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An Evaluation of ASTM Method P-42-97 for Sampling and Analysis of Metalworking Fluids

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Exposure to certain metalworking fluids (MWF) has been correlated with outbreaks of occupational asthma, hypersensitivity pneumonitis (HP), and, to a lesser extent, with cancer. There are many components of MWF but these fluids are generally categorized according to the amount of mineral oil that they contain. Straight fluids are primarily composed of mineral oils with other organic additives, are water-insoluble, and are used undiluted. The three other types of MWF are diluted with water during use. Soluble fluid concentrates contain up to 80 percent mineral oil with emulsifying agents added to form emulsions when mixed with water. Semi-synthetic fluid concentrates contain 5–30 percent mineral oil with surfactants added to make them water-soluble. Synthetic fluids contain no mineral oil and are completely water-soluble.

In a 1998 criteria document,[1] the National Institute for Occupational Safety and Health (NIOSH) promulgated a recommended exposure limit (REL) for metalworking fluids of 0.4 mg/m^3 measured as thoracic particulate (or 0.5 mg/m^3 measured as total particulate). The criteria document further recommended that the exposure standard be supported using NIOSH Method 0500 (for total particulate), but recognized that "when there are simultaneous exposures to nontoxic particulate materials, NIOSH Method 5026 *or a similar method* [emphasis added] may be useful to estimate the soluble component of the workroom aerosol."

The separation of the soluble MWF from the insoluble particulate may be necessary due to interferences from many sources; for example, metal particulate from the metalworking processes themselves, fumes from nearby welding operations, agricultural debris in manufacturing plants located in rural areas, background dust generated during in-plant construction, and urban ambient air particulate material. Exposures to atmospheres containing MWF commingled with such solid particulates are not properly classified as exposure only to MWF.

In recognition of this distinction, the British Health and Safety Executive (HSE) analytical method for MWF monitors the concentrations of marker elements that are specific to MWF (e.g., boron from added borates or boric acid); since there are virtually no marker elements in straight MWF, the HSE technique does not permit specific analysis of straight fluids.[2]

The German Berufsgenossenschaftliches Institut für Arbeitsschutz (or BIA) employs a Fourier transform infrared analytical method that monitors the C-H infrared stretching frequency of mineral oil hydrocarbons present in MWF; since there are no mineral oils present in synthetic fluids, the technique cannot generally be used for analysis of such fluids.[3]

To analyze all four classes of MWF, NIOSH has adapted an American Society for Testing and Materials (ASTM) method PS-42-97 for MWF to support the recommended standard.[4] In this procedure, samples are collected on tared 37-mm polytetrafluoroethylene (PTFE) filters using a closed-face cassette sampler or a thoracic sampler. The samples are desiccated prior to gravimetric analysis, then weighed and the total weight (W_T) of each sample is recorded. The filter is then placed in a specialized extraction funnel and extracted with a ternary blend of 1:1:1 methylene chloride, methanol, and toluene[5,6] to separate MWF from commingled solid particulate. The filter is then reweighed and the MWF is reported as the extractable weight (W_E) of the samples. For each sample, the fraction extracted ($FE = W_E/W_T$) is generally also recorded.

The ASTM method was employed in a survey of 79 machining or metalworking operations across the United States.[7] Of the 155 individual MWF encountered in this survey, 154 were soluble in the ternary blend. The lone insoluble fluid was a synthetic fluid that was successfully extracted with a 1:1 blend of methanol and water. An evaluation of the ASTM procedure used in that survey was recently published[8] and is summarized as follows:

- There were problems with high filter blank levels, which resulted in relatively high limits of quantitation (LOQs) of approximately 0.1 mg per sample for both the total

weight measurements and the extracted weight measurements. The upper 95th percentile of both was also about 0.3 mg per sample.

- Quality assurance (QA) samples were prepared by spiking known quantities of each of the four types of MWF at each of four levels onto the PTFE filters; the sample filters were purged with pure air for 8 hours to simulate a real sampling situation. The quality assurance samples were submitted to the contractor performing the analysis. A parallel set of QA samples was also prepared and weighed in-house over a period of 30 days. The in-house QA samples lost weight during storage according to the simple linear relationship

$$FR = At + B \qquad [1]$$

where FR is the fraction recovered relative to the original amount spiked, t is the time in days, and A and B are constants. The decreases in weight were especially significant for the synthetic and semi-synthetic fluids (up to 25%); this may be related to the removal of water from those samples during storage or desiccation. For each fluid, for each level spiked, the amounts reported by the contractor for storage times (t) were compared to those expected from the in-house equations, solved for the times, t that the QA samples were actually stored by the contractor. The contractor's results were, on average, 101 percent, 103 percent, 104 percent, and 116 percent of what were expected for the straight, soluble, semi-synthetic and synthetic samples, respectively. Fractions extracted for the QA samples were ≥ 0.90, indicating quantitative extraction of all of these samples.

- For all samples for all fluids, the fractions extracted increased with sample weight but generally decreased in the order straight > soluble ~ semi-synthetic > synthetic. To determine if interactions between operations and fluid type affected the fractions extracted, samples were grouped according to the four fluid types and the three major operations encountered—grinding, milling, and turning. A statistical analysis using a maximum likelihood technique was employed to determine the significance of differences in the fractions extracted by operation and fluid type. Statistically significantly lower fractions extracted (FE) were observed for synthetic fluids relative to straight fluids for grinding operations only. This may be related to many factors. The weights of the straight grinding fluid samples were higher than those of the synthetic grinding fluid samples. If there is a constant background of insoluble particulate in the atmospheres being sampled, straight fluids might, on average, be expected to exhibit higher fractions extracted relative to the synthetic fluids. It is also possible that there were small amounts of unextracted, water-soluble components in synthetic fluid samples.

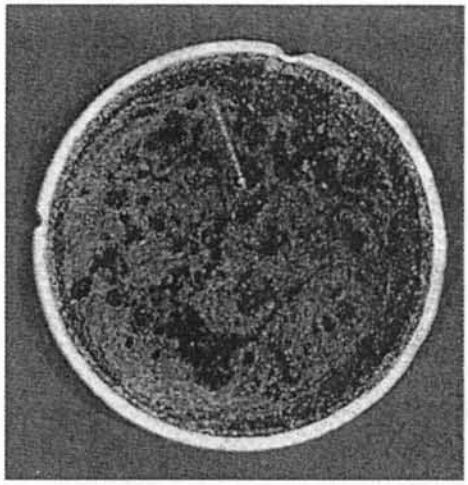

FIGURE 1
A 6.4-mg/m^3 thoracic exposure sample from a welder. Sample contained 16% MWF (i.e., $W_E = 1.0$ mg/m^3).

NIOSH has recently released Method 5524,[9] which incorporates the ternary blend as well as a 1:1 binary blend of methanol and water to facilitate the removal of any water-soluble components as well as the single MWF found to be insoluble in the ternary blend. To minimize sample loss during storage, the NIOSH method also imposes rather strict storage requirements. A major advantage of using an extraction technique is illustrated in Figure 1, which is an extracted thoracic breathing zone sample taken from a welder who was working near a metalworking operation that used semi-synthetic fluids. Approximately 6.4 mg of aerosol was collected, consisting of 84 percent solid particulate and 16 percent extractable MWF. Since the major industrial hygiene concern here was with the welding fume, such samples would generally be analyzed gravimetrically or for the presence of metals only. Without an extraction procedure, it would not have been known that the worker had been overexposed to welding fume (NIOSH REL = 5 mg/m^3) and to MWF at 2.5 times the NIOSH recommended exposure limit concentration.

The process by which such samples become loaded with MWF is of interest. For this welding sample, there may be three major sources of the extractable materials. The most obvious is the MWF aerosol from the nearby machining operation. Secondly, there may be MWF or other metal treatments, for example, preservatives on the metal in the vicinity of the weld that were volatilized and/or aerosolized by the high temperatures of the welding process. Finally, and perhaps most intriguing, is the possibility that the welding aerosol particles act as nuclei for the condensation of MWF *vapors* that are present in the shop environment. For the simple system—triethanolamine in water—a surface tension-based model has indicated that as much as 9 percent of the mass of a welding fume sample may originate from vapor-phase condensation on the fume. While additional research is needed to confirm these estimates, the significance of such a model and these findings cannot be overlooked,

for they suggest a novel inhalation mechanism—MWF-coated metal welding particles. Without an extraction-based analytical method, it would not have been possible to readily investigate this phenomenon.

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DISCLAIMER

Mention of products or services in this manuscript does not constitute endorsement by NIOSH.

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