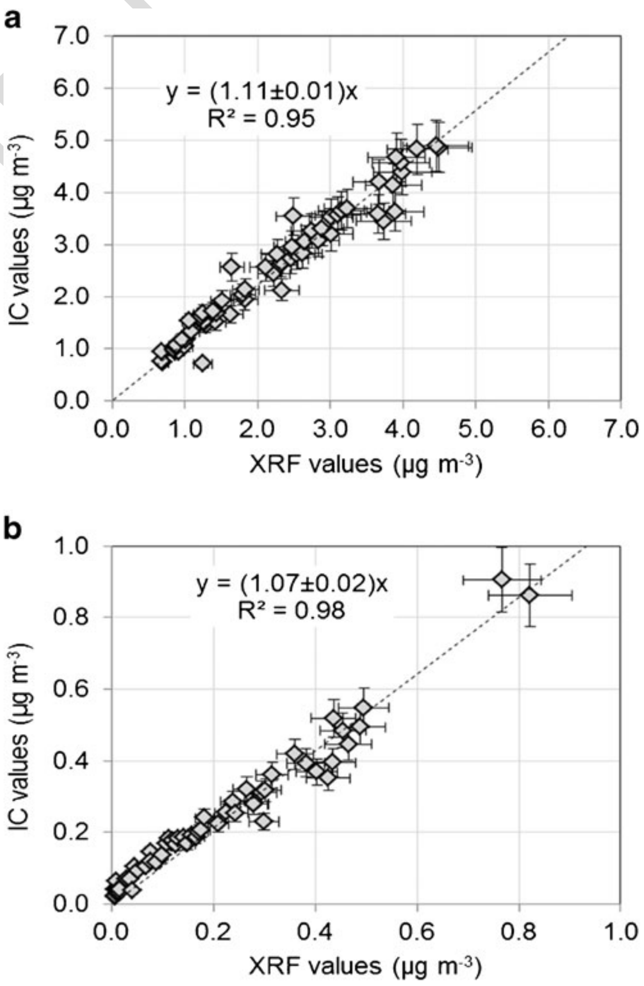

Fig. 1 Example of Ca^{2+} (**a**) and sulphate (**b**) inter-comparison between ion chromatography and ED-XRF. As for ED-XRF, sulphate content is estimated as 3× S assuming that all S is present in the sulphate form

exceptions can be ascribed to samples impacted by carbonates (see 'Methodologies for carbonate determination' section for further details).

Efficiency of the extraction procedure for carbonate solubilisation

Carbonate solubilisation during the extraction procedure and its transformation into CO_2 can lead to an anionic deficiency in samples heavily impacted by carbonate. In such cases, the ionic balance approach is widely used for carbonate estimation [36, 37]. In this method, possible anionic deficit is totally ascribed to carbonate, assuming that no residual acidity and no other undetected ions are present.

It is noteworthy that not all the water extraction procedures ensure the complete carbonate solubilisation. In these cases, the ionic balance approach could underestimate the carbonate contribution in the sample, as the corresponding cations are not released into the water solution. On the contrary, it is demonstrated that the extraction of the samples in a diluted MSA solvent ensures complete solubilisation [18].

We tested the efficiency of our water extraction procedure (see 'Ion chromatography' section) for $CaCO_3$ and $MgCO_3$ solubilisation. To this aim, a set of atmospheric particulate matter samples collected on PTFE filters and impacted by carbonate due to marble extraction in Massa Carrara (details on the monitoring campaign can be found in Cuccia et al. [16]) was extracted both by water and by using MSA.

Figure 2 shows Mg^{2+} and Ca^{2+} quantification using the two extraction approaches. It is noteworthy that Carrara marble is mainly composed by $CaCO_3$, but also $MgCO_3$ can be found. The good agreement obtained between the two approaches suggests that our extraction procedure is effective for carbonate decomposition in aerosol samples (see more details in 'Methodologies for carbonate determination' section) even if they are highly impacted by carbonate.

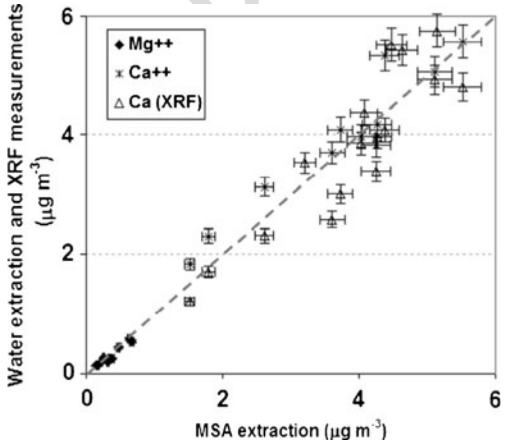

Fig. 2 Comparison of Mg^{2+} and Ca^{2+} measured in samples impacted by carbonate (from Carrara marble quarries, [16]) after water and MSA extraction. Also IC vs. ED-XRF Ca measurements [in the legend Ca (XRF)] are reported

Quality assurance in levoglucosan analysis

During the set-up phase of our HPAEC–PAD system [28], a comparison between levoglucosan results obtained by our methodology and an independent GC–MS determination (following Pashynska et al. [38]) was carried out. Very good agreement was found between the techniques (slope=1.02, R^2=0.97 and intercept comparable to zero within 2σ).

In the present study, NIST 1649a standard was also analysed for levoglucosan content and the result was in very good agreement with the certified value (Fig. 3a); moreover, an inter-comparison was carried out with the group of the Vienna University of Technology on particulate matter winter samples collected in Milan. This group uses HPAEC–PAD coupled to a de-convolution methodology for levoglucosan/arabitol determination [39]. Therefore, this approach to levoglucosan determination is free from possible interferences from arabitol. Very good agreement was found between the two approaches (see Fig. 3b).

It is noteworthy that the good results obtained in the inter-comparisons with other techniques demonstrated that possible interference by arabitol which can occur in HPAEC–PAD analysis is negligible in winter samples (in fact arabitol is emitted by fungi spores mainly in the warm seasons [39]).

Optimisation of a TGA–FTIR system

The quantification of OC/EC by means of a home-made TGA–FTIR instrument has been proposed for the first time by our research group some years ago [40, 41]. If compared to the TOT technique, TGA–FTIR presents some main advantages: (1) it is a system easy to be achieved and assembled in an analytical chemistry laboratory where both instruments TGA and FTIR are usually present (on the

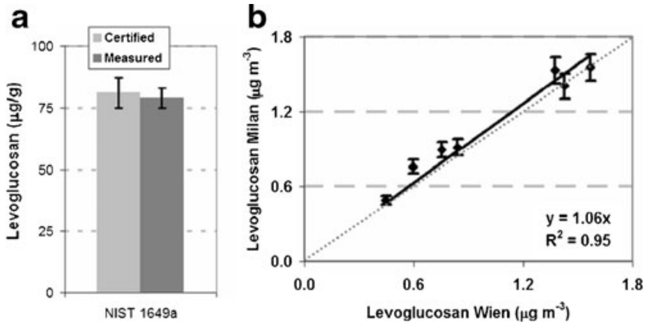

Fig. 3 **a** Comparison between measured and certified levoglucosan value in the NIST1649a standard. **b** Inter-comparison between levoglucosan measurements carried out using the HPAEC–PAD technique at Milan University and HPAEC–PAD with levoglucosan/arabitol peaks de-convolution at Wien University on wintertime samples collected in Milan

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contrary, TOT is a dedicated system), (2) it gives the possibility to work on powder samples which—in some specific applications—could be useful although PM ~~normally is~~ collected on filters, and (3) FTIR can allow the simultaneous determination of other compounds too (e.g. nitrate, sulphate and ammonium) [40].

Our TGA–FTIR was optimised for what concerns carrier gas, temperature ramp slope and duration of plateaus [40]. Following literature indications (e.g. [32] and our laboratory tests [41]~~)~~, we chose to work in oxygen atmosphere with flash heating (160 °C/min). The temperature of the separation step between OC and EC was set to 435 °C and the duration of the plateau was set to 25 min after laboratory tests carried out on different organic standards, ambient particulate matter samples and vehicle exhaust samples [41].

Analyses were carried out using both TGA–FTIR with the described protocol and the TOT instrument using the NIOSH protocol [30]. Uncertainties were 10 % and 5 % and limits of detection were 108 and 32 ng/m^3 (24-h samplings at 2.3 m^3/h) for TGA–FTIR and TOT methods, respectively. Comparing the results by the two methods, the average differences observed were 6±5 % and 8±6 % for TC and OC, respectively, and they were within the measurement uncertainties. As regards EC, data are shown in Fig. 4. It is noteworthy that only EC measurements by TOT method lower than 15 μg/cm^2 were considered to ensure that the laser in the TOT instrumentation operated in optimal conditions (see 'The role of filter load and field blanks in TOT analysis: influence on sampling strategies' section). The two approaches showed a 25±19 % difference compared to the average value. Nevertheless, significant differences between analytical methods for EC determination are expected, as already stated in the introduction. In this case, they can be ascribed to possible problems connected to EC quantification by the TOT method due to different attenuation coefficients of PyC and EC [42] or to a possible contribution from EC pre-combustion or not complete OC evolution in the TGA–FTIR. However, considering the differences in the applied methodologies, our results were considered fairly good.

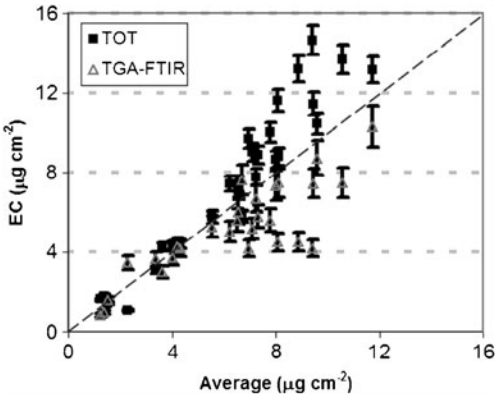

Fig. 4 EC results obtained by TGA–FTIR and TOT methods. Only samples showing EC by TOT <15 μg/cm^2 are shown (see 'The role of filter load and field blanks in TOT analysis: influence on sampling strategies' section)

Insights into the TOT method

The role of filter load and field blanks in TOT analysis: influence on sampling strategies

The correction of pyrolytic carbon by the TOT method occurs measuring the transmittance of a laser signal through the sample. Subramanian et al. [42] evidenced that the variation of the laser transmission through the filter cannot be correctly monitored for light absorbing material on the filter higher than 15 μg/cm^2. This prevents the correct assessment of the split-point in such loaded filters. The 15 μg/cm^2 value corresponds to 3 and 7.5 μg/m^3 of EC in air when 24-h sampling is performed on 47-mm filters using a flow rate of 2.3 and 1 m^3/h, respectively.

In our laboratory, 800 samples collected in the Po Valley between February 2005 and July 2007 were analysed in the frame of the ParFiL (Particolato Fine in Lombardia—fine particulate matter in the Lombardy region) project. PM10 was sampled by the Environmental Agency of Lombardy using low-volume samplers operating at 1 m^3/h equipped with the EPA (Environmental Pollution Agency, USA) PM10 inlet. Further details can be found in Piazzalunga et al. [25]. In these samples, the EC concentration in air ranged between 0.1 and 19 μg/m^3, ~~meaning that~~ 4 % of the samples showed EC concentrations higher than 15 μg/cm^2. It is noteworthy that if the campaign had been carried out using CEN-equivalent samplers (i.e. flow rate of 2.3 m^3/h), 31 % of the collected samples would have shown concentrations higher than 15 μg/cm^2 and the results from all these samples would have to be rejected. Therefore, in heavily polluted areas such as the Po Valley, it is important the development of suitable sampling strategies (e.g. the use of low flow-rate samplers or sampling time shorter than the standard 24-h interval) to ensure the possibility to perform TOT analysis in optimal conditions for the split-point determination avoiding data rejection.

It is noteworthy that TGA–FTIR can be useful to gain information on EC when heavily loaded samples—which cannot be correctly analysed by TOT—have to be analysed.

Another problem affecting TOT analysis is due to field blanks. Indeed, the TC limit of detection of the technique is about 0.15 μg/cm^2. However, the variability of TC measurements on field blanks can easily exceed this value. As an example, TC in field blanks obtained in sampling campaigns carried out in Milan [24, 25, 43] and measured at our laboratory were in the range 0.67–2.37 μg/cm^2 and the variability (standard deviation) in a single campaigns reached 0.35 μg/cm^2. As no EC is measured on field blanks,

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all the uncertainty related to field blanks has to be reported on OC measurements and from now on we will refer to OC field blanks.

Assuming three times the field blanks variability as the limit of detection (LOD) of airborne OC (after the correction for field blanks), in our conditions it can reach about 1 μg/cm^2 in the worst case. Converting this value into OC concentration in air for 24-h sampling at 1 and 2.3 m^3/h, we obtain about 0.5 and 0.2 μg/m^3, respectively. It is noteworthy that the limit of quantification of the method can be assessed as 10 times the field blanks variability (i.e. about 1.7 and 0.7 μg/m^3 for 24-h samplings at 1 and 2.3 m^3/h, respectively, in the worst case). Such low values are rarely registered in heavily polluted areas such as the Po Valley, but they can be found at other sites (e.g. in Northern Europe [44]).

Therefore, we would like to highlight the importance of performing preliminary campaigns at the site of interest to gain information on the expected carbon concentrations and on field blanks variability. This can allow the development a suitable sampling strategy to perform the TOT analysis in the optimal conditions.

The role of organics evolving at high temperature in He for the most correct EC assessment

A detailed study aimed to identify possible biases in the TOT due to the presence of peculiar organic classes in the sample analysis was carried out at our laboratory [45]. We tested three thermal protocols mainly differing for the highest temperature in the He atmosphere, but the discussion in the following will be a deeper insight into the comparison between a NIOSH-like protocol (He-870, highest temperature in the He step=870 °C, [45]) and the EUSAAR_2 protocol [46] (highest temperature in the He step=650 °C).

Our work showed the importance of studying the thermogram features of the collected samples to choose the best protocol for the analysis. Indeed, we showed that the differences between the EC quantification by He-870 and EUSAAR_2 protocols could be mainly ascribed to the carbon evolving during the highest temperature step in the He phase using the He-870 protocol (C_He4_{870}) (see Fig. 5). It is thus important to understand the nature of C_He4_{870} in the analysed samples, i.e. whether it is light absorbing (and therefore possibly connected to EC pre-combustion) or not (therefore representing resilient organics).

The monitoring of the laser signal throughout the highest temperature step in He-870 gives information on the nature of C_He4_{870}. The evaluation of the apparent attenuation coefficient in such step can give important information on the most suitable thermal protocol to be applied. As an example, C_He4_{870} was mainly not light-absorbing in Milan winter samples [45]. In these cases, lower temperature protocols such as EUSAAR_2 could lead to an EC overestimation due to the incomplete evolution of resilient organics during the He phase.

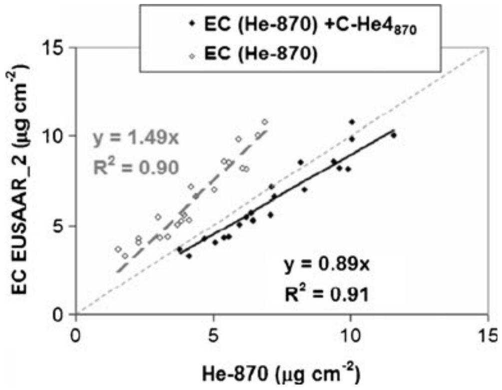

Fig. 5 Comparison between EC measured by EUSAAR_2 (*y*-axis) and EC and EC+C_He4_{870} by He-870 protocol (*x*-axis)

A recent technical report (CEN/TR 16243:2011 [47]) gives guidance on the measurement of elemental carbon and organic

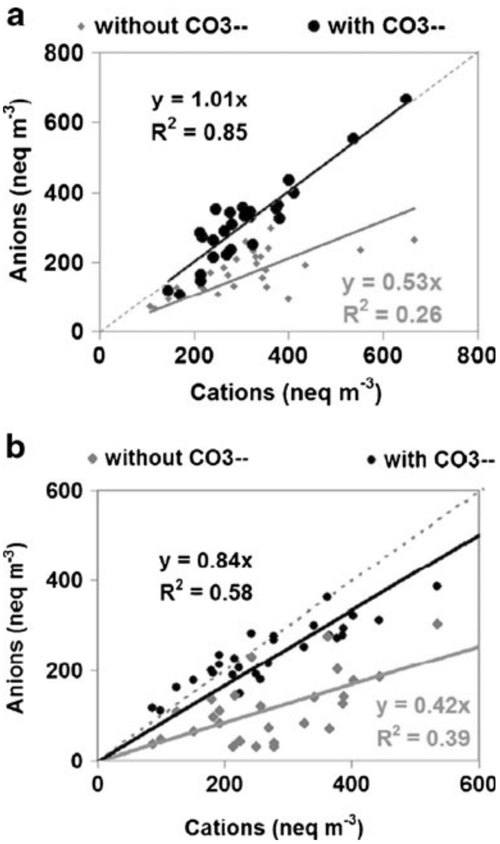

Fig. 6 Ionic balance obtained with and without considering carbonate contribution. CO_3^{2-} determined by the de-convolution of TOT thermogram in the He phase by He-870 protocol (**a**) and by FTIR on PTFE filters (**b**)

carbon as requested by the Council Directive 2008/50/EC [2] on ambient air quality and cleaner air for Europe. The methodology described in the report is thermal–optical transmittance/reflectance and four different thermal protocols are reported (both low- and high-temperature protocols in the He step are suggested). The choice among the different protocols should consider the characteristics of the aerosol in the sampling site to minimise possible biases. Therefore, as already mentioned in 'The role of filter load and field blanks in TOT analysis: influence on sampling strategies' section, a preliminary assessment of the aerosol features at the sampling site of interest can be helpful in performing analyses in optimised conditions.

Methodologies for carbonate determination

A standard methodology for carbonate determination does not exist yet. In the literature [32, 48], different approaches basically based on the sample pre-treatment with HCl are presented. Nevertheless, the exposure of the sample to HCl smokes increases the charring and therefore the uncertainty in the OC/EC separation [18]. In addition to acidification and thermal analysis of the samples, the ionic balance approach is widely used for carbonate quantification [36, 37]; there are several drawbacks in this approach [18] like the possible residual acidity in PM or the presence of not detected ions (e.g. organic anions or compounds produced by phytoplankton activity in the sea as methanesulphonic acid—MSA). Moreover, the complete carbonate solubilisation in PM samples can depend on the extraction procedure chosen (e.g. on the water quantity used or on the number of extractions).

At our laboratory, the de-convolution method presented in Perrone et al. [14] was developed. In this approach, CC determination is carried out de-convolving the FID signal during TOT analysis of the sample as is.

Another technique developed at our laboratory is based on the FTIR analysis of ambient samples collected on PTFE filters as described in [16]. In this case, carbonate determination is performed on samples collected on PTFE filters, which are commonly used in monitoring campaigns and cannot be analysed by thermal methods.

It is noteworthy that when IC is carried out on samples heavily impacted by CC contributions, a significant anionic deficit appears. On the contrary, the ionic balance significantly improves considering the CO_3^{2-} evaluated by de-convolution of the thermogram obtained by the analysis of samples collected on quartz fibre filters or by the FTIR analysis of samples collected on PTFE filters (see Fig. 6a and b, respectively). As we showed in 'Efficiency of the extraction procedure for carbonate solubilisation' section, our extraction procedure is efficient in carbonate solubilisation; thus, the results shown in Fig. 6a and b demonstrate the effectiveness of the methodologies for carbonate quantification developed at our laboratory.

Conclusions

In this work, we presented an overview of technical developments and insights into analytical techniques for aerosol samples analysis performed at the environmental chemistry laboratory of the Department of Chemistry of the University of Milan during the last decade.

Focus was posed on the main aerosol components (secondary ions and carbonaceous material) and on source markers (levoglucosan and carbonate). Different techniques were set up and QA procedures were applied. Moreover, deep insight into open problems concerning the TOT method was carried out and an innovative approach for CC quantification was developed and presented.

All this work allowed the chemical characterisation of thousands of aerosol samples in the frame of different projects. Such analyses allowed also the application of receptor models for source identification [16, 24] and the development of innovative approaches for the identification of real-world emission factors [25].

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