A methodology for calculating the effect of puffing on desorption of condensate in HCI and ISO smoking

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Introduction

The requirement for review of ISO standards for analytical smoking has triggered a debate on the most appropriate regime that should be smoked for routine analysis. The Health Canada method T-115 [1] has emerged as a possible candidate for a complementary regime to the established ISO regime.

In reviewing this method it has been noted by collaborative studies that there is a systematic difference in yield between the two main smoking machine types – the rotary and linear smoking machines [2].

The causes of these discrepancies have been investigated and two causes have been identified, firstly the dead volume inherent in rotary machine design and secondly the influence of puffing on condensate delivered to the pad [3, 4].

Understanding the influence of puff action under different smoking regimes on the measured TPM deposition on a Cambridge filter holder is essential to providing comparative measurements using different conditions and equipment.

Understanding the action of puffing for a "model" system must therefore be a cornerstone of making meaningful comparisons between different machine types

Experimental

A model "TPM" equivalent was found in the literature [5] which consists of a mixture of propylene glycol, glycerol and water in the proportions by weight of 1.7:45.5:53. 44mm. Conditioned Cambridge filter pads were placed in holders, capped and weighed then loaded by micropipette with the mixture, capped and left to rest for 24 hours then reweighed for an initial reference point. The table 1 shows the loading and puffing conditions for the experimental protocol. Puffing was conducted on a Cerulean SM450 smoking machine operated in fixed puff mode with a monoacetate filter rod of the same approximate PD as a CORESTA monitor #6 cigarette in place.

Table 1: Parameters for desorption experiments Linear smoking machine

	Puff volume	Puff duration	Puff interval	Target Loading	Puff numbers (fixed)
Run Ex1	35ml	2s	60s	85 µL	3,5,7,10,13,15,17,20
Run Ex2	55ml	2s	30s	130 µL	3,5,7,10,13,15,17,20,25,30,35,40, 45,50,55,60
Run Ex3	35ml	2s	30s	85 µL	3,5,7,10,13,15,17,20
Run Ex4	20ml	2s	30s	130 µL	3,5,7,10,13,15,17,20,23,25,27,30
Run Ex5	65ml	2s	30s	130 µL	3,5,7,10,13,15,17,20,23,25,27,30

Multiple determinations were made to build a picture of both the loss caused by successive puffs but also the influence of puff volume on the proportion of the mixture lost for each puff.

Results

The percentage losses for linear smoking for different puff volumes are shown in figure 1.

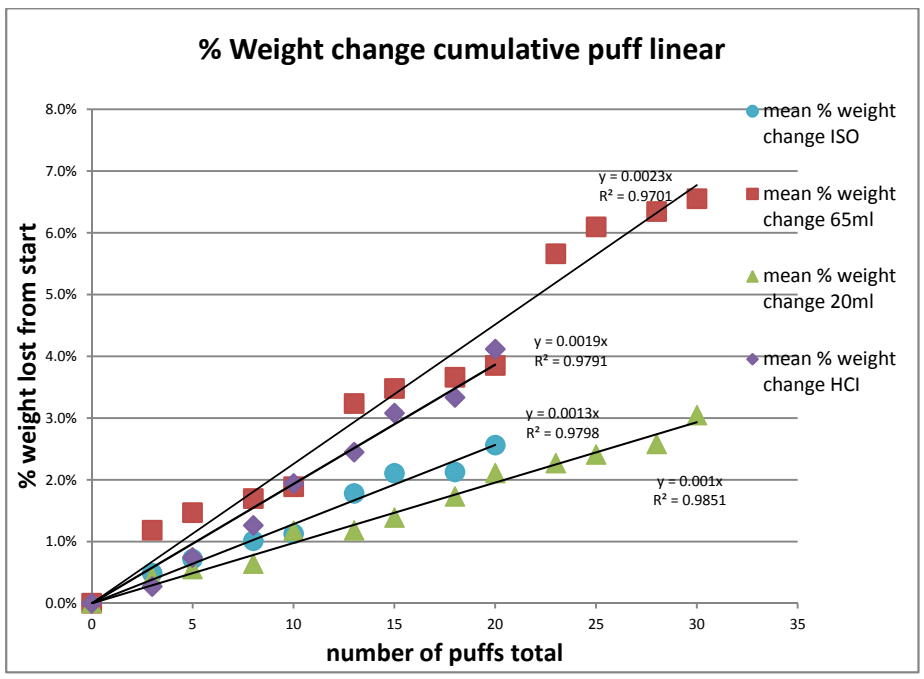

Figure 1: Plot of % weight loss of model compound with puff number for various puff volumes

It can clearly be seen that increasing the puff volume increases the proportionate loss. Each proportionate loss curve can be approximated by a straight line for the early stages of puffing which becomes increasingly nonlinear as the puff cycle progresses. If considered to be linear approximations, and the slope of the curve plotted against puff volume (figure 2) then a linear curve can be drawn allowing an approximation for the loss that may be observed with only information on puff number and volume (note changing interval did not influence the % loss of the model compound).

Discussion

From the curves presented an equation can be prepared that describes the apparent measured yield as a function of the true yield before pad desorption occurs as a function of puff volume and puff number.

$$Y_o = \frac{Y_m}{(1 - \sum_1^N f(x))}$$

Y_o = original yield of TPM if no puffing had occurred
Y_m = measured yield of TPM,
N = total number of puffs
f(x) = function of %loss related to the puff volume

This becomes based upon the observed results above and generalised for multiple cigarettes and different puff volumes;

$$Y_M = Y_O \left((1 - 4.10^{-5}VN) + (1 - 4.10^{-5}V(N - B)) + \cdots (1 - 4.10^{-5}V(N - SB))\right)$$

Where

Y_O = per cigarette yield before puffing loss
Y_M = measured yield of TPM,
N = total number of puffs
B = Per cigarette puff number
V= puff volume
S = number of puffs per channel

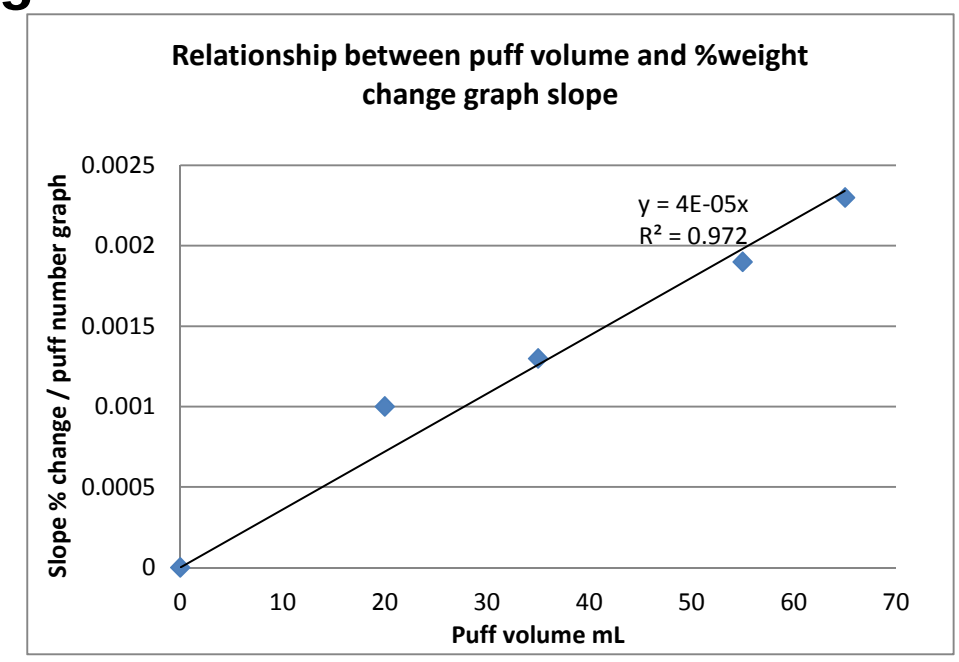

Figure 2: Plot of slope of %loss graph as a function of puff volume.

Using these equations it should be possible to predict the measured yield for a known number of puffs IF a calibration has been made using a known number of puffs. Comparing the results from the above equation for multiple rods and the experimental results shown in figure 3 it can be seen there is tolerable agreement between the theory and experimental values for 55ml puffs at 30 second intervals.

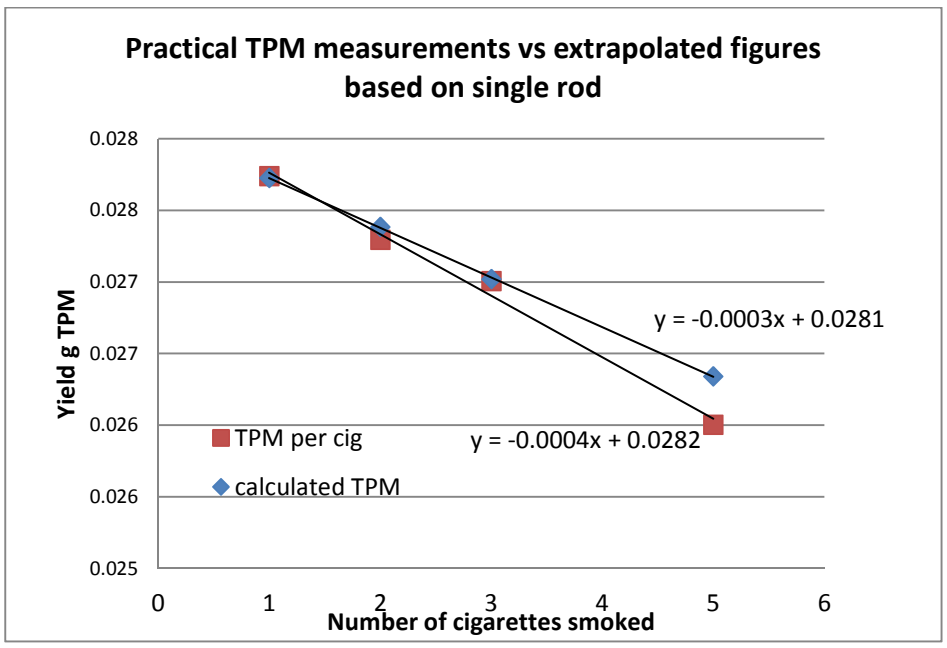

Figure 3: Actual yield for 55mL puffs and 30 second interval and calculated yield based on a single rod calibration using the derived equation (2)

As the volatile component desorbed is both puff number and volume dependant and is predictable, this has particular significance where volatile components are being considered such as some in the Hoffmann list which can be described as "semi volatile" such as the phenols. The manner of the experiment performed on the cigarettes, and equipment used, will influence the composition of the residue on the CFH and in consequence, for some analytes, the subsequent quantitative analysis. Simply considering the difference between linear and rotary smoking machines gives an insight to the nature of this effect.

As the puff number on the pad increase then desorption also increases. Where there are differences in composition on a puff by puff basis then this desorption will also have a significant impact on the pad composition. This is magnified when the high puff count from the single pad of a rotary smoking machine is considered. Here all the first puffs in a HCI experiment would encounter (for a 10 puff test) 100+ puffs whilst comparably for a linear machine the first puff would experience on average 20 puffs (1 x30, 1x20, 1x10). This moves pro rata with the puff number only achieving equivalence with the rotary system for the final puff. This has been observed in practice, significant yield differences being observed for phenols between linear and rotary machines [6].

Conclusion

A model can be prepared that predicts the loss of TPM from a theoretically "loaded" CFH. In itself this has limited use: however it does form the basis for an understanding of the errors inherent in comparative experiments where different smoking machine types are used or different numbers of cigarettes smoked.

The risks in comparing quantitative data for volatile and semi-volatile components of TPM are clarified through comparison of the losses in the rotary and linear machine set ups. For the more volatile components of TPM the rotary machine arrangement runs the risk of significantly underestimating the quantity of the component actually generated during smoking due to the greater desorption of these components.

References

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[3] "Smoking machine design and yield errors under intense smoke regimes. Part 1: The influence of dead volume on yield" Tindall, Crumpler, Mason ,TSRC 2012
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[5] Borgerding, Milhous, Hicks, Giles: "Cigarette smoke composition. Part 2 Method for determining major components in smoke of cigarettes that heat instead of burn"; J.Assoc.Off. Anal. Chem. 73 1990
[6] Rickert, Wright: "Yields of selected mainstream constituents in relation to smoking regime and smoking machine type"; 60th TSRC Montreal 2006

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