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

MDHS95/3

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Scope

1   This method describes a procedure for the measurement of time-weighted average concentrations of water-mix metalworking fluid originating from metalworking machine operations. The method is only suitable when the machine sump fluid (liquid circulating in the machine) contains an element which is unlikely to emanate from a source other than the water or metalworking fluid concentrate used to prepare the fluid and this element is present at a high enough concentration to facilitate its use as a marker.

2   Elements that have been found to be suitable markers are boron, potassium and sodium.

Summary

3   A measured volume of air is drawn through a filter mounted in an inhalable aerosol sampler. The filter is then desorbed with caesium chloride solution.

4   The concentration of the marker element in the filter samples and a sample of the sump fluid can then be measured by either flame atomic absorption spectrometry (AAS) or inductively coupled plasma – atomic emission spectrometry (ICP-AES).

5   The strength of water-mix metalworking fluid in the sump is then measured by comparison of refractometry results of the sump fluid with solutions of known strength prepared from the concentrate used to prepare the metalworking fluid.

6   Together these measurements allow the calculation of the concentration of the metal working fluid concentrate in the air sample.

7   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

8   A minimum sampling time of 2 hours is recommended when boron or potassium is the marker element; and a minimum sampling time of 8 hours is recommended when sodium is the marker element. However, if sampling is carried out in a dusty environment, the sampling time should 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.[1] Advice on monitoring strategies for toxic substances is given in HSG173.[2]

9   If employing background sampling, samplers should be positioned at approximately head height, away from obstructions, fresh air inlets or strong winds. The sampling procedures are otherwise the same as for personal sampling.

10   The examples of the lower limit of the working range of the method given in Table 1 (Appendix 1) may be used to estimate the minimum sampling time required to enable personal exposure measurements to be made with acceptable expanded uncertainty at the concentration of water-mix metalworking fluid concentrate in air of interest, eg 0.1 mg.m^{-3}. A more accurate assessment of the minimum sampling time required can be achieved by following the procedure described in Appendix 2. If in doubt, sample for at least 4 hours and preferably over a full working day.

Prerequisites

11   Users of this method will need to be familiar with the content of MDHS14.[3]

Safety

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

Equipment

13   Inhalable aerosol samplers with protective cover as described in MDHS14.[3] The samplers should be cleaned and operated according to the manufacturer's instructions.

14   Personal sampling pumps that meet the requirements of BS EN 13137.[4]

15   Filters: Quartz fibre filters should be used when boron is the marker element.[5] For sodium or potassium, filters with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter are required. Mixed cellulose ester filters of 0.8 µm mean pore diameter are suitable.

16   A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than ±2%.

17   Flexible plastic tubing of a suitable diameter for making a leak-proof connection from the sampling head to the pump; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes and containers to transport samples to the laboratory.

Laboratory apparatus and reagents

18   During the analysis use only reagents of a recognised analytical grade. Use only deionised water.

19   Water: Complying with the requirements of ISO 3696[6] grade 2 water (electrical conductivity less than 0.1 m.S.m^{-1} and resistivity greater than 0.01 MΩ.m at 25 °C

20   Concentrated nitric acid (HNO$_3$): Density about 1.42 g.ml^{-1} (69%–71% (m/m)).

21   Dilute nitric acid (10%): Add approximately 800 ml of water to a 1 litre volumetric flask. Carefully add 100 ml of concentrated nitric acid and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

22   Stock standard solutions of sodium, potassium and boron (1000 µg.ml^{-1}): Use commercially available standard solutions. Observe the manufacturer's expiry date and storage conditions.

23   Working standard solutions (100 µg.ml^{-1}): Accurately pipette 5 ml of stock standard solution into a 50 ml volumetric flask, dilute to the mark with water and mix thoroughly. Prepare these solutions fresh weekly.

24   Caesium chloride solution, approximately 0.2% (m/v): Dissolve 2.5 g of caesium chloride in water. Quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water and mix thoroughly. This solution may be stored in a polypropylene bottle for an indefinite period.

25   Cellulose filter papers.

26   Laboratory detergent solution: Suitable for cleaning of laboratory glassware, diluted with water according to the manufacturer's instructions.

27   Borosilicate laboratory glassware (suitable plastic beakers may also be used): Beakers; funnels; watch glasses; measuring cylinders; and volumetric flasks complying with the requirements of BS ISO 3585.[7] Cleaned before use with laboratory detergent and laboratory washing machine followed by rinsing with water. An additional cleaning by soaking in the 10% nitric acid for at least 24 hours and then thoroughly rinsing with water is required.

28   Micropipettes complying with the requirements of BS EN 8655-6.[8]

29   Orbital mixer: variable speed.

30   Polypropylene bottles: with screw cap for collection of bulk samples, cleaned by soaking in 10% nitric acid for at least 24 hours and rinsed with water. Bottles made of an alternative plastic may be used provided that they are suitable for the intended use.

31   Spectrometer: Either an atomic absorption spectrometer (AAS), fitted with an air-acetylene burner, supplied with compressed air and acetylene, and equipped with a sodium or potassium hollow cathode lamp or an inductively coupled plasma – atomic emission spectrometer (ICP-AES), supplied with argon, and capable of measuring boron at 249.773 nm (or an alternative suitable wavelength).

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

Preparation and sampling

33   Preparation of samplers and air sampling should be carried out in accordance with the procedures described in MDHS14[3] for inhalable aerosol.

34   Consult the material safety data sheet for information on the composition of the metalworking fluid and select quartz fibre filters if boron will be the marker element, otherwise mixed cellulose ester membrane filters may be used. Boron or potassium are suitable for use as the marker element if present in the sump fluid at

a concentration of at least 100 µg.ml^{-1}, while sodium concentration must be at least 400 µg.ml^{-1}. However, avoid using sodium, where possible, since the lower limit of the analytical range is much higher than for boron or potassium, and there is a greater likelihood of interference from secondary sources of sodium in the workplace. Other elements may be used as markers if the concentration permits.

35   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 work piece 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.

36   Set aside a minimum of three unused samplers as blanks, or for batches of more than thirty, one blank for every ten samples collected. Ensure that the blank samplers are handled in the same way as the samples but draw no air through them.

37   An appropriate sampling period should be selected (Appendix 2).

38   After sampling, remove the filter from each sampler and place in a labelled filter transport cassette. Alternatively, transport the sample filters to the laboratory in the samplers with their protective cover in place in a suitable container. For samplers which have an internal filter cassette, remove the filter cassette from each sampler and fasten with its lid or transport clip before transport.

39   Using a labelled polypropylene bottle, take a sample of sump fluid from each machine where 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/work piece while the fluid is circulating.

40   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 labelled polypropylene bottle. Also take a 1 litre sample of the water used to prepare the working strength water-mix metalworking fluids at the work area.

Calibration

41   Prepare calibration solutions by diluting appropriate volumes of the sodium, potassium or boron 100 µg.ml^{-1} solutions with caesium chloride solution (0.2 %m/v Cs). At least six (three for boron) calibration solutions should be used covering the range 0 to 5 µg.ml^{-1} (0 to 2.5 µg.ml^{-1} for sodium).

Sample analysis

42   Analyse the sump fluid sample before analysing the air samples to confirm the marker element. If necessary, also analyse the metalworking fluid concentrate and the water used to prepare the working strength water-mix metalworking fluids at the work area.

43   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.

Preparation of air sample and blank solutions

44   Transfer each sample and blank filter into a labeled 50 ml beaker using clean flat-tipped tweezers. Discard any samples that display evidence of splash contamination.

45   Accurately dispense 10 ml of caesium chloride solution into each beaker and place on the orbital mixer for 60 minutes.

46   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, wash any particulate material adhering to the internal surfaces into the beaker using the caesium chloride solution. Ensure that the liquid drains from the sampler into the beaker as completely as possible and the total volume is 10 ml.

47   Remove each beaker from the mixer and analyse immediately. Alternatively, transfer each solution to a labelled polypropylene bottle 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.

Preparation of sump fluid sample solutions

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

49   Dilute each sump fluid sample to bring the marker element concentration within the calibration range. Accurately pipette 1 ml of each sample into a 100 ml volumetric flask and dilute to the mark with caesium chloride solution. Stopper and mix thoroughly.

Analysis by flame atomic absorption spectrometry

50   Set up the AAS 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 $\mu g.ml^{-1}$ of sodium and about 0.03 $\mu g.ml^{-1}$ of potassium.

51   Adjust the spectrometer zero while aspirating the blank calibration solution. Repeat this procedure regularly throughout the analysis and readjust the zero if the baseline drifts.

52   Aspirate the calibration solutions into the flame in order of increasing concentration and make absorption measurements for each solution. Generate a calibration function by carrying out a linear regression.

53   Aspirate the air sample and blank solutions and the diluted sump fluid sample solutions into the flame.

54   Aspirate a mid-range calibration solution 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 ±5%, take one of the following appropriate corrective measures: either use the available software facilities to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer; and in either case reanalyse the solutions analysed during the period in which the sensitivity change occurred.

55   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 into a, labeled 50 ml volumetric flask. Dilute to the mark with caesium chloride solution, stopper and mix thoroughly. Record the dilution factor.

56   Determine the mean sodium or potassium concentration of the blank solutions in $\mu g.ml^{-1}$.

Analysis by inductively coupled plasma – atomic emission spectrometry

57   Set up the ICP-AES to determine boron at 249.773 nm (or a suitable alternative wavelength), sodium and potassium may also be measured by this technique. 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 $\mu g.ml^{-1}$ of boron.

58   Aspirate the calibration solutions into the plasma in order of increasing concentration and make emission measurements for each solution. Generate a calibration function for boron by carrying out a linear regression.

59   Aspirate the air sample and blank solutions and the diluted sump fluid sample solutions into the plasma and make emission measurements for each solution. Use the calibration function to determine the concentration of boron in the sample and blank solutions in $\mu g.ml^{-1}$.

60   Boron can take a considerable period of time to wash out of the sample introduction system of the ICP-AES. 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 ICP-AES system when deciding on the length of this rinse time.

61   Aspirate the low calibration solution 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 ±5%, take one of the following appropriate corrective measures: either use the available software facilities to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer. In either case, reanalyse the solutions that were analysed during the period in which the sensitivity change occurred.

62   If high concentrations of boron 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 into a, labeled 50 ml volumetric flask. Dilute to the mark with caesium chloride solution, stopper and mix thoroughly. Record the dilution factor.

63   Calculate the mean boron concentration of the blank solutions in µg.ml^{-1}.

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

64   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 metalworking fluid concentrate into 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.

65   Set up the refractometer 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, and take refractometer readings for each calibration solution, rinsing the refractometer with water between readings.

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

67   Take refractometer readings for each filtered sump fluid sample, rinsing the refractometer with water between readings. If necessary, dilute the sump fluid to bring its strength within the range of the calibration.

68   Use the calibration graph to determine the strength of water-mix metalworking fluid in each sump fluid sample.

69   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 1, and an acid split procedure is described in Appendix 2. 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.

Calculations

Volume of air sample

70   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

71   Calculate the concentration of the marker element in air, $\rho(E)_A$, in milligrams per cubic metre (mg.m^{-3}), using equation 1:

$$\rho(E)_A = \frac{(\rho(E)_1 \times V_1 \times DF_1) - (\rho(E)_0 \times V_0 \times DF_0)}{V} \qquad \text{Equation 1}$$

where:

$\rho(E)_0$ = mean concentration of the marker element in the blank solutions, in $\mu g.ml^{-1}$

$\rho(E)_1$ = concentration of the marker element in the sample solution, in $\mu g.ml^{-1}$

V = volume of the air sample, in litres

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

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

DF_0 = dilution factor for the blank solutions, ie 1

DF_1 = dilution factor for the sample solutions

Concentration of the marker element in the sump fluid

72   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 equation 2:

$$\rho(E)_S = \frac{\rho(E)_2 \times V_3 \times DF}{V_2 \times 1000} \qquad\qquad \text{Equation 2}$$

where:

$\rho(E)_2$ = concentration of the marker element in the diluted sump fluid sample solution, in $\mu g.ml^{-1}$

V_2 = volume of sump fluid sample used to prepare the diluted solution, in ml, ie 1 ml

V_3 = volume to which the sump fluid sample was diluted, in ml, ie 100 ml

DF = secondary dilution factor, applicable if a dilution was required to bring the sample into the calibration range

1000 = factor required to convert the concentration units from $\mu g.ml^{-1}$ 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

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

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

Personal exposure to the aqueous aerosol

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

$$\rho(A) = \frac{\rho(E)_A \times 1000}{\rho(E)_S} \qquad\qquad \text{Equation 3}$$

where:

$\rho(E)_A$ = concentration of the marker element in air, in mg.m^{-3}

$\rho(E)_S$ = concentration of the marker element in the sump fluid, in mg.g^{-1}

1000 = factor required to convert the concentration units from g.m^{-3} to mg.m^{-3}

Personal exposure to water-mix metalworking fluid concentrate

75   Calculate the personal exposure of the operator to the water-mix metalworking fluid concentrate, $\rho(C)$, in mg.m^{-3}, using equation 4:

$$\rho(C) = \rho(A) \times S/100 \qquad\qquad \text{Equation 4}$$

where:

$\rho(A)$ = personal exposure of the operator to aqueous aerosol, in mg.m^{-3}

S = strength of water-mix metalworking fluid, in % (v/v)

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

Appendix 1: Method performance

1   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.

2   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 determined for boron, by ICP-AES; and for sodium and potassium, by AAS. The qualitative and quantitative detection limits for boron were 0.007 µg.ml^{-1} and 0.024 µg.ml^{-1}, respectively; for sodium 0.084 µg.ml^{-1} and 0.28 µg.ml^{-1}, respectively; and for potassium 0.008 µg.ml^{-1} and 0.028 µg.ml^{-1}, respectively.[10]

3   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 µg.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.

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

4   Lower limits of the working range determined 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.[10] 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 µg.ml^{-1}, and sump fluid strengths in the range 2–5%.

Overall uncertainty

5   The overall uncertainty, as defined in BS EN 48211 has been estimated 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 ICP-AES;
- 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 AAS;
- 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 AAS.

Interferences

6   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.

7   Determination of the strength of water-mix metalworking fluid in the sump by refractometry gives accurate results if the sump fluid is in good condition. 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.

8   Measurement of sodium and potassium by AAS is subject to possible ionisation interferences, but these are eliminated through the use of caesium chloride as an ionisation buffer.

9   Measurement of boron by ICP-AES 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.

Appendix 2: Calculation of the minimum sampling time required to ensure that measurements are made with acceptable expanded uncertainty

1   Determine the quantitative detection limit of the analytical method under the working analytical conditions. Prepare ten blank solutions by leaching ten blank filters using the procedure described for air samples, and prepare calibration solutions for determination of the selected marker element.

2   Analyse the blank solutions by AAS or ICP-AES, as appropriate.

3   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).

4   Determine the concentration of the marker element in the sump fluid and the strength of water-mix metalworking fluid in the sump fluid and then calculate the minimum sampling time, t, using equation 5:

$$t = \frac{DL \times V_1 \times S \times 1000}{q \times \rho(E)_S \times \rho(C) \times 100} \qquad \text{Equation 5}$$

where:

DL = quantitative detection limit of the analytical method under the working analytical conditions

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

S = strength of water-mix metalworking fluid, in % (v/v)

q = design flow rate of the samplers used, in litres per minute

$\rho(E)_S$ = concentration of the marker element in the sump fluid, in mg.g-1

$\rho(C)$ = minimum concentration of water-mix metalworking fluid concentrate-in-air of interest, in $mg.m^{-3}$

1000 = factor required to convert the concentration units from $g.m^{-3}$ to $mg.m^{-3}$

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

Appendix 3: Potentiometric titration procedure for determination of the strength of water-mix metalworking fluid in the sump fluid by measurement of total alkalinity

1   This procedure is beneficial 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. This can occur when the sump fluid is near the end of its useful life. Results of the analysis of twenty sump fluid samples have shown good correlation with results obtained by refractometry and other methods.9

2   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.

3   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 can be 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 and laboratory apparatus

4   Hydrochloric acid, 0.5 mol.l-1: Use commercially available 0.5 mol.l-1 hydrochloric acid volumetric solution, or concentrated volumetric solution diluted with water according to the manufacturer's instructions.

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

5   Potentiometric titration system: Automated or manual, suitable for measuring the total alkalinity of water-mix metalworking fluid, comprising:

- 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, compatible with the pH meter; or combination pH electrode which incorporates both pH measurement and reference electrodes. The electrode(s) should have a suitable, rapid response time if an autotitration system is used.
- Either burette, 25 ml, class A, graduated in 0.05 ml increments; for manual titration or autotitration system, equipped with a 25 ml autoburette, featuring automatic adaptation of the titration speed to the slope of the titration curve. 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, 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, 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, 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.

6   Maintain, prepare and test the electrodes in accordance with the manufacturer's instructions.

Preparation for analysis

7   Calibrate the pH meter using the pH buffer solutions. Follow the manufacturer's instructions for the appropriate calibration procedure.

8   Fill the burette or autoburette with 0.5 mol.l^{-1} hydrochloric acid.

Determination of total alkalinity

9   Determine the total alkalinity of the calibration solutions of known water-mix metalworking fluid strength and the filtered sump fluid samples by titrating to an end-point of pH 5.5.

10   Introduce 50 ml of the calibration solution or filtered sump fluid sample into the titration vessel. Place the titration vessel on the titration assembly so that the electrodes are about half immersed. Start the stirrer 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.

Manual titration

11   Add suitable small aliquots of 0.5 mol.l^{-1} hydrochloric acid 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 from the titration assembly and wash the electrodes and stirrer paddle or stir with water.

Automatic titration

12   Adjust the apparatus in accordance with the manufacturer's instructions. Programme the instrument to titrate with 0.5 mol.l^{-1} hydrochloric acid 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 from the titration assembly and wash the electrodes and stirrer paddle or stir bar with water.

Calculation of total alkalinity

13   Calculate the total alkalinity of the calibration solution or sump fluid sample, $\rho(CO_3^{2-})$, expressed in mol.l-1 of carbonate, using equation 6:

$$\rho(CO_3^{2-}) = \frac{\rho(H^+) \times V_2}{V_1 \times 2} \qquad\qquad \text{Equation 6}$$

where:

$\rho(H^+)$ = concentration of the titrant (hydrochloric acid) in mol.l^{-1}, ie 0.5 mol.l^{-1}

V_2 = volume of titrant added to reach the end-point

V_1 = volume of calibration solution or sump fluid sample titrated, ie 50 ml

2 = number of moles of H^+ required to titrate 1 mole of CO_3^{2-}

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

13   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 4: Acid split procedure for determination of the strength of water-mix metalworking fluid in the sump

1   Recently water-mix metalworking fluids have been formulated containing much less mineral oil than older conventional fluids. Conventional water-mix metalworking fluids are typically water-in-oil emulsions, typically containing 50–90% oil. Newer products, known as semisynthetic 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.

2   Although acid split is a primitive method for determining the strength of water-mix metalworking fluid in sumps, results of the analysis of twenty sump fluid samples have shown good correlation with results obtained by refractometry and other methods.[9]

3   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 and laboratory apparatus

4   Concentrated hydrochloric acid: density about 1.18 g.ml^{-1}, 36.5% to 38% (m/m), general purpose reagent grade.

5   Hydrochloric acid (50% v/v): Carefully add 500 ml of concentrated hydrochloric acid to 450 ml of water 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.

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

7   Water bath.

Analysis

8   For each proprietary product, prepare a calibration solution at a concentration of 5% (v/v). Accurately pipette 5 ml of each concentrate into a labelled 100 ml volumetric flask. Dilute to volume with water, stopper and mix thoroughly.

9   Transfer each calibration solution to a 250 ml phenol flask, and add sufficient 50% (v/v) hydrochloric acid to bring the level of the liquid to approximately one-third the way up the graduated neck of the flask.

10   Transfer 100 ml of filtered sump fluid to an individual, labelled 250 ml phenol flask, and add sufficient 50% (v/v) hydrochloric acid to bring the level of the liquid to approximately one-third the way up the graduated neck of the flask.

11   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

12   Calculate the strength of water-mix metalworking fluid in each sump fluid sample, S, in % (v/v), using the equation 7:

$$S = \frac{V_{SF} \times 5}{V_{CS}} \qquad\qquad \text{Equation 7}$$

where:

V_{SF} = volume of mineral oil separated from the sump fluid sample, in ml

V_{CS} = volume of mineral oil separated from the calibration solution, in ml

5 = volume of concentrate used to prepare the calibration solution, in ml

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5   Bradley S D and Howe A M *Assessment of the suitability of filters for sampling
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6   BS EN ISO 3696:1995 *Water for analytical laboratory use. Specification and
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8   BS EN ISO 8655-6:2002 *Piston operated volumetric apparatus. Gravimetric
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metalworking machine operators to airborne water-mix metalworking fluid:* Backup
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11   BS EN 482:2012 *Workplace exposure General requirements for the
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You should use the current edition of any standards listed.

Further information

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