

Evaluation of an online, puff by puff method for the determination of nitric oxide, nitrogen dioxide and total mono-nitrogen oxides in fresh mainstream smoke.

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Purpose

The determination of mono nitrogen oxide species in tobacco smoke by the chemiluminescence method is well established¹, but can suffer inaccuracies from poor methodology. It has been shown that retaining gas phase in a tedlar bag for up to 30 seconds before NO_x analysis can reduce NO_x measured values by up to 30%.² It has also been shown that the “condition” and path length before measurement can reduce measured yields of NO_x.³

The goal of this study was to develop a method that could accurately determine the NO/NO₂ concentration in fresh mainstream smoke similar to that experienced by the smoker. In order to do this it is critical to develop methods that measure NO_x near instantaneously and without introducing experimental artefacts. A methodology based on fast analysis and puff by puff measurement in real time would appear to fit these criteria.

Methods

Smoke samples were collected with a semi-automatic Cerulean CR20i, 20 port rotary smoking machine interfaced with an Ecophysics chemiluminescent analyser equipped with a molybdenum converter. Data were collected over three days of smoking. Cigarettes were conditioned and smoked according to ISO standards. Gas samples were measured on a puff by puff basis and reported per puff and total mass per cigarette. For all each puff and cigarette NO, NO₂ and total NO_x were determined for the 1R5F, 3R4F and CM7 cigarette. Mainstream smoke was collected under ISO conditions. The NO_x analyzer was calibrated using certified reference gases that spanned from 500 to 1500 ppm.

Results

Analytical smoking results are shown in Table 1. Results for the determination of the concentration of NO, NO₂ and NO_x in the fresh 3R4F, 1R4F and CM7 mainstream smoke of are given in Tables 2-4. The puff by puff composition of fresh 3R4F mainstream smoke is shown in Figure 1.

Table 1: Analytical smoking results

(N=15)	3R4F	1R5F	CM7
MS TPM (mg)	10.4	2.1	15.9
Puffs/cigt	8.5	7.2	8.7

Table 2: Data for reference cigarette samples collected over three days of smoking

(N=15)	3R4F	1R5F	CM7
NO µg/cigt	227.9	105.7	95.4
NO %RSD	7.7	6.9	5.4
NO ₂ µg/cigt	58.2	19.2	33.4
NO ₂ % RSD	18.5	27.6	17
NO _x µg/cigt	286.2	125.4	129.2
NO _x %RSD	3.9	4.7	4.4

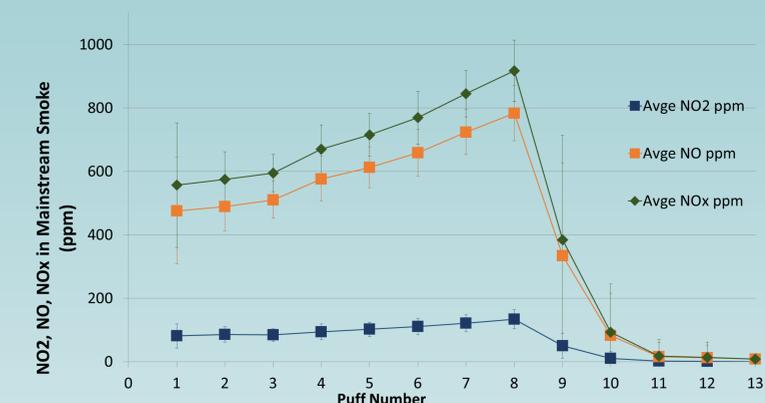
Table 3: Composition of fresh mainstream smoke

% of Total NO _x	3R4F	1R5F	CM7
% NO	79.6	84.3	73.8
% NO ₂	20.3	15.3	25.9

Table 4: Comparison with data from a linear smoking machine

	3R4F this method	3R4F from [1]	% Decrease
NO _x µg/cigt	286	198	30.8
Stdev	11.2	8.3	NA
%RSD	3.9	4.2	NA

Figure 1: 3R4F: Average Over 9 Runs of NO₂, NO and NO_x Concentration by Puff Number (Error Bars 1 Std Dev)



Conclusion

The quasi real time analysis of nitrogen oxides using a 20 port rotary machine fitted with a fast acting chemiluminescence analyser and designed specifically for the purpose has shown that puff by puff analysis is not only possible but gives highly repeatable results for monitor products. Comparisons with values obtained using systems that use smoke that may have been resident in the smoke matrix for a matter of tens of seconds show that the faster analysis is performed after formation of tobacco smoke the higher the apparent NO_x concentration. The initial first puff concentration in systems with extended dead volumes can be a factor in underestimating NO_x values, this is mitigated with the described system. It is postulated that this higher NO_x concentration would be a more representative measure of the smokers' experience. The generation of puff by puff profiles and mean rod data for a variety of monitor products allows comparison of system and laboratory performance which will be of assistance in determining the proficiency of any test performed. The increase in yield of NO_x with puff number is supported by published results.

References

- Health Canada Method T-110 "determination of oxides of nitrogen in mainstream tobacco smoke" 1999
- R.Frye, D.Urban, D.Allen "Validation of a new smoking system for detection of nitrogen oxides" TSRC 2012
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