The comprehensive understanding of the biological responses to in vitro aerosol exposures requires knowledge of the chemical composition of the test aerosol. The term test aerosol thereby refers to what gets into direct contact with the biological test system. Since between generation and interaction with a biological test system, an aerosol may be changed due to interactions with the used aerosol exposure system and due to ageing, it is not necessarily the same as the aerosol originally generated. Aerosol characterization in close proximity to the biological test system is therefore required.

The challenge thereby is to not disturb the exposure or the biological test system, whilst still reaching a high analytical sensitivity, selectivity and accuracy. We developed a procedure for using a Single Photon Ionization Time of Flight (SPI TOF) Mass Spectrometer (Photonion GmbH, Schwerin, Germany) for the on-line chemical characterization of diluted tobacco product derived aerosols within the Vitrocell 24/48 aerosol exposure system. A physical system setup and procedures for aerosol sampling and the quantification of eight targeted smoke constituents were established and tested.

Equipment, Materials and Methods

The Vitrocell 24/48 aerosol exposure system (Figure 1): The test aerosol (in this work smoke generated from 3R4F reference cigarettes (University of Kentucky) according to the Health Canada smoking regime (Health Canada Test Method T-115:1999) or aerosols generated by electronic cigarettes) passes through a dilution system. It is serially diluted and sampled into exposure trumpets projecting into the exposure chambers. In each dilution row, one sampling line allows on-line quantification of aerosol mass deposition by Quartz Crystal Microbalances (QCM). The volume flow rate through the exposure trumpets and the QCM channels are kept at 2 mL/minute. The dilution airflow rates applied in the present work are indicated in Figure 1.

The Photonion SPI TOF-MS (Figure 2): The heated sampling capillary takes samples of 3 – 5 mL/minute. The samples are ionized by VUV light of -320-160 nm (ionization energy of ~10.3 eV) and enter the TOF by linear extraction. Mass spectra are reported at a frequency of 1 Hz, the covered mass range is 10-2000 m/z. Absolute quantification is based on compound specific cross sections (ionizabilities) relative to toluene, determined using 100 ppm reference gases. Photo-ionization results in only limited fragmentation of analytes. Known aerosol constituents can therefore be identified based on their molecular mass (= risk of biased quantification in presence of isobaric molecules).

Sampling within the Vitrocell 24/48 aerosol exposure system (Figure 3): The sampling capillary (heated to 280°C) was directly inserted into the tube connecting the dilution system to the QCM modules. Special holders for the transfer line were developed for this purpose. The length of the uncovered (hot) heated capillary segment was kept to below 5 mm, thereby avoiding aerosol condensation and clogging.

Results and Conclusions

Table 1: Mass of the targeted 3R4F smoke constituents reaching the exposure chambers. Only values for highly diluted smoke are listed, the calculated dilution ratios and the observed decrease in concentration are listed for each dilution step. The table further shows a comparison to expected yields per cigarette and the according delivery efficiencies. The molecular masses are listed for assisting peak identification in Figure 4.

A setup for sampling and analyzing complex aerosols on-line during exposures was established

Quantitative data for eight targeted aerosol constituents were obtained
- Aerosol dilution is reflected by the measured concentrations
- Calculated delivery efficiencies are not commonly equal to 1, which can be attributed to:
  i) Presence of isobaric molecules (= delivery efficiency > 1)
  ii) Losses in the Vitrocell system due to condensation (= delivery efficiency < 1)
  iii) Selective sampling into sampling capillary

The puffing profile could be resolved at low aerosol concentrations
- Puff-wise chemical aerosol analysis is possible
- With increasing aerosol concentration the resolution decreases drastically (puff-to-puff carry over)

No compounds of molecular masses higher than 200 Da were detected in significant amounts
- These compounds are potentially lost in the Vitrocell system due to condensation

Future steps:
- Verification of complete aerosol sampling at capillary tip
- Increasing the set of targeted compounds
- Increasing specificity, e.g. by identification of mass fingerprints for compounds for which fragmentation occurs

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