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**Stationary source emissions — Sampling  
and determination of gaseous fluoride  
content**

*Émissions de sources fixes — Échantillonnage et détermination de la  
teneur en fluorure gazeux*



Reference number  
ISO 15713:2006(E)

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15713 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

## Introduction

This International Standard describes a method for the measurement of the concentration of gaseous fluoride compounds in flue gas passing through ducts or chimneys.

The effects of fluoride containing species are of concern as irritants to humans when inhaled at high concentration and because of the potential for adverse effects on vegetation.

For the purposes of this International Standard, the fluoride measured is quoted as hydrogen fluoride. The aim of the method is to measure hydrogen fluoride, but, in practice, the parameter assessed is operationally defined. The fluoride measured is from those compounds that pass through a filter and dissolve in dilute sodium hydroxide and which produce fluoride ions which remain present in solution when analysed.



# Stationary source emissions — Sampling and determination of gaseous fluoride content

## 1 Scope

This International Standard is applicable to the measurement of the gaseous fluorides that are entrained in gases carried in stacks or ducts. The gaseous fluoride content is expressed as a mass of hydrogen fluoride in the stack gas.

This International Standard is applicable to all stacks emitting gases with fluoride concentrations of below 200 mg/m<sup>3</sup>. It can be used for higher concentrations, but then the absorption efficiency of the bubblers should be checked before the results can be regarded as valid. The detection limit of the method is estimated as 0,1 mg m<sup>-3</sup>, based on a sample volume of 0,1 m<sup>3</sup>. All compounds that are volatile at the filtration temperature and produce soluble fluoride compounds upon reaction with water are measured by this method. The method does not measure fluorocarbons. The concentration of fluoride in the adsorbent solution is then measured using an ion selective electrode. The amount of fluoride measured is then expressed as hydrogen fluoride by convention, though this may not reflect the chemical nature of the compounds, which are measured.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 9096:2003, *Stationary source emissions — Manual determination of mass concentration of particulate matter*

ISO 10780, *Stationary source emissions — Measurement of velocity and volume flowrate of gas streams in ducts*

## 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

### 3.1

#### **isokinetic sampling**

sampling at a flowrate such that the velocity and direction of the gas entering the sampling nozzle is the same as that of the gas in the duct at the sampling point

[ISO 9096:2003]

### 3.2

#### **sampling point**

specific position on the sampling section at which a sample is extracted

**NOTE** Sampling points are spread out over the sampling section in order to be representative of subsections of equal areas.

**3.3**  
**STP**

standard conditions for temperature, 273,15 K, and pressure, 101,325 kPa

## **4 Principle**

As a result of the high reactivity and solubility of hydrogen fluoride, particular precautions are required to minimize irreversible loss of the species of interest and to take a representative sample. Firstly, if incorrect materials are selected for the sampling probe, impingers and connecting tubing they could react irreversibly with the species of interest. Secondly, if condensed liquid droplets are present in the probe before the impingers the species of interest may dissolve in them and so not be included in the measurement. Further, where droplets are present in the flue, if the sample is not taken isokinetically, then it may not be representative.

The flow conditions at a sampling plane are determined before sampling. If there are droplets present, then isokinetic sampling at a number of sampling points is necessary. The homogeneity of the spatial profiles of the flue gas velocity, temperature and oxygen concentration is investigated. If there is significant variability in any of these parameters, but no droplets, then sampling is carried out at a number of sampling points but at a constant flow rate. If these parameters exhibit homogeneity, then sampling is carried out at a single point at a constant flow rate.

To determine the gaseous fluoride content of the flue gas, a representative metered sample of that gas is drawn through a heated sampling probe and filter. Any droplets, which may contain dissolved gaseous fluoride compounds, are evaporated in the heated probe. Particulate bound fluoride species that may be present as solid materials are removed by filtration of particulates at a controlled temperature. Gaseous fluoride compounds or more precisely those water-soluble fluoride compounds that pass through the filter are absorbed using a sampling train made up of a series of impingers containing a sodium hydroxide solution.

The concentrations of dissolved fluoride ions in the collected solutions are measured using the ion selective electrode technique.

## **5 Reagents**

To carry out the method, the following reagents are required to be of a recognized analytical grade. If they have changed visibly, they should be discarded.

**5.1 Absorber solution**, 0,1 mol/l NaOH solution.

**5.2 Sample gas drying agent**, self-indicating coarse grade silica gel.

**5.3 Total ionic strength adjustment buffer (TISAB).**

Sodium chloride

Sodium acetate trihydrate

Trisodium citrate monohydrate

Glacial acetic acid

Deionized or distilled water

5,0 mol/l NaOH



#### 5.4 Calibration solutions.

Deionized or distilled water

Sodium fluoride

## 6 Apparatus

### 6.1 Introduction

A schematic diagram of the equipment for the sampling of gaseous fluorides is given in Figure 1. The apparatus consists of a sampling probe and filter assembly that may be heated if required, an impinger train containing sodium hydroxide solution to capture gaseous fluorides, a pressure gauge, a suction control valve, a suction pump, a gas meter, and a sample gas volume flow rate measurement system. A thermometer and manometer shall be included in the sample train to allow the temperature and relative pressure of the metered gas to be determined. A barometer shall be used to measure atmospheric pressure during the test in order that the volume of the gas sampled can be normalized to standard conditions of 273,15 K and 101,325 kPa.

### 6.2 Probe

The probe shall be a length of rigid tubing and shall be capable of withstanding the temperature within the duct. It shall be resistant to chemical attack from the various pollutants in the duct. In particular, the probe shall be resistant to fluoride attack to avoid sample loss. Suitable materials for fluoride sampling are silica or Monel<sup>®</sup> type alloys<sup>1)</sup>.

The probe shall have a heating system capable of maintaining a gas temperature at its exit of at least 423 K or  $> 20 \text{ K} \pm 5 \text{ K}$  above the dew point temperature, whichever is the higher.

The internal surfaces of the sample probe shall be cleaned thoroughly before each sample run by rinsing it with deionized water. Between samples, it will first be necessary to allow the probe to cool. The probe rinse shall be repeated until the rinse water shows no evidence of particulate matter.

### 6.3 Filter and filter housing

A filter shall be used to capture particulate material to prevent dissolution of any soluble particulate fluoride. Filters can be placed in the duct between the nozzle and the probe only if there are no droplets present, or out of the duct before the first impinger. If a filter is used outside the duct, it shall be heated to a temperature of at least 423 K or  $> 20 \text{ K} \pm 5 \text{ K}$  above the dew point temperature, whichever is the higher, to avoid condensation. If the amount of particulate fluoride within the sample is below 10 % of the total, then the filter can be omitted.

Filters and filter holders shall be made of material resistant to attack by fluorides; for example, glass frits will remove gaseous fluoride and therefore cannot be used as filter supports. Filter holders shall have an airtight seal against leakage from outside or around the filter.

The filter shall be capable of withstanding prolonged exposures up to 40 K above the temperature setting and have at least 99,5 % collection efficiency for 0,3  $\mu\text{m}$  diameter particles.

The filter housing shall be cleaned thoroughly prior to use and before each sample run using deionized distilled water until no particulate matter is present on the inner surfaces of the filter holder.

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1) Monel<sup>®</sup> type alloys is an example of a suitable product(s) available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

#### 6.4 Sampling train

The impingers shall be connected to the sampling probe using HF resistant materials. Suitable materials are polypropylene, polyethylene or Viton® tubing<sup>2)</sup>. The sampling train consists of a series of four impingers through which the sample gases are passed and the fluorides are removed into solution. The impingers can be made of quartz, polypropylene or polyethylene. Convenient sizes for impingers are 125 ml to 250 ml.

The first two impingers shall contain between 50 ml and 100 ml of 0,1 mol/l NaOH solution of analytical grade.

The third impinger shall be left empty to catch any carryover of the absorption solution.

The fourth impinger shall be used a drying unit. Its materials of construction need not be resistant to HF. It shall be filled with silica gel to dry the sample gas prior to the suction unit, gas meter and volume flow meter. Prior to use, the impingers shall all be rinsed and cleaned with distilled or deionized water and a bottlebrush.

During sampling, the gases shall enter the first impinger at its base and bubble up through the sodium hydroxide solution before entering the second impinger at its base.

The geometry of the impingers and quantity of absorbing solution employed shall be such that a gaseous fluoride absorbance efficiency of not less than 95 % is achieved at the chosen sampling flow rate and in the concentration range examined. Evidence that this criteria is met shall be demonstrated on at least one occasion at the maximum flow rate used with that design of equipment.

#### 6.5 Suction unit

The pump is used to draw the sample through the sampling train. It shall be an airtight pump capable of maintaining the selected sampling flow rate throughout the sampling period and shall be adjusted using a flow regulator.

#### 6.6 Thermometer

An airtight thermometer shall be fitted into the sample line after the drying unit and before the gas meter. The thermometer shall be capable of measuring absolute temperature to within 1 % of the absolute temperature.

#### 6.7 Differential pressure gauge

The differential pressure gauge shall be used to measure the difference in pressure between the gas entering the volume meter and atmospheric pressure. It shall be capable of measuring pressure difference to within 1% of the differential pressure.

#### 6.8 Gas volume meter

The volume of the dried sample gas shall be measured using a calibrated gas meter. The gas meter shall be capable of measuring the sampled gas volume to within 2 % of the actual volume.

#### 6.9 Sample gas flow rate meter

A flow rate meter shall be used to ensure that the sample flow rate stays within the limits specified in section 6.4 and to perform the actions described in 7.5, 7.7 and 7.8. This meter shall be capable of measuring the flow rate to within  $\pm 10$  % of the flow.

#### 6.10 Barometer

A barometer shall be used to measure the local atmospheric pressure in kilopascals (kPa) to within 1 % of the absolute pressure.

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2) Viton® tubing is an example of a suitable product(s) available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

## 6.11 Working platform

A safe working platform shall be provided at the sampling position so that all the sampling points can be reached with safety.

# 7 Sampling

## 7.1 Sampling position and sampling points

The sampling position shall comprise of suitable access port(s) through which the sampling probe can be passed into the duct. The port(s) shall be capable of being sealed when not in use. Sampling can be performed either isokinetically (if droplets are present) or non-isokinetically at points according to the relevant requirements of ISO 9096. Multipoint sampling at a constant flow rate shall be carried out according to the relevant requirements of ISO 9096. Sampling will normally be carried out on at least two duct diameters and at a number of sampling points on each line.

Where this is not possible, due to constraints of either duct design or safety considerations, the sampling plane shall be situated in a length of straight duct, preferably vertical with a constant shape and constant cross-sectional area. It shall be as far as practicable downstream from any obstruction that may cause a disturbance or produce a change in the flow (for example, a bend, a fan or a damper).

The position at which a representative sample of the gas is to be taken is an important part of the sampling procedure. Representative sampling requires the gas to be taken from a homogenous flow in the duct. To achieve this, the velocity, temperature, and the oxygen concentration, shall first be determined at representative sampling points across the chosen sampling plane. The object of this procedure is to confirm that the velocity profile conforms to the requirement of ISO 9096. The temperature and oxygen shall not vary across the duct by more than 5 % from the mean value to avoid stratification affecting the measured concentration. If no stratification is detected, then a representative location shall be chosen for sampling.

## 7.2 Minimum sampling duration and minimum sample volume

The minimum sampling period and number of samples taken will depend on the nature of the process that is producing the emissions. The sampling duration shall be at least 30 min. If emissions from a cyclical process are to be measured, the total sampling period shall cover at least one cycle of the process operation.

The minimum sampling time also needs to take into account the detection limit of the sampling and analytical method. If the process is operating under steady state conditions, the minimum sampling time and volume can be calculated prior to sampling, by using the expected emitted gas concentration or a tenth of the emission limit value if appropriate and the sample train detection limits given in 10.1. If multiple point sampling is employed, the minimum sampling time at any one point shall not be less than 3 min.

## 7.3 Number and location of sampling points

An appropriate representative location shall be chosen for sampling. The number and location of the sampling points on the sampling plane shall conform to ISO 9096, unless this is not practicable.

Sampling at a single point shall only be acceptable if the flue gas velocity, temperature, and oxygen concentrations meet the requirements stated in 7.1.

If sampling from a number of points is required, then the sampling time chosen shall be the same at each sample point.

## 7.4 Other measurements to be made prior to sampling

### 7.4.1 Volumetric gas flow through duct at the sampling plane

The measurement of the volumetric gas flow through the duct at the sampling plane will be necessary if the results are to be reported in terms of mass of pollutant emitted per unit time. The measurements shall be carried out in accordance with ISO 10780.

### 7.4.2 Moisture content of gas

The measurement of the moisture content of the gas will be necessary if the results are to be reported as a fluoride concentration on a wet basis or if the sampling is to be carried out isokinetically.

### 7.4.3 Oxygen content of gas

If sampling is to be carried out of emissions from a combustion plant and the results are to be reported after correction to a particular oxygen concentration, measurement of the flue gas oxygen concentration will be necessary during the sampling period.

## 7.5 Assembly of sampling apparatus

Sampling is carried out with the apparatus assembled as illustrated in Figure 1.

NOTE The filter can be positioned in the duct or out of the duct before the first impinger (see 6.3).

Preheat all relevant parts of the sampling train and insert the probe into the duct, so that the sampling tip is positioned at the first sampling point. Avoid contact between the probe and any deposits in the duct or sampling port. Seal the opening of the access port to minimize air in-leakage.

## 7.6 Sampling

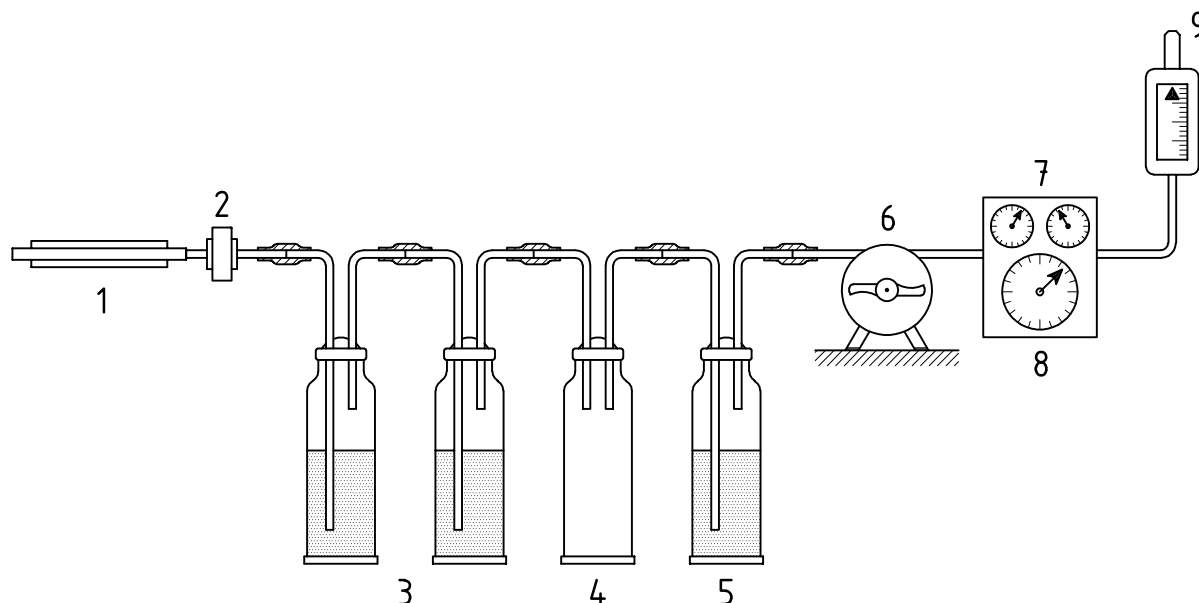
If the sampling is to be carried out isokinetically, this shall be done according to the relevant requirements of ISO 9096.

If sampling is to be carried out at multiple sampling positions, this shall be done according to the relevant requirements of ISO 9096.

Otherwise, record the time and the current gas meter reading, then start the pump. Set the sampling flow rate to the desired level using the suction control valve and the flow rate meter. The sampling rate shall be sufficient to allow vigorous bubbling within the first two impingers of the sampling train but not so vigorous that the solution is carried over into the third empty impinger. A constant sampling flow rate shall be maintained at each point (to within  $\pm 10\%$  of the chosen rate). Meter temperature and pressure should be recorded periodically. If more than one sampling point is employed on a sampling line, then move the sampling probe directly to the next point once the sampling period at that point is complete — do not switch off the pump. In this way, complete the sampling operations at all points on one line. If another line is to be employed, the suction control valve shall be closed at the end of sampling on the first line and the sampling pump switched off. The gas meter should be read and sampling operations carried out on the second line as before.

At the end of the final sampling period, the suction control valve shall be closed and the sampling pump switched off. The gas meter shall be read. A leak test of the equipment should then be carried out.

NOTE A sample rate of between 2 l/min and 6 l/min may be sufficient to allow vigorous bubbling.



### Key

- 1 heated probe
- 2 filter and housing
- 3 0,1 molar NaOH impingers
- 4 catchpot
- 5 drying tube or silica gel dreschel
- 6 pump
- 7 temperature and pressure gauges
- 8 gas meter
- 9 rotameter

Figure 1 — Schematic diagram of a sampling train

## 7.7 Leak-check procedure

A pre-test leak-check is required before and after all sampling and also if any of the sampling train components are replaced during a test. The leak rate shall not exceed 2 % of the nominal sample gas flow rate to be used.

## 7.8 Leak-checks during sample run

If, during the sampling run, a component (e.g. filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak-check shall be carried out as the initial leak check, except that it shall be done at a vacuum equal to or greater to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 2 % of the average sampling rate, the results are acceptable. If a higher leakage rate is measured, the sample is void.

## 7.9 Post-test leak-check

A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be carried out as the initial leak check, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 2 % of the average sampling rate, the results are acceptable. If a higher leakage rate is measured, the sample is void.

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## 7.10 Quality assurance

Prior to sampling make a note of the time and the current gas meter reading. During sampling, the flow rate of the sample gas shall be noted periodically, together with the temperature and pressure at the gas meter to allow the calculation of the average temperature and pressure during the sampling period.

During sampling, operatives shall periodically check and correct the following:

- that the flow rate has not drifted by more than  $\pm 10\%$  of the chosen flow rate;
- that the silica gel has not been exhausted. If the colour of the silica gel indicates that it is nearly exhausted, then the pump shall be switched off and the sampler withdrawn from the duct to be leak tested while a new bottle of silica gel is fitted into the system.

If any of the components are replaced, then the leak test shall be performed again.

The leak rate measured during any leak test shall not be greater than 4 % of the nominal flow rate. If the leak rate is greater than this, then the concentration measured will be an underestimate of the true value. If the measured concentrations are above the appropriate limit value then the result can be used as a lower estimate of the true concentration in the flue gas. However, in other circumstances, the result is invalid.

## 7.11 Sample recovery

Analysis of the particulate bound fluorides on the filter is not required by this International Standard and so it may be discarded.

The fluorides contained in the impingers shall be carefully recovered as soon as possible.

Withdraw the probe from the stack and allow it to cool so that it can be handled.

Wipe off all external particulate matter near the tip of the probe.

If a filter following the probe was used, then disconnect the probe from the sampling train and check to see if there is any condensation present within the probe. If there is evidence of condensation, the test shall be rejected. The contents of the three impingers shall be carefully poured into a sample container, each impinger shall be rinsed with approximately 20 ml of deionized distilled water, and these washings shall be added to a sample container. Repeat the process for each impinger. If the adsorption efficiency of the sampler is being determined, the impinger solutions should be kept separate.

Rinse through all the connecting tubes using 10 ml of distilled or deionized water. Repeat this three times and add the washings to the sample container. Record the volume of water used.

Seal the sample container and clearly label with the date, and a unique identifier to enable the sample to be traced back to the measurement. Take a sample of the water used.

## 7.12 Equipment field blank

An equipment field blank shall be taken at each site at which measurements are carried out by performing all of the steps of the sampling gas procedure, but without drawing exhaust gas through the sampling equipment. The resulting solution shall be treated, labelled and handled in the same manner as the test solutions. The results for the field blank shall be reported along with the samples from that site. Any samples in which the mass of fluoride ion in the field blank is greater than 10 % of the measured amount of fluoride ion shall be identified in the report.

## 8 Analytical procedure by ion selective electrode

### 8.1 Introduction

The standard method for the determination of fluoride ion content in the sample is by ion selective electrode. Fluoride ion-selective electrodes are available from several manufacturers. The manufacturer's instructions shall always be consulted particularly in the preparation of reagents and the care and storage of electrodes. The analysis may be carried out by the method of standard additions if a significant matrix effect is detected, and in some circumstances alternative TISAB solutions may be required to complex certain specific interfering ions.

### 8.2 Analytical equipment and reagents

#### 8.2.1 Equipment

- 8.2.1.1 **Fluoride ion-selective electrode.**
- 8.2.1.2 **Voltage meter**, with a direct reading of both pH and fluoride ion concentration is advisable.
- 8.2.1.3 **Reference electrode – either silver chloride or calomel.**
- 8.2.1.4 **pH electrode.**
- 8.2.1.5 **Polyethene or polypropylene coated stirrer bar and magnetic stirrer.**
- 8.2.1.6 **Polyethene or polypropylene volumetric flasks**, 1 l and 100 ml.
- 8.2.1.7 **Polyethene bottles.**
- 8.2.1.8 **Pipettes.**
- 8.2.1.9 **Polyethylene or polypropylene beakers.**

#### 8.2.2 Reagents

##### 8.2.2.1 0,1 mol/l standard fluoride solution.

0,1 mol/l standard fluoride solutions are to be made from dissolving analytical grade sodium fluoride in water. Add 4,2 g of NaF to a 1 l flask, add water and dissolve the NaF. Dilute to 1 l with water and store in a polyethene or polypropylene bottle.

##### 8.2.2.2 Total ionic strength adjustment buffer (TISAB).

Prepare the buffer, made from 800 ml water, 58,5 g sodium chloride, 14 ml glacial acetic acid, 102 g sodium acetate trihydrate and 0,3 g of sodium citrate dissolved in a 1 l flask. Adjust the pH to between 5,0 and 5,5 using sodium hydroxide solution or acetic acid. Dilute to 1 l and store in a polyethene or polypropylene bottle.

### 8.3 Calibration of ion-selective electrode

#### 8.3.1 pH Meter

For a pH meter, the calibration will be done by plotting a calibration curve using solutions prepared from the 0,1 mol/l fluoride standard solution. Pipette 10 ml of the 0,1 mol/l fluoride standard solution into a 100 ml volumetric flask and dilute to 100 ml using deionized distilled water to produce a  $10^{-2}$  mol/l solution. Use 10 ml of the  $10^{-2}$  mol/l solution to make a  $10^{-3}$  mol/l solution in the same manner. Repeat this procedure to make up  $10^{-4}$  and  $10^{-5}$  mol/l solutions.

Pipette 50 ml of each standard solution into a separate polyethylene or polypropylene beaker and add 50 ml TISAB to each beaker. The temperature of the solutions in the beakers and standards shall be kept constant to within 5 K.

Place the electrode in the most dilute solution, the  $10^{-5}$  mol/l standard, and record the mV reading once it becomes stable. This may take several minutes. Repeat the process for the other standards by moving from the dilute to more concentrated solutions, ensuring that the electrode is rinsed in deionized distilled water and then soaked in clean deionized distilled water for at least 30 seconds prior to and between measurements. If the meter reading is the electrode voltage, plot the voltage against the log of the calculated calibration solution concentration. This should produce a straight-line calibration curve for fluoride concentrations between  $10^{-1}$  and  $10^{-5}$  mol/l. Some electrodes may be slightly non-linear between  $10^{-4}$  and  $10^{-5}$  mol/l. If this non-linearity is detectable, make up additional concentrations standards between these concentrations and recalibrate in this range. The fluoride electrode shall be calibrated fully each day it is used and checked hourly against a calibration solution near to the range at which it is being used. Prepare fresh calibration solutions from the fluoride standard solution daily.

### 8.3.2 Direct reading fluoride meter

For a pH meter with direct reading of the fluoride concentration, use the calibration procedure described by the manufacturer.

## 8.4 Measurement procedure

Pipette a 50 ml aliquot from the sample into a plastic beaker. Add 50 ml of TISAB, place the stirrer bar in the beaker and place on the magnetic stirrer.

The sample shall be at the same temperature as the standard solutions used in the calibration procedure. The stirring action during mixing and measurement may increase the temperature of the sample. Hence, it may be found advisable to keep the beaker in a temperature controlled water bath.

Insert the fluoride and reference electrodes into the solution. When a steady reading is obtained, which may take several minutes, record it. If the pH meter does not have a direct concentration readout, use the calibration graph to determine the fluoride ion concentration.

Rinse the electrode thoroughly with deionized distilled water and soak in deionized distilled water for at least 30 s prior to the measurement of any subsequent sample.

NOTE As with the calibration procedure, it is good practice to measure the samples containing the lowest concentration of fluoride ions first (if known).

The selective ion electrode should be stored in buffer solution, not in distilled or deionized water.

The total mass of fluoride contained within the solution is determined by finding the product of the solution concentration in milligrams per millilitre (mg/ml) by the volume of the sample in millilitres (ml) at the point of measurement, that is after dilution by the buffer and the water used to wash the impingers and connecting tubing. The concentration of fluoride in the sodium hydroxide solution, in the water used for washing the impingers and tubing and in the buffer solution shall be determined. The mass of fluoride added from the sampling and analytical reagents may then be calculated by adding the product of the volume of each of these solutions by the fluoride concentration in each solution. This mass of fluoride shall be subtracted from the mass of fluoride in the sample.



## 9 Expression of results

### 9.1 Determination of the fluoride content of the sample, $m_F$

The fluoride content of the sample,  $m_F$ , is determined from the fluoride concentration measured in the sample as analysed in milligrams per litre and the total volume of the sample as analysed in millilitres, including the water volume used to wash the impingers and connecting tubing. The measurement shall be corrected both for the dilution of the analytical solution by the rinsing water and for the fluoride present in the reagents and rinsing water used (see 8.4).

### 9.2 Calculation of the volume of flue gas sampled at meter conditions, $V_m$

The volume of dry gas sampled ( $V_m$ ) is calculated by subtracting the final gas meter reading ( $V_f$ ) from the initial gas meter reading ( $V_i$ ) correcting for any air drawn through the gas meter during leak checks when equipment is replaced, or if carried out between sampling lines. It is assumed that the gas volume measured is on a dry basis.

$$V_m = V_f - V_i - V_l \quad (1)$$

where

$V_m$  is the volume of dry gas sampled as cubic metres ( $m^3$ );

$V_f$  is the final gas meter reading at the end of sampling expressed as cubic metres ( $m^3$ );

$V_i$  is the initial gas meter reading at the beginning of sampling expressed as cubic metres ( $m^3$ );

$V_l$  is the volume of air drawn through the gas meter during any intermediate leak tests expressed as cubic metres ( $m^3$ ).

### 9.3 Calculation of the volume of dry flue gas, $V_d$ , sampled normalized to standard temperature and pressure

$$V_d = V_m \times \frac{(p_{atm} + p_{av}) \times 273,15}{T_{av} \times 101,325} \quad (2)$$

where

$V_d$  is the volume of dry flue gas sampled normalized to standard temperature and pressure as cubic metres ( $m^3$ );

$V_m$  is the uncorrected volume of sample gas in cubic metres ( $m^3$ );

$p_{atm}$  is the local atmospheric pressure in kilopascals (kPa);

$p_{av}$  is the average pressure of the sample gas before the volume flow meter in kilopascals (kPa);

$T_{av}$  is the average temperature of the sample gas before the volume flow meter in kelvins (K).

**9.4 Mass concentration of gaseous fluorides,  $\rho_{\text{HF,dry}}$ , expressed as hydrogen fluoride in the flue gas on a dry basis at STP**

$$\rho_{\text{HF,dry}} = \frac{m_{\text{F}}}{V_{\text{d}}} \times \frac{20,0}{19,0} \quad (3)$$

where

$\rho_{\text{HF,dry}}$  is the mass concentration of gaseous fluorides expressed as hydrogen fluoride in the flue gas on a dry basis at STP in milligrams per cubic metre ( $\text{mg}/\text{m}^3$ );

$m_{\text{F}}$  is the mass of fluoride in the sample after correction for the mass of fluoride added in the blank solutions and buffer solution in milligrams (mg).

NOTE This is used along with the total sample volume of the solution to calculate the total mass of fluoride captured by the method expressed in milligrams.

**9.5 Mass concentration of gaseous fluorides,  $\rho_{\text{HF,std}}$ , expressed as hydrogen fluoride in the flue gas on a dry basis at STP and reference oxygen volume fraction**

$$\rho_{\text{HF,std}} = \rho_{\text{HF,dry}} \times \left( \frac{20,9 - \varphi_{\text{O,ref}}}{20,9 - \varphi_{\text{O,d}}} \right) \quad (4)$$

where

$\rho_{\text{HF,std}}$  is the mass concentration of gaseous fluorides expressed as hydrogen fluoride in the flue gas on a dry basis at STP and reference oxygen concentration in milligrams per cubic metre ( $\text{mg}/\text{m}^3$ );

$\varphi_{\text{O,ref}}$  is the volume fraction, in percent, of the reference oxygen for the process;

$\varphi_{\text{O,d}}$  is the volume fraction, in percent, of the average oxygen on a dry basis measured during the sampling.

**9.6 Rate of mass discharge of gaseous fluorides expressed as hydrogen fluoride,  $q_{m,\text{HF}}$**

Rate of discharge can be determined by finding the product of the concentration of HF at reference conditions in milligrams per cubic metre by the average flow rate in the stack at reference conditions.

$$q_{m,\text{HF}} = \frac{c_{\text{HF},i} \times q_{V,\text{fg},i}}{1000} \quad (5)$$

where

$q_{m,\text{HF}}$  is the rate of mass discharge of gaseous fluorides expressed as hydrogen fluoride in grams per second (g/s);

$c_{\text{HF},i}$  is the mass concentration of gaseous fluorides expressed as hydrogen fluoride at conditions  $i$  of temperature, pressure, oxygen and moisture conditions in milligrams per cubic metre ( $\text{mg}/\text{m}^3$ );

$q_{V,\text{fg},i}$  is the volume flow rate of flue gas (fg) through the sampling plane at the same conditions  $i$  of temperature, pressure, moisture and oxygen content at which the fluoride concentration is expressed in cubic metres per second ( $\text{m}^3/\text{s}$ ).

### 9.7 Mass concentration of gaseous fluorides expressed as hydrogen fluoride in the stack on a wet basis at STP expressed as HF, $\rho_{\text{HF,wet}}$

$$\rho_{\text{HF,wet}} = \frac{m_{\text{F}}}{V_{\text{d}}} \times \frac{20,0}{19,0} \times \frac{(100 - w_{\text{W}})}{100} \quad (6)$$

where

$\rho_{\text{HF,wet}}$  is the mass concentration of gaseous fluorides expressed as hydrogen fluoride in the stack on a wet basis at STP in milligrams per cubic metre ( $\text{mg}/\text{m}^3$ );

$w_{\text{W}}$  is the average water vapour content of stack gas at the sampling plane during the sampling period expressed as a percentage.

### 9.8 Mass concentration of gaseous fluorides expressed as hydrogen fluoride in the flue gas on a wet basis at STP and reference oxygen concentration, $\rho_{\text{HF,wetO}}$

$$\rho_{\text{HF,wetO}} = \rho_{\text{HF,wet}} \times \left( \frac{20,9 - \varphi_{\text{O,ref}}}{20,9 - \varphi_{\text{O,m}}} \right) \quad (7)$$

where

$\rho_{\text{HF,wetO}}$  mass concentration of gaseous fluorides expressed as hydrogen fluoride in the flue gas on a wet basis at STP and reference oxygen concentration in milligrams per cubic metre ( $\text{mg}/\text{m}^3$ ).

## 10 Performance characteristics

### 10.1 Detection limits

The detection limit of the test method can be estimated to be  $0,1 \text{ mg}/\text{m}^3$  with a sample volume of  $0,1 \text{ m}^3$  (based on a flow rate of  $4 \text{ l min}^{-1}$  for a sample period of 25 min) and a limit of detection of 1 mg for the mass of fluoride in solution.

### 10.2 Standard deviation under repeatability conditions

No information is available.

### 10.3 Uncertainty associated with the measurement

No information is available.

## 11 Test report

The test report shall refer to this International Standard and shall include at least the following information:

- a) identification of the sampling site, the date, time and duration of sampling and the sampling and analytical personnel;
- b) description of the plant or process operation conditions, including:
  - 1) any variation to the process that occurred during sampling,
  - 2) the load on the plant during monitoring,
  - 3) the maximum loading conditions of the plant;

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- c) identification of the sampling location, duct dimensions, sampling position, number and position of sampling points;
- d) flue gas characteristics at the sampling location:
  - 1) flue gas velocity,
  - 2) flue gas static pressure,
  - 3) temperature and oxygen profiles,
  - 4) flue gas water vapour content;
- e) measurement procedure:
  - 1) whether sampling was carried out isokinetically, at sampling points according to ISO 9096 with justification or at a single point with justification,
  - 2) entry nozzle diameter,
  - 3) location of filter,
  - 4) filtration temperature,
  - 5) duration of each sample;
- f) test results:
  - 1) sampled flue gas volume at meter conditions,
  - 2) average sample gas flow rate, any special circumstances or incidents,
  - 3) the volume of sample submitted for analysis,
  - 4) the concentration of fluoride in the sample measured in the laboratory,
  - 5) the corrected calculated concentration at standard conditions;
- g) quality assurance:
  - 1) leak test result,
  - 2) overall blank value from sampling and analytical reagents,
  - 3) the field blank value and information on measurement uncertainty,
  - 4) if isokinetic sampling was carried out, the relevant parts of the sampling report from ISO 9096;
- h) comments:
  - 1) indicate any special circumstances that may have influenced the results,
  - 2) any modification to the method shall be reported.

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