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From: H. R. Randolph and M. E. Parrish

Subject: MS and SS Benzene and Toluene Deliveries for Cigarette Models With and Without Mg(OH), Paper at 17, 20 and 24.8 mm Circumference

BACKGROUND

A method has been developed for determining both benzene and toluene in mainstream (MS) and sidestream (SS) smoke on a single cigarette. The cigarette was smoked using a single-port, continuously cycling smoking machine. Both MS and SS smoke were collected using traps having 25 mL of 95% ethanol. The MS collection system used one trap, while the SS required two traps in series to minimize losses due to breakthrough. Using the rectangular designed SS chamber at the optimum flow rate of 2.4 L/min., a trapping efficiency of >98% was obtained for benzene and toluene in both MS and SS smoke. After the contents of the traps were quantitatively transferred and adjusted to volume using 25 mL volumetric flasks, gas chromatography was performed using a GC equipped with a flame ionization detector (FID) and an automatic sampler (1). A J&W fused silica capillary column was used having the following characteristics: length of 60 M and 0.323 mm ID, DB-1 liquid phase, and 3 um film thickness (2). Two uL of each sample was injected with an initial oven temperature of 40°C. The temperature program profile was: 40°C for 2 minutes, 40 to 75°C at 5.0°C/min., 75 to 230°C at 15°C/min., and hold for 5 min. at the final temperature.

Benzene and toluene standards were made with cumene added as an internal standard. Standard curves were determined over the required range and found to be linear with an intercept through the origin. Mass spectral analysis of the benzene and toluene peaks in the chromatogram for Monitor 24 and several other 100% single blend component cigarettes showed that there were no interfering compounds being co-eluted (3). Figure 1 shows a chromatogram of a standard and Figures 2 and 3 show chromatograms of MS and SS smoke (1st trap only) for a Monitor 24 cigarette. All three chromatograms were obtained using the same attenuation and only the first twenty (20) minutes were printed. Using the above procedure for Monitor 24 cigarettes (n=9), the MS and SS benzene deliveries were 60±6 ug/cigt. (RSD@2σ=20%) and 280±15 ug/cigt. (RSD@2σ=11%), respectively. The MS and SS toluene deliveries were 105±10 ug/cigt. (RSD@2σ=20%) and 635±35 ug/cigt. (RSD@2σ=12%), respectively. The SS/MS ratios for benzene and toluene, based on the above data, were 4.5 and 6.0, respectively. These values are within the range reported in the literature. More precise interpretation of the SS data can be made when the SS deliveries are calculated based on the amount of tobacco and paper consumed (mg/g). The Monitor 24 benzene and toluene SS deliveries were calculated to be 0.410±0.025 mg/g and 0.925±0.055 mg/g, respectively. Interpretation of SS results based on this format is

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preferred to using only per cigarette deliveries, especially for comparisons between samples varying in tobacco weight.

Toluene/benzene ratios have been shown by Johnson and co-workers to be characteristic of the smoke formation temperature and to be independent of tobacco type (4). They reported toluene/benzene ratios for MS and SS of the Ky. Ref. 1R1 to be 1.7 and 2.0, respectively. In our work, the values for Monitor 24 were calculated to be 1.8 and 2.2, respectively, which demonstrated excellent agreement. Their work suggested that as the tobacco pyrolytic temperature increased, the toluene/benzene ratio decreased. The values obtained from this "chemical thermometer" were found to be less than the peak coal temperatures, as measured by physical means. However, changes in the toluene/benzene ratios suggest changes in the coal temperature profiles as well. Therefore, the calculation of toluene/benzene ratios may be beneficial for understanding the effects caused by changes in the physical or chemical parameters of cigarette prototypes.

The benzene and toluene method was applied to the evaluation of six (6) model cigarettes with and without $Mg(OH)_2$ paper at 17, 20, and 24.8 mm circumference. The purpose of this memo is to report the results obtained and to evaluate the data to determine what effect the $Mg(OH)_2$ paper or the circumference has on the benzene and toluene smoke deliveries. Cigarette conditioning, selection, and the data presentation format will be the same as reported previously for the ammonia and acrolein work (5-7).

SUMMARY

The toluene SS deliveries (mg/g) of the 17 and 20 mm $Mg(OH)_2$ models were lower compared to the controls, while the benzene SS deliveries (mg/g) for all all three $Mg(OH)_2$ models were higher compared to the controls. These differences were in the range of 5 to 10%. The calculation of the toluene/benzene ratios for all six samples using the SS deliveries (mg/g) suggests that the $Mg(OH)_2$ models have lower ratios relative to their respective controls. The magnitude of these reductions were 12% for the 17 mm, 11% for the 20 mm, and 8% for the 24.8 mm $Mg(OH)_2$ models. The lower toluene/benzene ratios indicate that the $Mg(OH)_2$ paper may cause an increase in the tobacco temperature of the cigarette compared to the control models.

The effect of cigarette circumference on smoke delivery was the second objective of this study. The SS deliveries (mg/g) for benzene were similar for both the 17 and 20 mm control models and they delivered ~15% more benzene than the 24.8 mm model. The same trend was observed for the SS toluene deliveries (mg/g), but the increase compared to the 24.8 mm control was less than 10%. These results were obtained with the $Mg(OH)_2$ models as well.

The conclusions made from this data set were based on real differences that were measured. However, additional experiments would be required to verify these observations since the data were a result of one model system composed of six (6) samples and the averaged smoke deliveries were based on five (5) determinations per sample.

RESULTS AND DISCUSSION

Five determinations were made for each of the six(6) model cigarettes in a random fashion over a two-week time frame. Nine (9) Monitor 24 cigarettes were analyzed along with the models. The calculated weights of the tobacco filler and paper consumed (mg), the puff counts and the burn times (min.) obtained for the benzene and toluene analyses are given below in Table I.

TABLE I

Cigarette Smoke Parameters

Sample Description	Filler & Paper Consumed (mg)		Puff Count		Burn Time (min.)	
	x	σ	x	σ	x	σ
Control - 24.8 mm (D7CZH)	871	10	12.4	0.5	11.7	0.4
$Mg(OH)_2$ - 24.8 mm (D7CZI)	912	10	10.6	1.9	10.1	1.7
Control - 20 mm (D7CZG)	546	5	9.8	0.4	9.1	0.3
$Mg(OH)_2$ - 20 mm (D7CZF)	599	5	8.0	0	7.3	0.2
Control - 17 mm (D7CZE)	414	5	7.8	0.4	7.7	0.3
$Mg(OH)_2$ - 17 mm (D7CZD)	470	5	8.2	0.4	7.6	0.4
Monitor 24	685	13	9.2	0.8	8.5	0.8

These data agree with those of previous analyses conducted within Project 6502 for this cigarette model system. The averaged MS benzene and toluene deliveries are given in Table II.

TABLE II

Averaged MS Benzene and Toluene Deliveries

Sample Description	Benzene Delivery (ug/cigt.)		(ug/puff)		Toluene Delivery (ug/cigt.)		(ug/puff)	
	x	σ	x	σ	x	σ	x	σ
Control - 24.8 mm (D7CZH)	91	13	7.3	1.0	151	20	12.2	1.6
$Mg(OH)_2$ - 24.8 mm (D7CZI)	97	11	9.2	1.0	144	8	13.6	0.8
Control - 20 mm (D7CZG)	66	6	6.7	0.6	99	8	10.1	0.8
$Mg(OH)_2$ - 20 mm (D7CZF)	65	5	8.1	0.6	97	4	12.1	0.5
Control - 17 mm (D7CZE)	40	5	5.1	0.6	62	6	7.9	0.8
$Mg(OH)_2$ - 17 mm (D7CZD)	53	6	6.5	0.7	92	9	11.2	1.1
Monitor 24	60	6	6.5	0.6	106	10	11.5	1.1

Since the cigarettes vary considerably in puff counts, comparisons should be made using the per puff deliveries. Both benzene and toluene show increased MS deliveries for cigarettes with the $Mg(OH)_2$ paper compared with their respective controls. The increase in benzene is ~25% for all three circumferences, while the toluene MS deliveries increase 10, 20 and 40% for the 24.8 mm, 20 mm and 17 mm $Mg(OH)_2$ models, respectively. In regards to the effect of circumference on the MS benzene deliveries, a reduction of 30% is achieved for the 17 mm control compared to the 24.8 mm control. A 35% reduction is obtained in the toluene MS delivery for these two models.

The SS deliveries for benzene and toluene for the six models are given in Table III.

TABLE III

SS Deliveries for Benzene and Toluene

Sample Description	Benzene Delivery (ug/cigt)		(ug/min)		(mg/g)		Toluene Delivery (ug/cigt)		(ug/min)		(mg/g)	
	x	σ	x	σ	x	σ	x	σ	x	σ	x	σ
Control-24.8 mm (D7CZH)	350	25	30	3	.40	.03	800	30	68	5	.92	.04
$Mg(OH)_2$-24.8 mm (D7CZI)	410	15	44	2	.45	.02	865	35	92	1	.95	.04
Control-20 mm (D7CZG)	250	20	27	3	.46	.04	540	50	59	6	.98	.09
$Mg(OH)_2$-20 mm (D7CZF)	295	10	40	2	.49	.02	555	10	76	2	.93	.01
Control-17 mm (D7CZE)	190	20	26	3	.46	.04	415	45	54	4	1.00	.11
$Mg(OH)_2$-17 mm (D7CZD)	225	5	30	1	.48	.01	435	20	57	2	.92	.04
Monitor 24	280	15	33	3	.41	.02	635	35	74	5	.93	.06

For all three $Mg(OH)_2$ models, the benzene SS deliveries are greater than their respective controls. The magnitude of the higher deliveries can be assessed more accurately by comparing the deliveries based on mg/g than on the per cigt. or per min. values. The increases are only 5 to 10% but this is observed for all three models. In the case of toluene, the SS deliveries (ug/cigt., ug/min., and mg/g) do not show the clear pattern as was observed for the benzene data. However, the best comparison would be using the mg/g values. These data show that the toluene SS deliveries for the 17mm and 20 mm $Mg(OH)_2$ models are reduced by 5 to 10% compared with their respective controls. The 24.8 mm $Mg(OH)_2$ model delivered 0.95 mg/g compared to 0.92 mg/g for the control. The weight difference between the control and $Mg(OH)_2$ model for the 24.8 mm circumference was much greater than for the other two circumference model samples (see Table I). The overall trend, however, suggests that the cigarettes having $Mg(OH)_2$ paper deliver 5 to 10% more benzene and 5 to 10% less toluene to the SS(mg/g) compared to their respective controls.

In regards to the effect of circumference on the SS smoke benzene and toluene deliveries (mg/g), it appears that similar results are obtained for the 17 mm and 20 mm controls, as well as the 17 mm and 20 mm $Mg(OH)_2$ models.

These smaller circumference models deliver 10 to 15% more benzene in the SS (mg/g) compared to the 24.8 mm circumference models and this is observed for the controls as well as the $Mg(OH)_2$ samples. For the above comparisons using the toluene SS delivery (mg/g), the 10 to 20% increase was only observed for the control models. The trend was not observed with the $Mg(OH)_2$ models.

The differences observed in the SS benzene and toluene deliveries between the control and $Mg(OH)_2$ cigarettes were explored in greater detail for two reasons. First, even though the measured differences were relatively small (5 to 10%), the change was positive for benzene and negative for toluene. Therefore, by obtaining a ratio of the two deliveries for each cigarette model, the individual changes detected for benzene and toluene are combined to provide a more accurate assessment of the effect $Mg(OH)_2$ paper may have on the SS smoke delivery. Secondly, it has been shown by Johnson and co-workers that the toluene/benzene ratio determined in cigarette smoke is characteristic of the smoke formation temperature (4). Therefore, these calculations may provide additional information important to understanding whether the smoke temperature is being affected by the $Mg(OH)_2$ paper. The calculated toluene/benzene ratios for MS and SS smoke for the six model cigarettes are given in Table IV.

TABLE IV

MS and SS Toluene/Benzene Ratios

Sample Description	MS Ratio (ug/cigt.)	SS Ratio (mg/g)
Control - 24.8 mm (D7CZH)	1.66	2.17
$Mg(OH)_2$ - 24.8 mm (D7CZI)	1.48	1.92
Control - 20 mm (D7CZG)	1.50	2.13
$Mg(OH)_2$ - 20 mm (D7CZF)	1.49	1.90
Control - 17 mm (D7CZE)	1.55	2.30
$Mg(OH)_2$ - 17 mm (D7CZD)	1.73	2.11
Monitor 24	1.77	2.27

While no pattern can be seen with the MS toluene/benzene ratios, the SS ratios show a definite trend, in that the models having $Mg(OH)_2$ paper show lower ratios than their respective controls. The magnitude of the decrease for the three models is ~10%. Based on the results of Johnson and co-workers, the lowering of the ratio indicates an increase in the tobacco pyrolytic temperature. Although static coal temperature measurements show a 30°C decrease for cigarettes made with $Mg(OH)_2$ paper compared with controls, there were no clear differences observed in the dynamic coal temperature measurements (8). Physical temperature measurements may not be sensitive or accurate enough to observe the pyrolytic temperature changes suggested by the "chemical thermometer" (toluene/benzene ratio data). Additional experiments would be required to verify these conclusions because the data

were a result of one model system and also were based on five (5) determinations per sample.

Immediate plans within our project are to collect quantitative data for benzene and toluene in MS and SS smoke for the 1988 fabricated 100% single blend component cigarettes in order to expand our data base for use in the SS program.

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3. We thank Ms. P. Grantham for validating the accuracy of the chromatographic separation procedure for benzene and toluene using the HP 5890 MSD system (PM Notebook # 8596, p.42.

4. W.R. Johnson, R.W. Hale, J.W. Nedlock, H.J. Grubbs, and D.H. Powell, "The Distribution of Products Between Mainstream and Sidestream Smoke", TOBACCO SCIENCE, Vol. XVIII, pp. 141-144 (1973).

5. M.E. Parrish, memo to R.A.Fenner, "MS/SS Gaseous Ammonia (TDL) and MS Total Ammonia (IC) Analyses for Cigarette Models with 17, 20, and 24.8 mm Circumference", Nov. 2, 1987.

6. H. Randolph, memo to J. Lephardt, "The Simultaneous Determination of the Total Ammonia Delivery in MS and SS Smoke for Cigarette Models with 17, 20, and 24.8 mm Circumference", Feb. 3, 1988.

7. M.E.Parrish, memo to R.A Fenner, "MS and SS Acrolein Deliveries for Cigarette Models With and Without $Mg(OH)_2$ Paper at 17, 20 and 24.8 mm Circumference, March 15, 1988.

8. B. Goodman, oral communication, June 22, 1988.

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