

MDHS 98/2

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

Hydroquinone in air

Laboratory method using high performance liquid chromatography

July 2007

Scope

1 This method describes how to measure hydroquinone in air using High Performance Liquid Chromatography (HPLC). It is suitable for exposures in the range 0.05 mg/m³ to 3.0 mg/m³ for 15 minute or 8 hour sampling.

Measurement principle

2 A measured volume of air is drawn through a glass fibre filter contained in a personal inhalable dust sampler which is backed-up with a Tenax sorbent tube. After sampling, the samplers are desorbed into acetonitrile and analysed by HPLC. Separation is achieved using a Zorbax CN column (25 cm x 4.6 mm id) or equivalent and separated species are detected using a photodiode array detector.

Recommended sampling

3 For expected exposures up to 1 mg/m³:

Max sampling time: 8 hours.
Sampling rate: 2 l/min.
Sampled volume: 960 litres.

Prerequisites

4 Users of this method should be familiar with the content of MDHS 14.¹

Safety

5 People using this method should be familiar with normal laboratory practice. This method does not

address all the safety problems associated with its use. It is the responsibility of the user to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

Equipment

6 Sampling medium: glass fibre filters contained in a suitable personal inhalable dust sampler¹ (multi-orifice or Institute of Occupational Medicine (IOM) type), with a back-up sorbent tube containing two layers of Tenax TA sorbent (50 and 100 mg), and having dimensions 8 x 100 mm (Tenax is a registered trademark of the Akzo Research Co).

7 Sampling pumps: capable of sampling up to 2 l/min and conforming to the requirements specified in MDHS 14.¹

8 Flow meter: calibrated against a primary standard and conforming to the requirements of MDHS 14.¹

9 Ancillary equipment: Flexible plastic tubing, of a diameter suitable for making a leakproof connection from the sample to the sampling pump; belts or harnesses to which the sampling pump can be conveniently fixed, unless the pump is sufficiently small to fit into the worker's pocket.

10 Glassware: A selection of laboratory glassware: including beakers and volumetric flasks.

11 Analytical balance: calibrated against a primary standard, capable of weighing ± 0.1 mg over the range 0-100 g.

12 Micropipettes: A range of adjustable positive displacement micropipettes, complying and tested in accordance with BS EN ISO 8655.²

- 13 4 ml screw top glass septum vials.
- 14 HPLC system: fitted with a photodiode array detector.

Chemicals

- 15 Acetonitrile: HPLC grade.
- 16 Hydroquinone: Pure (99%+).
- 17 Sodium dihydrogen orthophosphate.

Solutions

- 18 Sodium dihydrogen orthophosphate solution: Dissolve 1.56 g sodium dihydrogen orthophosphate dihydrate in 1 litre water.
- 19 Hydroquinone in acetonitrile calibration solutions.

Sample collection

- 20 Load the filter into the sampler, attach the back-up sorbent tube and set the flow rate to 2 l/min.
- 21 Set aside three unused sets of filters and sorbent tubes as field blanks. Subject the blanks to the same handling procedures as the samples, but without drawing air through them.
- 22 Fix the sampler on the worker's lapel, as close to the mouth and nose as possible. Place the sampling pump in a convenient pocket or attach it to the worker via a belt or harness.
- 23 After sampling, measure the flow-rate, switch off the sampling pump, and seal the sampler with its protective cover and cap the ends of the sorbent tube.
- 24 Check the sampler and pump periodically during sampling to see that they are still working and if necessary re-measure and adjust the flow rate.
- 25 Transport the filters to the laboratory for analysis either in the samplers or in a suitable container.
- 26 Samples may be stored at room temperature for no more than two days.

Sample preparation

- 27 Desorption of filters and sorbent tubes should be carried out as soon as possible and not more than two days after sampling.

28 Place each filter in a 4 ml glass screw top septum vial. Empty each Tenax section from the back-up tube into a similar vial.

29 Desorb the filters and Tenax sorbent into 3 ml acetonitrile.

30 Once desorbed, the samples may be stored for up to 4 weeks at room temperature.

Instrument conditions

- 31 HPLC:
- (a) Column: Zorbax CN.
 - (b) Dimensions: 25 cm x 4.6 mm id.
 - (c) Mobile phase: 30% acetonitrile/70% 0.01M sodium dihydrogen orthophosphate.
 - (d) Flow rate: 1.5 ml/min.
 - (e) Injection volume: 10 µl.
 - (f) Detector wavelength: 290 nm.
 - (g) Approximate elution time: 2.8 minutes.
 - (h) Total run time: 5 minutes.

Calibration

- 32 Prepare a fresh set of calibration standards with each batch of samples.
- 33 Prepare a stock calibration solution by weighing a known amount of hydroquinone into a volumetric flask and diluting with acetonitrile.
- 34 Dilute the stock solution to prepare at least six calibration standard solutions to cover the range 1.5 to 320 µg/ml.
- 35 Analyse the calibration standards in order of increasing concentration.
- 36 Determine the chromatographic peak areas.
- 37 Calculate the hydroquinone content of each standard. Plot the concentration against the peak area values, and determine the line of best-fit.
- 38 Check the calibration graph by analysing an independently prepared control solution. If the result does not agree with the previous calibration line within 10%, prepare fresh standards and carry out a new calibration.

Sample analysis

39 Analyse the samples and blanks and determine the analyte chromatographic peak areas.

40 Use the calibration graph to relate this to the concentration on the sample filter and tube.

41 Calculate the total analyte for each sample (CS, in µg), by adding the blank corrected filter and tube results together.

Calculation of results

42 Calculate the volume of air sampled for each sample, V_S , in litres.

43 Calculate the hydroquinone concentration in each air sample, ρ , in milligrams per cubic metre (mg/m^3), using the equation:

$$\rho = C_S / V_S$$

Sources of error

44 No interferences have been identified.

45 Sample stability has been considered in the Appendix.

Appendix 1: Additional information

1 Significant supplementary information can be found below. Further information can be found in the back-up data report, published online.⁴

Evaluation of the method

Precision

2 This method has been validated to EN 482,³ for an exposure limit of $0.5 \text{ mg}/\text{m}^3$. The overall uncertainty of the method was determined to be less than $\pm 14\%$ for samples in the range 0.1 to 0.5 times the limit value (ie 0.05 to $0.25 \text{ mg}/\text{m}^3$), and less than $\pm 11\%$ for samples in the range 0.5 to 2.0 times the limit value (ie 0.25 to $1.0 \text{ mg}/\text{m}^3$).

Recovery

3 The desorption efficiencies of the filter and Tenax tubes were tested at loadings equivalent to 8 hour samples taken at 2 l/min at hydroquinone concentrations between 0.05 and $10 \text{ mg}/\text{m}^3$. The mean desorption efficiency was found to be 101% for the filters, and 98% for the Tenax tubes.

Detection limits

4 The qualitative and quantitative detection limits for hydroquinone, defined as the concentration which gives a signal to noise ratio of 3:1 and 10:1 respectively, are typically around 0.3 µg and 1.2 µg per sample respectively. For an 8 hour sample taken at a flow rate of 2 l/min, these figures correspond to qualitative and quantitative detection limits of $0.3 \text{ µg}/\text{m}^3$ and $1.3 \text{ µg}/\text{m}^3$ respectively.

Sample stability

5 Sample stability was investigated by spiking filters and Tenax tubes with a solution of hydroquinone and determining the analytical recovery after 28 days. The results indicated that at low concentrations, Tenax tubes could lose a quarter of the material collected, and filters could lose almost half. Filter and Tenax tube extract solutions however were found to be stable for 28 days when stored at room temperature. It is recommended that exposed filters and Tenax tubes should be desorbed into acetonitrile as soon as possible after sampling.

References

- 1 MDHS 14/3 *General methods for sampling and gravimetric analysis of respirable and inhalable dust* HSE Books 2000 *
- 2 BS EN ISO 8655:2002 *Piston-operated volumetric apparatus Parts 1-6* British Standards Institution *
- 3 BS EN 482, 1994 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution ISBN 0 580 236447 *
- 4 Scobbie E *Measurement of Hydroquinone* Health and Safety Laboratory Report HSL/1992/02 Available at <http://www.hse.gov.uk/research/hsl/workenvn.htm>

* Amendments may be made occasionally and readers should ensure that they are using the current edition.

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