Validation of an online, real-time, soft photon ionisation (SPI) time of flight mass spectrometer for mainstream tobacco smoke analysis

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Mainstream tobacco smoke is a complex and dynamic aerosol, consisting of both particulate and vapour phases. Most analytical approaches for the determination of mainstream tobacco smoke toxicant yields employ off-line per-cigarette analytical techniques that limit understanding of the processes leading to smoke formation. Therefore analytical techniques which allow for online, real time, per-puff quantifiable yield measurements offer many advantages over traditional techniques. The LM2X-TOFMS (Borgwaldt GmbH, Munich, Germany), a coupling of a linear smoking engine and time of flight mass spectrometer is an example of a real-time per-puff analysis system for the vapour phase of mainstream cigarette smoke.

The system uses an E-Lux 126 vacuum ultraviolet (VUV, 126nm) lamp as its light source for soft photon ionisation (SPI), an ionisation technique which causes almost no fragmentation of the chemical species present in the sample (photons of 9.8eV). SPI allows substances to be measured directly in complex mixtures, such as mainstream tobacco smoke whilst not ionising background gases such as O_2, N_2 and CO_2. Currently, seven constituents of mainstream smoke can be quantified (Table 1) on the system (Adam, 2006). Three of which are present on the WHO eighteen priority toxicant list (WHO, 2008).

Table 1: Quantifiable vapour phase analytes on the LM2X-TOFMS.

Class	Analyte
Alkenes	1,3-Butadiene (m/z 54)*
	Isoprene (m/z 68)
Aromatics	Benzene (m/z 78)*
	Toluene (m/z 92)
Carbonyls	Acetaldehyde (m/z 44)*
	Acetone (m/z 58)
	2-Butanone (m/z 72)

*identified as toxicants of concern by a WHO study group

Validation of the system was split into two studies based on recommendations of the International Committee on Harmonisation (ICH). Initially, robustness testing was performed to determine whether the LM2X-TOFMS was able to remain unaffected by small but deliberate changes in operational factors such as capillary length, ferrule, time of day and the day on which measurements are performed. Secondly, measurements were performed to evaluate the linear response of the system based on an individual concentration range for each analyte.

3R4F Kentucky reference cigarettes, (9.4mg ISO pack tar) were used during the first part of the study; all samples were conditioned under ISO parameters: T: 22 ± 1°C RH: 60 ± 3%, and smoked using ISO puffing parameters (35ml puff over 2s every 60s). For the linearity measurements, six certified gas mixtures of varying concentrations as well as a 'blank' were analysed in 2L gas bags over three days. Gas bag analysis was performed using sampling parameters of ten 35ml, 2s "puffs" with a frequency of 20s. Separate gas bags were used for each gas mixture to avoid contamination.

The robustness results were analysed by One-way ANOVA, it showed that no vapour phase constituent had a statistically significant difference for any of the identified changes ($p = \geq 0.05$). I-MR control charts confirm that although there is day to day variation, some of which could be attributed to cigarette variation, the overall process shows good stability and control.

To establish analyte linearity, the measured puff yield (µg/puff) for each analyte was plotted against the relevant bottle concentration range. Figure 1 shows a comparison plot of measured benzene yields vs. calculated benzene yields (assuming ideal gas law).

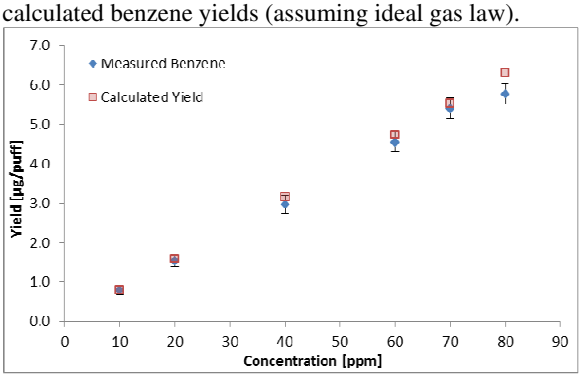

Figure 1. calculated vs. measured values for benzene.

These data will be used to determine reproducibility, repeatability and limits of detection (LOD) and quantification (LOQ).

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