Cigarette Smoke Formation Studies

II. Smoke Distribution and Mainstream Pyrolytic Composition of Added ^{14}C -Menthol (U)*

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INTRODUCTION

Menthol has long been a major cigarette additive and several investigators have reported limited smoke distribution data. Mitchell, Barbee, and Irby (1) have reported data on menthol transfer to mainstream cigarette smoke. Newell, Latimer, and Haefele (2) presented data on randomly labeled ^{14}C -menthol and its distribution in smoke, using non-equilibrated cigarettes; they obtained activity material balances of 85–89%. The tube pyrolysis products of menthol have been studied by Schmeltz and Schlotzhauer (3), who sought to establish the pyrolysis contribution of menthol towards the chemical properties of smoke.

This work describes the distribution of ^{14}C -menthol (U) in the total cigarette smoke, and also its distillation, combustion and pyrolysis contributions to mainstream smoke.

EXPERIMENTAL

Radiochemicals

^{14}C -Menthol, prepared biosynthetically, was isolated as described by Gager et al. (4). The chemical and radiochemical purities were determined by gas radiochromatography and were 99.5% and 99.6% respectively. The chief impurity was 0.4% of ^{14}C -labeled menthone (U) which was not separated in the gradient elution step of the isolation scheme.

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Labeled Cigarette Preparation

The cigarettes were prepared by spiking non-filtered 70 mm cigarettes with 1.1 μCi of ^{14}C -menthol (U) dissolved in 40 μl ethanol. Cold menthol was added to adjust the total concentration to 3 mg/cigarette. Spiking was accomplished by withdrawing the 50 μl syringe needle from the midpoint to each end of the cigarette. The cigarettes were equilibrated in individual glass bottles for four weeks.

Smoke Distribution Studies

The distribution of the ^{14}C -menthol (U), and/or its products, in the total cigarette smoke was determined by using a carbon-14 total recovery smoking machine (5).

The total particulate matter (TPM) was removed from the Cambridge filter pads by immediate extraction in 25 ml of ethanol (95%). The activity was extracted from the unconsumed tobacco (butt) in 25 ml of ethanol (95%). Total wet combustions conducted on Cambridge pads and butts verified complete activity recovery by the solvent extraction process used.

Using the described procedures, the sidestream and mainstream gas phases were continuously and totally converted to CO_2 , and absorbed directly into Hyamine-10X (Rohm & Haas). Aliquots of the Hyamine-10X® were taken for liquid scintillation counting.

The amount of ^{14}C -menthol (U) in the equilibrated cigarettes was determined by extracting controls in 25 ml ethanol (95%) and counting the extractant by liquid scintillation. The uniformity of dispersion of the activity along the cigarette rod was determined by sectioning cigarettes into three equal lengths. Each section was extracted and the activity was counted by liquid scintillation. The amounts were in excellent agreement because of the great ability of menthol to migrate during equilibration.

Mainstream ^{14}C -Smoke Analyses

The mainstream cigarette smoke analyses were conducted without any transfers or pre-separation by the use of a combination smoking machine and gas radiochromatograph (6).

The CO_2 from each smoke component peak was counted in a flow proportional counter as it exited from the combustion tube. Corrections were applied for the counter efficiency and split ratio to the FID. Counting efficiencies for the flow proportional counter were determined by the use of ^{14}C -toluene (New England Nuclear). Helium flow was constant from -190°C to 300°C as determined by a bubble flowmeter.

The total mainstream smoke was assayed as described by Jenkins et al. (7) by examining the following three smoke fractions separated on:

- A. Porapak®Q — This resolved compounds from C_1 to about C_7 , as well as CO and CO_2 .
- B. Carbowax-20M on Chromosorb G-HMDS — This column resolved compounds containing from 6 to 12 carbon atoms.
- C. OV-17 on Chromosorb G-HMDS — This region consists mainly of C_{12} – C_{36} containing compounds.

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Liquid Scintillation Counting

A Packard Tricarb Model 3003 liquid scintillation spectrometer with optimized gain and window settings was used. Aliquots of the ethanol extract were counted in a scintillator solution containing 72 gms naphthalene; 216 ml ethanol; 360 ml p-xylene and 360 ml dioxane. The Hyamine-10X[®] aliquots were counted in an Insta-Gel (Packard) scintillator cocktail. Counting times were regulated to give good counting statistics.

RESULT AND DISCUSSION

The distribution of activity in the smoke portions from the cigarettes containing ¹⁴C-menthol is presented in Table 1. Only a very small amount of activity is in the dropped ash, and this amount is included in the sidestream TPM values. The intact ash is included in the butt activity values. Since all cigarettes were smoked to a butt length of 20 mm from a beginning cigarette length of 70 mm, the expected menthol concentration in the butt would be 28.5% of the initial activity.

Because of the high degree of volatility of menthol, one would expect it to be present in the volatile portion of the particulate phase of smoke. Jenkins et al. (7) stated that perhaps the volatile portion of the TPM is filtered by diffusion into the leaf, whereas the non-volatile portion is filtered by impaction onto the leaf surface. From this speculation, an increase in menthol concentration in the unconsumed tobacco would be expected. The data in Table 2 show the opposite. In fact, a slight decrease in menthol concentration as a function of butt length was obtained. It would appear that menthol, when vaporized, condenses into nonvolatile smoke particles and is filtered mainly by the inefficient impaction procedure and therefore shows no concentration build-up in the butt. The slight loss in the 20 mm and even greater loss in the 10 mm butt is most likely the result of the temperature gradient that exists behind the coal at the smoking termination length. It has been reported that this gradient drops to 50° C at 10 mm behind the coal (8). Even at this temperature, some menthol vapor would be swept into the moving mainstream smoke. The percentage of menthol loss would become more significant at shorter butt lengths because of the cumulative volume of smoke and air passing over the uncombusted tobacco. This sweeping action should result in an increase in menthol delivery as a function of puff count.

Table 2. Cigarette butt menthol concentration.

Butt length (mm)	% Menthol (theoretical)	% Menthol (observed)
10	14.2	11.8
20	28.5	26.9
40	57.1	56.2
57	81.4	81.8

A puff-by-puff delivery of activity into the mainstream (Figure 1) was determined by mechanically switching in new TPM pads for each puff. As will be discussed later, menthol contributes almost 99% of this TPM pad activity, which is therefore representative of menthol delivery. These data are in contrast to those reported by Kamachi et al. (9) who reported a decrease in menthol per puff of delivery from the first until the ninth puff.

Figure 1. Puff-by-puff TPM delivery.

The mainstream smoke contribution by the ¹⁴C-menthol, its pyrolysis products, and its combustion products are presented in Table 3. The 0.1% of the mainstream activity found in the CO₂ peak is a measure of the amount of combustion products in the mainstream smoke. The amount of activity in the unidentified peaks (numbers 13 & 25) along with the 0.1% activity in peak number 18, (menthane) are indications of the amount of pyrolysis products in mainstream smoke (0.4% total). The presence of 0.4% of the mainstream activity in the menthone peak (number 22) is due mostly to the ¹⁴C-menthone concentration present in the ¹⁴C-menthol initially added to the cigarettes. By far the largest mainstream ¹⁴C-smoke product is ¹⁴C-menthol (98.9% of the total mainstream activity), indicating very little, if any, pyrolysis and combustion of menthol during the puffing of the cigarette. This mainstream compositional value of 98.9% of unchanged menthol

Table 1. Total smoke distribution.

Smoke phase	μ Ci						% Distribution
Cigarette number	1	2	3	4	5	Avg.	
Sidestream gas	0.20	0.23	0.21	0.23	0.22	0.22	21.2
Sidestream TPM	0.24	0.23	0.24	0.25	0.24	0.24	23.1
Mainstream gas	0.01	0.01	0.01	0.01	0.01	0.01	1.0
Mainstream TPM	0.30	0.29	0.27	0.30	0.30	0.29	27.9
Butt	0.27	0.29	0.27	0.29	0.26	0.28	26.9
Total recovery	1.02	1.05	1.00	1.08	1.03	1.04	100.1
Extracted average (three cigarettes)	1.03 $\pm$ 0.02						

Table 3. Distribution of activity in mainstream smoke.

GC peak number (Carbowax 20-M)	Smoke component	Activity* nCi	% of total mainstream activity
3	CO ₂	$<0.5 \pm 0.2$	0.1
13	?	0.6 ± 0.1	0.2
14-17	minor constituents total	$<0.5 \pm 0.3$	0.1
18	menthane	0.7 ± 0.1	0.2
22	menthone	1.3 ± 0.1	0.4
23	menthol	296.8 ± 4.0	98.9
25	?	$<0.5 \pm .3$	0.1
>25	—	0.0	0.0
Total recovered		301. $\pm$ 5.	100.

* Average values for five determinations corrected for system efficiency and split ratio.

is in good agreement with the value of 96.4% obtained by Newell et al. (2) by isotope dilution techniques. The small amount of activity found in the mainstream combustion and pyrolysis products and the large amount of activity present in the sidestream smoke (44.3%) may be directly related to the gas flow patterns within the cigarette during the static burning period. As stated before (7), we propose the explanation that as the momentum of the smoke stream due to the puff is lost, the flow of gases within the cigarette adjacent to the coal reverses and flows toward the burning zone. The vaporized menthol from its appropriate isotherm flows into the coal where combustion and pyrolysis can take place. A large amount of menthol escapes unchanged through and around the coal. Upon reaching the cooler air, the condensation of the unchanged menthol into smoke particles takes place. The low concentration of pyrolysis and combustion products present in the mainstream smoke may be due to the sudden reversal of flow when the cigarette is puffed, carrying small amounts of these products into the mainstream.

Schmeltz and Schlotzhauer (3), who studied the thermal decomposition products of menthol by chamber pyrolysis, found that at a temperature of 860°C only 16% of the neutral fraction remained as menthol. When the pyrolysis temperature was lowered to 600°C, 78% of the neutral fraction was menthol. If one continues to extrapolate to the boiling point of menthol (212°C), very little menthol pyrolysis would be expected. This we have shown to be the case. The data presented, showing very little menthol decomposition, reinforces earlier concern (7) about correlating pure pyrolysis data to mainstream cigarette smoke without first knowing the precursor-product relationship.

SUMMARY

The distribution of ¹⁴C-menthol (U) and its combustion and pyrolytic products in cigarette smoke is described. The mainstream smoke contains 28.9 percent of the total activity with 44.3 percent in the sidestream smoke and 26.9 percent in the butt. The major ¹⁴C-menthol smoke product in the mainstream smoke is unchanged

menthol (98.9 percent). A puff-by-puff plot of menthol delivery is presented. The results obtained are explained hypothetically.

ZUSAMMENFASSUNG

Die Arbeit behandelt die Verteilung von ¹⁴C-Menthol (U) und von dessen Verbrennungs- und Pyrolyseprodukten im Cigarettenrauch. Der Hauptstromrauch enthält 28,9%, der Nebenstromrauch 44,3% und der Stummel 26,9% der gesamten Aktivität. Überwiegend beruht die Aktivität im Hauptstromrauch auf unverändertem Menthol (98,9%). Die Mentholausbeute je Zug wird untersucht. Die Ergebnisse werden hypothetisch erklärt.

RESUME

On décrit la distribution du menthol marqué au carbone 14 (U) et de ses produits de combustion et de pyrolyse dans la fumée de cigarette. Le flux principal de fumée contient 28,9% de l'activité totale, le flux secondaire 44,3% et le mégot 26,9%. Dans le flux principal, la majeure partie des produits de combustion du 14 C-menthol est du menthol inchangé (98,9%). On présente un diagramme du dégagement de menthol bouffée par bouffée. On essaye d'expliquer les résultats obtenus par des hypothèses.

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