

# MDHS

## *Methods for the Determination of Hazardous Substances*

Health and Safety Laboratory



# 79

## Peroxodisulphate salts in air

Laboratory method using mobile phase ion chromatography

June 1995

**Note 1** Mobile phase ion chromatography is a patented technique which combines reversed phase ion-pair chromatography with chemical suppression.

### INTRODUCTION

#### Occurrence

1 Peroxodisulphate is a dianion, having the formula  $S_2O_8^{2-}$ . The ammonium, potassium and sodium salts are most commonly used, but the free acid is also known.<sup>1</sup>

#### Properties and uses

2 Peroxodisulphate salts are water soluble, odourless, white crystalline solids which decompose before melting. They are oxidising agents and are generally used as an aqueous solution, for example as an additive to 'boost' peroxide hair bleaches<sup>2</sup> and for removing copper backing from printed circuit boards.<sup>3</sup>

#### Health effects

3 Concern raised from cutaneous and respiratory responses of hairdressers and their clients revealed<sup>2, 4-6</sup> that peroxodisulphate exposure can result in a variety of conditions including: (i) irritant scalp dermatitis with temporary hair loss, (ii) irritant hand contact dermatitis, (iii) allergic eczematous contact dermatitis of hands and scalp, (iv) immediate edema of scalp, face and neck, (v) generalised urticaria, (vi) rhinitis and asthma, and (vii) syncope.

#### Precautions and first aid

4 If a person is thought to have suffered severe exposure to peroxodisulphate salts, the affected area should be flushed with copious quantities of water and medical attention sought.

#### Exposure limits

5 Occupational exposure limits for sodium, ammonium and potassium peroxodisulphate are set out in HSE Guidance Note EH 40.<sup>7</sup>

#### Analytical methods

6 This is not a 'reference' method in the strict analytical sense of the word. There are frequently several alternative methods available for the determination of a particular analyte (eg other methods in the MDHS series). With the exception of a few cases, where an exposure limit 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.

7 This method has been validated<sup>8</sup> to demonstrate that it complies with the *General requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres* described by the Comité Européen de Normalisation (CEN) in draft European Standard prEN 482.<sup>9</sup> If an alternative method is used it is necessary to demonstrate that it also meets these performance requirements.

#### Requirements of the COSHH Regulations

8 The Control of Substances Hazardous to Health (COSHH) Regulations<sup>10</sup> require that employers make an assessment of the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. The COSHH Regulations also include a requirement that persons who may 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 method.

## SCOPE

### Applicability

9 This MDHS describes a method for determination of the concentration of sodium, ammonium and potassium peroxodisulphate salts in workplace air using mobile phase ion chromatography. The method is suitable for sampling over the range 15 minutes to 8 hours.

**Note 2** HSE Guidance Note EH 42<sup>11</sup> advises employers about how they should conduct investigations into the nature, extent and control of exposure to substances hazardous to health which are present in workplace air. The objective of air monitoring is usually to determine worker exposure, and therefore the procedures described in this method are for personal sampling in the breathing zone. The method may be used for background or fixed location sampling, but it should be recognised that due to aerodynamic effects the samplers used do not necessarily exhibit the same collection characteristics as when they are used for personal sampling.

## METHOD PERFORMANCE

### Detection limits

10 The qualitative and quantitative detection limits for peroxodisulphate, defined as three times and ten times the standard deviation of a blank determination, are  $0.29 \mu\text{g ml}^{-1}$  and  $0.96 \mu\text{g ml}^{-1}$  respectively.<sup>8</sup> For an air sample volume of 30 litres and a sample solution volume of 10 ml, these qualitative and quantitative detection limits for peroxodisulphate correspond to peroxodisulphate in air concentrations of  $96 \mu\text{g m}^{-3}$  and  $320 \mu\text{g m}^{-3}$  respectively.

### Overall uncertainty

11 Laboratory experiments<sup>8</sup> indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 90 spiked filters in the range  $6 \mu\text{g}$  to  $1920 \mu\text{g}$  of peroxodisulphate was 96.5%.

12 The component of the coefficient of variation of the method that arises from analytical variability, CV (analysis), was less than 10% for spiked filters in the range  $6 \mu\text{g}$  to  $9 \mu\text{g}$  of peroxodisulphate and less than 5% for spiked filters in the range  $30 \mu\text{g}$  to  $1920 \mu\text{g}$  of peroxodisulphate.

13 The overall uncertainty of the method, as defined by CEN,<sup>9</sup> was determined to be less than 33% for samples in the range  $6 \mu\text{g}$  to  $30 \mu\text{g}$  of peroxodisulphate and less than 19% for samples in the range  $30 \mu\text{g}$  to  $1920 \mu\text{g}$  of peroxodisulphate. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from

pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN.<sup>9</sup>

### Interferences

14 The method is very specific for peroxodisulphate, and no interference from other anions has been identified.

### Stability

15 Sample stability was investigated<sup>8</sup> by spiking filters with a solution of potassium peroxodisulphate and determining analytical recovery after 7 days. Results indicate that samples of peroxodisulphate in the range  $6 \mu\text{g}$  to  $1920 \mu\text{g}$  are stable when collected on mixed cellulose ester filters. Other filters may be suitable for sampling peroxodisulphate, but it is advised that sample stability is investigated prior to use.

## PRINCIPLE

16 A measured volume of air is drawn through a filter mounted in an inhalable dust sampler. The filter and collected sample are then treated with 4 ml of water and the mixture swirled for 1 hour on an orbital shaker. The resulting solution is diluted to 10 ml with water and peroxodisulphate concentration determined using mobile phase ion chromatography. Separation is achieved using Dionex NG1 and NS1-5 $\mu$  guard and separator columns respectively and separated species detected by conductivity after eluent suppression using an Anion Micromembrane Suppressor (Dionex AMMS - MPIC). The eluent is 28% (v/v) acetonitrile, containing 2 mM tetrabutylammonium hydroxide and 3 mM sodium carbonate.

## REAGENTS

17 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 18). Do not pipette by mouth.

### Water

18 Water complying with the requirements of BS 3978<sup>12</sup> grade 1 water (electrical conductivity less than  $0.01 \text{ mS m}^{-1}$  and resistivity greater than  $0.1 \text{ M}\Omega\cdot\text{m}$  at  $25^\circ\text{C}$ ).

### Acetonitrile

19 'HPLC grade' acetonitrile.

**Warning** Acetonitrile is toxic by inhalation, in contact with the skin or if swallowed. Avoid exposure by contact with the skin or eyes, or by inhalation of the vapour. Personal protection (eg gloves and safety spectacles etc) shall be used when working with acetonitrile. All operations with acetonitrile shall be carried out in a fume cupboard.

### **Tetrabutylammonium hydroxide (TBAOH), 0.5 M solution**

20 'HPLC grade' TBAOH, 0.5 M solution.

**Warning** TBAOH solution causes severe burns. Avoid exposure by contact with the skin or eyes. Personal protection (eg gloves and safety spectacles etc) shall be used when working with TBAOH solution.

### **Sodium carbonate solution, 0.5 M solution**

21 Dissolve 26.50 g of sodium carbonate in 300 ml of water (paragraph 18) and swirl gently until completely dissolved. Quantitatively transfer the solution into a 500 ml volumetric flask, dilute to the mark with water (paragraph 18), stopper and mix thoroughly.

### **Eluent, 28% (v/v) acetonitrile containing 2mM TBAOH and 3mM sodium carbonate**

22 Prepare the eluent fresh each day prior to analysis, as follows. Add 280 ml of acetonitrile, 4 ml of TBAOH solution and 6 ml of sodium carbonate solution to a 1 litre volumetric flask. Dilute to the mark with water (paragraph 18), stopper and mix thoroughly.

### **Sulphuric acid, 200 mM**

23 Carefully add 10.7 ml of concentrated sulphuric acid to around 400 ml of water (paragraph 18) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water (paragraph 18), stopper and mix thoroughly.

**Warning** Concentrated sulphuric acid can cause severe burns. Avoid exposure by contact with the skin or eyes. Personal protection (eg gloves and safety spectacles etc) shall be used when working with concentrated sulphuric acid. Caution shall be exercised when diluting concentrated sulphuric acid. Always add acid to water with stirring.

### **Sulphuric acid, 20 mM (Regenerant)**

24 Quantitatively transfer 100 ml of 200 mM sulphuric acid (paragraph 23) to a 1 litre volumetric flask. Dilute to the mark with water (paragraph 18), stopper and mix thoroughly.

### **Stock standard peroxodisulphate solution, 1000 µg ml<sup>-1</sup> peroxodisulphate**

25 Dissolve 0.352 g of potassium peroxodisulphate in 75 ml of water (paragraph 18) and swirl gently until completely dissolved. Quantitatively transfer the solution into a 250 ml volumetric flask, dilute to the mark with water (paragraph 18), stopper and mix thoroughly. Prepare this solution fresh daily, prior to analysis.

**Warning** Peroxodisulphate salts are oxidising agents and irritating to the eyes, skin and respiratory system (paragraph 3). Avoid exposure by contact with the skin or

eyes, or by inhalation. Personal protection (eg gloves and safety spectacles etc) shall be used when working with peroxodisulphate salts. All operations with peroxodisulphate salts shall be carried out in a fume cupboard.

### **Laboratory detergent solution**

26 A laboratory grade detergent suitable for cleaning of samplers and labware, diluted with water (paragraph 18) according to the manufacturer's instructions.

### **Air**

27 Compressed and regulated to around 5 psi for controlling the flow of regenerant to the AMMS (paragraph 16), and regulated to around 100 psi for pneumatic valve switching.

### **Helium**

28 Compressed and regulated to around 5 psi for eluent degassing (paragraph 38).

## **SAMPLING EQUIPMENT**

### **Samplers for collection of the inhalable fraction of the airborne particles**

29 Samplers, with protective covers, for collection of the inhalable fraction of airborne particles, as defined in European Standard EN 481.<sup>13</sup> The seven-hole sampling head described in MDHS 14<sup>14</sup> and the IOM (Institute of Occupational Medicine) inhalable dust sampler are suitable for personal sampling. Samplers manufactured in non-conducting plastic shall not be used as these have electrostatic properties which may influence representative sampling.

**Note 3** In general, the collection characteristics of inhalable samplers (eg the seven-hole sampling head) are such that particulate material collected on the filter is the inhalable fraction of the airborne particles, and any deposited on the internal surfaces of the sampler is not of interest. However, some samplers are designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction, in which case any particulate material deposited on the internal surfaces of the sampler is part of the sample. Certain samplers of this type (eg the IOM inhalable dust sampler) incorporate an internal filter cassette which may be removed from the sampler to enable this material to be easily recovered.

### **Filters**

30 Filters, of a diameter suitable for use in the selected sampler (paragraph 29), with a retentivity of not less than 99% for 0.3 µm mass median aerodynamic diameter particles. The filters shall be suitable for collection of stable samples of peroxodisulphate (see paragraph 15). Mixed cellulose ester membrane filters are suitable.

## Sampling pumps

31 Sampling pumps, with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the appropriate flow rate (see paragraph 39) to within  $\pm 5\%$  of the nominal value throughout the sampling period (see paragraph 40), and capable of being worn by persons without impeding normal work activity. The pumps shall give a pulsation-free flow (if necessary, a pulsation damper shall be incorporated between the sampling head and the pump, as near to the pump as possible). Flow-stabilised pumps may be required to maintain the flow rate within the specified limits.

## Flowmeter

32 Flowmeter, portable, capable of measuring the appropriate flow rate (see paragraph 39) to within  $\pm 5\%$ , and calibrated against a primary standard.

**Note 4** The flowmeter incorporated in the pump may be used provided that it has adequate sensitivity, that it has been calibrated against a primary standard with a loaded sampler in line, and that it is read in a vertical orientation if it is of the supported float type. However, it is important to ensure that there are no leaks in the sampling train between the sampling head and the flowmeter, since in this event a flowmeter in the pump or elsewhere in line will give an erroneous flow rate.

**Note 5** A soap bubble flowmeter may be used as a primary standard, provided its accuracy is traceable to national standards (see Appendix 1).

## Ancillary equipment

33 Flexible plastic tubing, of a diameter suitable for making a leakproof connection from the sampler to the sampling pump; belts or harnesses to which the sampling pump can be conveniently 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 49), to transport samples to the laboratory.

## LABORATORY APPARATUS

### Glassware, made of borosilicate glass

34 A selection of laboratory glassware: including beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS 1792.<sup>15</sup>

## DISPOSABLE GLOVES

35 Disposable gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from contact with toxic and corrosive substances. PVC gloves are suitable.

## Piston operated volumetric apparatus

36 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,<sup>16-19</sup> for the preparation of calibration solutions (paragraph 58) and dilution of samples (paragraph 63). A suitable set might include micropipettes covering the ranges 10  $\mu\text{l}$  to 100  $\mu\text{l}$ , 100  $\mu\text{l}$  to 1000  $\mu\text{l}$ , and 1000  $\mu\text{l}$  to 5000  $\mu\text{l}$ .

## Orbital shaker

37 An orbital shaker with variable speed control. Other techniques suitable for desorbing the peroxodisulphate salt from the filter (paragraph 30) include periodic manual swirling or using an ultrasonic bath.

## Chromatograph

38 The chromatograph shall contain the following components. A 1 litre capacity glass eluent bottle plus a system for degassing the eluent with helium gas (paragraph 28). A load/injection valve fitted with a 40  $\mu\text{l}$  sample loop. Pneumatic load/injection valves require a compressed air supply (paragraph 27). Dionex NG1 guard column and NS1-5 $\mu$  separator column; the method also performs satisfactorily with a Dionex NS1 separator column. An eluent pump, preferably with a dual reciprocating piston pump for pulse-free flow and capable of maintaining the high pressures encountered in High Performance Liquid Chromatography (the Dionex NG1 plus NS1-5 $\mu$  columns generate a relatively high backpressure of over 2000 psi). An AMMS (Dionex AMMS - MPIC Part No 037106). A 4 litre capacity plastic regenerant bottle plus a system for delivering the regenerant to the AMMS. This is usually achieved by pressurising the regenerant bottle using compressed air (paragraph 27). A conductivity detector with a small volume (under 2  $\mu\text{l}$ ) flow cell.

**Note 6** Consult manufacturer's literature regarding compressed gas pressure settings for eluent degassing, regenerant delivery and for chromatographs with pneumatically actuated valves.

## SAMPLING

### Sampling procedure

39 Select a sampler to collect the inhalable fraction of the airborne particles and use at the flow rate at which the sampler (paragraph 29) exhibits the required collection characteristics. Refer to MDHS 14<sup>14</sup> for the flow rate to be used when sampling with a seven-hole sampling head, IOM inhalable dust sampler.

40 Select a sampling period of an appropriate duration, such that the filter does not become overloaded with particulate material. (An 8-hour time weighted average concentration may be derived from the results for two or more consecutive samples, as described in Guidance Note EH 42.<sup>11</sup>)

## Preparation of sampling equipment

41 Clean the samplers (paragraph 29) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 26), rinse thoroughly with water (paragraph 18), wipe with absorptive tissue and allow to dry thoroughly before reassembly.

42 Load the filters (paragraph 30) into clean, dry samplers (see paragraph 41) using clean, flat-tipped tweezers (paragraph 33). Connect each loaded sampler to a sampling pump (paragraph 31) using plastic tubing (paragraph 33), ensuring that no leaks can occur. Switch on the pump, attach the calibrated flowmeter (paragraph 32) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the appropriate flow rate (see paragraph 39) with an accuracy of  $\pm 5\%$ . Remove the flowmeter and allow the pump to operate for an appropriate period to enable it to warm up and the flow rate to stabilise (follow the manufacturer's recommendations). Then discard the used filter and load a new one into the sampler for collection of the sample. Finally, attach the calibrated flowmeter again, readjust the flow rate to the appropriate value with an accuracy of  $\pm 5\%$ , switch off the pump and seal the sampler with its protective cover to prevent contamination during transport to the sampling position.

## Collection of samples

43 Fix the sampler to the lapel of the worker, in the breathing zone and as close to the mouth and nose as practicable. Then, either place the sampling pump in a convenient pocket or attach it to the worker in a manner that causes minimum inconvenience, eg to a belt around the waist (paragraph 33). When ready to begin sampling, remove the protective cover from the sampling head and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, set this to zero.

44 Since it is possible for a filter to become clogged, monitor the performance of the sampler frequently, a minimum of once per hour. Measure the flow rate with an accuracy of  $\pm 5\%$  using the calibrated flowmeter (paragraph 32) 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.

**Note 7** Regular observation of the flow fault indicator is an acceptable means of ensuring that the flow rate of flow-stabilised sampling pumps is maintained satisfactorily, provided that the flow fault indicator indicates malfunction when the flow rate is outside  $\pm 5\%$  of the nominal value.

45 At the end of the sampling period (see paragraph 40), measure the flow rate with an accuracy of  $\pm 5\%$  using the calibrated flowmeter (paragraph 32), switch off the sampling pump, and record the flow rate and the time. Also observe the reading on the elapsed time indicator, if fitted, and consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling

pump do not agree to within  $\pm 5\%$ , since this may suggest that the sampling pump has not been operating throughout the sampling period. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

46 Carefully record the sample identity and all relevant sampling data (see Appendix 2). Calculate the mean flow rate by averaging the flow rate measurements taken throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the flow rate in litres per minute by the sampling time, in minutes.

47 With each batch of ten samples, submit for analysis two unused filters from the same lot of filters used for sample collection. Subject these blank filters to exactly the same handling procedure as the samples, but draw no air through them.

48 Proceed with the analysis as soon as possible after sampling. In particular, for short-term samples, analysis should be performed within three days to ensure that analytical recovery is acceptable (see paragraph 15).

## Transportation

49 For samplers which collect the inhalable fraction of airborne particles on the filter (eg the seven-hole sampling head and cyclone samplers), remove the filter from each sampler using clean flat-tipped tweezers (paragraph 33), place in a labelled filter transport cassette (paragraph 33) and close with a lid.

50 For samplers which have an internal filter cassette (eg the IOM sampler), remove the filter cassette from each sampler, fasten with the transport clip supplied by the manufacturer, and label appropriately.

51 For samplers designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction, but which do not have an internal filter cassette, and for samplers of the disposable cassette type, transport the samples to the laboratory in the samplers in which they were collected.

52 Transport the filter transport cassettes (paragraph 49), sampler filter cassettes (paragraph 50) or samplers (paragraph 51) to the laboratory in a container which has been designed to prevent damage to samples in transit and which has been labelled to ensure proper handling.

## ANALYSIS

Wear disposable gloves (paragraph 35) during analysis to reduce the possibility of contamination and to protect the hands from corrosive and oxidising reagents.

## Cleaning of glassware

53 Before use, clean all glassware (paragraph 34) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 26) and then rinse thoroughly with water (paragraph 18).

## Preparation of sample and blank solutions

54 Open the filter transport cassettes (paragraph 49), sampler filter cassettes (paragraph 50) or samplers (paragraph 51) and transfer each filter into an individual, labelled, tall-form 50 ml beaker using clean flat-tipped tweezers (paragraph 33).

55 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 3), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 18). Follow the same procedure for the blank filters (paragraph 47).

56 Add 4 ml of water (paragraph 18) to each beaker, cover with a watch glass, place the beaker on an orbital shaker (paragraph 37) and swirl the mixture for 1 hour at 60 rpm.

57 Carefully rinse the sides of each beaker with water (paragraph 18) and transfer each solution quantitatively to a labelled 10 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter which has been pre-washed with water (paragraph 18). Finally, dilute to the mark, stopper and mix thoroughly.

## Analysis of sample and blank solutions

### Preparation of calibration solutions

58 Prepare at least five calibration solutions to cover the range  $0 \mu\text{g ml}^{-1}$  to  $5 \mu\text{g ml}^{-1}$  peroxodisulphate by adding by pipette the appropriate volume of  $1000 \mu\text{g ml}^{-1}$  stock standard peroxodisulphate solution (paragraph 25) to separate, labelled 100 ml volumetric flasks. Dilute to the mark with water (paragraph 18), stopper and mix thoroughly. Prepare these solutions fresh daily.

## Chromatography

59 Set up the chromatograph (paragraph 38) according to the manufacturer's instructions for specific operating parameters. Degas the eluent (paragraph 38) for around 10 minutes. Set the full scale deflection of the conductivity detector to around  $30 \mu\text{S}$ . Pump regenerant (paragraph 24) through the AMMS (paragraph 16) at a flow rate of around  $4 \text{ ml min}^{-1}$ . Pump eluent (paragraph 22) through the Dionex NG1 and NS1-5 $\mu$  columns (paragraph 16) at a flow rate of  $1.0 \text{ ml min}^{-1}$ . Allow the column packing material and eluent to come to equilibrium (at least 30 minutes prior to analysis). Offset the conductivity reading of the detector to zero just prior to analysis.

**Warning** Acetonitrile vapour is toxic: vent exhaust gases and vapour produced from degassing outside the laboratory.

**Note 8** Mobile phase ion chromatography requires longer equilibration times than do standard reversed-phase separations.<sup>20</sup> An indication of equilibration is given

by the (suppressed) conductivity of the eluent, which should settle at around  $11 \mu\text{S}$ .

60 Allow a run time of eight minutes per injection.

61 Run the calibration solutions (paragraph 58) in order of increasing concentration. For chromatographs having commercial data handling software facilities, it is recommended that bracketed calibration is used, if available, when the number of injections is greater than or equal to ten. Limit the maximum number of injections controlled by this calibration method to ten. For chromatographs not possessing the latter facility, a calibration should be generated by manually plotting conductivity versus concentration and recalibrating after every five to ten injections.

62 Run the sample and blank solutions (paragraph 57) and determine the peroxodisulphate peak height for each solution. For instruments having commercial data handling software facilities, use the calibration function to directly determine the peroxodisulphate concentration in  $\mu\text{g ml}^{-1}$ . For instruments without this capability, determine the peroxodisulphate concentration in  $\mu\text{g ml}^{-1}$  by comparing the peroxodisulphate peak height with the calibration graph (paragraph 61).

63 If high peroxodisulphate concentrations are found, dilute the sample solutions with water (paragraph 18) to bring the concentration within the calibration range. Repeat the analysis and record the dilution factor.

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

## CALCULATIONS

### Volume of air sample

65 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.

### Concentration of peroxodisulphate salt in air

66 Calculate the concentration of sodium, ammonium or potassium peroxodisulphate in air,  $\rho(X_2S_2O_8)$ , in milligrams per cubic metre ( $\text{mg m}^{-3}$ ), using the equation:

$$\rho(X_2S_2O_8) = \frac{[\rho(S_2O_8^{2-})_1 \cdot V_1 \cdot DF_1 - \rho(S_2O_8^{2-})_0 \cdot V_0 \cdot DF_0] \cdot F}{V}$$

where

X is the counter ion, ie sodium, ammonium or potassium (paragraph 1);

$\rho(S_2O_8^{2-})_0$  is the mean concentration, in  $\mu\text{g ml}^{-1}$ , of peroxodisulphate in the blank solutions (see paragraph 64);

$\rho(S_2O_8^{2-})_1$  is the concentration, in  $\mu\text{g ml}^{-1}$ , of peroxodisulphate in the sample solution (see paragraph 62);

V is the volume, in litres, of the air sample (see paragraph 65);

$V_0$  is the volume, in ml, of the blank solutions, ie 10 ml (see paragraph 57);

$V_1$  is the volume, in ml, of the sample solution, ie 10 ml (see paragraph 57);

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

$DF_1$  is the dilution factor for the sample solutions (see paragraph 63);

F is the appropriate factor, depending on whether sodium, ammonium or potassium peroxodisulphate is determined. For sodium peroxodisulphate  $F = 1.239$ , for ammonium peroxodisulphate  $F = 1.188$  and for potassium peroxodisulphate  $F = 1.407$ .

## TEST REPORT

67 Appendix 2 gives recommendations for information to be included in the test report.

## APPENDIX 1

### Primary standard for calibration of portable flowmeter

The primary standard should preferably be a flowmeter whose accuracy is traceable to national standards, used with careful attention to the conditions of the calibration certificate. A bubble flowmeter may be used. This is an arrangement whereby the pump under test draws a soap film up a calibrated tube. The passage of the film is accurately timed between two marks whose separation defines a known volume. A one litre burette can form a suitable tube. The volume between the marks can be checked by filling the burette with water (paragraph 17), allowing temperatures to stabilise, drawing off a known volume and weighing the water, making allowance for the dependence of volume on temperature. A suitable bubble solution can be made by mixing one part of concentrated washing-up liquid, two parts glycerol and four parts water. The burette must be thoroughly wetted with the solution and several attempts at drawing the film up the tube may be necessary before the tube is wet enough for this to be achieved consistently. (Traceability of the calibration will require checking of the clocks and use of certificated weights.)

## APPENDIX 2

### Recommendations for the test report

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

- 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;
- a reference to this MDHS and a description of any deviation from the procedures described;
- the type and diameter of filter used;
- the type of sampler used;
- the type of sampling pump used;
- 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;
- the time at the start and at the end of the sampling period, and the duration of the sampling period in minutes;
- the volume of air sampled, in litres;
- the name of the person who collected the sample;
- the time-weighted average mass concentration of peroxodisulphate salt (ammonium, potassium or sodium) found in the air sample, in milligrams per cubic metre;
- the name of the analyst;

(l) the date of the analysis.

#### 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.

#### REFERENCES

- 1 Greenwood NN and Earnshaw A *Chemistry of the Elements* (1st ed) Pergamon Press 1984 835
- 2 Fisher AA and Dooms-Gossens A Persulphate Hair Bleach Reactions *Arch Dermatol* 112 (1976) 1407
- 3 Nethercoti JR, Albers J, Guirgus S, Ching G, Hofstader S and From L Erythema Multiforme Exudativum Linked to the Manufacture of Printed Circuit Boards *Contact Dermatitis* 8 (1982) 314
- 4 Pepys J, Hutchcroft BJ and Breslin ABX Asthma due to Inhaled Chemical Agents - Persulphate Salts and Henna in Hairdressers *Clinical Allergy* 6 (1976) 399
- 5 White IR, Catchpole HE and Rycroft RIG Rashes Amongst Persulphate Workers *Contact Dermatitis* 8 (1982) 168
- 6 Killit JK and Beck MH Ammonium Persulphate Sensitivity in Hairdressers *Contact Dermatitis* 13 (1985) 26
- 7 Health and Safety Executive *Environmental Hygiene Series Guidance Note. Occupational exposure limits* EH 40 HSE Books (updated annually)
- 8 Healy J and Howe AM *Development and validation of a method for the sampling and analysis of peroxodisulphate salts in workplace air using mobile phase ion chromatography* HSE Internal Report IR/L/IS/93/04 1993
- 9 Comité Européen de Normalisation *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents* prEN 482 CEN 1992
- 10 Health and Safety Commission *Control of substances hazardous to health / Control of carcinogenic substances Approved Codes of Practice* 1988 HSE Books 2nd ed 1990 ISBN 0 11 885698 7
- 11 Health and Safety Executive *Environmental Hygiene Series Guidance Note. Monitoring strategies for toxic substances* EH 42 HSE Books 1989 ISBN 0 11 885698 7
- 12 British Standards Institution *Specification for water for*

*laboratory use* BS 3978 BSI 1993 ISBN 0580163121

13 Comité Européen de Normalisation *Workplace atmospheres - Size fraction definitions for measurement of airborne particles* EN 481 CEN 1993 (now adopted as British Standard BS EN 481 1993 ISBN 0580221407)

14 Health and Safety Executive *Methods for the Determination of Hazardous Substances. General methods for the gravimetric determination of respirable and total inhalable dust* MDHS 14 (rev) HSE Books 1993 ISBN 0 7176 0509 4

15 British Standards Institution *Specification for one-mark volumetric flasks* BS 1792 BSI 1993 ISBN 0580127540

16 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA). Part 1: Glossary of terms* BS 7653-1 BSI 1993 ISBN 0580221148

17 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA). Part 2: Methods of operation* BS 7653-2 BSI 1993 ISBN 0580221237

18 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA). Part 3: Methods of test* BS 7653-3 BSI 1993 ISBN 0580221253

19 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA). Part 4: Specification for conditions of test, safety and supply* BS 7653-4 BSI 1993 ISBN 0580221245

20 Dolan JW *Ion-pairing problems* LC · GC 10 (1992) 744

HSE priced and free publications are available from:

HSE Books  
PO Box 1999  
Sudbury  
Suffolk CO10 6FS  
Tel: 01787 881165  
Fax: 01787 313995

Priced publications are available through all good booksellers.

ISBN 0-7176-0802-6



© Crown copyright 1995  
First published 1995

C10 6/95

£4.00 net

Applications for reproduction should be made to HMSO