Speciation of semivolatile organics in the Veneto’s bonfires aerosol

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Direct Thermal Desorption (DTD) of PM samples hyphenated to gas chromatography – mass spectrometry (GC-MS) or comprehensive bidimensional gas chromatography Time Of Flight MS (GCxGC-TOF MS) have been proposed for the characterization studies of the particle-bound Semivolatile Organic Compounds (SVOC) (Waterman et al., 2000; Falkovich et al., 2001; Larsen et al. 2003; Hays et al., 2003; Hays et al., 2004) and the routine characterization of PM2.5 on daily collected filters (Schnell-Kreis et al., 2005).

An application is presented for this technique employing a filtering media (glass fiber) for PM that has not been conditioned thermically before sampling, adopting only the requirements of the current procedure for the gravimetric measurement of PM. Tentatively also samples of the glass fiber ribbon from PM10 analysers in the air quality monitoring network of the Ente Zona Industriale di Porto Marghera (Venice mainland industrial area) have been tested.

PM10 samples have been sequentially collected on a 4 hours basis (sample volume: 4 m³) starting from January 5 h00:00 for three days at an urban site in Mestre (Venice mainland). Automatic analysers collected 2 hours PM10 spots (sample volume: 4.6 m³) on their glass fiber ribbon starting from January 5 h12:00 for two days.

The major PM contributing source at the monitoring site is traffic. However its relevance decrease in the time series of collected filter as the choosen period of sampling include the Twelfth Night (eve of Epiphany, Jan 5-6 night) when thousands bonfires are lit in the Veneto Region at suburban and rural sites from evening to midnight. As reported for the U.K. bonfires (Harrison et al., 1999; Farrar et al., 2004) the air concentration of PM rised according to the widespread combustion sources, but the peculiar meteorological conditions (wind calm) induced a relevant pollution episode leading to a PM10 air concentration of 470 µg/m³ between 00:00 and 04:00 January 6.

Aliquots of the collected PM10 filters (or ribbon) were thermally desorpted, without any preparation, directly to a gas chromatograph coupled with a quadrupole MS detector (DTD-GCMS). The GC-MS chromatograms showed a rather complex pattern of SVOC according to the variety and different blend of raw materials used to build and make up the bonfires, as well to the actual burning conditions of each of them. Selected ion traces (m/z) allowed an easy identification of several aliphatic homologues series (alkanes, esters, alkan-2-ones, alkenes), PAH(s), oxy-PAH(s), and thermal derivatives from terpenoids, lignin and vegetation waxes (Simoneit, 2002).

The results of the filters (4h sampling) are compared with those obtained from the PM spots on glass fiber ribbon sampled by the PM10 analysers of the survey network (2h sampling), allowing a better resolution of the different SVOC profile in the early traffic related samples and those collected during the bonfire flaming and smoldering phases. The the pros and cons of the technique as blank level of the DTD-GC introduction system and filtering media, lower and upper volatility range limits for the SVOC, and sensitivity will be discussed.