Tobacco smoke is an extremely complex and dynamic aerosol consisting of liquid/solid droplets (particulate phase) suspended in a mixture of gases and semi-volatiles (gaseous phase). It is formed during overlapping processes of burning, pyrolysis, pyrosynthesis, distillation, sublimation, condensation, filtration and elution\(^1\). Smoke is emitted either as the mainstream smoke inhaled by the smoker or emitted from the smoldering cigarette in the form of sidestream smoke.

Mainstream smoke consists of about 5600 identified compounds\(^2\) and some reports claim the number of unidentified compounds might reach up to 100 000\(^3\). Over 150 smoke constituents are toxic to humans\(^4\) and/or animals and around 80 have been classified by the International Agency for Research on Cancer (IARC) as known (Group 1), probable (Group 2A) or possible (Group 2B) carcinogens to humans\(^5\). These include toxicants such as metals, aromatic amines, nitrosamines, phenols, carbonyls, unsaturated-, aromatic- and polynuclear aromatic hydrocarbons, among others.

Classical GC cannot provide sufficient resolution to separate the number of constituents present in tobacco smoke. Consequently, most methods used for smoke analysis focus on a relatively small number of target analytes. This results in a multi-method approach for the analysis of toxicants.

Comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS) has proven in recent years its high resolving potential for the analysis of complex mixtures\(^6,7\). Thus, this technique might be very useful for unraveling the composition of mainstream smoke and identification of toxicants.

Cigarettes were smoked using a RM20 Smoking Machine and internationally agreed standard smoking conditions. Particulate matter (PM) was collected onto 44mm glass fibre filter pads which were afterwards analysed by means of dynamic headspace (DHS) sampling and solvent extraction. A combination of a thick phase primary column and a very polar ionic liquid secondary column was used. Identification of compounds was conducted by de-convolution of the mass spectrometric fragmentation patterns and script-based classification.

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