TECHNICAL NOTE

Robert A. Glaser[1]

Data Supporting a Provisional American Society for Testing and Materials (ASTM) Method for Metalworking Fluids, Part I: A Solvent Blend with Wide-Ranging Ability to Dissolve Metalworking Fluids

REFERENCE: Glaser, R. A., **"Data Supporting a Provisional American Society for Testing and Materials (ASTM) Method for Metalworking Fluids, Part I: A Solvent Blend with Wide-Ranging Ability to Dissolve Metalworking Fluids,"** *Journal of Testing and Evaluation,* JTEVA, Vol. 27, No. 2, March 1999, pp. 171–174.

ABSTRACT: Data are presented to support modification to a provisional American Society for Testing and Materials (ASTM) sampling and analytical technique for metalworking fluids (ASTM P-42-97). The method, tentatively recommended by ASTM Subcommittee D-22.04, involves collection of the aerosolized fluid on a filter and separation of the fluid from co-sampled particulate matter via solvent extraction of that fluid from the filter. The solubilities of nine metalworking fluids were tested in seven solvents: acetone, dichloromethane, ethyl acetate, isopropanol, methanol, toluene, water, and three solvent blends: dichloromethane:methanol, dichloromethane:methanol:toluene, and dichloromethane:methanol:hexane. A ternary blend of dichloromethane:methanol:toluene (1:1:1) was found to dissolve samples of the four classes of metalworking fluids within about 1 min.

KEYWORDS: metalworking fluids, ASTM analytical method, ternary solvent, solubility studies

Metalworking fluids (MWF) find widespread use throughout the metalworking industry. The Independent Lubricant Manufacturers Association (ILMA) estimated that 96 million gallons of these fluids were produced in 1995 [*1*]. There are four classes of metalworking fluid: insoluble (or straight), soluble, synthetic, and semisynthetic. These materials have a wide range of components generally classified along the following lines [*2*]:

1. *Straight*—nonwater soluble, containing 60 to 100% hydrocarbon mineral oil (petroleum distillates) or other oils.
2. *Soluble*—water soluble or miscible, containing large percentages (e.g., 30 to 85%) of hydrocarbon mineral oil, surfactants, and other additives.
3. *Semisynthetic*—water soluble, containing low percentages (e.g., 5 to 30%) of hydrocarbon mineral oil, water, and higher proportions of emulsifiers than the soluble oils.
4. *Synthetic*—water soluble containing no mineral oil, rather containing small amounts of surfactants and emulsifying agents, inorganic additives, and water.

The National Institute for Occupational Safety and Health (NIOSH) estimates that 1.2 million workers are exposed to these fluids in the United States; some data support an increased risk of cancer in workers exposed primarily to straight fluids [*2*]. An acute cross-shift drop in forced expiratory volume (FEV1) has been associated with exposure to all types of these fluids [*3*]. For these reasons, NIOSH has proposed lowering the recommended exposure limit (REL) for MWF from the current standard of 5.0 mg/m^3, measured as total particulate, to 0.4 mg/m^3 measured as thoracic particulate (corresponding to 0.5 mg/m^3 total particulate) [*2*].

It is important that adequate sampling and analytical methodology be available to support the proposed REL and anticipated increase in epidemiological monitoring. Many analyses for metalworking fluids rely on a gravimetric procedure for total weight similar to that outlined in NIOSH method 0500 for total particulate [*4*]. A serious problem with sampling total particulate as an indicator of exposure to MWF is that nuisance dust may be collected as well. Ambient particulate levels approaching 0.1 mg/m^3 have been reported in urban areas [*5*]. In addition, the concentrations of in-plant nuisance dust or particulate levels may be elevated in areas undergoing construction or during certain manufacturing operations, e.g., grinding. Particulate material generated at harvest time in certain agricultural areas may also present a problem. Infrared techniques, e.g., NIOSH Method 5026 [*6*], may circumvent these interference problems; however,

Manuscript received 5/15/98; manuscript accepted 12/16/98.
[1]National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226.

this technique is limited to fluids that are soluble in Freon or carbon tetrachloride and have a pronounced absorption at the C-H stretching frequency of 2940 cm^{-1}, i.e., primarily to straight oils.

One of the automotive manufacturers circumvents the nuisance dust problem by extracting the sample filter with trichlororethylene [*7*]; however, this solvent is primarily useful only for extraction of straight oils.

In August of 1996, at a meeting of the American Automobile Manufacturers Association (AAMA), NIOSH researchers and representatives of industry and labor participated under the auspices of ASTM subcommittee D-22.04 in an effort to propose a method for MWF. It was proposed that the sample be collected on tared Teflon® membrane filters. Those filters were to be weighed following sampling, then placed in a filtration funnel and extracted with organic solvents and reweighed. The weight of MWF would be the difference in the pre- and post-extraction weight of the filter. The procedure called for the extraction of the filter initially with two 5-mL washes of dichloromethane to remove primarily straight and soluble oils, then with two 5-mL washes of isopropanol for the remaining fluids, followed by a final wash with dichloromethane to "flash-remove" the isopropanol from the filter. A contact time of 15 to 20 s for the solvent with the filters was proposed. The technique was adapted from the auto industry approach described above [*7*].

In this paper, the author documents problems with the solvents initially recommended for extraction of MWF from the filter. The results of testing the solubility of a cross section of MWF in a variety of other solvents and solvent blends are presented. A solvent blend that dissolved samples of all four classes of metalworking fluids is proposed as the extraction solvent. An estimate of the required contact time of the solvent with the individual MWF is also provided.

Experimental

Solvents and Standards: Dichloromethane, methanol, and toluene were distilled-in-glass grade and obtained from Burdick and Jackson Co. (Muskegon, MI). All solvent blends were prepared by mixing equal volumes of the individual solvents. Nine samples of metalworking fluids were used as obtained from Cincinnati Milacron (Cincinnati, OH) and Castrol Industrial Lubricants (Downers Grove, IL). These fluids and their components are listed in Table 1.

TABLE 1—*Metalworking fluids evaluated in these studies.*

Fluid	Type	Listed Components
1-STR	Straight	Mineral oil
2-SOL	Soluble	*o*-Phenylphenol
		Mineral oil
		Triethanolamine
		Nonylphenoxy-polyethoxyethanol
3-SS	Semisynthetic	Ethanolamine
		Mineral oil
		Monoisopropanolamine
4-SYN	Synthetic	Ethanolamine
		Neodecanoic acid
		Pelargonic acid
		Triethanolamine
5-SYN	Synthetic	Triethanolamine
		Boric acid
6-SYN	Synthetic	Triethanolamine
		Boric acid
7-SYN	Synthetic	Triethanolamine
		Boric acid
8-SS	Semisynthetic	Petroleum distillates
		Triethanolamine
9-SS	Semisynthetic	Triethanolamine
		Petroleum distillates
		(light and heavy naphthenic)

Solubility Testing

The solubilities of each of the nine test fluids in each of the solvents tested were estimated as follows: A 500-μL aliquot of each MWF was separately placed in a 20-mL scintillation vial; a 10-mL aliquot of the test solvent or solvent blend was then added to the vial. The vial was initially not shaken. The solubility was determined visually by observation of the disappearance of solute streamlines in the solvent or solvent blend. The clarity or turbidity of the resulting solution or the presence of precipitates was also noted. As necessary, the vial was shaken to finally ensure that the fluids had completely dissolved in the solvent.

Results and Discussion

Solubility Screening Experiments

The nine fluids evaluated in this study are listed in Table 1, the components of each fluid are also presented in this table. Of the nine samples, one was a straight fluid, one a soluble fluid, four were synthetic fluids, and three were semisynthetic fluids. The results of the solubility tests for each fluid for each solvent or solvent blend are tabulated in Table 2. Note that there are a number of solvents that alone could be used for extraction of the straight fluid, e.g., toluene or dichloromethane or possibly ethyl acetate or isopropanol. However, no single solvent dissolved the remaining fluid classes. Only a 1:1 blend of dichloromethane:methanol would dissolve all other classes of MWFs tested. The only solvent or solvent blend that dissolves all four categories of the MWF concentrate is the ternary blend of dichloromethane:methanol:toluene. Sample 9-SS did produce a light precipitate on standing in the ternary blend; however, when the MWF fluid volume was reduced to 50 μL, this sample completely dissolved in the solvent blend. Since a 50-μL aliquot should contain many times the mass estimated to be collected at the REL, these experiments indicate a sufficient margin of error.

The solvents chosen for the ternary blend were selected on the basis of their expected ability to dissolve the individual components of the metalworking fluids. Nonpolar hydrocarbon components of the fluids (e.g., petroleum distillates) dissolve in dichloromethane and/or toluene. Methanol facilitates the solution of hydroxyl-containing compounds such as aminoethanols and amines themselves. However, it is evident that there are synergistic effects among the solvents. For example, methanol alone dissolved four of the nine fluids tested; dichloromethane dissolved only one of the nine test fluids. However, a 1:1 blend of these solvents dissolved eight of the nine fluids tested; the addition of an equal volume of toluene to that blend produced a solvent blend that dissolved all samples of metalworking fluids tested.

A blend of solvents with wide-ranging capability to extract MWF has several advantages:

1. There should be no need for the laboratory to perform sequential extractions with multiple solvents as was initially proposed

TABLE 2—*Solubility of nine metal working fluids in seven solvents and three solvent blends.*

Solvent	Metal Working Fluid								
	1-STR	2-SOL	3-SS	4-SYN	5-SYN	6-SYN	7-SYN	8-SS	9-SS
Toluene (TOL)	clear	sl cloudy	vv cloudy/phase sep + ppt	clear/globule ppt	clear/phase sep	clear/globule ppt	clear/ globule ppt	cloudy/med ppt std	v cloudy/med ppt std
Dichloromethane (DCM)	clear	sl cloudy	v cloudy/phase sep	v cloudy/phase sep	clear/phase sep	clear/phase sep	clear/phase sep	milky cloudy/ phase sep	v cloudy on std
Acetone	clear + oily ppt	clear/ppt std	phase sep/cloudy	cloudy	heavy ppt	v heavy ppt	cloudy/ppt	clear/lt ppt	clear/med ppt
Ethyl acetate	clear	clear/ppt std	clear + oily ppt	clear + oily ppt	clear + oily ppt	clear + oily ppt	clear + oily ppt	clear + oily ppt	clear + oily ppt
Isopropanol (IPA)	clear	clear	cloudy	v cloudy	cloudy/med ppt std	cloudy/med ppt std	v cloudy/med ppt std	clear	sl cloudy/lt ppt std
Methanol (MEOH)	vv cloudy/phase sep + ppt	vv cloudy/phase sep + ppt	vv cloudy	clear	clear	clear	clear	clear+ globule ppt	sl cloudy/ globule ppt
Water	phase sep	milky-cloudy/ but soluble	clear	clear	clear	clear	clear	sl cloudy	sl cloudy
MEOH:DCM(1/1)	phase sep	clear	clear	clear	clear	clear	clear	clear	clear/lt ppt std
IPA/DCM (1/1)	clear	clear	v cloudy	v cloudy	clear/globule ppt	cloudy	cloudy/ppt	clear	clear/globule ppt
Hexane/MEOH/DCM (1/1/1)	clear	clear	phase sep	clear	phase sep	phase sep	clear	clear	clear/lt ppt
TOL/MEOH/DCM (1/1/1)	clear	clear	clear	clear	clear	clear	clear	clear	sl cloudy/lt ppt std*

NOTE: ppt = precipitate; std = upon standing; lt = light; med = medium; hvy = heavy; sep = separation; sl = slightly; v = very.
* Sample was completely soluble (clear solution) for 50 μL dissolved in this solvent blend.

in the provisional ASTM method. Since this single blend has the apparent advantage of dissolving all four classes of MWF, it avoids problems with multiple extraction solvents, solvent extraction order, etc.

2. Analytical extraction efficiency should improve when sampling worker exposures from multiple machining operations. If two MWF are commingled on a filter, the use of a multiple stage solvent extraction regimen may be relatively inefficient, since it may be difficult to expose each fluid to a solvent which dissolves that fluid. For example, a straight oil could be sampled early on in the shift, followed by a synthetic oil later in the shift. If the straight oil is sufficiently covered by the synthetic fluid, that straight oil may be inefficiently extracted from the filter if the extraction solvent sequence is designed to first remove the straight oil. This situation may be even more problematical if the fluids are commingled with particulate.

The weights of MWF evaluated here are many times greater than the weights of MWF expected to be collected at the proposed REL. Since rates of solution of all MWF are unknown, a second extraction with a 10-mL aliquot of the ternary blend was proposed for incorporation into the provisional ASTM extraction procedure to remove any residual MWF from the filter (and also to clean the filtration apparatus). It is important to note that the "universality" of the solvent blend remains to be demonstrated with other MWF fluids. The ternary blend has been tentatively accepted by ASTM Subcommittee E34.50 into the provisional method for metalworking fluids. An evaluation of the provisional method employing this ternary blend to measure four of the test fluids is presented in the accompanying paper in this journal. The provisional method has been incorporated into the analytical methodology for analysis of filter samples generated from an extensive NIOSH survey of concentrations of metalworking fluids in various machining operations across the United States.

Conclusions

A solvent blend with the ability to dissolve a wide range of metalworking fluids is proposed as the extraction solvent in a provisional ASTM method for metalworking fluids. The blend consists of equal volumes of dichloromethane:methanol:toluene. Visual observations indicated that this ternary solvent blend dissolved nine different samples of MWF within 1 min.

Acknowledgments

The author wishes to thank William Lucke and John Howell for supplying the samples of metalworking fluids for this study.

Disclaimer

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

References

[*1*] "Report on the Volume of Lubricants Manufactured in the United States and Canada by Independent Lubricant Manufacturers in 1995," Independent Lubricant Manufacturers Association, Washington, DC, May 1996.

[2] NIOSH Criteria for a Recommended Standard: "Occupational Exposure to Metalworking Fluids," U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH, DHHS (NIOSH) Publication No. 98-10, 1998.

[3] Robins, T. G., Seixas, N. S., Burge, H., and Abrams, L., "Association of Cross-Shift Decrements in Pulmonary Function with Machining Fluid Exposure," *American Journal of Respiratory Critical Care Medicine,* Vol. 151, No. 4, Pt. 2, 1995, p. A 420.

[4] NIOSH, "Method 0500 for Nuisance Dusts," in *NIOSH Manual of Analytical Methods,* 4th ed., P. M. Eller, Ed., U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH, DHHS (NIOSH) Publication No. 94-113, 1994.

[5] National Air Quality and Emissions Trends Report 198, U.S. Environmental Protection Agency, Office of Air Quality, Planning and Standards Technical Support Division, Research Triangle Park, NC, EPA-450-91-0, 1993.

[6] "Method 5026 for Mineral Oils," *NIOSH Manual of Analytical Methods,* 4th ed., P. M. Eller, Ed., U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH, DHHS (NIOSH) Publication No. 94-113, 1994.

[7] "Sampling and Analytical Method for Metalworking Fluids," Method No. FIH-005, Ford Motor Company, Detroit, MI, 1995.