

# **QUANTITATIVE ON-LINE ANALYSIS OF FLAME-FORMED PAH BY MOLECULAR BEAM TIME OF FLIGHT MASS SPECTROMETRY (MB-TOFMS)**

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Polycyclic aromatic hydrocarbons (PAH), formed from incomplete combustion of a wide range of combustion sources, are believed to be hazardous to human health and to be soot precursors.

The current European legislation provides PAH monitoring from exhaust through time-consuming sampling by condensation, washing by solvent, filtration and off-line mass spectrometric analysis. Continuous on-line measurement of PAH inside and at the exhaust of combustion systems is still challenging. This is due to the small concentrations and limited selectivity of available measurement methods.

The development of on-line mass spectrometric analysis, such as flame-sampling Molecular-Beam Time of Flight Mass Spectrometry (MB-TOFMS), has enabled the selective and sensitive detection of PAH, since the expansion of the flame gases through a nozzle into a lower pressure region leads to the formation of a nearly collisionless molecular beam. In the past several years, substantial progress has been achieved by supplementing traditional electron ionization molecular-beam mass spectrometry (EI-MB-MS) with isomer-specific measurements using photo-ionization (PI-MBMS). However the inherent characteristics of on-line sampling and laser ionization allow PAH identification and comparative profiles along the flame evaluation whereas prevent PAH quantitative determination.

In this work a quantitative analysis of flame-formed PAH with a MB-TOFMS is proposed through a calibration made with off-line techniques.

Flame products from a premixed atmospheric pressure ethylene/oxygen laminar flame just above the soot formation threshold have been collected for several hours and concurrently analyzed on-line with the MB-TOFMS apparatus. The collected samples were extracted in solvent and off-line analysed by conventional GC-MS for quantitative determination of PAH. The GC-MS undetectable fraction was moreover analysed by other off-line chemical and spectroscopic techniques. From the on-line mass spectra acquired, the total area of each flame species has been evaluated and related to its concentration obtained by means of GC-MS, thus calibrating the MB-TOFMS apparatus. Moreover, a measure of the sensitivity of such experimental apparatus and a comparison with the common off-line, less sensitive and more time-expensive, GC-MS for PAH analysis is given.