

MDHS

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory



95/2

Measurement of personal exposure of metalworking machine operators to airborne water-mix metalworking fluid

Elemental marker method using flame atomic
absorption spectrometry or inductively coupled
plasma-atomic emission spectrometry

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Note 1: This MDHS describes a method for measuring the personal exposure of metalworking machine operators to airborne water-mix metalworking fluid. It does not apply to mineral oil mist, a method for which is described in MDHS 84.¹

Note 2: Refer to Appendix A for a glossary of the terminology used in this MDHS.

INTRODUCTION

Requirements of the Control of Substances Hazardous to Health Regulations 2002 (COSHH)

1 Those who carry out and supervise the procedures described in this MDHS could be exposed to various hazardous substances, and therefore should also be aware of the requirements of the COSHH Regulations.² These are designed to ensure that the exposure of people at work to substances that could cause health damage is either prevented or, where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH Regulations also require that persons who could 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 MDHS.

2 Guidance is given in the Approved Codes of Practice for the Control of Substances Hazardous to Health Regulations, which are included in a single publication with the COSHH Regulations.³

Properties and uses

3 Properties and uses of water-mix metalworking fluids are described in Guidance Note EH 62.⁴

Health effects

4 The health effects of water-mix metalworking fluids are summarised in Guidance Note EH 62⁴ and in leaflet INDG169.⁵ It should be noted that metalworking fluid formulations are continually changing due to advances in technology, and therefore health effects can only be characterised in general terms.

5 The primary health concern arising associated with the use of water-mix metalworking fluids is contact dermatitis resulting from repeated or prolonged dermal (skin) exposure. However, inhalation exposure to mist generated during use of water-mix metalworking fluids is also a significant health concern as it can cause irritation in the respiratory tract and impairment of lung function. There is limited evidence that some components of water-mix metalworking fluids can induce occupational asthma, but there is no consensus on which components are responsible. The most serious respiratory effects are related to exposure to endotoxin released from dead bacteria. Endotoxin can cause short-term effects, including flu-like symptoms and reduced lung function. Exposure may exacerbate symptoms in those with pre-existing asthma.

6 Although concerns have been raised about the potential for cancer in humans, these relate to historical exposures to unrefined mineral oils containing aromatic hydrocarbons (PAHs), which themselves are potential carcinogens, and not to water-mix metalworking fluids.

Health and safety precautions

7 HSE leaflet INDG169⁵ summarises the risks involved in working with water-mix metalworking fluids and what can be done to control them. Guidance on health surveillance, health risks and safe working practice are described more fully in HSE leaflets INDG165,⁶ INDG167⁷ and INDG365⁸ and in guidance booklet HSG231.⁹ An

information pack on working safely with metalworking fluids¹⁰ is also available, containing a copy of HSG231, a set of eight encapsulated task sheets, a 'Dos and Don'ts' wallchart and ten copies of INDG365.

Exposure limits

8 No occupational exposure limit has been set for water-mix metalworking fluids. However, the results of a survey of UK industry have been used as a basis for the development of guidance exposure limits for metalworking fluids.¹¹ A guidance limit value of 1 mg m^{-3} has been set for water-mix metalworking fluid mist.⁹

9 The guidance limit value for water-mix metalworking fluid mist is not health-based, but is an indicator of what can be achieved if good practice is followed. It is for guidance only and is not legally binding. If, as a result of a COSHH assessment, it can be demonstrated that use of a higher guidance limit value will not compromise the health of metalworking machine operators, or if, based on current technology, it is difficult to work to the guidance limit value in a particular process, an alternative in-house limit value may be established.¹¹

Analytical methods

10 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. 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.

11 This method has been validated¹² to demonstrate that it complies with BS EN 482 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents*.¹³ If an alternative method is used, it is necessary to demonstrate that it also meets these performance requirements.

SCOPE

12 This MDHS describes an elemental marker method for measurement of personal exposure of metalworking machine operators to airborne water-mix metalworking fluid, using flame atomic absorption spectrometry or inductively coupled plasma-atomic emission spectrometry.

13 The method is applicable only when the machine sump fluid contains a suitable element at a high enough concentration for its successful use as a marker. A suitable marker element is one that originates from the water-mix metalworking fluid concentrate or from the water used to prepare the working strength solution; and which is unlikely to emanate from a secondary source within the workplace. An element that originates from the workpiece is unsuitable, since it will be present in any airborne metal particles generated by the metalworking process, which will therefore interfere with the marker method.

14 The sampling time for which the method is suitable is dependent upon the sensitivity of the analytical technique used for measurement of the marker element; the concentration of the marker element in the machine sump fluid; and the sump fluid strength. A sampling time in the range 2 to 8 hours is recommended in order to comply with the overall uncertainty requirements of BS EN 482¹³ when boron or potassium is used as a marker element (see paragraphs 34 and 36). A sampling time of 8 hours is recommended in order to comply with the overall uncertainty requirements of BS EN 482¹³ when sodium is used as a marker element (see paragraph 35).

METHOD PERFORMANCE

Lower limit of the working range

15 The working range of the method is dependent upon the quantitative detection limit of the analytical technique used for measurement of the marker element; the concentration of the marker element in the machine sump fluid; the sump fluid strength; and the air sample volume.

16 Qualitative and quantitative detection limits for the analytical method, defined as three times and ten times the standard deviation of a blank determination, have been determined¹² for boron, by inductively coupled plasma-atomic emission spectrometry; and for sodium and potassium, by flame atomic absorption spectrometry. The qualitative and quantitative detection limits for boron were $0.007 \mu\text{g ml}^{-1}$ and $0.024 \mu\text{g ml}^{-1}$, respectively; for sodium they were $0.084 \mu\text{g ml}^{-1}$ and $0.28 \mu\text{g ml}^{-1}$, respectively; and for potassium they were $0.008 \mu\text{g ml}^{-1}$ and $0.028 \mu\text{g ml}^{-1}$, respectively.

17 Examples of the lower limit of the working range for water-mix metalworking fluid concentrate-in-air are given in Table 1. The values given are for a quantitative analytical detection limit of $0.025 \mu\text{g ml}^{-1}$, which is typical of that which can be obtained using boron or potassium as the marker element, and for a range of typical concentrations of marker element in the sump fluid and sump fluid strengths. The lower limit of the working range will be about ten times higher if sodium is used as the marker element.

18 Lower limits of the working range determined¹² from the results of measurements made on some 200 samples in a survey of personal exposure to water-mix metalworking fluids are 0.01 mg m^{-3} for potassium, 0.03 mg m^{-3} for boron and 0.12 mg m^{-3} for sodium. These are mean values for samples collected on quartz fibre filters, with sample volumes in the range 250 - 500 litres, sump fluid marker element concentrations in the range 200 - $400 \mu\text{g ml}^{-1}$, and sump fluid strengths in the range 2 - 5%.

Bias

Sampler bias

19 The bias of inhalable samplers has been shown¹⁴ to vary considerably. However, a bias of less than $\pm 5\%$ is typical for the samplers recommended in MDHS 14/3.¹⁵ This value was therefore used when estimating the bias of the measuring procedure as a whole using Equation 1.

Table 1 - Examples of the lower limit of the working range for measurement of water-mix metalworking fluid concentrate-in-air for a quantitative analytical detection limit of 0.025 µg ml⁻¹

Concentration of marker element in the machine sump fluid (µg ml ⁻¹)	Sump fluid strength (% v/v)	Lower limit of the working range for measurement of water-mix metalworking fluid concentrate-in-air (mg m ⁻³)		
		Air sample volume (litres)		
		250	500	1000
100	1	0.1	0.05	0.025
	2	0.2	0.1	0.05
	5	0.5	0.25	0.125
200	1	0.05	0.025	0.0125
	2	0.1	0.05	0.025
	5	0.25	0.125	0.0625
400	1	0.025	0.0125	0.00625
	2	0.05	0.025	0.0125
	5	0.125	0.0625	0.03125

20 The collection efficiency of quartz fibre filters for boron has been shown to be better than 99% (see note 10).

Analytical bias

21 The analytical recovery of marker elements from filters spiked with water-mix metalworking fluid has been shown¹² to be around 100%.

22 The mean analytical recovery for 200 filters spiked with between 0.048 µg and 38.4 µg of boron has been determined¹² to be 96.7 ± 4.0% using inductively coupled plasma-atomic emission spectrometry. The mean analytical recovery for 120 filters spiked with between 0.768 µg and 38.4 µg of sodium has been determined¹² to be 100.2 ± 4.1% using flame atomic absorption spectrometry; and the mean analytical recovery for 190 filters spiked with between 0.096 µg and 38.4 µg of potassium has been determined¹² to be 101.0 ± 5.4% using flame atomic absorption spectrometry.

23 Laboratory experiments¹² therefore indicate that the analytical method does not exhibit significant bias. An analytical bias of zero was therefore substituted in Equation 1 when estimating the bias of the measuring procedure as a whole.

Combination of sampling and analytical bias

24 The bias of the measuring procedure as a whole is given by:

$$(1 + \text{bias}) = (1 + \text{bias}_{\text{sampler}}) \times [1 + \text{bias}_{\text{analysis}}] \quad \text{Equation 1}$$

Precision

Imprecision of the aerosol sampling process

25 The imprecision of the aerosol sampling process usually depends strongly on the size distribution of the airborne particles sampled, and it can depend on other factors, such as windspeed. BS EN 13205¹⁶ suggests calculating approximate values of the imprecision of the

sampling process relevant to the workplace atmosphere to be sampled, using information given in the sampler test report.

26 However, this approach is not practicable for assessing the performance of a measuring procedure intended for general application. The results of a study to evaluate the performance of inhalable samplers¹⁴ suggest that the relative standard deviation of the aerosol sampling process is normally less than 5% for inhalable samplers that meet the requirements of BS EN 13205.¹⁶ The relative standard deviation of the aerosol sampling process, RSD_{sampler} , was therefore taken to be 5% when estimating the imprecision of the measuring procedure as a whole using Equation 2.

Imprecision arising from flow rate variability

27 In the case of aerosol samplers where there is no interaction between particle size selection characteristics and volumetric flow rate, at least for small changes in flow rate, the imprecision arising from flow rate variability can be estimated simply. BS EN 1232 *Workplace atmospheres - Pumps for personal sampling of chemical agents - Requirements and test methods*¹⁷ prescribes a maximum allowable error in the volumetric flow rate of ±5%. Assuming that this is met on 99% of all occasions, the flow-related relative standard deviation, RSD_{flow} , is equal to 0.05/3. This value was therefore used when estimating the imprecision of the measuring procedure as a whole using Equation 2.

Imprecision arising from analytical variability

28 The relative standard deviation of the analytical method, RSD_{analysis} , has been determined¹² to be less than 22% for samples in the range 0.048 µg to 9.6 µg of boron, and less than 5% for samples in the range 0.24 µg to 38.4 µg of boron, using inductively coupled plasma-atomic emission spectrometry; less than 18% for samples in the range 0.768 µg to 9.6 µg of sodium, and less than 3% for samples in the range 9.6 µg to 38.4 µg of sodium, using flame atomic absorption spectrometry; and less than 14%

for samples in the range 0.096 µg to 3.84 µg of potassium, and less than 9% for samples in the range 0.24 µg to 38.4 µg of potassium, using flame atomic absorption spectrometry. The determined relative standard deviations were substituted in Equation 2 to estimate the imprecision of the measuring procedure as a whole for each mass of marker element.

Combination of sampling and analytical precision

29 The imprecision of the measuring procedure as a whole is given by:

$$RSD^2 = RSD_{\text{sampler}}^2 + RSD_{\text{flow}}^2 + RSD_{\text{analysis}}^2 \quad \text{Equation 2}$$

Overall uncertainty

30 The overall uncertainty for a measuring procedure is defined in BS EN 482¹³ as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is expressed in percentage terms, by a combination of bias and precision according to the following equation:

$$OU = \frac{|\bar{x} - x_{\text{ref}}| + 2\sigma_{(n-1)}}{x_{\text{ref}}} \times 100\% \quad \text{Equation 3}$$

where:

OU is the overall uncertainty of the procedure;

\bar{x} is the mean value of results of n repeated measurements;

x_{ref} is the true or accepted reference value; and

$\sigma_{(n-1)}$ is the standard deviation of n repeated measurements.

31 Equation 3 can be rewritten as:

$$OU = [|\text{bias}| + (2 \times RSD)] \times 100\% \quad \text{Equation 4}$$

where:

bias is the difference between the mean measured concentration and the true or reference concentration, divided by the true or reference concentration, ie

$$\frac{(\bar{x} - x_{\text{ref}})}{x_{\text{ref}}}; \text{ and}$$

RSD is the relative standard deviation of n repeated measurements defined as

$$\frac{\sigma_{(n-1)}}{x_{\text{ref}}}$$

32 The overall uncertainty can then be estimated by substituting in Equation 4 the values for bias and relative standard deviation calculated using Equations 1 and 2. In

this manner, the overall uncertainty of the measuring procedure described in this method has been estimated¹² to be less than 50% for samples in the range 0.048 µg to 9.6 µg of boron, and less than 20% for samples in the range 0.24 µg to 38.4 µg of boron, using inductively coupled plasma-atomic emission spectrometry; less than 42% for samples in the range 0.768 µg to 9.6 µg of sodium, and less than 18% for samples in the range 9.6 µg to 38.4 µg of sodium, using flame atomic absorption spectrometry; and less than 35% for samples in the range 0.096 µg to 3.84 µg of potassium, and less than 25% for samples in the range 0.24 µg to 38.4 µg of potassium, using flame atomic absorption spectrometry.

33 BS EN 482¹³ prescribes that the overall uncertainty of procedures for the measurement of chemical agents in workplace air shall be <50% for measurements in the range 0.1 to 0.5 times the limit value, and <30% for measurements in the range 0.5 to 2.0 times the limit value.

34 The method using boron and inductively coupled plasma-atomic emission spectrometry therefore complies with the overall uncertainty requirements of BS EN 482¹³ when measuring water-mix metalworking fluid-in-air concentrations between 0.1 and 2 times a guidance exposure limit of 1 mg m⁻³ (see paragraph 8), using sampling times between 2 and 8 hours and a volumetric flow rate of 2 l min⁻¹, in circumstances where the marker element concentration in the sump fluid is greater than 0.1 g l⁻¹ and the sump fluid strength is less than 5%. It can also comply with the overall uncertainty requirements of BS EN 482¹³ when the marker element concentration in the sump fluid is less than 0.1 g l⁻¹, if the sump fluid strength is less than 5% and/or if sampling times in excess of 1 hour are used.

35 The method using sodium and flame atomic absorption spectrometry therefore complies with the overall uncertainty requirements of BS EN 482¹³ when measuring water-mix metalworking fluid-in-air concentrations between 0.1 and 2 times the guidance exposure limit of 1 mg m⁻³ (see paragraph 8) using a sampling time of 8 hours and a volumetric flow rate of 2 l min⁻¹, in circumstances where the marker element concentration in the sump fluid is greater than 0.4 g l⁻¹ and the sump fluid strength is less than 5%. It can also comply with the overall uncertainty requirements of BS EN 482¹³ when the marker element concentration in the sump fluid is less than 0.4 g l⁻¹, if the sump fluid strength is less than 5%.

36 The method using potassium and flame atomic absorption spectrometry therefore complies with the overall uncertainty requirements of BS EN 482¹³ when measuring water-mix metalworking fluid-in-air concentrations between 0.1 and 2 times the guidance exposure limit of 1 mg m⁻³ (see paragraph 8), using sampling times between 2 and 8 hours and a volumetric flow rate of 2 l min⁻¹, in circumstances where the marker element concentration in the sump fluid is 0.2 g l⁻¹ and the sump fluid strength is 5%. It can also comply with the overall uncertainty requirements of BS EN 482¹³ when the marker element concentration in the sump fluid is less than 0.2 g l⁻¹, if the sump fluid strength is less than 5% and/or if sampling times in excess of 1 hour are used.

Interferences

37 Secondary sources of the marker element in the workplace could interfere significantly with the method, and lead to spuriously high results. In particular, sodium is ubiquitous in the environment, and careful consideration should be given before selecting it as the marker element.

38 Determination of the strength of water-mix metalworking fluid in the sump by refractometry (paragraphs 124-128) gives accurate results if the sump fluid is in good condition.¹⁸ However, results can be subject to interference if significant amounts of tramp oil have entered the sump. This is most likely to be a problem if the water-mix metalworking fluid formulation includes emulsifiers to disperse tramp oil.

39 Measurement of sodium and potassium by flame atomic absorption spectrometry is subject to possible ionisation interferences, but these are eliminated by the use of caesium chloride as an ionisation buffer.

40 Measurement of boron by inductively coupled plasma-atomic emission spectrometry can be subject to interferences from concomitant elements in the sample solution, so careful attention should be given to wavelength selection and the need for background and/or spectral correction to ensure that accurate results are obtained. Carry over can also be a problem (see note 27).

PRINCIPLE

41 Personal exposure of a metalworking machine operator to airborne water-mix metalworking fluid is determined by using sodium, potassium or boron (or some other suitable element) present in the sump fluid as a marker.

42 A measured volume of air is drawn through a filter mounted in an inhalable sampler attached to the lapel of the metalworking machine operator. A sample of the fluid circulating in the machine is also taken.

43 The sump fluid sample and the air sample are analysed for the marker element by either flame atomic absorption spectrometry or inductively coupled plasma-atomic emission spectrometry, and the results are used to estimate the aqueous aerosol concentration to which the operator was exposed.

44 The strength of water-mix metalworking fluid in the sump is then measured by refractometry, and this result is used to calculate the operator's exposure to airborne water-mix metalworking fluid concentrate.

REAGENTS

45 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 46). Do not pipette by mouth.

Water

46 Water complying with the requirements of BS 3978¹⁹ grade 2 water (electrical conductivity less than 0.1 mS m⁻¹ and resistivity greater than 0.01 MΩ.m at 25°C).

Nitric acid (HNO₃), concentrated, ρ about 1.42 g ml⁻¹, 69% (m/m) to 71% (m/m)

47 General purpose reagent grade concentrated nitric acid.

WARNING - Concentrated nitric acid is corrosive and oxidising, and nitric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with concentrated or diluted nitric acid, and sample dissolution with nitric acid should be carried out in a fume cupboard.

Nitric acid, diluted 1 + 9

48 Add approximately 800 ml of water (paragraph 46) to a 1 litre volumetric flask. Carefully add 100 ml of concentrated nitric acid (paragraph 47) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Stock sodium standard solution, 1000 µg ml⁻¹ of sodium

49 Use commercially available standard solution at a concentration of 1000 µg ml⁻¹ of sodium. Observe the manufacturer's expiry date or recommended shelf life.

Alternatively prepare a stock sodium standard solution by the following procedure:

50 Dissolve 2.543 g of sodium chloride, NaCl, dried overnight at 110°C and cooled in a desiccator, in water (paragraph 46). Quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water and mix thoroughly.

Note 3: Sodium standard solution prepared according to the instructions in paragraph 50 may be stored in a polypropylene bottle (paragraph 67) for a period of one year without deterioration.

Working sodium standard solution, 100 µg ml⁻¹ of sodium

51 Accurately pipette 5 ml of stock sodium standard solution (paragraph 49 or 50) into a 50 ml volumetric flask, dilute to the mark with water (paragraph 46) and mix thoroughly. Prepare this solution fresh weekly.

Stock potassium standard solution, 1000 µg ml⁻¹ of potassium

52 Use commercially available standard solution at a concentration of 1000 µg ml⁻¹ of potassium. Observe the manufacturer's expiry date or recommended shelf life.

Alternatively prepare a stock potassium standard solution by the following procedure:

53 Dissolve 1.910 g of potassium chloride, KCl, dried overnight at 110°C and cooled in a desiccator, in water (paragraph 46). Quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water and mix thoroughly.

Note 4: Potassium standard solution prepared according to the instructions in paragraph 53 may be stored in a polypropylene bottle (paragraph 67) for a period of one year without deterioration.

Working potassium standard solution, 100 µg ml⁻¹ of potassium

54 Accurately pipette 5 ml of stock potassium standard solution (paragraph 52 or 53) into a 50 ml volumetric flask, dilute to the mark with water (paragraph 46) and mix thoroughly. Prepare this solution fresh weekly.

Stock boron standard solution, 1000 µg ml⁻¹ of boron

55 Use commercially available standard solution at a concentration of 1000 µg ml⁻¹ of boron. Observe the manufacturer's expiry date or recommended shelf life.

Alternatively prepare a stock boron standard solution by the following procedure:

56 Dissolve 8.819 g of di-sodium tetraborate decahydrate, Na₂B₄O₇·10H₂O, in water (paragraph 46). Quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water and mix thoroughly.

Note 5: Boron standard solution prepared according to the instructions in paragraph 56 may be stored in a polypropylene bottle (paragraph 67) for a period of one year without deterioration.

Working boron standard solution, 100 µg ml⁻¹ of boron

57 Accurately pipette 5 ml of stock boron standard solution (paragraph 55 or 56) into a 50 ml volumetric flask, dilute to the mark with water (paragraph 46) and mix thoroughly. Prepare this solution fresh weekly.

Caesium chloride solution, approximately 0.2% (m/v) of caesium

58 Dissolve 2.5 g of caesium chloride, CsCl, in water (paragraph 46). Quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water and mix thoroughly.

Note 6: Caesium chloride solution prepared according to the instructions in paragraph 58 may be stored in a polypropylene bottle (paragraph 67) for an indefinite period.

Laboratory detergent solution

59 A laboratory grade detergent suitable for cleaning of samplers and labware, diluted with water (paragraph 46) according to the manufacturer's instructions.

SAMPLING EQUIPMENT

Inhalable samplers

60 Samplers, with protective covers, designed to collect the inhalable fraction of airborne particles, as defined in

BS EN 481,²⁰ and complying with the provisions of BS EN 13205.¹⁶ Inhalable samplers suitable for personal sampling are described in MDHS 14/3.¹⁵

Note 7: Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge that can be removed from the sampler to enable this material to be easily recovered.) The operating instructions supplied by the manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample.

Note 8: Samplers manufactured in non-conducting material have electrostatic properties that can influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.

Note 9: Metalworking fluid operations often result in particulate being ejected from the workpiece and/or the formation of a coarse spray of metalworking fluid. If possible, the inhalable samplers selected for use should be of a design that minimises the occurrence of direct impaction of metal particles or the splashing of metalworking fluid droplets onto the sample filter.

Filters

61 Filters, of a diameter suitable for use in the samplers (paragraph 60), with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter (see subclause 2.2 of BS EN 481²⁰), for sampling when sodium or potassium is used as the marker element. Mixed cellulose ester membrane filters of 0.8 µm mean pore diameter are suitable.

62 Quartz fibre filters, of a diameter suitable for use in the samplers (paragraph 60), for sampling when boron is used as the marker element.

Note 10: It has been found²¹ that the boric esters present as additives in certain water-mix metalworking fluids are collected quantitatively by quartz fibre filters, but not by mixed cellulose ester membrane filters.

Sampling pumps

63 Sampling pumps, complying with the provisions of BS EN 1232,¹⁷ and compatible with the samplers used (paragraph 60).

Note 11: Existing users may continue to use sampling pumps that do not fully comply with the provisions of BS EN 1232,¹⁷ provided that they take steps to ensure that the required volumetric flow rate (see paragraph 78) is maintained to within ±5% of the nominal value throughout the sampling period.

64 BS EN 1232¹⁷ requires that sampling pumps have, as a minimum, the following features:

- an automatic control which keeps the volumetric flow rate constant in the case of changing back pressure;
- either a malfunction indicator, which, following completion of sampling, indicates that the air flow has been reduced or interrupted during sampling; or an automatic cut-out, which stops the pump if the flow rate is reduced or interrupted; and
- a facility for the adjustment of flow rate, such that it can only be actuated with the aid of a tool (eg screw driver) or requires special knowledge for operation (eg via software), so as to preclude inadvertent readjustment of the flow rate during use.

Note 12: *An integral timer is a highly desirable additional feature.*

65 BS EN 1232¹⁷ requires that the performance of the pumps is such that:

- the pulsation of the flow rate does not exceed 10%;
- a flow rate set within the nominal range does not deviate by more than $\pm 5\%$ from the initial value under increasing back pressure;
- within the range of ambient temperatures from 5°C to 40°C, the flow rate measured under operating conditions does not deviate by more than $\pm 5\%$ from the flow rate at 20°C;
- the operating time is at least 2 h, and preferably 8 h; and
- the flow rate does not deviate by more than $\pm 5\%$ from the initial value during the operating time.

Flowmeter

66 Flowmeter, portable, with an accuracy that is sufficient to enable the required volumetric flow rate (see paragraph 78) to be measured to within $\pm 5\%$. The calibration of the flowmeter shall be checked against a primary standard, ie a flowmeter whose accuracy is traceable to national standards.

Note 13: *It is recommended that the flowmeter used should be capable of measuring the volumetric flow rate to within $\pm 2\%$ or better.*

Note 14: *Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers (see note 22), provided they have adequate sensitivity.*

Polypropylene bottles

67 Polypropylene bottles, with leakproof screw cap, for collection of samples of sump fluid (see paragraph 94), concentrate (see paragraph 95) and water used to prepare the working strength water-mix metalworking fluids at the work area (see paragraph 96); and for storage of reagents (see paragraphs 50, 53, 56 and 58). Clean these before use by soaking in 1 + 9 nitric acid (paragraph 48) for at least 24 hours and then rinsing thoroughly with water (paragraph 46). Bottles made of an alternative plastic may be used provided that they are suitable for the intended use.

Ancillary equipment

68 Flexible tubing, of a diameter suitable for ensuring a leakproof fit, to connect the sampler to the pump; a belt to which the pump can conveniently be 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 89), in which to transport samples to the laboratory.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

69 A selection of laboratory glassware, including: beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS EN ISO 1042.²²

Note 15: *It is recommended that a set of glassware is reserved for the analysis of water-mix metalworking fluids by this method.*

Disposable gloves

70 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.

Disposable plastic beakers

71 Disposable plastic beakers, eg 30 ml capacity, as an alternative to 50 ml glass beakers, and containing less than 0.1 μg of the selected marker element (see paragraphs 100 and 101), extractable under the conditions of the test.

Piston-operated volumetric instruments

72 Pipettors and dispensors, complying with the requirements of BS EN ISO 8655-1²³ and tested in accordance with BS EN ISO 8655-6,²⁴ pipettors, complying with the requirements of BS EN ISO 8655-2,²⁵ for preparation of solutions for calibration of the atomic absorption spectrometer (see paragraphs 108 and 109), the inductively coupled plasma-atomic emission spectrometer (see paragraph 110), the refractometer (see paragraph 124) and the acid split procedure (see

paragraph E9) and for dilution of sample solutions (see paragraphs 107, 116, 122 and 127); and dispensers, complying with the requirements of BS EN ISO 8655-5,²⁶ for dispensing caesium chloride solution (see paragraph 104).

Note 16: *Micropipettes used for dispensing concentrate should be of the positive displacement type.*

Orbital mixer

73 Orbital mixer, variable speed.

Atomic absorption spectrometer

74 An atomic absorption spectrometer, fitted with an air-acetylene burner, supplied with compressed air and acetylene, and equipped with a sodium or potassium hollow cathode lamp.

Inductively coupled plasma-atomic emission spectrometer

75 Inductively coupled plasma-atomic emission spectrometer, supplied with argon, and capable of measuring boron at 249.773 nm (or an alternative suitable wavelength).

Refractometer

76 Refractometer, capable of measuring the refractive index of water-mix metalworking fluids over a suitable range of fluid strengths (eg 0 - 10%), and with a graduated scale having 0.1% divisions or better.

Note 17: *Small hand-held refractometers are available, and are quick and easy to use. Water-mix metalworking fluid is placed on the glass prism of the refractometer, and measurements are made by viewing this obliquely through a system of lenses and reading off a transparent scale.*

SAMPLING

Preliminary considerations

Filter selection

77 Consult the Material Safety Data Sheet provided by the supplier for information on the composition of the proprietary product, and determine whether boron is a possible candidate for the marker element. If this is the case, use quartz fibre filters (paragraph 62) to load the samplers (see paragraph 82). If not, use mixed cellulose ester membrane filters (paragraph 61).

Use of samplers

78 Use the samplers (paragraph 60) at their design flow rate, and in accordance with the instructions provided by the manufacturer, so that they collect the intended fraction of airborne particles.

Sampling period

79 Select an appropriate sampling period, taking into account the purpose of the measurement. A minimum

sampling time of 2 hours is recommended when boron or potassium is used as a marker element (see paragraphs 34 and 36); and a minimum sampling time of 8 hours is recommended when sodium is used as a marker element (see paragraph 35). However, if sampling is carried out in a dusty environment, the sampling time shall not be so long as to risk overloading the filter. (An 8-hour time weighted average concentration may be derived from the results for two or more consecutive samples, as described in HSE guidance note EH40.²⁷) Advice on monitoring strategies for toxic substances is given in guidance booklet HSG173.²⁸

Note 18: *The examples of the lower limit of the working range of the method given in Table 1 may be used to estimate the minimum sampling time required to enable personal exposure measurements to be made with acceptable overall uncertainty at the concentration of water-mix metalworking fluid concentrate in air of interest, eg in the region of the guidance exposure limit (see paragraph 8). A more accurate assessment of the minimum sampling time required can be achieved by following the procedure described in Appendix B. If in doubt, sample for at least 4 hours and preferably over a full working day.*

Handling of filters

80 To minimise the risk of damage or contamination, only handle filters using flat-tipped tweezers (paragraph 68), in a clean area. Wear disposable gloves (paragraph 70) to prevent the possibility of contamination.

Preparation for air sampling

Cleaning of samplers

81 Clean the samplers (paragraph 60) before use. Disassemble the samplers, soak in laboratory detergent solution, rinse thoroughly with water (paragraph 46), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

Note 19: *If the laboratory detergent used could contain a significant concentration of the marker element, it is important to ensure that the rinsing with water is very thorough.*

Loading the samplers with filters

82 Load clean samplers (see paragraph 60) with filters (see paragraph 77), label each sampler so that it can be uniquely identified, and seal with its protective cover to prevent contamination.

Setting the volumetric flow rate

Perform the following in a clean area, where the concentration of airborne water-mix metalworking fluid is low:

83 Connect each loaded sampler (paragraph 82) to a sampling pump (paragraph 63) using flexible tubing (paragraph 68), ensuring that no leaks can occur. Remove the protective cover from each sampler, switch on the

sampling pump, attach the calibrated flowmeter (paragraph 66) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the required volumetric flow rate (see paragraph 78). Switch off the sampling pump and seal the sampler with its protective cover to prevent contamination during transport to the sampling position.

Note 20: *If necessary, allow the sampling pump operating conditions to stabilise before setting the volumetric flow rate (refer to the manufacturer's instructions).*

Blanks

84 Retain, as blanks, one unused loaded sampler from each batch of ten prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but draw no air through the filters.

Sampling position

85 Position the sampler in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, eg fasten it to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, eg to a belt (paragraph 68) around the waist, or place it in a convenient pocket.

Collection of air samples

86 When ready to begin sampling, remove the protective cover from the sampler and switch on the sampling pump. Record the time and volumetric flow rate at the start of the sampling period, and if the sampling pump is fitted with an integral timer, check that this is reset to zero.

Note 21: *If the temperature or pressure at the sampling position is significantly different from that where the volumetric flow rate was set (see paragraph 83), the volumetric flow rate could change and it might need to be re-adjusted before sampling.*

Note 22: *If the sampling pump used does not comply with BS EN 1232¹⁷ (see note 11), monitor its performance frequently, a minimum of once per hour. Measure the flow rate using the calibrated flowmeter (paragraph 66) 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.*

87 At the end of the sampling period (see paragraph 79), record the time and calculate the duration of the sampling period. Check the malfunction indicator and/or the reading on the integral timer, if fitted, and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period. Measure the volumetric flow rate at the end of the sampling period using the calibrated flowmeter (paragraph 66), and record the measured value. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

88 Carefully record the sample identity and all relevant sampling data (see Appendix C).

Transportation of air samples

89 For samplers that collect airborne particles on the filter (see note 7), remove the filter from each sampler, place in a labelled filter transport cassette (paragraph 68) and close with a lid. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters. Alternatively, transport samples to the laboratory in the samplers in which they were collected.

90 For samplers that have an internal filter cassette (see note 7), remove the filter cassette from each sampler and fasten with its lid or transport clip.

91 For samplers designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, but which do not have an internal filter cassette (see note 7), transport the samples to the laboratory in the samplers in which they were collected.

Note 23: *Discard any samples that display evidence of splash contamination.*

92 Transport the samples (paragraphs 89-91) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

93 When appropriate, ensure that the documentation which accompanies the samples is suitable for a 'chain of custody' to be established.

Collection of water-mix metalworking fluid samples

Perform the following wearing disposable gloves (paragraph 68) to protect the hands:

94 Using a suitable, labelled polypropylene bottle (paragraph 67), take a sample of sump fluid from each machine at which the operator's personal exposure is to be measured. Collect 500 ml samples, as near as practicable to the points at which the water-mix metalworking fluid is applied to the cutting tool/workpiece, and while the fluid is circulating. Ensure that the screw-caps are tightly closed.

95 Record details of the concentrated proprietary products from which the working strength water-mix metalworking fluids were prepared, and take a 100 ml sample of each concentrate using a suitable, labelled polypropylene bottle (paragraph 67). Ensure that the screw-caps are tightly closed.

WARNING - Substances contained in water-mix metalworking fluids have been assigned various risk phrases in the *Approved Supply List*²⁹ for the *Chemicals (Hazard Information and Packaging for Supply) Regulations 2002*³⁰. Care should be taken when working with water-mix metalworking fluid concentrates, and the appropriate hazard warning sign(s) should be affixed to sample bottles for transport to the laboratory (refer to the manufacturer's safety data sheets).

96 Using a suitable, labelled polypropylene bottle (paragraph 67), take a 1 litre sample of the water used to

prepare the working strength water-mix metalworking fluids at the work area. Ensure that the screw-cap is tightly closed.

ANALYSIS

Wear disposable gloves (paragraph 70) during analysis to protect the hands from toxic, corrosive and oxidising reagents.

Cleaning of glassware

97 Before use, clean all glassware (paragraph 69) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 59) and then rinse thoroughly with water (paragraph 46).

98 After initial cleaning (paragraph 97), clean all glassware by soaking in 1 + 9 nitric acid (paragraph 48) for at least 24 hours and then rinsing thoroughly with water (paragraph 46).

99 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 97 and 98, and which has been reserved for determination of water-mix metalworking fluid by this method, can be adequately cleaned by rinsing thoroughly with 1 + 9 nitric acid (paragraph 48) and then with water (paragraph 46).

Selection of marker element

100 Analyse the sump fluid (paragraph 94) before analysing the air samples, in order to identify the most suitable marker element (see notes 24 and 25). If necessary, also analyse the concentrate (paragraph 95) and the water used to prepare the working strength water-mix metalworking fluids at the work area (paragraph 96).

Note 24: *A suitable marker element is one that originates from the water-mix metalworking fluid concentrate or from the water used to prepare the working strength solution, and which is unlikely to emanate from a secondary source within the workplace. An element that originates from the workpiece is unsuitable, since it will be present in any airborne metal particles generated by the metalworking process, which will therefore interfere with the marker method.*

Note 25: *Boron, sodium and potassium are often present in the additives included in water-mix metalworking fluid formulations, and in most instances the working strength metalworking fluid will contain one or other of these elements at a high enough concentration for its successful use as a marker. However, avoid using sodium, if possible, since the lower limit of the analytical range is much higher than for boron or potassium (see paragraphs 15-18), and there is much more likely to be interference from a secondary source of sodium in the workplace (see paragraph 37).*

101 Boron or potassium is suitable for use as the marker element if present in the sump fluid at a concentration of at least 100 $\mu\text{g ml}^{-1}$, while sodium is only suitable for use as the marker element if present in the sump fluid at a concentration of at least 400 $\mu\text{g ml}^{-1}$. Other elements could

also be suitable markers if they are present in the sump fluid at a high enough concentration.

Determination of marker element using flame atomic absorption spectrometry or inductively coupled plasma-atomic emission spectrometry

Preparation of air sample and blank solutions

102 Open the filter transport cassettes (see paragraph 89), sampler filter cassettes (see paragraph 90) or samplers (see paragraph 91) and transfer each filter into an individual, labelled 50 ml beaker (paragraph 69) or 30 ml disposable plastic beaker (paragraph 71) using clean flat-tipped tweezers (paragraph 68). Follow the same procedure for the blanks (paragraph 84).

Note 26: *Discard any samples that display evidence of splash contamination.*

103 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 7), wash any particulate material adhering to the internal surfaces into the beaker or disposable plastic beaker using the caesium chloride solution used to leach the sample filters (see paragraph 104). Ensure that the liquid drains from the sampler into the beaker or disposable plastic beaker as completely as possible.

104 Accurately dispense 10 ml of caesium chloride solution (paragraph 58) into each beaker or disposable plastic beaker. Place the beakers on the orbital mixer (paragraph 73) for 60 minutes.

105 Remove each beaker or disposable plastic beaker from the mixer and analyse immediately. Alternatively, transfer each solution to a suitable, labelled polypropylene bottle (paragraph 67) until ready to proceed with the analysis. If necessary, remove any particulate material by filtering each sample solution through a cellulose (paper) filter, which has been pre-washed with water (paragraph 46).

Preparation of sump fluid sample solutions

106 Shake each bottle of sump fluid sample (paragraph 94) thoroughly to re-emulsify any metalworking fluid that might have separated out. Allow the samples to stand for a few minutes and then check to see if any tramp oil can be observed on the surface of the samples. If tramp oil is present, remove it using a micropipette (paragraph 72). Finally, remove any particulate material by filtering each sample through a cellulose (paper) filter, which has been pre-washed with water (paragraph 46), into a second, labelled, polypropylene bottle (paragraph 67).

107 Dilute each sump fluid sample to bring the marker element concentration within the calibration range. Accurately pipette 1 ml of each sample into an individual, labelled 100 ml volumetric flask and dilute to the mark with caesium chloride solution (paragraph 58). Stopper and mix thoroughly.

Preparation of sodium calibration solutions

108 Prepare at least six calibration solutions to cover the range $0 \mu\text{g ml}^{-1}$ to $2.5 \mu\text{g ml}^{-1}$ of sodium. Accurately pipette the appropriate volume of working sodium standard solution (paragraph 51) into separate, labelled 100 ml volumetric flasks, dilute to the mark with caesium chloride solution (paragraph 58), stopper and mix thoroughly. Prepare these solutions fresh weekly.

Preparation of potassium calibration solutions

109 Prepare at least six calibration solutions to cover the range $0 \mu\text{g ml}^{-1}$ to $5 \mu\text{g ml}^{-1}$ of potassium. Accurately pipette the appropriate volume of working potassium standard solution (paragraph 54) into separate, labelled 100 ml volumetric flasks, dilute to the mark with caesium chloride solution (paragraph 58), stopper and mix thoroughly. Prepare these solutions fresh weekly.

Preparation of boron calibration solutions

110 Prepare at least three calibration solutions to cover the range $0 \mu\text{g ml}^{-1}$ to $5 \mu\text{g ml}^{-1}$ of boron. Accurately pipette the appropriate volume of working boron standard solution (paragraph 57) into separate, labelled 100 ml volumetric flasks, dilute to the mark with caesium chloride solution (paragraph 58), stopper and mix thoroughly. Prepare these solutions fresh weekly.

Analysis by flame atomic absorption spectrometry

Atomic absorption measurements

111 Set up the atomic absorption spectrometer (paragraph 74) to determine sodium at 589.0 nm or potassium at 766.5 nm using an oxidising air-acetylene flame. Follow the manufacturer's recommendations for specific operating parameters. The sensitivity, defined as the concentration required to produce a signal of 1% absorbance or 0.0044 absorbance units, is about $0.01 \mu\text{g ml}^{-1}$ of sodium and about $0.03 \mu\text{g ml}^{-1}$ of potassium.

112 Adjust the spectrometer zero while aspirating the blank calibration solution (paragraph 108 or 107). Repeat this procedure regularly throughout the analysis and readjust the zero if the baseline drifts.

113 Aspirate the calibration solutions (paragraph 108 or 109) into the flame in order of increasing concentration and make absorption measurements for each solution. For instruments controlled by a microprocessor or personal computer, generate a calibration function by carrying out a linear regression. For instruments without this capability, prepare a calibration graph by plotting the absorbance of the calibration solutions versus the sodium or potassium concentration.

114 Aspirate the air sample and blank solutions (paragraph 105) and the diluted sump fluid sample solutions (paragraph 107) into the flame. For instruments controlled by a microprocessor or personal computer, use the calibration function (see paragraph 113) to determine the concentration of sodium or potassium in the sample

and blank solutions and obtain a direct read-out of the results in $\mu\text{g ml}^{-1}$. For instruments without this capability, determine the concentration of sodium or potassium in $\mu\text{g ml}^{-1}$ from the calibration graph (see paragraph 113).

115 Aspirate a mid-range calibration solution (paragraph 108 or 109) into the flame after each five to ten sample solutions and make an absorption measurement. If this indicates that the sensitivity has changed by more than $\pm 5\%$, take one of the following appropriate corrective measures: either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer as described in paragraph 113; and in either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

116 If high concentrations of sodium or potassium are found, dilute the sample solutions to bring the concentration within the calibration range, and repeat the analysis. Accurately pipette an appropriate volume of each sample solution (paragraph 105 or 107) into an individual, labelled 50 ml volumetric flask. Dilute to the mark with caesium chloride solution (paragraph 58), stopper and mix thoroughly. Record the dilution factor.

117 Calculate the mean sodium or potassium concentration of the blank solutions.

Inductively coupled plasma-atomic emission measurements

118 Set up the inductively coupled plasma-atomic emission spectrometer (paragraph 75) to determine boron at 249.773 nm (or a suitable alternative wavelength). Follow the manufacturer's recommendations for specific operating parameters. The background equivalent concentration (BEC), defined as the concentration of a solution that results in an analyte emission signal of the same intensity as that of the background emission signal at the measurement wavelength, is about $0.06 \mu\text{g ml}^{-1}$ of boron.

119 Aspirate the calibration solutions (paragraph 110) into the plasma in order of increasing concentration and make emission measurements for each solution. Use the instrument's personal computer or microprocessor to generate a calibration function for boron by carrying out a linear regression.

120 Aspirate the air sample and blank solutions (paragraph 105) and the diluted sump fluid sample solutions (paragraph 107) into the plasma and make emission measurements for each solution. Use the calibration function (paragraph 119) to determine the concentration of boron in the sample and blank solutions and obtain a direct read-out of the results in $\mu\text{g ml}^{-1}$.

Note 27: Boron can take a considerable period of time to wash out of the sample introduction system of an inductively coupled plasma-atomic emission spectrometer. It is advisable to allow a lengthy rinse time between analysis of the calibration and sample solutions to avoid carry-over. However, give consideration to the long-term

stability of the inductively coupled plasma-atomic emission spectrometry system when deciding on the length of this rinse time.

121 Aspirate the low calibration solution (paragraph 110) into the plasma after each five to ten sample solutions and make an emission measurement. If this indicates that the sensitivity has changed by more than $\pm 5\%$, take one of the following appropriate corrective measures: either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer as described in paragraph 119. In either case, reanalyse the solutions that were analysed during the period in which the sensitivity change occurred.

122 If high concentrations of boron are found, dilute the sample solutions to bring the concentration within the calibration range, and repeat the analysis. Record the dilution factor.

123 Calculate the mean boron concentration of the blank solutions.

Determination of strength of water-mix metalworking fluid in the sump by refractometry

Preparation of calibration solutions

124 For each proprietary product, prepare water-mix metalworking fluid calibration solutions at strengths of 0, 2, 4, 6, 8 and 10% (v/v). Accurately pipette 0 ml, 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of each concentrate (paragraph 95) into separate, labelled 50 ml volumetric flasks, washing out the tip of the micropipette with water to ensure quantitative transfer of the viscous concentrate. Dilute to volume with water taken from the supply from which the working strength water-mix metalworking fluids were prepared (paragraph 96).

Calibration of the refractometer

125 Set up the refractometer (paragraph 76) according to the manufacturer's instructions. Adjust the zero using water from the supply from which the working strength water-mix metalworking fluids were prepared (paragraph 96), and take refractometer readings for each calibration solution (paragraph 124), rinsing the refractometer with water (paragraph 46) between readings.

126 For each proprietary product, plot a calibration graph of refractive index against water-mix metalworking fluid strength.

Measurement

127 Set the refractometer to zero using water from the supply from which the working strength water-mix metalworking fluids were prepared (paragraph 96) and take refractometer readings for each filtered sump fluid sample (paragraph 106), rinsing the refractometer with water (paragraph 46) between readings. If necessary, dilute the sump fluid to bring its strength within the range of the calibration, ie between 0 and 10% (v/v).

Note 28: If the refractometer reading is difficult to assess due to a haze on the scale, then the sump fluid is likely to be near to the end of its useful life. In this case, it is advisable to obtain corroborative evidence of the accuracy of the result by determining the sump fluid strength using one or more alternative methods. A potentiometric titration procedure for determination of the strength of water-mix metalworking fluid in the sump by measurement of total alkalinity is given in Appendix D, and an acid split procedure is described in Appendix E. If necessary, either or both of these methods may be used to check the refractometry results, in which case the sump fluid strength should be taken as the mean of the two closest results.

128 Use the appropriate calibration graph (paragraph 126) to determine the strength of water-mix metalworking fluid in each sump fluid sample.

CALCULATIONS

Volume of air sample

129 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 the marker element in air

130 Calculate the concentration of the marker element in air, $\rho(E)_A$, in milligrams per cubic metre (mg m^{-3}), using the equation:

$$\rho(E)_A = \frac{(\rho(E)_1 \times V_1 \times DF_1) - (\rho(E)_0 \times V_0 \times DF_0)}{V} \quad \text{Equation 5}$$

where:

$\rho(E)_0$ is the mean concentration, in $\mu\text{g ml}^{-1}$, of the marker element in the blank solutions (see paragraph 117 or 123);

$\rho(E)_1$ is the concentration, in $\mu\text{g ml}^{-1}$, of the marker element in the sample solution (see paragraph 114 or 120);

V is the volume, in litres, of the air sample (see paragraph 129);

V_0 is the volume, in ml, of the blank solutions, ie 10 ml (see paragraph 104);

V_1 is the volume, in ml, of the sample solution, ie 10 ml (see paragraph 104);

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

DF_1 is the dilution factor for the sample solutions (see paragraph 116 or 120).

Concentration of the marker element in the sump fluid

131 Calculate the concentration of the marker element in the sump fluid, $\rho(E)_s$, in milligrams per gram of water-mix metalworking fluid (mg g^{-1}), using the equation:

$$\rho(E)_s = \frac{\rho(E)_2 \times V_3 \times DF}{V_2 \times 1000} \quad \text{Equation 6}$$

where:

- $\rho(E)_2$ is the concentration, in $\mu\text{g ml}^{-1}$, of the marker element in the diluted sump fluid sample solution (see paragraph 114 or 118);
- V_2 is the volume, in ml, of sump fluid sample used to prepare the diluted solution, ie 1 ml (see paragraph 107);
- V_3 is the volume, in ml, to which the sump fluid sample was diluted, ie 100 ml (see paragraph 107);
- DF is the secondary dilution factor, if applicable (see paragraph 116 or 120); and
- 1000 is the factor required to convert the concentration units from $\mu\text{g ml}^{-1}$ to mg g^{-1} (assuming that 1 ml of sump fluid has a mass of 1 g).

Personal exposure to water-mix metalworking fluid aerosol

132 Personal exposure to water-mix metalworking fluid can be expressed in two ways:

- personal exposure to the aqueous aerosol (ie airborne sump fluid); or
- personal exposure to the water-mix metalworking fluid concentrate.

Personal exposure to the aqueous aerosol

133 Calculate the personal exposure of the operator to the aqueous aerosol, $\rho(A)$, in mg m^{-3} , using the equation:

$$\rho(A) = \frac{\rho(E)_A \times 1000}{\rho(E)_s} \quad \text{Equation 7}$$

where:

- $\rho(E)_A$ is the concentration, in mg m^{-3} , of the marker element in air (see paragraph 130);
- $\rho(E)_s$ is the concentration, in mg g^{-1} , of the marker element in the sump fluid (see paragraph 131); and
- 1000 is the factor required to convert the concentration units from g m^{-3} to mg m^{-3} .

Personal exposure to water-mix metalworking fluid concentrate

134 Calculate the personal exposure of the operator to the water-mix metalworking fluid concentrate, $\rho(C)$, in mg m^{-3} , using the equation:

$$\rho(C) = \frac{\rho(A) \times S}{100} \quad \text{Equation 8}$$

where:

- $\rho(A)$ is the personal exposure of the operator to aqueous aerosol, in mg m^{-3} (see paragraph 133);
- S is the strength of water-mix metalworking fluid, in % (v/v) (see paragraph 128, D16 or E13); and
- 100 is the factor required to convert the sump fluid strength in % (v/v) to the ratio of proprietary product in the sump fluid.

TEST REPORT

135 Appendix C gives recommendations for information to be included in the test report.

QUALITY CONTROL MEASURES

136 Analytical quality requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS 71.³¹

137 If analysis of water-mix metalworking fluid is performed frequently it is recommended that internal quality control is performed. In such instances, prepare quality control samples by spiking a large number of filters with microlitre volumes of a solution with a known concentration of the selected marker element (see paragraphs 100 and 101). Randomly select a suitable number (eg 20) of quality control samples, analyse them on separate occasions, and calculate the mean and standard deviation of the measured marker element concentrations. Assuming that the distribution of results is Gaussian, construct a Shewhart chart with warning and action limits at $\pm 2\text{SD}$ and $\pm 3\text{SD}$ respectively. Subsequently, analyse a quality control sample with each analytical batch and plot the result on the Shewhart chart. Compare the internal quality control result with the target value and take appropriate action if the warning or action limits are exceeded, as recommended in MDHS 71.³¹ Take care to ensure that the quality control samples are stored under conditions which ensure maximum stability.

138 It is strongly recommended that all laboratories undertaking the determination of personal exposure to the airborne water-mix metalworking fluid should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are given in MDHS 71.³¹ However, at present the WASP scheme does not encompass any of the recommended marker elements (see note 25).

APPENDIX A GLOSSARY

Aqueous aerosol: Airborne water-mix metalworking fluid produced from the sump fluid when a metalworking machine is in use.

Concentrate: A water-mix metalworking fluid proprietary product before it is diluted with water for use.

Sump fluid: A water-mix metalworking fluid in use on a metalworking machine, circulated to the cutting tool/workpiece as a lubricant and coolant.

Tramp oil: Contamination of the sump fluid by lubricating or hydraulic oils introduced during normal cutting operations.

Working strength water-mix metalworking fluid: A water-mix metalworking fluid proprietary product when it has been diluted with water for use.

APPENDIX B CALCULATION OF THE MINIMUM SAMPLING TIME REQUIRED TO ENSURE THAT MEASUREMENTS ARE MADE WITH ACCEPTABLE OVERALL UNCERTAINTY

B1 Follow the procedure described in paragraphs B2-B10 to determine the minimum sampling time required to enable personal exposure measurements to be made with acceptable overall uncertainty at the minimum concentration of water-mix metalworking fluid concentrate-in-air of interest, eg 0.1 times the guidance exposure limit of 1 mg m⁻³ (see paragraph 8).

Calculation of the quantitative detection limit of the analytical method

B2 Determine the quantitative detection limit of the analytical method under the working analytical conditions, following the procedure described in paragraphs B3-B5. Repeat this exercise if conditions change.

B3 Prepare ten blank solutions by leaching ten blank filters (see paragraph 84) using the procedure described in paragraphs 102-105, and prepare calibration solutions for determination of the selected marker element (see paragraph 108, 109 or 110).

B4 Analyse the blank solutions by flame atomic absorption spectrometry, following the procedure described in paragraphs 111-117, or by inductively coupled plasma-atomic emission spectrometry, following the procedure described in paragraphs 118-123, as appropriate.

B5 Calculate the standard deviation of the blank results (in µg) and multiply this by ten to determine the quantitative detection limit (99.99% confidence level).

Calculation of the minimum sampling time

B6 Determine the concentration of the marker element in the sump fluid (see paragraphs 106-123) and the strength

of water-mix metalworking fluid in the sump fluid (see paragraphs 124-128) and then calculate the minimum sampling time, *t*, using the following equation:

$$t = \frac{DL \times V_1 \times S \times 1000}{q \times \rho(E)_s \times \rho(C) \times 100} \quad \text{Equation 9}$$

where:

DL is the quantitative detection limit of the analytical method under the working analytical conditions (see paragraph B5);

V₁ is the volume, in ml, of the sample solution, ie 10 ml (see paragraph 104);

S is the strength of water-mix metalworking fluid, in % (v/v) (see paragraph 128);

q is the design flow rate of the samplers used, in litres per minute (see paragraph 78);

ρ(E)_s is the concentration, in mg g⁻¹, of the marker element in the sump fluid (see paragraph 114 or 118);

ρ(C) is the minimum concentration of water-mix metalworking fluid concentrate-in-air of interest (see B1);

1000 is the factor required to convert the concentration units from g m⁻³ to mg m⁻³; and

100 is the factor required to convert the sump fluid strength in % (v/v) to the ratio of proprietary product in the sump fluid.

APPENDIX C 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, including information about which marker element was used and which analytical technique was used to measure the sump fluid strength, 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;

- g) the time at the start and at the end of the sampling period, and the sampling time in minutes;
- h) the volume of air sampled, in litres;
- i) the name of the person who collected the sample;
- j) the sump fluid strength, the concentration of marker element in the sump fluid, and the measured personal exposure of the operator to the water-mix metalworking fluid concentrate, in micrograms per cubic metre;
- k) the name of the analyst;
- l) the date of the analysis.

APPENDIX D POTENTIOMETRIC TITRATION PROCEDURE FOR DETERMINATION OF THE STRENGTH OF WATER-MIX METALWORKING FLUID IN THE SUMP FLUID BY MEASUREMENT OF TOTAL ALKALINITY

Scope

D1 This appendix describes a potentiometric titration procedure for determination of water-mix metalworking fluid strength by measurement of total alkalinity. It is useful for obtaining corroborative evidence of the accuracy of refractometry results in instances when the refractometer reading is difficult to assess due to a haze on the scale (see note 28). This can occur when the sump fluid is near the end of its useful life.

D2 Degradation of nitrogen-containing water-mix metalworking fluids can occur by bacterial action, yielding alkaline products. The possibility of obtaining high results should be considered when using data obtained by this method to corroborate refractometry measurements.

Method performance

D3 Results of the analysis of the twenty sump fluid samples have shown good correlation¹⁸ with results obtained by refractometry and other methods.

Principle

D4 Water-mix metalworking fluid strength is directly proportional to its total alkalinity. This is measured by potentiometric titration of samples with aqueous hydrochloric acid using a glass pH electrode and reference electrode or a combination pH electrode. The strength of water-mix metalworking fluid in the sump is determined from a calibration graph of water-mix metalworking fluid strength against total alkalinity, obtained by measuring the total alkalinity of calibration solutions of known strength.

Reagents

Hydrochloric acid (HCl), 0.5 mol l⁻¹

D5 Use commercially available 0.5 mol l⁻¹ hydrochloric acid volumetric solution, or concentrated volumetric

solution diluted with water (paragraph 46) according to the manufacturer's instructions.

pH buffer solutions

D6 Commercially available pH buffer solutions, suitable for calibration of the pH meter, eg pH 2.0 and pH 7.0.

Laboratory apparatus

Potentiometric titration system, automated or manual

D7 A potentiometric titration system, automated or manual, suitable for measuring the total alkalinity of water-mix metalworking fluid, comprising:

pH meter

D8 pH meter, capable of measuring over the range 0-14 pH units, with an accuracy of at least ±0.1 pH unit.

Glass pH electrode and reference electrode

D9 Glass pH electrode and reference electrode, compatible with the pH meter; or combination pH electrode which incorporates both pH measurement and reference electrodes. The electrode(s) shall have a suitable, rapid response time if an autotitration system is used.

Either

Burette, 25 ml

D10 Burette, 25 ml, class A, graduated in 0.05 ml increments; for manual titration.

or

Microprocessor or personal computer-controlled autotitration system

D11 Microprocessor or personal computer-controlled autotitration system, equipped with a 25 ml autoburette, featuring automatic adaptation of the titration speed to the slope of the titration curve, and capable of recording the complete course of a titration by continuously printing out the relative cell potential versus volume of titrant added and of automatically calculating the volume of titrant required to reach the end-point.

Stirrer, mechanical or magnetic

D12 Stirrer, mechanical or magnetic, variable speed, equipped with chemically resistant paddle or stir bar. Electrical stirring apparatus shall be grounded to prevent electrical disturbances caused by the stirrer affecting the pH meter.

Titration vessel

D13 Titration vessel, 100 ml capacity; either a beaker, for manual titration, or the titration vessel supplied by the manufacturer, if an autotitration system is used.

Titration assembly

D14 Titration assembly, to support the electrodes, the stirrer and burette/titrant delivery system in position. An arrangement that allows the removal of the beaker or titration vessel without disturbing the electrodes, stirrer and burette is desirable.

Maintenance of the electrode system

D15 Maintain, prepare and test the electrodes (paragraph D9) in accordance with the manufacturer's instructions. In particular, clean the electrode system at frequent intervals (eg once a week if in regular daily use), in accordance with the manufacturer's instructions. Store the electrodes in pH 2.0 buffer solution when not in use.

Preparation for analysis

D16 Calibrate the pH meter (paragraph D8) using the pH buffer solutions (paragraph D6). Follow the manufacturer's instructions for the appropriate calibration procedure.

D17 Fill the burette or autoburette (paragraph D10) with 0.5 mol l⁻¹ hydrochloric acid (paragraph D5) and position on the titration assembly (paragraph D14) or autoburette drive unit (paragraph D11).

Determination of total alkalinity

D18 Determine the total alkalinity of the calibration solutions (paragraph 124) of known water-mix metalworking fluid strength and the filtered sump fluid samples (paragraph 94) by titrating to an end-point of pH 5.5.

D19 Introduce 50 ml of the calibration solution or filtered sump fluid sample (paragraph 124 or 92) into the titration vessel. Place the titration vessel on the titration assembly (paragraph D14) so that the electrodes are about half immersed. Start the stirrer (paragraph D12) and adjust the stirring rate to produce vigorous agitation without splashing and without stirring any air into the solution. Then titrate the calibration solution or sump fluid sample following the procedure described in paragraph D20 or D21, as appropriate.

Manual titration

D20 Add suitable small aliquots of 0.5 mol l⁻¹ hydrochloric acid (paragraph D5) to titrate to an end-point of pH 5.5. Wait until the pH reading stabilises before adding each aliquot, recording the burette and pH readings on each occasion. Add another aliquot of 0.5 mol l⁻¹ hydrochloric acid to verify that the end-point has been reached. Plot the volume of the titrant added against pH, and read off the volume of titrant added to reach the end-point. Remove the titration vessel (paragraph D13) from the titration assembly (paragraph D14) and wash the electrodes (paragraph D9) and stirrer paddle or stir bar (paragraph D12) with water (paragraph 46).

Automatic titration

D21 Adjust the apparatus in accordance with the manufacturer's instructions. Programme the instrument to

titrate with 0.5 mol l⁻¹ hydrochloric acid (paragraph D5) to an end-point of pH 5.5. Use a variable, continuous titrant delivery rate of less than 0.2 ml min⁻¹, and preferably 0.05 ml min⁻¹, through the end-point region. Record the volume of titrant added to reach the end-point. Remove the titration vessel (paragraph D13) from the titration assembly (paragraph D14) and wash the electrodes (paragraph D9) and stirrer paddle or stir bar (paragraph D12) with water (paragraph 46).

Calculation of total alkalinity

D22 Calculate the total alkalinity of the calibration solution or sump fluid sample, $\rho(\text{CO}_3^{2-})$, expressed in mol l⁻¹ of carbonate, using the equation:

$$\rho(\text{CO}_3^{2-}) = \frac{\rho(\text{H}^+) \times V_2}{V_1 \times 2} \quad \text{Equation 10}$$

where:

$\rho(\text{H}^+)$ is the concentration of the titrant (hydrochloric acid) in mol l⁻¹, ie 0.5 mol l⁻¹ (see paragraph D5);

V_2 is the volume of titrant added to reach the end-point (see paragraph D13 or D14);

V_1 is the volume of calibration solution or sump fluid sample titrated, ie 50 ml (see paragraph D12); and

2 is the number of moles of H⁺ required to titrate 1 mole of CO₃²⁻.

Calculation of the strength of water-mix metalworking fluid in the sump fluid

D23 For each proprietary product, plot a calibration graph of total alkalinity against water-mix metalworking fluid strength. Then use the appropriate calibration graph to determine the working strength of water-mix metalworking fluid in each sump fluid sample.

APPENDIX E ACID SPLIT PROCEDURE FOR DETERMINATION OF THE STRENGTH OF WATER-MIX METALWORKING FLUID IN THE SUMP

Scope

E1 This appendix describes an acid split procedure for determination of water-mix metalworking fluid strength. It is useful for obtaining corroborative evidence of the accuracy of refractometry results in instances when the refractometer reading is difficult to assess due to a haze on the scale (see note 28). This can occur when the sump fluid is near the end of its useful life.

E2 Over recent years, water-mix metalworking fluids have been formulated containing much less mineral oil than older conventional fluids. Conventional water-mix metalworking fluids are water-in-oil emulsions, typically containing 50-90% oil. Newer products, known as semi-synthetic fluids and synthetic fluids, are oil-in-water

emulsions, typically containing 10-40% oil and 0% oil, respectively. Since this method relies on measuring the volume of oil separated out of the emulsion, it is not recommended for use with semi-synthetic and synthetic water-mix metalworking fluids that contain little or no mineral oil.

Method performance

E3 Although acid split is a primitive method for determining the strength of water-mix metalworking fluid in sumps, results of the analysis of the twenty sump fluid samples have shown good correlation¹⁸ with results obtained by refractometry and other methods.

Principle

E4 Water-mix metalworking fluid strength is determined by splitting an aliquot of fluid into its aqueous and mineral oil components and measuring the resulting volume of mineral oil. Samples are mixed with strong mineral acid in a long-necked, graduated flask, heated for a period of time in a hot water bath, and allowed to cool. A clear, aqueous, lower layer is formed with a layer of mineral oil on top. The volume of the oil layer, which is usually about 1-2% of the total volume of sample and mineral acid used in the test, is read from the graduations on the neck of the flask. The strength of water-mix metalworking fluid in the sump fluid is determined from a calibration graph of water-mix metalworking fluid strength against volume of the oil layer, obtained by measuring the volume of the oil layer produced from calibration solutions of known strength.

Reagents

Hydrochloric acid (HCl), concentrated, ρ about 1.18 g ml⁻¹, 36.5% (m/m) to 38% (m/m)

E5 General purpose reagent grade concentrated hydrochloric acid.

WARNING - Concentrated hydrochloric acid is corrosive and hydrochloric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with concentrated or diluted hydrochloric acid, and heating of samples with hydrochloric acid should be carried out in a fume cupboard.

Hydrochloric acid, diluted 1 + 1

E6 Carefully add 500 ml of concentrated hydrochloric acid (paragraph E5) to 450 ml of water (paragraph 46) 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, stopper and mix thoroughly.

Laboratory apparatus

Phenol flasks

E7 Phenol flasks, class A, nominal capacity 150 ml, with a graduated scale having 0.1 ml divisions or better.

Water bath

E8 Water bath.

Analysis

E9 For each proprietary product, prepare a calibration solution at a strength of 10% (v/v). Accurately pipette 5 ml of each concentrate (paragraph 95) into an individual, labelled 100 ml volumetric flask. Dilute to volume with water (paragraph 46), stopper and mix thoroughly.

E10 Transfer each calibration solution (paragraph E9) to an individual, labelled 250 ml phenol flask (paragraph E7), and add sufficient 1 + 1 hydrochloric acid (paragraph E6) to bring the level of the liquid to approximately one third the way up the graduated neck of the flask.

E11 Transfer 100 ml of filtered sump fluid (paragraph 94) to an individual, labelled 250 ml phenol flask (paragraph E7), and add sufficient 1 + 1 hydrochloric acid (paragraph E6) to bring the level of the liquid to approximately one third the way up the graduated neck of the flask.

E12 Place each phenol flask in gently boiling water for 1 hour or until all the oil has separated and the emulsion cleared. Then read the volume of oil separated from the graduated neck of each phenol flask while the solution is still hot. Record these volumes.

Calculation of the strength of water-mix metalworking fluid in the sump fluid

E13 Calculate the strength of water-mix metalworking fluid in each sump fluid sample, S, in % (v/v), using the equation:

$$S = \frac{V_{SF} \times 5}{V_{CS}} \quad \text{Equation 11}$$

where:

V_{SF} is the volume of mineral oil separated from the sump fluid sample, in ml (see paragraph E12);

V_{CS} is the volume of mineral oil separated from the calibration solution, in ml (see paragraph E12); and

5 is the volume of concentrate used to prepare the calibration solution, in ml (see paragraph E9).

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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 289 2000).

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.

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