

# Hydrazine in air

Laboratory method with sampling either onto acid-coated glass fibre filters followed by solvent desorption or directly into modified impingers. Analysis by liquid chromatography after derivatisation

MDHS86/2

Methods for the  
Determination of  
Hazardous Substances

Health and Safety  
Laboratory

## Scope

1 Two sampling methods are described for airborne hydrazine (CAS No. 302-01-6). Both are suitable for the determination of time-weighted average concentrations of hydrazine vapour in workplace and environmental atmospheres. The first, employing sampling onto acid-coated glass fibre filters, is applicable to sampling periods of a few minutes to two hours. This method is suitable for personal sampling. The second method, using a modified impinger is applicable to long-term static sampling for periods up to 8 hours.

## Summary

2 Method 1 (filter sampling; recommended for personal sampling up to 2 hours): a measured volume of air is drawn through a phosphoric acid-coated glass fibre filter that is then desorbed into dilute sulphuric acid.

3 Method 2 (impinger sampling; recommended for long term static sampling): a measured volume of air is drawn through a modified impinger containing dilute sulphuric acid.

4 In both methods, hydrazine in the sample solution is derivatised by the addition of benzaldehyde at 80 °C, generating benzalazine, which is quantified by high-performance liquid chromatography (HPLC) with UV detection.

5 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

6 Method 1 (filter sampling): maximum sampling time 2 hours; sampling rate: 2 l.min<sup>-1</sup>; sampled volume: 240 litres.

7 Method 2 (impinger sampling): maximum sampling time: 8 hours; sampling rate: 1 l.min<sup>-1</sup>; sampled volume: 480 litres.

## Prerequisites

8 Users of this method will need to be familiar with the content of MDHS14.<sup>1</sup>

## Safety

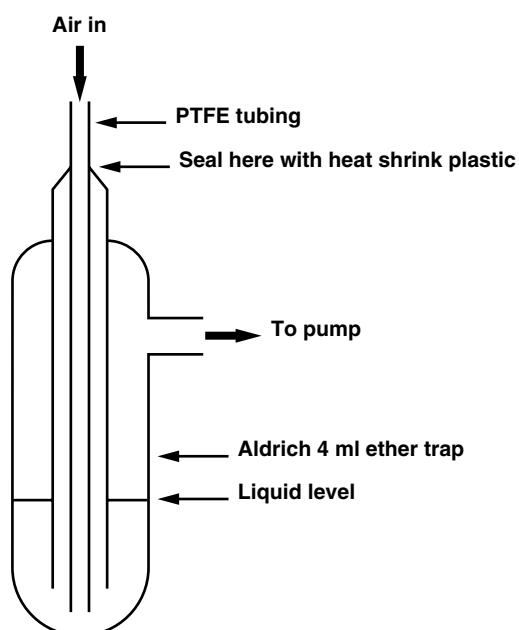
9 Users of this method should be familiar with standard laboratory practice and be able to carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

## Equipment

10 Filter method: binder-free glass fibre filters (25 mm Whatman GF/A have been found to be suitable).

11 Open face, chemically inert filter holder (eg Delrin type).

12 Impinger method: 25 ml midget impingers (see Figure 1) modified using, 1–2 mm i.d. Teflon tubing.



**Figure 1** Impinger for hydrazine sampling

13 Personal sampling pumps that meet the requirements of BS EN 13137.<sup>2</sup>

14 A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than  $\pm 2\%$ .

15 Flexible plastic tubing for making a leak-proof connection from the sampling train to the pump; belts or harnesses to facilitate attachment of sampling apparatus to sample subjects; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes to transport samples to the laboratory.

## Laboratory apparatus and reagents

16 During the analysis use only reagents of a recognised analytical grade. Use only distilled or deionised water.

- 17 Phosphoric acid in acetonitrile: Dilute 0.5 ml phosphoric acid (85% aqueous solution) to 25 ml with acetonitrile.
- 18 0.1 M sulphuric acid: Dilute 2.7 ml concentrated sulphuric acid to 500 ml with water (caution: carefully add acid to water).
- 19 Derivatisation reagent solution: Dilute 0.5 ml benzaldehyde to 100 ml with methanol.
- 20 Hydrazine sulphate.
- 21 Buffer solution: Dissolve 2 g sodium tetraborate in 100 ml water (stir continually until dissolved).
- 22 A selection of laboratory glassware, including beakers; 4 ml vials (with screw-top caps and teflon-silicone septa), and volumetric flasks, Class A, complying with the requirements of BS EN ISO 1042.<sup>3</sup>
- 23 Positive displacement micropipettes complying with the requirements of BS EN 8655-6.<sup>4</sup>
- 24 A balance, calibrated against a primary standard, for the preparation of the calibration standards. The balance should be capable of weighing to  $\pm 0.1$  mg over the range 0 to 100 g.
- 25 A heater block or oven, capable of maintaining samples (in sealed 4 ml vials) at 80 °C for 30 minutes.
- 26 Solvent-resistant plastic syringe filters (2  $\mu$ m pore size) for sample filtration prior to analysis.
- 27 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 dimensions	150 mm x 4.6 mm ID with guard column
Column packing	5 micron, reverse phase C18
Column temperature °C	20 °C
Mobile phase	70% acetonitrile/30% water
Flow rate	2.5 ml.min <sup>-1</sup>
Injection volume	20 $\mu$ l
UV detector	313 nm

- 28 Under the above conditions the retention time of benzalazine was 2.5 minutes and that of the excess benzaldehyde 1 minute.

## Preparation and sampling

### Filter samples

29 Lay out clean filters, in a fume cupboard, so that they are supported with a minimum amount of their surface area in contact with any solid surface. With 25 mm GF/A filters this may be achieved by resting the filter on the top rim of a 10 ml beaker. Add 0.25 ml of phosphoric acid in acetonitrile solution to each filter and allow 30 minutes to dry. The filters are then ready for use and may be stored for several weeks in an air-tight container before use.

30 Attach an acid-coated filter, mounted in a sampling head, to each pump with a length of flexible tubing. If personal sampling is being performed, the filter holder should be mounted on the sample subject's lapel, within 20 cm of the breathing zone. The sampling period should not exceed two hours under any circumstances. Do not allow filters to be exposed to test atmospheres before sampling commences since they may collect hydrazine passively. For this reason, samplers should be sealed before and immediately after sampling, using an appropriate cap. The filters are not suitable for sampling in extremely dry air, although they have been shown to perform adequately at humidities as low as 20% RH.

### Impinger samples

31 Remove the lower portion of the glass stem from a standard 25 ml midjet impinger and replace it with Teflon tubing, sealed in place with PTFE sleeving (heat shrink sleeving is suitable). On no account must the air sample pass through any glass tubing before the collecting solution, as this can lead to significant errors caused by hydrazine adsorption onto the glass. Place 10 ml of 0.1M sulphuric acid into the impinger body for sample collection.

32 Connect the acid-filled impinger to the sampling pump using a length of flexible tubing. This sampling train is best suited to static sampling, as liquid may be spilled from the impinger. It may be necessary to top up the solution with distilled water intermittently during and at the end of sampling if significant evaporation occurs.

### Blanks

33 A minimum of three field blanks of each sampler type should be included with a batch of samples.

## Calibration

34 Prepare a minimum of four calibration standards by accurately weighing hydrazine sulphate, a stable salt of hydrazine containing 24.6% w/w hydrazine, into volumetric flasks and diluting with 0.1 M sulphuric acid. Further serial dilutions will usually be necessary to obtain a suitable concentration range, eg 0.05  $\mu\text{g}\cdot\text{ml}^{-1}$  – 30  $\mu\text{g}\cdot\text{ml}^{-1}$ .

35 Transfer 1.0 ml of each calibration solution to a 4 ml vial, analyse in an identical manner to the samples and measure the peak areas of the target compound. Plot the peak areas against the corresponding hydrazine content of the standard, in  $\mu\text{g}$ , and construct the line of best fit. The slope of this line is the detector response factor (RF) for hydrazine.

36 Modern HPLC equipment is usually sufficiently stable that a new calibration is not required with each set of samples. However, to verify the equipment, a quality assurance (QA) solution of known concentration, must be analysed with each set of samples. The QA solution may be prepared using the procedure above (paragraph 34).

## Sample analysis

37 Analyse samples and blanks in an identical manner.

38 For filter samples, remove the filter from the sampling head using tweezers and place in a 4 ml vial and add 1.0 ml of 0.1 M sulphuric acid. If the samples are not to be analysed immediately, the vials may be sealed and stored at room temperature for up to 4 weeks. Note: Pre-desorbed filters are stable for a few hours only.

39 For impinger samples, it may first be necessary to make the liquid in the impinger back up to the original volume (10 ml, using de-ionised water). Take 1.0 ml of the sample solution and place in a 4 ml vial.

40 Add 1.0 ml of reagent (benzaldehyde in methanol) to each vial, followed by 1.0 ml of buffer solution. Seal the vials with caps fitted with Teflon-lined septa, and heat at 80 °C for one hour. Note: excess acidity inhibits the reaction between hydrazine and benzaldehyde. A significant peak on the chromatogram, eluting before benzaldehyde, is evidence that this has occurred.

41 Cool the samples to room temperature, then filter and analyse by HPLC. Measure the chromatographic peak area of the target compound and convert this peak area to a hydrazine content, in µg, by dividing by the RF value obtained from the calibration standards.

42 Calculate the mean mass of hydrazine, in µg, in the blanks.

## Calculation of results

43 Calculate the volume of air sampled for each sample,  $V_s$ , in litres.

44 For a filter sample, calculate the airborne concentration of hydrazine,  $C$ , in  $\text{mg}\cdot\text{m}^{-3}$ , using the equation:

$$C = (M_s - M_b) / V_s$$

For an impinger sample, calculate the airborne concentration of hydrazine,  $C$ , in  $\text{mg}\cdot\text{m}^{-3}$  using the equation:

$$C = (10 \times (M_s - M_b)) / V_s$$

Results for both sample types may also be expressed as a volume fraction in air,  $C'$ , in ppm, using the equation:

$$C' = C \times (24.5/M_w) \times (T/298)$$

Where:

$M_s$  = Mass of hydrazine in sample, in  $\mu\text{g}$

$M_b$  = Mean mass of hydrazine in blanks, in  $\mu\text{g}$

$V_s$  = Air volume of sample, in litres

24.5 = Molar volume of an ideal gas at 298K, in litres

$M_w$  = Molecular weight of hydrazine, in  $\text{g}\cdot\text{mol}^{-1}$

T = Temperature of sampled air, in K

## Appendix: Additional information

### Detection limit

1 The estimated limits of detection and quantification may be calculated from the mean and standard deviation (SD) of the blanks using the following formulae:

Limit of detection (LOD) =  $M_b + (3 \times \text{SD})$

Limit of quantification (LOQ) =  $M_b + (10 \times \text{SD})$

2 Using the recommended sampling conditions, both filter and impinger methods are suitable for the measurement of airborne hydrazine in the concentration range 0.002 to 2 ppm. The actual detection limit for an individual sample is dependent on the sample volume.

### Overall uncertainty

3 The overall uncertainty for both sampling procedures, as defined by BS EN 482,<sup>5</sup> determined by sampling laboratory generated standard atmospheres, was typically calculated at 15% (and no greater than 25%).<sup>6</sup>

## 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](http://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 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 BS EN 482:2012 *Workplace exposure. General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution

6 Keen C and Pengelly MI *Development of a method for measuring airborne hydrazine* HSE internal report IR/L/SP/95/07 1995

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/](http://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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