

MDHS

*Methods for the Determination of
Hazardous Substances*
Health and Safety Laboratory



35/2

Hydrogen fluoride and fluorides in air

Laboratory method using an ion selective
electrode or ion chromatography

April 1998

Note 1: This MDHS updates and replaces MDHS 35.¹ The principal changes which have been made are (i) to specify use of the sampling procedure for inhalable dust described in MDHS 14/2² for collection of samples of hydrofluoric acid mist and particulate fluorides, (ii) to specify use of a PTFE membrane pre-filter and a sodium carbonate-impregnated paper pad for sample collection, rather than a mixed cellulose ester membrane pre-filter and a sodium hydroxide-impregnated paper filter for sample collection, when measuring hydrogen fluoride-in-air concentrations for comparison with the short-term OES for Hydrogen fluoride, (iii) to specify use of a mixed cellulose ester membrane filter and a sodium carbonate-impregnated paper pad, rather than a mixed cellulose ester membrane filter and a sodium hydroxide-impregnated paper filter, when measuring total fluoride-in-air concentrations for comparison with the 8-hour TWA OES for Fluorides, and (iv) to describe analysis using ion chromatography as an alternative to analysis using an ion selective electrode when measuring hydrogen fluoride-in-air concentrations.

INTRODUCTION

Requirements of the Control of Substances Hazardous to Health (COSHH) Regulations 1994

1 Those who carry out and supervise the procedures described in this MDHS could be exposed to various hazardous substances, and therefore should also be aware of the requirements of the COSHH Regulations.³ These are designed to ensure that the exposure of people at work to substances that could cause health damage is either prevented, or where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH Regulations also require that persons who could be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this MDHS.

2 Guidance is given in the Approved Codes of Practices for the Control of Substances Hazardous to Health Regulations, the *General COSHH ACOP*, the Control of Carcinogenic Substances Regulations, the *Carcinogens ACOP*, and the Control of Biological Agents Regulations, the *Biological Agents ACOP*, which are included in a single publication with the COSHH Regulations.⁴

Occurrence, properties and uses

3 Fluorine, chemically bound as fluoride, is widely distributed in the earth's crust. The chief fluorine-containing minerals are fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$).

4 Hydrofluoric acid, which is an aqueous solution of hydrogen fluoride (HF), dissolves glass, reacting to form gaseous silicon tetrafluoride. Because of this property it is used for frosting, etching and polishing glass, and for removing sand from metal castings. It is also used as a catalyst in paraffin alkylation; in the separation of uranium isotopes; the manufacture of boron trifluoride and fluoride salts; in the dyeing industry; to arrest fermentation in brewing; in the production of polyfluorinated polymers; in the cleaning and weatherproofing of limestone facades; in metal pickling; and in the cleaning and polishing of cast iron, brass and copper.

5 Various alkali metal and alkaline earth fluorides have good fluxing properties for smelting, refining and melting a large variety of metals. Thus fluorspar is used as a flux in steelmaking, and calcium and sodium fluorides are used in the melting and refining of light metals and alloys. Fluorides are also used as fluxes in the smelting of nickel, copper, gold and silver. Cryolite, in the molten form, is used as an electrolyte in the production of aluminium from alumina. Fluorapatite is used extensively in the production of phosphorus, phosphoric acid phosphate fertilisers and phosphate feed supplements. Other uses of fluorides include the manufacture of hydrofluoric acid; the disinfection of hides and skins; the preservation of wood; and the coating of welding rods.

Fluorides are also produced as by-products during welding and in the manufacture of bricks, tiles, pottery, cements, glasses and enamels.

Health effects

6 Inorganic fluorides can be divided into four categories, based upon their toxicological effects:

- Group I Gaseous fluorine compounds, such as hydrogen fluoride and silicon tetrafluoride (SiF_4), which are very toxic and corrosive. The exception to this is sulphur hexafluoride, which appears to be physiologically inert when pure.
- Group II Solutions of hydrofluoric acid and fluorosilicic acid (H_2SiF_6), the acid fluorides (KHF_2 , NaHF_2) and acid solutions containing fluorides and fluorosilicates, all of which are extremely toxic and corrosive.
- Group III Soluble fluorides and fluorosilicates (NaF , KF , Na_2SiF_6 , etc), which are all highly toxic.
- Group IV Almost insoluble fluorides, such as fluorspar and cryolite, the toxicity of which is moderate or low.

Conditions which tend to increase the solubility of the less soluble fluorides make them readily absorbable and hence more toxic; the converse is also true.

7 Hydrofluoric acid is extremely corrosive. The principal health effects resulting from single exposure to the gas or to the acid mist are irritation and inflammation of the eyes, nose, upper respiratory tract and skin. Inflammation, congestion and haemorrhage of the lungs can also occur. Skin contact with anhydrous hydrogen fluoride liquid can cause painful and penetrating burns. Irreversible disfigurement and permanent eye damage may occur. Relatively brief exposure by inhalation can result in delayed symptoms of lung damage. Where there is dermal exposure to hydrogen fluoride gas, as distinct from actual splashing with the acid or the anhydrous liquid, skin irritation is especially marked in areas where the skin can be damp, ie in the flexures, such as at the elbows, and in the axillae and groin. Since hydrogen fluoride is very soluble it is easily absorbed into water, so the eyes are also very vulnerable to exposure to hydrogen fluoride gas.

8 Fluoride is an essential element in the body, and is present in most, if not all body tissues. Levels of fluoride are generally highest in the bones, dentine and tooth enamel. However, excessive exposure to fluoride from soluble fluoride salts can lead to a chronic form of fluoride poisoning known as fluorosis. Excess fluoride leads to mottling of the enamel of the teeth and can lead to weakening of the bone structure (skeletal fluorosis) and delayed healing of fractures.

9 The bifluoride salts of the alkali metals are very corrosive and locally can produce changes differing only

in degree from those of hydrofluoric acid itself. Neutral soluble fluorides are less irritant but produce the same effects as the fluoride ion following absorption into the bloodstream. Insoluble fluoride salts such as calcium fluoride do not release free fluoride ions into the bloodstream following oral ingestion.

10 Hydrogen fluoride and its solutions in water (hydrofluoric acid) are classified in the Approved Supply List⁵ of the Chemicals (Hazard Information and Packaging for Supply) Regulations 1994⁶ (the 'CHIP 2' Regulations) as:

R26/27/28 Very toxic by inhalation, in contact with the skin and if swallowed

R35 Causes severe burns

Health and safety precautions

11 Wear protective clothing and eye protection to prevent any possibility of skin or eye contact when working with hydrogen fluoride gas or hydrofluoric acid. Similar precautions might be necessary when working with corrosive inorganic fluoride compounds.

12 Each person working with hydrofluoric acid shall be provided with calcium gluconate gel and given instructions that it is always to be on his or her person. This is necessary because there can be a significant delay between dermal exposure and the onset of symptoms, particularly with lower strengths of hydrofluoric acid and with hydrogen fluoride gas.

First aid

13 If hydrofluoric acid or corrosive inorganic fluorides get into the eyes, irrigate immediately with isotonic saline for at least ten minutes and then seek medical advice.

14 If hydrofluoric acid or corrosive inorganic fluorides come into contact with the skin, immediately wash copiously with water for at least five minutes. Then apply calcium gluconate gel and massage gently into the affected area. Continue until 15 minutes after pain has subsided and then seek medical advice.

15 If a person is suspected of having suffered a high exposure by inhalation to hydrogen fluoride gas or hydrofluoric acid mist, or to corrosive and/or toxic inorganic fluoride dusts, move the person to fresh air immediately, apply artificial respiration (if necessary), administer six tablets of effervescent calcium gluconate (Sandocel tablets) in water by mouth, and get medical attention.

Exposure limits

16 The Health and Safety Commission has approved two occupational exposure standards (OESs) for fluorides. A short-term exposure limit of 2.5 mg m^{-3} , 15-minute reference period, has been set for *Hydrogen fluoride (as F)*; and a long-term exposure limit of 2.5 mg m^{-3} , 8-hour time-weighted average (TWA) reference period, has been set for *Fluorides (as F)*. These OESs are published in Table 2 of HSE Guidance Note EH 40.⁷ The criteria on

which the short-term OES for *Hydrogen fluoride* was based are documented in HSE Guidance Note EH 64.⁸

17 The European Commission's Scientific Committee on Occupational Exposure Limits (SCOEL) has considered hydrogen fluoride and inorganic fluorides, and has made recommendations for limits.⁹ These recommendations may form the basis for proposed Indicative Limit Values in the EU, but at any time the exposure limits applying in Great Britain are those appearing in the latest annual edition of EH40.⁷ The only significance of the recommendations to this publication is to define an extended validation range (see paragraph 21). At the time of writing, the recommendations made by SCOEL are for a short-term exposure limit of 5 mg m⁻³, 15-minute reference period, for *Hydrogen fluoride (as F)*; and for a long-term exposure limit of 1.5 mg m⁻³, 8-hour TWA reference period, for *Fluorides (as F)*.

Analytical methods

18 This is not a 'reference' method in the strict analytical sense of the word. There may be alternative methods available for the determination of a particular analyte. With the exception of a few cases, where an exposure is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided that they have been shown to have the accuracy and reliability appropriate to the application.

19 This method has been validated¹⁰ to demonstrate that it complies with BS EN 482 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents*.¹¹ If an alternative method is used it is necessary to demonstrate that it also meets these performance requirements.

SCOPE

20 This MDHS describes procedures for measuring the concentration of hydrogen fluoride and fluorides in workplace air using an ion-selective electrode or ion chromatography.

Note 2: *HSE's guidance booklet HSG173¹² advises employers about monitoring strategies for toxic substances. It describes how they may investigate the nature, extent and control of exposure. The objective of air monitoring is usually to determine the exposure of a worker by inhalation, and therefore the method described in this measuring procedure is written primarily for personal sampling in the breathing zone. However, it may also be used for fixed place or static sampling.*

21 The ion-selective electrode procedure is suitable for measuring hydrogen fluoride-in-air concentrations between 0.1 and 2 times the short-term OES for *Hydrogen fluoride* (see paragraph 16) and between 0.1 and 2 times the short-term exposure limit recommended by SCOEL for *Hydrogen fluoride* (see paragraph 17), using a sampling time of 15 minutes and a volumetric flow rate of 2 l min⁻¹ (see paragraph 47); and for measuring total fluoride-in-air concentrations between 0.1 and 2 times the 8-hour TWA OES for *Fluorides* (see paragraph 16) and between 0.1

and 2 times the 8-hour TWA exposure limit recommended by SCOEL for *Fluorides* (see paragraph 17), using sampling times between 1 and 8 hours and a volumetric flow rate of 2 l min⁻¹ (see paragraph 47).

22 The ion chromatography procedure is suitable for measuring hydrogen fluoride-in-air concentrations between 0.1 and 2 times the short-term OES for *Hydrogen fluoride* (see paragraph 16) and between 0.1 and 2 times the short-term exposure limit recommended by SCOEL for *Hydrogen fluoride* (see paragraph 17), using a sampling time of 15 minutes and a volumetric flow rate of 2 l min⁻¹ (see paragraph 48). However, it is not suitable for measuring total fluoride-in-air concentrations for comparison with the 8-hour TWA OES for *Fluorides* because the sample dissolution method described for analysis using ion chromatography (see paragraphs 122 and 123) is not effective for many commonly occurring particulate fluorides.

23 Certain particulate fluorides can only be taken into solution using a more vigorous sample dissolution method than the one described in this MDHS, eg an alkali fusion. The sample dissolution methods described in this MDHS are not applicable for the measurement of such substances.

METHOD PERFORMANCE

Detection limits

24 Using an ion-selective electrode, the qualitative and quantitative detection limits, defined as the concentration below which the deviation of the calibration from linearity is greater than 15% and 5% respectively, have been determined¹⁰ to be 3 µg and 9 µg of fluoride. For an air sample volume of 30 litres and a sample solution volume of 50 ml this corresponds to fluoride-in-air concentrations of 0.10 mg m⁻³ and 0.30 mg m⁻³.

25 Using ion chromatography, the qualitative and quantitative detection limits, defined as three times and ten times the standard deviation of a blank determination, have been determined¹⁰ to be 0.019 µg ml⁻¹ and 0.064 µg ml⁻¹ of fluoride. For an air sample volume of 30 litres and a sample solution volume of 50 ml this corresponds to fluoride-in-air concentrations of 0.03 mg m⁻³ and 0.11 mg m⁻³.

Bias

Sampler bias

26 The collection efficiency of sodium carbonate-impregnated paper pads for hydrogen fluoride was not determined in the validation of the measuring procedures described in this MDHS. However, a similar sampling method used in a measuring procedure described by ASTM¹³ has been evaluated, and it has been shown¹⁴ that sodium carbonate-impregnated paper pads exhibit a recovery of 99.1% for samples containing between 0.03 mg and 2.9 mg of fluoride. It is reasonable to expect that the collection efficiency of the sodium carbonate-impregnated paper pads will be similar for the slightly wider measuring range over which the analytical method described in this MDHS was validated, ie between 7.5 µg and 4800 µg of fluoride.

27 The bias of inhalable samplers has been shown¹⁵ to vary considerably. However, a bias of less than $\pm 5\%$ is typical for the samplers recommended in MDHS 14/2.²

28 In order to simplify the process of estimating the overall uncertainty of the measuring procedures described in this MDHS, the sampler bias was taken to be $\pm 5\%$ in all cases when estimating the bias of the measuring procedures as a whole using Equation 1.

Analytical bias

29 The sample dissolution method used in the ion-selective electrode procedure has been tested¹⁶ on two of the most common fluorides encountered in industrial use or occurring in workplace air, namely calcium fluoride and aluminium fluoride. The mean analytical recovery of fluoride was $101.5\% \pm 5.0\%$ for samples of between 0.1 mg and 5 mg of CaF_2 , and $99.6\% \pm 3.8\%$ for samples of between 0.1 mg and 5 mg of $\text{AlF}_3 \cdot 3\frac{1}{2} \text{H}_2\text{O}$.

30 Using an ion-selective electrode, the mean analytical recovery for 36 sodium carbonate-impregnated paper pads spiked with between 7.5 μg and 300 μg of fluoride has been determined¹⁰ to be $97.5 \pm 7.0\%$; and the mean analytical recovery for 96 membrane filters spiked with between 36 μg and 4800 μg of fluoride has been determined¹⁰ to be $100.4 \pm 3.3\%$.

31 Using ion chromatography, the mean analytical recovery for 36 sodium carbonate-impregnated paper pads spiked with between 7.5 μg and 300 μg of fluoride has been determined¹⁰ to be $102.3 \pm 10.8\%$.

32 Laboratory experiments^{10,16} therefore indicate that the analytical methods described do not exhibit significant bias. An analytical bias of zero was therefore substituted in Equation 1 when estimating the bias of the measuring procedures as a whole.

Combination of sampling and analytical bias

33 The bias of the measuring procedure as a whole is given by:

$$(1 + \textit{bias}) = (1 + \textit{bias}_{\text{ sampler }}) \times (1 + \textit{bias}_{\text{ analysis }}) \quad \text{Equation 1}$$

Precision

Imprecision of the aerosol sampling process

34 The imprecision of the aerosol sampling process usually depends strongly on the size distribution of the airborne particles sampled, and it can depend on other factors, such as windspeed. Draft European Standard EN (00137009)¹⁷ suggests calculating approximate values of the imprecision of the sampling process relevant to the workplace atmosphere to be sampled, using information given in the sampler test report.

35 However, this approach is not practicable for assessing the performance of a measuring procedure

intended for general application. The results of a study to evaluate the performance of inhalable samplers¹⁵ suggest that the relative standard deviation of the aerosol sampling process is normally less than 5% for inhalable samplers that meet the requirements of draft European Standard EN (00137009).¹⁷ The relative standard deviation of the aerosol sampling process, $RSD_{\text{ sampler }}$, was therefore taken to be 5% when estimating the imprecision of the measuring procedures as a whole using Equation 2.

Imprecision arising from flow rate variability

36 In the case of aerosol samplers where there is no interaction between particle size selection characteristics and volumetric flow rate, at least for small changes in flow rate, the imprecision arising from flow rate variability can be estimated simply. BS EN 1232 *Workplace atmospheres - Pumps for personal sampling of chemical agents - Requirements and test methods*¹⁸ prescribes a maximum allowable error in the volumetric flow rate of $\pm 5\%$. Assuming that this is met on 99% of all occasions, the flow-related relative standard deviation, $RSD_{\text{ flow }}$, is equal to 0.05/3. This value was therefore used when estimating the imprecision of the measuring procedures as a whole using Equation 2.

Imprecision arising from analytical variability

37 Using an ion-selective electrode, the relative standard deviation of the analytical method, $RSD_{\text{ analysis }}$, has been determined¹⁰ to be less than 6.9% for samples in the range 7.5 μg to 300 μg of fluoride on sodium carbonate-impregnated paper pads; and less than 1.6% for samples in the range 36 μg to 4800 μg of fluoride on membrane filters.

38 Using ion chromatography, the relative standard deviation of the analytical method, $RSD_{\text{ analysis }}$, has been determined¹⁰ to be less than 8.3% for samples in the range 7.5 μg to 300 μg of fluoride on sodium carbonate-impregnated paper pads.

39 The determined relative standard deviations were substituted in Equation 2 to estimate the imprecision of the measuring procedures as a whole for each mass of fluoride.

Combination of sampling and analytical precision

40 The imprecision of the measuring procedure as a whole is given by:

$$RSD^2 = RSD_{\text{ sampler }}^2 + RSD_{\text{ flow }}^2 + RSD_{\text{ analysis }}^2 \quad \text{Equation 2}$$

Overall uncertainty

41 The overall uncertainty for a measuring procedure is defined in BS EN 482¹¹ as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is expressed in percentage terms, by a combination of bias and precision according to the following equation:

$$OU = \frac{|\bar{x} - x_{ref}| + 2\sigma_{(n-1)}}{x_{ref}} \times 100\% \quad \text{Equation 3}$$

where: *OU* is the overall uncertainty of the procedure;

\bar{x} is the mean value of results of *n* repeated measurements;

x_{ref} is the true or accepted reference value; and

$\sigma_{(n-1)}$ is the standard deviation of *n* repeated measurements.

42 Equation 3 can be rewritten as:

$$OU = [bias + (2 \times RSD)] \times 100\% \quad \text{Equation 4}$$

where: *bias* is the difference between the mean measured concentration and the true or reference concentration, divided by the true or reference concentration, ie $\frac{(\bar{x} - x_{ref})}{x_{ref}}$; and

RSD is the relative standard deviation of *n* repeated measurements defined as $\frac{\sigma_{(n-1)}}{x_{ref}}$.

43 The overall uncertainty can then be estimated by substituting in Equation 4 the values for bias and relative standard deviation calculated using Equations 1 and 2.

44 In this manner, the overall uncertainty of the ion-selective electrode procedure has been estimated¹⁰ to be less than 23% for samples in the range 7.5 µg to 300 µg of fluoride on sodium carbonate-impregnated paper pads; and less than 16% for samples in the range 36 µg to 4800 µg of fluoride on filters.

45 Similarly, the overall uncertainty of the ion chromatography procedure has been estimated¹⁰ to be less than 25% for samples in the range 7.5 µg to 300 µg of fluoride on sodium carbonate-impregnated paper pads.

46 BS EN 482¹¹ prescribes that the overall uncertainty of procedures for the measurement of chemical agents in workplace air shall be < 50% for measurements in the range 0.1 to 0.5 times the limit value, and < 30% for measurements in the range 0.5 to 2.0 times the limit value.

47 The ion-selective electrode procedure therefore complies with the overall uncertainty requirements of BS EN 482¹¹ when measuring hydrogen fluoride-in-air concentrations between 0.1 and 2 times the short-term OES for *Hydrogen fluoride* (see paragraph 16) and between 0.1 and 2 times the short-term exposure limit recommended by SCOEL for *Hydrogen fluoride* (see paragraph 17), for a sampling time of 15 minutes and a volumetric flow rate of 2 l min⁻¹. It also complies with the overall uncertainty requirements when measuring total fluoride-in-air concentrations between 0.1 and 2 times the

8-hour TWA OES for *Fluorides* (see paragraph 16) and between 0.1 and 2 times the 8-hour TWA exposure limit recommended by SCOEL for *Fluorides* (see paragraph 17), using sampling times between 1 and 8 hours and a volumetric flow rate of 2 l min⁻¹.

48 The ion chromatography procedure complies with the overall uncertainty requirements of BS EN 482¹¹ when measuring hydrogen fluoride-in-air concentrations between 0.1 and 2 times the short-term OES for *Hydrogen fluoride* (see paragraph 16) and between 0.1 and 2 times the short-term exposure limit recommended by SCOEL for *Hydrogen fluoride* (see paragraph 17), using a sampling time of 15 minutes and a volumetric flow rate of 2 l min⁻¹.

Interferences

49 The fluoride ion-selective electrode measures the activity of free fluoride ions in solution (activity is directly proportional to fluoride ion concentration under the experimental conditions described). Interference can therefore occur through complexation or precipitation of the fluoride, both of which reduce the concentration of free fluoride ion. In particular, polyvalent cations such as Si⁴⁺, Al³⁺, Fe³⁺ and Cr³⁺ form complexes with fluoride. The effect of these species is substantially reduced or eliminated by the addition of tri-sodium citrate, which preferentially complexes these interferents.

50 Airborne particles collected on the filter can adsorb hydrogen fluoride, thus reducing the amount collected on the sodium carbonate-impregnated paper pad. However, it has been reported¹⁰ that loss of hydrogen fluoride would only be a significant problem at very high particle loadings.

Stability

51 Samples collected and transported in the specified manner are stable, and require no special storage conditions.

PRINCIPLE

52 When making measurements for comparison with the short-term OES for *Hydrogen fluoride* (see paragraph 16), samples are taken by drawing a measured volume of air through a PTFE membrane filter and a sodium carbonate-impregnated paper pad mounted in an inhalable sampler. The filter removes particulate fluorides, whilst the sodium carbonate-impregnated paper pad collects the hydrogen fluoride. Hydrofluoric acid mist is not retained on the filter, so it is also collected on the sodium carbonate-impregnated paper pad. After sampling, the filter is discarded and the sodium carbonate-impregnated paper pad is analysed using the ion-selective electrode procedure or the ion chromatography procedure.

53 When making measurements for comparison with the 8-hour TWA OES for *Fluorides* (see paragraph 16), samples are taken by drawing a measured volume of air through a mixed cellulose ester membrane filter and a sodium carbonate-impregnated paper pad mounted in an inhalable sampler. If there is only potential for exposure

to particulate fluorides, the sodium carbonate-impregnated paper pad may be omitted. After sampling, the filter and the sodium carbonate-impregnated paper pad are analysed together using the ion-selective electrode procedure. The sample dissolution method described for particulate fluorides is not compatible with analysis by ion chromatography.

54 For analysis using an ion-selective electrode, 2.5 M hydrochloric acid is used to leach soluble fluoride from the sodium carbonate-impregnated paper pad and to dissolve insoluble fluoride compounds collected on the filter. Tri-sodium citrate solution is added to complex interfering ions such as aluminium, calcium and silicon, thus releasing free fluoride ions. It also acts as a pH and ionic strength buffer.

55 For analysis using ion chromatography, soluble fluoride is leached from the sodium carbonate-impregnated paper pad with water.

REAGENTS

56 During the analysis, use only reagents of a recognised analytical grade. Suitable personal protection (eg gloves and safety spectacles) should be used when handling the reagents listed below.

Water

57 Water complying with the requirements of BS 3978²⁰ grade 2 water (electrical conductivity less than 0.1 mS m⁻¹ and resistivity greater than 0.01 MΩ.m at 25°C).

Sodium carbonate, 1 mol l⁻¹ (1 M), in 5% (v/v) glycerol solution

58 Weigh 10.6 g sodium carbonate (Na₂CO₃) into a 250 ml beaker (paragraph 84). Add 5 ml glycerol and 50 ml of water (paragraph 57) and swirl to dissolve. Quantitatively transfer the solution into a 100 ml volumetric flask (paragraph 84), dilute to the mark with water, stopper and mix thoroughly.

Laboratory detergent solution

59 A laboratory grade detergent suitable for the cleaning of samplers and labware, diluted with water (paragraph 57) according to the manufacturer's instructions.

Reagents for analysis using an ion-selective electrode

Hydrochloric acid (HCl), concentrated, ρ about 1.18 g ml⁻¹, 36.5% (m/m) to 38% (m/m)

60 The fluoride content should be less than 0.01 µg ml⁻¹.

Hydrochloric acid, 2.5 mol l⁻¹ (2.5 M)

61 Carefully add 215 ml of concentrated hydrochloric acid (paragraph 60) to 450 ml of water (paragraph 57) in

a 2 litre beaker (paragraph 84). Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask (paragraph 84). Dilute to the mark with water, stopper and mix thoroughly.

Tri-sodium citrate, 1 mol l⁻¹ (1 M)

62 Weigh 294 g of tri-sodium citrate (Na₃C₆H₅O₇ • 2H₂O) into a 2 litre beaker (paragraph 84). Add 500 ml of water (paragraph 57) and swirl to dissolve. Quantitatively transfer the solution into a 1 litre volumetric flask (paragraph 84), dilute to the mark with water, stopper and mix thoroughly.

Stock standard fluoride solution, 10⁻¹ mol l⁻¹ (10⁻¹ M)

63 Use a commercially available 10⁻¹ M fluoride standard solution. Observe the manufacturer's expiry date or recommended shelf life. Alternatively prepare a stock fluoride standard solution by the following procedure:

64 Accurately weigh 4.199 g ± 0.001 g of sodium fluoride, NaF, into a 250 ml plastic beaker (paragraph 85), add 50 ml of water (paragraph 57) and swirl to dissolve. Quantitatively transfer the solution into a 1 litre plastic volumetric flask (paragraph 85), dilute to the mark with water, stopper and mix thoroughly. Transfer the solution to a polypropylene bottle (paragraph 86) and label it with the date when it was prepared. Store the solution for a maximum of 12 months.

Reagents for analysis using ion chromatography

Stock standard fluoride solution, 1000 µg ml⁻¹ of fluoride

65 Use a commercially available standard solution at a concentration of 1000 µg ml⁻¹ of fluoride. Observe the manufacturer's expiry date or recommended shelf life. Alternatively prepare a stock fluoride standard solution by the following procedure:

66 Accurately weigh 0.5525 g ± 0.001 g of sodium fluoride (NaF) into a 100 ml plastic beaker (paragraph 85), add 50 ml of water (paragraph 57) and swirl gently until completely dissolved. Quantitatively transfer the solution into a 250 ml plastic volumetric flask (paragraph 85), dilute to the mark with water (paragraph 57), stopper and mix thoroughly. Transfer the solution to a polypropylene bottle (paragraph 86) and label it with the date when it was prepared. Store the solution for a maximum of 12 months.

Working standard fluoride solution, 25 µg ml⁻¹ of fluoride

67 Accurately pipette 1.25 ml of 1000 µg ml⁻¹ stock standard fluoride solution (paragraph 65 or 66) into a 250 ml plastic volumetric flask (paragraph 85), dilute to volume with water (paragraph 57), stopper and mix thoroughly. Transfer the solution to a polypropylene bottle (paragraph 86) and label it with the date when it was prepared. Store the solution for a maximum of 12 months.

Sodium bicarbonate solution (0.5 M NaHCO₃)

68 Accurately weigh 21.00 g of sodium bicarbonate into a 500 ml beaker (paragraph 84), add 250 ml of water (paragraph 57) and swirl gently until completely dissolved. Quantitatively transfer to a 500 ml volumetric flask (paragraph 84), dilute to the mark with water, stopper and mix thoroughly. Transfer the solution to a polypropylene bottle (paragraph 86) and label it with the date when it was prepared. Store the solution for a maximum of 12 months.

Sodium carbonate solution (0.5 M Na₂CO₃)

69 Accurately weigh 26.50 g of sodium carbonate into a 500 ml beaker (paragraph 84), add 250 ml of water (paragraph 57) and swirl gently until completely dissolved. Quantitatively transfer to a 500 ml volumetric flask (paragraph 84), dilute to the mark with water, stopper and mix thoroughly. Transfer the solution to a polypropylene bottle (paragraph 86) and label it with the date when it was prepared. Store the solution for a maximum of 12 months.

Sodium bicarbonate/sodium carbonate eluent (1 mM NaHCO₃/3.5 mM Na₂CO₃)

70 Prepare sodium bicarbonate/sodium carbonate eluent on the day required. Accurately pipette 2.0 ml of 0.5 M sodium bicarbonate solution (paragraph 68) and 7.0 ml of 0.5 M sodium carbonate solution (paragraph 69) into a 1 litre volumetric flask (paragraph 84). Dilute to the mark with water, stopper and mix thoroughly. Transfer the solution to the eluent bottle of the IC system and label it with the date when the solution was prepared. Store the solution for a maximum of one week.

Sodium bicarbonate/sodium carbonate 10x strength eluent (10 mM NaHCO₃/35 mM Na₂CO₃)

71 Accurately pipette 2.0 ml of 0.5 M sodium bicarbonate solution (paragraph 68) and 7.0 ml of 0.5 M sodium carbonate solution (paragraph 69) into a 100 ml volumetric flask (paragraph 84). Dilute to the mark with water (paragraph 57), stopper and mix thoroughly. Transfer the solution to a polypropylene bottle (paragraph 86) and label it with the date when it was prepared. Store the solution for a maximum of one month.

Air

72 Compressed and regulated to around 100 psi for pneumatic valve switching.

Helium

73 Compressed and regulated to around 5 psi for eluent degassing (paragraph 145).

SAMPLING EQUIPMENT

Samplers

Inhalable samplers

74 Samplers, with protective covers, designed to collect the inhalable fraction of airborne particles, as

defined in BS EN 481,²¹ complying with the provisions of draft European Standard EN (00137009),¹⁷ for use when sampling hydrofluoric acid mist or particulate fluorides (see notes 3, 4 and 5). Inhalable samplers suitable for personal sampling are described in MDHS 14/2.²

Note 3: *In general, personal samplers for collection of the inhalable fraction of airborne particles do not exhibit the same size-selective characteristics if used for static sampling.*

Note 4: *Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge which can be removed from the sampler to enable this material to be easily recovered.) The operating instructions supplied by the manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample.*

Note 5: *Samplers manufactured in non-conducting material have electrostatic properties which can influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.*

Sample collection substrates

Filters for use when measuring hydrogen fluoride-in-air concentrations

75 Filters, hydrophobic, of a diameter suitable for use in the samplers (paragraph 74), with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter (see subclause 2.2 of BS EN 481²¹) and compatible with subsequent analytical procedures. PTFE membrane filters of 1.0 µm mean pore diameter are recommended.

Note 6: *It is necessary to use hydrophobic filters when measuring hydrogen fluoride-in-air concentrations using an inhalable sampler because the filters are mounted directly on top of the sodium carbonate-impregnated paper pads. If hydrophilic filters were used there might be a risk of transfer of sodium carbonate from the impregnated paper pads to the filters. Hydrogen fluoride could then be trapped on the filters rather than on the sodium carbonate-impregnated paper pads, leading to low results.*

Filters for use when measuring total fluoride-in-air concentrations

76 Filters, of a diameter suitable for use in the samplers (paragraph 74), with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter (see subclause 2.2 of BS EN 481²¹) and compatible with subsequent analytical procedures. Mixed cellulose ester membrane filters of 0.8 µm mean pore diameter are recommended.

Note 7: It is not necessary to use hydrophobic filters when measuring total fluoride-in-air concentrations because the filters and sodium carbonate-impregnated paper pads are analysed together. It is therefore of no consequence if there is transfer of sodium carbonate from the impregnated paper pads to the filters. Mixed cellulose ester membrane filters are preferred because they are wettable, and therefore easier to work with during sample dissolution.

Sodium carbonate-impregnated paper pads

77 Cellulose (paper) pads, supplied as supports for membrane filters, of a diameter suitable for use in the samplers (paragraph 74), and impregnated with sodium carbonate solution (paragraph 58) using the procedure described in paragraph 78.

78 Place the paper pads on a clean PTFE sheet or a similar, inert, flat surface in an area where the concentration of hydrogen fluoride and fluorides in air is low. Establish the volume of sodium carbonate solution (paragraph 58) required to just wet the entire paper pad after the solution has been allowed to spread for a few minutes. Pipette this volume of sodium carbonate solution onto each paper pad and allow to dry for several hours at room temperature. Store the sodium carbonate-impregnated paper pads in an airtight container for a maximum of one year.

Note 8: The volume of sodium carbonate solution required to impregnate the paper pads is typically 175 µl for a 25 mm diameter paper pad or 400 µl for a 37 mm diameter paper pad.

Sampling pumps

79 Sampling pumps, complying with the provisions of BS EN 1232,¹⁸ and compatible with the samplers used (paragraph 74).

Note 9: Existing users may continue to use sampling pumps that do not fully comply with the provisions of BS EN 1232,¹⁸ provided that they take steps to ensure that the required volumetric flow rate (see paragraph 95) is maintained to within ±5% of the nominal value throughout the sampling period.

80 BS EN 1232¹⁸ requires that sampling pumps have, as a minimum, the following features:

- an automatic control which keeps the volumetric flow rate constant in the case of changing back pressure;
- either a malfunction indicator, which, following completion of sampling, indicates that the air flow has been reduced or interrupted during sampling; or an automatic cut-out, which stops the pump if the flow rate is reduced or interrupted; and
- a facility for the adjustment of flow rate, such that it can only be actuated with the aid of a tool (eg screw driver) or requires special knowledge for operation (eg via software), so as to preclude

inadvertent readjustment of the flow rate during use.

Note 10: An integral timer is a highly desirable additional feature.

81 BS EN 1232¹⁸ requires that the performance of the pumps is such that:

- the pulsation of the flow rate does not exceed 10%;
- a flow rate set within the nominal range does not deviate by more than ±5% from the initial value under increasing back pressure;
- within the range of ambient temperatures from 5°C to 40°C, the flow rate measured under operating conditions does not deviate by more than ±5% from the flow rate at 20°C;
- the operating time is at least 2 hours, and preferably 8 hours; and
- the flow rate does not deviate by more than ±5% from the initial value during the operating time.

Flowmeter

82 Flowmeter, portable, capable of measuring the required volumetric flow rate (see paragraph 95) to within ±1%, and calibrated against a primary standard, ie a flowmeter whose accuracy is traceable to national standards.

Note 11: Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers (see note 21), provided they have adequate sensitivity.

Ancillary equipment

83 Flexible tubing, of a diameter suitable for ensuring a leakproof fit, to connect the sampler to the pump; a belt to which the pump can conveniently be fixed, unless the pump is sufficiently small to fit in the worker's pocket; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes, or similar, if required (see paragraph 108), in which to transport samples to the laboratory.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

84 A selection of laboratory glassware: including beakers and volumetric flasks, class A, complying with the requirements of BS 1792.²²

Plastic labware

85 A selection of labware for use in the preparation and storage of fluoride solutions: including beakers and volumetric flasks, made of polypropylene or an alternative plastic suitable for the intended use.

Note 12: Glassware should not be used to contain fluoride solutions, since fluoride can be adsorbed onto glass.

Polypropylene bottles

86 Polypropylene bottles, with leakproof screw caps, for storage of stock standard solutions (paragraphs 64 and 66) and reagents (paragraphs 67-69 and 71), cleaned before use by soaking in water (paragraph 57) for at least 24 hours and then rinsing thoroughly. Bottles made of an alternative plastic may be used provided that they are suitable for the intended use.

Disposable gloves

87 Disposable gloves, impermeable, to protect the hands from contact with toxic and corrosive substances. PVC gloves are suitable.

Piston operated volumetric apparatus

88 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,²³⁻²⁶ for the preparation of the working standard fluoride solution (see paragraph 67) and calibration solutions (see paragraphs 125-131 and 143) and dilution of samples (see paragraphs 140 and 149). A suitable set might include micropipettes covering the ranges 10 µl to 100 µl, 100 µl to 1000 µl and 1000 µl to 5000 µl. Dispensers for dispensing 2.5 M hydrochloric acid (see paragraphs 119, 125-131 and 140), 1 M tri-sodium citrate solution (see paragraphs 120, 125-131 and 140), and 10x strength eluent (see paragraphs 123, 143 and 149).

Orbital shaker

89 An orbital shaker with variable speed control, for desorbing fluoride from filters (see paragraphs 119, 120 and 122).

Note 13: Alternatively, manual swirling may be used.

Selective ion meter and measuring electrodes

90 A selective ion meter or suitable high-impedance mV meter, capable of reading to ± 0.1 mV, and fitted with a fluoride ion-selective electrode and a silver/silver chloride double junction reference electrode which have been maintained according to the manufacturer's instructions.

Note 14: Calomel electrodes are not recommended because of the health risk and environmental concern associated with the use of mercury.

Ion chromatography system

91 A Dionex ion chromatography system having the following components: an eluent bottle of at least 1 litre capacity, equipped with a system for degassing the eluent with helium gas (paragraph 73); an injection valve, fitted with a 40 µl sample loop, and connected to a compressed air supply (paragraph 72) if pneumatically actuated; a Dionex AG14 guard column; a Dionex AS14 anion separator column; a Dionex ASRS-I electronic suppressor; an eluent pump, capable of maintaining the high pressures used in high performance liquid chromatography, and preferably with

a dual reciprocating piston pump for pulse-free flow; and a conductivity detector having a low volume (< 2 µl) flow cell.

Note 15: Other columns and suppressors or ion chromatography systems supplied by other manufacturers may be used, provided that they exhibit adequate resolution of the fluoride peak and have adequate sensitivity. However, the method performance data given in paragraphs 25, 31, 38 and 45 might not be applicable.

SAMPLING

Preliminary considerations

Selection of sample collection substrate(s)

92 Select an appropriate combination of sample collection substrate(s) according to the measurement task.

93 When making measurements for comparison with the short-term OES for *Hydrogen fluoride* (see paragraph 16) use PTFE membrane filters (paragraph 75) and sodium carbonate-impregnated paper pads (paragraph 78) to load the samplers (see paragraph 101).

Note 16: Alternatively, if there is no possibility of exposure to hydrofluoric acid mist, commercially available disposable, three-piece, plastic filter cassettes may be used. These are intended for use in the measuring procedures described by ASTM,¹² NIOSH,^{27,28} and OSHA.²⁹ They are convenient to use because they come pre-loaded with a mixed cellulose ester membrane filter and porous plastic support pad in the front section of the cassette, and a sodium carbonate-impregnated paper pad in the back section. However, they should not be used if there is possible exposure to hydrofluoric acid mist in addition to hydrogen fluoride, since they do not collect the inhalable fraction of airborne particles, as defined in BS EN 481.²¹

94 When making measurements for comparison with the 8-hour TWA OES for *Fluorides* (see paragraph 16) use mixed cellulose ester membrane filters (paragraph 76) and sodium carbonate-impregnated paper pads (paragraph 78) to load the samplers (see paragraph 101).

Note 17: If only particulate fluorides are present in the test atmosphere, and there is no possibility of exposure to hydrogen fluoride and/or hydrofluoric acid mist, the sodium carbonate-impregnated paper pads may be omitted and mixed cellulose ester membrane filters alone used to load the samplers.

Use of samplers

95 Use the samplers (paragraph 74) at their design flow rate, and in accordance with the instructions provided by the manufacturer, so that they collect the intended fraction of airborne particles.

Sampling period

96 Select an appropriate sampling period, taking into account the purpose of the measurement. Advice on monitoring strategies for toxic substances is given in HSE's booklet HSG173.¹²

97 When making measurements for comparison with the short-term OES for *Hydrogen fluoride* (see paragraph 16), use a 15-minute sampling time.

98 When making measurements for comparison with the 8-hour TWA OES for *Fluorides* (see paragraph 16), use a sampling time between 1 and 8 hours. However, if sampling is carried out in a dusty environment, the sampling time shall not be so long as to risk overloading the filter. (An 8-hour time weighted average concentration may be derived from the results for two or more consecutive samples, as described in HSE Guidance Note EH 40.⁶)

Handling of filters

99 To minimise the risk of sample loss or contamination, only handle filters using flat-tipped tweezers (paragraph 83), in a clean area. Wear disposable gloves (paragraph 87) to prevent the possibility of contamination.

Preparation for air sampling

Cleaning of samplers

100 Clean the samplers (paragraph 74) before use. Disassemble the samplers, soak in laboratory detergent solution, rinse thoroughly with water (paragraph 57), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

Loading samplers

101 Load each clean, dry sampler (paragraph 100) with a sodium carbonate-impregnated paper pad and a filter, as required (see paragraphs 93 and 94), in such a manner that the filter is upstream in relation to the paper pad when air is drawn through the sampler. Label each sampler so that it can be uniquely identified, and seal with its protective cover to prevent contamination.

Note 18: *Samplers which are assembled by means of screw threaded fittings can be unsuitable for use with a filter and a back-up paper pad. The high restriction of a filter compared with that of a paper pad means that there can be a tendency for air to take the path of least resistance and be drawn along screw threads and in through the edges of the paper pad, rather than through the filter. Leakage can usually be eliminated by tightening screw threaded fittings as much as possible to compress and seal the edges of the paper pads, but this is not always fully effective. Samplers with push-fit components can, in general, be used more reliably.*

Setting the volumetric flow rate

Perform the following in a clean area, where the concentration of hydrogen fluoride and fluorides in air is low:

102 Connect each loaded sampler (paragraph 101) to a sampling pump (paragraph 79) using flexible tubing (paragraph 83), ensuring that no leaks can occur. Remove the protective cover from each sampler, switch on the sampling pump, attach the calibrated flowmeter (paragraph 82) to the sampler so that it measures the flow

through the sampler inlet orifice(s), and set the required volumetric flow rate (see paragraph 95). Switch off the sampling pump and seal the sampler with its protective cover to prevent contamination during transport to the sampling position.

Note 19: *If necessary, allow the sampling pump operating conditions to stabilise before setting the volumetric flow rate (refer to the manufacturer's instructions).*

Blanks

103 Retain as blanks, one unused loaded sampler from each batch of ten prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but draw no air through the filters.

Sampling position

104 Position the sampler in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, eg fasten it to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, eg to a belt (paragraph 83) around the waist, or place it in a convenient pocket.

Collection of air samples

105 When ready to begin sampling, remove the protective cover from the sampler and switch on the sampling pump. Record the time and volumetric flow rate at the start of the sampling period, and if the sampling pump is fitted with an integral timer, check that this is reset to zero.

Note 20: *If the temperature or pressure at the sampling position is significantly different from that where the volumetric flow rate was set (see paragraph 102), the volumetric flow rate could change and it might need to be re-adjusted before sampling.*

Note 21: *If the sampling pump used does not comply with BS EN 1232¹⁸ (see note 9), monitor its performance frequently, a minimum of once per hour. Measure the flow rate using the calibrated flowmeter (paragraph 82) and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within $\pm 5\%$ of the nominal value throughout the sampling period.*

106 At the end of the sampling period (see paragraphs 96-98), record the time and calculate the duration of the sampling period. Check the malfunction indicator and/or the reading on the integral timer, if fitted, and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period. Measure the volumetric flow rate at the end of the sampling period using the calibrated flowmeter (paragraph 82), and record the measured value. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

107 Carefully record the sample identity and all relevant sampling data (see Appendix A).

Transportation

108 For samplers which collect airborne particles on the filter (see note 4), open each sampler and remove the filter and paper pad, if used (see note 17). Discard PTFE membrane filters, if used (see paragraph 93). Then place each paper pad and each mixed cellulose ester membrane filter, if used (see paragraph 94), in an individual, labelled, filter transport cassette (paragraph 83) and close with a lid. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters. Alternatively, transport samples to the laboratory in the samplers in which they were collected.

109 For samplers which have an internal filter cassette (see note 4), remove the filter cassette from each sampler and fasten with its lid or transport clip. Pack the filter cassettes in an airtight container or plastic bag if there is any possibility that the samples will be exposed to hydrogen fluoride during transportation.

110 For samplers designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, but which do not have an internal filter cassette (see note 4), and for disposable filter cassettes (see note 16), transport samples to the laboratory in the samplers in which they were collected.

111 Transport the samples (paragraphs 108-110) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

112 When appropriate, ensure that the documentation which accompanies the samples is suitable for a 'chain of custody' to be established.

ANALYSIS

Wear disposable gloves (paragraph 87) during analysis to protect the hands from toxic and corrosive reagents.

Cleaning of labware

113 Before use, clean all glassware (paragraph 84) and plastic labware (paragraph 85) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 59) and then rinse thoroughly with water (paragraph 57).

Preparation of sample and blank solutions

Unloading of the sample collection substrates

114 Open the filter transport cassettes (see paragraph 108), sampler filter cassettes (see paragraph 109) or samplers (see paragraph 110) and transfer each filter and/or paper pad into an individual, labelled 100 ml plastic beaker (paragraph 85) using clean flat-tipped tweezers (paragraph 83), as described in paragraphs 115-117. Follow the same procedure for the blanks (paragraph 103).

115 If inhalable samplers were used with PTFE membrane filters and sodium carbonate-impregnated paper pads for the purpose of making measurements for comparison with the short-term OES for *Hydrogen fluoride* (see paragraph 16), discard the PTFE membrane filter and transfer only the sodium carbonate-impregnated paper pad into the beaker for analysis.

116 If inhalable samplers were used with mixed cellulose ester membrane filters and sodium carbonate-impregnated paper pads for the purpose of making measurements for comparison with the 8-hour TWA OES for *Fluorides* (see paragraph 16), transfer both filters into the same beaker for combined analysis.

117 If pre-loaded disposable plastic cassettes were used for the purpose of making measurements for comparison with the short-term OES for *Hydrogen fluoride* (see note 16), discard the mixed cellulose ester membrane filter and transfer only the sodium carbonate-impregnated paper pad into the beaker for analysis.

118 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see note 4), carefully wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 57).

Preparation of sample and blank solutions for analysis using an ion-selective electrode

119 Add 5 ml of 2.5 M hydrochloric acid (paragraph 61) to each beaker, cover, and swirl the contents by placing on an orbital shaker (paragraph 89) for 30 minutes. Alternatively, simply allow to stand with occasional manual swirling.

120 Add 25 ml of tri-sodium citrate solution (paragraph 62) and swirl again for at least one hour.

121 Carefully rinse the sides of each beaker with water (paragraph 57), and quantitatively transfer the solution to a labelled 50 ml plastic volumetric flask (paragraph 85). If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter which has been pre-washed with water (paragraph 57). Finally, dilute to the mark with water, stopper and mix thoroughly.

Preparation of sample and blank solutions for analysis using ion chromatography

122 Add 25 ml of water (paragraph 57) to each beaker, cover, and swirl the contents by placing on an orbital shaker (paragraph 89) for 30 minutes. Alternatively, simply allow to stand with occasional manual swirling.

123 Carefully rinse the sides of each beaker with water (paragraph 57), and quantitatively transfer the solution to a labelled 50 ml plastic volumetric flask (paragraph 85). Add 5 ml of 10x strength eluent (paragraph 71), dilute to the mark with water, stopper and mix thoroughly.

Analysis using an ion-selective electrode

Preparation of calibration solutions

Note 22: Acidity and ionic strength affect the measurement of fluoride using an ion-selective electrode. It is therefore very important that the sample, blank and calibration solutions are all prepared in the same matrix, ie 0.25 M hydrochloric acid and 0.5 M tri-sodium citrate.

124 Prepare calibration solutions with pF values (ie negative logs of fluoride concentration) of 3, 3.5, 4, 4.5, 5, 5.5, and 6, as described in paragraphs 125-131. Prepare fresh calibration solutions daily.

10^{-3} M calibration solution

125 Accurately pipette 2.50 ml of 10^{-1} M stock standard fluoride solution (paragraph 63 or 64) into a 250 ml plastic volumetric flask (paragraph 85). Add 25 ml of 2.5 M hydrochloric acid (paragraph 61) and 125 ml of 1M tri-sodium citrate solution (paragraph 62), dilute to volume with water (paragraph 57), stopper and mix thoroughly.

3.162×10^{-4} M calibration solution

126 Accurately pipette 0.791 ml of 10^{-1} M stock standard fluoride solution (paragraph 63 or 64) into a 250 ml plastic volumetric flask (paragraph 85). Add 25 ml of 2.5 M hydrochloric acid (paragraph 61) and 125 ml of 1 M tri-sodium citrate solution (paragraph 62), dilute to volume with water (paragraph 57), stopper and mix thoroughly.

10^{-4} M calibration solution

127 Accurately pipette 5.00 ml of 10^{-3} M calibration solution (paragraph 125) into a 50 ml plastic volumetric flask (paragraph 85). Add 4.5 ml of 2.5 M hydrochloric acid (paragraph 61) and 22.5 ml of tri-sodium citrate solution (paragraph 62), dilute to volume with water (paragraph 57), stopper and mix thoroughly.

3.162×10^{-5} M calibration solution

128 Accurately pipette 5.00 ml of 3.162×10^{-4} M calibration solution (paragraph 126) into a 50 ml plastic volumetric flask (paragraph 85), add 4.5 ml of 2.5 M hydrochloric acid (paragraph 61) and 22.5 ml of tri-sodium citrate solution (paragraph 62), dilute to volume with water (paragraph 57), stopper and mix thoroughly.

10^{-5} M calibration solution

129 Prepare a 10^{-5} M calibration solution by serial dilution of the 10^{-4} M calibration solution (paragraph 127), in the same manner as that described in paragraph 127.

3.162×10^{-6} M calibration solution

130 Prepare a 3.162×10^{-6} M calibration solution by serial dilution of the 3.162×10^{-5} M calibration solution (paragraph 128), in the same manner as that described in paragraph 128.

10^{-6} M calibration solution

131 Prepare a 10^{-6} M calibration solution by serial dilution of the 10^{-5} M calibration solution (paragraph 129), in the same manner as that described in paragraph 127.

Preparation for analysis

132 Allow the temperature of the calibration, blank, and sample solutions to come to room temperature (within $\pm 2^\circ\text{C}$), since electrode potential is a function of temperature.

133 Connect the fluoride ion-selective electrode and the reference electrode to the selective ion meter or high-impedance mV meter (see paragraph 90), following the manufacturer's instructions.

134 Pre-condition the fluoride ion-selective electrode before use. Place the ion-selective electrode and the reference electrode in the low calibration solution (paragraph 131), and stir, either magnetically or mechanically, until the electrode potential becomes sufficiently stable, eg when it has remained constant to ± 0.1 mV for 1 minute. (If magnetic stirring is used, take care to ensure that there is no heat transfer from the stirrer to the solution.)

Calibration

135 Measure the mV readings of the calibration solutions (paragraphs 125-131) in increasing order of concentration, following the instructions in paragraphs 136 and 137.

136 Transfer an aliquot of calibration solution into a plastic beaker (paragraph 85), immerse the fluoride ion-selective electrode and the reference electrode in the solution, and stir, either magnetically or mechanically. If magnetic stirring is used, take care to ensure that there is no heat transfer from the stirrer to the solution. Record the electrode potential when it has become sufficiently stable, eg when it has remained constant to ± 0.1 mV for 1 minute.

Note 23: The electrode potential typically takes up to 5 minutes to stabilise, and with very dilute solutions this time can become considerably longer. As far as possible, measure calibration, blank, and sample solutions in order of increasing concentration to minimise this response time.

137 Rinse the electrodes thoroughly with water (paragraph 57) between readings, and blot dry with tissue paper. This prevents carry over of fluoride to the next solution measured.

138 Plot a calibration graph of mV against pF value (see paragraph 124).

Note 24: The calibration graph should be linear over the range pF 3 to pF 5. Its slope should be $-59 \text{ mV} \pm 3 \text{ mV}$ per decade of concentration at 25°C , if the meter and the electrodes are functioning correctly.

Determination of fluoride concentrations

139 Determine the mV reading of the blank and sample solutions (paragraph 121), following the same procedure described for the calibration solutions in paragraphs 136 and 137. Obtain the pF values of these solutions from the calibration graph (paragraph 138).

140 If fluoride concentrations above the upper limit of the calibration range are found, dilute the sample solutions by a factor of 10, and repeat the analysis. Make all dilutions so that the matrix of diluted sample solutions matches the calibration solutions. Accurately pipette 5.00 ml of sample solution (paragraph 121) into a 50 ml plastic volumetric flask (paragraph 85), add 4.5 ml of 2.5 M hydrochloric acid (paragraph 61) and 22.5 ml of tri-sodium citrate solution (paragraph 62), dilute to volume with water (paragraph 57), stopper and mix thoroughly. Record the dilution factor.

141 Calculate fluoride concentrations of the blank and sample solutions, in $\mu\text{g ml}^{-1}$, from the pF values using the formula given in paragraph 152.

142 Calculate the mean fluoride concentration of the blank solutions in $\mu\text{g ml}^{-1}$.

Note 25: As fluoride ions can 'poison' the reference electrode, it is recommended that the electrolyte in the reference electrode be renewed before each series of measurements.

Analysis using ion chromatography

Preparation of calibration solutions

143 Prepare at least five calibration solutions to cover the range $0 \mu\text{g ml}^{-1}$ to $2.5 \mu\text{g ml}^{-1}$ of fluoride. Accurately pipette appropriate volumes of $25 \mu\text{g ml}^{-1}$ working standard fluoride solution (paragraph 67) into individual, labelled 50 ml plastic volumetric flasks (paragraph 85). Add 5 ml of 10x strength eluent (paragraph 71), dilute to the mark with water (paragraph 57), stopper and mix thoroughly. Prepare these solutions fresh daily.

Preparation for analysis

144 Set up the ion chromatography system (paragraph 91) according to the manufacturer's instructions.

145 Degas the eluent (paragraph 70) for about 10 minutes. Pump the eluent through the guard, separator and suppressor columns at the flow rate recommended by the manufacturer, and allow the column packing material and eluent to come to equilibrium for at least 30 minutes prior to analysis.

Determination of fluoride concentrations

146 Analyse the calibration solutions (paragraph 143) and the blank and sample solutions (paragraph 123) and determine the fluoride peak height for each solution. Analyse the calibration solutions in order of increasing concentration at the start of the analysis sequence and thereafter at appropriate intervals.

147 Use the data handling system to perform a linear regression and give a direct measurement of the fluoride concentration of the blank and sample solutions in $\mu\text{g ml}^{-1}$.

148 Review the chromatograms after the analysis sequence has run to check that the baselines drawn for both calibration, blank and sample solutions are satisfactory. If not, enter new parameters and reprocess the raw data.

149 If high fluoride concentrations are found, dilute the sample solutions by a factor of 10, and repeat the analysis. Make all dilutions so that the diluted sample solutions are eluent-matched. Accurately pipette 5.00 ml of sample solution (paragraph 123) into a 50 ml plastic volumetric flask (paragraph 85), add 5 ml of 10x strength eluent (paragraph 71), and dilute to volume with water (paragraph 57), stopper and mix thoroughly. Record the dilution factor.

150 Calculate the mean fluoride concentration of the blank solutions in $\mu\text{g ml}^{-1}$.

CALCULATION OF RESULTS

Volume of air sample

151 Calculate the mean flow rate during the sampling period by averaging the flow rate measurements taken at the start and end of the sampling period. Then calculate the volume, in litres, of the air sample by multiplying the mean flow rate, in litres per minute, by the sampling time, in minutes.

Conversion of fluoride concentrations from pF to $\mu\text{g ml}^{-1}$ of fluoride

152 Convert each pF reading to the concentration of fluoride in solution, $\rho(F)_s$, in micrograms per millilitre ($\mu\text{g ml}^{-1}$), using the equation:

$$\rho(F)_s = 10^{-pF} \times 19000 \quad \text{Equation 5}$$

where

pF is the pF reading of the blank or sample solution (see paragraph 139); and

19000 is the factor required to convert the fluoride concentration from mol l^{-1} (M) to $\mu\text{g ml}^{-1}$.

Concentration of fluoride in air

153 Calculate the concentration of fluoride in air, $\rho(F)$, in milligrams per cubic metre (mg m^{-3}), using the equation:

$$\rho(F) = \frac{[\rho(F)_1 \times V_1 \times DF_1] - [\rho(F)_0 \times V_0 \times DF_0]}{V} \quad \text{Equation 6}$$

where

$\rho(F)_0$ is the mean concentration, in $\mu\text{g ml}^{-1}$, of fluoride in the blank solutions (see paragraph 142 or 150);

$\rho(F)_1$ is the mean concentration, in $\mu\text{g ml}^{-1}$, of fluoride in the sample solution (see paragraph 141 or 147);

V is the volume, in litres, of the air sample (see paragraph 151);

V_0 is the volume, in ml, of the blank solutions, ie 50 ml (see paragraph 121 or 123);

V_1 is the volume, in ml, of the sample solutions, ie 50 ml (see paragraph 121 or 123);

DF_0 is the dilution factor for the blank solutions, ie 1; and

DF_1 is the dilution factor for the sample solution (see paragraph 140 or 149).

154 Compare results with the short-term OES for *Hydrogen fluoride* or the 8-hour TWA OES for *Fluorides*, as appropriate.

TEST REPORT

155 Appendix A gives recommendations for information to be included in the test report.

QUALITY CONTROL MEASURES

156 Analytical quality requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS 71.³⁰

157 If fluoride analysis is performed frequently it is recommended that internal quality control is performed. In such instances, prepare quality control samples by spiking a large number of filters or sodium carbonate-impregnated paper pads, as appropriate, with microlitre volumes of a solution of known fluoride concentration. Randomly select a suitable number (eg 20) of quality control samples, analyse them on separate occasions, and calculate the mean and standard deviation of the measured fluoride concentrations. Assuming that the distribution of results is Gaussian, construct a Shewhart chart with warning and action limits at ± 2 SD and ± 3 SD respectively. Subsequently, analyse a quality control sample with each analytical batch and plot the result on the Shewhart chart. Compare the internal quality control result with the target value and take appropriate action if the warning or action limits are exceeded, as recommended in MDHS 71.³⁰

Take care to ensure that the quality control samples are stored under conditions which ensure maximum stability.

158 It is recommended that all laboratories undertaking the determination of hydrogen fluoride or fluorides in workplace air should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are given in MDHS 71.³⁰ However, at present the WASP scheme does not encompass fluoride.

ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Broad Lane, Sheffield S3 7HQ (telephone 0114 2892000).

The Health and Safety Executive wishes, wherever possible, to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

APPENDIX A RECOMMENDATIONS FOR THE TEST REPORT

It is recommended that the test report should include the following information:

- (a) a complete identification of the air sample, including the date of sampling, the place of sampling, and the identity of the individual whose breathing zone was sampled;
- (b) a reference to this MDHS, including information about which analytical technique was used, and a description of any deviation from the procedures described;
- (c) the type and diameter of sample collection substrates used;
- (d) the type of sampler used;
- (e) the type of sampling pump used;
- (f) the type of flowmeter used, the primary standard against which it was calibrated, and the range of flow rates for which the flowmeter was calibrated;
- (g) the time at the start and at the end of the sampling period, and the sampling time in minutes;
- (h) the volume of air sampled, in litres;
- (i) the name of the person who collected the sample;
- (j) the time-weighted average mass concentration of fluoride found in the air sample, in micrograms per cubic metre;
- (k) the name of the analyst;
- (l) the date of the analysis.

REFERENCES

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