

Hydroquinone in air

Laboratory method using high performance liquid chromatography

MDHS 98/3

Methods for the
Determination of
Hazardous Substances

Health and Safety
Laboratory

Scope

1 This method describes a procedure for measurement of time-weighted average concentrations of hydroquinone in air using high performance liquid chromatography (HPLC). It is suitable for both short-term (15 minute) and long-term (up to 8 hour) sampling durations and for hydroquinone concentrations in the range 0.05 mg.m^{-3} to 3.0 mg.m^{-3} .

Summary

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 filter and sorbent tube are desorbed into acetonitrile and analysed by HPLC with UV detection.

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: 960 litres. For short-term exposures: Sampling time: 15 mins; Sampling rate: 2 l.min^{-1} ; Sampled volume: 30 litres.

Prerequisites

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

Safety

6 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

7 Sampling medium: glass fibre filters contained in a suitable personal inhalable dust sampler¹ (Institute of Occupational Medicine (IOM) type has been found suitable), with a backup sorbent tube containing two sections of Tenax sorbent

(100 and 50 mg front and back sections respectively), and having dimensions typically 8 x 100 mm.

- 8 Personal sampling pumps that meet the requirements of BS EN ISO 13137.²
- 9 A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than $\pm 2\%$.
- 10 Ancillary equipment: Flexible plastic tubing for making a leak-proof connection from the sampling head to the sampling pump; belts or harnesses to which the sampling pump can be conveniently fixed; tweezers for handling glass fibre filters.

Laboratory apparatus and reagents

- 11 During the analysis, use only reagents of a recognised analytical grade.
- 12 Glassware: A selection of laboratory glassware: including beakers and volumetric flasks, Class A, complying with the requirements of BS EN ISO 1042.³
- 13 Analytical balance: Calibrated against a primary standard, capable of weighing ± 0.1 mg over the range 0 to 100 g.
- 14 Positive displacement micropipettes complying with the requirements of BS EN 8655-6.⁴
- 15 4 ml screw-top glass septum vials.
- 16 HPLC system with UV detector: 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: Zorbax CN, dimensions: 25 cm x 4.6 mm id.
 - Mobile phase: 30% acetonitrile/70% 0.01M sodium dihydrogen orthophosphate.
 - Flow rate: 1.5 ml.min⁻¹.
 - Injection volume: 10 μ l.
 - Detector wavelength: 290 nm.
 - Approximate elution time: 2.8 minutes.
 - Total run time: 5 minutes.
- 17 Acetonitrile: HPLC grade.
- 18 Hydroquinone: Pure (99%+).
- 19 Sodium dihydrogen orthophosphate solution: Dissolve 1.56 g sodium dihydrogen orthophosphate dihydrate in 1 litre water.

Preparation and sampling

- 20 Load the filter into the sampler in a clean area; attach the backup sorbent tube to the outlet of the sampler using a short piece of flexible tubing.
- 21 Attach the sampling head to the subject's lapel within 200 mm of the nose and mouth and attach the sampling pump using a belt or harness if required.
- 22 Set the flow rate to 2 l.min⁻¹ using the portable flow meter.

- 23 Check the sampler and pump periodically during sampling and if necessary adjust the flow rate.
- 24 After sampling, check and record the flow rate, switch off the pump, seal the sampler with its protective cover and cap the ends of the sorbent tube.
- 25 Transport the filters to the laboratory for analysis either in the sampling heads or in a suitable container with the sorbent tubes and blanks.
- 26 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 draw no air through them.
- 27 Samples may be stored at room temperature for no more than two days before analysis.

Calibration

- 28 Modern HPLC equipment is usually sufficiently stable that a new calibration is not required with each set of samples. However, in order to verify the equipment and calibration, a quality assurance (QA) solution of known concentration, prepared using the hydroquinone stock solution below, must be analysed prior to each set of samples. If the result obtained from the QA solution shows an error of more than 10%, when compared with the known concentration, prepare a fresh set of standards and carry out a new calibration.
- 29 Prepare a stock solution of hydroquinone by accurately weighing approximately 100 mg of hydroquinone into a 100 ml volumetric flask and making up to volume with acetonitrile.
- 30 If calibration is required, prepare at least five standards to cover the range 1.5 to 320 $\mu\text{g}\cdot\text{ml}^{-1}$ by dilution of the stock solution.
- 31 Analyse the calibration standards, in order of increasing concentration, by HPLC and measure the peak areas of the target compounds. Plot the peak areas against the corresponding hydroquinone concentration of the standard, in $\mu\text{g}\cdot\text{ml}^{-1}$, and construct the line of best fit. The slope of this line is the detector response (RF) for hydroquinone at 290 nm.

Analysis

- 32 Desorption of filters and sorbent tubes should be carried out as soon as possible and not more than two days after sampling.
- 33 Analyse samples and blanks in an identical manner.
- 34 Place each filter in a 4 ml glass screw-top septum vial.
- 35 Empty each Tenax section from the backup tube into a similar vial.
- 36 Desorb the filters and Tenax sorbent into 3 ml acetonitrile with shaking.
- 37 Once desorbed, the samples may be stored for up to 4 weeks at room temperature.

38 Analyse the sample and blank solutions by HPLC in an identical manner to the calibration solutions.

39 Measure the peak areas of the target compound at 290 nm and convert these peak areas to a hydroquinone concentration, in $\mu\text{g}\cdot\text{ml}^{-1}$, by dividing by the R_F value obtained from the calibration standards.

40 If the hydroquinone concentration of any sample solution is greater than that of the highest standard, dilute with distilled water to bring the concentration back within the calibration range. Record the dilution factor and repeat the analysis.

Calculation of results

41 Calculate the total analyte concentration for each sample (C_S), in $\mu\text{g}\cdot\text{ml}^{-1}$, by summing the filter and tube results (taking into account any dilution factor).

42 Calculate the volume of air sampled for each sample, V_S , in litres, of each air sample by multiplying the mean volumetric flow rate, in litres per minute, during the sampling period, by the sampling time, in minutes.

43 Calculate the hydroquinone concentration in each air sample, C , in $\text{mg}\cdot\text{m}^{-3}$, using the equation:

$$C = \frac{(C_S - C_B) \times 3}{V_S}$$

Where:

C_S = total concentration ($\mu\text{g}\cdot\text{ml}^{-1}$) of hydroquinone in the sample

C_B = mean concentration ($\mu\text{g}\cdot\text{ml}^{-1}$) of hydroquinone in the blanks

V_S = volume of air sampled (litres)

3 = volume of sample solution

Appendix: Additional information

1 Supplementary information concerning this method can be found in the backup data report.⁵

Detection limit

2 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 $\text{l}\cdot\text{min}^{-1}$, these figures correspond to qualitative and quantitative detection limits of 0.3 $\mu\text{g}\cdot\text{m}^{-3}$ and 1.3 $\mu\text{g}\cdot\text{m}^{-3}$ respectively.

Overall uncertainty

3 The overall uncertainty for the method, as defined by BS EN 482,⁶ for a target value of 0.5 $\text{mg}\cdot\text{m}^{-3}$ was determined to be less than $\pm 14\%$ for samples in the range 0.05 to 0.25 $\text{mg}\cdot\text{m}^{-3}$ and less than $\pm 11\%$ for samples in the range 0.25 to 1.0 $\text{mg}\cdot\text{m}^{-3}$.

Recovery

4 The desorption efficiencies of the filter and Tenax tubes were tested at loadings equivalent to 8-hour samples taken at 2 l.min^{-1} at hydroquinone concentrations between 0.05 and 10 mg.m^{-3} . The mean desorption efficiency was found to be 101% for the filters, and 98% for the Tenax tubes.

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.

Interferences

6 No interferences have been identified.

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 ISO 13137:2013 *Workplace atmospheres: Pumps for personal sampling of chemical and biological agents. Requirements and test methods* British Standards Institution

3 BS EN ISO 1042:2000 *Laboratory glassware: One-mark volumetric flasks* British Standards Institution

4 BS EN ISO 8655-6:2002 *Piston-operated volumetric apparatus. Gravimetric methods for the determination of measurement error* British Standards Institution

5 Scobbie E *Measurement of Hydroquinone* Health and Safety Laboratory Report HSL/1992/02 Available at www.hse.gov.uk/research/hsl/workenvn.htm

6 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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