Measurement of personal exposure to airborne water-mix metalworking fluids

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What are MWFs?

MWFs
- are applied to the work piece in processes such as grinding, milling, drilling, cutting etc to provide lubrication, cooling, swarf removal and corrosion protection (Figure 1)
- can be divided into two basic types: traditional ‘neat’ mineral oils and water-mix MWFs

Water-mix MWFs
- contain mineral oils and/or synthetic materials such as emulsifiers, corrosion inhibitors, biocides/biostats, etc, and water
- are supplied as concentrates, which are diluted with water to form a 2 - 5 % working strength solution
- can cause a variety of health effects in machine operators by skin contact or inhalation.

Water-mix MWF types
Water-mix MWFs can be classified into 3 sub-groups, as shown in Figure 2. The yellow, so-called ‘conventional’ concentrate has a large amount of mineral oil in its formulation (typically 80 %), the greenish-brown ‘semi-synthetic’ fluid contains about 20 % mineral oil, whilst the green and blue ‘synthetic’ fluids contain no mineral oil at all.

Glossary

Water-mix MWF concentrate is the proprietary product, as supplied by the manufacturer that needs to be diluted with water before use.

Working strength water-mix MWF is concentrate that has been diluted with water ready for use. A typical working strength solution is between 2 % and 5 % (v/v).

Sump fluid is the water-mix MWF circulating in a metalworking machine, as applied to the cutting tool and workpiece as a lubricant and coolant.

Aqueous aerosol is airborne water-mix MWF produced from the sump fluid when a metalworking machine is in use.
**Fluid management**

Proper fluid management is crucial to maintaining the performance of MWFs to a high standard. Deterioration of fluids has a significant influence on the nature and concentration of chemical and biological agents present in the sump, and this has a direct effect on workers' exposure.

The standard of fluid management varies considerably. Figure 3 shows the condition of 3 sump fluid samples. All are conventional water-mix MWFs, which typically produce a milky working strength fluid. The 1st fluid is clearly in good condition. The 2nd has a layer of tramp oil on the top. Whilst the 3rd is a fluid in very poor condition, containing significant amount of tramp oil and metal fines.

**MWF aerosols**

When metalworking machines are in operation, fluid from the sump is applied directly to the workpiece to achieve the required lubrication and cooling effect. This can lead to the formation of a MWF aerosol that can be inhaled by the machine operator (Figure 4).

A variety of health effects can result from the exposure of machine operators to the additives present in water-mix MWFs and the chemical and biological contaminants produced by deterioration of the fluids during use. These health effects are caused by direct skin contact or by inhalation or skin deposition of MWF aerosol generated during machine operation.

Inhalation health effects caused by water-mix MWFs include irritation of the upper respiratory tract, occupational asthma, chronic inflammatory reaction of the lungs and a form of pulmonary fibrosis. A recent survey in the UK suggested that 6-7 % of occupational asthma is due to exposure to water-mix MWFs.

**Requirement for a new method**

In the past, exposure to water-mix MWF aerosols has been assessed as for mineral oil mists, i.e. by comparing gravimetric results to the exposure limit for mineral oil mists (5 mg m$^{-3}$). This approach is unsatisfactory because

- a simple gravimetric method is affected by the presence of other airborne particles; and
- water-mix MWF formulations are very variable in terms of their mineral oil content, and some contain no mineral oil at all.

**Method selection**

Various methods with potential for measuring water-mix MWF aerosols were assessed, including gravimetry with solvent extraction, an elemental marker method used successfully by UK engineering firms; and various other options. After careful consideration the elemental marker method was selected for further development.

**Elemental marker method**

**Principle**

An element present in the sump fluid is used as a marker to estimate the amount of aqueous aerosol to which the machine operator is exposed. Personal exposure to the MWF concentrate is then calculated using the determined strength of MWF in the sump. The most useful marker elements are boron (from borate added to MWF fluid formulations as an anti-bacterial agent), potassium and sodium.

**Sample collection**

A sample of airborne water-mix MWF is collected by drawing a measured volume of air through a filter mounted in an inhalable dust sampler. At the same time a sample of the fluid circulating in the machine is also collected, and a sample of the water-mix MWF concentrate is also taken for calibration purposes.
### Analysis

The sample of airborne water-mix MWF is leached from the filter and the resulting solution is analysed to determine the concentration of the marker element in air.

The sump fluid is diluted and analysed to determine the concentration of marker element in the sump fluid.

The two results are then used to calculate the aqueous aerosol concentration, $\rho(A)$, in mg m$^{-3}$, using the following equation:

$$\rho(A) = \frac{\rho(E)_A \times 1000}{\rho(E)_F}$$

where $\rho(E)_A$ is the concentration of the marker element in air, in mg m$^{-3}$; and $\rho(E)_F$ is the concentration of the marker element in the sump fluid, in mg g$^{-1}$.

Finally, the sump fluid strength, $S$, in % (v/v), is determined and used to calculate the personal exposure of the operator to water-mix MWF concentrate, $\rho(C)$, in mg m$^{-3}$:

$$\rho(C) = \frac{\rho(A) \times S}{100}$$

### Experimental

#### Development of air sampling method

At the outset it was decided to use cellulose ester membrane filters for sample collection, since these have low blanks and adequate retentivity (> 99.5 % for particles with a 0.3 µm diffusion diameter). However, initial experiments with laboratory-generated MWF aerosols yielded low results for boron. Further tests with other filters showed that boron was collected quantitatively by quartz fibre filters, so these are used for sampling boron-containing water-mix MWFs.

#### Development of elemental analysis methods

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and flame atomic absorption spectrometry (FAAS) are used for analysis, as they are widely available and suitable for boron, potassium and sodium measurement.

Sample preparation is straightforward. Sump fluid samples are prepared simply by filtering to remove foreign material (if necessary) and diluting with caesium chloride solution. Filter samples are prepared for analysis by desorbing filters with caesium chloride solution.

Caesium acts as an ionisation suppressor for FAAS analysis, and it ensures a consistent response for analysis of boron by ICP-AES.

#### Development of a method for measuring sump fluid strength

There are many techniques that can be used to determine the sump fluid strength, including:

- refractometry; in which the refractive index of light is measured as it enters a thin film of fluid;
- measurement of total alkalinity, which involves acid titration; and
- acid split, in which oil separated by the addition of mineral acid is measured volumetrically.

Not all the techniques are suitable for all types of water-mix MWF, and their performance deteriorates if the sump fluid is in poor condition.

After a detailed assessment of the methods, refractometry was selected as the method of choice. However, if the sump fluid is in extremely poor condition, the fluid strength is redetermined by the acid split and total alkalinity methods, and the mean of the two closest results is reported.

#### Validation of the elemental marker method

The elemental marker method was tested to demonstrate compliance with the overall uncertainty requirements prescribed in EN 482.

The test protocol used was that given in EN 13890. This involved estimating sampling errors, experimentally determining analytical errors, and combining these to estimate the overall uncertainty of the measurement procedure as a whole.

Various assumptions had to be made in this process, and an educated guess had to be made about the value of any future UK exposure limit for water-mix MWF concentrate, which was taken to be 1 mg m$^{-3}$.

Table 2 gives an illustration of conditions when the elemental marker method was found to meet the EN 482 performance requirements. Full details of the validation work are given in the back-up data report for the new method.
Tests on a simulated MWF aerosol
Tests were also carried out on a laboratory generated MWF aerosol to compare results obtained using the different elemental markers with gravimetry. As can be seen from Table 3, there was excellent agreement.

Discussion
Advantages of the new MDHS 95 method
The new MDHS 95 method has a number of advantages over other available methods, including ASTM PS 42 – 97. In particular, it:

- has a lower detection limit, by up to an order of magnitude;
- its detection limit is not affected by the type of water-mix MWF involved, e.g. a synthetic fluid that is 90% water can have a detection limit as good as a conventional fluid that is 90% mineral oil; and
- results may be used to estimate exposure to other sump fluid components, e.g. endotoxin.

Disadvantages of the MDHS 95 method
Measurements made using the MDHS 95 have a few disadvantages, some of which it has in common with the other methods. In particular:

- results are expressed as water-mix MWF concentrate, so to be meaningful a relevant limit value is required to compare them with
- the method may not be suitable for assessing the exposure of operators tending multiple machines; and
- a secondary source of the marker element in the workplace can interfere with results.

MWFs Technical Development Survey (TDS)
The MDHS 95 method has been used in a major survey of the UK engineering industry. Table 4 presents some of the findings, full details of which have been published elsewhere.

Conclusions
An effective method for measuring personal exposure to airborne water-mix MWFs has been developed, validated and published as MDHS 95.

Data obtained with the MDHS 95 method has helped HSE develop new guidance for UK industry on the control of health risks from MWFs.

Further work is planned to compare the relative effectiveness of the MDHS and ASTM methods.

References
3. European Standard EN 482, Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents, CEN, Brussels, 1996.

Table 2
Conditions when EN 482 performance requirements are met

<table>
<thead>
<tr>
<th>Marker elements</th>
<th>Minimum marker element concentration in sump fluid (µg ml⁻¹)</th>
<th>Maximum sump fluid strength (% v/v)</th>
<th>Minimum air sample volume (litres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>100</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>K</td>
<td>200</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>Na</td>
<td>400</td>
<td>5</td>
<td>1000</td>
</tr>
</tbody>
</table>

Therefore, for example, if boron is present in the sump fluid at a concentration in excess of 100 µg ml⁻¹ and the sump fluid strength is less than 5%, the EN 482 requirements are satisfied if the air sample volume is > 250 litres.

Table 3
Results of tests on a simulated MWF aerosol

<table>
<thead>
<tr>
<th>Marker element method</th>
<th>Water-mix MWF concentrate-in-air (mg m⁻³)</th>
<th>Gravimetric method</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4.35</td>
<td>4.29</td>
</tr>
<tr>
<td>K</td>
<td>4.42</td>
<td>4.57</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4
Summary of MWF TDS results

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Number</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-mix MWF aqueous aerosol (mg m⁻³)</td>
<td>298</td>
<td>0.07</td>
<td>944</td>
<td>2.34</td>
</tr>
<tr>
<td>Sump fluid strength (% v/v)</td>
<td>269</td>
<td>0.3</td>
<td>37.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Water-mix MWF concentrate (mg m⁻³)</td>
<td>298</td>
<td>&lt; 0.01</td>
<td>13.2</td>
<td>0.12</td>
</tr>
<tr>
<td>Total particulate (mg m⁻³)</td>
<td>296</td>
<td>0.02</td>
<td>23.1</td>
<td>0.32</td>
</tr>
</tbody>
</table>