Atmospheric particles phase-transitions and Time-of-Wetness in Milan

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Phase-transitions of atmospheric particles are a field of interest for many applications such as estimation of radiative forcing and climate change, remote sensing, atmospheric chemistry and effects on materials (Martin, 2004; Randriamiarisoa, 2009; Schindelholz, 2010). However, the majority of studies focused their attention on the deliquescence and crystallization processes of pure inorganic and/or organic acids because of the lack of a standardized method to study the behavior of particles exposed at ambient relative humidity (RH).

For these reasons, a conductance method (Ferrero, 2014; Casati, 2015) was applied to observe the response of atmospheric $PM_{2.5}$ particles between 30 and 90% RH. Samples were collected in Milan (Italy) on Teflon filters according to EN-14907 (2.3 m^3 h^{-1}, sampling time 24 h) and exposed to an increasing and decreasing RH ramp in Aerosol Exposure Chamber. At each step of 1% RH conductance measures were obtained to determine a humidograph (Fig.1)., allowing the identification of a RH range in which the water-soluble fraction deliquesces (during the increasing ramp) and crystallizes (during the decreasing ramp). In order to consider the variability in chemical composition of atmospheric particles during different seasons, two wintertime and two summertime sampling campaigns were carried out and deliquescence and crystallization relative humidity range were evaluated

Ionic chromatography highlighted that the wintertime nitrate-rich samples showed lower DRH range (51.6±0.7% – 58.5±0.7% RH) than the summertime sulfate-rich samples (68.3±1.0% – 72.8±1.0% RH). This seasonal trend was also observed for the CRH range: 48.1±0.5 – 44.3±0.6% RH in winter and 63.0±1.2% – 59.3±1.3% RH during hot seasons. A gravimetric method was also applied for a sub-dataset of the seasonal samples. Results showed that the two methods are perfectly comparable (Tab.1) and a good relation between an increase (decrease) in conductance signal and increase (decrease) in sample mass was found (Fig.2).

Finally, an estimation of Time-of-Wetness was carried out considering the RH values in which the transitions showed a maximum rate in signal variation. Milan historical data series of relative humidity and temperature were considered to evaluate hysteresis of the phase-transitions relative humidity as well. Since experimental DRH and CRH were obtained at 298 K, E-AIM II model by Clegg et al. (1998) was used to estimate the temperature dependence of DRH. Because of the lack of information of how CRH varies with temperature, the dependence estimated for DRH was applied to CRH as well. Results showed the importance of considering the hysteresis behavior of atmospheric particles to avoid the underestimation of the Time-of-Wetness.

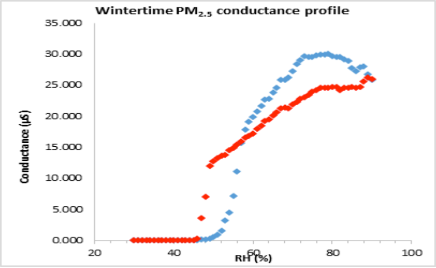

Figure 1. Typical conductance profile of wintertime PM2.5 samples collected in Milan.

Table 1. DRH and CRH range by means conductance and gravimetric method

		CONDUCTANCE METHOD				GRAVIMETRIC METHOD			
		MDRH (%)		MCRH (%)		MDRH (%)		MCRH (%)	
		start	end	start	end	start	end	start	end
summertime	average	64.5	69.0	63.7	59.2	63.2	69.5	61.0	56.0
	σ ±	2.3	2.1	2.1	2.1	2.5	2.3	1.9	1.7
wintertime	average	51.1	57.2	48.5	47.4	48.5	55.7	48.1	45.1
	σ ±	0.8	0.8	0.6	0.7	1.0	1.4	1.0	1.0

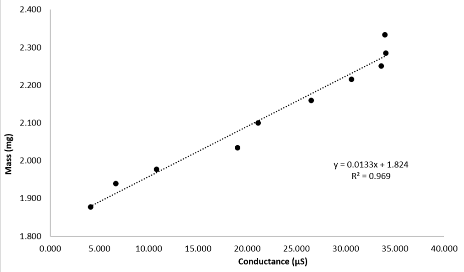

Figure 2. Correlation between increasing in conductance and mass during the DRH range.

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