

Thermal desorption coupled with resonance enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS) for the analysis of PAH content of urban aerosol particles

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Pyrolysis and methods of thermal analysis are useful techniques for the investigation of e.g. polymers, biomass, or urban aerosol particles, the latter held responsible for serious health effects such as cardiovascular disease. In this instance, the role of organic species such as polycyclic aromatic hydrocarbons (PAH), which are adsorbed on the particle surface, has been discussed intensively in recent years. However, relatively little is known about the distinct components of aerosol particles; and analysis of the carbon content is often limited to the determination of the total organic and elemental carbon fractions. By means of Thermal desorption-Photoionization Mass Spectrometry (TD/PI-MS) at different temperatures evaporated organic compounds from the particles are analysed. The soft resonance-enhanced multiphoton ionization (REMPI) is applied in this work, which is in combination with time-of-flight mass spectrometry (TOFMS) well suited for the sensitive detection of PAH with almost no fragmentation occurring in the mass spectra. In addition, single photon ionization with VUV photons (118 nm) was utilized for the detection of aliphatic hydrocarbons, BTX, and some smaller PAH such as naphthalene to either analyze possible decomposition products from PAH or substantiate the REMPI results. The applicability of these methods for on-line analysis of pyrolysis off-gases and tobacco smoke has been demonstrated recently [2, 3].

Urban aerosol samples are heated sequentially to 120, 250, and 340°C. These temperatures are widely used in the aerosol field to define specific fractions of organic carbon (OC) content from the particles. The respective effluent gases are injected into a heated transfer line composed of a deactivated quartz capillary and subsequently introduced into the ionization source of the mass spectrometer. Three TOFMS spectra are recorded per second as long as evaporated compounds are visible before moving on to the next temperature. The spectra that can be allocated to each temperature are averaged.

The total ion signal of all detected masses during the holding of a given temperature is summed up. The shape of the obtained curve is comparable to the shape of the OC fractions determined by thermal/optical methods [1], although it has to be remarked that the REMPI signal represents only a subset of the whole organic content. However, it could be interpreted as a sum parameter for the aromatic fraction of the particle. At 120 °C, there is relatively little aromatic content visible, which could mainly be attributed to phenanthrene/anthracene and their alkylated derivatives as well as pyrene. When a temperature of 250°C is attained, a large variety of PAH with masses higher than 200 amu appear such as 228 m/z (e.g. chrysene) and 252 m/z (e.g. perylene) as well as many alkylated homologues thereof. Moreover, the whole content of PAH increases significantly. At 340°C, even six ring PAH such as benzo[g,h,i] perylene could be detected, whereas smaller PAH and BTX are still visible. This may be due to pyrolytic decomposition of either the large PAH or even larger polymeric substances present on the surface of the particles, which are not detectable with REMPI-TOFMS. The respective SPI-TOFMS spectra, albeit their value is limited in terms of PAH detection, showed comparable trends.

Future work should comprise further improvement of the measurement technique for the application of aerosol analysis by thermal desorption and subsequent PAH analysis with REMPI-TOFMS of real aerosol samples with differing organic content such as summer/winter samples or samples taken on a daily basis.

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[2] Cao, L., Mühlberger, F., Adam, T., Streibel, T., Wang, H.Z., Kettrup, A., and Zimmermann, R., *Anal. Chem.* **75**, 21, 5639 (2003)

[3] Mitschke S., Adam T., Streibel T., Baker R.R., and Zimmermann R. (2005) *Anal. Chem.* **77**: 2288-2296