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*Data Supporting a Provisional American Society for Testing and Materials (ASTM) Method for Metalworking Fluids, Part 2: Preliminary Report of Evaluation of a Ternary Solvent Blend in a Provisional ASTM Method for Metalworking Fluids (P-42-97)

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ABSTRACT: Samples of straight, soluble, semi-synthetic, and synthetic metalworking fluids (MWF) were spiked onto polytetrafluoroethylene (PTFE) membrane filters, stored overnight, and analyzed using a provisional American Society for Testing and Materials (ASTM) method for metalworking fluids. That technique involves collection of aerosolized fluid on PTFE membrane filters and separation of the fluid from co-sampled particulate matter via extraction of the filter with a blend of dichloromethane: methanol:toluene. The extraction of all fluids from the filters was quantitative over the range 200 to 815 μg for the straight fluid, from 223 to 878 μg for the soluble fluid, from 51 to 189 μg for the semisynthetic fluid, and from 102 to 420 μg for the synthetic fluid. For those weights of all four fluids spiked at levels ≥200 μg, the precision (%relative standard deviation or %RSD) was estimated to be 4% for the total weight procedure and 5% for the extraction procedure. Limits of quantitation, estimated from blanks carried through the entire analytical procedure, were 30 μg for the weighing technique and 60 μg for the extraction technique.

KEYWORDS: metalworking fluids, analytical method, spiking study, limits of detection and quantitation

The National Institute for Occupational Safety and Health (NIOSH) has proposed lowering the recommended exposure level (REL) for metalworking fluids (MWF) from 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); the thoracic standard is conditioned on the availability of an adequate thoracic sampler [*1*]. A provisional method for sampling and analysis of metalworking fluids, developed under the jurisdiction of Subcommittee D-22.04 of the American Society for Testing and Materials (ASTM) [*2*], is being evaluated by NIOSH researchers to support the reduced REL. That procedure involves collection of the sample on a tared Teflon (PTFE) filter, determination of the total weight of collected particulate, separation of the MWF from co-sampled particulate via solvent extraction, and a final determination of the filter's weight. The weight of MWF is estimated from the weight loss of the filter following extraction. Evaluation of a ternary solvent for extraction of the MWF is described in a companion paper in this journal [*3*]. In this paper, we present the results of a preliminary study that incorporated the ternary solvent into an analytical regimen for evaluation of the provisional ASTM method. Samples of four metalworking fluids were spiked onto PTFE membrane filters, stored overnight, and analyzed according to a protocol, which is presented below (under **Experimental**). Estimates of the method precision for each fluid are made along with estimates of the limits of detection and quantitation for each fluid. Improvements are recommended for inclusion into the provisional ASTM method for metalworking fluids.

Experimental

Solvents and Standards—Dichloromethane, methanol, and toluene (analytical grade) were obtained from Burdick and Jackson Co. (Muskegon, MI); the purity of these solvents was specified to be ≤1 ppm residue upon evaporation. Samples of metalworking fluids, obtained from a major manufacturer of metalworking fluids, were evaluated in this study: straight oil—1-STR; soluble oil—2-SOL; semisynthetic—3-SS; and synthetic—4-SYN.

Apparatus

Filters and Filter Funnels—The proposed ASTM method calls for analysis of samples collected on 37-mm filters. At the time of this study, there were no commercially available filter funnels for extraction of 37-mm filters; consequently, it was necessary to employ 47-mm filters and filter funnels for this purpose. Samples were spiked onto 2-μm, 47-mm PTFE membrane filters (Zefluor®, Gelman Sciences, Ann Arbor, MI). Samples were extracted from

* Part 1 follows this paper in the Technical Note Section.

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the filters and placed in 47-mm glass filter holders (Kontes Ultraware, Vineland NJ).

Balance—All weights were determined to six decimal places using a Mettler MT-5 microbalance (Mettler-Toledo, Hightstown, NJ). Prior to each weighing, any static charge that had developed on the filters was dissipated using a ^{210}Po static strip.

Sample Spiking and Analysis Protocol

1. A solution of dichloromethane and methanol and toluene was prepared by blending equal volumes of each solvent together in a clean, dust-free container, which was sealed with a glass stopper.
2. Stock solutions of each fluid in the ternary solvent were prepared by metering 500 μL of each MWF into a 10-mL volumetric flask, using a gas-tight syringe equipped with a Teflon-sealed plunger and large bore (12 to 16 gauge) needle. The samples were diluted to the mark with the ternary solvent.
3. For each fluid, eighteen 47-mm PTFE filters were weighed and separated into three sets of six (one set for each of three sets of spikes).
4. For each fluid type, six of the pre-weighed filters were spiked at each of three levels (18 filters/fluid, total = 72 samples) by metering 5-, 10-, or 20-μg of each fluid onto the filters (one spike/filter). The spikes were placed as close to the center of the sampling surface of each filter as possible.
5. The spiked samples were stored on a metal screen in a dust-free environment to facilitate evaporation of the solvent. The solvent was allowed to evaporate for at least 1 h.
6. After the initial storage for 1 h, the samples were stored in a chemical desiccator over $CaSO_4$ overnight. Following overnight storage in the desiccator, these filters were conditioned in the weighing room and their weights determined. The difference between these weights and the filter tare weight (Step 3) is referred to as the "total weight."
7. The filters were then loaded into the filtration funnel. The MWF spikes were then extracted from each filter with two 10-mL aliquots of the ternary solvent. The solvent was poured along the inside of the filter funnel to avoid splashing the solvent directly against the sample. The first aliquot was passed through under no vacuum (approximately 1 min) in order to allow the MWF to dissolve; remaining solvent was then extracted under slight vacuum. A second 10-mL aliquot of the ternary solvent was then passed through the filter under slight vacuum to remove the remaining sample.
8. The filters were then removed from the extraction funnel and the solvent allowed to evaporate for at least 1 h at ambient conditions. The samples were then equilibrated in the weighing room for at least 2 h prior for determination of their weights. The differences between this weight and the weight of the spiked filters (Step 6) is called the "extractables weight."
9. *Blanks*—In these experiments, extraction of four fluids over

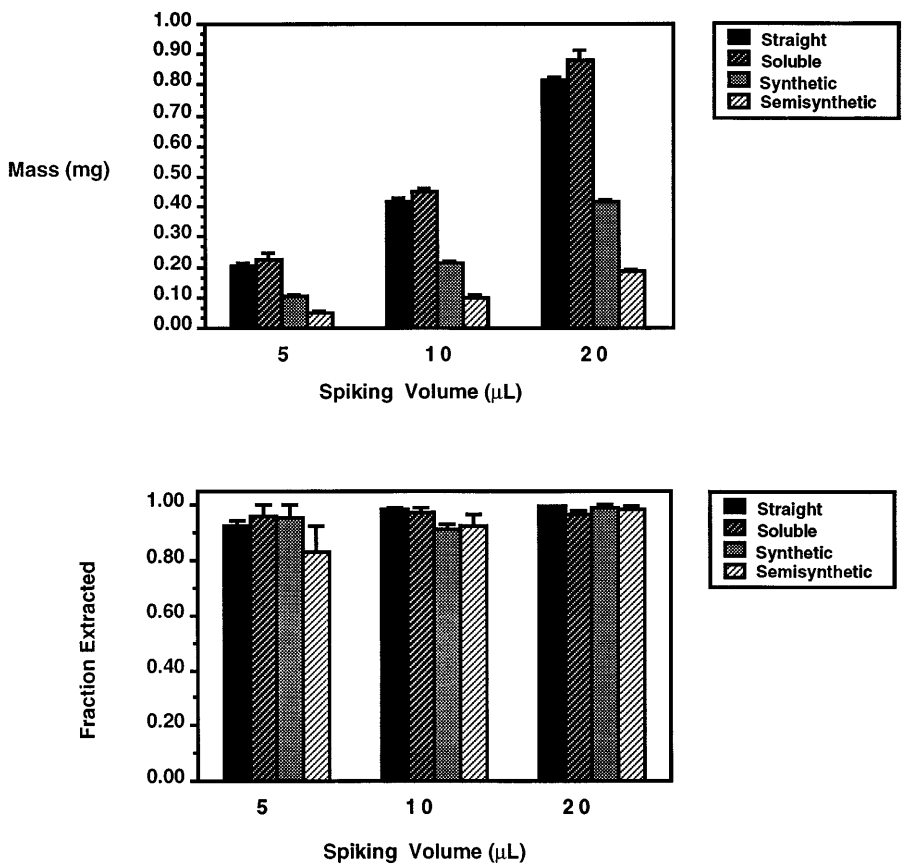

FIG. 1—(a) *Mean total weights (mg) of four metal-working fluids spiked onto Zefluor filters in 5-, 10-, or 20-μL aliquots, error bar = plus one standard deviation (+1 SD);* (b) *mean fraction(s) extracted (+1 SD) of the four metalworking fluids spiked on Zefluor filters at the weights indicated in (a)—all samples were extracted with ternary solvent;* (c) *relative standard deviations (RSDs) with which the total weights of MWF could be determined—spiking imprecision has been removed from these estimates (see Note 1);* (d) *RSDs of the fraction extracted data presented in (b)—spiking imprecision has been removed from these estimates (see Note 1).*

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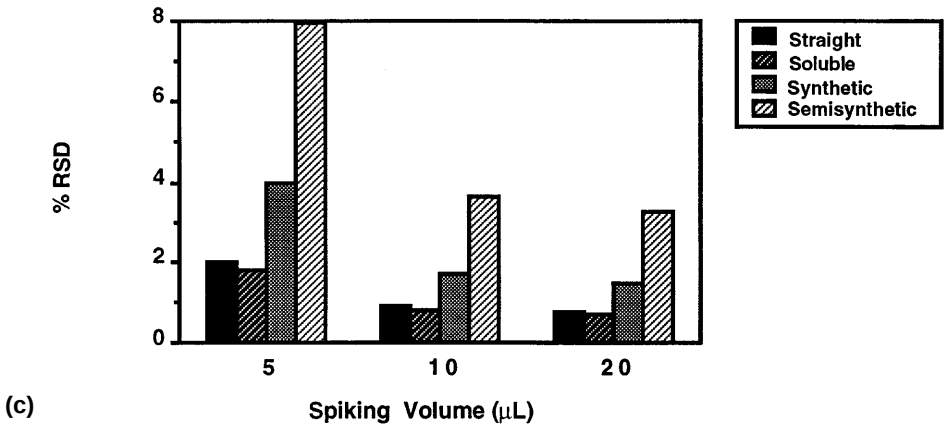
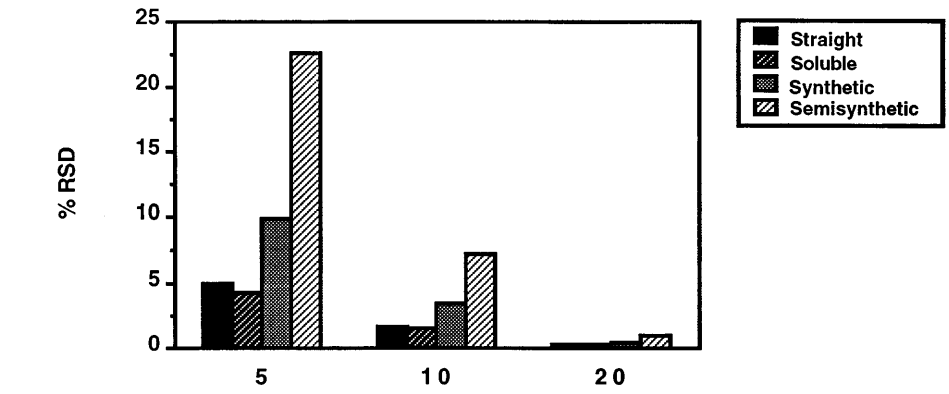


(c)



(d)

FIG. 1—*Continued.*

three levels was evaluated. This 4 by 3 matrix, therefore, contained twelve sample sets, with each set containing six replicate samples. A blank was analyzed with each six-sample set (twelve blanks total). Each blank was spiked with a volume of the ternary solvent equal to the volume of MWF solution used for spiking the sample filters in that blank's corresponding set, i.e., 5- or 10- or 20-μL. These solvent-spiked blank samples were placed on the metal screen and the solvent was permitted to evaporate for at least 1 h. After drying over $CaSO_4$ for 16 h, these blank filters were conditioned for 2 h in the weighing room and then weighed. The blank filters were then extracted with the ternary solvent following the same procedure used for the samples, dried for 1 h, then equilibrated and weighed. In this way, separate blanks for "total weight" and for "extractable weight" were obtained for each block. The weights obtained for the spiked samples in each block were corrected for the total weight blank values; the corresponding post-extraction weights of these samples were corrected for the "extraction weight blank values."

Results and Discussion

Sample Loading, Recovery, and Precision

Figures 1*a-d* summarize the results of the spiking and extraction tests for the four MWF evaluated. The average weight loading of each fluid on the filters for each of the three spiking levels is shown in Fig. 1*a*. While the loading weights were targeted to range from 250 to 1000 μg, or approximately 0.5 to 2.0 times the weight anticipated to be collected at the proposed REL for total particulate, these levels were only approached for the straight and the soluble oils. The much lower loadings obtained for synthetic and semisynthetic fluids were apparently due to the relatively large amount of water in these samples. The spiking solutions were made by dissolving 500 μg of each fluid in the ternary solvent. The straight and soluble fluids contained little if any water. Thus, delivery of the target loadings was straightforward for these fluids. The synthetic and semisynthetic fluids contained relatively high proportions of water. Since the entire 500-μg aliquot was soluble in the ternary solvent, that water was also spiked on the filters. The water component of these fluids evaporated during the storage/desiccation stage of sample workup.

The error bars in Fig. 1*a* (one standard deviation of the mean weight) indicate the total precision with which those weights were spiked. The average relative standard deviations are 17% (5-μL spike), 7% (10-μL spike), and 6% (20-μL spike); these estimates include spiking error as well as weighing error. We have estimated the relative standard deviation of the spiking error to be 16% (5-μL spike), 6% (10-μL spike), and 6% (20-μL spike). As Note 1 illustrates, the major source of error in these analyses was the spiking error rather than analytical (weighing) error.

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NOTE 1. In order to estimate the spiking precision, it was assumed that the variance of total weight was composed of weighing error and spiking error. The weighing error variance is estimated from the variability of the four blank samples (1 per fluid) at each loading. The variability due to spiking was computed by subtracting the estimated weighing variance from the total variance associated with measurement of the weights of the six samples of each metalworking fluid type. For example, the standard deviation of the four blank samples at the lowest loading was 2.9 μg (variance = 2.9^2 = 8.3). The total variance for the six straight metalworking fluid samples at this loading was 378. Thus, the variance associated with spiking was (378 − 8.3) = 370, and the spiking standard deviation = 19.2 μg. The mean weight recovered for this sample set was 206 μg, and the spiking relative standard deviation was 19.2/206 = 0.094; this compares with a total relative standard deviation of 0.095. Thus, the spiking variability accounts for virtually all of the sample variability. The same pooled estimate of the blank standard deviation (2.9) was used for estimating each of the spiking components of the total weight variability of each metalworking fluid at the lowest loading. Similar computations were made at the two higher levels using standard deviations ranging from 2.5 to 4.5 μg (total weight), and 1.2 to 6.8 μg (extractable weights). The results were averaged across all four fluids at each level to estimate the overall spiking error for that level.

Figure 1*b* shows that the fraction extracted exceeded 0.83 for all fluids and for each of the three spiking levels. The error bars given in the figure are within 1 standard deviation of the mean weight. Figure 1*b* shows a tendency towards better extraction efficiency at higher spiking levels. Note that the lowest recoveries were observed for the semi-synthetic fluid at the 5-μL spiking level, corresponding to a weight spiked of about 50 μg. These lower recoveries of the semi-synthetic spike may have been related to the low level of sample spiked onto the filter. In fact, for the semi-synthetic fluid, the average weight extracted at the 5-μL level was less than the estimated limit of quantitation for the extraction procedure of 58.5 μg (see below).

Figure 1*c* shows the precision (RSD or relative standard deviation) with which the total weight could be determined; Figure 1*d* shows the precision with which the extracted weight could be determined. Since the spiking error was so large, only the error associated with weighing was used in calculating the RSD (see Note 2). These plots demonstrate that the precision of both total and extractable weighings improves somewhat with increasing weight of fluid spiked on the filter. This effect is dependent on the weight spiked on the filter. For example, for the total weight of the semi-synthetic fluid, an RSD of 8% was observed for the 50-μg samples, whereas an RSD of 3.6% was observed for the 100-μg samples. Here the standard deviations of the blanks were comparable (2.87 μg versus 2.58 μg); however, the weight spiked increased by a factor of two. Thus, it is quite reasonable for the relative standard deviations to decrease with increasing weight spiked if the standard deviations of the blanks remain relatively constant.

NOTE 2: These RSDs were determined for each fluid at each level tested by dividing [(✓2)* standard deviation of the blank, total or extracted, at that level] by the matched blank-corrected mean weight (total or extracted) determined at that level. In the determination of a final weight for these samples, there are actually two pairs of weighings, one for determination of the filter's weight and another to determine the level of blank correction for that weight. Assuming that the precision of the weighing process is comparable for both sets of samples, the overall variance = σ^2 (total weight blank) + σ^2 (blank correction) = $2\sigma^2$ (i.e., twice the variance of the blank signal) and the standard deviation = (✓2)(σ). For instance, at the lowest spiking level, the standard deviation of the *four* blanks for determination of the total weight samples was 2.9 μg; the average value of the *six* determinations for the straight fluid was 206 μg. The *single* blank for that set was zero. Thus, the RSD = {(✓2)[2.9]/[206 − 0.00]} * 100, or 2.0%. This RSD is associated with a single determination as opposed to several determinations. The same numerator is used for all four total weight RSDs at this level. A similar approach was taken for both extractables and total weight RSDs at each level, although a different standard deviation was used for each level by extractables and each level by total weight combination.

The relative standard deviations presented in Figs. 1*c* and 1*d* are not homogeneous across the three levels for any of the fluids investigated. Therefore, these RSDs cannot be pooled to estimate overall method precision for each fluid. An estimate of the precision of the method can be obtained by considering those weights of fluid spiked greater than approximately 200 μg (0.5 times the thoracic REL). For samples exceeding this level, Figs. 1*c* and 1*d* indicate that the total and extracted weights could be determined with maximum estimated %RSDs of 4 and 5%, respectively.

Note that these are estimates only of analytical method precision and must be used very carefully. They do not include sampling imprecision resulting from variations in the sample pump flow, nor do they include variations in the analytical procedure, e.g., the possibility of a less precise extraction efficiency if the metalworking fluid is co-sampled with large amounts of particulate on the filter.

In these extractions, two 10-mL aliquots of the ternary solvent were used. The volume of each aliquot was kept relatively low in order to minimize the possibility of particulate material floating above the solvent and coating the inside surfaces of the filter funnel. Per the recommendations in Ref *3*, the contact time of the fluid with the solvent was established to be about 1 min per each 10-mL extraction. A second aliquot of solvent was used as a means of assuring complete extraction of the fluid from the sample.

Blanks

Figure 2*a* is a plot of the blank values (see Note 3) obtained for determination of total weight; the average weights of these blank filters increased from 3.8 to 9.8 μg as the solvent volume spiked increased from 5 to 20 μL. Overall, the blanks are not very large. Given the quality of the solvents used in these studies (≤1ppm or 1 μg/mL), the post-evaporation residues from 5 to 20 μL of solvent could not have accounted for the blank weights. Thus, the blanks are likely not due to contaminants dissolved in the microliter volumes of solvent used for the blank spiking experiments or to traces of particulate suspended in the solvent. Furthermore, it is unlikely that they are related to incomplete evaporation of the spiking sol-

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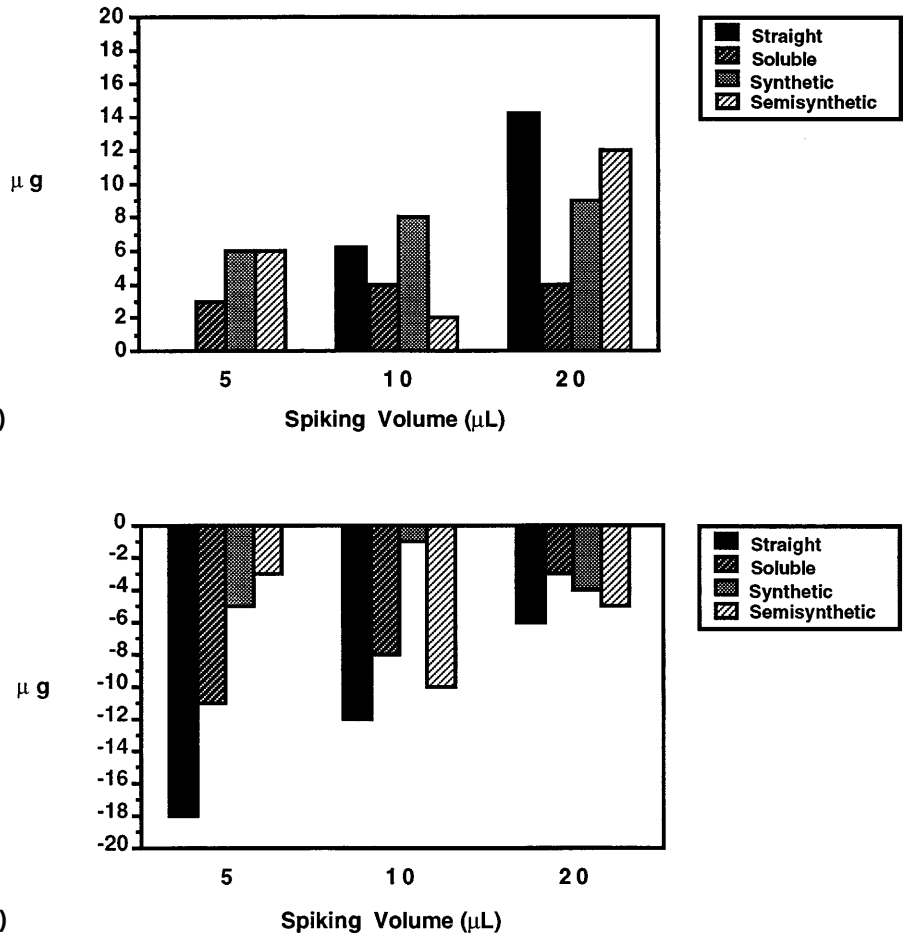

FIG. 2—(a) *Total blank correction values (μg) for twelve Zefluor blank filters spiked with 5, 10, or 20 μL of the ternary solvent after evaporation of the solvent;* (b) *extraction blank correction values (μg) of the same twelve ternary-solvent spiked blank Zefluor filters following extraction with two 10-mL aliquots of the ternary solvent, drying, dessication, and conditioning in the weighing room—the values are negative because the post-extraction weights were greater than the pre-extraction weights.*

vent because these blanks were carried through the same analytical finish as were the spiked samples (dried for 1.5 h, desiccated for 16 h, equilibrated for 2 h in weighing room); such prolonged storage should have permitted adequate time for the micro-liter volumes of spiking solvent to evaporate. The standard deviations of the determination of total weights were estimated to range from 2.5 to 4.5 μg (see Note 1); thus, weighing imprecision cannot entirely account for these blanks. Other than random variations in the weights of the blank filters themselves, the magnitude of these blanks cannot be readily explained.

NOTE 3. Although the MWF designations, e.g., "straight," were retained for the respective blocks of these blank filters, the solvent used to spike them contained no MWF; all seven filters from each block (6 samples + 1 blank) were analyzed on the same day.

Figure 2*b* is a plot of the weight changes in those same blank filters obtained after extraction. For these blanks, the post-extraction weights exceeded the pre-extraction weights. Since these blank weights were determined by subtracting the post-extraction weights of the filters from the pre-extraction filter weights, Fig. 2*b* shows all of these values as negative weights even though these filters actually gained weight after extraction. The average weight gain of the extracted filters decreased from a mean of 9.3 μg to a mean of 4.5 μg as the spiking volume increased from 5 to 20 μL. Here again, the standard deviations of the weighing procedure for extracted samples were estimated to range from 1.2 to 6.8 μg (see Note 1); thus, the variation in the balance used to obtain the weights cannot entirely account for these blanks. Incomplete evaporation of the extraction solvent may partly explain the blanks; however, it cannot account for the apparent negative correlation of volume spiked with blank level observed. Although the filters were treated with differing (micro-liter) amounts of the carrier solvent, they were later treated with much larger (milliliter) quantities of the extraction solvent. Incomplete evaporation of the final wash extraction solvent from the filters would have, perhaps, been expected to randomly affect the weights of the blank filters. Although the change in the weight decrease with increasing solvent volume spiked is not readily explained, the possibility of contributions from unevaporated solvent cannot be overlooked. Thus, it may be prudent to increase the filters' post-extraction drying time from 1.0 to 1.5 h.

The standard deviations obtained from the blank spiked data, shown in Fig. 2, were pooled together across the two lower spiking levels to estimate limits of detection (LOD) and quantitation

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(LOQ) for the total weight and for the extractables weight. Using techniques outlined in Ref *4*, the LOD and LOQ for the weighing procedure were computed to be 8.2 and 28 μg, respectively; the LOD and LOQ for the extractables weight were 18 and 59 μg, respectively. These estimates of the LOD and the LOQ likely understate the sampling and analytical method limits of detection and quantitation to be expected during an actual sampling situation. Much higher limits of detection for total weight (e.g., 33 μg) and quantitation (e.g., 130 μg) have been reported for unextracted Teflon membrane field blanks that have been sent to and returned from the field [*1*].

Further Method Evaluation

A NIOSH study of MWF mist levels in small to medium machine shops has been completed. This survey should provide the Occupational Safety and Health Administration (OSHA) with an estimate of MWF mist levels and the types of controls in place in these machine shops, an assessment of the feasibility of the proposed REL, and an opportunity to further refine or develop rules to minimize harmful health effects of metalworking fluids. The survey will also permit an assessment of the provisional ASTM analytical method's ability to handle actual field samples. Preliminary results from that study [*5*] have been presented; a more thorough analysis of the method will be provided in a future publication.

Conclusions

The extraction of four metalworking fluids spiked onto PTFE membrane filters was studied using a provisional ASTM method. The fluids were extracted from the filters using a ternary blend of solvents that has a wide-ranging ability to dissolve MWF. The amounts of each fluid spiked ranged from 200 to 900 μg for the straight and soluble fluids, from 50 to 200 μg for the semisynthetic fluid, and from 100 to 400 μg for the synthetic fluid. Despite the large variations in the amounts of each fluid spiked, the fraction extracted was ≥0.83 across all three levels studied for each fluid. Estimates of the analytical method precision were 4% for the total weight procedure and 5% for the extraction procedure if the weight of fluid spiked exceeded 200 μg. Limits of detection and quantitation were well below the amounts expected to be encountered at the proposed REL.

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Disclaimer

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

References

[*1*] 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. 98-102, 1998.

[*2*] Provisional Standard Test Method for Metal Removal Aerosol in Workplace Atmospheres (PS 42-97), American Society for Testing and Materials, West Conshohocken, PA, 1997.

[*3*] Glaser, R., Technical Note: "Data Supporting a Provisional American Society for Testing and Materials (ASTM) Method for Metalworking Fluids, Part 1: A Solvent with Wide-Ranging Ability to Dissolve Metalworking Fluids," American Society for Testing and Materials, *Journal of Testing and Evaluation*, this issue, pp. 171–174.

[*4*] Kennedy, E., Fischbach, T., Song, R., Eller, P., and Shulman S., 1995, NIOSH Technical Report: "Guidelines for Air Sampling and Analytical Method Development and Evaluation," DHHS(NIOSH) Publication No. 95-117, Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH, Standard Operating Procedures No. 018, p. 65.

[*5*] Piacetelli, G., Hughes, R., Catalano, J., Sieber, W., Glaser, R., and Kent M., "Exposures to Metalworking Fluids in Small Size Machine Shops," unpublished paper presented at the "The Industrial Metalworking Environment: Assessment and Control of Metal Removal Fluids" Symposium, Detroit, MI, September 1997.

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