Inorganic Toxicant Levels in Contemporary Smokeless Tobacco Products

K.G. McAdam[1], A. Faizi[1], M. Mola[1], and B. Rodu[2].

[1]British American Tobacco, Group Research and Development, Regents Park Road, Southampton, SO15 8TL, United Kingdom

[2] University of Louisville, Clinical Translational Research Building, 505 South Hancock Street, Louisville, KY 40202, USA

Contact: kevin_mcadam@bat.com

1. Introduction:

IARC monograph 89 (1) summarised historical literature on the presence of carcinogens in smokeless tobacco products. 28 Chemical agents are listed, including nitrosamines, carbonyls, benzo(a)pyrene, angelica lactones, coumarin, ethyl carbamate, and a series of metallic and radioactive species.

There are significant data in the literature concerning the levels of a number of nitrosamines in smokeless tobaccos, but relatively little information available for many of the other species. Much of the data is 20-30 years old but smokeless tobacco product styles, ingredients and production practises have undergone significant changes over this time. Moreover most of the existing data have been generated on a small number of brands in each study; with little comprehensive comparative information available on the contents of different product styles.

A study was initiated in 2008 to examine the levels of the agents in contemporary smokeless tobacco products from the US and Sweden. 70 Smokeless tobacco brands: loose (S-L) and pouched snus (S-P), chewing tobacco (C.T.), dry (D.S.) and moist snuff (M.S.), moist and hard tobacco pellets (P.M. and P.H.) and plug tobacco (P.G.), were sourced covering all major manufacturers and representing 80-90% market share in both markets.

2. IARC Classification of Metallic and Radioactive Species (2):

Chemical Agents	IARC Classification:
Metallic species	
Arsenic and arsenic compounds	1
Lead compounds (inorganic/organic)	2A/3
Nickel compounds	1
Beryllium & Beryllium compounds	1
Cadmium & Cadmium compounds	1
Chromium (III) compounds	3
Chromium (VI) compounds	1
Mercury (depending upon chemical form)	2B/3
Selenium	3
Radioactive species	
α- Particle emitting radionuclides, internally deposited (e.g. ^{234}U, ^{235}U, ^{238}U, ^{228}Th, ^{230}Th)	1
Polonium-210	1
Radium-226	1
Thorium-232	1
β-Particle emitting radionuclides, internally deposited (e.g. ^{210}Pb)	1

3. Focus of investigation:

The smokeless tobacco products were analysed for the metallic species identified in Monograph 89 (Arsenic, Nickel, Beryllium, and the radioactive species Polonium-210, Uranium-235 and -238), as well as other toxic metalloids and radioactive species previously identified in tobaccos and other plant materials (3) (Cadmium, Chromium, Lead, Mercury, Selenium; the alpha emitters Uranium-234; Thorium-228, -230, -232; Radium-226; and beta emitter Lead-210).

4. Methods:

The metalloid species were analysed by FERA, York, UK (www.fera.defra.gov.uk), as follows:

Metal yields were measured by digesting 5*0.5g aliquots of each test sample, plus certified reference material NIST 1547 (Peach leaves), in nitric acid using quartz high pressure closed vessels and microwave heating, prior to quantification by high resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS). Reagent blanks, and a reagent blank spiked with a known amount of each analyte, were analysed with the test samples for recovery estimate purposes. Three reference samples: a cigarette tobacco, a reference olive leaf material and a reference spinach leaf material were included in each analytical batch. All results were corrected for reagent blank and spike recovery.

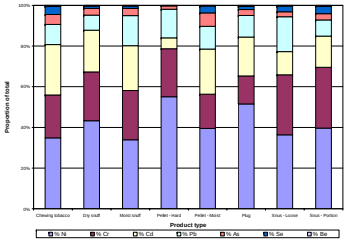
Radioactive species were analysed by Scientifics, Harwell, UK (www.scientifics.com), as follows:

Lead-210 was determined via measurement of Bismuth-210 through gas flow proportional counting after addition of lead internal tracer, ashing, acid treatment, filtering, addition of barium carrier, precipitation of lead sulphate, separation from barium sulphate using EDTA and TEA, ashing, separation by anion exchange chromatography, addition of bismuth carrier, co-precipitation of lead/bismuth sulphate, filtration and mounting on a planchette.

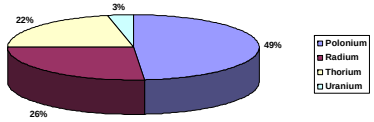
Polonium-210 was determined by alpha spectrometry after addition of Po-208 as internal tracer, prior to wet oxidation and homogenisation using HF/HNO3, and auto deposition onto a silver disc. **Radium-226** was measured by determination of alpha activity using a Berthold low-level proportional counter following addition of Ba-133 internal standard, ashing, acid digestion, precipitation with lead and barium sulphates, isolation, dissolution in alkaline EDTA and TEA, co-precipitation with barium sulphate, and mounting on a stainless-steel planchette. **Thorium** isotopes were measured by alpha spectrometry, following addition of Th-229 internal standard, ashing, dissolution in HF, co-precipitation with iron (III) hydroxide, acid dissolution, ion-exchange chromatography and electrodeposition onto a stainless-steel disc. **Uranium-234, 235 & 238** were determined by alpha-spectrometry following addition of U-232 internal tracer, ashing, dissolution in HCl/HF/HNO3, co-precipitation with iron, ion-exchange chromatography, and electro-deposition onto stainless-steel discs.

5. Results:

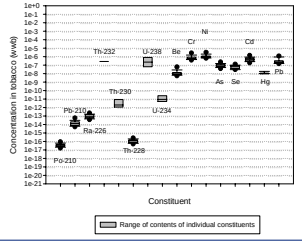
5.1 Relative contents of individual metal species in all measured smokeless tobaccos



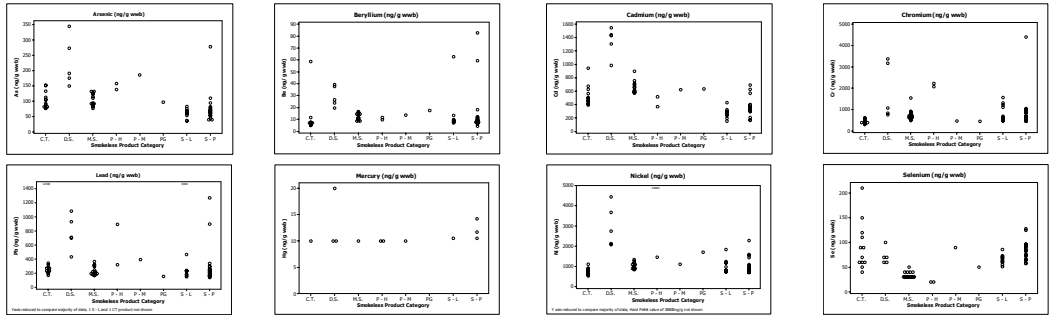
5.2 Comparison of alpha activities of radioactive species averaged across all measured smokeless tobaccos



5.3 Comparison of inorganic species levels (g/g) in contemporary smokeless tobacco products

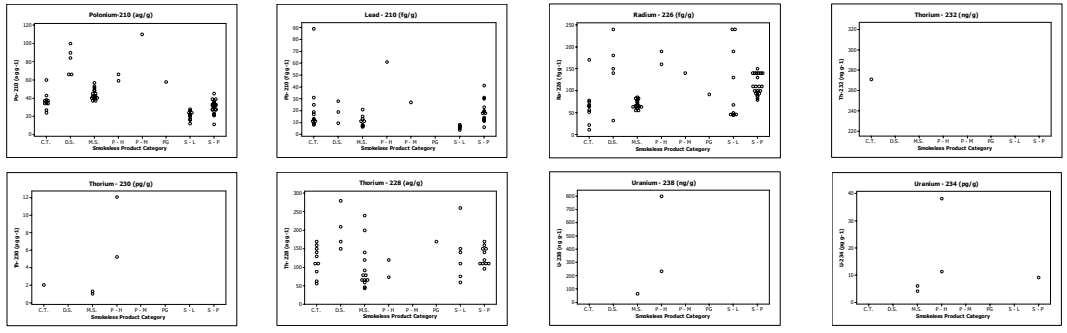


5.4 Comparison of metal levels across smokeless tobacco categories



Key to Figures: C.T. = Chewing Tobacco; D.S. = Dry Snuff; M.S.= Moist Snuff; P – H = Hard Pellet; P-M = Moist Pellet; PG = Plug; S – L = Loose Snus; S – P = Pouched Snus, ag = 10^{-18}g, fg = 10^{-15}g, pg = 10^{-12}g, ng = 10^{-9}g

5.5 Comparison of the content of radioactive species across smokeless tobacco categories (wwb)



6. Discussion:

The metal contents of moist snuff products reported from this study compare very well with those reported by Pappas et al (4), and are in good agreement although generally slightly higher than those reported by Rickert et al (5) for Canadian sourced products. Comparing metal contents across different categories of smokeless products shows a 3-4 fold range of values. For the majority of metals studied dry snuff occupies a high position in the ranking of product styles; some of this is due to the low moisture content, and therefore high tobacco content of the products in comparison to most of the other tobacco products. The hard pellet products also ranked relatively high in comparison to other smokeless tobacco products for some of the metals, again the low moisture and high solids content contributes to the relatively high ranking.

The α radioactivity of smokeless tobaccos is dominated by Po-210, Ra-226 and Th-228. However, these species are present at very low quantities (10^{-17} to 10^{-12}g/g). The radioactive species present in greatest quantity are U-238 and Th-232, which have relatively low activity. Due to the very short path length of an emitted α particle in liquid and solid media, and the nature of the measurement process, these measured alpha activities strongly overestimate the actual dose of alpha radiation that a smokeless tobacco user would receive during use. Reasonably similar levels of radioisotopes were measured across different product styles, other than higher Th-230, U-238 and U-234 levels in hard pellet products. U-235 was not present in measurable levels with any of the smokeless tobacco products, in contrast to earlier reported findings (1).

7. Conclusions:

This work has significantly expanded the database of available information on inorganic toxicant levels in US and Swedish smokeless products. Fresh insight has been provided into the relative levels of carcinogenic species, particularly in respect of Swedish smokeless products, and the presence and relative activity of different radioactive species in contemporary US and Swedish smokeless tobaccos.

8. References:

1) IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 89 (2007), http://monographs.iarc.fr/ENG/Monographs/vol89/index.php

2) "Overall Evaluations of Carcinogenicity to Humans", htttp://monographs.iarc.fr/ENG/Classification/crthallalph.php

3) Rodgmann, A. and Perfetti, T.A., Chemical Components of Tobacco and Tobacco Smoke. *CRC Press*

4) Pappas, R.S. et al, (2008), *J. Anal Toxicol.* **32**, 281-291,

5) Rickert, W. et al., (2009), Regulatory Toxicology and Pharmacology, 53, 121-133

Poster POS1-75 at SRNT Annual Meeting, February 24-27, 2010, Hilton Baltimore Hotel, Baltimore, Maryland, USA

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