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Data Supporting a Provisional ASTM Method for Metalworking Fluids* Part 3. Evaluation of an ASTM Method for Metalworking Fluids in a Survey of Metalworking Facilities

Testing+Evaluation

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ABSTRACT: An interim ASTM method for analysis of metalworking fluids was evaluated for estimation of personal exposure concentrations in a 79-plant survey of machine shops and metalworking facilities across the United States. Both thoracic and total particulate samples were collected on tared polytetrafluoroethylene filters. Metalworking fluid concentrations were estimated by determination of the total- and extractable-sample weights using ASTM Method PS-42-97. This procedure employs a ternary solvent blend of dichloromethane:methanol:toluene to separate the fluids from comingled insoluble particulate. Following the initial extraction, re-extraction of 322 samples with the ternary solvent removed, on average, <2.5% of the sample weight, indicating that the majority of extractable material had been removed during the first extraction. Evaluation of the field study blank data permitted estimation of the mean, median, and upper 95th percentile of the limits of quantitation to be 0.1 mg, 0.1 mg, and 0.3 mg, respectively, for both the total weight and the extractable weight samples.

For the 79-plant survey, the fractions extracted (weight extracted/weight of sample) were studied as a function of four metalworking fluid types and three main work operations—grinding, milling, and turning—according to a restricted maximum likelihood statistical procedure. This evaluation of the data indicated that the fractions extracted generally decreased in the order: straight > semisynthetic or soluble > synthetic; the differences in the fractions extracted for the straight and the synthetic fluids were statistically significant only for the grinding operation at two sample levels tested.

Studies of the stability of quality assurance (QA) samples spiked separately with a straight, a soluble, a semisynthetic, and a synthetic fluid indicated that the QA samples all lost weight according to simple linear decay equations. These decay equations were used to estimate the amounts expected to be reported for QA filters by the performing laboratory. For storage periods ranging from 18–26 days, the total weight of sample recovered for each QA sample was ≥80% of that expected from the decay equations. For these QA samples, the fractions extracted (extracted weight/total sample weight) from all four fluid types were ≥0.90.

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KEYWORDS: metalworking fluids, blanks, fraction extracted, recommended exposure level, quality control measures

Introduction

The National Institute for Occupational Safety and Health (NIOSH) recommends that "exposures to metalworking fluid aerosol (MWF) be limited to 0.4 mg/m^3, measured as thoracic particulate (or 0.5 mg/m^3 total particulate) as a time-weighted average (TWA) for up to 10 h/day during a 40 h workweek" [1]. To support this recommended exposure level (REL), a provisional method for sampling and analysis of MWF, promulgated by ASTM, has been evaluated by NIOSH researchers. That procedure involves collection of the sample on a tared polytetrafluoroethylene (PTFE) filter; determination of the weight of that filter; extraction of the MWF from the filter using a ternary solvent blend of dichloromethane: methanol:toluene; and reweighing the filter to obtain the weight of the unextracted material. The weight of MWF is the difference between the post sampling and post extraction weights of the filter. In previous papers in this journal, the development of the ternary solvent blend was described [2], and the initial evaluation of the interim ASTM method was discussed [3]. To assess the feasibility of the NIOSH REL, the Occupational Safety and Health Administration (OSHA) and NIOSH undertook a large survey of MWF concentrations in 79 small- to medium-sized plants across the United States. The results of this 79-plant survey have been reported elsewhere [4]. In this paper, we present an in-depth analysis of the analytical data collected in that survey, including an evaluation of extraction trends by fluid weight, type, and operation, and a presentation of the measures implemented to assure the quality of the sample analyses. Those quality assurance/quality control (QA/QC) measures included:

- Use of blank filters for correction of the weight data and computation of the limits of detection (*LOD*) and quantitation (*LOQ*)
- Determination of the solubility of each survey MWF in the ternary solvent; approximately 155 individual products were encountered in this survey
- Re-extraction of approximately 25% of the filters to assure that all of the MWF had been completely removed during the first extraction

- Submission of blind spikes containing known amounts of MWF to the laboratory performing the analysis
- Studies of the storage stability of spiked MWFs

The fractions extracted (extracted weight/sample weight) for each of the types of fluids and manufacturing operations surveyed are presented. The limits of detection and quantitation for both the total weight measurements and for the extractable weight measurements are determined. An in-depth statistical evaluation of the data was conducted to assess the effects of sample weight, fluid type, and operation on the fractions extracted of the various samples.

Experimental

Solvents and Standards

All solvents were analytical grade and obtained from Burdick and Jackson Co. (Muskegon, Mississippi). A solution of dichloromethane, methanol, and toluene was prepared by blending equal volumes of each solvent together in clean, dust-free, 1-gallon (4-L) glass solvent containers that were sealed with PTFE-lined caps.

Apparatus

Filters and filter funnels—Samples were collected with 2-μm, 37-mm PTFE membrane filters (Zefluor® Gelman Sciences, Ann Arbor, Michigan.) At the outset of this survey, there were no commercially available filter funnels for extraction of 37-mm filters; consequently, special stainless steel filter funnels were made for determining the extractable fraction of each sample. A commercial version of these funnels is now available from the SKC Corporation, Pittsburgh, Pennsylvania.

Samplers—The sampling units used to collect the thoracic and the total particulate samples have been described elsewhere [4].

Weight Determinations

All weights were determined to six decimal places using a Mettler MT-5 microbalance (Mettler-Toledo). Prior to each weighing, any static charges that had developed on the filters were dissipated using a ^{210}Po static strip. The samples were placed in a dessicator for 8 h prior to analysis. All samples were equilibrated to the conditions of the weighing room for a period of 1–2 h, prior to analysis. The mean weight of the field blanks at each site was subtracted from the weight of each sample at that site.

Solubility Testing

The solubility of each fluid in the extraction solvent was tested in the manner previously described [2] by metering 250 μL of the bulk fluid into 10 mL of the ternary blend. If the resulting solution was clear and free of precipitates or phase separation, the fluid was determined to be soluble in the ternary blend.

Extractions

All filter samples were weighed and extracted using the procedures outlined in Ref. 2. The filters were extracted twice with two 10 mL aliquots of the ternary blend. Following the second solvent wash of each filter, the inner walls of the filtration apparatus were washed with 2 mL of dichloromethane delivered from a PTFE squeeze bottle (VWR Scientific). This procedure was intended to flush any insoluble particulate material from the funnel's inner walls back onto the filter. For one synthetic fluid, Glacier (Solutia Inc., St. Louis, Missouri), which was not completely soluble in the ternary blend, a different extraction regimen was employed. This involved extraction using two 10 mL aliquots of the ternary blend, followed by a 10 mL aliquot of a binary blend—methanol:water (1:1)—and finally by a 2 mL rinse of methanol.

Quality Assurance Audit Samples

Quality assurance (QA) audit samples were prepared by spiking aliquots of four MWFs—a straight, a soluble, a semisynthetic, and a synthetic—onto tared 37-mm Zefluor filters. A stock solution of each fluid was prepared by diluting 500 μL of the fluid concentrate to 10 mL with the ternary solvent. The quality assurance samples were prepared by spiking 5, 15, 25, and 35 μL of the stock solutions onto preweighed 37-mm filters. These loadings nominally corresponded to levels ranging from 220 to 1900 μg/filter. The amount of each fluid metered onto the filters was estimated from the density of the fluid. Three replicate samples were prepared at each of the four test levels. The filters were allowed to dry on a screen in the balance room; an initial weight was recorded after 3–4 h storage. These samples were then loaded into cassettes, sealed with shrink bands, and stored overnight. The following day, the samples were purged with purified air for 8 h at nominal flow rates of about 2 L/min. The QA samples were then sealed and submitted as blind audit samples to the laboratory performing the analysis. Simultaneously, another set of samples was prepared by spiking filters with the same amounts of fluid; those samples were purged with purified air in an identical fashion as the audit samples and stored in cassettes at room temperature. The weights of these filters were also recorded post purge and at regular intervals over a 30-day period. There were three blanks per level investigated; the mean of the blanks for each level was subtracted from the weight of each sample at that level.

Results and Discussion

Distribution of Survey Fluids and Solubility Studies

Figure 1*a* is a pie chart showing the types of MWF encountered in the 79-plant survey. This distribution counts each of the 210 fluids encountered as a single fluid even though that same formulated product may have been encountered several times at multiple sites. In order to provide a more realistic estimate of the applicability of the extraction procedure, each unique fluid formulation was counted only once. Figure 1*b* is the pie chart for the resulting data set. Note that the number of fluids has been reduced from 210 to 155; the distribution of MWF has also changed. No accurate estimates of the total number of the four types of MWF currently used in the United States could be found.

Since the number of fluids evaluated in this survey was so large, it is impractical to list them in this manuscript. Therefore, the results of the solubility testing done using each of those fluids will be listed as an appendix to the MWF analytical method being issued by NIOSH (number 5524) at the NIOSH web site (www.cdc.gov/niosh/nmam/nmampub.html). These solubility data can be summarized as follows. Of the 155 individual fluids encountered in this survey, 99.4% (154 out of 155) were soluble in the ternary solvent, at approximately the 25 mg/mL level. This concentration far exceeds the levels expected in extraction of a full-shift, 1 m^3 field sample, at the REL (0.4–0.5 mg in 10–20 mL of solvent).

The only fluid that was insoluble in the ternary solvent was a synthetic fluid, Glacier, manufactured by Solutia Inc. (St. Louis, Missouri). However, this fluid was found to be completely soluble in a binary blend of methanol:water (1:1). The alternative extrac-

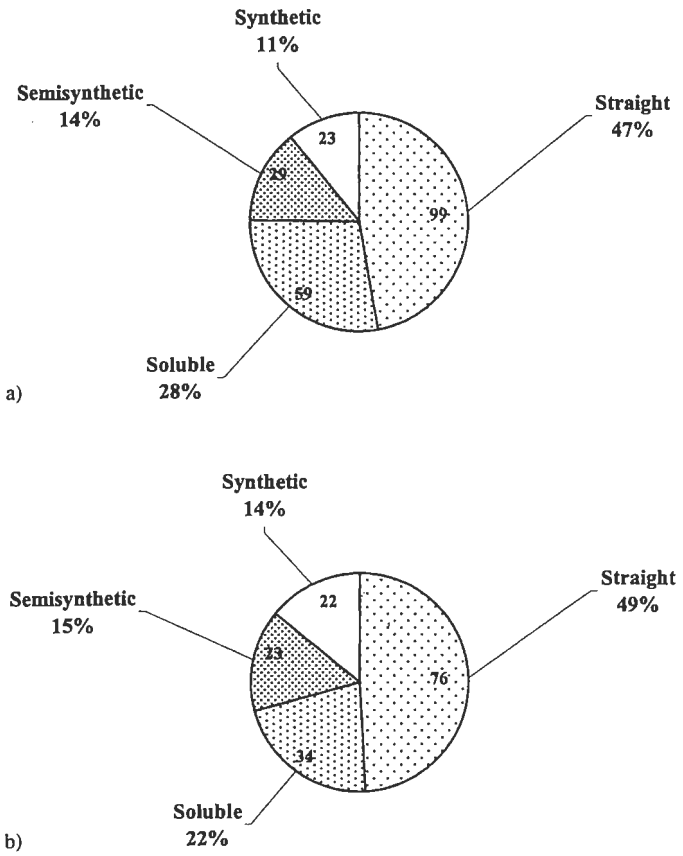


FIG. 1—*a) Top: Number and distribution of 210 MWFs encountered in the 79-plant survey by fluid type. b) Bottom: Number and distribution of surveyed MWFs with replicates removed (155 total) to indicate individual formulations encountered.*

tion procedure for Glacier, involving the ternary and the binary blends, is described in the Experimental section of this paper.

Blanks, Limits of Detection, and Quantitation

From three to five blank samples were submitted with the field samples for each site surveyed. These blanks were sent to the field, opened momentarily in a noncontaminated area, and returned to the laboratory with the field samples. The blank samples were carried through the same analytical procedures as the field samples, i.e., they were tared, weighed upon receipt at the lab, extracted, and reweighed.

Figure 2*a* shows the mean field blank weights for the total-weight samples for each of the 79 sites. While the 0.05 mg level was exceeded at one site, the absolute value of the blank sample means at most of the sites (77/79 or 97%) was 0.03 mg or less. These blank weights are mostly positive, indicating weight gain rather than loss during storage. The average blank weights ranged from −0.022 mg to nearly 0.060 mg and are within the range of those expected from previous studies [5]. The origin of these blank responses is not completely understood. They may be related to incomplete dissipation of the static charge during the weighing process. This can result in a gain or loss of weight (depending at what point in the analysis the spurious weight gains occurred). Gains or losses in weight also may relate to the relative state of hydration of the filter during storage. If the relative humidity of the weighing room changes from the initial to the final weighing process, so may the weight of the filters due to different levels of hydration.

Figure 2*b* shows the mean field blank weights for the extractable-weight samples for each of the 79 sites. Here, 76/79 or 96% of the mean field blanks had absolute values of 0.03 mg or less. In contrast to the total-weight blanks, the extractable-weight blanks are relatively symmetrically distributed on both sides of zero, indicating greater balance between weight gains and losses. In addition to the sources of blank responses discussed above, the extractable-weight blanks could be affected by incomplete evaporation of the solvent following the extraction. However, this should generally produce only positive blanks. It is unlikely that the extractable-weight blanks are due to either dissolved residue or undissolved particulate material (e.g., dust particles) in the extraction solvent. The manufacturer specified that the solvent(s) contained ≤ 1 μg/mL (1 ppm) residue upon evaporation to dryness. Thus, in the 20 mL of the solvent blend used in the extractions, no more than 0.02 mg of dissolved residue should have been present. Since no concentration of the extraction solvent occurred, dissolved residue could not have been a major source of the blank response. Any suspended particulate in the extraction solvent would be expected to affect all samples equally if that particulate were distributed uniformly throughout the solvent; however, randomly distributed particles suspended in the solvents could yield spurious (and presumably positive) blank weights.

The mean and median weights for the total-weight and extractable-weight blanks are given in Table 1. While there may have been more sources of contamination for extracted-weight blank measurements, the mean extracted-weight blank was actually lower than the comparable blank for the total-weight measurements (0.001 mg compared with 0.004 mg). The median blank weights for each were 0.002 mg.

The standard deviations of the blanks are shown in Fig. 3*a* for the total-weight samples and in Fig. 3*b* for the extractable-weight samples. The majority of standard deviations (84% total-weight samples and 92% extractable-weight samples) were ≤ 0.020 mg. No standard deviation of the total-weight blanks exceeded the 0.04 mg level. The standard deviations of the extractable-weight blanks equaled or exceeded the 0.04 mg level at three sites and the 0.05 mg level at two sites.

The standard deviations of the blanks were used to compute the limits of detection (*LOD*) and quantitation (*LOQ*) for the method at each sample site [6]. The *LOD*s were determined for each site using 3X the standard deviation of the blank weights; the *LOQ*s were determined for each site using 10X the standard deviation of the blank weights. The *LOQ*s for the total-weight samples are shown in Fig. 4*a*; the *LOQ*s for the extractable-weight samples are shown in Fig. 4*b*. Note that the total-weight *LOQ*s approached 0.4 mg (the amount expected in a 1000-L sample at the thoracic REL) at two sites. The extractable-weight *LOQ*s exceeded 0.5 mg (the amount expected in a 1000-L sample at the total particulate REL) for two sites and equaled or exceeded the expected thoracic REL sample mass of 0.4 mg at two sites.

The mean and median standard deviations are presented in Table 1 along with the mean and median *LOD*s and *LOQ*s and the upper 95% confidence limits of the *LOD*s and the *LOQ*s. The mean and median *LOQ*s were approximately 0.1 mg for both the total-weight estimation and the extraction technique. The computed 95% confidence intervals indicate that the upper boundaries on the *LOQ*s for both procedures are approximately 0.3 mg. Given the large size of these data sets, we can expect approximately 95% of the time that both quantitation limits will be lower than the masses expected in 1.0-m^3 samples of air at the RELs—0.40 mg (thoracic sample) or 0.50 mg (total particulate sample).

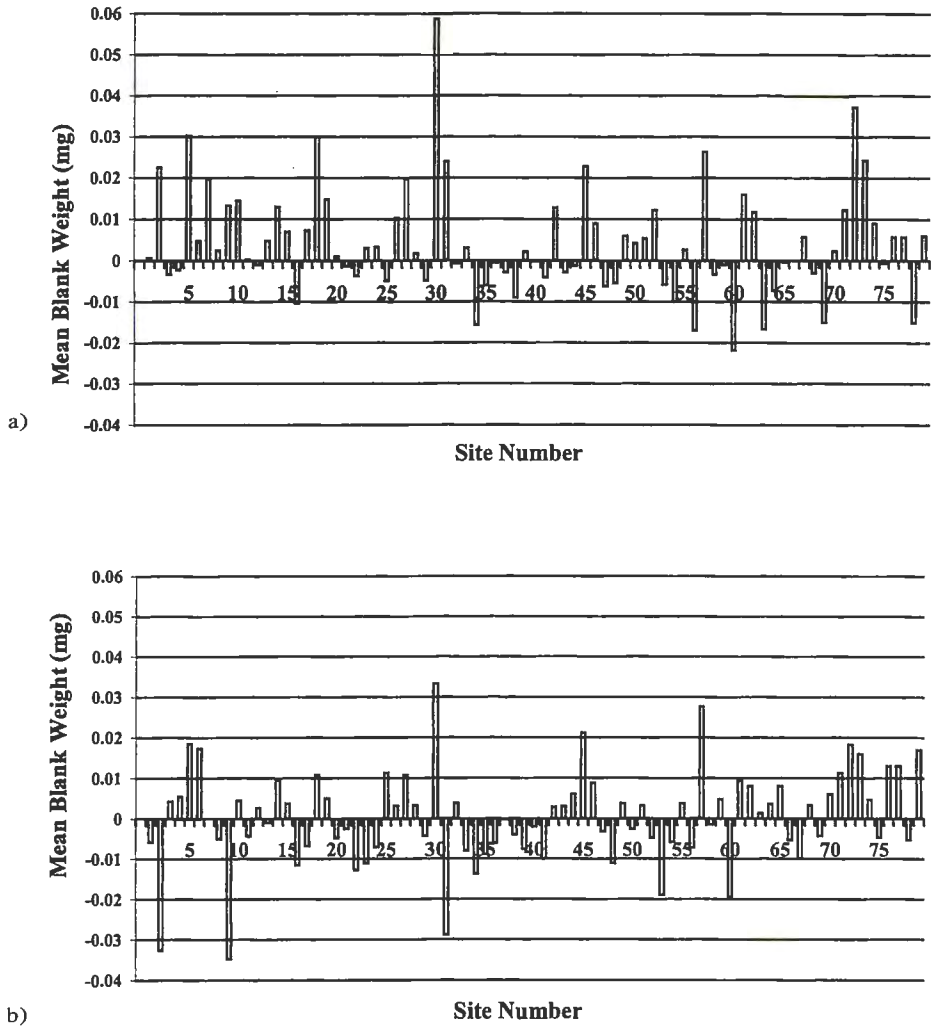


FIG. 2—*a) Top: Means of the total weight blanks by site. b) Bottom: Means of the extractable weight blanks by site.*

TABLE 1—*Estimates of the mean and median blank weights ($Wt_{mean\ or\ median}$) standard deviations ($SD_{mean\ or\ median}$), limits of detection ($LOD_{mean\ or\ median}$) and quantitation ($LOQ_{mean\ or\ median}$) obtained from the total-weight blank samples and the extractable-weight blank samples for the 79-site survey. The upper 95th percentile (+95%) of the LODs and LOQs are also given.*

	Wt_{median} (mg)	Wt_{mean} (mg)	SD_{median} (mg)	SD_{mean} (mg)	LOD_{median} (mg)[a]	LOD_{mean} (mg)[a]	LOQ_{median} (mg)[a]	LOQ_{mean} (mg)[a]	$LOD_{+95\%}$ (mg)[a]	$LOQ_{+95\%}$ (mg)[a]
Total weight	0.002	0.004	0.010	0.012	0.029	0.036	0.096	0.120	0.087	0.290
Extractable weight	0.002	0.001	0.009	0.011	0.026	0.032	0.086	0.107	0.095	0.318

[a] The *LOD* and *LOQ* values given above are the median, mean, or upper 95th percentile of the distribution of three times the blank standard deviations (*LOD*) or of the distribution of ten times the blank standard deviations (*LOQ*) over the 79 surveyed sites.

Fraction(s) Extracted, by Type of Fluid, Operation, and Mass Sampled

Approximately 1200 total particulate weight and 300 thoracic particulate weight samples were collected in this survey. The fractions extracted, (FE_1 or $Weight_{extracted}/Weight_{total}$) were computed for the four types of fluid—straight, soluble, semisynthetic, and synthetic. Figure 5 shows the fractions extracted by fluid type for each of the major operations monitored in this study—grinding, milling, and turning. The samples listed as "other" in this figure include those collected at broaching, drilling, hobbing, and stamping operations; there were too few of these samples for these operations to be considered separately. The number of samples encountered by each operation is also shown in Fig. 5. With the exception of the "other" samples, the fractions extracted decrease approximately in the order $FE_{1\ straight} > FE_{1\ semisynthetic} \sim FE_{1\ soluble} > FE_{1\ synthetic}$. The fraction extracted can obviously be quite variable by operation.

FE_1 is plotted against the sample weight for total particulate weight samples weighing ≤2 mg in Fig. 6. An increase in FE_1 with sample weight is apparent. A similar plot and trend were obtained for the thoracic particulate samples.

There was also a substantial extractable fraction ($FE_1 = 0.58$) for 54 samples classified as "dry" samples (not included in Figs. 5 or 6). These samples were collected at metalworking operations in

the 79 monitored plants; however, they cannot be classified according to fluid since no MWF was in use at these operations. Dry machining may not typically be thought to expose the worker to MWF; however, these results suggest the ubiquitous presence of MWF aerosol about the shop area. This aerosol could result from vapor phase or aerosol MWF components that eventually condense on particulate material (e.g., dust) that becomes distributed about the shop atmosphere. The presence of significant amounts of extractable material in these "dry" samples argues in favor of using an extraction technique to analyze for the presence of MWF. Otherwise, these may not be recognized as exposures to MWF and the effect of the exposure to MWF would remain confounded with the effect of exposure to comingled insoluble particulate.

Model

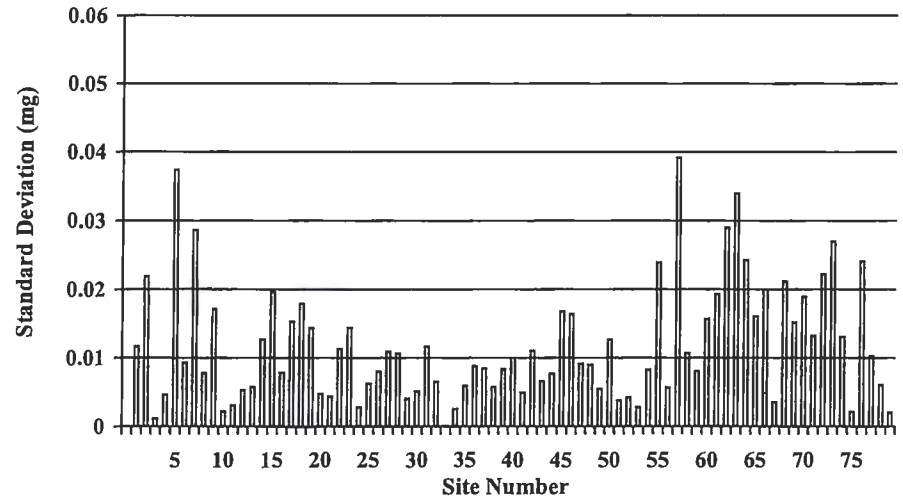
The discussion above suggests that the fraction extracted may be affected by several factors, including the sample weight, the type of fluid, and the type of operation. To more accurately quantify the relationship between FE_1 and these variables, an analysis of covariance statistical procedure was used [6,7]. As discussed further in the Appendix, the data analysis was restricted to 875 total particulate samples; there were too few thoracic samples for a comparable analysis.

This model assumed that the fraction extracted could vary with total weight (Wt), with operation (Op) and fluid (F), and that interactions of these variables with each other were possible, i.e., operation with weight ($Wt * Op$), operation with fluid ($Op * F$), total weight with fluid ($Wt * F$), operation with fluid and total weight ($Wt * F * Op$), as well as the Wt^2 terms ($Wt^2 * F$), ($Wt^2 * Op$), and ($Wt^2 * F * Op$).

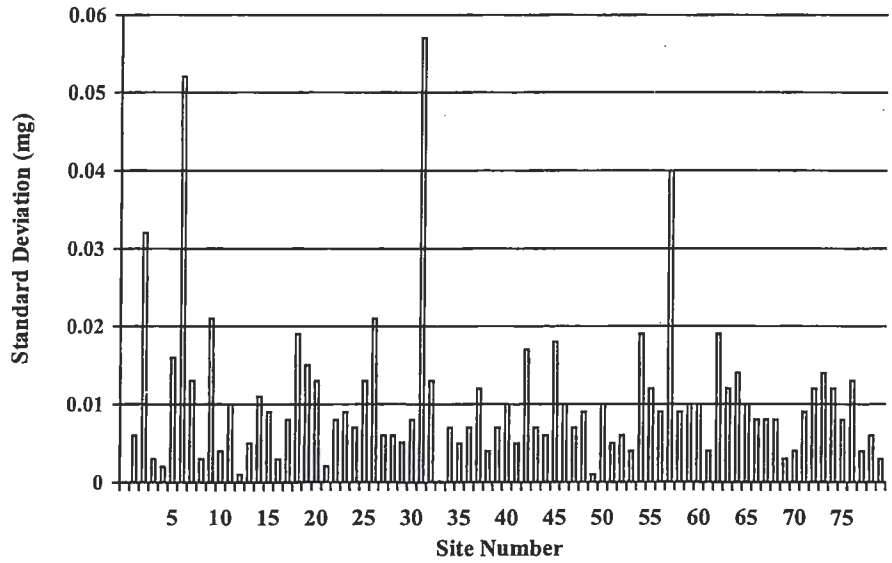
The relationship can be stated as follows:

$$FE_1 \cong \{Op + F + Wt + Wt^2 + (Wt * Op) + (Op * F) + (Wt * F) + (Wt^2 * Op) + (Wt^2 * F) + (Wt * F * Op) + (Wt^2 * F * Op)\} \quad (1)$$

In an F-test for the full model, the major factors governing FE_1 were the weight, operation, and the type of fluid; in this model, the two- and three-way interaction terms were of marginal signifi-



a)



b)

FIG. 3—*a) Top: Standard deviations of the total particulate weight blanks by site. b) Bottom: Standard deviations of the extractable weight blanks by site.*

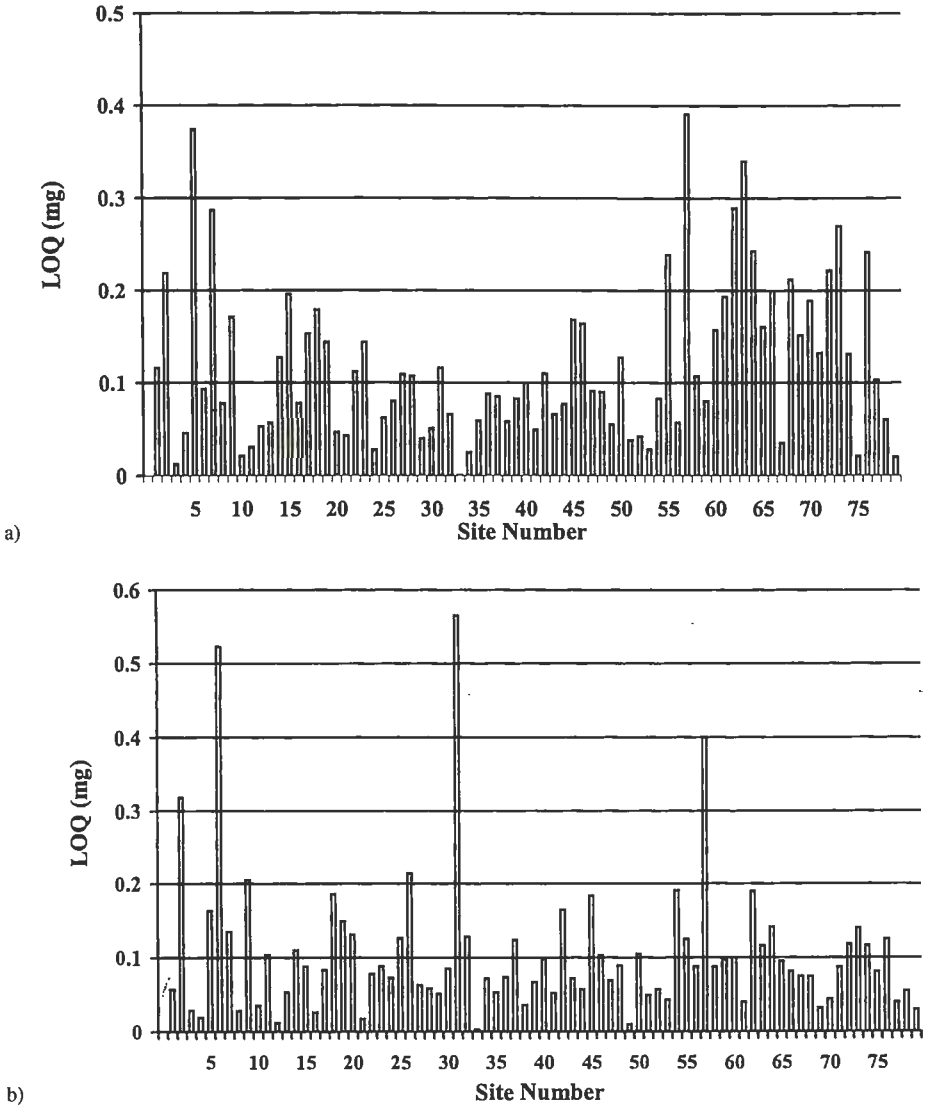


FIG. 4—*a) Top: Limits of quantitation estimated for total particulate weight samples by site. b) Bottom: Limits of quantitation estimated for extractable weight samples by site.*

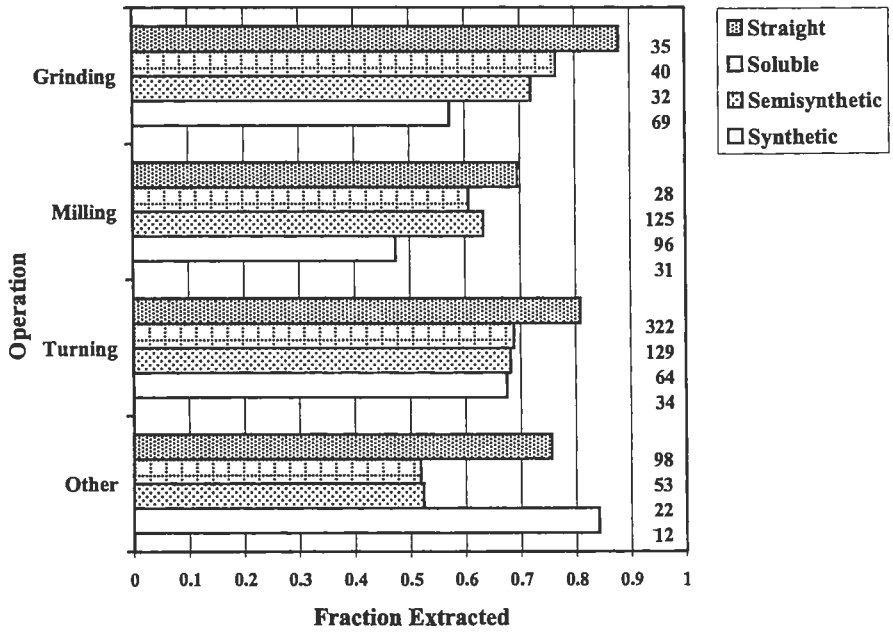


FIG. 5—*Fraction extracted (FE_1) by type of operation and type of fluid. The numbers of each fluid sample encountered in each operation are also given to the right of the FE_1 bars.*

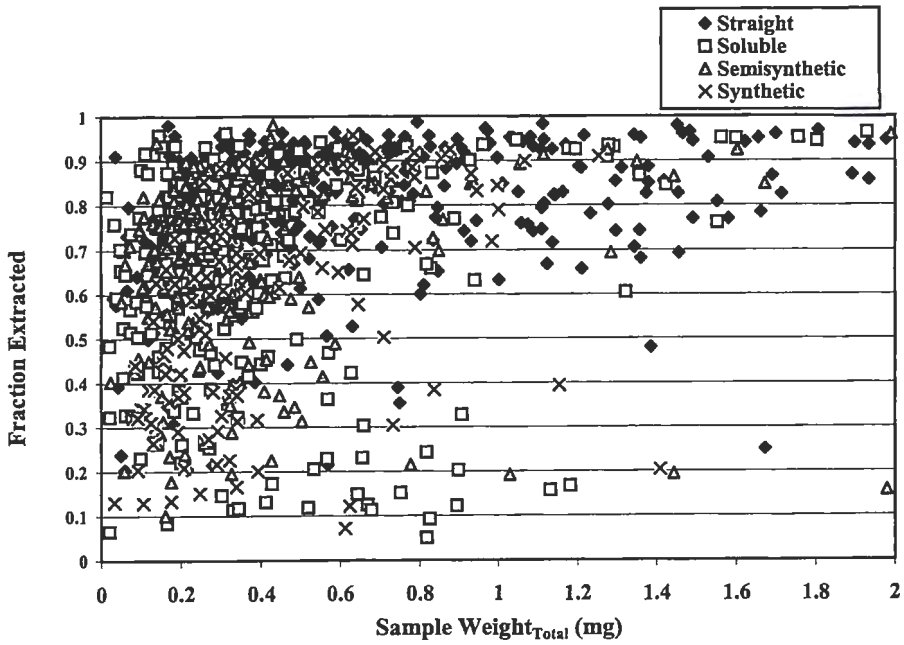


FIG. 6—*Fraction extracted (FE_I) as a function of sample weight for the total particulate samples weighing ≤ 2.0 mg. For simplicity of presentation, 35 samples, weighing 2–12 mg, have been excluded from this plot.*

cance. The significance of the 2- and 3-way interaction terms for individual fluids was further investigated via a likelihood ratio procedure that was based on a restricted maximum likelihood and a maximum likelihood technique [7], using the Statistical Analysis System (SAS) PROC MIXED estimation program [8] (See Appendix). By this technique, statistically insignificant terms are removed from the overall model, one at a time. The results of this iterative procedure indicated that the only significant interaction terms were the 2-way $Op * F$ (the straight and synthetic fluids interacting with the grinding operation) and the $F * Wt$ and $F * Wt^2$ (synthetic fluid interacting with the Wt and Wt^2 terms).

FE_I was found to be a quadratic function of the sample weight for all fluids for all operations. It was possible to reduce the four fluid-three operation combinations (twelve total) to five sets of separate parameters, i.e., a series of five individual curves. These are shown in Fig. 7. Three of these curves—straight (grinding), straight (milling or turning), and soluble or semisynthetic (all operations)—are parallel to one another. The two other curves—synthetic (grinding), and synthetic (milling or turning)—are parallel to one another but not to the others. These curves demonstrate:

- the increase in FE_I with increasing sample weight. This result might be expected if there are relatively fixed background levels of insoluble particulate in plants having widely varying MWF exposure levels. For example, if the total exposure levels at two operations in a plant having a background insoluble particulate level of 0.05 mg/m^3 are 0.1 mg/m^3 and 1.0 mg/m^3, the low and high exposure samples should exhibit $FE_I = 0.5$ and 0.95, respectively.
- a tendency towards lower values of FE_I in the order straight > soluble ~ semisynthetic > synthetic, possibly indicating lower extraction efficiencies for the synthetic fluids relative to the other fluids and operations. Interestingly, the grinding operation using straight fluids produced the highest fractions extracted, whereas the grinding operation using synthetic fluids produced the lowest fractions extracted.

Computation of Differences in FE_I by Fluid Type

In order to assess the possibility of an extraction bias by fluid type and operation, the magnitude and statistical significance of the differences in FE_I (ΔFE_I) were computed. Since the curves obtained for the synthetic fluids were not parallel to those obtained for the other fluids, the bias was estimated by measuring the values of FE_I at $Wt = 0.27$ mg and 0.69 mg. These values are approximately the mean weights for all data <0.5 mg and >0.5 mg, respectively.

The percent differences in the values of FE_I for all fluids across the three operations studied are plotted in Fig. 8. Since the statistical procedure had produced identical curves for the semisynthetic and soluble fluids over the range studied, there were no differences in FE_I between these fluids for either level for any operation. For most operations, decreasing values of ΔFE_I were generally observed in the order (straight-synthetic), (soluble or semisynthetic-synthetic), and (straight-soluble or semisynthetic). The differences in FE_I are especially apparent for the grinding operations, where the fractions extracted for the synthetic fluids are significantly lower than for the straight fluids. The percent difference is greater at the lower sample level ($\Delta FE_I = 0.28$ or 35%) than at the higher sample level ($\Delta FE_I = 0.19$ or 22%). These are the only two statistically significant differences in the values of ΔFE_I among all four fluids across the three operations tested.

Grinding may produce more metal or other insoluble particulate fines than other operations, so relatively low values of FE_I might be expected. However, extraction of all fluids in grinding operations should have been equally affected. While these results suggest that further investigation of the extraction of synthetic fluids may be warranted, it is useful to consider the following:

- The average weight of the straight grinding samples (0.57 mg) was greater than the average weight of the synthetic samples (0.44 mg). Thus, the differences in FE_I may reflect the fact that the average sample weights were lower and that background particulate levels contributed proportionally more to the weights of these samples.

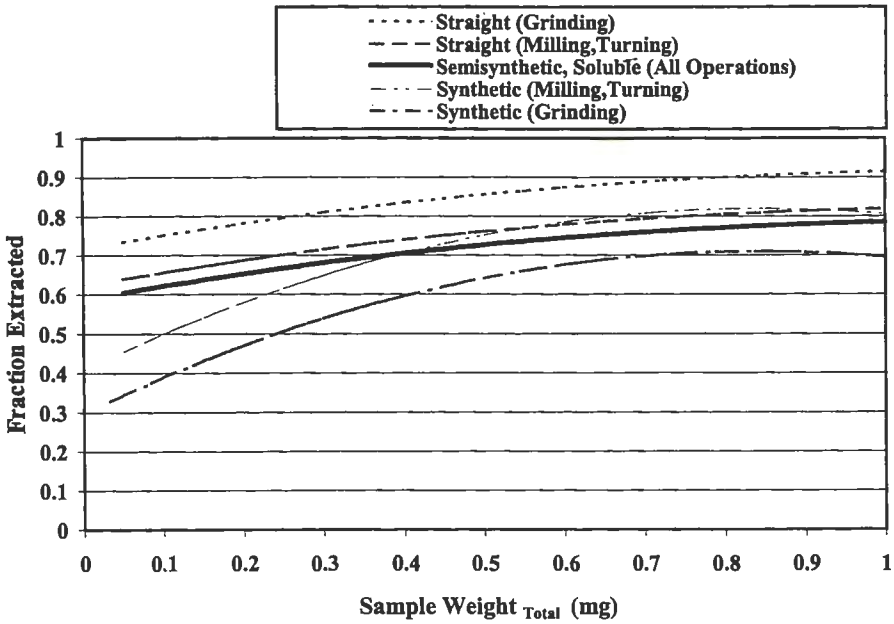


FIG. 7—*Curves predicting the fraction extracted (FE_1) as a function of total particulate sample weight using the quadratic model (see Appendix) over the fluid/operation combinations studied.*

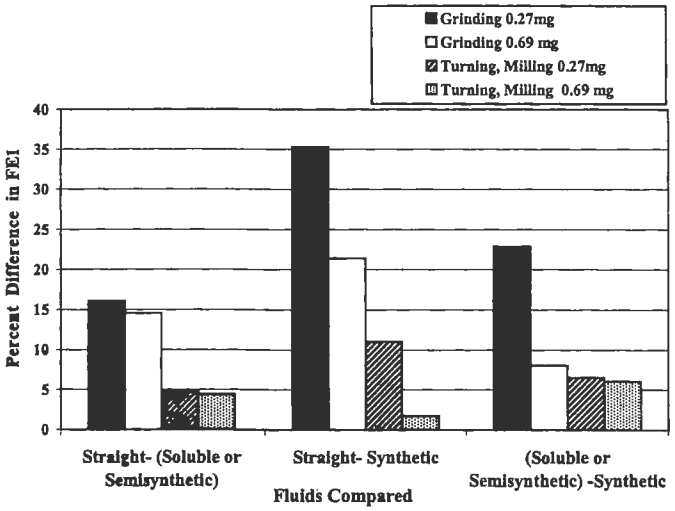


FIG. 8—*Percent differences in the fractions extracted (FE_1) among all fluids over the three operations studied or 100* [$FE_{1\ Fluid\ 1} - FE_{1\ Fluid\ 1\ or\ 2}$ /$FE_{1\ Fluid\ 1\ or\ 2}$], where $\Delta/FE_{1,\ Fluid\ 1\ or\ 2}$ is the higher value of FE_1 for Fluid 1 or Fluid 2.*

- These sample classifications represent the primary MWF to which each worker was exposed. Some workers were exposed to multiple fluids at different workstations throughout the workday.
- While significant differences in FE_1 were found between the straight and synthetic fluids at both sample levels for the grinding operation, that operation contained the fewest number of data points (131) relative to the milling (270) and turning operations (474). Thus, for 85% (744/875) of all samples evaluated, the difference between the highest (straight) and lowest (synthetic) values of FE_1 was 2–11% and not statistically significant ($p = 0.05$).

Sample Re-extraction

To assure that the extractions were complete, a large set of extracted samples was re-extracted. The fraction re-extracted (FE_2) was computed as the sample weight following the second extraction divided by the total (unextracted) weight of the sample. The guidelines for the re-extraction of these samples were that they be the highest weight samples and exhibit relatively low values of FE_1; the average FE_1 of these samples was 0.74. Approximately 25% (322/1190) of the total particulate weight samples and 27% (77/285) of the thoracic samples were re-extracted in this manner. The overall value of FE_2 for the total particulate samples was ~0.001; for the thoracic samples, the average value of FE_2 was ~0.008. Figure 9 summarizes the results for the total particulate samples over the range from $FE_2 < 0$ to > 0.15. For the vast majority of the samples (98.2%), FE_2 was less than 0.10. Note that there are 108 samples where FE_2 is < 0, i.e., the mass extracted during the re-extraction of these samples was less than the mean field blank used to adjust the masses of these samples. Excluding these samples, the overall average FE_2 is still ~0.024. This study provides substantial evidence that the extractable components of the total weight samples had been effectively removed during the first extraction. Similar results were obtained for the thoracic samples.

To determine if lower values of FE_2 were related to extraction of any one fluid type, the re-extraction data in Figure 9 were examined by fluid type. While there were small differences apparent by fluid type, the average FE_2 for each fluid was <0.01 and the differences between fluids were not statistically significant ($p = 0.05$). This indicates that there was no diminished extraction of any one type of fluid in the first set of extractions and that there was no preferential bias towards increased extraction of any one type of fluid in the second set of extractions. A comparable analysis could not be made for the thoracic data due to the limited number of samples available.

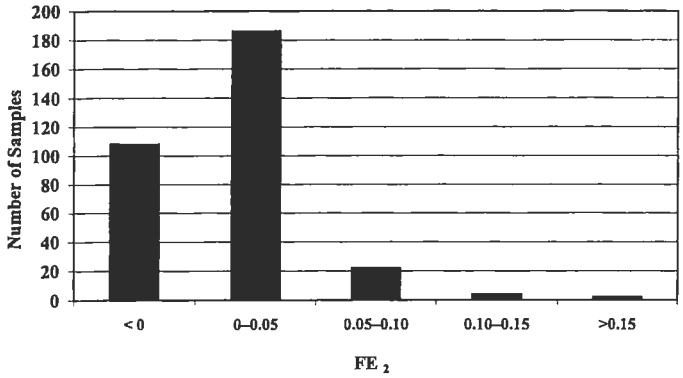


FIG. 9—*Bottom: Ranges of fractions re-extracted (FE_2) for the 322 re-extracted metalworking fluid samples.*

Quality Assurance Audit Samples

A preliminary set of quality control audit samples prepared independent of this work was submitted to the laboratory conducting the analyses for MWF. Overall, relatively low recoveries were observed for these samples; ranging from 0.41(SD = 0.24) for the semisynthetic samples to 0.80 (SD = 0.11) for the straight samples. These samples ranged in nominal weight from 0.02 to 1.0 mg and had been spiked onto the filters and stored overnight prior to shipment to the laboratory. These recovery estimates were made on the basis of the volume of MWF dissolved in the ternary blend carrier solvent that was metered onto the filter. As discussed in a previous paper [3], this approach is problematic, especially for semisynthetic and synthetic fluids, since it does not account for the large amount of water in the sample concentrates. Water is dissolved in the ternary solvent and is metered onto the filters; however, it will evaporate as the filter dries. Thus, for fluids containing relatively large amounts of water, e.g., synthetic and semisynthetic fluids, the amount placed on the filter will be proportionally overestimated by the amount of water in the fluid. It was also recognized that a major source of these low and imprecise recoveries may have been due to incomplete evaporation of the spiking solvent or release of high vapor pressure MWF components from the filter.

It is reasonable that a field sample will be purged of a large proportion of volatile material as air passes through the filter during a full-shift sampling period. Leith et al. [9] and Volckens et al. [10] have estimated weight losses of up to 50% from MWF filter samples that have been purged of volatile components. In preliminary experiments, PTFE filters, spiked with all four types of MWF and purged with air for 8 h, lost an average of 10–17% of their prepurge weight. This was despite the fact that these samples had been allowed to air dry prior to purging. Due to these sample losses, all spiked quality assurance sample filters were purged with pure air for 8 h at 2 L/min prior to submission to the laboratory that performed the analyses. Another set of purged samples was also prepared in the same manner as the QA samples and weighed periodically over a 30-day storage period. This second set of samples permitted simultaneous tracking of the changes in weight of the MWF samples on the filters. The preparation of the QA and tracking samples is described in the Experimental section of this paper.

For the tracking filter set, we found that all samples lost weight during the storage period; the weight decay generally obeyed the simple linear equation:

$$F_R = A + bt \quad (2)$$

where F_R is the fraction recovered (relative to the original mass spiked), A and b are constants, and t is the storage period (in days). The ratios of F_R (computed for t = 1 to 30 days) to F_R (computed immediately post purge) provide an estimate of the sample recovery during the 30-day storage period. These ratios have been plotted in Figs. 10*a–d* for all four fluids over the four spiking levels for the 30-day storage period. Figures 10*a–d* generally indicate lower recoveries for the lowest spiking levels. Recoveries did exceed 80% for all straight, soluble, and semisynthetic samples for storage periods approaching 30 days. However, for the two lower spiking levels of the synthetic fluid, the recoveries dropped below 80% at about 20 days post purge.

As discussed below, the actual masses used for computation of the fractions recovered in Figs. 10*a–d* are much lower than those predicted from the densities of the fluids spiked. For example, based on density alone, the lowest-level spikes of the semisynthetic and synthetic fluids should have contained ~0.25 mg. However, the masses actually deposited on these filter samples were only ~0.12 mg (based on post purge analysis). These masses are lower than those expected in a 1.0-m^3 air sample collected at either REL. For all QA samples containing >0.4 mg or 0.5 mg (the masses in a 1.0-m^3 sample at the REL), recoveries exceeded 80% following storage for 30 days.

These results thus indicate that volatile material was removed from the filters during the initial 8 h purge and that further loss of volatile and semivolatile material occurred during storage. For water-soluble fluids, a major source of weight decrease during storage may be the loss of water itself. An applied spike of a water-based sample may be expected to penetrate the filter matrix forming a multilayered but generally amorphous spot. Water from the innermost layer(s) is likely to be removed at a much slower rate than the water on the surface. The surface material will air dry before the subsurface material, trapping water and other volatile material in the subsurface sample. Innermost water molecules may be hindered in passage through not only the hydrophobic PTFE filter matrix but also through the outer layers of the semisolid MWF components. Slow weight loss could result during storage or dessication.

For the straight, soluble, and semisynthetic MWF samples, lower molecular weight volatile components, including the lighter mineral oils, may evaporate during sampling as well as storage. Low molecular weight fatty acid components of synthetic fluids have appreciable vapor pressure [11] and may be lost during either sampling or storage.

Samples containing soluble, semisynthetic, and synthetic fluids may lose volatile ethanolamines during sampling. Kenyon et al. [12] reported losses ranging from 11–26% of 50 μg spikes of triethanolamine (TEA) from PTFE cascade impactor filters that had been purged for 8 h at 2 L/min. However, loss of TEA during storage will be contingent on the sample makeup. In the same study, MWF and TEA concentrations were monitored at a variety of operations in a plant that employed soluble, semisynthetic, and synthetic MWF. It was found that the amounts of TEA collected on individual samples were quite variable and dependent on the amount of TEA in the bulk fluid as well as the operation. If the bulk MWF contained ≥10% TEA, the masses of TEA collected could be as high as 33% of the total sample mass. However, if the bulk MWF contained ≤10% TEA, the masses of TEA collected were generally ≤1% of the total sample mass. Evaporation of TEA cannot account for the significant weight losses during storage of the latter samples.

These QA sample results and the previous discussion suggest

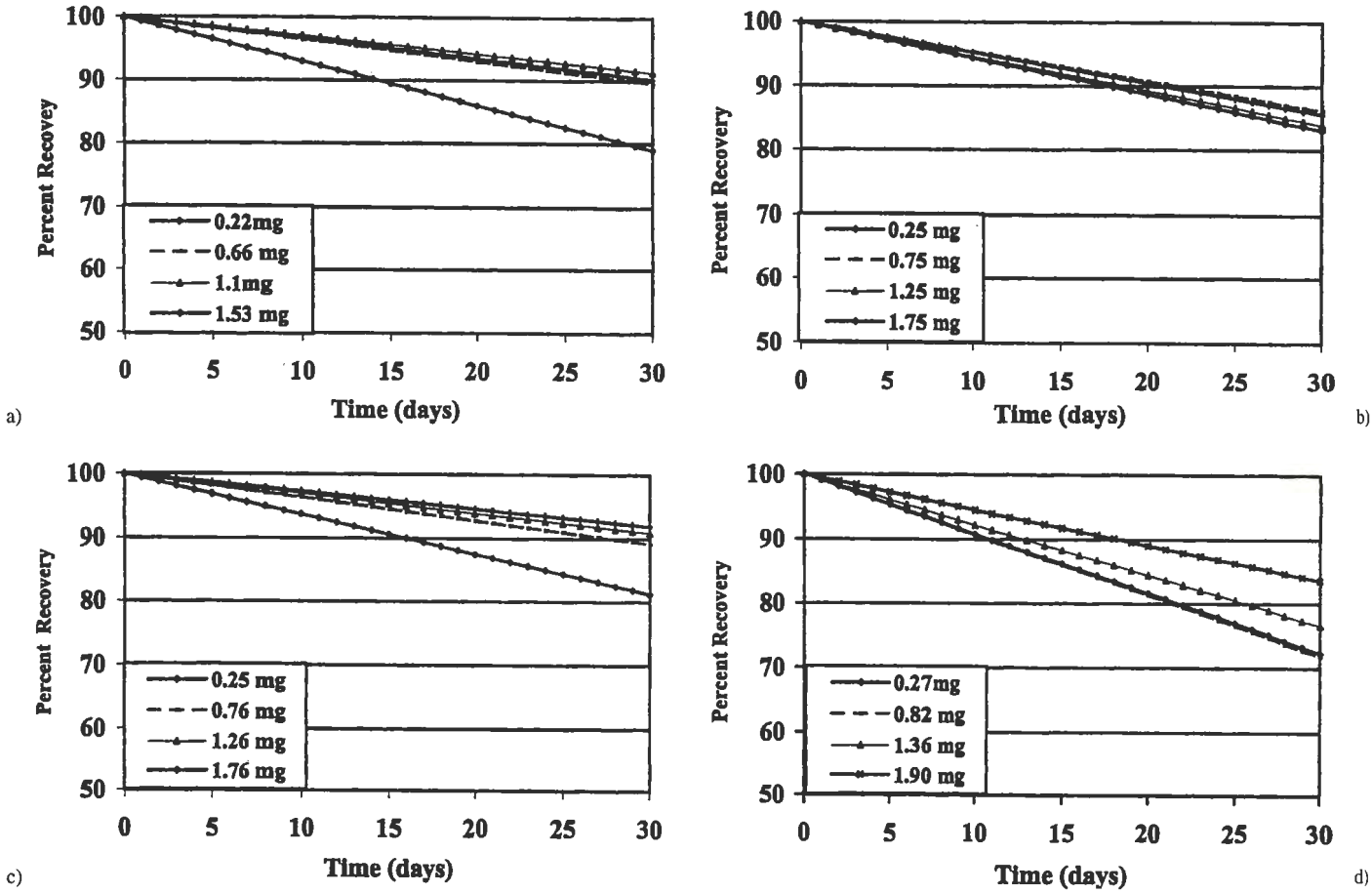


FIG. 10—*Recoveries of the QA samples versus storage time. Percent recovery computed as F_R (storage time t = 0–30 d)/F_R (post purge)*100 and plotted for: a) Straight fluid—Top left; b) Soluble fluid—Bottom left; c) Semisynthetic fluid—Top right; d) Synthetic fluid—Bottom right.*

that storability of MWF samples may be affected by the amount of water or volatile organic components in the MWF itself, the mass of sample collected, the length of time that the samples are stored, and the temperature of storage. These issues will likely require further investigation. In the interim, it is prudent to implement techniques to minimize sample loss during storage. These include overnight transportation of MWF samples from the collection point to the laboratory, refrigeration of MWF samples immediately upon receipt at the laboratory, and analysis of MWF samples as soon as possible after collection.

The QA samples were in storage for periods ranging from 18–26 days. Since the exact storage times of the audit samples were known, Eq 2 also could be used to estimate the audit sample weight that should have been reported back by the contracting laboratory for each set of QA samples.

Figure 11*a* compares the theoretical amounts spiked onto the filters (based on the density of the fluids), the average amounts found post purge, the amounts estimated by Eq 2 (using the sample storage period), and the results reported by the contractor. Several things should be apparent from the figure. First, for the straight and soluble fluids, the amounts determined, whether post purge, reported by the laboratory, or predicted on the basis of Eq 2, agree much better with the amount estimated from the fluid density than do the comparable estimates for the semisynthetic and synthetic fluids. This is related to the loss of large amounts of water in the semisynthetic and synthetic samples as discussed above. In spite of the weight loss from the purged filters during the storage periods, there is still reasonable agreement between the amounts found immediately post purge, those estimated by Eq 2, and those reported back from the performing laboratory. The reported values are within 86–100% of the post purge values and those estimated using Eq 2.

Figure 11*b* presents the fractions extracted for the audit samples. Here, the contractor-reported total and extracted weights were used to compute FE_1. With the exception of the soluble fluid QA samples, the fractions extracted generally increased with the mass of the samples spiked. Extraction of spiked MWF from these filters was very good ($FE_1 > 0.90$) across all spiking levels for all four fluids studied.

Conclusions

Data from a NIOSH/OSHA-sponsored survey of 79 machine shops were evaluated. Approximately 1200 MWF samples were analyzed for total particulate weight; approximately 400 samples were analyzed for thoracic particulate weight. Full-shift samples were collected on PTFE membrane filters. Extractable fractions of these samples were determined by elution of the MWF samples from the filters using a 1:1:1 blend of dichloromethane:methanol: toluene according to ASTM Method PS-42-97.

The solubility of bulk samples of all study fluids in the extraction solvent was determined. Of the 155 individual fluids encountered in the survey, only a single synthetic fluid was not completely soluble in the ternary blend; however, this fluid was completely soluble in a 1:1 blend of methanol:water. The samples containing

this fluid were analyzed using the ternary blend and the methanol:water blend. Although the ternary blend is not a universal solvent for all MWFs, the extraction technique had universal application to all MWFs encountered.

The blank weight data were evaluated to determine the *LOD* and *LOQ*. The mean, median, and upper 95th percentiles of the *LOQ* were approximately 0.1 mg, 0.1 mg, and 0.3 mg, respectively, for both the total particulate weight and the extractable weight samples. This finding indicates that the total particulate REL of 0.5 mg/m^3 and the thoracic particulate REL of 0.4 mg/m^3 can readily be supported if 1.0 m^3 of air is sampled.

Large extractable fractions of samples from *dry* machining operations were obtained, indicating an ubiquitous presence of MWF about certain shops and the utility of an extraction-based analytical method to recognize exposures to MWF that might have been overlooked previously. The effects of operation, fluid type, and sample weight on the fraction extracted (FE_1) data were evaluated using a statistical analysis of covariance technique for a reduced set of the total and extractable particulate data. For each fluid over the three major operations studied—grinding, milling, and turning—a curve of FE_1 was obtained as a function of sample weight. For all fluids and operations, the data could be reduced to five quadratic curves. This statistical analysis indicated that FE_1 increased with increasing sample weight and that FE_1 varied with operation and with fluid. Overall, the increase with weight may reflect the lower proportional contribution of background solid particulate to the over-

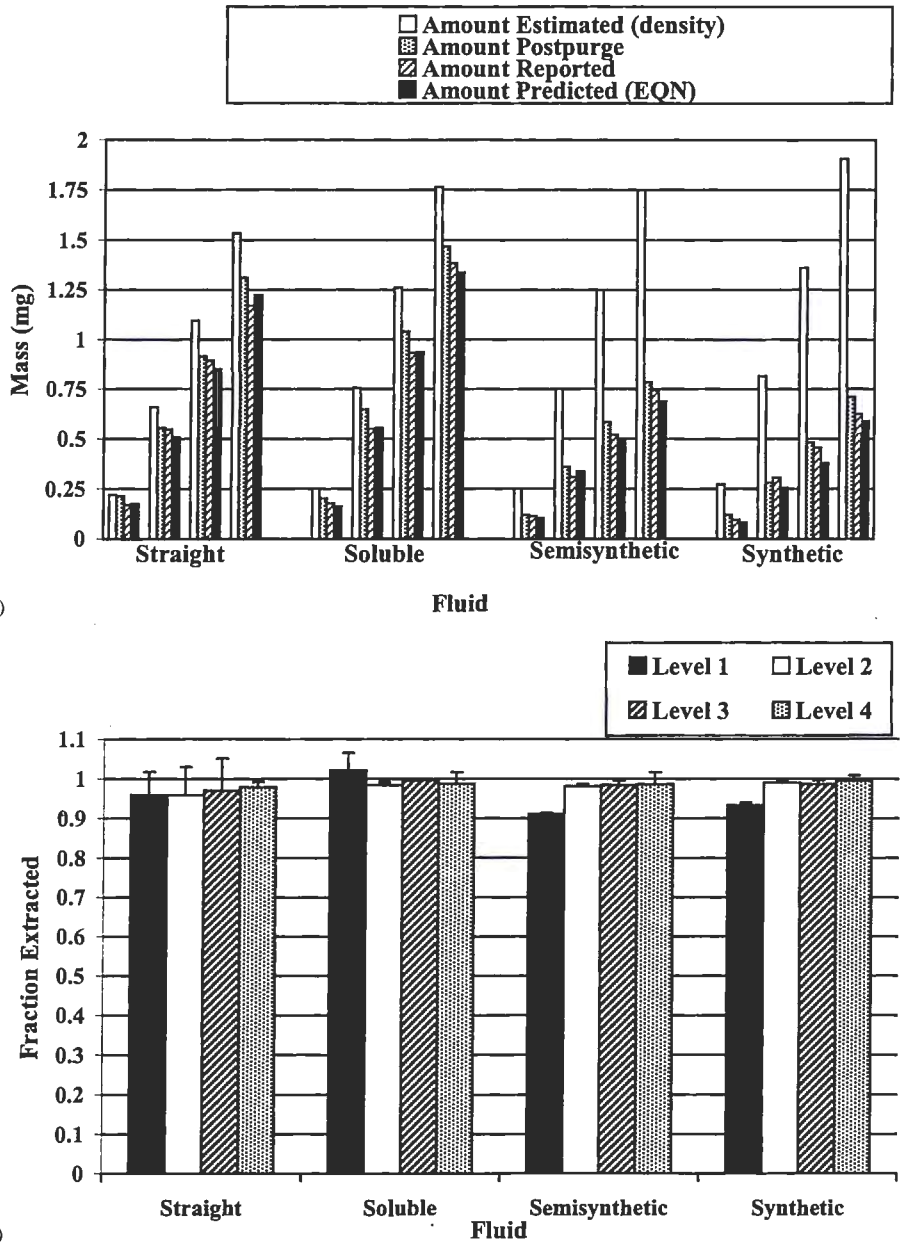


FIG. 11—*a) Top: QA audit results for four MWF, spiked on PTFE filters at four test levels and stored for 17–30 days prior to analysis. Weight spiked based on density of each fluid; weight reported obtained from the performing laboratory; weight post-purge obtained from a parallel tracking set of QA samples following an 8 h air-purge; weight predicted (Eq 2) obtained from the fitted curves (Fig. 10) for the QA tracking samples for storage periods equal to those of the actual QA samples. b) Bottom: FE_1 computed for the metalworking fluid QA audit samples by dividing the reported extractable weight by the reported total weight at each of the four spiking levels for each of the four test fluids. Brackets indicate the relative standard deviations of FE_1.*

all weight. With few exceptions, the fractions extracted generally decreased in the order: $FE_{1straight} > FE_{1semisynthetic} \sim FE_{1soluble} > FE_{1synthetic}$ for all operations. The significance of the differences in FE_1 among the fluids was evaluated at two loading levels—0.27 mg and 0.69 mg. For the milling and turning operations, which comprised the majority (85%) of the samples, these differences were relatively small (2–11%) and statistically insignificant for both sample levels. Statistically significant differences in FE_1 (2–36%) were found between the straight and synthetic fluids in the grinding operations at both levels. The reasons for these differences are unknown; they may suggest that removal of the synthetic fluids from grinding samples is less efficient than for straight fluids. Alternatively, there may be other factors affecting FE_1, including differences in sample weights, numbers of samples of each fluid type, fluid exposure classifications, and lack of fit of the model to the data. This is an area that deserves further study.

To assure that the initial extraction had been efficient, approximately 25% of the total particulate samples and 20% of the thoracic samples were re-analyzed for extractable weight by re-extraction of these samples with the ternary blend. The filters selected for re-extraction were the most heavily loaded samples; yet the mean fraction re-extracted (FE_2) was only 0.001 for the total particulate samples and 0.008 for the thoracic samples. These re-extraction experiments indicated effective removal of the MWF from the filters during the first extraction. There were no significant trends in FE_2 for any fluid type.

Quality assurance (QA) samples were prepared by spiking aliquots of solutions containing samples of all four types of fluid onto filters. Following air drying, these QA samples were purged for 8 h to simulate sampling. These QA samples were then submitted to the laboratory performing the analyses. The masses of the QA samples recovered were in very good agreement (86–100% recovery) with amounts predicted from a simple linear decay model that was developed by studying the loss in weight of MWF samples over a 30-day storage period. The decay equation(s) predicted that samples could be stored from 20 days (synthetic samples) to 30 days (all others), with average recoveries $\geq \sim 80\%$, relative to the immediate post purge weight of the spikes. All test fluids were extracted efficiently ($FE_1 > 0.90$) from these QA filter samples. Refrigerated sample storage and analysis of MWF samples as soon as possible after collection are recommended to mitigate sample loss.

Acknowledgments

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APPENDIX

The model used all data for grinding, milling, and turning for the four fluid types that satisfied the following conditions:

a) FE_1 between 0 and 1.0;
b) Total weight and extractable weight after blank correction must be greater than 0.0 mg;

c) Total weight after blank correction must be between 0.0 and 1.0 mg.

The data were truncated in this manner since there were too few synthetic and semisynthetic samples containing more than 1.0 mg for comparison to the soluble and straight fluids. Of the 1190 samples available, there were 875 total particulate samples that satisfied these criteria; approximately 13% of the available samples had weights that were >1.0 mg. Samples with a value of FE_1 > 1.0 were also excluded. Such steps were taken to eliminate the undue weighting of FE_1 outside the weight range of the vast majority of the data, i.e., from 0.0 to 1.0 mg. Only the total particulate data for grinding, milling, and turning operations were evaluated; there were insufficient total particulate "other" samples and thoracic particulate measurements to perform an analysis of that data. The range studied included approximately 70% of all total particulate samples; the majority of these samples (75%) contained <0.5 mg.

A statistical model for FE_1 was constructed using approaches similar to those found in Refs. 6 and 8; the parameter FE_1 was modeled as a function of total weight, fluid type, and operation as described by Eq 1 in the text. The dependence of FE_1 on weight was allowed to vary by companies; each set of data from each company was treated as a random sample. While there was some lack of fit of the model to the data, on average, the predicted values were within 10% of the actual values. Better fitting, but more complicated log-transformed models (of FE_1) gave results that were similar to those obtained with the untransformed FE_1 data.