Simultaneous On-line Size and Chemical Analysis of Gas Phase and Particulate Phase of Mainstream Tobacco Smoke

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INTRODUCTION

Tobacco smoke is a complex and dynamic matrix consisting of gaseous and particulate material, in which about 4800 constituents have been identified (Baker, 1999). The chemical composition and partition between both phases of the smoke can change continuously and is strongly influenced by time, temperature, chemistry and dilution of smoke. Therefore, in order to gain dosimetric predictions of smoke components relevant for human smokers, it is helpful to investigate both phases simultaneously in real time, in fresh rather than aged smoke.

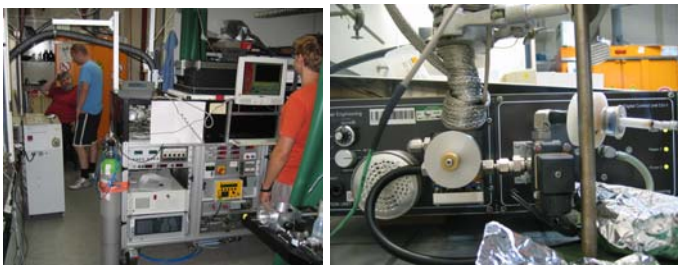

Figure 1 : Measurement apparatus

EXPERIMENTAL

The smoke is provided by a smoking engine and diluter (Model MD-19E, Matter Engineering, Wohlen, Switzerland), set to a square-wave smoking profile controlling puff volume, puff duration, and puff frequency. A rotating disk diluter allows a 50:1 real-time dilution of the whole smoke, prior to particle diameter and concentration measurement by an electrical mobility spectrometer at 10 Hz resolution in the range 5–1000 nm (Model DMS-500, Cambustion, Cambridge, UK) (Reavell *et al*, 2002). The excess non-diluted smoke was sampled directly, in real-time, for mass spectrometry where two soft photo-ionisation techniques were applied. These avoid fragmentation, and allow improved interpretation and quantification of spectra of highly complex matrices such as smoke (Figure 2).

The resonance-enhanced multi-photon ionisation (REMPI) technique uses at least two ultraviolet (UV) photons for photoionisation. In practice, REMPI is highly sensitive for aromatic compounds. The single photon ionisation (SPI) technique uses vacuum ultraviolet (VUV) photons for ionisation. With SPI, additional compounds e.g. aliphatic hydrocarbons, carbonyl compounds and nitrogen-containing substances are accessible. In principle, both ionisation methods can be applied in an alternating mode with a time-resolution of up to 10 Hz. Combining REMPI and SPI with time-of-flight mass spectrometry (TOFMS) results in a fast measurement system for trace compounds in complex gaseous matrices (Mitschke, 2005)

Cigarettes were smoked at two flow regimes of 1.05 and 2.10 l.min-1 over eight puffs of 2s duration and 60s intervals. Cigarettes consisted solely of Burley, Virginia or Oriental tobacco and were filter ventilated at 0, 35 or 70%.

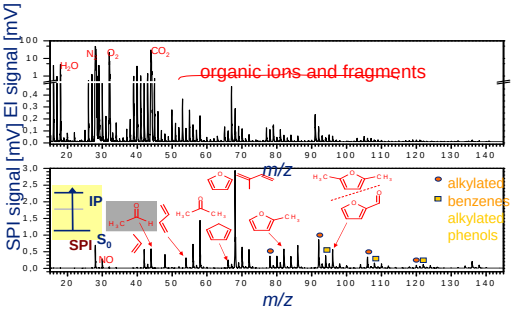

Figure 2 : SPI (9.86 eV) versus EI (70 eV) spectra

RESULTS

Count median diameter (CMD) averaged over the cigarette varied from 182 – 260 nm and increased with increasing filter ventilation and lower puff flow rates, a consequence of increasing smoke residence time and coagulation within the rod. Puff-by-puff data showed increasing particle concentration and decreasing diameter as the tobacco was consumed and the coagulation period decreased (Figure 3).

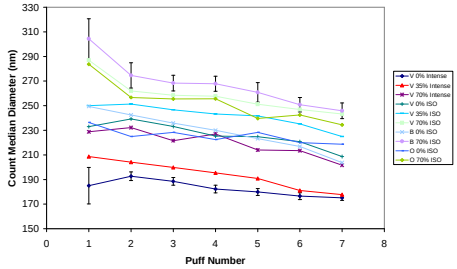

Figure 3 : Variation of particle diameter with cigarette ventilation and smoking regime

Initial mass spectrometry data show that most smoke constituents feature a continuous increase from the first to the last puff, as filtration by the tobacco rod, air dilution and outward gaseous diffusion decrease. However, there are some substances, in particular unsaturated hydrocarbons e.g. butadiene, isoprene, and propyne, which show different behaviour by having the highest amounts in the first puff. This is likely to be related to the different combustion and pyrolysis conditions when the cigarette is lit (Adam, 2006).

Absolute concentrations of individual species, in general, follow the cigarette yield, as determined by the cigarette design and smoking intensity parameters (Figure 4). Relative mass measurements in contrast show the proportion of many species in smoke stays the same, despite significant changes in particle diameter (Figure 5), implying mixing by coagulation as the predominant mechanism.

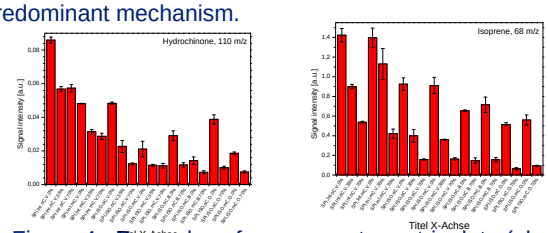

Figure 4 : Examples of mass spectrometric data (absolute)

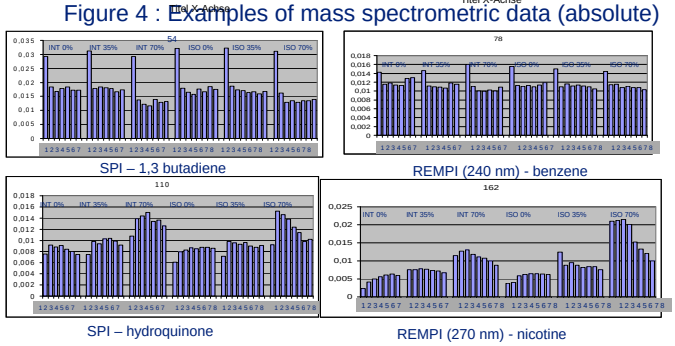

Figure 5 : Examples of mass spectrometric data (relative)

REFERENCES

Adam, T. *et al.* (2006). Chem. Res. Toxicol., 19, 511 - 520.
Baker, R.R. (1999). Smoke Chemistry. In *Tobacco: Production, Chemistry, and Technology*; Blackwell: Oxford, U.K.; 398 - 439.
Mitschke, S. *et al*. (2005). Anal. Chem., 77, 2288-2296.
Reavell, K. *et al*. (2002). *A fast response particulate spectrometer for combustion aerosols*. SAE Technical Paper, 2002-01-2714.