

Analytical method research for metalworking fluids at the National Institute for Occupational Safety and Health (NIOSH)

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1 Introduction

Metalworking fluids (MWFs) remove metal debris from the work surfaces of metal parts that are being turned, ground, milled, or drilled and provide lubrication and cooling to the work piece and to the work tool. These fluids are also used to cool and lubricate in cold metal-forming operations such as stamping, punching, hobbing, or drawing.

There are hundreds of compounds in MWFs, including mineral oils, emulsifiers, water, alkanolamines, polyethoxyethanols, biocides, surfactants, chlorinated paraffins, and boron compounds. Despite the complexity of their formulations, MWFs are generally classified according to the amount of mineral oil that they contain. Straight fluids contain essentially 100 % mineral oils or other organic additives but no water; they are used undiluted. The remaining three types of fluids – soluble, semisynthetic, and synthetic – are all diluted with water prior to use. Undiluted soluble fluids contain up to 80 % mineral oil; undiluted semisynthetic fluids contain 5 % to 30 % mineral oil. Synthetic fluids contain no mineral oil.

Worker exposure to certain MWFs has been related to occupational illnesses, specifically occupational asthma and hypersensitivity pneumonitis (HP). In addition, there have been concerns about the carcinogenic potential of these fluids.

To support the recommended exposure limit to MWFs, NIOSH recently released Method 5524 in the NIOSH Manual of Analytical Methods [1]. The method employs an extraction technique for MWF that lends itself to further analysis of sample components. Since occupational illnesses (e. g. HP) have been reported at low mist levels, further analysis of the composition of MWF samples will likely be required to identify individual causative agents.

NIOSH currently has an extensive analytical research program for metalworking fluids. Three areas of immediate analytical focus are:

- Techniques to separate and identify individual components in the MWF.
- Biocides, especially hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine, which has been implicated in outbreaks of HP.
- Nitrosamines, especially N-nitrosodiethanolamine (NDELA) and N-nitrosomorpholine (NMORPH); both are potential carcinogenic contaminants of MWFs.

A new liquid chromatographic (LC) procedure is being investigated for separation of MWF into its ionic, polar, and neutral components. The biocide and the nitrosamine analyses are currently being investigated using electrospray-mass

Abstract Exposure to certain metalworking fluids (MWFs) has been related to occupational asthma, hypersensitivity pneumonitis (HP), and possibly to cancer. NIOSH recommends that exposure to MWF aerosols be limited to 0.4 mg/m³ measured as thoracic particulate or 0.5 mg/m³ measured as total particulate. Method 5524, a sampling and analytical method for MWF, issued by the National Institute for Occupational Safety and Health (NIOSH) to support the standard, is described. This technique separates MWF from commingled particulate by extraction with a ternary blend of methylene chloride, methanol, and toluene. Despite lowered exposure limits, occupational disease due to MWF is still observed, indicating further analyses of MWF samples may be needed to isolate causative agents. A NIOSH analytical research program for metalworking fluids which employs liquid chromatographic techniques to separate and classify major components of the MWF according to chemical class is discussed. The analysis of biocides and nitrosamines using an electrospray-mass spectrometric technique is also described. Miscellaneous other analytical issues are also addressed.

Entwicklung von Analysenverfahren für Kühlschmierstoffe im National Institute for Occupational Safety and Health (NIOSH)

Zusammenfassung Die Exposition gegenüber bestimmten Kühlschmierstoffen (KSS) wird mit berufsbedingtem Asthma, hypersensitiver Pneumonitis (HP) und möglicherweise auch Krebs in Zusammenhang gebracht. Das National Institute for Occupational Safety and Health (NIOSH) empfiehlt, die Exposition gegenüber KSS-Aerosolen auf 0,4 mg/m³, gemessen als thorakale Fraktion, bzw. auf 0,5 mg/m³, gemessen als einatembarer Anteil, zu begrenzen. Die hierzu vom NIOSH herausgegebene Methode 5524, ein Probenahme- und Analyseverfahren für KSS, wird beschrieben. Bei diesem Verfahren werden KSS durch Extraktion mit einem ternären Gemisch aus Methylenchlorid, Methanol und Toluol von anderen Partikeln getrennt. Trotz abgesenkter Expositionsgrenzwerte treten weiterhin durch KSS verursachte Berufskrankheiten auf. Dies weist darauf hin, dass weitere Untersuchungen an KSS-Proben notwendig sind, um auslösende Substanzen zu ermitteln. Ein Forschungsprogramm des NIOSH zur Analyse von KSS, bei dem flüssigchromatografische Verfahren zur Trennung und Klassifizierung der Hauptbestandteile von KSS angewendet werden, wird diskutiert. Des Weiteren wird die Analyse von Bioziden und Nitrosaminen mit der Elektrospray-Massenspektrometrie beschrieben und verschiedene andere analytische Aspekte werden angesprochen.

spectrometry (ES-MS) techniques. Extensive further LC and gas chromatographic (GC) analyses of MWFs are also underway.

2 Method 5524

The NIOSH criteria document [2] for MWFs states that the exposure limits for MWFs can be supported using a simple gravimetric procedure such as NIOSH Method 0500. "However, when there are simultaneous exposures to non-toxic particulate materials, NIOSH Method 5026 or a similar method [emphasis added] may be useful to estimate the soluble component of the workroom aerosol."

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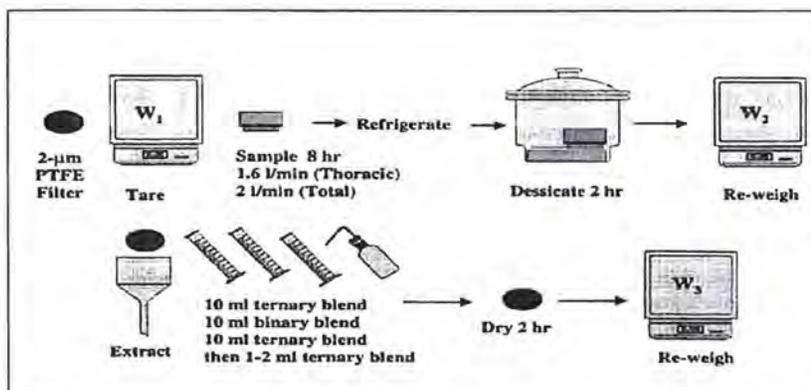


Figure 1 | Measurement of MWF using Method 5524. (1st line) The filter is tared (W_1). Sampling is conducted as indicated; samples are refrigerated during storage, then desiccated prior to weighing (W_2). (2nd line) The filter is extracted using the ternary (1:1:1 methylene chloride : methanol : toluene) and binary (1:1 methanol : water) blends, dried, and reweighed (W_3). Total weight, $W_T = W_2 - W_1$; MWF is measured as extractable weight, $W_E = W_3 - W_2$; and the fraction extracted, $FE = W_E/W_T$.

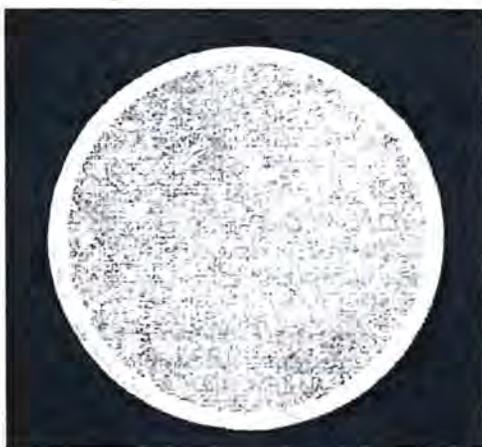


Figure 2 | Residual particulate after extraction of an 0.8 mg/m^3 thoracic exposure sample from a welder who was also exposed to MWF. $W_E = 0.57 \text{ mg/m}^3$, indicating sample was primarily MWF.

In rural areas of the USA where there are metalworking facilities, agricultural debris may be a significant source of interference, especially during planting and harvest times. Background dust levels from in-plant construction and, in urban areas, ambient air particulate material may also interfere with measurements of MWF concentrations. Furthermore, there may be significant levels of metal particulate generated during many metalworking processes, in particular, during welding.

For these reasons, NIOSH has adapted American Society for Testing and Materials (ASTM) Method PS-42-97 for metalworking fluids to support the standard. This procedure collects samples on a 37-mm PTFE filter and extracts MWF from commingled solid particulate using a ternary blend of 1 : 1 : 1 methylene chloride, methanol, and toluene [3; 4]. The new NIOSH Method 5524 is described in detail in Figure 1.

The ASTM method was employed in a 79-plant survey of small-to-medium sized machining operations across the United States [5]. Approximately 155 individual MWFs were encountered in this survey; 154 of these fluids were soluble in the ternary blend. The one insoluble fluid was successfully extracted with a 1 : 1 blend of methanol : water. One of the authors (*R. Glaser*) recently published an evaluation of the ASTM procedure [6]. As with most gravimetric analyses, the ASTM method has problems with blanks. Sample loss during

storage or desiccation may also occur. Statistical analysis indicated that the limits of quantitation for both the total-weight measurements and the extracted-weight measurements were approximately 0.1 mg. That analysis also indicated that the fractions extracted (FE) for straight fluids were significantly higher than those for the synthetic fluids for grinding operations only ($P = 0.05$). This may be related to many factors. The sample weights of the straight-grinding samples were higher than those of the synthetic-grinding samples. If there is a constant background of insoluble particulate in the atmospheres being sampled, the straight fluids would be expected to exhibit higher FE values relative to the synthetic fluids. Alternatively, there may be small amounts of unextracted, water-soluble components of synthetic fluid samples. Method 5524 incorporates a 1 : 1 binary blend of methanol : water to facilitate removal of any of these water soluble components and the lone MWF found to be insoluble in the ternary blend. To mitigate sample losses during storage, NIOSH Method 5524 also imposes relatively strict storage requirements.

The benefits of using an extraction technique for the analysis of MWFs can be seen in Figure 2, which shows an extracted fume sample taken from a welder who was working near a metalworking operation that used semisynthetic fluids. Note that the sample contained only 0.8 mg of thoracic aerosol, which consisted of 30 % unextracted particulate (0.23 mg/m^3) and 70 % MWF (0.57 mg/m^3). The measured MWF concentration exceeded the NIOSH REL (REL, recommended exposure limit). Typically, such samples would be analyzed gravimetrically or for the presence of metals only. Without the sample extraction, it would not have been known that the worker was primarily exposed to MWF and **not** welding fume; furthermore, the MWF exposure exceeded the NIOSH REL.

3 Sample fractionation

While Method 5524 permits extraction of personal exposure samples, further procedures may still be required to fractionate the components of such samples into appropriate chemical classes for identification. In addition, bulk samples of both new and used MWFs require analysis both for health hazard evaluations and toxicological assays. Two techniques, being investigated under the direction of one author (*K. Brown*), are multi-modal liquid chromatography and solid phase extraction.

4 Multi-modal liquid chromatography (MM-LC)

This chromatography scheme combines the principles of ion exchange, normal, and reverse phase liquid chromatography into a single column system for the separation of complex mixtures. An MM-LC system with UV detection is being tested to fractionate MWF into cationic, anionic, polar, and neutral components. Fractions containing cationic (e. g. alkanolamines, quaternary ammonium salts), anionic (ionic surfactants), and the majority of high molecular weight polar components (e. g. non-ionic surfactants) will likely be analyzed using liquid chromatography with confirmation by LC-MS. Liquid chromatographic fractions containing non-ionic polar and intermediate polarity organics (e. g. chlorinated paraffins) and neutral components (e. g. waxes and mineral oils) should be amenable to analysis via gas chromatography with confirmation via GC-MS.

Another MM-LC system is being studied (by *K. Brown* and *J. Arnold*) using an evaporative light scattering detector (ELSD) to further analyze and classify MWFs. The ELSD is a general detector, with a response approximately proportional to the mass of MWF components that can be aerosolized; however, this restriction limits its ability to detect vaporized contaminants.

5 Solid phase extraction (SPE)

Due to the possibility of high levels of contamination in field samples, additional sample pretreatment may also be required. Solid phase extraction cartridges are small, disposable, low resolution liquid chromatography columns that can concentrate analytes using normal phase, reverse phase, or ionic retention/exchange mechanisms. The retained analyte is then eluted from the column via an appropriate solvent or ionic solution. Cleanup using SPE not only simplifies the final analytical finish but also prevents damage to expensive instrumentation from highly contaminated samples. Some preliminary work has been done using SPE technology to rapidly fractionate a mock MWF sample containing mineral oil, stearic acid, triethanolamine, and a non-ionic surfactant, nonylphenol ethoxylate (Tergitol® NP-9), into its cationic, anionic, non-ionic polar, and non-polar fractions prior to instrumental analysis. One limitation of this technique that has been discovered is the extraction of artifacts from the SPE cartridge which can cause significant analytical interferences. Another limitation may be irreversible adsorption of the analyte into the adsorptive matrix of certain SPE cartridges.

6 Gas chromatography-mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry is a useful technique for screening MWF components. There are well-established libraries of known mass spectra for reliable matching and identification of unknown compounds in MWF. Screening of thermally stable MWF components at NIOSH will eventually be done by GC-MS analysis of solvent extracts of the MWF that have been run through the MM-LC or SPE cleanup procedures. This technique will be directed towards analysis of volatile and semivolatile, non-polar, and moderately polar components, such as mineral oils and chlorinated paraffins.

Under certain circumstances, where rapid answers are required, more direct screening approaches may be used. In an investigation of a semisynthetic sump sample from a plant where HP had been diagnosed, three of the authors (*S.-H. Park*, *K. Brown* and *R. Glaser*) employed a rapid screening GC-MS procedure, diluting the fluid with methanol or acetone (1% to 5% solutions) and directly injecting aliquots of the resulting solution into the GC-MS system. This technique successfully identified ethanolamines, an ethanolamine borate, an isothiazalone biocide, and waxy esters, among other components of the MWF samples. This procedure is only used for selected samples because it can severely shorten GC column life. Furthermore, thermal degradation of nitrosamines (see below), aminoethanols, and glycol ethers limits the use of GC-MS for quantitative purposes.

7 Electrospray-mass spectrometry (ES-MS)

In contrast to conventional mass spectrometry, electrospray-mass spectrometry is a soft ionization technique which takes advantage of the fact that neutral molecules can become charged, e. g. by loss of a proton (acids) or complexation with species such as H^+ , Na^+ , or NH_4^+ . The charged (ionized, protonated, sodiated, or ammoniated) species are then detected by the ES-MS technique. Generally, the charged moiety is analyzed under low energy analytical conditions such that it is not fragmented. However, it may be fragmented at higher energies to provide further structural evidence and confirm species identity. The primary limitation of this procedure is that the analyte must be capable of forming an ion or charged complex in solution. Many of the components of MWFs are thermally labile or high molecular weight species, e. g. anionic surfactants, quaternary ammonium compounds, and ethanolamines, among others. Such compounds should be amenable to analysis via ES-MS. One of the authors (*J. Pretty*) is investigating the use of ES-MS for analysis of thermally labile biocides and nitrosamines in metalworking fluids.

8 Biocides

Biocides are an important area of current focus at NIOSH. Biocides are added to sumps containing MWFs to control bacterial levels. Of particular interest is the formaldehyde releasing biocide, hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine, (structure 1 in **Figure 3**). This triazine forms a protonated complex (4) which can decompose, presumably through an oxazolidine (5), or directly to ethanolamine (6) and formaldehyde (7). Overdosing of MWF with this triazine may induce an overgrowth of biocide-resistant mycobacteria, which have been linked to outbreaks of hypersensitivity pneumonitis [7; 8]. Thus, there is a need for a method to analyze this triazine in MWF sumps. There are analytical methods involving conversion of the triazine to CH_2O with subsequent analysis, e. g. as the 2,4-dinitrophenylhydrazones. Such techniques provide no estimate of the residual biocide levels. Attempts to analyze the triazine by gas chromatography were unsuccessful due to its high thermal lability. For that reason, a procedure is being developed to analyze the triazine using ES-MS. **Figure 3** shows the triazine

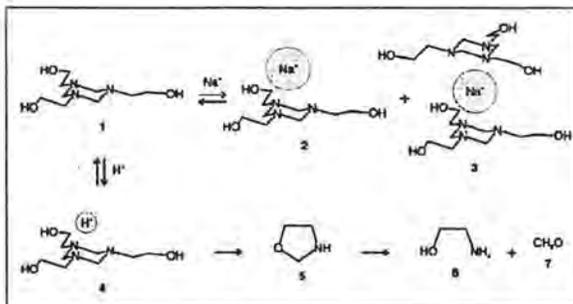


Figure 3 | Triazine biocide (1), observed by electrospray-mass spectrometry as the sodiated monomer (2) (m/z 242), dimer (3) (m/z 461), and the protonated species (4) (m/z 220). At low pH, the biocide decomposes, presumably through an oxazolidine intermediate (5), or directly to ethanolamine (6) and formaldehyde (7).

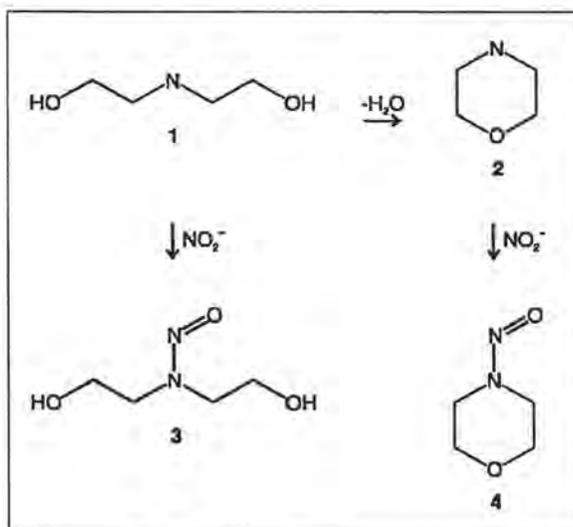


Figure 4 | Reaction of diethanolamine (m/z 101, protonated) (1) and its dehydration product, morpholine (2), with nitrite to form N-nitrosodiethanolamine (3) (NDELA, m/z 135, protonated), and N-nitrosomorpholine (4) (NMORPH, m/z 117, protonated).

molecule as observed by ES-MS in the form of protonated and sodiated complexes.

By controlling the sodium ion concentration, the equilibrium can be forced towards the 1 : 1 sodium adduct and, as appropriate, an analytical method can be developed for that species. Calibration curves using simple flow injection analyses have been shown to be linear for the 1 : 1 sodium adduct ($R^2 > 0.99$). Techniques to stabilize samples of the triazine during storage are also under investigation. The analytical method is being ruggedized for application to field samples. It is currently unknown if the complexed triazine can survive the liquid chromatographic process. Thus, the technique may be limited to a flow-injection ES-MS system. Samples of the triazine spiked into actual metalworking fluids have been successfully analyzed without chromatography using the flow-injection approach. There are many other biocides as well as corrosion inhibitors used in metalworking fluids that

should be amenable to analysis via ES-MS. It is anticipated that a generalized LC-MS technique will be developed for such analytes.

9 Nitrosamines

Nitrosamines are carcinogenic compounds that have been found in metalworking fluids [2]. They may be formed from the reaction of nitrites with secondary amines. Of major concern in MWFs is the nitrosation of diethanolamine to produce N-nitrosodiethanolamine (NDELA) and of morpholine to produce N-nitrosomorpholine (NMORPH). This process is shown in Figure 4.

Generally NDELA has been analyzed using GC-MS by conversion of its hydroxyl moiety to a trimethylsilyl ether to permit ready vaporization and transport past the high temperature surfaces encountered in gas chromatography. The analysis of NDELA and NMORPH has also been investigated using ES-MS. Both nitrosamines can be analyzed as protonated moieties (not shown). Initial results indicate at least ten additional nitrosamines can be detected in protonated form using this technique. Analytical procedures for all of these nitrosamines are anticipated from this research.

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