Comparison among un-denuder filter based, denuder filter pack and continuous techniques for inorganic artefact assessment

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The particulate matter consists of thousands of chemical species characterized by several physical and chemical properties. Sulphate, nitrate and ammonium are the main components of the inorganic fraction and account for 30-40% of total mass of PM2.5 (Minguillóna et al., 2012).

Traditionally in measuring the ambient concentrations of aerosols, water-soluble inorganic fraction of PM are determined by filter-based method. This method has several shortcomings such as labor intensity, lengthy analysis time, poor resolution time and the sampling artefacts. The most studied sampling artefact regards the nitrate content determined on filter. PM2.5 nitrate concentrations, in fact, can result overestimated due to the absorption of gas-phase nitric acid on the filter, and underestimated due to the evaporation of ammonium nitrate collected on filter during the sample collection (Vecchi et al., 2009). The most rigorous methods recommended by United States Environmental Protection Agency (USEPA Compendium Method IO-4.2) for avoiding gas/aerosol artefacts is the use of diffusion denuders and a filter pack. These denuders first denude the air stream of condensable gases and then sample the aerosols with a filter pack that can collect both the aerosol and any volatilized products from it. Nowadays semi-continuous instruments that provide data of PM ionic component have been developed. Among the most modern automated systems equipped with denuders, the Ambient Ion Monitor AIM 9000D (by URG&Co) has been used for this work. The AIM is a real-time analytical instrument capable of simultaneous sampling and measurements of water-soluble PM2.5 constituents and ion gas precursors.

In this study, in order to assess the inorganic artifact and the AIM performance for avoiding them, the results obtained measuring nitrate and nitrite determined by an un-denuded filter based sampler, a denuder filter-pack sampler and a semi-continuous system have been reported.

The preliminary results analysis highlighted a noticeable difference in nitrate and nitrite amount determined on 24h filters and on three 8h filters samples simultaneously; especially for nitrite concentration when lower NOx and higher Ozone concentrations were registered (for example in fig. 1 are reported only few days). Moreover, as shown in figure 2, the nitrate concentrations determined by AIM showed a good correlation with those determined by the rigorous artefact free methods based on denuder filter pack sampler. However in specific days, the particulate nitrate concentrations determined by AIM result unexpectedly lower than those determined by denuder filter pack method. In these days, characterized by higher ozone concentrations, the particulate nitrite concentrations on filter for denuder filter pack methods were very lower than those determined by AIM and usually not determined. These findings suggested a possible oxidation of nitrite to nitrate on filter during PM collection (Yu et al., 2005). Therefore, this reaction probably determines another important artefact in nitrate determination on filter. Finally, these results showed also the potentiality of the automatic instrument in nitrate artefact free measurements and taking into account the user-friendliness and lower time and cost consumption, AIM could be an useful tool for an accurate determination of PM ionic composition.



Fig. 1: Comparison among nitrate amount determined on 24 and 8 hours filters. NOx and Ozone concentrations behavior



by denuder filter pack method and by AIM

Vecchi, R. et al., 2009. Atm. Env. 43 (2009) 1713–1720. Minguillóna, M.C., et al. 2012. Sci.Tot.Env.427–428: 191–202 Yu et al., 2005. J. Air & Waste Manag. Ass. 55, 1100–1110.