

Peroxodisulphate salts in air

Laboratory method using sample collection on filters and analysis by ion chromatography

MDHS79/2

Methods for the
Determination of
Hazardous Substances

Health and Safety
Laboratory

Scope

1 This method describes the measurement of time-weighted average concentrations of the peroxodisulphate dianion ($S_2O_8^{2-}$) in workplace air using ion chromatography which may then be expressed as the ammonium, potassium or sodium salt as required. The method is suitable for sampling over the range 15 minutes to 8 hours.

Summary

2 A measured volume of air is drawn through a filter mounted in an inhalable dust sampler. After extraction of the filter with water, the peroxodisulphate dianion is determined by ion chromatography.

3 The use of alternative methods not included in the MDHS series is acceptable provided they can demonstrate the accuracy and reliability appropriate to the application.

Recommended sampling

4 For long-term exposures: maximum sampling time: 8 hours; sampling rate: 2 l.min⁻¹; sampled volume: up to 960 litres.

5 For short-term exposures: sampling time: 15 minutes; sampling rate: 2 l.min⁻¹; sampled volume: 30 litres.

Prerequisites

6 Users of this method will need to be familiar with the content of MDHS14.¹

Safety

7 Users of this method should be familiar with normal laboratory practice and carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

Equipment

8 An inhalable dust sampler (with filter cassette transport clips), pre-cleaned as specified by the manufacturer: An IOM sampler operated as described in MDHS14¹ has been found suitable.

- 9 Mixed cellulose ester membrane filters (25 mm, pore size 0.45 μm , handle with flat-tipped tweezers during all manipulations).
- 10 Personal sampling pumps that meet the requirements of BS EN 13137.²
- 11 A portable flow meter, calibrated against a primary standard, with a measurement uncertainty typically less than $\pm 2\%$.
- 12 Flexible plastic tubing for making a leak-proof connection from the sampling head to the pump; belts or harnesses to facilitate attachment of the sampler to the subjects; flat-tipped tweezers for loading and unloading the filters into filter cassettes.

Laboratory apparatus and reagents

- 13 During the analysis, use only reagents of a recognised analytical grade.
- 14 Deionised water: Complying with the requirements of ISO 3696 grade 1 water (electrical conductivity less than 0.01 m.S.m^{-1} max at $25 \text{ }^\circ\text{C}$).³
- 15 Acetonitrile: HPLC grade.
- 16 Tetrabutylammonium hydroxide (TBAOH) solution, 0.5 M: HPLC grade.
- 17 Sodium carbonate solution, 0.5 M: Dissolve 26.50 g of sodium carbonate in 300 ml of water and make up to 500 ml with water in a volumetric flask.
- 18 Ion chromatography eluent, 28% (v/v) acetonitrile containing 2 m.M TBAOH and 3 mM sodium carbonate: 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. Prepare fresh eluent each day prior to analysis.
- 19 Sulphuric acid, 200 m.M: Carefully add 10.7 ml of concentrated sulphuric acid to around 400 ml of water in a 2 litre beaker. Mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water.
- 20 Sulphuric acid, 20 mM (regenerant): Quantitatively transfer 100 ml of 200 mM sulphuric acid to a 1 litre volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.
- 21 Stock standard peroxodisulphate solution ($1000 \mu\text{g.ml}^{-1}$ peroxodisulphate): dissolve 0.352 g of potassium peroxodisulphate in 75 ml of water. Quantitatively transfer the solution into a 250 ml volumetric flask, dilute to the mark with water. Prepare this solution fresh daily, prior to analysis.
- 22 Borosilicate laboratory glassware: including beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS EN ISO 1042.⁴ The glassware should be cleaned in a laboratory washing machine or soaked overnight in laboratory detergent solution and then rinsed in water.
- 23 Ion chromatography system: Operated according to the manufacturer's specifications. Suitable operating conditions are listed below but the use of other columns and conditions are acceptable provided they have the accuracy and reliability appropriate to the application:

Column	Dionex NG1 and NS1-5 µm guard and separator columns respectively
Mobile phase	28% (v/v) acetonitrile/water, containing 2 mM tetrabutylammonium hydroxide and 3 µM sodium carbonate
Eluent flow rate (ml.min ⁻¹)	1.5
Detection	Conductivity with chemical suppression using Dionex MMS suppressor and 20 mM sulphuric acid regenerant
Run time (min)	8

Preparation for air sampling

24 In a clean environment, load the filters into clean filter cassettes using flat-tipped tweezers, then into clean IOM samplers and cap.

25 Connect each sampler, excluding the blanks, to a sampling pump using plastic tubing, ensuring that no leaks can occur, and set the flow rate to 2 l.min⁻¹ using the calibrated flow meter.

26 Set aside two samplers per 10 samples to be used as blanks. Treat the blanks as for the samples but draw no air through them.

Sampling

27 Sampling should be carried out in accordance with the procedures described in MDHS14¹ for inhalable dust and is summarised below:

28 Select a suitable sampling time, such that the filter does not become overloaded with aerosol. (An 8-hour time-weighted average concentration may be derived from the results for two or more consecutive samples).

29 Attach the sampler in the breathing zone of the subject within 200 mm of the mouth and nose.

30 When ready to begin sampling, remove the protective cover from the sampler, switch on the pump and check and adjust the flow rate if necessary using the calibrated flow meter.

31 Record the time and sample details at the start of the sampling period.

32 At the end of the sampling period, measure the flow rate using the calibrated flow meter, switch off the sampling pump, and record the flow rate and the time and the elapsed time indicator, if fitted.

33 Reseal the sampler with its protective cover and disconnect it from the sampling pump.

34 In a clean area, remove the filter cassette from each sampler and place in the transport clip and transport back to the laboratory in a suitable container. Alternatively transport the samples in the capped sampling heads.

35 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 quantitative analytical recovery.

Calibration

36 Prepare at least five calibration solutions to cover the range 0 $\mu\text{g}\cdot\text{ml}^{-1}$ to 5 $\mu\text{g}\cdot\text{ml}^{-1}$ peroxodisulphate by pipetting the appropriate volume of 1000 $\mu\text{g}\cdot\text{ml}^{-1}$ stock standard peroxodisulphate solution into separate 100 ml volumetric flasks. Dilute to the mark with water and stopper. Prepare these solutions fresh daily.

Analysis

37 Transfer each sample and blank filter into a 50 ml beaker and rinse the internal surfaces of the filter cassette with a few millilitres of water if material deposited on these forms part of the sample (eg if an IOM sampler is used).

38 Add a further 4 ml of water to each beaker, cover with a watch glass, and place on an orbital shaker for 1 hour at 60 rpm.

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

40 Run the calibration solutions in order of increasing concentration using a bracketed calibration procedure. Limit the maximum number of sample injections controlled by this calibration method to ten.

41 Run the sample and blank solutions and determine the peroxodisulphate concentration in $\mu\text{g}\cdot\text{ml}^{-1}$ for each solution.

42 If high peroxodisulphate concentrations are found, dilute the sample solutions with water to bring the concentration within the calibration range, repeat the analysis and record the dilution factor.

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

Calculation of the concentration of peroxodisulphate salt in air

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

Note If it is not known which salt the peroxodisulphate exists as then a peroxodisulphate alone value can be obtained by omitting the factor, F.

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

Where

X = the counter ion, ie sodium, ammonium or potassium

$\rho(\text{S}_2\text{O}_8^{2-})_0$ = the mean concentration, in $\mu\text{g. ml}^{-1}$, of peroxodisulphate in the blank solutions

$\rho(\text{S}_2\text{O}_8^{2-})_1$ = the concentration, in $\mu\text{g. ml}^{-1}$, of peroxodisulphate in the sample solution

V = the volume, in litres, of the air sample; determined by averaging the flow rate measurements taken at the start and end of the sampling period and then multiplying by the sampling time, in minutes.

V_0 = the volume, in ml, of the blank solutions, ie 10 ml

V_1 = the volume, in ml, of the sample solution, ie 10 ml

DF_0 = dilution factor for the blank solutions, ie 1

DF_1 = dilution factor for the sample solutions

F = 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; for potassium peroxodisulphate F = 1.407.

Appendix: Additional information

Detection limits

1 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. For an air sample volume of 30 litres and a sample solution volume of 10 ml, these qualitative and quantitative detection limits correspond to peroxodisulphate in air concentrations of $96 \mu\text{g.m}^{-3}$ and $320 \mu\text{g.m}^{-3}$ respectively.

Overall uncertainty

2 Laboratory experiments 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%.

3 The overall uncertainty⁵ of the method 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, was negligible and that the coefficient of variation of the method that arises from pump flow rate variability was 5%. The overall uncertainty is therefore within the criteria specified by BS EN 482.⁵

Interferences

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

Stability

5 Sample stability was investigated by spiking filters with a solution of potassium peroxodisulphate and determining the analytical recovery after 7 days. Results indicate that samples in the range 6 µg to 1920 µg 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.

References

- 1 *General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable aerosols* MDHS14/4 HSE 2014
www.hse.gov.uk/pubns/mdhs/index.htm
- 2 BS EN 13137:2013 *Workplace atmospheres: Pumps for personal sampling of chemical and biological agents. Requirements and test methods* British Standards Institution
- 3 BS EN ISO 3696:1995 *Water for analytical laboratory use. Specification and test methods* British Standards Institution
- 4 BS EN ISO 1042:2000 *Laboratory glassware. One-mark volumetric flasks* British Standards Institution
- 5 BS EN 482:2012 *Workplace exposure. General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution

You should use the current edition of any standards listed.

Further information

For information about health and safety, or to report inconsistencies or inaccuracies in this guidance, visit www.hse.gov.uk/. You can view HSE guidance online and order priced publications from the website. HSE priced publications are also available from bookshops.

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