

Speciation of arsenic in tobaccos from reference materials and cigarettes using HPLC-ICP-MS

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Tobacco (*Nicotiana tabacum* L.) use is predicted to be the prime cause of one billion deaths this century, globally. Agents and mechanisms that cause smoking-related disease are still uncertain. The chemical form and bioavailability of the metalloid Arsenic (As), one of several hazardous components recognised in tobacco, is poorly constrained despite its importance to toxicity mechanisms. It has been suggested that the heavy metal content of tobacco products should be controlled by regulators. The burning coal of a cigarette produces mainstream smoke (inhaled through the filter) and side-stream smoke that escape into the surrounding air; a relatively high transfer rate of 7–18 % total As is volatilized from cigarette tobacco to smoke. Inorganic and organic metal(oid) species formation in smoke are poorly documented, but first it is important to determine As species present in tobacco, in order to understand the transfer pathways of As species from tobacco to smoke and human uptake. The research aims of this study were to speciate As, using HPLC-ICP-MS, in tobacco using certified reference materials, leading authentic US, UK and Chinese cigarette brands, and also some counterfeit cigarettes known to contain elevated levels of As, in order to gain a sense of the variability among globally diverse smoking materials. Total concentrations analytical recoveries for the stand-

ard reference materials correlated well to reference values, and further analyses for error determination gave confidence in the analyses protocols, accuracy and precision; values ranged from 144 - 4012 $\mu\text{g As kg}^{-1}$ ($n = 14$); reference standards and genuine brand samples (144 - 1008 $\mu\text{g As kg}^{-1}$; $n = 11$), counterfeits of Chinese (2339 - 4012 $\mu\text{g As kg}^{-1}$; $n = 3$). Speciation error was determined to be $\pm 12 \mu\text{g DMA kg}^{-1}$ (mean = 145; $n = 3$), $\pm 14 \mu\text{g MMA kg}^{-1}$ (mean = 44; $n = 3$), $\pm 44 \mu\text{g inorganic As kg}^{-1}$ (mean = 946; $n = 3$). DMA concentrations ranged from 21 - 176 $\mu\text{g kg}^{-1}$ (median = 40 $\mu\text{g kg}^{-1}$; $n=14$), MMA from 30 - 116 $\mu\text{g kg}^{-1}$ (median = 42 $\mu\text{g kg}^{-1}$; $n=14$), and inorganic As from 16 - 955 $\mu\text{g kg}^{-1}$, (median = 101 $\mu\text{g kg}^{-1}$; $n=14$). Organic As species were significantly low relative to inorganic As species in tobacco samples, with MMA concentrations generally lower than DMA, or below detectable limits. This study found that samples selected for this study were representative of other widely available tobaccos, and that As was found to be present in tobacco principally in inorganic form, although minor DMA and MMA were detected. As-thiol complexes may represent a significant proportion of the species not extracted or detected in this analysis, thus their inclusion would be pertinent in future studies. Ongoing synchrotron studies are being used to resolve inorganic AsIII and AsV.

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