Simultaneous on-line size and chemical analysis of gas phase and particulate phase of mainstream tobacco smoke

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Abstract. Tobacco smoke is a complex and dynamic physical and chemical matrix in which about 4800 components have been identified. It is known that deposition efficiencies of smoke particles in the lung (60–80%) are greater than expected for smoke particles of 150–250 nm count median diameter (CMD). Various mechanisms have been put forward to explain this enhanced deposition pattern, including coagulation, hygroscopic growth, condensation and evaporation, changes in composition, or changes in inhalation behaviour. This paper represents one of three studies seeking to better quantify smoke chemistry, inhalation behaviour and cumulative particle growth. This information will improve dosimetry estimates in quantitative risk assessment tools as part of a harm reduction process. In this study smoke particle size and chemistry were measured simultaneously in real-time using electrical mobility spectrometry and soft-ionisation, time-of-flight mass spectrometry respectively. Qualitative puff-by-puff resolved yields of three selected compounds (acetaldehyde, phenol, and styrene) are shown and compared with particle number and count median diameter from different smoking intensities and filter ventilation. Yields of chemical analysis, particle diameter and concentration are in good agreement with the intensity of the smoking regime and the dilution of smoke by filter ventilation.

1. Introduction
Tobacco smoke is a complex and dynamic matrix consisting of more than 4800 compounds. It is composed of a gas phase and a particulate phase and many semi-volatile substances are partitioned between these two phases. The majority of substances can be found in the particulate phase; the gas phase consists of 400 to 500 individual compounds of which about 300 can be classified as semi-volatiles. Most of these smoke constituents are at trace levels. The chemical composition and partition between both phases can change continuously and is strongly influenced by time, temperature, chemistry and dilution of smoke [1].
Tobacco smoke analysis is usually carried out by off-line techniques with phases separate. Moreover, many analytical methods involve such techniques as trapping, storage, separation and derivatisation, all of which may alter smoke composition and phase. In addition, the results obtained are mostly for total yields in smoke from whole cigarettes. Therefore, short-time fluctuations and variations in concentration by puff are not resolved. This may be of particular interest for smoke particles which are known to be changing rapidly through coagulation and condensation [2].

In order to gain dose-based predictions of smoke components relevant for human smokers, it would be helpful to investigate particle diameter and the chemistry of both phases simultaneously during the smoking process in real time, in fresh rather than aged smoke.

Gas phase measurements by puff have been characterised for example by Fourier transform infrared spectroscopy [e.g.3] and gas chromatography-mass spectrometry [e.g. 4]. However, limiting factors for many techniques are either low time resolution, ageing of smoke, risk of artefact formation due to usage of chemicals or the fact that only a few substances can be analysed at the same time within complex spectra of primary compounds and their fragments.

In this context, two photon ionisation techniques (Single Photon Ionisation: SPI, Resonance Enhanced Multiphoton Ionisation: REMPI) coupled to time-of-flight mass spectrometry (TOFMS) have recently proven to be well suited for on-line analysis of gaseous and semi-volatile compounds of the cigarette smoking process [5].

**Figure 1.** Schematic of experimental set-up of SPI/REMPI-TOFMS for on-line gas phase analysis, Cambustion DMS-500 electrical mobility spectrometer for on-line size particle analysis coupled to a Matter MD-19E combined cigarette smoking machine and diluter.
The REMPI technique uses at least two photons for photo-ionisation, which takes place via an optical resonance absorption step. Only those molecules that exhibit a suitable electronic transition with a respective excitation wavelength together with an ionisation energy (IE) lower than the combined energy of the photons, may be ionised by two-photon ionisation. The REMPI technique, in particular, is well suited for the on-line analysis of aromatic compounds [e.g. 6].

The SPI technique using vacuum ultraviolet (VUV) photons for ionisation can be applied to detect additional compounds, e.g. aliphatic hydrocarbons or carbonyl compounds [e.g. 7]. As with REMPI, SPI generally causes no fragmentation of molecules. However, the selectivity of the SPI process is less compared to REMPI, because all compounds with an IP lower than the photon energy may be ionised. Despite this, most background gases such as nitrogen, oxygen, carbon dioxide and water are not subject to ionization, because their IEs are higher than the energy of the most commonly used VUV sources (<11 eV) and thus are not detected in the mass spectrometer. In this context, puff-by-puff resolved quantification of several potential toxicants in mainstream smoke by SPI-TOFMS has been reported recently [8,9].

For real-time particle sizing, a differential mobility particle spectrometer was used (Model DMS-500, Cambustion, Cambridge, UK). This technique enables real-time particle diameter and concentration measurements at 38 channels at 10 Hz resolution in the range 5 to 1000 nm [10].

A range of cigarettes of different tobacco type (Virginia, Burley and Oriental) and filter ventilation (0, 35 and 70%) were analysed for gas phase and whole smoke chemistry under two smoking regimes with measurements of particle diameter and concentration. Whilst multiple compounds were quantified, this paper will focus on chosen examples of vapour phase, particle phase and semi-volatile behaviour.

2. Methods

The smoke was 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. Two puffing regimes were used; either a 35 ml (ISO) or 70 ml puff (INT) of 2 seconds duration, once every sixty seconds. 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). A sub-sample from the excess non-diluted smoke was sampled directly by capillary at 10 ml.min$^{-1}$, in real-time, for mass spectrometry. Two soft photo-ionisation techniques were applied; SPI with VUV ionisation at 118 nm and REMPI with laser pulses at 240 nm and 270 nm. For vapour phase only measurements, particulate material was intercepted with a 44mm diameter Cambridge filter pad located directly behind the cigarette filter. Cigarettes with Virginia tobacco were pre-conditioned at 22°C and 60% relative humidity for at least 48 hours prior to measurement.

A schematic of the combined sampling system is shown in Figure 1.

Measurements were carried out in triplicate. In order to qualitatively account for the total amount per cigarette all on-line recorded mass spectra were summed up resulting in a single summed mass spectrum and mean as well as standard deviation were calculated for the three measurements. The same procedure was carried out for all individual puffs of all measurement series leading to puff-by-puff resolved results for the SPI/REMPI-TOFMS. In principle, quantification of several compounds is possible by applying external gas standards as demonstrated previously [8,9]. In this study, the focus was on gaining a qualitative overview on a large number of species where there were known differences in the smoke particle size.

Regarding the DMS-500 results count median diameter, particle number, total surface area, and mass load were calculated for each individual puff as well as the whole cigarette by usage of the provided software package. Mean and standard deviation were calculated for the nine corresponding measurements ($3 \times \text{SPI}$, $3 \times \text{REMPI at 240 nm}$, $3 \times \text{REMPI at 270 nm}$) of each cigarette type.
3. Results

The use of different levels of filter ventilation in the cigarettes and different flow rates of 1.05 l.min\(^{-1}\) (ISO) and 2.1 l.min\(^{-1}\) (INT) were chosen to give different transit times of smoke through the cigarette. As coagulation is the driving force for particle growth in this phase, it was anticipated that differences in particle diameter would be observed, against which any differences in chemical composition might be related.

Count median diameter (CMD) averaged over the cigarette varied from 182–260 nm (Table 1) 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 2a).

Table 1. Average count median diameter for 7 puffs per cigarette at 1.05 l/min (ISO) and 2.1 l/min (INT) (n=9)

| Filter ventilation | 0 %     | 35 %    | 70 %    |
|--------------------|---------|---------|---------|
| ISO                | 182.8 ± 2.6 | 194.0 ± 2.7 | 219.8 ± 4.5 |
| INT                | 226.4 ± 5.7 | 241.9 ± 5.5 | 258.1 ± 4.3 |

Particle concentration also changes with ventilation, smoking intensity and puff number as shown in Figure 2b; generally increasing coagulation time tends to give fewer, larger particles.

Figure 2: Puff resolved count median diameter and particle number for Virginia cigarettes of 0, 35 and 70% filter ventilation under two puffing regimes

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 and isoprene (not shown here), 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 [8,9].
Figure 3 shows typical summed mass spectra demonstrating the wide variety of compounds accessible by the used photo-ionisation techniques, SPI at 118 nm (top), REMPI at 240 nm (middle), and REMPI at 270 nm (bottom). In all measurements a pure Virginia tobacco cigarette having a filter ventilation of 0 % was smoked under the 35 ml puffing smoking conditions from the first to the last puff. The, all on-line recorded mass spectra were summed with the three illustrations on the left side showing whole smoke, with vapour phase post-filter shown on the right. It can be seen that SPI is suited to detect lower molecular weight organic species, with a list of all accessible tobacco smoke constituents published elsewhere [11]. It can also be noted that the Cambridge filter does not greatly affect the compounds in the lower mass range below about 100 \textit{m/z}. With the REMPI technique aromatic compounds and their homologues can be determined with great sensitivity.

![Figure 3: Summed mass spectra of filtered (gas phase) and unfiltered mainstream (whole smoke) smoke of a complete Virginia cigarette (0 % ventilation; ISO smoking regime) when ionised by SPI, REMPI at 240 nm, and REMPI at 270 nm.](image)

To illustrate the physical behaviour of smoke constituents in different phases, puff-by-puff resolved yields for acetaldehyde (44 \textit{m/z}), styrene (104 \textit{m/z}) and phenol (94 \textit{m/z}) were determined and plotted in Figure 4. For all measurements the yields increase with increasing puff number. In addition, it can be noted that the yields for the ventilated cigarettes decrease as the ventilation rate increases and increase when smoking under the more intense flow conditions [INT].

Comparing whole smoke (WS) and gas phase (GP) spectra highlights differing behaviour. For acetaldehyde, there are few observable differences for the puff-resolved values demonstrating that
acetaldehyde is completely present in the gaseous phase. The same holds for various other species most of them having rather low molecular weights.

In contrast, styrene (104 m/z) features a different behaviour whereby the yields are lowered when a particle filter is applied to the smoke stream, supporting the hypothesis that styrene exhibits semi-volatile behaviour, partitioning between the vapour and particle phases.

A different behaviour was observed for phenol (94 m/z) which was almost completely trapped by the Cambridge filter, implying it is almost wholly associated with the particulate phase.

Figures 4 A to C: Puff-resolved signals of acetaldehyde (m/z=44), styrene (m/z=104), and phenol (m/z=94) for Virginia tobacco research cigarettes having 0 %, 35 % or 70 % filter ventilation, smoked
under the ISO or the intense smoking regime with the Cambridge filter pad incorporated (gas phase) or not (whole smoke)

In conclusion, the combined measurement system for aerosol size, concentration and composition in real-time using combined electrical mobility and soft-ionisation mass spectrometry has proven successful. The techniques have illustrated the influence of smoking intensity and filter ventilation on yields with clear discrimination between volatile semi-volatile, and involatile particulate-bound species. Further preliminary data analysis suggests that when normalised for puff by puff mass yield and excluding the lighting puff, many species remain at a relatively consistent proportion of the smoke composition, regardless of particle diameter. However, significant first puff elevations are observed for a number of chemical species. Further work will focus on improving real-time quantitative measurement by MS particularly for key toxicants and nicotine and sampling exhaled smoke. This will allow improved estimates of the efficiency and regional deposition of toxicant chemical species and particles to better improve dosimetry and quantitative risk assessment.

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