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Smokeless tobacco: Assessing potential constituent exposures in US snus users.

This study estimated the potential exposure to a number of snus constituents experienced by US consumers that regularly use snus. A total of 54 snus users, aged 21 to 55, who reported using at least 15 snus pouches per week for three or more months were recruited. The participants used one of three brand-styles of a 600 mg snus product and collected the used snus pouches under normal life conditions for seven days. Participants completed a survey regarding their tobacco usage. During the study, 13% of the participants used snus exclusively, 50% used both snus and cigarettes, 37% used snus plus a variety of tobacco products. The average number of pouches used per day was 3.5 for all participants, 5.4 for exclusive snus users and 3.2 for users of both snus and cigarettes. Nicotine, N-nitrosonornicotine (NNN), 4-(methylnitrosamino)-1- (3-pyridyl)-1-butanone (NNK), N'-nitrosoanatabine (NAT), N'-nitrosoanabasine (NAB), arsenic, cadmium, chromium, lead, nickel and benzo[a]pyrene (B[a]P) levels were measured in the used pouches and in unused product. The amount of a constituent extracted by a participant was estimated by the difference between the constituent levels in the collected used and unused products. For all participants, mean nicotine extracted equaled 2.8 mg/pouch and 9.4 mg/day, corresponding to an extraction level of 39%. NNN extraction averaged 97.1 ng/pouch and 302.4 ng/day (23%), NAT extraction averaged 34.1 ng/pouch and 94.1 ng/day (16%), and NNK extraction averaged 37.5 ng/pouch and 124.4 ng/day (30%). B[a]P extraction averaged 0.2 ng/pouch and 0.68 ng/day (29%). Previous reports indicated snus users in Sweden extracted up to five times more of some constituents. Because determinations of trace metals in the used and unused pouches showed considerable variability, metals results were inconclusive. The results of this study suggest exposure to snus constituents by US market adopters may be substantially different than users in other markets.

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Ignition Propensity: some further information that can be gained from cigarettes that have been subjected to ASTM E2187 testing.

Low Ignition Propensity (LIP) products are of interest to cigarette designers and regulatory bodies in various parts of the world. To date the ASTM test or a derivative of it has been the basis on which LIP regulation is formulated. Thus further information that can be gained on cigarettes that have been subjected to ASTM testing is of interest to the tobacco industry.

During LIP testing the cigarettes in question are placed on a number of layers of a particular substrate. An issue that sometimes arises is that part or all of a series of experimental cigarettes can give 100% LIP pass rates. Although a 100% pass rate meets regulatory needs, data interpretation from a scientific perspective can then, in certain instances, become more problematic. This can be potentially overcome by further testing of all the cigarettes in the series in question on a reduced number of layers of substrate. This in turn can be viewed as being somewhat wasteful and time consuming. We have developed an alternative approach in which the individual cigarettes that had been ASTM tested were retained, and the residual length of non burnt tobacco column was measured and recorded.

Subsequent analyses utilising this technique gave good correlations between residual length values and LIP pass rates between 0% and 100%. Residual length data can be used to help resolve the effect of cigarette design variable changes that consistently gave 100% pass rates. We will illustrate the residual length technique using studies including tobacco types, cigarette paper and cigarette circumference.

This technique has been developed as a method to gain further information from individual cigarettes that have been subjected to ASTM E2187 testing and as such it is not aimed at either replacing or enhancing the said method.

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Studies on molecularly imprinted materials for selective reduction of TSNAs in cigarette smoke.

Silica gel surface graft polymers molecularly imprinted polymer Si-MIP and non molecularly imprinted polymer Si-NMIP were prepared. The synthesized samples after removing the inside template and other residues were characterized by FT-IR. The characterization results indicated that the essential organic functional groups were grafted onto the surface of the silica gel. SEM observation proved that the surface morphology between Si-MIP and Si-NMIP were significantly different. The difference was further verified by equilibrium absorption that Si-MIP exhibited higher affinity and selectivity to template molecules than Si-NMIP. The Si-MIP and Si-NMIP were added to filter tip at a rate of 40 mg/cig, test data showed that the additives had little influence on the contents of TPM and CO in cigarette mainstream smoke, TSNAs in cigarette mainstream smoke were decreased significantly by Si-MIP (24.6%) while not by Si-NMIP (3.8%). This result suggested that the molecularly imprinted polymer was a promising material for selectively reducing TSNAs in cigarette smoke.

Key words: molecularly imprinting, molecularly imprinted material, TSNA, mainstream smoke, selectivity, silica gel

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Analysis of free amino acids by two-dimensional capillary electrophoresis on micro-fluidic chip.

An in-house built two-dimensional electrophoresis system based on a microfluidic chip with laser induced fluorescence (2D-MCE-LIF) detection was used for amino acids analysis. The microfluidic chip had a glass base made by photolithographic etching, wet chemical etching, and bonding techniques. The 2D electrophoresis system combined two different separation mechanisms, including a micellar electrokinetic chromatography (MEKC) in the first dimensional separation channel and a capillary zone electrophoresis (CZE) in the second dimensional separation channel. We employed sample feed-in and separation were switched through. Electrophoretic parameters were optimized and an optimal condition was obtained. 21 amino acid mixtures labelled with fluorescent dyes were completely separated and detected, and analysed qualitatively and quantitatively. Based on the 2D chip electrophoresis of five different concentrations of amino acid samples, calibration curves were established for each amino acid. Their linear ranges spanned over two orders of magnitude with linear correlation coefficients $\gamma > 0.99$. The results indicated that the said system has the advantage over the traditional methods, such as high performance liquid chromatography (HPLC) and capillary electrophoresis (HPCE). Though the said system offers substantially the same efficiency, it takes far less time for amino acids analysis. The system is also competent for analysing free amino acids in tobacco leaf.

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Semi-quantitative analysis of cigarette by inductively coupled plasma mass spectrometry.

Inductively coupled plasma mass spectrometry (ICP-MS) has become a popular technique in multi-element analysis since the first commercial instrument became available in 1980s. Semi-quantitative analysis by ICP-MS has proven to be a powerful tool for fast screening, in addition, it does not require the element of interest to be present in the calibration standard, making it especially useful for the analysis of unknown samples.

In this study, fifteen cigarette samples were analyzed by the rapid semi-quantitative analysis method based on the ICP-MS. For each cigarette sample, cut tobacco, cigarette paper, filter (after smoking), smoke condensate and ash were analyzed. The accuracy and reproducibility of the analysis technique were evaluated by comparing results obtained from CRM (NIST SRM 1570a Trace Elements in Spinach Leaves) analysis and calibration method. Furthermore, to evaluate the performance of semi-quantitative analysis mode, two batches (5 samples per batch) of cigarette samples were examined.

The results concerning accuracy and reproducibility were more than 90% in analyzed samples at concentrations equal to or greater than 10 times the detection limit. Compared to full quantitative analysis by calibration method, the results for cigarette samples showed average error within ± 15%.

From these results, it seems that the semi-quantitative analysis technique by ICP-MS is a very useful tool for surveying many samples rapidly and it can provide analysts with valuable information. It is especially useful for survey studies and for tracer or "fingerprinting" analysis.

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Effect of blend styles on cigarette performance in low or reduced ignition propensity testing.

Lower or reduced ignition propensity cigarettes (LIP or RIP) is a term used to describe modified cigarettes that demonstrate lowered ignition propensity under specific laboratory tests. These cigarettes must meet standard performance criteria described by the test method established by the ASTM E2187-04 standard in which lit cigarettes must self-extinguish under controlled conditions.

Internal studies have shown that cigarettes made with the same paper may perform differently in the ASTM when they are manufactured with different blends. The uptake of legislation in different regions of the world where product blends and styles may differ means that it would be beneficial to understand the implication of tobacco styles on the ASTM performance at a more fundamental level.

Therefore, this study aimed to investigate the impact of blend style on the LIP performance of cigarettes, more specifically:

- The effect of tobacco types, Virginia, Burley and Oriental, in a systematic experimental design. These blends are 100% lamina in design to avoid influence from other common blend components, such as stem or reconstituted tobaccos.
- The impact of the substitution of stem for equal proportions of lamina from a tobacco blend on ASTM performance

Both of these experiments were conducted using consistent cigarette construction, and utilised both banded and non-banded styles of LIP paper from a number of suppliers.

Data from these studies show that high Burley tobacco content, and high stem inclusion rates in tobacco blends have a negative impact on the performance of cigarettes in the ASTM test.

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Estimation of exposure to snus constituents amongst Swedish pouched and loose snus users.

Measurement of the quantity of constituents in snus before and after use provides a flexible and convenient approach for estimating exposure to a range of tobacco constituents.

Consumer studies were conducted in Sweden as central location trials, with volunteer users of loose and pouched snus. Snus was held in the mouth for 60 minutes, consistent with average consumption times for Swedish snus users. A multi-analyte methodology was developed to quantify exposure to a range of constituents from the same snus portion. Used snus, and unused control portions were analysed for nicotine, humectants, TSNAs, nitrate, sodium and chloride ions, ammonia nitrogen, and five flavour compounds. Moisture content and pH levels were also examined. Benzo(a)pyrene, dimethyl nitrosamine and selected heavy metals were incompatible with the multi-analyte methodology due to either excessive variability, levels at or near analytical quantification thresholds, or apparent interactions/ interferences with saliva in validation tests.

Similar quantities of constituents were found to be extracted from loose and pouched snus portions, although differences in the initial content levels resulted in different percentage extractions. Greater levels of variability in the results were observed with loose snus, in comparison to pouched snus, due at least in part to greater variability in portion weight. Nicotine extraction at 23.8% (loose) and 33.3% (pouched), and TSNA extraction at 24.2-26.0% (loose) and 34.6-37.9% (pouched), were both consistent with the limited amount of previously reported work. These results also provide some indications of potential mechanisms underlying constituent extraction by users, such as constituent solubility and accessibility of the constituents to saliva.

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Online chemical analysis for threshing and redrying process control.

Rapid online analysis methods of sugar and nicotine contents in tobacco were developed for threshing and redrying process control. The near infrared spectra of tobacco in threshing and redrying line were collected with FT-NIR spectrometer. Meantime the chemical contents of online tobacco was sampled and the contents of sugar and nicotine in the samples were determined with continuous flow analyzer. The online FT-NIR model was optimized, it completed a test of sugar and nicotine contents in tobacco on the threshing and redrying line in 4 seconds. Base on the analysis of chemical constituents in tobacco during the threshing and redrying process, an EWMA (Exponentially Weighted Moving Average) control chart with dynamic control ranges was chosen for the process control. The tobacco which was out of the set tolerance would be rejected. The application of this online chemical analysis system proved that it is practical and beneficial to the quality of redried tobacco.

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The effectiveness of cigarette paper properties for controlling smoke yields under intense smoking regimes.

Some intense smoking regimes prescribe that the ventilation holes in the tipping paper should be fully or partially blocked, which reduces the effectiveness of the perforation in the tipping paper for controlling the smoke yields. Consequently, under these intense regimes the cigarette paper becomes more important as a design tool.

This study investigates whether the effectiveness of the cigarette paper as a design tool is influenced by the smoking regime and especially by the blocking of the ventilation holes. To this end cigarettes were produced from cigarette papers with varying air permeability and citrate content. These cigarettes were smoked under the ISO regime, the Massachusetts regime (45/2/30) and the Canadian regime (55/2/30) without blocking of ventilation. The measured smoke yields were compared with results from a numerical simulation and a good agreement (R^2>0.98) was found. The simulations were then extended to 50% and 100% blocking of ventilation holes.

The results show that the air permeability of the cigarette paper remains an effective tool to control NFDPM yields, while nicotine and CO react about 15% less sensitively on changes of the air permeability. The effectiveness of the citrate level is higher for all smoke yields when switching from ISO to intense smoking regimes, the effect is especially pronounced for tar.

When ventilation holes are blocked, the smoke yields react much stronger on changes in the air permeability of the cigarette paper for all smoking regimes, which is plausible from simple considerations of the flow in the cigarette. In contrast, the effectiveness of citrate level modifications does not depend on the blocking of ventilation holes.

In conclusion the cigarette paper remains an effective tool to influence smoke yields, but adjusting CO levels to meet regulations may become more difficult under intense smoking regimes.

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A comparison of selected volatile aldehyde levels in US and Swedish smokeless tobacco products.

To date, researchers have reported 28 toxicants in smokeless tobacco products (STP) including the volatile aldehydes formaldehyde, acetaldehyde and crotonaldehyde. According to the International Agency for Research on Cancer (IARC), formaldehyde is classified as a Group 1 carcinogen, acetaldehyde as Group 2B, and crotonaldehyde as Group 3.

Previous studies have shown that the contents of these volatile aldehydes in STPs ranged from 0.2 µg/g to 27.4 µg/g on a dry weight basis (DWB) for moist snuff, dry snuff and natural tobacco. However, approximately 20 years have passed since these measurements were carried out. Research has shown changes in levels of other toxicants in STPs over this time period. Therefore, a more up to date survey was necessary to reflect current STPs on the market.

70 major STPs were sampled from Sweden and the US in October 2008. They consisted of 32 Swedish loose and pouched snus products and 38 US products including chewing tobacco, dry snuff, pellets, moist snuff and plug. The STPs were sampled to include products from all major manufacturers within Sweden and the US. The target analytes were analysed by water extraction of the STP, derivatisation to carbonyl-hydrazones and analysis by HPLC/UV. The analytical approach was also capable of analysing acrolein, itself a Group 3 carcinogen, but not on the list of 28 toxicants, and these values are also reported.

Contemporary volatile aldehydes values ranged from below detection limit (BDL) to 10.6 µg/g DWB (BDL to 4.9 µg/g on a wet weight basis (WWB)) for both Swedish and US STPs.

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New methodologies for qualitative and semi-quantitative determination of carbon-centered free radicals in cigarette smoke using liquid chromatography-tandem mass spectrometry and gas chromatography-mass selective detection.

Several approaches were explored to develop a high throughput procedure for relative determination of 14 different carbon-centered free radicals, both acyl and alkylaminocarbonyl type, in cigarette smoke. Two trapping procedures using cyanoproxyl radical (3-CNP) were designed for this study: a) trapping in solution and b) trapping on a solid support which was a Cambridge filter pad. Fresh mainstream cigarette whole smoke and gas phase smoke, as partitioned via an unadulterated Cambridge filter pad, from Kentucky Reference Cigarette 2R4F, were collected into each trapping system in separate experiments. The 3-CNP coated Cambridge filter pad approach was shown to be superior to the impinger procedure as described in this study. Gas chromatography coupled with mass selective detection (GC-MS) was employed for the first time as an alternate means of detecting several relatively highly concentrated radical adducts. Liquid chromatography tandem mass spectrometry (LC-MS/MS) with either precursor ion monitoring (PIM), selected reaction monitoring (SRM) or selected ion monitoring (SIM) was used for detecting the large array of radicals, including several not previously reported: formyl, crotonyl, acrolein, aminocarbonyl, and anilinocarbonyl radicals. Relative quantitation was achieved using external calibration standards of 4-[1-pyrrolindino]benzaldehyde and nicotine. It was determined that the yield of carbon-centered free radicals for reference cigarette 2R4F was approximately 265 nmoles/cigarette at 35 cc puff/60 sec interval/2 sec duration smoking conditions.

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Qualitative and relative quantitative determination of carbon-centered free radicals in whole smoke from various cigarette types.

Free radicals in cigarette smoke may contribute to harm associated with cigarette smoking, more specifically, contribute to oxidative stress and subsequent biological activity. Recently, a high throughput procedure for relative determination of 14 different carbon-centered free radicals, both acyl and alkylaminocarbonyl type, was developed. This procedure used the radical scavenger 3-cyanoproxyl radical (3-CNP), which was diluted in acetone and spiked onto a 44 mm fiberglass Cambridge filter pad, which had the acetone subsequently evaporated. Fresh whole smoke from various cigarettes was collected onto the 3-CNP coated Cambridge filter pads. Cigarettes evaluated afforded a representative range of standardized 'tar' yields (14, 10, and 5 mg/cigarette, respectively by the Cambridge filter method), and also included a carbon filtered prototype, as well as Kentucky reference cigarettes 2R4F, 3R4F, and 1R5F. Cigarettes were exposed to coated filter pads using 2 different smoking regimes: 35 cc puff/ 60 sec interval/ 2 sec puff duration / 0% vent block (35/60/2/0) and 55 cc puff/ 30 sec interval/ 2 sec puff duration / 100% vent block (55/30/2/100). Liquid chromatography tandem mass spectrometry (LC-MS/MS) with precursor ion monitoring was used for detecting the large array of radicals. High resolution mass spectrometry was used to confirm several previously proposed 3-CNP:radical (3-CNP-R) adducts, the formyl and ethyl radical adducts. The range of carbon-centered free radical concentration was related to 'tar' delivery and was found to be 41-348 nmoles/cigarette with the 35/60/2/0 regime, and 349-647 nmoles/cigarette with the 55/30/2/100 regime.

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Research on measuring thermal properties of cut tobacco by transient plane thermal source method.

The thermal properties of bulk cut tobacco, such as thermal conductivity, thermal diffusivity, volume specific heat, are essential to the analysis of heat and mass transfer in various tobacco processing conditions. Based on transient plane thermal source technique, an experimental equipment was set up. Working parameters of the equipment were calculated. Thermal conductivity, thermal diffusivity, and volume specific heat of cut tobacco were measured simultaneously at different moisture contents and bulk densities. Moreover, the repeatability of the experimental data was investigated with this method at different measuring levels. The results were as follows: (1) The experimental data showed good repeatability. (2) the precision ranges of thermal conductivity, thermal diffusivity, and volume specific heat were 0.00012 $W \cdot m^{-1} \cdot K^{-1}$ - 0.00471$W \cdot m^{-1} \cdot K^{-1}$, 0.00371 $mm^2 \cdot s^{-1}$ - 0.02598 $mm^2 \cdot s^{-1}$, and 0.00921$MJ \cdot m^{-3} \cdot K^{-1}$ - 0.06537$MJ \cdot m^{-3} \cdot K^{-1}$, respectively. (3) thermal conductivity, and volume specific heat increased with the increase of moisture content and bulk density, while thermal diffusivity decreased with the increase of moisture content and bulk density.

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A new microprobe construction for *in-situ* smoke analysis inside a burning cigarette with single photon ionization - time of flight mass spectrometry.

Routine smoke analyses are mostly conducted with offline GC/MS or HPLC methods. However, tobacco smoke is a highly dynamic and extremely complex mixture of aerosol particles and vapour phase compounds. Recently, on-line sampling methods coupled with time-of-flight mass spectrometry with single photon ionisation (SPI-TOFMS) have proven to be useful to allow puff-resolved detection of many organic smoke constituents in real time. The main advantages of the SPI-TOFMS technique are its soft and sensitive ionisation without fragmentation as well as high time resolutions. It is therefore suited to investigate cigarette smoke formation mechanisms in real dynamic fashion.

Most published puff-resolved and/or on-line studies have been carried out on smoke exiting from the cigarette filter. For fundamental understanding of the combustion/pyrolysis processes during smoke generation, it is desirable to analyse these complex reactions directly inside the burning coal and also along the tobacco rod. For this purpose, a microprobe was constructed which can take samples inside the burning coal. The tip of the microprobe has to be temperature-stabile up to ca. 1100 °C and has a sufficiently small thermal mass to minimise any influence on the actual burning process. The entire microprobe and the subsequent transfer line should be heated to ca. 250-300 °C to avoid condensation and blocking. This work will demonstrate a prototype microprobe with a stainless steel tip. Results obtained from this microprobe linked with SPI-TOFMS will be presented to demonstrate the feasibility for puff-resolved online analysis on semi-volatile aromatic, aliphatic species (1,3 butadiene, isoprene, acetone and acetaldehyde) and nicotine inside the burning cigarette. Comparison with mainstream smoke yields using 2R4F reference cigarettes reveals different behaviours that are determined by the analyte's mass, volatility and relative yields.

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Synchrotron X-ray analysis of the oxidation states of arsenic and cadmium in cut tobacco, cigarette ash and mainstream smoke.

Mainstream smoke from cigarettes is known to contain various toxic metals, including As, Cd, Cr, Pb, Ni and Se. It is of interest to study the potential contribution of these metals to the overall toxicity of smoke. The oxidation state and chemical species of metals in cigarette smoke may be an important factor determining the extent of their toxicity. However, few studies have been carried out to identify the chemistry of these species in tobacco products. This study describes synchrotron-based X-ray analyses of the metal oxidation states in cut tobacco, cigarette ash and mainstream smoke, specifically on As and Cd. Impaction trapping for cigarette mainstream smoke was developed and found to be a suitable method for collecting the total particulate matter (TPM) from 2R4F reference cigarettes. The TPM samples were collected from the mainstream smoke with the impaction trap device immersed in an ice box and could be stored in dry ice for more than seven days before analysis. The X-ray Absorption Near Edge Structure (XANES) spectra showed that the mainstream smoke contained a mixture of As(III) and As(V) , while As(V) dominated the cigarette ash and cut tobacco samples. It was also established that cadmium in smoke, cut tobacco and cigarette ash is almost exclusively in the +2 oxidation state.

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Establishment of functional relationships for predicting mainstream smoke constituent yields for conventional cigarettes from Japanese market.

Some papers about functional relationships for predicting mainstream smoke constituent yields using tar or other parameters as independent variables have been previously published. Since these functional relationships can predict the mainstream smoke constituent yields in cigarettes within a reasonable range, these are useful methods for monitoring the mainstream smoke constituent yields. For the long-term use of the prediction formulas, stability should be checked because they are generated by a data set obtained in a specific time range. The objective of this study was to check the stability of the prediction formulas and to compare predicted values and measured values, using the data obtained at different times. In this study, data obtained in 2002, 2005 and recent data from the Japanese market were used. Their mainstream smoke constituent yields were all analyzed in the same laboratory under ISO smoking conditions. The stability of the prediction formulas was examined by comparing slopes and Y-intercepts in simple linear regression models between the formulas derived from the data of 2002 and the ones derived from the data of 2005. The measured values for the brands obtained recently were compared with the predicted values derived from the prediction formulas using the data of 2005. Slopes and Y- intercepts of the prediction formulas derived from the data of 2002 and the ones from 2005, show no significant differences for most of the smoke constituents. Comparison of predicted values by the prediction formulas derived from the data of 2005, and measured values obtained from recent products, shows that most of the smoke constituent yields could be predicted within a reasonable range.

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Effect of puff conditions on smolder burn rate of cigarettes smoked on a smoking machine.

The equilibrium static burn rate (SBR) of a cigarette is different from the static burn rate [smolder burn] observed during the actual smoking process (SMBR). It is therefore essential that the propagation of the cigarette burn after puffing should be studied for predicting the TPM delivery precisely during the smoking cycle.

In earlier studies, it was reported that a cigarette paper char line stayed stationary after puffing, and then moved. In other words, the cigarette paper extinguishes once and then ignites again. Moreover, the effect of the cigarette paper and cigarette design on the SMBR has been well known. For example, a high cigarette paper basis weight and high packing density exhibit a reduction in SMBR compared to SBR.

The objective of this study was to determine the effect of the puff conditions on the SMBR of cigarettes (2R4F) smoked on a smoking machine producing three different puff volumes (17.5 ml, 35 ml, 60 ml) and two different puff interval times (28 s, 58 s).

An image analysis system with a CCD camera was applied to monitor the movement of the paper char line.

As a result, we found that the burn rate after restarting of the paper char line movement was the same as the SBR, and the re-ignition interval time (Re-time), meaning the time between the stopping and restarting of the paper char line, was nearly constant (almost 15 s) in all puff conditions.

These results indicated that the SMBR is lower than the SBR and is proportional to the time obtained by subtracting the Re-time from the puff interval time, regardless of the puff conditions.

This study concludes that the Re-time is the most important factor for improving the precision of the TPM delivery during the smoking cycle for any cigarette.

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Will the Food and Drug Administration's new authority over manufacturing affect analytical testing of cigarettes? - A discussion of current Good Manufacturing Practices (GMPs).

President Obama signed legislation on June 22, 2009 granting the United States Food and Drug Administration (FDA) sweeping authority to regulate the manufacturing, marketing and sale of tobacco products. The legislation will empower the FDA to require changes in tobacco products, such as the removal or reduction of harmful ingredients or the reduction of nicotine levels. Therefore, there most likely will be additional scrutiny on analytical data and the quality systems surrounding it. This poster will discuss some aspects of cGMPs and how their potential implementation could affect the tobacco testing laboratory. Some of the key aspects explored include instrumentation, documentation, training, validation, and change control.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 11

Use of two GC-MS scan techniques for the characterization of reference smokeless tobacco products.

The recent LSRO report, ***Differentiating the Health Risks of Categories of Tobacco Products***, called for the use of smokeless tobacco reference products (STRP) in research to help characterize the health risks associated with smokeless tobacco product (STP) use. The report discussed the current set of STRP: the 2S1 Loose-leaf Chewing Tobacco, the 1S2 Dry Snuff, and the 2S3 Moist Snuff, including approximate composition and some routine analytical data. The 1S2 was made in 1986, and 2S1 and 2S3 were 1998 remakes of the 1986-produced 1S1 and 1S3. While much is known about many cigarette blends and additives, there is little public information on detailed chemistries of the STRP, commercial STP, and the differences among the older and newer versions of the STRP. Furthermore, it is not known if the analytes reported for STRP are responsible for the health risks associated with STP use. Consequently, we characterized all five STRP with two GC-MS scan techniques: 1) the Direct Silylation Scan (*in situ* silylation of tobacco before analysis), which provides identifications and semi-quantitative data on acids, humectants, sugars, and certain other compounds (Moldoveanu et al., 46th TCRC, Paper #28); and 2) the HFP Scan (*in situ* extraction of tobacco with hexafluoroisopropanol before analysis), which allows the analysis of the semivolatile compounds ranging, from low molecular-weight ketones to neophytadiene and some sterols (Dong *et al*., 47th TCRC, Paper #16). Both GC-MS techniques were performed on an Agilent 6890 GC coupled with an Agilent 5972 MS. A DB-5MS capillary GC column (25 m X 0.25 µm film thickness and 0.25 mm ID) was used. In general, the total ion chromatograms and mass spectra were reflective of published data on the STRP and expected tobacco chemistry. However, there were unexpected compounds found and they may have originated during storage.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 11

Study on the enhancement of mass transfer in convective drying process of cut tobacco.

The cylinder drier is widely used in the tobacco primary process. It combines the convective heat from the hot air inside the cylinder with the conductive heat from the cylinder wall to dry cut tobacco. Most of the former researches have focused on the hot air temperature. In this study, the enhancement of mass transfer in convective drying process of cut tobacco (temperature and velocity of hot air and temperature of cylinder wall) was investigated. The cylinder drier was simulated by a fixed bed drier in the laboratory, in which the convective heat from hot air and the conduction heat from thin wall were provided. Three kinds of cut tobacco (A: Burley from China; B and C: flue-cured tobacco from China and Brazil respectively) were chosen as experimental materials. The ranges of hot air temperature, hot air velocity and thin wall temperature were chosen as 60~100°C, 0.37~0.93 m/s and 50~90°C respectively. The results shows that: 1) A mathematical model which characterizes the enhancement of mass transfer in cut tobacco drying process was set up based on Fick's Second Law. The effects of hot air temperature, velocity and thin wall temperature on mass transfer of cut tobacco drying process can be expressed by the calculated effective diffusion coefficient (De) using this mathematical model. 2) The Arrhenius Equation can be used to describe the effect of hot air temperature on De. According to the Arrhenius Equation, the apparent activation energies (Ea) are 8.31, 12.11 and 21.13 kJ/mol for samples A, B and C respectively. 3) The effects of thin wall temperature and hot air velocity on De can be expressed by using the dimensionless analysis method based on Fick's Second Law. The calculated enhancement factors of thin wall temperature are 10.08, 12.21, 10.82 for samples A, B and C respectively. The calculated enhancement factors of hot air velocity are 0.65, 0.42, 0.81 for samples A, B and C respectively.

Key words: cut tobacco, drying process, enhancement of mass transfer, effective diffusion coefficient

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 24

Novo435® lipase-catalyzed biosynthesis of glucose esters.

In order to develop novel flavour enhancers for tobacco, a series of biosynthesis experimentations were carried out by using 6 common organic acids (iso-pentanoic acid, n-hexanoic acid, n-octanoic acid, lauric acid, propanedioic acid and malic acid) and glucose as raw materials. Six glucose fatty esters were synthesized separately in one reaction step and at the presence of the catalyst Novo435® lipase in tert-butanol, glucose and fatty acid were dissolved in tert-butanol at a mole ratio of 1:1 in a flask. Then Novo435® lipase was added and the mixture obtained was shaken at 45 °C for 24 hours prior to vacuum distillation and purification. All of the synthesis products were white powders. These 6 glucose-ester products were identified qualitatively by ESI-MS (Electron Spray Ionisation) and HPLC-ESI-MS. The analysis results showed that the products were dominated by monoesters, with only a small part of diesters. In addition, the pyrolysis products of the glucose fatty esters were studied by Pyrol/GC/MS, most of the identified degradation components were volatile aromatic compounds of low molecular weight. The cigarettes spiked with the glucose fatty esters were evaluated by an expert panel, it was found that the glucose fatty acid esters could enhance smoke flavor, reduce offensive taste and improve smoothness and mildness.

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Simulating the lip-release effect of tipping paper and its influence on the end use application of cigarette products.

A large variety of commercial tipping papers has been investigated by using various experimental techniques yielding an empirical mathematical model, which describes and simulates the absorptivity of coated or printed tipping paper for aqueous liquids in order to reveal its lip-release properties. The proposed theoretical approach makes exclusively use of macroscopic physical and chemical base paper specifications and rotogravure printing process parameters and provides a simplified image of the water transport mechanisms through the tipping paper without considering the details of the microscopic fibrous paper structure. The potential advantages of the outlined absorption model are its simple and rapid application without any huge experimental efforts and the high predictive quality for the expected theoretical lip-release efficiency. However, the physiological perception of the lip-release properties is beyond doubt subjective and depends strongly on the individual smoking habits of cigarette smokers. By taking into account the survey performed with a professional smoker panel on the one hand and evaluating field reports from regular cigarette smokers on the other hand the correlation between the calculated lip-release efficiency and the real sensation on the human lips will be outlined. Consequently, the findings open the potential to predict and control the quality of the generated lip-release properties during tipping paper production and to customize the tipping paper overprint for specific target groups of cigarette consumers.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 18

New insights into the mainstream gas-phase smoke formation process.

Understanding the mainstream smoke formation process is an important step in the development of cigarettes with potentially reduced yields of toxicants. In this respect, on-line smoke detection with fast scanning mass spectrometry is an effective means of observing smoke formation processes occurring in a burning cigarette. This technique provides mechanistic insights which are otherwise inaccessible through use of conventional routine smoke analysis methods.

In this work, a novel sampling mechanism was designed which directly connected a fast mass spectrometer to the mouth end of a cigarette filter; this design enabled real-time sampling and analysis of volatile gases and other smoke toxicants under conditions close to those experienced in human smoking. The formation profiles of individual compounds during puffing and within inter-puff periods have been monitored using cigarettes of different tar yields and constructions, such as filters containing activated carbon. The results revealed that the inter-puff smouldering burn period generates significant amounts of gas-phase smoke analytes, which become either sidestream smoke or are trapped within the cigarette rod. The trapped smoke constituents contribute to the subsequent mainstream smoke to which the smoker is exposed upon puffing. The extent of this contribution depends on the cigarette design (1 mg, 5 mg and 10 mg tar levels), smoking regimes applied, properties of the analytes (combustion gases like nitrogen oxide and carbon dioxide, volatile gases like acrolein and butadiene, or semi-volatile gases like acetaldehyde and acetone) and their interaction with the remaining tobacco rod and any other filtration media (cellulose acetate fibre or activated carbon) present.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 12

Application of FT-NIR in rapid and simultaneous determination of physical and chemical indices of tobacco flavor and fragrance.

Flavor and fragrance play a key role in cigarettes. Therefore, it is very important to control the qualities of these additives. The current method of quality control is to determine physical and chemical indices of tobacco flavor and fragrance, but it is complicated to measure so many indices one by one. The objective of this study was to use FT-NIR for rapid and simultaneous determination of four physical and chemical indices including refraction index, pH, relative density and total volatile constituents. Spectra of 18 different kinds of samples were collected to develop calibration models using partial least squares (PLS). The effect of spectra pre-treatment on models had been studied, and it was indicated that second-derivative transformation of spectra could improve the models' performance. To avoid low signal-to-noise ratio, only wavelengths in the region of 6200-5500cm-1 were employed for the calculations. The correlation coefficients of four models were 0.99926, 0.99106, 0.99990 and 0.99527 with the RMSEC values of 0.000844, 0.127, 0.00183 and 2.01, respectively. At the same time, the reliability and repeatability of this method were evaluated. Result showed that this method was applicable for four indices of different flavor and fragrance, and the RMSEP values were 0.00182, 0.374, 0.00393 and 3.04, respectively. Besides, RSD values of four indices of some random samples were all very low. In conclusion, tobacco flavor and fragrance indices could be determined rapidly and simultaneously without any damage by FT-NIR, which would achieve on-line determination and real-time control of products.

Key words: FT-NIR, tobacco flavour and fragrance, refraction index, pH, relative density, total volatile constituents

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 38

Using diffusion measurements to predict the ignition propensity of cigarettes.

The dominant technology used on cigarette paper to help reduce the ignition propensity of cigarettes is to apply bands of a coating material to the cigarette paper.

The role of these bands is to reduce the burn intensity of the cigarette as the combustion cone reaches the bands, helping the cigarette to self extinguish. For conventional non-banded cigarette paper, the main parameter used to control the burn rate of cigarettes is air permeability, measured in CORESTA units.

The goal of this presentation is to demonstrate that oxygen diffusion is an effective alternative to air permeability for predicting the self extinguishing characteristics of banded cigarette papers.

In this paper, we will present studies on the influence of these parameters on ASTM results, showing that diffusivity is a viable and effective alternative to air permeability.

Other studies will also show that at same band permeability, paper having different base air permeability can give significantly different results in the ASTM test.

Further, the relationship between diffusivity and ASTM results has proven to be more consistent, whatever the permeability of the base paper.

From these studies we conclude oxygen diffusion can be an effective, and potentially more consistent, alternative to air permeability testing for predicting the ASTM self extinguishing characteristics of banded cigarette papers.

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Characterization of water distribution in cut tobacco using a low-field 1H NMR technique.

Cut tobacco was studied by low-field ^{1}H NMR at various water contents and temperatures. The spin-spin relaxation times (T_2) were measured with Carr-Purcell-Meiboom-Gill (CPMG) sequences. Three populations were observed in cut tobacco, namely, population T21, with relaxation times in the range of 0.1-1ms; population T22, with relaxation times in the range of 1-10ms; and population T23, with relaxation times in the range of 10-100ms. The population T21 was referred to free water which was significantly affected by the moisture content in cut tobacco. An increase in the relaxation time of this population was observed when water content was increased. The intensity of T21 evidently increased with the increase of water content from 8% to 18% w/w. The population T22 was referred to bound water. The intensity of T22 was relatively stable, however, its ratio to total water decreased with the increase of water content in tobacco. The population T23 was an intermediate state of water which was less sensitive to the moisture content in tobacco. In addition, the spin-spin relaxation times (T_2) were also measured at -15.8 °C, -6.8 °C, 0 °C and 32 °C. Results showed that the intensities of T22 and T23 were relatively stable with temperature, as opposed to the population T21 which intensity sharply decreased with the temperature decreased from 32 °C to -15.8 °C.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 17

Cross-sectional study of cigarette smoke exposure in eight countries.

The development of the scientific basis for global tobacco product regulation can be assisted by cigarette smoke exposure data from a wider range of countries since most current data come from North America and Europe. Cigarette smoke exposure can be estimated by the analysis of biomarkers in human body fluids, the measurement of human smoking behaviour followed by machine duplication or the analysis of spent cigarette filters and the calculation of human smoke yields from the filtration efficiency. Filter analysis enables the estimation of the nicotine and tar yields obtained by smokers in their everyday environment.

Leading (by market share) products across the range of ISO tar yields were selected from Australia, Brazil, Canada, Germany, Japan, New Zealand, South Africa and Switzerland. At least fifty smokers were recruited per product to represent the demographics of consumers of the products being assessed. All smokers, ≥21 yrs of age and smoking ≥5 cigarettes per day, were asked to collect ≥15 filters from cigarettes they had smoked, subject to written informed consent being obtained. The collected filters were analysed for nicotine and UV absorbance to enable the smokers' exposure to nicotine and tar (respectively) to be estimated. Smoking history data were also collected.

The overall data set comprises eight countries, 106 products and 5710 smokers, and is based on the analysis of filters from more than 80000 cigarettes smoked by the subjects. Mean±sd estimated nicotine exposure ranged from 0.93±0.34 mg/cigarette (Brazil) to 1.77±0.69 mg/cigarette (South Africa) and from 17.5±11.3 mg/day (Brazil) to 36.9±28.7 mg/day (New Zealand). Some gender differences were noted. Significant correlations were found between estimated nicotine exposure and ISO nicotine yield, and between estimated tar exposure and ISO tar yield ($p<0.001$).

These data confirm the wide variation in smoke exposure between smokers of individual products and between smokers of different products. It is the first time these data have been collected on such a large scale and is believed to be the first smoke exposure data of any description in some of the countries.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 16

Cigarette-to-cigarette variation in smoking intensity over a 24 hour period.

The analysis of smoked cigarette filters has been shown to provide a reliable estimate of smokers' exposure to nicotine and other smoke constituents. Previous studies have used the analysis of a random sub-sample of all smoked cigarette filters collected over a fixed period to estimate a smoker's average per cigarette or daily exposure. However, because smokers' behaviour may vary at different times of the day it is possible that the random sample may not be a true representation of the actual smoke exposure. Consequently a study was undertaken to determine the cigarette to cigarette variation in estimates of smoke exposure over a 24 hour period. 54 Swiss smokers of a 4mg ISO tar product collected smoked cigarette filters after smoking in their everyday environment. A newly developed data-logging filter cutter was used to record when the cigarette filters were collected. The tar and nicotine content of individual mouth-end sections of the smoked filters were used to estimate the tar and nicotine yields in-use. The majority of the cigarettes analysed were collected by subjects between the hours of 7am and midnight. Subjects returned between 8-40 filter tips and on a tip to tip basis, the estimated yields in-use ranged from 1.4-29.4mg.cig^{-1} for tar and 0.19-2.98mg.cig^{-1} for nicotine. The mean±SD yields in-use for in this study were 13.0±3.4mg.cig^{-1} for tar and 1.35±0.34mg.cig^{-1} for nicotine. Despite subject to subject variation in yield in-use values, there were no discernable trends during the 24 hour period. In addition, there did not appear to be a correlation between the estimates of yield in-use and the recorded average daily cigarette consumptions.

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Simultaneous determination of ethylene oxide, propylene oxide, vinyl chloride, 1,3-butadiene, benzene, toluene, acrylonitrile, acetamide and isoprene in mainstream smoke.

In this paper, a modification of the Health Canada method for volatile compounds in mainstream smoke in one analytical run, is described. The goal behind developing this method was to extend the number of target compounds of potential health risk that could be analyzed from one sample. Existing methods for the determination of ethylene oxide in mainstream smoke either employ Tedlar® bags for collection of the volatiles, therefore limiting the compounds which can be collected, or chemical absorbants which are specific to ethylene oxide alone. Compared to methods based on the collection of gaseous samples, this method is easier to calibrate, more amenable to automation, and has the potential to be extended to less volatile compounds.

In this new method, mainstream smoke is passed through a 92 mm pad followed by dry ice cooled impingers containing methanol. Volatile compounds are determined by a combination of ion-trap and selective ion monitoring GC-MS on both a pad extract and the impinger solution. Typical analytical run times were 25 minutes.

For control cigarettes (Kentucky Reference 3R4F) smoked under ISO (35/60/2) conditions, the concentration of ethylene oxide and propylene oxide determined (n=18) using this method was 20 µg/cig. and 460 ng/cig. respectively, and for intense smoking conditions (55/30/2, vents blocked), 53.4 µg/cig. and 1162 ng/cig. respectively. These results are comparable to those obtained using the Tedlar® bag method for other control cigarettes. Ethylene oxide can be determined with a limit of detection (LOD) of 0.4 µg/cig., and propylene oxide 15 ng/cig. Relative standard deviations for measurements of the epoxides under both ISO and intense conditions were between 10 and 15%. The other analytes were determined within 95-108% of the expected values, with relative standard deviations less than 10% and LOD's between 0.1 and 2.5 µg/cig.

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Superslim carbon filters - Effect of carbon weight and smoking regimes.

Super slim cigarettes are increasing in popularity globally and are probably at the moment showing the most rapid growth of any market segment. These products are generally defined as less than 17 mm circumference and typically use longer filters and much lower tobacco weights. The lower circumference means that smoke velocities passing through the filter are much higher than in standard products. Typically the smoke velocities in super slim cigarettes are more than twice that of standard products. Smoke velocity is an important parameter governing the performance of filters in terms of both particulate retention and vapour adsorption. The smoke velocities for intense smoking of super slim cigarettes are much higher than any experienced in standard products. More super slim products are using special filters including those containing carbon, so how does the carbon perform at such high smoke velocities?

Experimental findings will be presented for the measurements of yields and retentions of selected vapour phase compounds measured by gas chromatography for a range of carbon weights and activities tested using two smoking regimes (ISO and Canadian intense). Comparisons will be made with previous work carried out with standard circumference products.

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Determination of menthol in mentholated tobacco by headspace GC-MS.

There are various methods for the analysis of menthol in tobacco, which consists of multi-step sample preparation involving refluxing of the samples with a solvent, cooling and subsequently making duplicate injections of the same into the Gas Chromatograph. These methods are very tedious and require more analyst input and analytical time.

The static headspace technique developed is a very simple and rapid method with no tedious sample preparation steps and reduced solvent usage, sample preparation and analysis time.

In a typical analysis, about 0.5 gm of sample is taken into a headspace vial, sealed and allowed to equilibrate at 80 deg C for half hour. The headspace is then injected into the GC-MS. The method has been validated for standard parameters i.e. linearity, limit of detection, limit of quantification, repeatability, reproducibility and recovery. There is an excellent linearity in the concentration range from 0.2 to 1% with a correlation coefficient of 0.999. Recovery studies have been carried out by spiking tobacco with a defined amount of menthol and subsequently analyzing the menthol content. A minimum recovery of 93% is observed and the minimum detection limit of this method is 35 ppm.

Initial studies indicate method applicability to cigarettes with minor modifications.

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Prediction of menthol distribution during storage of mentholated cigarette packs.

During storage of mentholated tobacco products, the menthol is redistributed among the tobacco, filter and paper independently of the application method, and permeates through the wrapping material. Therefore, menthol migrates from the tobacco to the filter or from the filter to the tobacco until the menthol reaches the adsorption equilibrium. In this study, first a mathematical model was developed for predicting the menthol distribution within a pack of cigarettes. The model represents the three physicochemical properties dominating the rate of menthol transfer: the vapor adsorption equilibrium relationship among the tobacco, filter, papers and packing materials, the permeation coefficient of the wrapping film, and the apparent diffusion coefficient through the packed tobaccos and packed filters assuming that the packed components can be treated as a uniform packed bed of components. The validity of the mathematical model was confirmed by comparing the experimental results with ones calculated using these properties, which had been experimentally determined in advance. Finally, the changes in menthol distribution in the pack of mentholated cigarettes during storage were predicted, based on the mathematical model. The results showed that the influences of the parameters on the menthol distribution, i.e. the storage conditions of temperature, initial menthol placement and menthol loading amounts, as well as the various cigarette designs, had been systematically assessed. Therefore, the menthol distribution within a pack of various on-market mentholated products can be estimated once these properties have been measured.

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A novel method to determine ash appearance of cigarettes.

Ash appearance has been a persistent issue in the tobacco industry for many years.

Most notably in the Asian market ash appearance can be an important cigarette benchmark.

In the past there has not been an objective method to determine the ash appearance of a cigarette. The combination of tobacco and cigarette paper influences mainly the ash appearance. However, several other factors have a significant impact on the result of the measurement. These are climate condition, type of light source or the background.

The developed method minimizes the influence of all these factors leading to a semi automated procedure to quantify the ash appearance of a cigarette.

The method consists of an apparatus to burn down cigarettes under constant conditions including a digital camera to take pictures of the ash. Finally the digital pictures are processed with an imaging software to receive a value expressed as percentage dark area in the ash.

The apparatus called “ash appearance box” allows the analysis of 3 cigarettes at once.

Results are given for 26 different cigarette brands. 9 cigarettes of each brand have been analysed. The ash appearance value of the different brands was in the range of 1-10% dark area in the ash. The overall coefficient of variation found was 42,4%. The lowest variation of one cigarette brand was 23,1%, the highest 63,4%. The high variation of the results is obviously caused by differences in the tobacco composition, for instance the amount of heterogeneous tobacco components like stems. It is acceptable to exclude the highest and lowest value of each cigarette sample to normalize the data. In this case the average coefficient of variation found was 31,7%. The error of the method itself is less than 10% (5% digital camera, 5% position of cigarette in the box).

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Evaluation of the effect of phytol on the formation of PAHs in cigarette smoke.

Pyrolysis of phytol has been studied with various purposes, including the potential formation of polycyclic aromatic hydrocarbons (PAHs). When pyrolyzed in a quartz tube at 860 ± 5 °C in a flow of nitrogen (30 mL/min) phytol was reported to generate benzo[a]pyrene at a level of about 3.9 mg/g from the initial material. However, in a flash pyrolysis experiment performed at 900 °C for 10 s the pyrolysis products were found more similar to those of a long chain hydrocarbon that typically generate only very low levels of PAHs. Since phytol is naturally present in tobacco at levels around 100-150 µg/g dry leaf, where it is bound in the form of an ester to form chlorophyll, the compound has been considered a PAHs precursor in cigarette smoke. This study evaluated the formation of PAHs when several levels of phytol were added on 3R4F cigarettes. The resulting phytol levels were up to about 15 times higher than those expected in cigarettes. These cigarettes were smoked under two different smoking conditions, 35 mL puff of 2 s every 60 s (35/60) and intensive 60 mL puff of 2 s every 30 s (60/30). A statistical evaluation of the dependence of total PAHs and the added level of phytol showed that the hypothesis of a zero slope for the dependence line cannot be rejected (with a P = 0.101 for 35/60 smoking and P = 0.626 for 60/30 smoking). Flash pyrolysis of free phytol and of chlorophyll a provided results that indicated that phytol bound in chlorophyll is not likely to generate different PAHs level compared to free phytol. The study showed that phytol is not a significant contributor/precursor to the PAHs formation in cigarette smoke.

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Fate of tobacco ingredients: application of isotope mass spectrometry to study the behaviour of humectants, geranyl acetate and tetramethyl pyrazine during combustion.

The fate of tobacco ingredients during combustion is of major interest and has been discussed in many publications and CORESTA papers. Pyrolysis experiments have been used to identify possible breakdown products and to estimate their potential contribution to Hoffmann Analytes yield. However, reliable predictions are limited since combustion of ingredients applied onto tobacco cannot be simulated by pyrolysis in a straightforward manner. Tracer experiments with radioactive (^{14}C) or stable ^{13}C labelled compounds have been described as an alternative technique to track volatile and non-volatile ingredients and their combustion products in mainstream and sidestream tobacco smoke.

For this study, ^{13}C labelled glycerol, propylene glycol, geranyl acetate, and tetramethyl pyrazine were applied on tobacco. The test cigarettes were smoked and smoke collected using the sidestream fishtail chimney device. For the examination of fate and behaviour of these ingredients, ^{13}C concentrations in CO, CO_2 and volatile hydrocarbons were determined for mainstream and sidestream smoke, the smoked cigarette butt and ash. The $^{12}C/^{13}C$ ratio for the different smoking traps was determined using isotope mass spectrometry and the contribution of tracer labelled ingredient to the natural abundance was estimated. The newly developed experimental set-up for the simultaneous determination of CO and CO_2 and for oxidation of volatile hydrocarbons is described.

It is confirmed that ^{13}C labelled humectants and semi-volatile ingredients significantly contribute to the ^{13}C concentration in CO and CO_2. Experimental recovery rates for ^{13}C ranged from 92 to 103%.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 21

Effect of smoking parameters on the temperature in cigarette filters during smoking.

The filtration efficiency of cigarette smoke depends on filter design. Adsorption of smoke constituents in carbon-containing filters is likely to be influenced by the temperature generated in the filter during smoking. Our work with carbon-filtered cigarettes smoked under more intense conditions than ISO has shown that vapour phase compounds partly desorbed from the carbon filter which was probably due to the high temperatures these filters experienced during both puffing and smouldering.

In this study, the filter temperature was measured for cellulose acetate and carbon filtered cigarettes during smoking using a thermocouple probe inserted into the filter. The probe tip was inserted 5 and 20 mm from the filter end and cigarettes were smoked under the following regimes: ISO (35 mL/60 sec/0 % vent block), Massachusetts (45 mL/30 sec/50 % vent block), WG9 Option B (60 mL/30 sec/50 % vent block), and Canadian Intense (55 mL/30 sec/100 % vent block).

For ISO smoking, temperature rises were only detected for the last two puffs (last 15 % of the cigarette burnt), while much higher filter temperatures were measured when cigarettes were smoked under more intense conditions over a greater percentage of the cigarette burnt, particularly the Canadian intense regime. This significant temperature rise was observed for low tar products in particular when smoked under intense conditions.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 16

Optimized analytical method of hydrogen cyanide in mainstream smoke using continuous flow analyzer.

Hydrogen cyanide (HCN) is present in both the particulate phase and vapour phase of cigarette smoke. It is one of the 44 harmful substances on the Hoffmann list and is known to be a major ciliatoxic agent in cigarette smoke.

Typically the determination of HCN in cigarette smoke has been done through colorimetric and electrochemical techniques, such as UV-spectrophotometry (UV), continuous flow analyzer (CFA), ion chromatography (IC) and capillary GC-ECD. In particular, CFA is commonly used for analysis of hydrogen cyanide in cigarette smoke and the analysis reaction is the pyridine-pyrazolone reaction.

In this study, an optimized analytical method rather than the previous pyridine-pyrazolone reaction method is suggested, using an isonicotinic acid-pyrazolone reaction method. This is a commonly used method for the determination of cyanide in water and air using CFA. The sample collection method is optimized by trapping separately smoke of particulate phase and vapour phase (%RSD ±4). Tripping solution concentration of 0.2 mol L^{-1} (3 hour) is more stable than 0.1 mol L^{-1} (1 hour) after cigarette smoking. The sensitivity of this method is sufficient to permit hydrogen cyanide analysis in mainstream smoke.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 08

Switching from usual brand cigarettes to a tobacco heating cigarette or snus - a multi-center evaluation of biomarkers of exposure and harm.

A randomized, multi-center, 3-group study was conducted in subjects who smoke (n=131) and were switched to a Tobacco Heating (TH) cigarette, Snus (S) or a Tobacco Burning (TB) cigarette (5 mg 'tar' by the Cambridge filter method), with a non-treatment group of never-smokers (NS) (n=32). Clinical confinement, with biomarker evaluation, was conducted in smokers at baseline, 12 and 24 weeks and in NS at baseline only. Samples for 24-h urine and blood were collected and analyzed for tobacco-related biomarkers. Urinary biomarkers included those for total nicotine equivalents (NicEq-T), NNK, benzene, acrolein, crotonaldehyde, 1,3-butadiene, acrylamide, polycyclic aromatic hydrocarbons (PAH), aromatic amines (AA), and urine mutagenicity (UM), among others. Blood biomarkers included carboxyhemoglobin (COHb), 4-aminobiphenyl-Hb adducts (4-ABP-Hb), C-reactive protein (hsCRP), sICAM-1, fibrinogen, homocysteine, platelets, sister chromatid exchange (SCE) in peripheral lymphocytes and circulating endothelial precursor (CEP) cells, among others. Smokers on usual brand (UB) at baseline constituted the intent to treat (ITT) sample. Usage of study product and other tobacco/nicotine forms was tracked daily via telephone diary and compliance was computed. Mean compliance >50% in week 24 defined the per protocol (PP) sample (n=88; with dual use noted particularly in the Snus group). For all urinary biomarkers listed, mean values (mass/24-h) in ITT smokers exceeded ($p<0.05$) those in NS. For listed blood biomarkers, mean values in ITT smokers exceeded ($p<0.05$) those in NS except for hsCRP, fibrinogen, platelets and CEP cells (these are not discussed further). Among matched PP subjects at week 24 (vs. UB baseline), the following significant differences were noted: in urine, TH<UB for NicEq-T, NNK, AA, PAH (4 of 6), acrylamide, butadiene, crotonaldehyde, benzene, UM; and, in blood, for 4-ABP-Hb and sICAM-1. TH>UB only for acrolein in urine. In urine, Snus<UB for NNK, AA, PAH (4 of 6), acrylamide, butadiene, crotonaldehyde, acrolein, benzene, UM and, in blood, for COHb and sICAM-1. Switching from UB cigarettes to TH cigarettes or Snus (even non-exclusively) significantly reduced exposure to several important tobacco toxicants.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 44

Comparison of *in vitro* micronucleus assay among four procedures.

The *in vitro* micronucleus (MN) assay has been used as one of the tools for assessment of the genotoxic potencies of cigarettes in the tobacco industry. It is recognized that the difference in results among laboratories is larger in the MN than in the widely-used Ames assay. The variation in results would be due to several factors, mainly the diversity in procedures and/or the difference of laboratory conditions. However there is little information regarding these aspects.

We tried comparing four procedures in terms of reproducibility and relative activity among cigarettes. Since the comparative study was conducted in the same facility with consistency of environment, the variation factors associated with laboratory conditions were eliminated.

The key factors of the four procedures selected were: Procedure-A (Chinese Hamster Ovary cells, without cytochalasin B (CB)), Procedure-B (V79 cells, with CB), Procedure-C (Chinese hamster lung (CHL/IU) cells, without CB), and Procedure-D (CHL/IU cells, without CB, *in situ*).

The reproducibility was investigated based on three replicates of the experiment using 3R4F, and the relative activity was analyzed based on two replicates of each experiment using Flue-cured, Blend and Burley cigarettes.

For the evaluation of the results, the effective concentration for three times the solvent control value (EC3SC), was used as the MN activity index.

As a result, the reproducibility in EC3SC of 3R4F with a coefficient of variation of about 20% was realized in all procedures with and without S9.

Furthermore, the order of the MN activity of the sample cigarettes was the same (Flue-cured > Blend > Burley) in all procedures with and without S9, although there were slight differences in the ratios between the MN activities of cigarettes among four procedures with S9.

It is suggested that comparable results are obtained under these four procedures when the tests are examined in the same laboratory.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 34

Analysis of four tobacco specific nitrosamines in cigarette smoke by LC-MS/MS: impact of APCI and ESI ionisation on the quantification of different cigarette smoke matrices.

Tobacco Specific Nitrosamines (TSNA) are formed during the ageing, curing and fermentation process in tobacco leaf and are transferred into smoke by vaporisation or formed by pyrosynthesis at very low concentration levels. The determination of TSNA in cigarette smoke is a commonly monitored analytical parameter in tobacco industry. Four of the routinely determined TSNA are N-nitrosonornicotine (NNN), 4-(methylnitrosamino)-1-(3-pyridyl)-1butanone (NNK), N-nitrosoanatabine (NAT), and N-nitrosoanabasine (NAB).

The most widely spread techniques for the quantification of TSNA in cigarette smoke are GC-TEA (ISO draft published) and LC-MS/MS.

The GC-TEA technique comprises the highly nitrogen-specific determination of TSNA in cigarette smoke samples. However, extensive sample cleanup and a concentration step are necessary for the detection at low concentration levels. Therefore, the GC-TEA methods are relatively time consuming.

Due to high selectivity and sensitivity of LC-MS/MS systems, a decreased sample preparation and analysis time are feasible compared to traditional GC-TEA methods. The LC-MS/MS methods use liquid chromatography coupled to a tandem mass spectrometer. For the ionisation, different techniques are applied, e.g. electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI). The type of ionisation is of particular importance, since the influence of cigarette smoke matrices during ionisation is a well-known challenge in LC-MS/MS analysis. In this work, different ionisation methods (ESI and APCI) for LC-MS/MS systems are assessed for the determination of four TSNA (NNN, NAT, NNK, NAB) in smoke of reference cigarettes on different tar levels. Each analyte is quantified by two specific mass transit ions using deuterated standards. The results of the different ionisation techniques are compared and discussed.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 09

Some observations on biomarker study design to assess potentially reduced exposure products.

Two double crossover biomarker studies in Germany and the UK were conducted on two different ISO tar levels with 50 male heavy smokers in each group and 25 non-smoking study subjects for comparison. People smoked their own brand for 6 weeks, switched to a test product over a period of 6 weeks and switched back to their main brand for another 6 weeks. Blood and urine samples for biomarker measurements were taken every 3 weeks to obtain two data points for each period. The experience gained was used to develop a simplified design for a third study to reduce the assessment period to 3 weeks which enabled us to include female smokers and representative groups of smokers without setting limits on the daily consumption or selecting only certain brands. The change in marker levels between subjects smoking their main brand and after switching to a test product with reduced level of smoke constituents was measured.

Observations were also made on the appropriate selection of smoke exposure biomarkers: half-life of markers in the human body; sufficient number of study subjects; changes in daily consumption; differences between gender and the effect of blend styles in two markets.

One of the main results of the two double crossover switching studies was that the marker level did not change between the two visits to the clinical site after 3 and 6 weeks. This was found for all three periods (twice smoking the main brand and once smoking the test product). Hence, we concluded that a 3-week test period would be sufficient to assess differences between products.

Significant differences between test products and commercial brands were measured in all studies for those biomarkers which are related to smoke constituents with different levels in the compared products. In conclusion the chosen study design was appropriate for measuring reduced exposure levels in smokers.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 01

Role of product design and smoking behaviour on mouth level exposure to tar and nicotine among Brazilian and German smokers.

Results from studies to estimate smokers' mouth level exposure or Yield In-Use (YIU) to tar (TIU) and nicotine (NIU) across a number of countries showed that German smokers obtained significantly higher average YIU per cigarette than Brazilian smokers of similar ISO yield cigarettes. Therefore, a study was conducted to investigate the influence of product and smoker differences on YIU per cigarette between Brazilian and German smokers.

Commercial products assessed previously in the German and Brazilian market surveys were selected from the 1 mg, 6 mg and 10 mg ISO tar levels, and a 6 mg product was selected from the Swiss market to act as a cross-market control.

The study was conducted in Brazil and Germany. Three groups of approximately 50 smokers of 1 mg, 6 mg and 10 mg cigarettes in Brazil and Germany were recruited to smoke the study products in their usual ISO tar level. Statistical comparisons were conducted by ISO tar level to investigate the influence of smoker and product differences on YIU per cigarette.

For each of the groups studied the German smokers obtained significantly higher mean NIU per cigarette than the Brazilian smokers for all except the Brazilian 10 mg product and significantly higher mean TIU per cigarette for the German 1 and 10 mg, the Swiss 6 mg and the Brazilian 1 mg product.

In conclusion, both smoker and product differences between the two countries influenced YIU per cigarette. Smoker differences tend to contribute most towards the NIU variation across the range of ISO deliveries and TIU variation for 1mg ISO products. Product differences tend to contribute most towards TIU variation for 6 mg and 10 mg ISO tar products.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 25

The environmental degradation of cellulose acetate filters by multiple mechanisms.

Current emphasis on product sustainability and continued interest in the environmental impact of materials used in consumer products reinforces the need to understand the degradation of cellulose acetate tow used in cigarette filters.

Accelerated laboratory exposure tests and specialized chemical analyses have shown that cellulose acetate biodegrades into non-toxic components by a two step mechanism, which involves naturally occurring micro-organisms. Cellulose acetate filters have also been shown to photo-degrade and to degrade chemically under natural conditions.

In addition to the laboratory tests, procedures for measuring total degradation under natural exposure conditions have been established. These conditions include soil burial, soil surface, and soil-free environments. Results show that in natural environments degradation occurs by a combination of mechanisms, and that the balance of active mechanisms and the ultimate degradation rate varies widely with different environments. Mechanisms which dominate in one environment may not contribute in other environments. For example, in soil-free environments biodegradation is minimal and photo-degradation dominates. However, when soil is present, even in soil-surface environments, photo-degradation is significantly reduced and biodegradation is the dominant mechanism.

One of the factors limiting the rate of degradation is the exposure of individual fibers to the environment. A general approach which accelerates all of the degradation mechanisms is to increase the dispersibility of filter fibers. Filters made with short segments or partial-cut filters have been shown as a potential approach for reducing the visual impact of filters.

Recognition of the interaction of the multiple degradation mechanisms involved in natural environments enables a realistic assessment of the potential benefits of alternative filter designs and materials for reducing environmental impact.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 15

Human smoking intensity before and after introduction of the public place smoking ban in Scotland.

Scotland introduced a public place smoking ban in all wholly or substantially enclosed public places in March 2006. It has been reported that people who smoke outside of their work-place, due to public place smoking bans, smoke cigarettes 'harder' than in social settings. This study investigated whether cigarettes smoked in public places following the ban were smoked more intensely than those smoked before the ban came into force.

Smokers (343 in total) of four leading products participated in 3 consecutive studies: a) immediately preceding the ban, b) 1 month and c) 6 months after the ban. The maximum mouth level exposures to tar and nicotine from cigarettes smoked under normal conditions of use (yield in-use) were determined by filter analysis. Subjects collected at least 20 filters from cigarettes that they smoked at hotels, restaurants and recreational venues over 72 hours spanning a weekend. Filters were then analyzed for tar and nicotine content. Yield in-use was calculated from calibration graphs derived from machine smoking the 4 products over a range of intensities. Yield in-use estimates for individuals across the 3 filter studies were compared using paired t-tests. The subjects also completed a questionnaire at each stage to provide information on the numbers of cigarettes smoked inside and outside the selected locations.

The number of cigarettes smoked indoors after the ban fell dramatically and there was a corresponding rise in smoking incidence in outdoor locations. When the tar and nicotine yields in-use per product were compared across the three studies there was either no change or, for some products, a slight decrease after the ban. Self reported total cigarette consumption over the 72 hour period was unchanged, but a difference between this and reported consumption in the selected locations indicated that a significant number of cigarettes were smoked in locations not investigated in this study.

The public place smoking ban in Scotland was effective in eliminating smoking in enclosed public places. The ban did not appear to change total cigarette consumption and it did not increase smoking intensity.

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Report of the Sub-Group Smokeless Tobacco.

The recently formed Smokeless Tobacco Sub-Group (STS) has met three times since its inception November 2008: the first on 28 January 2009 in Nashville, Tennessee, the second on 14 May 2009 in Madrid, Spain, and the third on 1 October 2009 in Amelia Island, Florida - each with around 33 attendees.

The Scientific Commission charged the STS with meeting the following objectives:

1. To create a report on product definition and definitions of terms to support harmonization of nomenclature
2. To perform collaborative studies on main chemical parameters of smokeless products
3. To develop CORESTA Recommended Methods (CRM's) as agreed by the Scientific Commission
4. To develop a technical report on sample handling and sampling procedures
5. To define and set standards for the manufacture of reference products and storage requirements for long term stability

To that end the STS formed three working groups to address the following topics as the first responsibilities, as adjusted during the second meeting:

1. Working Group on Definitions (WG1)
   - To produce a glossary of terms for smokeless tobacco product categories and associated terms, agreed by the STS Sub-group members, by October, 2009.
2. Working Group on Collaborative Studies (WG2)
   - To develop a protocol, execute the same, and evaluate the data from a collaborative study to measure and compare product pH, water, moisture, nicotine and TSNAs, to be conducted in Q3, 2009. Scope includes sample handling procedures.
3. Working Group on Reference Products (WG3)
   - To recommend the design and specifications for new smokeless reference products, and to produce those products by fall, 2009.

Each working group has been very active, and the goals are being well met, as summarized below.

1. WG1 Definitions: Extensive email communication has resulted in at least three draft documents. Various existing sets of definitions have been collated, including those from ESTOC, IARC, SCENHIR, LSRO, BIS, and suggested STS alternatives discussed. WG1 planned to circulate to all STS members the best summary of definitions in September 2009.
2. WG2 Collaborative studies: Utilizing questionnaires submitted by each of the nine working group members, a collaborative study protocol was drafted by May, and has been executed with 23 labs participating. The goal of this study was to establish how much variation will be extant using current methods, and provide direction in what steps must be taken to develop CRM's for smokeless tobacco. Nine samples were distributed for analysis: snus (loose and pouched), moist snuff (natural & flavoured), chewing tobacco (loose leaf & twist), hard snuff, nasal snuff, and gutkha). From an extensive potential list, WG2 agreed to focus on the following analyses for initial testing: pH, moisture, water, nicotine, & TSNA. Data analysis is expected to be completed in October, 2009. The "sample handling and sampling" objective will be addressed at least partially by WG2, but subsequently to this first study - using both experience from the current study, input from members, and relevant data.
3. WG3 Reference products: Production specifications were agreed upon for four representative reference products (CRP's) - snus, moist snuff, dry snuff, loose leaf. Three manufacturers agreed to cooperate (USSTMC, BAT, Conwood), and production is expected to be completed by October. An extensive list of some 32 analytes has been suggested for measurement in the initial characterization of each CRP, with a much smaller list targeted for annual monitoring. After production is complete, the WG3 will coordinate an initial collaborative analyses of the CRP's, with hopeful completion in Q4/2009. After evaluating two permanent storage & distribution options, WG3 recommended using

the site of storage for the current smokeless reference products (North Carolina State University), and plans are underway to have the new CRP's replace the existing inventory as soon as feasible.

The CSTS plans to meet again in January 2010.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 14

A comparison of consumption behaviour in Swedish users of loose and portion snus.

Snus in Sweden is principally available in two forms – one where the tobacco is loose and the consumer takes a pinch of tobacco from the tin, and one where the tobacco has been sealed in pouches and the consumer typically takes one pouch from the tin at a time. The objective of this paper is to analyse and compare data on consumption behaviours of male users of loose snus to male users of pouched snus. A telephone survey of around 3000 snus users was conducted between March and April of 2007. The male population was relatively evenly distributed between use of loose snus (41.9%) and pouched snus (54.0%). In this study the average daily consumption was considerably higher in loose snus users (mean around 30 g per day) than pouched snus users (around 12 grams per day). In our study sample there were very few loose snus users taking less than 10 grams per day, and a significant portion using 50 grams per day, as compared with pouched snus where 50% were consuming less than 10 g per day and very few subjects consumed over 25 grams per day. Frequency of use and duration for each use was similar for both loose and pouched use, and the key factor governing the increased amount of tobacco used seemed to be the fact that loose snus users take a much larger amount of tobacco for each use than is found in a pouch.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 06

Urinary S-phenylmercapturic acid (SPMA) as a biomarker for exposure to benzene.

Benzene is a Class 1 carcinogen ('carcinogenic to humans') according to the International Agency for Research on Cancer (IARC). It occurs at various workplaces, in combustion exhausts, ambient air and tobacco smoke. The urinary benzene metabolites phenol (at high exposure levels), *trans*,*trans*-muconic acid and S-phenylmercapturic acid (SPMA) have been used as biomarkers of exposure to benzene. Although urinary SPMA represents only about 0.2% of the benzene dose, this biomarker has turned out to be the most suitable for low level exposure to benzene, including tobacco smoking. Recently, it was reported that the unstable pre-mercapturic acid of SPMA (pre-SPMA) occurs in urine in varying amounts and is converted to the stable SPMA under acidic conditions. We characterized urinary pre-SPMA in terms of its chromatographic and mass spectrometric properties as well as the pH-dependent conversion to SPMA. Furthermore, we applied various modifications of an LC-MS/MS method (differing mainly in pre-treatment of samples) to urine samples of non-smokers, smokers and subjects occupationally exposed to benzene. The average ratio of pre-SPMA/SPMA in urine at pH 2 was found to be 1.35 in smokers and occupationally exposed persons, with a relative standard deviation > 50%. No measurable amounts of pre-SPMA were observed in non-smoker urine samples. Complete conversion of pre-SPMA to SPMA occurred at pH < 1.1. We conclude that urine samples should be adjusted to pH < 1 before analysis, in order to completely convert pre-SPMA to SPMA.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. IG 01

Report of the Sub-Group Pest and Sanitation Management in Stored Tobacco.

The Sub-Group Pest and Sanitation Management in Stored Tobacco was set up 1993 with the following objectives:

1. To share information on methods to control pests in stored tobacco.
2. To conduct collaborative studies on pest control and sanitation practices for tobacco in storage.
3. To investigate new technologies and issues related to infestation control methods.

The main focus of the Sub-Group is on the cigarette beetle and the tobacco moth, and work is ongoing to provide the tobacco industry with the knowledge and resources needed to implement the best practices for controlling these two primary tobacco pests.

The Sub-Group currently comprises 17 members from 13 companies including tobacco processors, leaf companies, fumigation services and laboratories. The Sub-Group holds regular meetings that are usually combined with an Infestation Control Conference (ICC) - a workshop open to all parties associated with the tobacco industry.

The Sub-Group established phosphine fumigation parameters for the control of cigarette beetle and tobacco moth and published these guidelines as CORESTA Guide No. 2 in 2004. A revised and updated edition was published in 2009.

Current work focuses on new chemical and non-chemical control tools, pheromone trap options, phosphine fumigation developments and issues and potential alternatives to phosphine.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 43

Effect of new charcoal filter on the *in vitro* pulmonary toxicity induced from cigarette mainstream smoke.

The effect of a new charcoal filter on pulmonary toxicity was investigated using an *in vitro* cell culture system. The human bronchial epithelial cell NCI-H292 was used to measure the acute toxicological response to two mainstream smoke fractions: total particulate matter (TPM) deposited on Cambridge filter pad and gas vapor phase (GVP) prepared by bubbling through a buffer solution. The cytotoxic activity of smoke fraction was determined by neutral red uptake assay. Based on the reports suggesting injurious effects by lung toxicants in humans, we chose four pulmonary toxicity biomarkers including tumour necrosis factor-α (TNF-α), interleukin-8 (IL-8), transforming growth factors-α (TGF-α) and matrix metalloproteinases-1 (MMP-1). Production of biological markers was quantified in the media from control and treated cells by ELISA. For the validation of *in vitro* lung cell model used in this study, Kentucky Reference Cigarette 2R4F was performed. TPM (10-100 μg/ml) and GVP (60-300 μg TPM-equivalent/ml) not only significantly induced cytotoxicity but also enhanced the production of biomarkers in a dose-dependent manner, suggesting that this model is appropriate for the evaluation. In this study, we compared *in vitro* pulmonary toxicity of the new charcoal filter cigarette with existing charcoal filter cigarettes. As a result, pulmonary toxicity parameters from GVP of the new charcoal filter cigarette were almost not shown in the concentration showing dose-dependent increase in general charcoal filter cigarette. Our data indicated that the new charcoal filter could be useful for the reduction of pulmonary toxicity from cigarette smoke.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 02

Investigation of filter temperatures and desorption of volatiles from carbon filters under different smoking regimes.

There is a current regulatory interest in smoke yields obtained under both ISO and more intense smoking regimes and the relative advantages or disadvantages of using each regime.

Smoke temperatures in filters of 1-mg and 13-mg ISO "tar" products were measured when smoking under various smoking regimes. These temperatures were much higher under the Canadian intense regime (55 mL puff volume every 30 seconds for 2 seconds with 100% vent blocking) than under any of the three other regimes where the smoke was cooled with air entering through the filter ventilation holes. These other regimes were the current ISO regime, the Massachusetts regime using a 45 mL puff every 30 seconds for 2 seconds with 50% blocking and a regime recommended in the ISO Working Group 9 using a 60 mL puff every 30 seconds for 2 seconds. High temperatures seemed to be associated with a tendency for desorption of vapour phase from carbon filters as seen in per puff smoke profiles.

In subsequent investigations, cigarettes were smoked under the ISO regime and carbon was removed from the smoked filters and heated at temperatures equivalent to those generated when smoking under the Canadian regime. This confirmed that desorption of volatiles from carbon occurs indeed at these temperatures. The released volatiles were identified using thermal desorption - gas chromatography - mass spectrometry analysis. The relative contribution of desorbed components to the total yield of the same components was estimated.

The work confirmed that the high filter temperatures associated with the Canadian intense smoking regime lead to a significant desorption from carbon of some volatiles leading to an increase of vapour phase yield.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPTPOST 01

Post manufacture automatic track identification of mixed populations of rods from a dual track making machine.

Quality assurance measurements of manufactured cigarette rods can be made by sampling from the mass flow at the exit from a making machine either by "grab sampling" or various forms of autosampling. From the analysis of defects in the rod manufacture, or through SPC trends, adjustments can be made to the making process that ensures consistency of manufacture. However in the new generation of makers, to achieve high speeds, two making tracks are combined and mix the population of rods from both tracks in the mass flow. When data is obtained from a conventional test station on these rods that indicates a defect, or requires a process change, it is not possible to pinpoint the origin of the rod and so make the correct adjustment.

A method has been devised that uses a special optical configuration and utilizes a contact image sensor (CIS) that can determine the track of origin in a twin track maker. The method is reliant on differences in contrast in a line image of the rod and utilizes a discrimination algorithm to deconvolute seam information from a surface plot of time/intensity/location.

Data is presented that shows how not only track information can be determined but also how this method can be used to determine if the rod is "front" or "back". The influence of lighting conditions and cigarette substrate colour is discussed with respect of detection efficiency. The implications for quality control in the making process and pinpointing of corrective actions at the maker level are discussed in the context of other measurement parameters such as rod density profile.

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Comparison of the effectiveness of tape and simple holder based vent blocking devices when used in intensive smoking regimes.

The complete blocking of ventilation features has been mandated in Health Canada standards for a number of years. In contrast some US states mandate blocking of 50% of ventilation holes during smoking and the current ISO standards require no ventilation blocking. However as smoking methods are reviewed it is becoming increasingly likely that the current ISO method will be supplemented by some form of intensive smoking regime which will include vent blocking. However some difficulties arise in the manner of vent block prescribed by the Health Canada method, namely the use of adhesive tape to block holes.

This is a time consuming activity that relies on the skill and dedication of the person taping. A conceptually simpler method that would reduce the human element present in applying tape for vent blocking, would be to devise a holder that occludes the ventilation holes and is equivalent to the taping method.

A simple holder was devised that allowed occluding of the ventilation holes and was suitable for a range of product diameters. This holder was compared against the tape method using 15 different commercially available brands of different styles and constructions. Comparisons were made on the basis of pressure drop of taped and holder based rods and smoking yields.

Statistical equivalence was shown with a 95% confidence limit for paired t tests for pressure drop measurements and two sample t tests for smoked rods.

The R and r implications are discussed with considerations of reducing variability of intensive smoking methods explored.

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Effect of storage conditions on LIP cigarettes and papers.

Lower or reduced ignition propensity cigarettes (LIP or RIP) is a term used to describe modified cigarettes that demonstrate lowered ignition propensity under specific laboratory tests. These cigarettes must meet standard performance criteria described by the test method established by the ASTM E2187-04 standard in which lit cigarettes must self-extinguish under controlled conditions.

One solution for LIP cigarettes in the market places to comply with this legislation is the use of banded LIP papers. These papers have a solution applied in bands that reduces the air permeability/ diffusivity of the paper, so that the cigarettes will only self-extinguish in the test when the burning zone reaches these discrete regions.

Currently there is little understanding of how the ambient storage conditions may modify these papers; especially the banded areas applied to them. Therefore an extended storage trial with both banded LIP papers and cigarettes was carried out in specified control environments. More specifically, this study was conducted in two stages that ran in parallel in order to investigate:

- The effect of temperature and humidity on the performance in the ASTM test of the LIP cigarettes at discrete time intervals.
- The effect of temperature and humidity on the physical properties of the LIP paper bobbins stored for 6 months. Additional cigarettes were manufactured from these papers post-storage to evaluate their performance in the ASTM test.

Two LIP papers from different suppliers and a standard control paper, for comparative purposes, were used for this study. Two different blends, flue-cured Virginia and US style blend, were used to produce the cigarettes.

Detailed results will be presented of the physical properties of the papers and of the performance in the ASTM test of the cigarettes.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 15

Comparison of tobacco extracts: a strategy based on GCxGC-MS analysis and chemometric data processing.

The extraction of tobacco, obtained either by Likens Nickerson or supercritical fluid extraction, generates samples that contain a high number of different compounds. The characterization and the comparison of these tobacco extracts, requires the use of a powerful analytical technique. Thanks to its high peak capacity enabling the separation of several hundreds of compounds in a single run, comprehensive two-dimensional gas chromatography (GCxGC) is now considered as the most efficient technique for the analysis of complex volatile mixtures.

However, taking into account all the information contained in the whole 2D chromatogram for comparison purposes is far from trivial. A simple transposition of traditional data processing based on individual peak integration would be tedious and time consuming, given the large number of peaks often observed. Thus, the data processing is often reduced to a rather subjective visual examination of colour plots to determine which spots are similar and which are different. This is the reason why an approach based on chemometrics is proposed for the global comparison of the GCxGC chromatograms.

The idea is to perform a processing based on picture comparison. Each point of the colour plot is taken as a response and multivariate analysis tools are used to determine to what extent these responses differ or not from one sample to another. Nevertheless, this strategy failed to give satisfactory results because the comparison is blurred by variability of retention times, especially along the second chromatographic dimension. To handle this problem, a preliminary alignment of the chromatograms is carried out. Effectiveness of different time alignment strategies, including Dynamic Time Warping is considered.

The proposed approach was successfully applied to the comparison of the volatile fraction of tobacco extracts to discriminate various types of tobaccos. Moreover the discriminant components obtained from multivariate analysis could also be interpreted from a chemical point of view as markers and identified with Mass Spectrometry data.

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Determination of plasticizer profile in mono acetate filters using the microwave method.

Plasticizer is a vital addition to cellulose acetate tow in filter production to harden the filters. This ensures that they pass cleanly through the cigarette assembly process and maintain their designed filter characteristics during smoking. A microwave-based method to determine the total content of plasticizer in a filter rod has recently been announced.

This presentation will describe the further development of the technique to provide quantitative information about the distribution of plasticizer in a filter using a scanning microwave unit. This provides information about obvious process issues, such as melt hole formation and more generally about the uniformity of the product that is ultimately experienced by the consumer.

Melt holes are caused by a local excess of plasticizer that dissolves the tow, which derives most commonly from poor set-up such that drops of plasticizer fall onto the tow from the hood of the spray unit. There is no visual evidence of this problem in the product at the time of manufacture. We show that the additional plasticizer is likely to be within the normal range of variation, so would not be detected reliably by a whole-rod measurement. The presentation describes how the microwave scan can quantify the presence of a local concentration of plasticizer and its validation using coloured drops of triacetin so that deliberately created 'process faults' could be identified and linked to the formation of melt holes. The technique is shown to be quantitative and sufficiently sensitive to detect plasticizer concentrations well before they cause melt holes. The technique can also determine the plasticizer content of the individual tips in a filter and so identify any non-uniformity of plasticizer application even in a process that is apparently under control. The correlation between microwave measurements and GC analysis of triacetin in the corresponding tips is presented.

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Preparation of hemoglobin immobilized mesoporous hydrogel filter material for selective reduction of hazardous constituents in cigarette smoke.

To reduce hazardous constituents in cigarette smoke, the polyethylene glycol (PEG) grafted Poly methacrylic acid mesoporous hydrogel (PMH) particles were prepared. The particles were further verified by infrared spectra (IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and *in vitro* analysis. The results showed that the particles are hollow spheres with particle size <300 nm in diameter, pore size <100 nm in diameter. The results of cytotoxic test indicated that the PMH was harmless. Then, hemoglobin was immobilized into the pores to obtain hemoglobin immobilized mesoporous hydrogel. The hemoglobin filter effectively reduced total particle matter (TPM), tar, nicotine, CO and HCN in cigarette smoke. Depending on the amount of hemoglobin immobilized in hydrogel, CO decreases by 20.12-58.77%, HCN decreases by 7.96-41.76%, however cigarette's smoking quality is affected a little.

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Determination of citrate, phosphate and acetate in cigarette paper by ion chromatography.

A simple method has been developed to separate and quantify citrate, phosphate and acetate anions in cigarette paper using Ion Chromatography with conductivity detection. Citrate, phosphate and acetate in cigarette paper influence the ash appearance of a burning cigarette and the burning rate of the cigarette paper and therefore the puff number of the cigarette. Citrate, phosphate and acetate react in an acid solution and are measured photometrically according to traditional analysis methods. Compared with the CORESTA Recommended Methods for the determination of these three anions in cigarette paper, the new method is simple and convenient, and has lower limits of determination. The three anions were analyzed simultaneously in the same column, fluoride, formate and propionate did not affect the quantification of acetate. Cigarette papers were extracted with deionised water, ultrasonicated for 30 min, and separated on a IonPac® AS15 anion-exchange column, with the gradient elution of OH- from 2 mM to 50 mM. The LOD of citrate, phosphate and acetate were 0.105 mg/g, 0.153 mg/g, and 0.084 mg/g respectively, the precisions and recoveries of the method were also discussed and found satisfactory. The concentrations of 3 anions in 11 different cigarette papers were measured.

Key words: ion chromatography, citrate, phosphate, acetate, cigarette paper

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 20

Simultaneous determination of nicotine, tar and carbon monoxide in the mainstream smoke of flue-cured tobacco by Fourier transform near infrared spectrometry.

The prediction of these contents plays an important role in the quality control of cigarette manufacturing and the development of new products. A novel method for simultaneous prediction of nicotine, tar and carbon monoxide (CO) in the mainstream smoke was developed based on the Fourier transform near infrared (FT-NIR) diffusing reflectance spectra of tobacco powder. The calibration models for nicotine, tar and CO contents were established by the help of partial least square (PLS) and these values measured by the traditional methods. The coefficients of determination of the obtained models are 0.9678, 0.9115, 0.9312, the root mean square errors of cross validation (RMSECV) are 0.0804, 0.6142, 0.2190, and the predictive ranges are 0.4255~3.000mg, 9.770~21.72mg and 10.67~15.37mg respectively. The method was capable of predicting the contents of nicotine, tar and CO in the mainstream smoke of various flue-cured tobacco samples with a mean relative deviation smaller than 5% and good reproducibility. The advantages of this method are that the sample preparation is very simple and the measurement of NIR is pretty fast. Moreover, this method is safe, economic and environmentally friendly, as it avoids the use of any chemical solvent.

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Comparison of *in vitro* smoke toxicity of novel charcoal filter cigarettes and benchmark cigarettes from the UK market.

The *in vitro* cytotoxicity of test cigarettes with highly effective charcoal filters and leading brands from the UK market was compared. The objective of the study was to assess the differences of smoke toxicity of test cigarettes vs marketed cigarettes of similar ISO tar yields. For this purpose, test cigarettes with ISO tar yields of 10, 6 and 3 mg were manufactured and compared with two leading UK brands of similar tar yields.

Smoke was generated according to the ISO Standard (35 mL/60 sec/2 sec, no vent blocking) and the Canadian Intense regime (CINT, 55/30/2, 100% vent blocking), respectively.

The human liver cell line Hep-G2, cultured in serum free medium, was used for bio testing. Human hepatocytes may be regarded as the most suitable *in vitro* model for biotransformation in human liver and are of great importance for toxicological and pharmaceutical studies. Hep-G2 cells are easy to handle and provide, with some limitations, a reproducible human system.

Cells were exposed to fresh whole smoke aerosol in the Bt020 exposure apparatus and toxicity determined by Neutral Red Uptake (NRU). Toxicity of smoke condensates dissolved in DMSO, fresh whole smoke and vapour phase extracted in culture medium was assessed by NRU and the MTS assay.

These methods offer opportunities to describe important aspects of cigarette smoke toxicity. As regards the smoker, characterisation of fresh whole smoke is most relevant. Gaining additional knowledge on smoke condensate and vapour phase toxicity might help to improve our understanding of whole smoke toxicity and its changes. In particular, characterising charcoal filters and estimating their efficiency regarding vapour phase and ultimately whole smoke toxicity, necessitates a tiered approach.

Our data demonstrate that, under both ISO and CINT smoking conditions, the vapour phase of charcoal filtered test cigarettes was significantly less toxic compared to leading brands with similar tar yields from the UK market. In most cases, the positive influence of a less toxic vapour phase was readily identifiable in experiments with extracted whole smoke. All tests with cells directly exposed to fresh whole smoke (Bt20) confirmed this positive effect of charcoal filters.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 45

Tobacco relative risk continuum: the role of cadmium in tobacco-related chronic disease risk.

Cadmium (Cd) concentrations in tobacco products and cigarette mainstream smoke (MSS) are of concern in the tobacco industry and some regulatory organizations, although whether or not Cd has an etiological role in tobacco-related disease is unknown. In this study, we evaluated the association between tobacco-related disease and Cd exposure at levels observed in tobacco users through an analysis of epidemiological data, biomonitoring data, and probabilistic risk assessment (PRA). Data from a biomonitoring study of the U.S. population suggests blood Cd levels are higher in cigarette smokers than in smokeless tobacco (SLT) (moist snuff, loose leaf) users, with levels in SLT users being not significantly different than in non-tobacco users. A PRA of SLT Cd concentration and MSS Cd yield data show that average noncancer risk estimates fall below U.S. regulatory risk guidelines for SLT users, but not for smokers. Similarly, comparison of urinary Cd values with a Biomonitoring Equivalent (BEq) based on proteinuria—a low-dose effect of Cd exposure—suggests that <10% of smokers and <5% of SLT users exceeded the BEq value. Available evidence suggests that Cd is not carcinogenic via the oral route, but inhalation exposure to Cd is associated with lung cancer. The calculated mean lung cancer risk estimate for MSS Cd inhalation exposure was 2.5E-4, lower than risk estimates reported for Cd levels in occupational exposure. These results suggest that Cd, at levels currently measured in MSS and SLT, would not be expected to play a significant, independent role in tobacco-related diseases observed at higher exposure levels (e.g., cardiovascular disease).

Together with the biomonitoring and epidemiological analyses, these PRA results for Cd are consistent with epidemiological observations that some forms of SLT may present lower chronic disease risk than cigarette smoking.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 37

Influence of low ignition propensity (LIP) cigarette paper on ignition strength and combustion coal temperature of cigarette.

The ignition behaviour of 6 cigarette samples wrapped in papers of different ignition propensities (2 ordinary cigarette papers, 4 LIP cigarette papers) was studied. The influence of burning additive and band width/space on ignition behaviour of cigarette was studied on the basis of the mean surface temperature of combustion coal while smouldering and CO content in mainstream cigarette smoke. The results showed that 1) especially the content of burning additive in and the band width/space on the LIP cigarette paper play an important role in the ignition strength of cigarette; 2) the ignition strength of LIP cigarette correlates to the mean surface temperature of combustion coal. 3) the content of burning additive has an influence on the mean surface temperature of combustion coal and CO yield, while the influence of band width/space is not observed.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 05

Selective solid-phase extraction of nicotine and cotinine from human urine using a uniform molecularly imprinted microsphere.

Nicotine and cotinine have been widely used as biological markers for the assessment of direct or passive exposure to tobacco or tobacco smoke. A method using a nicotine molecularly imprinted polymer microsphere (MIP) as the selective sorbent for solid-phase extraction (SPE) has been developed. It is applied to the assay of nicotine and cotinine level from human urine with high-performance liquid chromatography (HPLC).

The nicotine MIP microsphere has been prepared by a precipitation polymerization method using methacrylic acid as a functional monomer and divinylbenze as a cross-linker in mixture of toluene and acetonitrile. The imprinted polymers were monodispersed particles which exhibited a regular spherical shape of about 3.5 μm in diameter. The selectivity factor was 9.8 for nicotine and 6.3 for cotinine on the MIP.

The MIP microsphere was evaluated for use as a SPE sorbents, in tests with aqueous standards, by comparing recovery data obtained using the imprinted form of the polymer and a non-imprinted form (NIP). The optimal extraction conditions were obtained when 2.0 mL ammonium acetate-ammonia buffer (pH 9.1) and 1.0 mL acetonitrile was used in the washing step, respectively, and the target analytes were eluted with 3.0 mL acetonitrile-H2O-trifluoroacetic (95:2.5:2.5 v/v). Extraction recoveries resulted in more than 98% for nicotine and 82% for cotinine, respectively.

This MIP-SPE-HPLC method provided inherent selectivity and sensitive response to both nicotine and cotinine with detection limit of 0.02 μg/mL and the limit of quantification was 0.05 μg/mL. Calibration curves of nicotine and cotinine showed good linearity in the range of 0.05–5.0 μg/ml (r = 0.995) and 0.05–4.0 μg/ml (r = 0.991), respectively. The intra-day precision (R.S.D.) of both ingredients was less than 6.5%.

This investigation provided a reliable method for determination of nicotine and cotinine in human urine for the evaluation of the exposure to tobacco smoke.

Key words: molecularly imprinted microsphere, solid-phase extraction, human urine, nicotine and cotinine

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The mesoporous silica MCM-41 *in situ* coated with carbon for the adsorption and catalysis of volatile nitrosamines.

Synthesis of a new material to reduce the level of nitrosamines in cigarette smoke is important to reduce smoker exposure. Accordingly, a novel composite was obtained by using the template micelle as the carbon precursor to form a composite with a layer of carbon *in situ* coated on the pore wall of the mesoporous silica MCM-41, which will not only reduce the cost, but also increase the adsorption ability. The template micelle used in the synthesis of MCM-41 was the hydrocarbon that could be utilized as a kind of carbon precursor to prepare the carbon containing mesoporous silica similar to the activated carbon with a lot of porous structure. Introducing the carbon can create a suitable curvature or defects in channels of MCM-41, which were beneficial to accommodate the incorporated active components and to form high active site to capture nitrosamines. To examine the influence of carbonization temperature on the performance of the resulting composite, the instantaneous adsorption, temperature programmed surface reaction (TPSR) methods were employed and the results proved the promotion of carbon modification on the adsorption and catalysis of *N*-nitrosopyrrolidine (NPYR) by the mesoporous silica. Compared with MCM-41, the carbon modified MCM-41 prepared in the range of 773 - 973 K possessed a higher adsorption ability of volatile nitrosamines NPYR in gaseous phase. Especially the sample made at 773 K adsorbed 7 times more NPYR than parent MCM-41 when the total amount of NPYR injection amount reached 1 mmol g^{-1}.

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Influence of potassium on the formation of benzo[a]pyrene in tobacco pyrolysis.

It is known that potassium, which is the most abundant alkali metal in tobacco leaves, affects the thermal degradation of biomass and cigarette combustion. However, there is little information on the relationship between potassium and the formation of benzo[a]pyrene (B[a]P) from tobacco. In this study, tobacco samples with various potassium contents were pyrolyzed using an infrared image furnace to evaluate their B[a]P yields, and their pyrolysis behaviours were investigated by thermogravimetric analysis (TGA). Both pyrolysis studies were carried out under inert conditions.

Potassium-extracted samples were prepared by washing tobacco samples with water, and potassium-added samples were prepared by adding potassium lactate, potassium carbonate (K_2CO_3) and potassium chloride (KCl) to individual tobacco samples.

It was found that the removal of potassium by water extraction increased the yield of B[a]P significantly. However, the influence of potassium addition on the yield of B[a]P was different according to the types of salts and tobacco. The addition of potassium lactate or K_2CO_3 to flue-cured tobacco decreased the yield of B[a]P, while the KCl addition increased it. The addition of potassium lactate to Burley tobacco did not decrease the yield of B[a]P.

As the results of the TGA, the addition of potassium lactate or K_2CO_3 to flue-cured tobacco lowered the temperature at which cell wall components such as cellulose and lignin decomposed. On the other hand, no significant change in temperature was observed in the case of the KCl addition to flue-cured tobacco and for the addition of potassium lactate to Burley tobacco.

These results indicate that the modification of the pyrolysis process of cell wall components by potassium influences the formation of B[a]P and the influence of potassium depends on the form of potassium that is present.

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CORESTA Meeting Smoke Sci.-Prod. Techno Groups, Aix-en-Provence, 2009, abstr. SSPT 07

Simultaneous determination of mercapturic acids derived from benzene, 1,3-butadiene, acrolein and crotonaldehyde in human urine.

A method based on liquid chromatography tandem mass spectrometry (LC-MS/MS) was developed for the simultaneous determination of the mercapturic acids derived from Benzene, 1,3-butadiene, acrolein and crotonaldehyde in human urine. The urine samples were cleaned up by an Isolute ® ENV+ solid phase extraction column from Biotage Co. and separated by a C18 reversed-phase column, and then detected by tandem mass spectrometry in the mode of multiple reaction monitoring under electrospray ionization, using isotope-labeled analogs as internal standards. The analytes were S-phenylmercapturic acid (S-PMA), hydroxyl-butyl mercapturic acid (including monohydroxybutenyl-mercapturic acids MHBMA and dihydroxy-butyl-mercapturic acid DHBMA), 3-hydroxy-propyl mercapturic acid (3-HPMA) and 3-hydroxy-1-methylpropyl mercapturic acid (3-HMPMA). These calibration curves all showed good linearity. The detection limits of the developed method ranged from 0.8 to 4.2 ng/ml, recoveries were between 97.17% and 112.49% and relative standard deviations for six separated determinations were between 1.02% and 9.03%. With this method, the mercapturic acids in the urine samples of smokers and non-smokers were determined and analyzed.

Key words: HPLC-MS/MS, mercapturic acids, benzene, 1, 3-butadiene, acrolein, crotonaldehyde

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On-line detection of tobacco smoke constituent by EBEL photo ionisation mass spectrometry: Applications and determination of the photo ionisation cross-sections of relevant compounds.

In the last years a single photo ionisation time-of-flight mass spectrometry (SPI-TOFMS) technology was developed for on-line monitoring of tobacco smoke constituents. One of the main advantages of the SPI-TOFMS approach is the possibility to investigate dynamic processes during the smoking process. For example, different smoking regimes were investigated (mainstream and sidestream smoke), the pyrolysis behaviour of different tobacco sorts were studied and exhaled smoke/breath was monitored. A prototype on-line tobacco smoke profiler has been developed. This prototype is operated with an improved ***E***lectron ***B***eam pumped rare gas ***E***xcimer ***L***ight source, EBEL. In this work some on-line cigarette smoke monitoring applications of the prototype are shown. Furthermore, results on the determination of SPI cross sections of tobacco smoke constituent are given. For the latter measurements, a gas chromatograph was coupled to a SPI-TOFMS device.

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