Cooperation Centre for Scientific Research Relative to Tobacco

Smoke Analytes Sub-Group

CORESTA Recommended Method No. 104

DETERMINATION OF OXIDES OF NITROGEN (NOx) IN MAINSTREAM CIGARETTE SMOKE BY CHEMILUMINESCENCE

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0. INTRODUCTION

The CORESTA Smoke Analysis Sub-Group (SA), launched a project to develop a CORESTA Recommended Method (CRM) for the determination of oxides of nitrogen in the mainstream smoke of cigarettes generated under ISO 3308 and ISO 20778 smoking regimes.

The CRM is based on a proficiency study involving 12 laboratories from 9 countries smoking 3 samples of monitor test cigarettes 2R5F, 1R6F and CM9 under both, ISO 3308 and ISO 20778 smoking regimes. Based on the reported results, it was noted that vast majority of laboratories used the same methodology, automated chemiluminescence with in-line (11 data sets) gas analysis. Only one laboratory used the off-line analysis after outlier exclusion. Therefore, this CRM describes the in-line methodology, but off-line technique could also be used when demonstrated that the results are comparable.

1. FIELD OF APPLICATION

This method is applicable to the determination of oxides of nitrogen (NOx) in mainstream cigarette smoke by chemiluminescence.

The described method is specified using ISO 3308 and ISO 20778 smoking parameters.

The use of these machine smoking parameters reflects their inclusion in the reporting requirements of various national regulations rather than an endorsement of their appropriateness by CORESTA.

2. NORMATIVE REFERENCES

2.1 *ISO 3308*
Routine analytical cigarette-smoking machine – Definitions and standard conditions.

2.2 *ISO 8243*
Cigarettes – Sampling.

2.3 *ISO 3402*
Tobacco and tobacco products – Atmosphere for conditioning and testing.

2.4 *ISO 4387*
Cigarettes – Determination of total and nicotine-free dry particulate matter using a routine analytical smoking machine.

2.5 *ISO 20778*
Cigarettes — Routine analytical cigarette smoking machine — Definitions and standard conditions with an intense smoking regime.

2.6 *ISO 20779*
Cigarettes — Generation and collection of total particulate matter using a routine analytical smoking machine with an intense smoking regime.

3. METHOD SUMMARY

Cigarettes are smoked on a routine analytical smoking machine under ISO 3308 or ISO 20778 smoking regimes and the total particulate matter of mainstream smoke is trapped on a glass fibre filter pad (CFP). The gas phase is directly transferred on a puff-by-puff basis to an in-line connected gas analyser to determine the amounts of oxides of nitrogen. The yield is reported on a per cigarette basis.

4. APPARATUS AND EQUIPMENT

Laboratory apparatus and equipment, in particular the following items:

- Equipment for conditioning of tobacco products.
- Equipment for marking the butt length if necessary.
- Analytical smoking machine with accessories for smoking of tobacco products complying with ISO 3308 and ISO 20778 including equipment for smoking according to ISO 4387 and ISO 20779. The smoking machine needs to be connected to a chemiluminescence analyser capable to draw the mainstream smoke gas phase into the analyser measuring cell between the puffs.
- Chemiluminescence Gas-Analyzer.

5. REAGENTS AND SUPPLIES

All reagents shall be, at the least, recognized as analytical reagent grade.

- NO Calibration Gas.
    - 500 ppm was found as an appropriate concentration, but other concentrations could be used depending on the amount expected.
- Ethanol for cleaning purposes

Note: The solvents and chemicals used in this method are classified as toxic, highly toxic, harmful, carcinogenic, mutagenic, sensitising, teratogenic, irritant, corrosive, easily flammable and dangerous for the environment. The instructions specified in the individual material safety data sheets concerning safe handling, storage and waste disposal as well as protective equipment are to be followed.

6. SAMPLING

Sampling is performed in accordance with ISO 8243.

7. SAMPLE PREPARATION

Cigarettes are conditioned in accordance with ISO 3402.

Cigarettes are butt marked in accordance with ISO 4387 respectively ISO 20779.

8. SAMPLE GENERATION – SMOKING OF CIGARETTES

The smoking parameters for which the method has been studied are set out in ISO 3308 and in ISO 20778.

Table 1: Smoking parameters for ISO 3308 and ISO 20778 smoking regimes

Smoking regime	Puff volume (ml)	Puff frequency (seconds)	Puff duration (seconds)	Ventilation blocking (%)
ISO 3308	35	60	2	0
ISO 20778	55	30	2	100

The cigarettes are smoked according to ISO 4387 respectively ISO 20779.

9. PROCEDURE

9.1 Calibration of the analyser

After warming up the instrument according to the manufacturer's recommendations, purge the instrument with air and adjust to read zero.

Fill a previously evacuated gas phase collection container with the calibration gas of about 500 ppm NO, re-evacuate and refill with gas. Ensure that the gas in the container is at ambient temperature and pressure. Introduce the gas into the measuring cell of the analyser using the system sampling pump. Note the value when a steady reading has been obtained.

If necessary, adjust the instrument reading to agree with the certified value of the calibration gas.

9.2 Smoking and gas phase supply to the analyzer

9.2.1 Set up the gas phase collection system. Proceed in accordance with the instructions pertinent to the equipment used. Ensure that the collection device (tube) is properly connected and flushed before the start of smoking.

Note: Ensure that the system pump is collecting the gas phase pressure free. For example by by-passing the overrun.

9.2.2 Set up the smoking machine in accordance with ISO 3308 or ISO 20778 and smoke the cigarettes in accordance with ISO 4387 or ISO 20779.

9.2.3 After the completion of the smoking run remove the cigarette butt and take five clearing puffs.

9.2.4 Record the total number of puffs taken on each channel, i.e. smoking puffs plus clearing puffs.

9.3 Measurement of the nitrogen oxide content on a puff-by-puff basis

9.3.1 Read the analyser output and determine the observed nitrogen oxide concentration puff-by-puff.

Note: A zero-reading between the puffs could give a clear indication for the deviation of the single puffs.

9.3.2 At the end of each smoking run the gas phase collection tube must be emptied and flushed with air. The apparatus is then ready for the next smoking starting at 9.2.1.

10. CALCULATIONS

The content of NO and/or NO_2 is normally calculated by the analyzer directly by the following formula:

$$C = \frac{X * V * N * P * T_0 * M}{S * P_0 * T * V_0}$$

C Mass of NO or NO_2 concentration in per cigarette [µg/cig]

X Measured NO or NO_2 concentration [ppm]

V Puff volume e.g., 35 mL (ISO 3308) or 55 mL (ISO 20778)

N Number of puffs

P Atmospheric pressure [kPa]

P_0 Normal atmospheric pressure 101,325 [kPa]

S Number of smoked cigarettes

T Temperature during smoking [K]

T_0 Temperature triple point of water 273,15 [K]

M Molar masses of NO (30,0061 g/mol) and NO_2 (46,0055 g/mol)

V_0 Molar volume of an ideal gas (22414 mL/mol)

$$C_{NOx} = C_{NO} + C_{NO2}$$

C_{NOx} NO_x concentration per cigarette [µg/cig]

C_{NO} NO concentration per cigarette [µg/cig]

C_{NO2} NO_2 concentration per cigarette [µg/cig]

11. REPEATABILITY AND REPRODUCIBILITY

A CORESTA study was conducted in 2021 with the objective to establish a CRM for analysis for oxides of nitrogen (NOx) in mainstream cigarette smoke.

The study was conducted using 2R5F (Sample A) and 1R6F (Sample B) reference cigarettes and CM9 (Sample C) monitor cigarette smoked under ISO intense (ISO 20778) and non-intense (ISO 3308) smoking regimes. Twelve laboratories participated in the study. Based on the reported results the vast majority of laboratories used the same methodology, automated chemiluminescence with in-line (11 data sets) gas analysis.

Based on the 11 data sets received using the in-line method repeatability (r) and reproducibility (R) were calculated following the ISO 5725 Part 1 and 2 statistical procedures.

Following values for repeatability (r) and reproducibility (R) of this method were calculated for both smoking regimes and for each of the three tested reference products.

Table 2. Estimated r & R values

One test result consists of 20 cigarettes for ISO 3308 and 10 cigarettes for ISO 20778.

Sample	Mean	r	r (%)	R	R (%)
NO ISO 3308 (µg/cig)					
A	64	5,3	8,2 %	17,4	27,2 %
B	153	9,7	6,3 %	23,0	15,1 %
C	64	3,8	5,9 %	16,6	25,9 %
NO ISO 20778 (µg/cig)					
A	323	28,3	8,8 %	66,9	20,7 %
B	369	26,4	7,1 %	80,9	21,9 %
C	131	9,7	7,4 %	65,0	49,7 %
NO_x ISO 3308 (µg/cig)					
A	71	6,0	8,6 %	26,3	37,3 %
B	177	11,8	6,7 %	34,8	19,7 %
C	77	4,9	6,3 %	19,4	25,3 %
NO_x ISO 20778 (µg/cig)					
A	386	34,0	8,8 %	83,4	21,6 %
B	437	30,4	7,0 %	88,5	20,2 %
C	154	12,1	7,9 %	72,1	46,9 %

Outlying data have been removed.

12. REPORT

12.1 Test results

The expression of the laboratory data depends on the purpose for which the data are required, and the level of laboratory precision. Confidence limits shall be calculated and expressed based on the laboratory data before any rounding has taken place.

13. BIBLIOGRAPHY

[1] ISO 5725-1: Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions.

[2] ISO 5725-2: Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability (r) and reproducibility (R) of a standard measurement method.

[3] CORESTA Technical Report: 2021 Study for NOx in Mainstream Cigarette Smoke – June 2022 [SA-295-1-CTR]