

Identification and estimation of atmospheric aerosol main components: hit the target by means of a single analytical method

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1- INTRODUCTION

Atmospheric aerosol main components are represented by some principal ions (sulphate, nitrate and ammonium) and by the carbonaceous fraction, i.e. total carbon (TC) which is mainly formed by organic carbon (OC) and elemental carbon (EC). These two components (main ions and TC) account for about 40 and 50% of the particulate matter mass.

Ions determination in aerosol is commonly achieved by means of ion chromatography (IC) (Chow and Watson, 1999) after extraction of the filter. The methods most commonly applied for OC and EC quantification are based on thermal evolution and reflectance/transmission measurements (Birch and Cary, 1996), i.e. TOT and TOR. In a recent study (Fermo *et al.*, 2006) a new application of TGA/FT-IR (thermo-gravimetric analyzer combined with an infrared spectrophotometer) for carbon determination has been proposed and validated through the comparison with TOT.

We have investigated the possibility to monitor, simultaneously by TGA/FT-IR, CO₂, deriving from OC and EC decomposition, with other species (SO₂, NO, NO₂, N₂O, NO₃⁻ and NH₄⁺) which volatilize during the decomposition of sulphates and nitrates contained in the particulate matter. While the system turned out to be reliable for OC and EC quantification, the assessment of ammonium, sulphate and nitrate concentrations is still in progress and here we present some preliminary results.

2- METHODS

TGA/FT-IR system is based on the continuous acquisition of IR spectra for the gaseous species of interest while the filter is thermally decomposed following a program consisting of two heating steps as described in Fermo *et al.*, 2006.

This allows, for each examined sample, to obtain 64 IR spectra in the region 4000-600 cm⁻¹. By monitoring the infrared absorbance of the single species an evolution curve is obtained. The evolution curve peak areas are proportional to the compounds concentration.

In table 1 the compounds of interest in the aerosol characterization, the gaseous or ionic species deriving from their thermal decomposition and the corresponding IR absorptions are reported.

Compound	Analyzed species	Wavenumber (cm ⁻¹)
OC	CO ₂	2361
EC	CO ₂	2361
SO ₄ ²⁻	SO ₂	1360
NO ₃ ⁻	NO ₂	1628
	NO	1896
	N ₂ O	2236
	NO ₃ ⁻	1360, 830
NH ₄ ⁺	NH ₄ ⁺	3200, 1420

Table 1: analyzed compounds, species and their typical IR absorptions

Sometimes, the species observed in the IR spectrum are in ionic form, because of a condensation process probably occurring in the White cell for gas analysis, placed inside the spectrophotometer.

The measurements have been carried out on both standard materials (NH₄NO₃, (NH₄)₂SO₄ and mixtures of these two salts) and about 150 real urban PM₁ samples, collected during a campaign carried out in Milan, Genoa and Florence in 2004 (Vecchi *et al.*, 2005) using low volume CEN-equivalent samplers (flow rate: 2.3 m³/h) equipped with PM₁ inlet.

The analysis of the standard samples allowed the identification the peaks of interest.

In order to verify the method reliability in the assessment of ions concentrations, different portions of the same filter have been analyzed by both TGA/FT-IR and IC (after sample ultrasonic extraction with MQ water).

4- CONCLUSIONS

It is worthy to note that the hyphenated method TGA/FT-IR is here proposed for the first time to our knowledge for the simultaneous quantification of particulate matter main components, by means of a single analytical method.

The first advantage is represented by the direct measurement of the filters without any pre treatment, generally a tricky step which could introduce further sample contamination.

Furthermore, TGA/FT-IR is a cheaper technique (no chemical reagents and expensive spare parts are required).

Moreover, analyses required a lower time consumption: no sample treatment and simultaneous assessment of both ionic and carbonaceous components.

Finally, the quantification of all the components is performed on the same sample portion, saving the remaining filter for further analyses.

Since the sensitivity is lower than the one achievable by means of IC, a drawback is that concentrations lower than about 1 µg/m³ are, at the moment, cannot be quantified, because of the IR signal to noise ratio.

On the other hand, a drawback of IC is represented by the complex and time consuming extraction procedure in order to obtain good recoveries.

It is also noteworthy that while IC allows the measurement of only the soluble fraction of ions, by means of TGA/FT-IR total species (soluble and insoluble) are quantified.

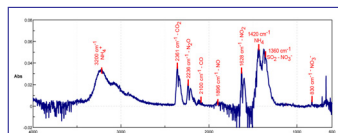


Figure 1a

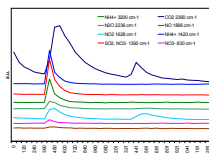


Figure 1b

Figure 1: a) example of IR spectrum (a) and the corresponding evolution curves (b) for the different species

3- RESULTS AND DISCUSSION

The target of the present work is the simultaneous analysis of OC and EC together with the major ions by TGA/FT-IR system.

The evolution curves obtained for the different species on a real PM sample are shown in figure 1 together with an IR spectrum belonging to the collected series.

It is worthy to note that each species has a different response factor in the IR spectrum; as a consequence comparing different compounds, the peaks intensities are not proportional to real concentrations. The evolution curves in figure 1b are reported with their real intensities.

In the following picture (figure 2) the more significant temporal trends of the major compounds obtained by the two methods (IC and TGA/FT-IR) are compared.

It has to be pointed out that the validation of OC/EC concentrations determined by TGA/FT-IR has been performed by an inter-comparison with another technique, i.e. TOT, and this is the subject of another poster presentation (4G12).

At present, compounds concentration determined by TGA/FT-IR are not reported in µg/m³ since the optimization of the calibration procedure is still in progress. Values obtained are therefore reported as evolution curves peaks areas, expressed in a.u..

Generally good agreements between TGA/FT-IR and IC data on PM samples are observable. For nitrates the best accordance has been observed in Milan and Florence during wintertime (figures 2a and 2b) when ammonium nitrate concentration is higher (since the signal at 830 cm⁻¹ is less intense than that at 1628 cm⁻¹, the trend of the first one is shown only for Milan (2b), where NH₄NO₃ is present in a higher quantity than in Florence).

For sulphates the agreement is good in all the cases (figure 2c) with the exception of Milan during wintertime. As shown in table 1 the 1360 cm⁻¹ signal is due to both SO₂, coming from sulphate decomposition, and NO₃ but it has to be noted that the signal intensity due to nitrate is not comparable with those of the other to signals previously used, i.e. 830 cm⁻¹ and 1628 cm⁻¹. When nitrate concentration is not particularly high, the contribution of this species to the band at 1360 cm⁻¹ is negligible, and sulphates determined by IC are in accordance with TGA/FT-IR data.

In figure 3, the correlations between data turned out by the two methods are shown.

Likewise what observed for the trends, the correlations are good with the exception of SO₄²⁻ for Milan-wintertime. This poor correlation is due, as previously mentioned, to the high nitrate concentration and to the spectral interference between SO₂ and NO₃ at 1360 cm⁻¹. Nitrate low concentration points (figure 3b) are spread because of the interference due to the water signal.

At the moment, by means of reference materials analysis and calculation of the sensitivity factors, we are trying to separate the different interfering contributions, in order to go back to sulphates and nitrates concentrations.

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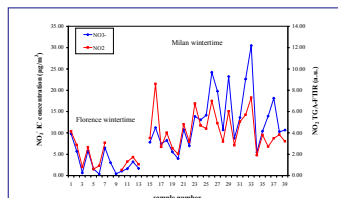


Figure 2a: NO₃⁻ (IC) and NO₂ (TGA/FT-IR) patterns (Wavenumber=1628 cm⁻¹)

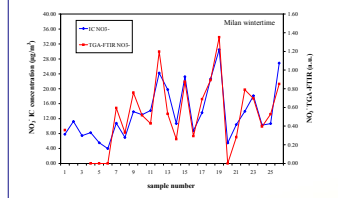


Figure 2b: NO₃⁻ (IC) and NO₂ (TGA/FT-IR) patterns (Wavenumber=830 cm⁻¹)

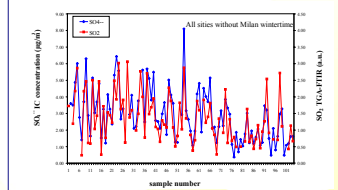


Figure 2c: SO₄²⁻ (IC) and SO₂ (TGA/FT-IR) patterns

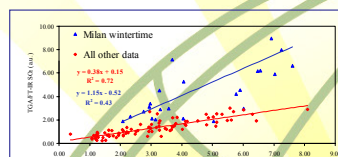


Figure 3a: SO₄²⁻ (IC) and SO₂ (TGA/FT-IR) correlation

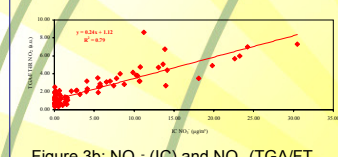


Figure 3b: NO₃⁻ (IC) and NO₂ (TGA/FT-IR) correlation (Wavenumber=1628 cm⁻¹)