CORESTA RECOMMENDED METHOD N° 55

DETERMINATION OF CARBON MONOXIDE IN THE VAPOUR PHASE OF CIGARETTE SIDESTREAM SMOKE USING A FISHTAIL CHIMNEY AND A ROUTINE ANALYTICAL/LINEAR SMOKING MACHINE

(May 2011)

0. INTRODUCTION

Cigarettes are manufactured to close tolerances using strict quality control procedures. However, all the constituents involved in the manufacture are derived from natural products and this results in a final product which is intrinsically variable. Further complexity arises as the cigarette is combusted during smoking to yield the cigarette smoke.

The quantitative measurement of carbon monoxide is therefore dependent on the arbitrary definition of the means used to generate and collect the smoke. In particular, the ambient conditions (*e.g.*, temperature, humidity, air movement within the laboratory) under which the test pieces are conditioned and smoke is collected, play a critical role in the accuracy of the measurement.

Sidestream Smoke in this Recommended Method is understood as the smoke that is evolved from the cigarette during the smoking run other than from the mouth end.

> ***Note:*** *this has to be distinguished from Environmental Tobacco Smoke (ETS), which is a mixture of aged and diluted exhaled mainstream smoke and aged and diluted sidestream smoke, and for the assessment of which the present method does not apply.*

From the time that scientists have attempted to determine carbon monoxide yields in sidestream smoke, many different methods have been adopted. However, experience has shown some procedures to be more reliable and more amenable to handling of large numbers of samples. With these factors in mind, during the 1999-2002 period, collaborative studies by a Task Force composed of CORESTA members have shown that improvements in repeatability and reproducibility result when some restrictions are placed upon the wide variety of methods and practices described in existing methods.

This Recommended Method, produced after much collaborative experimentation by many laboratories in many countries, reflects the results of the optimizations proposed and validated by the Task Force and provides one set of procedures which are the accepted reference procedures and for which repeatability and reproducibility of the determinations were assessed. Experience in the Task Force has shown how the strict adherence to the detailed set up and conditions of the method as well as the degree of proficiency of the operator affect the precision of the results.

Further, the selected method should be compatible with different modes of cigarette equilibration or puffing parameters for the smoking of the tested pieces. The standards defined by CORESTA for the determination of mainstream yields were however followed to the largest possible extent, although the machines used by the different laboratories were all of a linear type.

This method is a machine method and it allows cigarettes to be smoked using a strictly controlled set of parameters. Thus it enables the sidestream carbon monoxide yields from cigarettes, when smoked by this procedure, to be compared and ranked. In the course of its studies, the Task Force demonstrated the value of comparing the analytical processes and their stability by use of the CORESTA monitor test piece for sidestream CO yields.

Since the determination of sidestream CO yield is by nature more complex and delicate than its counterpart performed on mainstream smoke, it is highly recommended to include a control test piece in the smoking plans, as is done in mainstream determinations. It is possible to use the CORESTA monitor or any other internally designed control cigarette for this purpose. The use of an internationally recognized monitor test piece is recommended.

1. FIELD OF APPLICATION

This recommended method is applicable to the determination of carbon monoxide present in the sidestream smoke from cigarettes. The described method is specified using the ISO 3308:2000 smoking parameters (puff volume, duration and frequency) and butt length, but it is technically compatible with other smoking regimes. The method may not be directly applicable to other sidestream smoke analytes.

2. DEFINITIONS

For the purposes of this Recommended Method, the following definitions apply:

2.1. *Sidestream Vapour Phase*

That portion of the sidestream smoke which passes through a Cambridge filter pad under the conditions specified in the method.

2.2. *Smoking Process*

The use of a smoking machine to smoke cigarettes from lighting to final puff.

2.3. *Smoking Run*

A specific smoking process to produce such sidestream smoke from a sample of cigarettes as is necessary for the determination of the smoke components.

2.4. *Laboratory Sample*

The sample intended for laboratory inspection or testing and which is representative of the gross sample or the sub-period sample.

2.5. *Conditioning Sample*

The cigarettes selected from the test sample for conditioning prior to tests for sidestream carbon monoxide yield.

2.6. *Test Sample*

Cigarettes for test taken at random from the laboratory sample and which are representative of each of the increments making up the laboratory sample.

2.7. *Test Portion*

A group of cigarettes prepared for a single determination and which is a random sample from the test sample or conditioned sample as appropriate.

2.8. *Conditioned sample*

Conditioned cigarettes smoked for sidestream carbon monoxide tests.

3. REFERENCES

ISO 2971:1998
Cigarettes and filter rods - Determination of nominal diameter

ISO 3308:2000
Routine analytical cigarette-smoking machine – Definitions and standard conditions

ISO 3402:1999
Tobacco and tobacco products – Atmosphere for conditioning and testing

ISO 6488-1:1997
Tobacco -- Determination of water content -- Part 1: Karl Fischer method

ISO 6565:1999
Tobacco and tobacco products -- Draw resistance of cigarettes and pressure drop of rods -- Standard conditions and measurement

ISO 8243:1991
Cigarettes -- Sampling

ISO 8454:1995
Determination of carbon monoxide in the vapour phase of cigarette smoke (NDIR method)

CORESTA Recommended Method N° 5 (September 1993)
Determination of carbon monoxide in the mainstream smoke of cigarettes by non-dispersive infrared analysis

CORESTA Recommended Method N° 21 (August 1991)
Atmosphere for conditioning and testing tobacco and tobacco products

CORESTA Recommended Method N° 22 (August 1991)
Routine analytical cigarette-smoking machine specifications, definitions and standard conditions

CORESTA Recommended Method N° 24 (August 1991)
Cigarettes – Sampling

4. PRINCIPLE

Sampling of the test cigarettes.

Conditioning of the test cigarettes.

Smoking of the test cigarettes on a smoking machine complying with ISO 3308:2000, with the exception of the specifications on air velocity control, and equipped with a fishtail chimney and a glass-fibre filter pad for sidestream smoke collection from each channel.

Collection of sidestream smoke vapour phase and determination of its carbon monoxide content.

NOTE: The determination of the carbon monoxide content may be done either by an on-line measurement or by off-line measurement. In the latter method, the vapour phase, or a proportion of it, is first collected in a gas bag.

5. APPARATUS

Normal laboratory apparatus and in particular the following items:

5.1. *Fishtail chimneys*

Manufactured in glass, of design and dimensions shown in Figure 1 (Appendix).

NOTE: These fishtail chimneys are commercially available and may be obtained from, but not restricted to, Borgwaldt Technik GmbH and Cerulean.

5.2. *Routine analytical cigarette-smoking machine*

Modified to accept fishtail chimneys and complying with the requirements of ISO 3308:2000 with the exception of the specifications on air velocity control. A plate shall be fixed underneath each channel, with a minimal length of 120 mm and a minimal width of 50 mm, as shown in Figure 2 (Appendix).

5.3. *Non-dispersive infrared (NDIR) analyser*

Selective and calibrated for the measurement of CO in vapours and gases. Analysers are available from several manufacturers and should have a preferred working range of: 0-2% (V/V) with a linear output. The analyser should have a precision of 1% of full scale, a linearity of 1% of full scale, and a repeatability of 0.2% of full scale, under conditions of constant temperature and pressure. Its response to 10% (V/V) of CO_2 should not exceed 0.05% (V/V) as CO. Its response to 2% (V/V) of water vapour should not exceed 0.02% (V/V) as CO.

5.4. *Gas Sampling bags*

Needed only if vapour phase collection is done in bags rather than by a continuous flow system.

When a bag is used as the gas-collecting device, it should be large enough to avoid the final pressure of its contents exceeding the ambient atmospheric pressure. The volume of the bag shall also be no greater that twice the volume of the gas content collected at atmospheric pressure.

NOTE: Collection bag material must be suitable for CO and also for CO_2 if it is intended to determine the latter. Tedlar bags are suitable for CO analysis, but will allow CO_2 to gradually leak out upon storage, so that their use would mandate an immediate quantification of the latter. Saran has been shown to be an effective material for the sampling of both gases.

5.5. *A vacuum pump or pumps and flow control devices*

Capable of maintaining an air flow of 3 litres per minute through each fishtail chimney and collection train.

5.6. *PVC Tubing*

Tubing of approximately 8 mm I.D., 11 mm O.D., to connect the sidestream trap, in-line flow meter, flow regulator, vacuum pump, gas sampling bag (if used) and CO analyser.

5.7. *Timer*

A stopwatch, clock or timing device capable of measuring the elapsed time in seconds.

5.8. *Flow monitoring and regulating system on each channel*

Comprising an in-line continuous-reading flow meter, capable of monitoring the flow with a resolution of 0.2 litre per minute, followed by a precision flow-regulating device.

5.9. *Primary flow meter*

Capable of accurately measuring a flow-rate of 3 litres per minute to a precision of 0.1 litre per minute, to be used in setting the air flow in each fishtail chimney before a smoke run. As this is a primary measurement, the flow meter should measure the time needed to flush a known volume.

5.10. *Soap bubble flow meter or alternative displacement flow meter*

Capable of measuring a displaced volume of at least the desired puff volume with an accuracy of +/- 0.2 cm^3 and a resolution of 0.1 cm^3.

5.11. *Apparatus for the determination of puff duration and frequency.*

5.12. *Analytical balance*

With a resolution of 0.1 mg.

5.13. *Draw resistance testing equipment*

As specified in ISO 6565:1999

5.14. *Conditioning enclosure*

Carefully maintained in accordance with the conditions specified in ISO 3402:1999.

5.15. *Length-measuring device*

Suitable for measuring to the nearest 0.5 mm.

5.16. *Apparatus for the determination of diameter*

In accordance with ISO 2971:1998.

5.17. *Barometer*

Capable of measuring atmospheric pressures to the nearest 0.1 kPa.

6. REAGENTS

Use only reagents of recognised analytical reagent grade.

6.1. *Standard gas mixtures*

Nominally: 0.20% CO

Nominally: 0.75% CO

Gas standards with actual values within 25% of the above are acceptable.

Other gas standards may be used, when alternative calibration procedures are adopted.

The precision of the concentration of gas standard mixture should be 3% relative or better.

NOTE: If CO_2 is also to be determined, it is recommended that nominally: 0.70% CO_2, and nominally: 2.00% CO_2 standard gas mixes be used. In this case calibration gases may be a mixture of CO and CO_2, with concentrations as described above. Laboratory grade nitrogen or synthetic air is to be used for zeroing the analysers.

7. SAMPLING AND PREPARATION OF CIGARETTES

Provide a laboratory sample (see **2.4.**), by using a suitable sampling scheme. Guidance may be found in ISO 8243:1991. The sample will normally contain cigarettes taken from different parts of the population. Make up the test sample required for the test by randomly selecting cigarettes from the different parts of the population represented in the laboratory sample.

In **7.1.**, **7.2.** and **8.1.** below, the following symbols are used:

N is the number of cigarettes of a given type to be smoked, resulting from sampling at one point in time or from a sub-period sample.

C is a multiplying factor, value greater than 1, to allow for loss due to damage or selection procedures between initial sampling and smoking;

n is the number of replicate determinations of total sidestream particulate matter;

q is the number of cigarettes smoked into the same sidestream trap;

P is the total number of packets of cigarettes available;

Q is the total number of cigarettes available (laboratory sample, see **2.4**).

7.1. *Preparation of the Cigarettes for Smoking*

If N cigarettes of a given type are to be smoked, C x N cigarettes should be prepared from Q for conditioning and butt marking. The multiplier C is usually at least 1.2 to provide extra cigarettes in case some are damaged. If selection by mass or draw resistance (or any other parameter) is necessary, C will have to be much larger (experience suggests 2.0 to 4.0) depending on the selection process.

NOTE: The precision data given in this method are based on 8 replicates of 3 cigarettes. Any reduction in the number of replicates will affect the precision. It is not recommended to smoke less than 5 replicates.

The N cigarettes to be smoked will be tested in n = N/q determinations if q cigarettes are smoked into one trap. As far as possible these n determinations should correspond to different test portions of the test sample. Selection of each test portion will depend upon the form of the test sample.

7.2. *Selection of test portions of cigarettes*

7.2.1 *Selection of test portions from a bulk of Q cigarettes.*

If the test sample is in the form of a single bulk, consisting of Q cigarettes, C x N cigarettes should be selected at random so that every cigarette has an equal probability of being chosen.

7.2.2. *Selection of test portions from P packets.*

If the test sample consists of P packets, the selection procedure depends upon the number of cigarettes in each packet (Q/P) compared with q.

If Q/P ≥ C x q, select a test portion by choosing a single packet at random, then randomly select C x q cigarettes from that packet.

If Q/P < C x q, select the smallest number of packets (k) such that:

$$Q \times k / P \geq C \times q$$

and randomly choose an equal (or as near equal as possible) number of cigarettes from each packet to form the test portion of C x q cigarettes.

7.2.3. *Duplicate test portions.*

Provided that the test sample is sufficiently large (≥ 2 C x N), it would be prudent to reserve a duplicate set of n test portions. In this event the parallel selection of a test portion and its duplicate would seem sensible. In this case the two selection conditions of Section 7.2.1 would need to be changed to:

$$Q/P \geq 2\ C \times q \quad \text{and} \quad Q/P < 2\ C \times q.$$

7.3. *Marking the butt length*

7.3.1. *Standard butt length.*

The standard butt length to which cigarettes shall be marked shall be the greatest of the following three lengths:

- 23 mm
- length of filter + 8 mm
- length of overwrap + 3 mm

where the overwrap is defined as any wrapper applied to the mouth end of the cigarette and the length of the filter is defined as the total length of the cigarette minus the length of the tobacco portion.

NOTE: Butt length is defined in ISO 3308:2000 as the length of unburnt cigarette remaining at the moment when smoking is stopped.

7.3.2. *Measurement of length of filter.*

The length of filter as defined in **7.3.1.** shall be the mean value of 10 cigarettes taken from the laboratory sample measured to an accuracy of 0.5 mm. The mean shall be expressed to the nearest 0.5 mm.

NOTE: In some instances, it may be necessary to measure more than 10 cigarettes, but when the variation in filter length can be demonstrated to be well controlled, a smaller number of measurements may be sufficient.

7.3.3. *Measurement of length of overwrap.*

The length of overwrap as defined in **7.3.1** shall be the mean value of 10 overwraps taken from the laboratory sample measured to an accuracy of 0.5 mm. The mean shall be expressed to the nearest 0.5 mm.

NOTE: In some instances, it may be necessary to measure more than 10 cigarettes, but when the variation in overwrap length can be demonstrated to be well controlled, a smaller number of measurements may be sufficient.

7.3.4. *Butt length to be marked on the cigarettes before conditioning*

Draw a line, using a fine soft-tipped marker, at the standard butt length, to an accuracy of 0.5 mm, from the mouth end for the particular cigarette type.

Care should be taken to avoid damaging the cigarettes during butt marking. Any cigarettes accidentally torn or punctured during marking, or any found during marking to be defective, shall be discarded and replaced with spare cigarettes from the test portion.

If cigarettes are to be smoked on a smoking machine on which the butt length in accordance to **7.3.1.** can be pre-set, it is not necessary to mark the butt lengths on the cigarettes themselves.

7.4. *Selection of Cigarettes*

If a selection by mass or draw resistance (or any other parameter) is necessary because of the nature of the problem being studied, the selection is not to be considered as a method of reducing the number of cigarettes to be smoked.

7.5. *Conditioning*

Condition all the test portions in the conditioning atmosphere specified in ISO 3402:1999 for a minimum of 48 h and a maximum of 10 days.

If for any reason test samples are to be kept longer than 10 days store them in original packaging or in airtight containers just large enough to contain the sample.

The testing atmosphere in the laboratory where the smoking is to be carried out shall also be in accordance with ISO 3402:1999.

Transfer the test portions to the smoking location in airtight containers (just large enough to contain the portions) unless the smoking location and the conditioning location are adjoining and have identical atmospheres.

7.6. *Preliminary Tests before Smoking*

The following data may be required in the test report:

Total length of the cigarette.

Nominal diameter determined in accordance with ISO 2971:1998.

Draw resistance of the cigarette determined in accordance with ISO 6565:1999.

Average mass of the conditioned cigarettes selected for the smoking operation (milligrams per cigarette).

Water content (% mass/mass) of the conditioned cigarettes in accordance with ISO 6488-1:1997.

8. PREPARATIONS FOR THE SMOKING RUN

8.1. *Smoking Plan*

A smoking plan shall be chosen; examples are given in the annex to this Recommended Method.

The plan shall show the number of cigarettes to be smoked into each trap (q) and the number in the test sample for conditioning (C x N).

8.2. *Preparation of Mainstream and Sidestream Smoke Traps and Cigarette Holders*

For all operations the operator shall prevent contamination from the fingers by wearing gloves of a suitable material.

Prepare the mainstream smoke traps and cigarette holders according to ISO 3308:2000.

Insert into the sidestream smoke traps filter discs which have been conditioned in the test atmosphere for at least 12 h, and assemble placing the rough side of the filter disc so that it will face the oncoming smoke. After assembly, examine the filter holders to ensure that the discs have been properly fitted.

8.3. *Setting up the smoking machine*

Set up the smoking machine in accordance with ISO 4387:2000.

8.4. *Assembly of fishtail chimney and sidestream trap*

Each fishtail chimney shall be attached to an adjustable-height mounting block in such a way that it is securely held. Depending on the type of smoking machine and the degree of automation available, the mounting block may be manually or automatically raised and lowered. In its lowered position, the bottom of the fishtail chimney shall be a distance of 6 mm from the horizontal plate of the smoking machine. The raised position shall be at a height sufficient for convenient access for loading cigarettes and removing extinguished butts. An intermediate position may be used for lighting the cigarettes while maintaining the fishtail as close as possible to the cigarettes. A distance of about 60 mm above the horizontal plate has been found to be suitable.

The sidestream glass-fibre pad holder is attached to the top of the fishtail chimney by means of a suitable connector or a short piece of vacuum tubing.

8.5. *Calibration of carbon monoxide NDIR analyser*

8.5.1. *Calibration procedure*

Adjust the analysers to read zero whilst purging the measuring cell at the required flow rate.

Introduce the high gas (nominally 0.75% CO) to the analysers. Allow the digital display to stabilise and then set the analyser span. Once the analyser span is set, take a reading of the concentration for the high gas.

Introduce the low gas (nominally 0.20% CO) and allow the digital display to stabilise. Take a reading of the concentration for the low gas.

NOTE 1: For CO_2 determinations, a background reading from laboratory air should be performed to correct for the presence of CO_2 in the air when the bag collection method is used.

NOTE 2: The design of the calibrated flow meter must be such that it does not introduce a significant flow impedance (*i.e.* additional pressure drop) at a flow of 3 l/min.

NOTE 3: It is good practice when using a needle valve to control the airflow and a float type flow meter to monitor the set flow, to have the needle valve downstream of the flow meter (Figure 2).

NOTE 4: The calibration gases can be sampled into the gas analysers either directly from a continuous flow from the gas cylinders, or indirectly from gas sampling bags previously filled from the cylinders. It is very important to make sure that the gas pressure in the measurement cell of the analysers during calibration is the same as when measurements are subsequently made on the sidestream vapour phase. It is good practice to keep the gas pressure in the measurement cell as near to atmospheric pressure as possible by leaving its outlet directly open to the atmosphere, excluding any pump or flow restriction.

Plot a calibration curve of the average response factors from each calibration gas versus the concentrations of the gas mixtures used (nominally zero, 0.20%, 0.75% CO). A linear regression should be performed on the data set.

8.5.2. *Alternative Calibration Procedure*

Other procedures for calibration may be adopted. For example, the calibration gas mixture may be fed at a rate distinctly lower than 3 litres/minute into the fishtail and thence via the pump to the CO detector. The gas may be supplied from a compressed gas cylinder, or by other means (see schematic in Figure 3 (Appendix)). If the CO detector signal is recorded by an integrator, "peak" area can be calibrated against CO volume.

9. PROCEDURE FOR SMOKING RUN AND COLLECTION OF SIDESTREAM SMOKE

9.1. *Preparation of fishtail chimney*

Secure each fishtail chimney in its lower position, measuring the distance from the horizontal plate with a suitable 6-mm spacer. Raise the chimney to its upper position.

9.2. *Setting the fishtail chimney flow rate*

Switch on the vacuum pumps. By means of the associated flow indicator and needle valve, adjust the flow through each sidestream filter pad holder to 3.0 ± 0.1 litres/minute, using a suitable primary flow meter attached to the inlet of the sidestream filter pad holder. Switch off the vacuum pumps.

9.3. *Connection of sidestream glass-fibre pad holders*

Attach each sidestream trap securely to its fishtail chimney by means of a short piece of vacuum tubing or suitable connector.

9.4. *Record the atmospheric conditions*

Measure the temperature and relative humidity of the air surrounding the smoking machine and note the atmospheric pressure.

9.5. *Loading the cigarettes*

Insert the conditioned cigarettes into the cigarette holders to the insertion depth recommended in ISO 3308:2000 (9 mm). Avoid any leaks or deformations. Any cigarettes found to have obvious defects, or which have been damaged during insertion, shall be discarded and replaced with spare conditioned cigarettes.

Ensure that the cigarettes are positioned correctly so that the angle formed by the longitudinal axis of the cigarette and the horizontal plane shall be as small as possible. It shall not exceed 10° if the centre of the butt end is lower than the centre of the other end and 5° if the centre of the butt end is higher than the centre of the other end.

Adjust the position of each cigarette so that when the burning coal reaches the butt mark, the puff termination device (if applicable) is activated. If the burning through of 100 % cotton thread (40 denier) is used to terminate smoking at the butt mark, the cotton shall just touch the cigarettes at the butt mark, without modifying the cigarette positioning.

Ensure that the cigarette position is centred with respect to the fishtail, and that the fishtail covers a maximum length of the cigarette while ensuring that the distance between the end of the cigarette and the front wall of the chimney is never less than 5 mm. In the case of long cigarettes this requirement may mean that the chimney may need to be moved along the axis of the cigarette as smoking progresses, in order to ensure that the fishtail covers the butt mark of the cigarette well before this is reached. The central axis of the cigarette will be positioned at a minimum of 15 mm above the bottom edge of the fishtail chimney.

Return the fishtail chimneys to the lighting position.

9.6. *Smoking the cigarettes*

Switch on the vacuum pumps. Simultaneously (where gas bags are used to collect the smoke vapour phase) start the time recorder which will record the total time taken for the smoking run. Zero the puff counters and light each cigarette at the beginning of its first puff as specified by ISO 4387:2000. Lower each chimney to the smoking position as quickly as possible. As each butt mark is reached, immediately raise the fishtail chimney and remove the burning coal from the cigarette. Record the final reading of the puff counters. After the smoking process is complete, wait a minimum of 30 seconds before raising the chimney, in order to clear any sidestream smoke from the chimney. If required, new cigarettes shall be inserted immediately and the smoking process repeated until the predetermined number of cigarettes (normally three) has been smoked on each channel. Allow the vacuum pump to run for a minimum of 30 seconds after the last cigarette has been smoked. Stop the vacuum pump and time recorder and note the elapsed time.

NOTE: Avoid disturbance of the smoking by artificial removal of ash. Allow ash to fall naturally into the ash tray.

10. DETERMINATION OF CARBON MONOXIDE

10.1 *General Principles*

The parameters needed to calculate the sidestream carbon monoxide yield are the average volumetric concentration in the collected smoke vapour phase, the volumetric flow rate and the time taken for collection. The product of these three parameters, i.e. *concentration* x *flow rate* x *collection time*, is used to determine the total volume of carbon monoxide in the collected smoke vapour phase.

Either the on-line or the off-line method may be used to determine sidestream carbon monoxide yields.

10.1.1. *On-line Method*

A large number of carbon monoxide concentration measurements are recorded and mathematically averaged on-line. For on-line measurements, it is not necessary to independently record the collection time as this will be known from the data sampling rate and the number of data points included in the calculation of the average concentration.

10.1.2 *Off-line Method (Gas Bag Collection)*

The average sidestream carbon monoxide concentration is derived from a single measurement off-line, after allowing the sidestream vapour phase to mix in a gas sampling bag. A single measurement is recorded for each of the three parameters *concentration*, *flow rate* and *collection time,* and for each cigarette, or group of three cigarettes, smoked.

10.2. *Calculation of carbon monoxide on an on-line (continuous flow) data acquisition system*

In the case of on-line sampling, it is not appropriate to specify in detail how the data should be recorded and manipulated to calculate the volume of carbon monoxide, as there are many valid options. However an example is given here for purposes of illustration.

During data collection, read the sidestream analysers at least once per second, and store the collected data values in data arrays while logging the time. At the end of the run for each cigarette store the data arrays in a data file associated with the cigarette just smoked. For analysis of these data, ensure that data points (at least 20 seconds) are available to calculate a baseline for the data. This baseline will be used to determine what actual data will be used in the gas calculations.

The data are integrated (an average can for instance be computed using a spreadsheet) over the time between the initial deflection of the signal and the return of the detector signal to base line. The base line level has to be subtracted. If the front and back baselines do not match, an averaged value is used. The averaged signal deflection "CO data array" is recorded. The percentage by volume of carbon monoxide is determined from this averaged signal and the calibration line.

The CO yield in ml, corrected to standard temperature and pressure, is computed from the CO-analyser output (expressed as per cent CO) by the following equation:

$$V_{as} = C \times F \times R \times p \times T_0 /(S \times 100 \times p_0 \times (t + T_0))$$

where: V_{as} is the average volume of carbon monoxide per cigarette in ml
C is the percentage by volume of CO observed
F is the volumetric flow rate in ml per second
R is the vapour phase sampling time in seconds
S is the number of cigarettes smoked during the sampling period
p is the ambient pressure in kPa
t is the ambient temperature in ° Celsius
p_0 is the standard pressure (101.325 kPa)
T_0 is the temperature for the critical point of water in Kelvin (273 °K)

This yield (in ml per cigarette) can be converted to mg per cigarette by applying the following equation:

$$m_{cig} = V_{as} \times M_{CO} / V_m$$

where: m_{cig} is the average mass of carbon monoxide per cigarette in mg
M_{CO} is the molar mass of carbon monoxide in grams per mole (28)
V_m is the molar volume of an ideal gas in litres per mole (22.4 litres)

NOTE: The CO_2 if measured is calculated in the same way except the M_{CO2} for CO_2 is 44.

10.3. *Calculation of CO yields using an off-line (bag collection) system*

The volume of CO in the sidestream vapour phase collected in the bag must be calculated from the set flow rate from each port connected to the bag, and from the duration of the smoke run, *i.e.* the time elapsing between switching on the pump and switching it off. The concentration of CO (and CO_2 if measured) is determined by sampling the bag contents through the off-line NDIR analyser(s). This will then allow the calculation of the CO delivery in mg/cigarette, following the equations given in Section 9 of ISO 8454, but substituting the collected sidestream volume for the mainstream volume.

Thus,

$$V_{as} = C \times F \times R \times p \times T_0 /(S \times 100 \times p_0 \times (t + T_0))$$

where: V_{as} is the average volume of carbon monoxide per cigarette in ml
C is the percentage by volume of CO observed
F is the volumetric flow rate in ml per second
R is the vapour phase sampling time in seconds
S is the number of cigarettes smoked into the bag
p is the ambient pressure in kPa
t is the ambient temperature in degrees Celsius
p_0 is the standard atmospheric pressure (101.325 kPa)
T_0 is the temperature for the critical point of water in Kelvin (273°K)

This yield (in ml per cigarette) can be converted to mg per cigarette by applying the following equation:

$$m_{cig} = V_{as} \times M_{CO} / V_m$$

where: m_{cig} is the average mass of carbon monoxide per cigarette in mg
M_{CO} is the molar mass of carbon monoxide in grams per mole (28)
V_m is the molar volume of an ideal gas in litres per mole (22.4 litres)

NOTE: The CO_2 if measured is calculated in the same way except the M_{CO2} for CO_2 is 44.

11. SUMMARY OF OTHER TEST SAMPLE CALCULATIONS

$$\text{Puffs per cigarette} = \text{Total \# puffs per port/\# cigarettes smoked}$$

$$\text{Mainstream Pad TPM}(\text{mg/cigt}) = \frac{\text{Wt. 2 (g)} - \text{Wt. 1(g)}}{\text{\# cigts}} \times \frac{1000\text{ mg}}{\text{g}}$$

Wt. 2 = weight of mainstream filter holder after smoking
Wt. 1 = weight of mainstream filter holder prior to smoking

$$\text{Sidestream Pad TPM}(\text{mg/cigt}) = \frac{\text{Wt. 2 (g)} - \text{Wt. 1(g)}}{\text{\# cigts}} \times \frac{1000\text{ mg}}{\text{g}}$$

Wt. 2 = weight of sidestream filter holder after smoking
Wt. 1 = weight of sidestream filter holder prior to smoking

NOTE: These data should be recorded and monitored as a check on smoking conditions, but will not form part of the statistical analysis.

12. TEST REPORT

The test report shall show the method used and the results obtained. It shall also mention any operating conditions not specified in this recommended method, or regarded as optional, as well as any circumstances that may have influenced the results.

The test report shall include all details required for complete identification of the sample. Where appropriate, record the information in **12.1.** to **12.4.**

12.1. *Characteristic Data about the Cigarette*

Cigarette identification. In the case of a commercial cigarette this may include:

a) name of manufacturer, country of manufacture;
b) product name;
c) date of sampling;
d) place of purchase or sampling;
e) kind of sampling point;
f) sampling point (e.g. address of retail outlet or machine number);
g) packet number (of that product sampled that day);
h) marks on any tax stamp;
i) printed mainstream smoke yields (if any);
j) length of cigarette;
k) length of filter;
l) length of overwrap.

12.2. *Sampling*

Type of sampling procedure.
Number of cigarettes in laboratory sample.
Date and location of purchase.

12.3. *Description of Test*

Date of test.
Type of smoking machine used.
Type of smoke trap used.
Total number of cigarettes smoked in the entire determination on that cigarette type.
Number of cigarettes smoked into each smoke trap.
Butt length.
Room temperature (°C) during smoking operation.
Relative humidity (%) during smoking operation.
Atmospheric pressure (kPa) during smoking operation.

12.4. *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 on the basis of the laboratory data before any rounding has taken place.

Average length of the cigarettes to the nearest 0.1 mm.
Average length of the filter to the nearest 0.1 mm.
Average length of the overwrap to the nearest 0.1 mm.
Butt length to which cigarettes were smoked to the nearest 0.1 mm.
Average lengths of tobacco portion smoked to the nearest 0.1 mm.
Average diameter of the cigarettes (mm).
Average draw resistance of the conditioned cigarettes.
Average mass (milligrams per cigarette) of the conditioned cigarettes selected for the smoking operation.
Water content (% mass/mass) of the conditioned cigarettes (see ISO 6488-1:1997).
Average number of puffs per cigarette for each channel to the nearest 0.1 puff.

Carbon monoxide sidestream delivery (milligrams per cigarette) for each channel to the nearest 0.1 mg and the average per cigarette to the nearest 1 mg.

13. REPEATABILITY AND REPRODUCIBILITY

A major international collaborative study involving 14 laboratories and 7 cigarette samples including the CM3 test piece and spanning a wide range of blends and construction was conducted in 2002 and gave the following values for repeatability (r) and reproducibility (R) of this method.

The difference between two single results found on matched cigarette samples by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability value (r) on average not more than once in 20 cases in the normal and correct operation of the method.

Single results on matched cigarette samples reported by two laboratories will differ by more than the reproducibility (R) on average not more than once in 20 cases in the normal and correct operation of the method.

Data analysis for the 7 cigarette samples gave the estimates as summarised in the following table:

Cigarette Sample	CO (mg/cigarette)		
	Mean	**r**	**R**
A	53.96	7.06	14.27
B	60.50	7.45	14.94
C	55.93	6.92	13.46
D	58.66	6.18	11.70
E	50.87	5.63	9.39
F	50.17	5.71	10.55
CM3	58.51	6.40	12.57

For the purposes of calculating r and R, one test result was defined as the mean yield obtained from smoking 3 cigarettes in a single run. Eight test results were obtained for each cigarette sample type by each of the participating laboratories.

13.1. *Confirmation of r and R*

In 2008 the CORESTA Scientific Commission requested that the Routine Analytical Chemistry Sub Group organize a collaborative study to establish the r and R statistics for CM6. In June 2008 the experimental protocol and results template for the collaborative experiment to establish the r and R values for sidestream yields of the CM6 were circulated to the participating laboratories. Eight replicates were requested for each analyte. Twelve laboratories participated in the work and the number of data sets received from laboratories that were able to follow the protocol for each analyte were:

Conditioned weight of the CM6	11
Sidestream (SS) CO yield	12
Sidestream (SS) CO_2 yield	5

Repeatability (r) & reproducibility (R) values were calculated on the remaining data after the exclusion of outliers and these are shown in Table 1 below.

Parameter	No of Labs	Average	Repeatability r	Reproducibility R
Conditioned weight mg/CM6	11	972.49	24.16	37.71
Sidestream CO mg/CM6	11	53.02	6.24	12.35

The results from this study are comparable to those obtained from the 2002 study.

ANNEX Smoking Plans

(Informative, this Annex does not form an integral part of the Recommended Method)

In the majority of cases the results of mechanical smoking permit a comparison of types of cigarettes (treatments). This comparison should be made according to a smoking plan established in advance. The smoking plan should take account of:

the capacity and the variability of the smoking machine: number of channels;

the capacity of the sidestream smoke collection system: it determines the number of cigarettes to be smoked in each channel;

required precision: the results of smoking always give a certain variability; the distributions of the treatments in each smoking run and of the smoking runs in time should reduce the effects of uncontrolled or badly controlled factors (mechanical or personal); in general the larger the test portion, the greater the precision.

The order of magnitude of the number N of cigarettes in a test portion is fixed for each type as a function of various factors in particular:

the precision sought;

the time necessary for the smoking processes, itself related to the capacity of the machine.

The exact value to be selectedfor N, chosen in the ranges above (see Section **7.1.**) taking into account the preceding factors, is determined by calculation for each experiment taking into account the parameters which characterise it.

Also if

t	denotes the number of types to be compared (treatments);
s	denotes the number of smoking runs to be carried out;
c	denotes the number of channels on the machine;
q	denotes the number of cigarettes smoked into the same sidestream smoke collection system;

then the different parameters are related by the equation

$$t \times N = s \times c \times q$$

The examples of smoking plans proposed below illustrate the preceding remarks. They could correspond to the following objectives:

Example I
Comparison of two types of cigarettes on one single channel smoking machine. The sidestream smoke collection system can collect the sidestream condensate of three cigarettes.

Example II
Comparison of three types of cigarettes on one single channel smoking machine. The sidestream smoke collection system can collect the sidestream condensate of three cigarettes.

Example III
Comparison of two types of cigarettes on one four channel smoking machine. The sidestream smoke collection system can collect the sidestream condensate of three cigarettes.

Example IV
Comparison of five types of cigarettes on one twenty channel smoking machine. The sidestream smoke collection system can collect the sidestream condensate of three cigarettes.

Example I

Comparison of two types of cigarettes on one single channel smoking machine:

- Number of treatments	t = 2 (A, B)
- Number of cigarettes in the test sample	N = 24
- Number of cigarettes per channel	q = 3
- Number of channels	c = 1
- Number of smoking runs	s = 16 (1, 2, ... 16)

2 x 24 = 16 x 1 x 3

The number N of cigarettes to be smoked is limited to 24 of each type, so that the duration of the smoking process is not too long. Each smoking run carries only one treatment. Distribute the runs in time while repeating the following sequence four times (k represents successive values 0, 4, 8 and 12) :

Runs	Treatments
1 + k	A
2 + k	B
3 + k	B
4 + k	A

Example II

Comparison of three types of cigarettes on one single channel smoking machine

- Number of treatments	t = 3 (A, B, C)
- Number of cigarettes in the test sample	N = 24
- Number of cigarettes per channel	q = 3
- Number of channels	c = 1
- Number of smoking runs	s = 24 (1, 2, ... 24)

3 x 24 = 24 x 1 x 3

Each smoking run carries only one treatment. The runs are distributed in time in an ordered fashion, eg, by means of a matrix of the following type:

B	A	C
C	B	A
A	C	B

Example III

Comparison of two types of cigarettes on one four channel smoking machine

- Number of treatments	t = 2 (A, B)
- Number of cigarettes in the test sample	N = 24
- Number of cigarettes per channel	q = 3
- Number of channels	c = 4 (a, b, c, d)
- Number of smoking runs	s = 4 (1, 2, 3, 4)

2 x 24 = 4 x 4 x 3

Allocate the smoking channels in the two treatments utilising the matrix below, which is constructed for four treatments but which is easily adapted to the case of two treatments by identifying A with C on the one hand and B with D on the other. (In general all matrices of dimension g can be utilised for a number of treatments which are sub-multiples of g).

A	B	C	D
D	C	A	B
B	A	D	C
C	D	B	A

Channel Run	a	b	c	d
1	A	B	A	B
2	B	A	A	B
3	B	A	B	A
4	A	B	B	A

In each smoking run, two channels are allocated to each treatment. For example, in run 2:

- cigarette A is smoked in channels b and c
- cigarette B is smoked in channels a and d.

Each type is smoked twice in each of the four channels

Example IV

Comparison of five types of cigarettes on one twenty channel smoking machine

- Number of treatments	t = 5 (A, B, C, D, E)
- Number of cigarettes in the test sample	N = 24
- Number of cigarettes per channel	q = 3
- Number of channels	c = 20 (a, b, ... t)
- Number of smoking runs	s = 10 (1, 2, ... 10)

$$5 \times 24 = 2 \times 20 \times 3$$

Allocate the smoking channels to five treatments using the matrix below:

D	B	E	A	C
A	D	B	C	E
B	A	C	E	D
C	E	D	B	A
E	C	A	D	B

Channel Run	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t
1	D	B	E	A	C	C	E	D	A	B	E	C	B	A	D	B	D	A	C	E
2	A	D	B	C	E	A	C	E	B	D	C	E	A	D	B	A	B	D	E	C

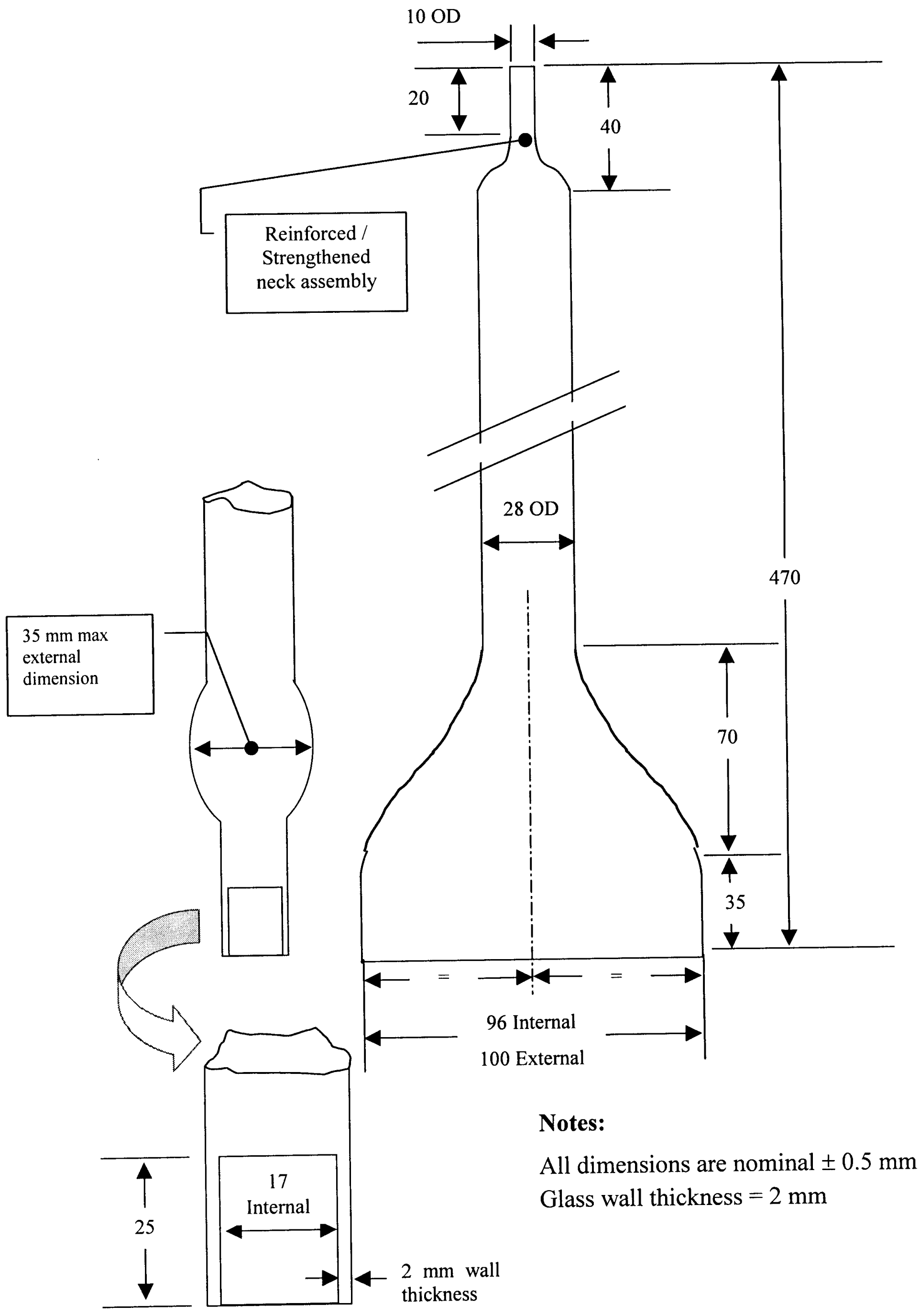
In each smoking run each treatment is smoked in four channels. For example in run 1:

- cigarette A is smoked in the channels d, i, n, r
- cigarette B is smoked in the channels b, j, m, p
- cigarette C is smoked in the channels e, f, l, s
- cigarette D is smoked in the channels a, h, o, q
- cigarette E is smoked in the channels c, g, k, t

Thus each treatment is smoked in 8 different channels.

APPENDIX - FIGURES REFERENCED IN THE TEXT

Figure 1: FISHTAIL CHIMNEY DIMENSIONS



Notes:

All dimensions are nominal ± 0.5 mm

Glass wall thickness = 2 mm

Figure 2: SIDESTREAM SMOKE COLLECTION SYSTEM

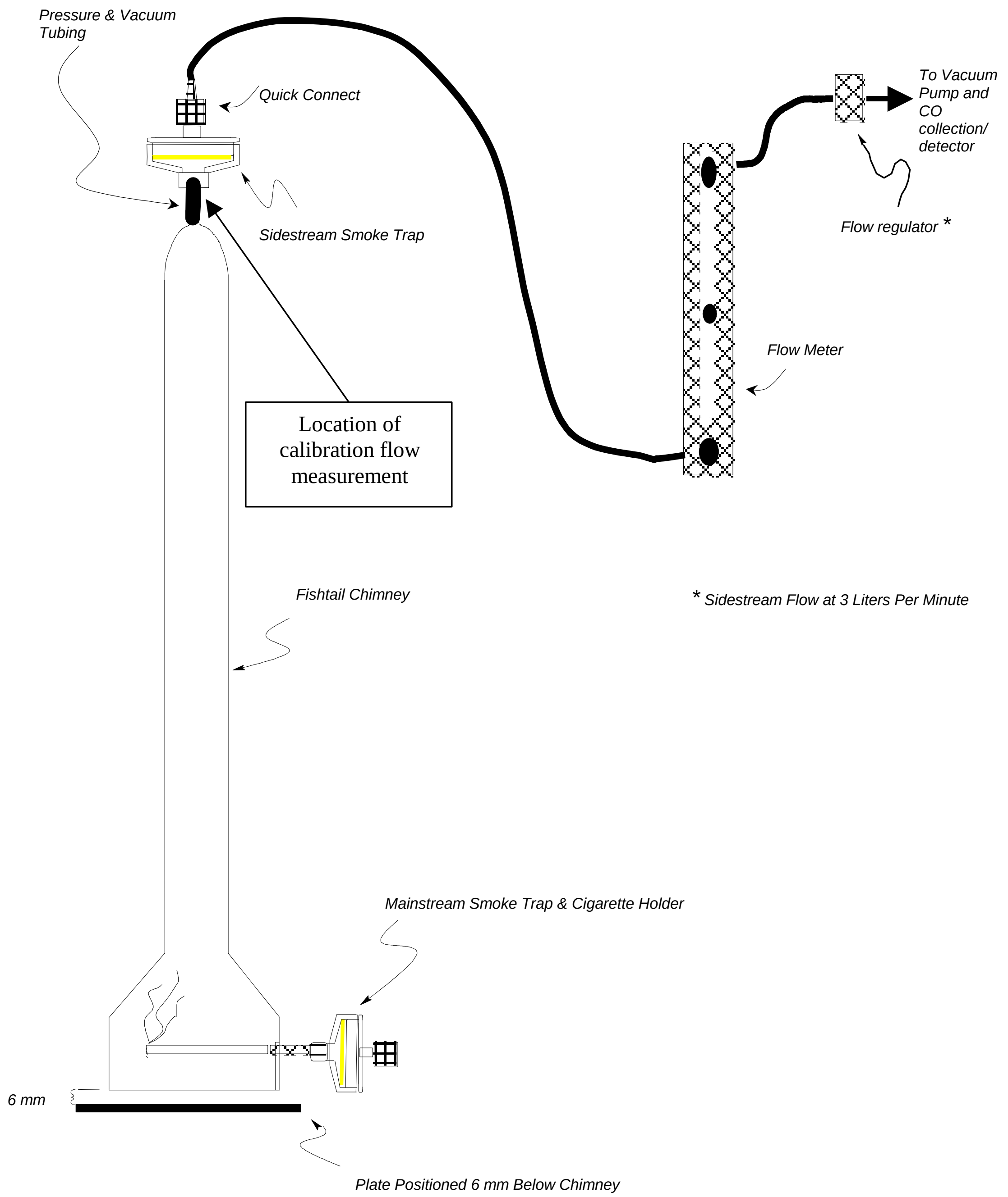


Figure 3: ALTERNATIVE PROCEDURE FOR CO CALIBRATION