Determination of Mainstream and Sidestream Cigarette Smoke Components for Cigarettes of Different Tobacco Types and a Set of Reference Cigarettes

by

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SUMMARY

The yield of selected components in the mainstream and sidestream smoke for cigarettes of different tobacco types and a set of Kentucky Reference cigarettes have been measured. The BAT "fishtail" chimney apparatus was used in conjunction with standard FTC Cambridge pad collection apparatus for the simultaneous collection of both sidestream (SS) and mainstream (MS) cigarette smoke, respectively. Comparison of MS FTC yields and MS yields from the BAT MS/SS smoke collection device showed that the smoke yields for the products of this study were similar for the two methods. Sidestream to mainstream smoke ratios (SS/MS) for TPM, nicotine, H₂O, "tar", CO and CO₂ were similar to those reported in the literature, despite the variety of collection devices employed in literature reports. The total nicotine accountabilities for the single tobacco cigarettes and the set of Reference cigarettes of this study were relatively constant (~ 53 %). Enantiomeric separation of the alkaloids in the different smoke streams was accomplished by chiral gas chromatography-mass selective detection. The levels and the enantiomeric ratios of nicotine and nornicotine varied in the smoke streams of the different cigarettes. The level and enantiomeric ratios of anabasine and anatabine in sidestream smoke

were below detection limits of the method employed. The enantiomeric ratios of these secondary alkaloids could not be calculated. The fraction of *d*-nicotine transferred to sidestream smoke did not change significantly when compared to that yielded in mainstream smoke even though the temperatures experienced during the sidestream smoke formation process are quite different (lower) from those occurring in the mainstream smoke formation process. Relatively low concentrations of the secondary alkaloids provided only a preliminary evaluation of their enantiomeric distribution in cigarette smoke. [Beitr. Tabakforsch. Int. 18 (1998) 95–113]

ZUSAMMENFASSUNG

Der Gehalt bestimmter Substanzen im Hauptstromrauch und Nebenstromrauch von Zigaretten unterschiedlicher Tabaksorten und einer Reihe verschiedener Kentucky-Referenz-Zigaretten wurde bestimmt. Der BAT 'fishtail'-Kamin wurde in Kombination mit der FTC Cambridgefiltermethode angewendet, um gleichzeitig sowohl Nebenstromrauch (NSR) als auch Hauptstromrauch (HSR) der Zigarette aufzufangen. Der Vergleich der Rauchausbeuten im HSR nach FTC-Standardrauchanalyse mit den durch die BAT HSR/NSR-Auffangvorrichtung erhaltenen HSR-Aus-

beuten hat gezeigt, dass das Vorkommen der in dieser Studie untersuchten Substanzen bei beiden Nachweismethoden gleich war. Das Nebenstromrauch zu Hauptstromrauch Verhältnis (NSR/HSR) von Rohkondensat (TPM), Nikotin, H₂O, nikotinfreies Trockenkondensat, CO und CO₂ stimmte mit den in der Literatur angegebenen Werten überein, trotz der in der Literatur beschriebenen Vielzahl unterschiedlicher Sammelvorrichtungen. Der Gesamtgehalt an Nikotin in Zigaretten, die aus einer Tabaksorte hergestellt waren, und in den verschiedenen in dieser Studie untersuchten Referenz-Zigaretten war relativ konstant (~53 %). Die Auftrennung der Enantiomere der Alkaloide in die verschiedenen Rauchströme erfolgte mittels chiraler GC-MS. Das Vorkommen und das Verhältnis der Enantiomere von Nikotin und Nornikotin war in den Rauchströmen der verschiedenen Zigaretten unterschiedlich. Das Vorkommen und das Verhältnis der Enantiomere von Anabasin und Anatabin im Nebenstromrauch war unterhalb der Nachweisgrenze der verwendeten Methode. Das Verhältnis der Enantiomere dieser sekundären Alkaloide konnte nicht berechnet werden. Der Anteil des *d*-Nikotins, der in den Nebenstromrauch überging, war nicht signifikant verschieden von dem Anteil des *d*-Nikotins im Hauptstromrauch, obwohl die Temperaturen, die bei der Entstehung von Nebenstromrauch auftreten, deutlich von den Temperaturen bei der Entstehung von Hauptstromrauch abweichen (sie sind niedriger). Die relativ niedrigen Konzentrationen von sekundären Alkaloiden ermöglichten lediglich eine vorläufige Abschätzung der Verteilung ihrer Enantiomere im Zigarettenrauch. [Beitr. Tabakforsch. Int. 18 (1998) 95–113]

RESUME

Le rendement en composants sélectionnés du courant principal et du courant secondaire de la fumée de cigarettes de différents types de tabacs a été déterminé. A l'aide de la cheminée en queue de poisson de BAT combiné avec des tampons de filtre Cambridge de standard FTC la fumée du courant principal et du courant secondaire de cigarettes pouvaient être piégées simultanément. La comparaison des rendements du courant principal obtenus au moyen de la méthode FTC standard aux résultats correspondants obtenus à l'aide de la méthode BAT a démontré que les rendements en composants sélectionnés de cet étude étaient pareils pour les deux méthodes. Le rapport du courant principal au courant secondaire quant au rendements en TPM, nicotine, H₂O, goudron, CO et CO₂ correspondait aux valeurs calculés dans la littérature malgré les différents dispositifs de piégeage décrits dans la littérature. Le

taux total en nicotine dans les cigarettes constituées d'un seul type de tabac et dans les cigarettes de référence de cette étude étaient relativement constants (~53 %). Les énantiomères des alcaloïdes présents dans les différents courants de fumée étaient séparés au moyen de GCMS. Le rendement en nicotine et nornicotine et leur taux respectif d'énantiomères dans la fumée de cigarettes variaient en fonction du type de cigarettes. Le rendement en anabasin et anatabin et leur taux respectif d'énantiomères dans le courant secondaire était au-dessous de la limite de détection de la méthode appliquée. Le taux des énantiomères de ces alcaloïdes secondaires ne pouvait pas être calculé. La fraction en *d*-nicotine transférée dans le courant secondaire ne changeait pas significativement comparée à la teneur en *d*-nicotine présente dans le courant principal, malgré les températures assez différentes (inférieures) qui existent pendant la formation du courant secondaire comparé au températures pendant la formation du courant principal. La teneur relativement faible en alcaloïdes secondaire permettait seulement une évaluation préalable de la distribution des énantiomères dans la fumée de cigarettes. [Beitr. Tabakforsch. Int. 18 (1998) 95–113]

INTRODUCTION

In 1965, LIPP (35) was the first to describe the concepts and components of mainstream and sidestream cigarette smoke. Thirty-five years earlier, WENUSCH (51) was the first to recognize the qualitative and quantitative difference in the composition of mainstream *versus* sidestream smoke. Since that time, numerous studies have been conducted to determine the yields of various mainstream and sidestream tobacco smoke constituents, employing a variety of procedures and smoke collection devices (1, 2, 3, 6, 8–12, 14, 16, 17, 23, 24, 28–34, 36, 48). Today, in the United States, the preferred methodology for the collection of mainstream smoke is the FTC (Federal Trade Commission) method (7). In other parts of the world the ISO (International Organization for Standardization) and DIN (German Industrial Standards) methods are accepted and used as a means to relate and compare the mainstream yields of "tar", nicotine and carbon monoxide of cigarette products (6, 11, 15, 18, 19). Although there is no accepted, official, or approved methodology for the determination of sidestream cigarette smoke, one such method described by PROCTOR (17) of the British American Tobacco Company (BAT) has been shown to be very practical for the routine analysis of sidestream cigarette smoke. The collection apparatus, known as the "fishtail" chimney, can be easily attached to a standard smoking machine and can be used to collect sidestream gas and particulate phases of sidestream

cigarette smoke. The "fishtail" chimney apparatus can be used in conjunction with standard FTC Cambridge pad collection apparatus for the simultaneous determination of both mainstream (MS) and sidestream (SS) cigarette smoke.

The MS and SS yields of individual smoke constituents can vary considerably. The 1982 article by KLUS and KUHN (36) reviewed the published MS and SS data available for a wide variety of cigarette smoke constituents. The ratios of the SS to MS yields for individual smoke constituents vary widely depending on the types of cigarette, the tobaccos employed in the cigarettes, and the methods used to burn (49) and collect the smoke streams (5, 13, 16, 32, 34, 42, 44-47).

Data on the distribution of nicotine in MS and SS cigarette smoke were first published over 60 years ago (50, 37). The reported ratios of SS to MS smoke nicotine vary considerably and were found to be between 2.4 and 13.11 (36). In general, non-filtered cigarettes employing a single type of tobacco (Burley, flue-cured or Oriental) or a blend of tobaccos gave slightly lower SS/MS for smoke nicotine (3.3-2.6), while filtered cigarettes generally had slightly higher ratios (> 3.5). Filter ventilation (21) and cigarette paper porosity (52) affect the SS/MS for smoke nicotine. BROWNE *et al.* (4) found that as ventilation increases (0-83 %), the SS/MS for smoke nicotine increased (3.49-13.11). NEURATH (27) found that tobacco moisture has a large effect on the SS/MS for smoke nicotine. As tobacco moisture increased (3.1-22.2 %) the SS/MS for smoke nicotine increased (2.11-3.24). Therefore, not only tobacco type but also the construction properties and the moisture of the cigarettes have been found to affect the SS/MS ratio for smoke nicotine (32, 39, 40, 42, 43). The method of smoke collection has been often cited in the literature as a major factor affecting the SS/MS ratio for smoke nicotine. Unfortunately, a comparative study testing the many different collection devices and employing appropriate control and Reference cigarettes has not been published.

A set of experimental Reference cigarettes is available through the University of Kentucky Tobacco and Health Research Institute (57). These cigarettes have been used in the past and a good set of data is available on mainstream yields for a number of smoke constituents, including smoke nicotine. Unfortunately, very little information has been reported on the composition of the sidestream smoke for this set of research cigarettes (16, 20). In a 1977 review on the nitrogen-containing compounds in tobacco and tobacco smoke, SCHMELTZ and HOFFMANN (22) made the point that "except for nicotine, no reports are available on the chirality of the optically active alkaloids as they are present in tobacco smoke". Recently, PERFETTI and

COLEMAN (53, 54) have published reports on the chiral-gas chromatography-selected ion monitoring-mass selective detection analyses of alkaloids in tobacco and tobacco smoke. These reports contain data on the ratios of *d*- and *l*-isomers of nicotine, nornicotine, anabasine and anatabine in tobacco and mainstream smoke for cigarettes of a single tobacco type and on a set of University of Kentucky Reference cigarettes. In those reports no sidestream smoke analyses were conducted.

The objective of the present study was to simultaneously determine the MS and SS yields for a common set of smoke components in a set of University of Kentucky Reference cigarettes and cigarettes of different tobacco types. The fate of smoke nicotine was determined in a number of ways. Additionally, the isomeric ratios of nicotine, nornicotine, anabasine and anatabine were determined in these cigarettes. The BAT "fishtail" chimney SS smoke collection apparatus was employed in this study. MS smoke was collected via Cambridge pads. Information gathered from these experiments fills a void in the cigarette smoke literature.

EXPERIMENTAL

Cigarettes / Reagents

Reference cigarettes (1R1, 2R1F, 1R3F, 1R4F, and 1R5F) were purchased from the University of Kentucky Tobacco and Health Research Institute (Lexington, KY). These cigarettes have been described in detail by DIANA *et al.* (57). Three 70 mm non-filtered cigarettes were prepared from either flue-cured, Burley or Oriental tobaccos.

Standard solutions were prepared in methylene chloride or chloroform (Burdick and Jackson, Muskegon MI). The (S)-(-)-isomer of nicotine (*l*-nicotine) was purchased from Eastman Kodak (Rochester, NY, USA). The (R)-(+)-isomer (*d*-nicotine) and racemic nicotine (*d,l*-nicotine) were prepared by T. D. C. Research (Blacksburg, VA, USA) using an established method (64), substituting di-*p*-toluyl-tartaric acid for tartaric acid in diastereomer formation. The (±) anabasine and the (±) nornicotine were purchased from ICN Biochemicals, Aurora, OH, USA. The (±) anatabine was purchased from Midwest Research Institute, NCI Chemical Repository, Kansas City, MO, USA.

Instrumentation

Separations were performed on a Hewlett Packard (HP) 6890 Gas Chromatograph (GC) equipped with a HP 5973 Mass Selective Detector (MSD) and a HP 6890 Autoinjector. Automatic injections, 1 µL, were

made in the split mode with a split ratio of 20 to 1. The GC column consisted of two columns connected with a SGE (Austin, TX) capillary column low dead volume mini union. The first column was a J&W Scientific (Folsom, CA) CyclodexB, 30 meters long, 0.25 mm I.D., 0.25 μ m film thickness fused silica column. The second column was a Restek (Bellefonte, PA) Rt-BDEXsm, 30 meters long, 0.25 mm I.D., 0.25 μ m film thickness fused silica column. For the separation of the enantiomers of nicotine, the oven initial temperature was set at 50 °C. For the separation of the other enantiomers of the secondary alkaloids the oven initial temperature was set at 130 °C. The oven was temperature programmed to 200 °C at 1 °C/min. Throughout the entire chromatographic run, the column flow rate was held constant at 2.1 mL/min. The injection port and MSD transfer line were held at 230 °C. The MSD was operated in the selected ion monitoring (SIM) mode for the analytes of interest. The analytes and *m/z* ratios employed were as follows: 1) nornicotine: 147, 148; 2) anabasine: 105; 3) anatabine: 105 and 4) nicotine: 84.

Smoke collection

Mainstream cigarette smoke samples were obtained by smoking in accordance with accepted procedures of the Federal Trade Commission (FTC) (25). Gas chromatographic vials (1.8 mL volume) used in the FTC method for analysis of nicotine and water were used without further work-up for the alkaloid analyses than described in this report. Simultaneous collection of mainstream and sidestream smoke streams were conducted employing Cambridge pads (MS (1 pad) and SS (2 pads), both particulate), the "fishtail" chimney device (SS particulate) and an impinger (SS vapor phase). The gas chromatographic analyses (nicotine and water) and near-infrared analyses (CO and CO₂) employed were those described by PROC-TOR (17). Gas chromatographic vials of the chimney TPM wash solution and the impinger solution were prepared and used without further work-up for the alkaloid analyses. This collection method/analysis described above will be referenced as the BAT MS/SS smoke alkaloid enantiomeric analysis in this report.

Tobacco extractions

The alkaloids were quantitatively extracted from tobacco samples in accordance with accepted procedure (55) for the determination of specific alkaloids. Gas chromatographic vials from the specific alkaloid analysis were used without further work-up for the alkaloid enantiomeric analyses.

RESULTS AND DISCUSSION

Analytical technique

The introduction of stable cyclodextrin derivatives as stationary phases has been a milestone in the GC separation of enantiomers (56). Enantiomeric separation is fundamental in the understanding of the chemistries associated with enantiomeric pairs. Of particular interest in this report is the distribution of the *d*- and *l*-isomers of several tobacco alkaloids found in the mainstream and sidestream smoke streams of Reference cigarettes and cigarettes containing a single tobacco type. Nicotine, nornicotine, anabasine and anatabine enantiomers were previously analyzed in a variety of tobaccos and mainstream cigarette smoke (53, 54). Under the conditions described in the experimental section, near baseline resolution was obtained for the enantiomers, yielding a lower limit of detection of approximately 2 % for the *d*-isomers in a mixture of *d*- and *l*-isomers (53, 54). Based on these chromatographic separations, the analysis of the *d*- and *l*-isomer distribution of alkaloids in sidestream cigarette smoke was conducted for the cigarettes of this study. Due to the relatively low abundance of the *d*-isomer compared with the abundance of the *l*-isomer in almost all of the samples, close attention was directed towards manual and automated integration of all chromatograms. Using both manual and automated integration approaches and multiple (6 $\times$) injections of the same sample, the average % relative standard deviation (RSD) for the determination of the % *d*-isomer in the total isomer mixture was ~5 %. This % RSD value was obtained by determining the standard deviation from the injections/integrations, multiplying the value by 100, and dividing by the average % *d*-isomer value of the sample.

Historical data

The scientific literature contains numerous references to the yields of alkaloids in mainstream (MS) and sidestream (SS) smoke. Table 1 contains a representative sample of tobacco alkaloid MS and SS data for cigarettes prepared from Burley, flue-cured or Oriental tobaccos, and the 1R1, 2R1, 1R4F and 1R5F Reference cigarettes. Several points should be made concerning the data in Table 1. Several different methods were used to collect and analyze the smoke alkaloids. The Burley, flue-cured and Oriental tobaccos employed in the different studies were not identical and the origin and alkaloid content of the different tobaccos varied. None of the studies that are cited in Table 1 report both MS and SS yields for all four of the major alkaloids (nicotine, nornicotine, anabasine, and anatabine). There were only three

References that reported the SS/MS for nicotine for Reference cigarettes (16, 20, 60). SAKUMA *et al.* (1) reported the only known SS/MS data for anatabine. Interestingly, the SS/MS for anatabine was less than one. The low SS/MS for anatabine may indicate that there is a substantial difference in thermal stability of anatabine *versus* nicotine, a difference in trapping efficiency for anatabine *versus* nicotine, or perhaps it is indicative of the greater difficulty in recovery and analysis for this secondary alkaloid. It is generally known that the concentrations of secondary alkaloids are one to three orders of magnitude more dilute than nicotine in the tobacco and the tobacco smoke. There are very few references in the literature concerning the MS yields of nornicotine and anabasine (25, 26, 32, 43, 41). No literature could be found on the SS yield of anabasine. Only one reference was found on the SS smoke yield of nornicotine (32). It is because of the lack of a complete data set on the MS and SS smoke yields for tobacco alkaloids that this study was initiated. This study employed a set of cigarettes containing only one type of tobacco (Burley, flue-cured or Oriental) as well as a set of Reference cigarettes and employed a single collection method for MS and SS, as mentioned above (17).

SIDESTREAM AND MAINSTREAM SMOKE RESULTS

A series of experiments was performed to determine if the simultaneous collection of MS and SS smoke, employing the modified BAT "fishtail" collection device with Cambridge pad attachment, gave MS smoke yields similar to the FTC method. Table 2 contains data comparing the FTC MS smoke yields to the MS yields collected with the BAT MS/SS methodology. The average values for puff count, TPM, nicotine, H₂O, "tar", CO and CO₂ are given along with the standard deviation between samples. The FTC method analyzed 5 ports of 5 cigarettes per port and the BAT method analyzed 5 ports of 3 cigarettes per port. The two methods were located in different conditioned laboratories. Although, there were several cases in the data set where there was statistical significance associated with differences between the two methods, the differences were small and were not considered of practical significance. Both methods employed the same gas chromatographic determination for nicotine and water. The CO and CO₂ analyzer used for the two methods were different but were calibrated employing the same gas standards. The CO data for the BAT method is biased slightly high while the CO₂ data for the BAT method is biased slightly low. Since only small differences in the analytes were found, it was

assumed that the differences in the two collection devices did not substantially affect the normal combustion processes of the burning cigarette.

Table 3 contains the BAT sidestream and mainstream smoke chemistry results. The table also lists the SS/MS for each analyte. Since it is believed that the BAT smoke collection device did not affect the normal combustion processes of the burning cigarette (FTC smoking combustion processes), the BAT SS and MS yields of smoke components from the cigarettes of this study are considered to be accurate representations of each smoke stream. It is well known that different types of cigarettes can have dramatically different overall MS and SS smoke yields and different individual yields of smoke constituents. Numerous cigarette design considerations and smoking and collection parameters affect the ultimate yields of smoke constituents in the various smoke streams associated with the burning cigarette. Some important variables are:

- ◇ The tobacco blend or tobacco type used in a cigarette
- ◇ Tobacco preparation (cut-width, additives, moisture, etc.)
- ◇ The dimensions and design of the cigarette
- ◇ Weight of the tobacco rod
- ◇ Specifications of the cigarette wrapper (permeability, caliper, basis weight, level and type of filler, type and level of burn chemical or ash conditioner, etc.)
- ◇ The presence and type of filter element and the level of filter ventilation used in the cigarette
- ◇ The smoking methodology (puff volume, frequency, duration, type of smoking machine, smoke collection device, laboratory environmental conditions, butt length, etc.)

The data in Table 3 illustrate how some of these variables affect the yields of selected smoke constituents in MS and SS smoke. The flue-cured, Burley and Oriental cigarettes exhibited different puff counts, 11, 7.7 and 15.6, respectively. These three cigarettes were prepared in a single format (70 mm length × 24.8 mm circumference) and had similar cigarette rod firmness, but the tobacco rod weight of the three cigarettes varied considerably, 896 mg – 1264 mg (Table 3). The weight differential among cigarettes containing a single type of tobacco is well known in the industry. Generally, Oriental tobacco prepared into cut filler tends to have a lower filling capacity (65), lower nicotine content and contains higher levels of sugars *versus* flue-cured or Burley cut filler. Although, flue-cured tobacco has a higher sugar content than Burley, it generally has less tobacco nitrate, which tends to decrease the burn rate relative to Burley. Considering the weights of the cigarettes, Burley cut

Table 1.

Sidestream (SS) and mainstream (MS) smoke yields (µg/cigarette) reported in the literature for Burley (B), flue-cured (FC), flue-cured "Cherry Red" (CR), Oriental (O), Maryland (M), and University of Kentucky Reference cigarettes.

Tobacco type	B	FC	CR	O	M	1R1	2R1	1R4F	1R5F	Comment/Reference
Smoke component (µg/cigarette)										
SS Nicotine	5380	5830		3210						SAKUMA; Bases, 1984 (1)
SS Nicotine	6588	6193		2987						SAKUMA; Middle & higher boiling comp., 1984 (2)
SS Nicotine	6090	6050								YOSIDA; 1976 (42)
SS Nicotine								5600		RJR Monograph; 1988 (20)
SS Nicotine						4720		4520		EVANS; 1992
SS Nicotine		5570	1670							KOBASHI; 1963 (32)
MS Nicotine	2940	3330		1720						SAKUMA; Bases, 1984 (1)
MS Nicotine	3100	3149		1483						SAKUMA; Middle & higher boiling comp., 1984(2)
MS Nicotine	2483	2262								YOSIDA; 1976 (42)
MS Nicotine	4500	3500		3300						SCHMELTZ ;1964 (43)
MS Nicotine						2310				DAVIS; 1977 (41)
MS Nicotine								790		RJR Monograph; 1988 (20)
MS Nicotine						2390		840		EVANS; 1992 (60)
MS Nicotine						2160		800		DIANA; 1990 (57)*
MS Nicotine		5050	1890							KOBASHI; 1963 (32)
MS Nicotine	950	2520		970						KOBASHI; 1960 (62)
MS Nicotine										KOBASHI; 1961 (63)
MS Nicotine							2200	800	200	BOMBICK; 1997 (66)
SS/MS Nicotine	1.8	1.8		1.9						SAKUMA; Bases, 1984 (1)
SS/MS Nicotine	2.1	2.0		2.0						SAKUMA; Middle & higher boiling comp., 1984(2)
SS/MS Nicotine	3.2	3.3		2.8		2.6				JOHNSON; 1973 (16)

* MS nicotine on all Reference cigarettes given

Table 1 (contd).

Tobacco type	B	FC	CR	O	M	1R1	2R1	1R4F	1R5F	Comment/Reference
Smoke component (µg/cigarette)										
SS/MS Nicotine	2.44	2.67								YOSIDA; 1976 (42)
SS/MS Nicotine								7.09		RJR Monograph; 1988 (20)
SS/MS Nicotine						1.97		5.36		EVANS; 1992 (60)
SS/MS Nicotine		1.1	0.9							KOBASHI; 1963 (32)
SS Normicotine		BLOD**	220							KOBASHI; 1963 (32)
MS Normicotine						73				DAVIS; 1977 (41)
MS Normicotine		90			90					KOBASHI; 1961 (63)
MS Normicotine		BLOD	340							KOBASHI; 1963 (32)
SS/MS Normicotine			0.6							KOBASHI; 1963 (32)
SS Anabasine										-
MS Anabasine	11	5.7		6.2						SCHMELTZ; 1964 (43)
MS Anabasine	11									QUIN; 1959 (25,26)
MS Anabasine						7				DAVIS; 1977 (41)
SS/MS Anabasine										-
SS Anatabine	11	0.5		0.5						SAKUMA; Bases, 1984 (1)
MS Anatabine	20.1	9.2		2.4						SAKUMA; Bases, 1984 (1)
MS Anatabine	14									QUIN; 1959 (25,26)
MS Anatabine						18				DAVIS; 1977 (41)
SS/MS Anatabine	0.5	0.1		0.2						SAKUMA; Bases, 1984 (1)

**BLOD = Below limit of detection.

Table 2.
Comparison of FTC and BAT methods for analysis of mainstream smoke constituents.

Tobacco Type	FTC	BAT	FTC	BAT	FTC	BAT	FTC	BAT
	Puffs/cigarette (SD)		MS Pad TPM mg/cigarette (SD)		MS Nicotine mg/cigarette (SD)		MS H ₂ O mg/cigarette (SD)	
Flue-cured	11 (0.55)	11 (0.48)	31.3 (1.1)	33.6 (1.16)	3.43 (0.13)	3.51 (0.10)	3.2 (0.19)	3.6 (0.24)
Burley	8 (0.51)	7.7 (0.62)	30.6 (0.65)	31.4 (1.51)	3.69 (0.26)	3.49 (0.27)	3.9 (0.18)	4 (0.25)
Oriental	15 (0.25)	15.6 (1.33)	32.3 (1.08)	31.5 (1.76)	1.06 (0.04)	0.96 (0.08)	3.5 (0.43)	3.7 (0.13)
1R1	10.7 (0.19)	10.3 (0.3)	40.4 (2.65)	38 (0.67)	2.52 (0.14)	2.39 (0.04)	6 (0.88)	5.1 (0.33)
2R1F	10.9 (0.22)	10.4 (0.11)	28.8 (0.99)	28.3 (0.64)	1.68 (0.04)	1.68 (0.05)	4.6 (0.44)	4.3 (0.16)
1R3F	7.8 (0.37)	7.4 (0.38)	18.7 (0.62)	18 (1.63)	1.18 (0.06)	1.04 (0.09)	2.7 (0.17)	2.9 (0.24)
1R4F	9 (0.18)	8.7 (0.16)	11.7 (0.28)	11.1 (0.19)	0.88 (0.05)	0.87 (0.04)	1.2 (0.08)	1.2 (0.08)
1R5F	7 (0.05)	6.7 (0.14)	2 (0.09)	2.1 (0.22)	0.18 (0.02)	0.17 (0.01)	0.2 (0.01)	0.2 (0.01)

Tobacco Type	FTC	BAT	FTC	BAT	FTC	BAT
	MS "Tar" mg/cigarette (SD)		MS CO mg/cigarette (SD)		MS CO ₂ mg/cigarette (SD)	
Flue-cured	24.7 (0.88)	26.5 (0.99)	10 (0.52)	12.3 (0.95)	44.1 (3.66)	43.8 (2.79)
Burley	23 (0.31)	23.9 (1.36)	11.8 (0.40)	13.6 (1.02)	44.9 (1.44)	43.5 (3.38)
Oriental	27.9 (1.01)	27.6 (0.86)	12.1 (0.40)	12.7 (1.09))	56 (1.71)	45.7 (1.13)
1R1	31.9 (1.69)	30.5 (0.42)	18.8 (0.61)	20.6 (0.30)	61 (1.73)	58.7 (1.37)
2R1F	22.7 (0.59)	22.4 (0.45)	23.2 (0.68)	25.5 (0.91)	70.5 (1.46)	69.2 (1.85)
1R3F	14.9 (0.42)	14.7 (0.55)	14.4 (0.39)	15.2 (0.94)	47.4 (1.15)	45.8 (3.58)
1R4F	9.6 (0.15)	9 (0.25)	12 (0.40)	14.3 (0.58)	44.6 (1.05)	41.8 (1.49)
1R5F	1.6 (0.08)	1.7 (0.18)	3 (0.15)	3.7 (0.17)	14.8 (0.17)	12.3 (.88)
				Bias high		Bias low

Bold = Significantly different

Table 3.
Complete data set on BAT sidestream and mainstream smoke chemistry.

Sample name	Flue-cured	Burley	Oriental	1R1	2R1F	1R3F	1R4F	1R5F
Cigarette length (mm)	70	70	70	85	85	85	85	85
Butt length (mm)	23	23	23	23	30	30	35	35
Filter (filtered/plain)	Plain	Plain	Plain	Plain	Filtered	Filtered	Filtered	Filtered
Filter ventilation (%)	None	None	None	None	0	0	29	74
Static burn rate (mm/min)	3.2	4.71	2.18	4.18	2.82	4.94	4.08	6.01
Tobacco rod weight (mg)	1014	896	1264	1173	920	808	808	623
Tobacco nicotine (%)	3.03	3.47	0.80	1.90	1.73	1.67	1.93	1.71
Tobacco reducing sugar (%)	10.5	1.3	13.1	9.8	11.3	8.6	7.6	5.8
Tobacco total sugar (%)	11.7	1.6	14.8	11.1	13.5	10	8.3	7.1
Tobacco nitrate (%)	0.35	0.96	0.15	0.67	0.75	1.22	1.37	1.36
BAT mainstream smoke results								
Puffs/cigarette	11	7.7	15.6	10.3	10.4	7.4	8.7	6.7
MS Pad TPM (mg/cigarette)	33.6	31.4	31.5	38	28.3	18	11.1	2.1
MS Nicotine (mg/cigarette)	3.51	3.49	0.96	2.39	1.68	1.04	0.87	0.17
MS H ₂ O (mg/cigarette)	3.6	4	3.7	5.1	4.3	2.9	1.2	0.2
MS "Tar" (mg/cigarette)	26.5	23.9	27.6	30.5	22.4	14.7	9	1.7
MS CO (mg/cigarette)	12.3	13.6	12.7	20.6	25.5	15.2	14.3	3.7
MS CO ₂ (mg/cigarette)	43.8	43.5	45.7	58.7	69.2	45.8	41.8	12.3
MS CO ₂ /CO	3.6	3.2	3.6	2.9	2.7	3	2.9	3.3
BAT Sidestream smoke results								
SS Pad TPM (mg/cigarette)	31.8	28.2	36.5	33	27.2	26.6	27.1	19.9
Total SS Nicotine (mg/cigarette)	8.42	7.33	2.67	6.64	5.59	5.01	6.07	4.01
SS Pad H ₂ O (mg/cigarette)	2.2	2.1	2.9	3.7	3.3	3.2	3	2.6
Total SS "Tar" (mg/cigarette)	26.1	22.4	35.7	28	22.6	23	21.8	16.2
SS CO (mg/cigarette)	65	55.1	71.3	51.9	47.3	55	59.1	43.6
SS CO ₂ (mg/cigarette)	484.1	370.9	584.5	516.3	418.4	385.2	477.1	362.6
SS CO ₂ /CO	7.5	6.7	8.2	9.9	8.9	7	8.1	8.3
BAT SS/MS smoke ratios								
SS/MS TPM	0.9	0.9	1.2	0.9	1.0	1.5	2.4	9.5
SS/MS Nicotine	2.4	2.1	2.8	2.8	3.3	4.8	7.0	23.6
SS/MS H ₂ O	0.6	0.5	0.8	0.7	0.8	1.1	2.5	13.0
SS/MS "Tar"	1.0	0.9	1.3	0.9	1.0	1.6	2.4	9.5
SS/MS CO	5.3	4.1	5.6	2.5	1.9	3.6	4.1	11.8
SS/MS CO ₂	11.1	8.5	12.8	8.8	6.0	8.4	11.4	29.5

filler tobacco generally exhibits a higher filling capacity compared to flue-cured cut filler tobacco. Flue-cured cut filler tobacco, in turn, has more filling capacity than

Oriental cut filler tobacco (65). The tobacco nicotine content for the flue-cured and Burley tobaccos were similar, 3.03 and 3.47 %, respectively. These factors associated

with the different types of tobacco cut filler used in the three cigarettes result in the puff counts and the associated MS yields of TPM, nicotine, "tar", CO and CO₂ shown in Table 3.

Total yields of SS TPM, "tar", nicotine and water for the three single-tobacco type cigarettes reflect fundamental differences in tobacco chemistry (nicotine and nitrate level) and rod packing density. Differences in these fundamental parameters are manifested in the exhibited puff count and the static burn rate of these cigarettes (67). For example, the Oriental cigarette which had the highest puff count, packing density and lowest content of nicotine (0.8 %) and nitrate (0.15 %), had the slowest static burn rate of the cigarettes tested. The Oriental cigarette had the highest yield of SS TPM, the lowest SS nicotine yield and the highest SS "tar" compared to the other single tobacco cigarettes (67). The Burley cigarette, which had the lowest packing density and puff count, the highest content of nicotine (3.47 %) and nitrate (0.96 %) had a high static burn rate. The Burley single tobacco cigarette had the lowest total SS "tar" *versus* the flue-cured and Oriental cigarettes. The values for SS nicotine are consistent with literature reports (Table 1). Sidestream CO and CO₂ data for the flue-cured, Burley and Oriental cigarettes are well within the reported ranges cited by GUERIN (12) and for similar single-type cigarettes cited by JOHNSON (16).

Mainstream cigarette smoke data for the Kentucky Reference cigarettes agrees well with the results reported by DIANA (57). Sidestream smoke yields of TPM, nicotine, H₂O, "tar", CO and CO₂ for the majority of the Reference cigarettes have not been reported before. The SS yields of nicotine reported by EVANS *et al.* (60) for the 1R1 and 1R4F in Table 1 are lower than the yields reported in Table 3. The "fishtail" collection device employed by EVANS apparently did not contain an inline acid trap or impinger behind the SS particulate trap as described by PROCTOR (17) for the collection of vapor phase nicotine. The nicotine trapped by the impinger in our study was found to account for 10–15 % of the total SS nicotine. The SS nicotine reported by R. J. Reynolds Tobacco Co. (20) for the 1R4F cigarette, which was collected employing the "fishtail" chimney with an impinger, was 5.6 mg. The SS nicotine yield for the 1R4F Reference cigarette reported in this study was 6.07 mg.

The Reference cigarettes are constructed to represent non-filtered, filtered, and ventilated filtered cigarettes sold in the United States cigarette market, today. The set has cigarettes representing the high, medium and low MS "tar" cigarette categories. The tobacco blends used in the cigarette series vary both in the ratio of flue-cured/Burley/Oriental tobacco

lamina and in the use and level of processed tobaccos (reconstituted tobacco sheet, expanded tobacco) employed as cut filler (57). The cigarettes vary in rod weight, tobacco weight, cigarette wrapper porosity and cigarette wrapper burn chemical or ash conditioner levels employed. The cigarette length and circumference for the set of Reference cigarettes studied were similar (~85 mm × ~25 mm). The reported static burn rate varies considerably (2.82–6.01 mm/min, 2R1F–1R5F, respectively) (57). These products provide a good range of cigarette properties for reference products and for comparison purposes. However, these products' diversity also prevents the influence of any single construction parameter on SS yields from being clearly found although a number of observations can be made. The 1R1 Reference cigarette yielded the highest levels of SS TPM, nicotine, H₂O, "tar", and CO₂ of all the Reference cigarettes tested. The 1R5F Reference cigarette yielded the lowest levels of SS TPM, nicotine, H₂O, "tar", CO and CO₂ of all the cigarettes tested. The 2R1F, 1R3F and 1R4F Reference cigarettes had intermediate yields of SS TPM, nicotine, H₂O, "tar", CO and CO₂. More SS smoke is expected to be generated when the amount of tobacco burned during smolder intervals increases compared to the amount of tobacco burned during puffing (e.g., static burn rate increases, puff count decreases). The reported yields of SS TPM, nicotine, "tar" and CO₂ for most of the Reference cigarettes were within the range of the single grade cigarettes. BROWNE (4, 21) reported that the yields of SS smoke constituents increased with increased filter ventilation. In BROWNE's report all cigarettes were of the same type and weight. In this report, the SS smoke yields for all SS smoke constituents measured were lower for the 1R5F product compared to the 1R4F Reference cigarette, although filter ventilation was higher for 1R5F. In addition to differences in filter ventilation and static burn rate, the 1R5F Reference cigarette in this report weighed substantially less than the 1R4F cigarette. Differences in tobacco mass, static burn rate and filter ventilation account for the differences between the results reported here and in BROWNE's work.

Table 3 also contains the SS/MS of TPM, nicotine, H₂O, "tar", CO and CO₂ for the cigarettes tested. The SS/MS of constituents for the flue-cured, Burley and Oriental cigarettes are very similar to those reported in the literature (36). The SS/MS for TPM for the single tobacco cigarettes of the current study was 1, on average. The SS/MS for nicotine varied slightly (2.1–2.8, average = 2.4), and was on average comparable to the average value of 2.7, reported by KLUS and KUHN in their review of the literature (36). The SS/MS for H₂O are very different from those reported in the literature (36). The reason for the

Table 4.
Sidestream (SS) to mainstream (MS) smoke yields (ADAMS, *et al.* (5)).

Cigarette type*	Non-filtered (NF)	Filtered (F1)	Filtered (F2)	Ventilated Filter (F3)
Smoke component				
SS/MS "Tar"	1.1	1.6	2.9	15.6
SS/MS Nicotine	2.3	2.8	4.4	21.1
SS/MS CO	2.1	2.7	3.5	14.9
SS/MS CO ₂	11.3	9.8	11.7	35.3

* Four U.S. commercial 85 mm cigarettes purchased on open market in 1985. Tar yields of NF, F1, F2, and F3 were 20.1, 15.6, 6.8 and 0.9 mg/cigarette, respectively.

Table 5.
Effects of filter ventilation on sidestream (SS) to mainstream (MS) smoke nicotine yields (BROWNE (21)).

	Stream	Nicotine (mg)	SS/MS	Total MS + SS Nicotine (mg)
Filter ventilation %				
0	MS	1.70	3.49	7.64
	SS	5.94		
33	MS	1.45	4.64	8.18
	SS	6.73		
48	MS	1.07	5.94	7.43
	SS	6.36		
83	MS	0.55	12.55	7.45
	SS	6.90		
100 (Static burning)	MS	0.08*	95.25	
	SS	7.62		

discrepancy is due to the collection devices employed and the objective of each study. NEURATH (61) determined the SS/MS for H₂O to be 24. NEURATH's value of 24 for the SS/MS of H₂O was confirmed by BROWNE (4). The SS/MS for H₂O determined in the present study for the single tobacco cigarettes, was 0.6, on average. Only water on the Cambridge pads was analyzed in this study. The water content of the remainder of the "fishtail" chimney collection apparatus was not measured. The SS/MS for "tar" for the single grade cigarettes has not been previously reported. The flue-cured, Burley and Oriental cigarettes of this study gave an average SS/MS for "tar" of 1.1. The SS/MS for CO and CO₂ of 5 and 10.8, respectively, reported in this

study for the single tobacco cigarettes were slightly higher on average compared to the SS/MS values for CO and CO₂ reported by JOHNSON (16), of 3.9 and 9.7, respectively. Similar discrepancies in findings *versus* JOHNSON's data for SS/MS CO and CO₂ were noted by BROWNE (4), who attributed the differences to the collection devices employed in each study. The SS/MS values for nicotine, CO and CO₂ for the 1R1 Reference cigarette reported by JOHNSON (16) (2.6, 2.5, 8.1) are nearly identical to the values reported in this study, (2.8, 2.5, 8.8, respectively). The SS/MS for nicotine reported by R. J. Reynolds Tobacco Co. (20) for the 1R4F Reference cigarette was the same as found in this study, 7.0. Several trends are evident in the data collected for the Reference

cigarettes of this study. In moving from the non-filtered 1R1 to the filtered 2R1F and 1R3F, and further to the ventilated filtered 1R4F and 1R5F, the SS/MS for nearly all the smoke constituents increase. The increase in SS/MS is primarily the result of large decreases in MS yields with smaller relative decreases in SS yields. The changes in construction parameters discussed earlier, especially reductions in rod weight, the presence of a filter, and increased filter ventilation in the cases of 1R4F and 1R5F cigarettes, cause these trends. ADAMS *et al.* (5) and BROWNE (4, 21) have reported the same trends. Data from those studies can be seen in Tables 4 and 5.

Total nicotine accountability has been discussed in the literature for a number of years. Values of nicotine accountability in the literature range from ~40 % (44) to ~80 % (32, 59). The discrepancies have arisen because of differences in the definition of accountability, the products evaluated and the methodologies used to collect and measure the collected nicotine. The definition of % total nicotine accountability used in this report was the sum of the total SS and total MS smoke nicotine mass multiplied by 100 and divided by the mass (mg) of nicotine present in the tobacco consumed when the cigarette was burned to a set butt length. The total SS and total MS smoke nicotine was collected on the BAT "fishtail" / the SS Cambridge pads / the SS impinger and the MS Cambridge pad (17). Table 6 shows the calculated % total nicotine accountability from information in the literature. The data from the different investigators were generated from cigarettes that varied in blend and configuration (presence of a filter element, with or without ventilation, having varied types of cigarette wrappers). The nicotine present in the cigarettes evaluated was either endogenous (natural, ^{12}C or ^{14}C) or exogenously applied as nicotine salts to the tobacco. Additionally, a variety of different smoke collection devices were employed in the studies represented in Table 6. The % total nicotine accountability from these studies varied from ~25–55 %.

Table 7 contains the calculated % total nicotine accountability from the cigarettes of this report. The % total nicotine accountability for the single tobacco cigarettes were 57.9, 51.8 and 53.5 % (average = 54.4 %) for the cigarettes made with flue-cured, Burley and Oriental tobacco, respectively. The % total nicotine accountabilities for the set of Reference cigarettes containing 1R1, 2R1F, 1R3F, 1R4F and 1R5F were 55.7, 54.2, 53.2, 51.7 and 45.7 %, respectively (average = 52.1 %). The % total nicotine accountability for the single tobacco cigarettes and the set of Reference cigarettes of this study remained relatively constant (53 %) despite the wide ranges in construction parameters. The remainder of the tobacco nicotine is decomposed

(20–30 %) and trapped in the cigarette butt (filter and unburned tobacco upstream of the filter element) (20–30 %) (58, 59). The % total nicotine accountability was essentially unchanged and unaffected by the presence of a filter element. BROWNE (4) stated that the total smoke (SS + MS) nicotine yield was not affected by filter ventilation. Close inspection of the data in his report (4) indicated that there was a small but consistent decrease in the total smoke nicotine yield with increased filter ventilation. The range of ventilated filtered products studied was between 33–83 % (Table 5). In this study, the 1R5F Reference cigarette, at 74 % filter ventilation also showed a small decrease in total smoke (MS + SS) nicotine. The % total nicotine accountability of the 1R5F Reference cigarette was 45.7 %. It is speculated that the small decrease in % total nicotine accountability for cigarettes with high levels of filter ventilation may be due to a slightly greater degradation of nicotine that may occur during the dynamic smolder (smolder during active smoking) of these products. In mouthend unrestricted smoking of unventilated cigarettes and in restricted and unrestricted smoking of ventilated cigarettes it is known that there is a smoke stream that can travel down the rod (35, 36). It is believed that this additional smoke stream carries volatile materials downstream during the active smoking process. This explanation is often used to account for the greater than expected MS yield of nicotine in highly diluted cigarettes. If this additional smoke stream transfers additional nicotine downstream, then during each subsequent smolder, that additional nicotine will undergo distillation and pyrolysis. These processes may account for the noted slight decrease in total nicotine accountability for cigarettes with highly ventilated filters.

Enantiomeric ratios of alkaloids in mainstream and sidestream smoke

As previously mentioned, SCHMELTZ and HOFFMANN (22) in the 1977 review on the nitrogen containing compounds in tobacco and tobacco smoke pointed out that "except for nicotine, no reports are available on the chirality of the optically active alkaloids as they are present in tobacco smoke". PERFETTI and COLEMAN (53, 54) have published reports on the chiral-gas chromatography-selected ion monitoring-mass selective detection analyses of alkaloids in tobacco and tobacco smoke. These reports contain MS data on the ratios of *d*- and *l*-isomers of nicotine, nornicotine, anabasine and anatabine in tobacco and mainstream smoke for single tobacco cigarettes and for a set of University of Kentucky Reference cigarettes. No sidestream smoke analyses were conducted. In this report, samples of

Table 6.
Nicotine accountability in sidestream and mainstream smoke / total nicotine as a percentage of original contained in tobacco burnt.

Reference	NEURATH (58)	HOUSEMANN (59)	HOUSEMANN (59)	SCHMELTZ (44)	EVANS (60)	EVANS (60)
Source of nicotine	Natural	Natural	Natural + Exogenous	Plant grown in ¹⁴ C CO ₂	Natural	Natural
Cigarette type/format	80 mm Non-filtered cigarette	70 mm Filtered cigarette	70 mm Filtered cigarette	85 mm Non-filtered cigarette	1R1 Reference cigarette	1R4F Reference cigarette
Nicotine in MS TPM (%)	12.4	14.1	14.9	16.8	18.4	6.6
Nicotine in MS vapor (%)	0	0	0	NR	NR	NR
Nicotine in SS TPM (%)	33.4	39.2	37	24	36.2	35.4
Nicotine in SS vapor (%)	0	0	0	NR	NR	NR
Nicotine in tobacco burnt (mg)	11.94	10.43	10.43 mg natural nicotine + 3.99 µg ¹⁴ C nicotine			
Total nicotine accountability (%)	45.8	53.3	51.9	40.8	54.6	42
SS/MS	2.69	2.78	2.48	1.43	1.97	5.36
Reference	ADAMS (5)	ADAMS (5)	ADAMS (5)	ADAMS (5)	CHORTYK (14)	
Source of nicotine	Natural	Natural	Natural	Natural	Natural	
Cigarette type/format	85 mm Non-filtered cigarette	85 mm Filtered high 'tar' cigarette	85 mm Filtered low 'tar' cigarette	85 mm Filtered ultra low 'tar' cigarette	85 mm Non-filtered cigarette	
Nicotine in MS TPM (%)	15.7 (2.04)	11.5 (1.5)	6.2 (0.81)	1.2 (0.15)	10.0 (1.3)	
Nicotine in MS vapor (%)	NR	NR	NR	NR	NR	
Nicotine in SS TPM (%)	35.5 (4.62)	31.9 (4.14)	27.2 (3.54)	24.3 (3.16)	40.7 (5.29)	
Nicotine in SS vapor (%)	NR	NR	NR	NR	NR	
Nicotine in tobacco burnt (mg)	13.0*	13.0*	13.0*	13.0*	13.0*	
Total nicotine accountability (%)	51.2	43.4	33.5	25.5	50.7	
SS/MS	2.26	2.77	4.38	20.25	4.07	

NR = Not reported; * estimated on a % tobacco nicotine content of ~ 2 %

Table 7.
Calculated values of nicotine accountability in tobacco smoke streams.

Sample name	Flue-cured	Burley	Oriental	1R1	2R1F	1R3F	1R4F	1R5F
Cigarette length (mm)	70	70	70	85	84	84	84	84
Filter length (mm)	Non-filtered	Non-filtered	Non-filtered	Non-filtered	20	20	27	27
Butt length (mm)	23	23	23	23	30	30	35	35
Tobacco nicotine (% (GC))	3.028	3.469	0.799	1.896	1.727	1.669	1.934	1.709
Cigarette circumference (mm)	24.8	24.8	24.8	25.1	25.1	24.8	25.0	24.7
Tobacco rod weight (mg)	1014	896	1264	1173	920	808	808	623
Filter weight (mg)	Non-filtered	Non-filtered	Non-filtered	Non-filtered	187	179	249	245
Total cigarette weight (mg)	1014	896	1264	1173	1107	987	1057	868
Weight of tobacco consumed (mg)	680.8	601.6	848.7	855.6	776.2	681.8	694.6	535.6
Weight of nicotine consumed (mg)	20.6	20.9	6.8	16.2	13.4	11.4	13.4	9.2
BAT mainstream smoke results								
MS nicotine (mg)	3.51	3.49	0.96	2.39	1.68	1.04	0.87	0.17
BAT sidestream smoke results								
SS pad nicotine (mg/cigarette)	5.88	4.92	1.93	4.83	4.06	3.66	4.6	3.11
Chimney nicotine (mg/cigarette)	1.16	1	0.38	0.98	0.71	0.84	0.56	0.41
Impinger nicotine (mg/cigarette)	1.43	1.33	0.32	0.88	0.8	0.54	0.83	0.48
Total SS nicotine (mg)	8.42	7.33	2.67	6.64	5.59	5.01	6.07	4.01
Impinger/total SS nicotine (%)	16	17.7	11.9	13.2	14.4	10.8	13.7	11.8
Calculated values of nicotine accountability in tobacco smoke streams:								
SS + MS nicotine (mg)	11.93	10.82	3.63	9.03	7.27	6.05	6.94	4.18
Total nicotine accountability (%)	57.9	51.8	53.5	55.7	54.2	53.2	51.7	45.7

Table 8.
Isomeric ratios (%) of alkaloids in MS and SS smoke.

Flue-cured		Burley		Oriental		1R1		2R1F		1R3F		1R4F		1R5F			
<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>	<i>l</i>	<i>d</i>		
FTC mainstream smoke results																	
MS nicotine pad (54)		≥97.5	≤2.5	≥97.5	≤2.5	96.4	3.6	≥97.5	≤2.5	97.3	2.7	97.0	3.0	97.4	2.6	96.6	3.4
BAT Mainstream smoke results																	
MS nicotine pad		98	2	97	3	97	3	97	3	97	3	97	3	97	3	95	5
BAT Sidestream smoke results																	
SS nicotine pad		99	1	98	2	98	2	97	3	≥97.5	≤2.5	98	2	98	2	98	2
Chimney nicotine		98	2	97	3	97	3	96	4	96	4	96	4	96	4	95	5
Impinger nicotine		97	3	97	3	95	5	96	4	96	4	96	4	96	4	94	6
FTC Mainstream smoke results																	
MS normicotine pad		87	13	90	10	80	20	76	24	84	16	78	22	75	25	85	15
BAT Mainstream smoke results																	
MS normicotine pad (54)		96	4	92	8	BLOD*	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD
BAT Sidestream smoke results																	
SS normicotine pad		BLOD	BLOD	BLOD	11	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD
Chimney normicotine		≥97.5	≤2.5	≥97.5	≤2.5	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD
Impinger normicotine		BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD	BLOD

*BLOD = Below limit of detection (50 µg/cigarette)

the cigarette smoke extracts from the SS Cambridge pads, the "fishtail" chimney and the impinger obtained from the BAT MS/SS smoke procedure were evaluated employing the chiral-gas chromatography-selected ion monitoring-mass selective detection analysis for alkaloids (53, 54). The same set of single tobacco cigarettes and Reference cigarettes were smoked as in references 53 and 54. The BAT MS/SS smoking procedure described above was used for collection. Table 8 contains the isomeric ratios of the analyzable alkaloids employing that method. Table 8 also contains data collected previously with the FTC smoking procedure (54).

The isomeric ratio of *d*- and *l*-nicotine in MS smoke is nearly identical to that obtained in SS smoke. As previously determined by PERFETTI and COLEMAN (53) *d*-nicotine is not present in tobacco. The mechanism for the generation of *d*-nicotine in smoke is not known. Yet on average, about 2 % of the total reported smoke nicotine was determined as *d*-nicotine. There was excellent agreement with the previously reported FTC generated smoke results of PERFETTI and COLEMAN (54) *versus* the results reported here obtained with the BAT MS/SS smoke procedure. It is interesting to note that the fraction of *d*-nicotine in sidestream smoke was not significantly different from that in mainstream smoke even though the temperatures experienced during the sidestream smoke formation process are quite different (lower) from those occurring in the mainstream smoke formation process. Very limited data was obtained on the isomeric ratio of nornicotine in SS cigarette smoke. The concentrations of nornicotine, anabasine and anatabine in the extracts obtained from the BAT smoking procedure were, in general, too dilute for an accurate determination of these secondary alkaloids using the current analytical approach. The current analytical approach has a limit of detection for the secondary alkaloids in the range of 50 $\mu\text{g}/\text{cigarette}$. Only in the cases of the flue-cured and Burley single tobacco cigarettes were there measurable levels of nornicotine. In these samples, it appears that there was only a slight change in the isomeric ratio of *l*- to *d*-nornicotine, in favor of increased *l*-nornicotine, but nothing definite can be stated, as the data set was too small.

Although understanding of nicotine chemistry in tobacco and tobacco smoke is quite extensive, there is comparatively little quantitative information on the presence and fate of the secondary alkaloids in tobacco and smoke. The yield of nicotine in mainstream cigarette smoke is somewhere between 20 and 50 times greater than the mainstream smoke yield of nornicotine (24). The mainstream cigarette smoke yields of anabasine and anatabine are in the range of 500–1000 times lower than mainstream smoke yield of nicotine (24). The SS/MS for nicotine is about 2.5 for the non-filtered cigarettes

tested. There are no reported values of SS/MS for anabasine. The reported SS/MS values for anatabine range between 0.1–0.5 (1) (Table 1). Pyrolysis studies (30, 31) of the secondary tobacco alkaloids (particularly nornicotine) indicate that they are less thermally stable at relatively low temperatures ($\sim 300^\circ\text{C}$) compared to nicotine (24). KOBASHI (30) found that the *N*-methylpyrrolidine ring of nicotine was thermally unstable at temperatures above 300°C when heated in an air stream. The pyrolysis of nornicotine in an air stream produces nearly the same type of volatile products produced by nicotine under similar conditions (24, 30, 31). Although the simplified conditions of pyrolysis experiments were well controlled, the results of those studies should not be used to draw conclusions concerning the processes that occur during the burning of cigarettes. KOBASHI (63) performed smoking experiments on cigarettes to address this concern. KOBASHI and his collaborators (32, 62, 63) studied the transfer of tobacco alkaloids into mainstream smoke and determined that the transfer rate of nornicotine was 0.25–0.07 that of nicotine. They concluded that the lower MS transfer rate of nornicotine was due to a higher rate of decomposition of nornicotine (32). Nornicotine, as well as, anabasine and anatabine have higher boiling points compared to nicotine. As a result, these secondary alkaloids tend to stay within the tobacco during the smoking process and therefore tend to decompose to a greater extent than nicotine. This would lead to a lower MS smoke transfer rate for the secondary alkaloids as seen by DAVIS (41). If the secondary alkaloids tend to remain stationary within the tobacco, then during the smolder process (at temperatures $> 300^\circ\text{C}$) these compounds would also tend to decompose to a greater extent than nicotine, which distills down the tobacco rod. These observed results would lead to the conclusion that there should be a very low SS transfer rate for the secondary alkaloids. The very low SS/MS for anatabine (~ 0.1) reported by SAKUMA (1) supports these postulates.

In general, the BAT MS/SS smoke collection device and methodology are not well suited for the determination of secondary alkaloids, when the gas chromatography techniques employed in this report are used. The limit of detection for each secondary alkaloid was approximately 50 $\mu\text{g}/\text{cigarette}$ from the chiral-gas chromatography-selected ion monitoring-mass selective detection analysis used for this study. If anabasine and anatabine were present in the sidestream smoke then their concentrations were below 50 $\mu\text{g}/\text{cigarette}$. The flue-cured and Burley single grade cigarettes, for which the isomeric ratio of nornicotine could be measured, had MS and SS smoke yields that were above the limit of detection. This is in agreement with the data of KOBASHI (63) where the flue-cured cigarette MS smoke yield for

nornicotine was reported to be 90 µg/cigarette. KO-BASHI has also reported (32) SS smoke for nornicotine at 220 µg/cigarette for "cherry red" (Koyo) flue-cured tobacco cigarettes. All other reported MS and SS smoke yields for anabasine and anatabine were below the limit of detection for the method presented in this report (Table1).

Additional work is presently planned to improve the detection limits for the chiral-gas chromatography-selected ion monitoring-mass selective detection analysis used for this study. When this is accomplished, the isomeric ratios of the secondary alkaloids in MS and SS smoke should be measurable.

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