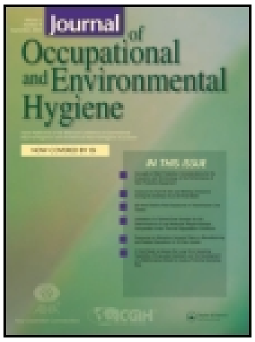

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Performance Testing of NIOSH Method 5524/ASTM Method D-7049-04, for Determination of Metalworking Fluids

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A performance test of NIOSH Method 5524/ASTM Method D-7049-04 for analysis of metalworking fluids (MWF) was conducted. These methods involve determination of the total and extractable weights of MWF samples; extractions are performed using a ternary blend of toluene:dichloromethane:methanol and a binary blend of methanol:water. Six laboratories participated in this study. A preliminary analysis of 20 blank samples was made to familiarize the laboratories with the procedure(s) and to estimate the methods' limits of detection/quantitation (LODs/LOQs). Synthetically generated samples of a semisynthetic MWF aerosol were then collected on tared polytetrafluoroethylene (PTFE) filters and analyzed according to the methods by all participants. Sample masses deposited (∼400–500 μg) corresponded to amounts expected in an 8-hr shift at the NIOSH recommended exposure levels (REL) of 0.4 mg/m^3 (thoracic) and 0.5 mg/m^3 (total particulate). The generator output was monitored with a calibrated laser particle counter. One laboratory significantly underreported the sampled masses relative to the other five labs. A follow-up study compared only gravimetric results of this laboratory with those of two other labs. In the preliminary analysis of blanks; the average LOQs were 0.094 mg for the total weight analysis and 0.136 mg for the extracted weight analyses. For the six-lab study, the average LOQs were 0.064 mg for the total weight analyses and 0.067 mg for the extracted weight analyses. Using ASTM conventions, h and k statistics were computed to determine the degree of consistency of each laboratory with the others. One laboratory experienced problems with precision but not bias. The precision estimates for the remaining five labs were not different statistically ($\alpha = 0.005$) for either the total or extractable weights. For all six labs, the average fraction extracted was ≥0.94 (CV = 0.025). Pooled estimates of the total coefficients of variation of analysis were 0.13 for the total weight samples and 0.13 for the extracted weight samples. An overall method bias of –5% was determined by comparing the overall mean concentration reported by the participants to that determined by the particle counter. In the three-lab follow-up study, the nonconsistent lab reported results that were unbiased but statistically less precise than the others; the average LOQ was 0.133 mg for the total weight analyses. It is concluded that aerosolized MWF sampled at concentrations corresponding to either of the NIOSH RELs can generally be shipped unrefrigerated, stored refrigerated up to 7 days, and then analyzed quantitatively and precisely for MWF using the NIOSH/ASTM procedures.

Keywords ASTM Method D-7049-04, limits of detection and quantitation, metalworking fluids, NIOSH method 5524, performance evaluation, storability

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INTRODUCTION

Metalworking fluids (MWFs) lubricate, cool, and remove debris from the work surfaces of metal parts that are being drilled, ground, milled, or turned. These fluids are generally classified according to the amount of mineral oil that they contain. *Straight* fluids are composed primarily of mineral oils but may also contain a wide range of components, including chlorinated paraffins, tricresyl phosphate, and sulfur compounds, among many others. Straight fluids are not water soluble and are used undiluted. The three other types of MWF are all mixed with water prior to use. They include *soluble* fluids that contain up to 80% mineral oil, *semisynthetic* fluids that contain up to 40% mineral oil, and *synthetic* fluids that contain no mineral oil. Water-mixed fluids may also contain alkanolamines, biocides, boron compounds, emulsifiers as well as ionic and nonionic surfactants.

The National Institute for Occupational Safety and Health (NIOSH) issued a 1998 criteria document recommending that exposures to MWF be limited to ≤0.4 mg/m^3 measured as thoracic particulate material, or ≤0.5 mg/m^3 measured as total particulate material.(1) This criteria document recognized that workers exposed to MWF may be at risk of developing occupational asthma, hypersensitivity pneumonitis, and cancer. It further recommends that exposures be evaluated via gravimetry using a technique such as NIOSH Method 0500. However, it also recommends that, "when there are simultaneous exposures to nontoxic particulate materials, NIOSH Method 5026 or a similar method may be useful to estimate the soluble component of the workroom aerosol."(1,p.147)

In 1997, ASTM released Method PS 42-97 for metalworking fluids.(2) This is a gravimetric/extraction technique that involves sampling MWF-contaminated air with a tared polytetrafluoroethylene (PTFE) filter, reweighing of the filter, and separation of MWF from co-sampled solid particulate via extraction of that filter using a ternary blend of toluene, methanol, and methylene chloride. The development of the ternary blend was described by Glaser in 1999;(3) an initial evaluation of the method was also described in 1999.(4) The analytical method, revised in 2004 to include not only extraction with the ternary blend but also a secondary extraction with a binary blend of methanol:water, has now been designated ASTM Method D-7049-04.(5) Documentation of laboratory-based performance studies of the revised method is provided in reference.(6) Because the development work for this method was conducted at NIOSH, it has released its own version of this technique as Method 5524.(7) Both the NIOSH and ASTM methods are functionally equivalent and are finding increased acceptance by the industrial hygiene community, for example, where co-exposures to insoluble particulate (e.g., welding fumes) and MWF occurs.(8) The sampling and analytical method(s) have been used to support a NIOSH survey of 79 metalworking facilities across the United States(9,10) and 21 NIOSH surveys of MWF exposures in machining operations. It is estimated that at least 2000 samples have been analyzed at NIOSH using NIOSH Method 5524. Recently, the NIOSH/ASTM methods were adopted by and incorporated into the French Institut National de Recherche et de Sécurité (INRS) methods manual.(11)

Although ASTM currently includes Method D-7049-04 as a standard method, it recognizes that the technique has not been fully validated because it has not yet been performance tested. ASTM grants *full* recognition only to methods that have been performance evaluated by multiple laboratories. Major concerns with the use of the NIOSH/ASTM methods include the following:

- Significant changes in the weights of blank filters during transit and storage may elevate the limits of detection and quantitation and may result in otherwise useful data being discarded.(10)
- Previous laboratory evaluations of the MWF analytical methods have been performed using spiked samples, that is, samples in which a bolus of MWF dissolved in the ternary blend was delivered onto filters. In at least four reports(4,6,12,13) significant losses of *spiked* MWF samples have been indicated or reported as a function of storage time
- Previous investigations of the performance of the methods(4,6,9,12,13) represented results obtained by single labs only. Much better estimates of the bias and precision of the methods as well as the limits of detection (LOD) and quantitation (LOQ) are likely to be obtained from a multilaboratory comparison of results.

In this article we present the results of a multilab evaluation of the methods, which included the following:

- A preliminary, blank stability study conducted to evaluate the intra- and interlaboratory gravimetric and extraction variability of the blanks and to estimate multilab LOQs.
- The calibration of a synthetic atmosphere generator of aerosolized MWF with a laser particle counter; this permitted reproducible deposition of quantities corresponding to those collected in an 8-hr sample at either of the NIOSH recommended exposure limits (RELs) of 0.4 mg/m^3 (thoracic particulate) and 0.5 mg/m^3 (total particulate).
- Performance testing of six laboratories for analysis of synthetically generated MWF aerosol samples. From this data, multilab estimates of the limits of detection and quantitation, and the sampling and analytical methods bias and precision were obtained.
- Follow-up performance testing of three laboratories for analysis of synthetically generated MWF aerosol samples. This study was conducted to further evaluate one of the six original labs that reported concentrations that were lower and significantly less precise than the other labs. This lab was retested against the NIOSH lab and a seventh check lab.
- A discussion of factors affecting the stability of MWF samples.

EXPERIMENTAL

Samples and Standards

All laboratories were required to use solvents that were analytical grade or higher. All laboratories used Omega brand 2 μm, 37-mm polytetrafluoroethylene (PTFE) filters (SKC Inc, Pittsburgh, Pa.). A semisynthetic MWF (Clearedge 6519, Castrol Inc., Downers Grove, Ill.) having approximately 30–35% naphthenic oil content and 40% water content was used as the test fluid.

Preliminary Blank Study

The NIOSH Cincinnati laboratory was the staging point for this study. Each of the participating labs provided 20 tared blank samples to the NIOSH lab, where they were stored for 2 weeks and then returned to the originating labs. These blanks were analyzed for total weight and for extractable weights within 2 weeks of receipt using the revised NIOSH/ASTM methods.

Sample Generation

Generator Construction

A generation system that had been built for the production of solid aerosols(14) was modified to produce liquid MWF aerosols. A diagram of this system is shown in Figure 1. High-pressure air, 21 psi (144.8 kpA) (A) was passed through a Collison nebulizer (model C-27; BGI Inc., Waltham Mass.) (B) to produce a stream of aerosol. To mitigate problems with adiabatic cooling and formation of significant levels of precipitates of higher molecular weight MWF components

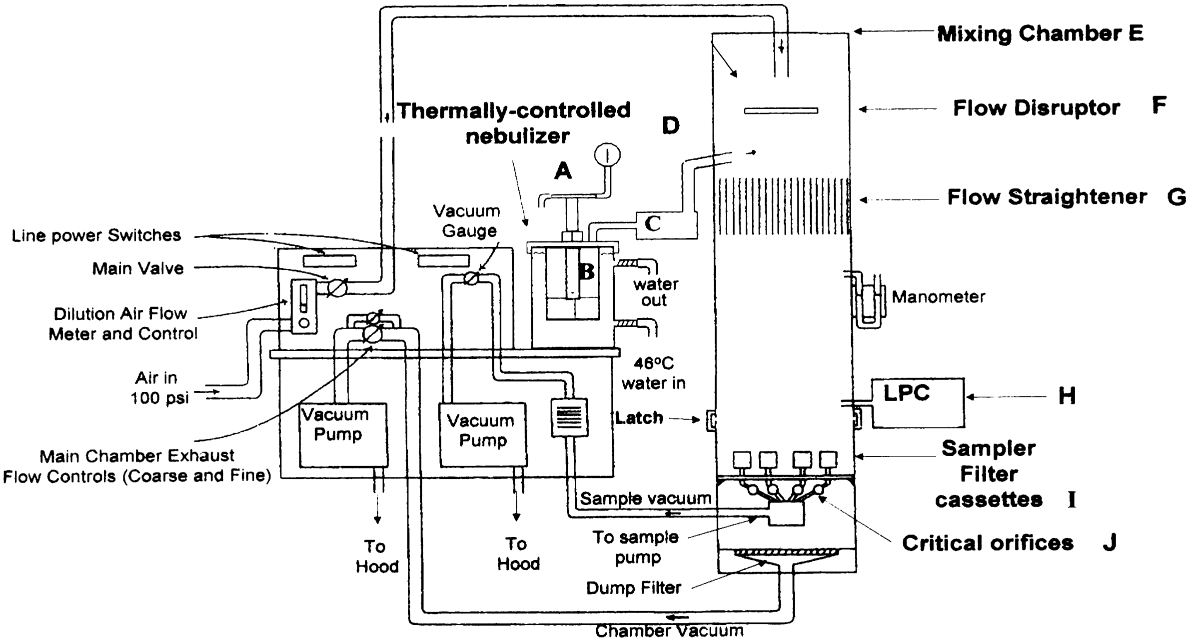

FIGURE 1. Aerosol sampling assembly for generation of aerosols of MWF. See Carsey[14] and Experimental section for details of the operation of the generator.

during aerosolization, the nebulizer was thermally jacketed with a leakproof plastic cylinder connected to a water bath that circulated water at constant temperature (46°C) around the nebulizer housing during operation.

From the nebulizer, the aerosol then passed through a large particle dropout zone (C) to a heated copper pipe (D) and was transported into a 1 ft (0.3 m) diameter × 8 ft (2.44 m) long cylindrical mixing chamber (E), where it was diluted with air supplied at ~ 400 ft^3/hr (11.3 m^3/hr). Flow was disrupted by a metal plate at (F) in the mixing chamber. A 1 ft (0.3 m) diameter × 4 inch (10.2 cm) thick section of metal aviation honeycomb was provided at point (G) to provide laminar airflow. Diluted samples of the airstream were obtained at point (H) using a laser particle counter (MDL 217A; Met One Inc., Grants Pass, Ore.) capable of monitoring the number of particles $\geq$500 nm generated.

Samples were collected at 2 L/min at the bottom of the mixing chamber by mounting sampler cassettes (I) on an 18-port sampling manifold. Flows through each port in the manifold were controlled by critical orifices (J) dedicated to that port. The critical orifices were connected to a central manifold that in turn was connected to a series of tandem sampling pumps (Gast, Benton Harbor, Mich.).

Sampling

For all performance testing, each laboratory submitted sample cassettes and blank samplers to the NIOSH labs where the samples were generated. For the six-lab performance testing, each of the six participating labs submitted 16 tared samples, 12 for sampling and 4 to be used as blanks. A total of 72 samples were collected in four sets of 18 sample batches. Three samples for each lab were collected in each 18-sample batch. All samples were assigned positions on the sampling manifold using a randomization procedure. Samples were collected at nominal flow rates of 2 L/min for ~140 min to collect approximately 280 L. Each time that a set of 18 samples was collected, one blank cassette from each lab was opened and closed (four blanks for each set of 12 lab samples). All samples and blanks were shipped back to the labs with instructions to keep them refrigerated until analysis. Using tracking information provided by the overnight delivery service, it was determined that all samples had arrived at the participating laboratories within ~24 hr of their shipment from the NIOSH labs.

A further performance test of the method compared data from one nonconsistent lab in the initial six-lab survey with a new lab (Lab 7) and to Laboratory 5, which acted as a control lab in this evaluation. Each of the three participating labs submitted 18 tared samples, 12 for sampling and 6 to be used as blanks. A total of 36 MWF samples were collected in two sets of 18-sample batches. Six samples for each lab were collected in each 18-sample batch. Each time that a set of 18 samples was collected, three blank cassettes from each lab were opened and closed. Samples were collected at nominal flow-rates of ~2 L/min for approximately 120 min (240 L) . All samples were assigned to positions on the 18-port manifold of the generation system using a randomization procedure.

Sample Analysis

Blank Study and Six-Lab Performance Study

All samples were refrigerated on receipt at each of the participating laboratories. All samples were kept refrigerated

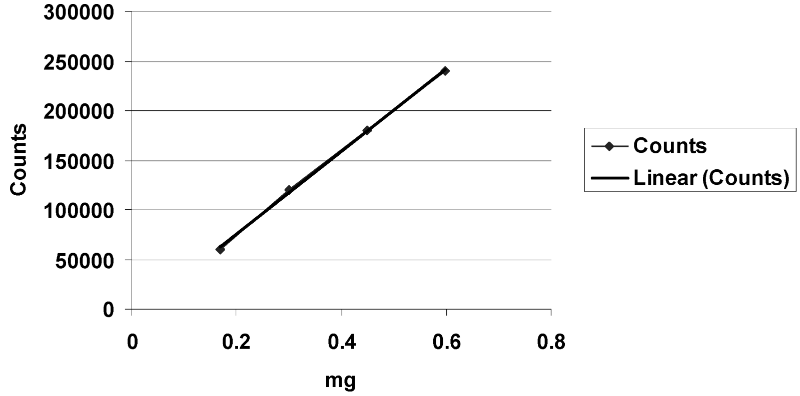

FIGURE 2. Calibration curve of total particulate count versus mass of MWF sampled.

until they were analyzed. During the analysis, the sample cassettes were initially opened and placed in a desiccator for 2 hr; then the filters were equilibrated in each participant's weighing room for 1 hr prior to determination of their weights. All measurements of the total weights of the samples were completed within 7 days of receipt. All extractable weight measurements were completed within 14 days of receipt. All data were entered into customized electronic spreadsheets supplied to each lab, allowing recording of the tare weights and postsampling and postextraction weights and the dates of receipt and analyses. All data were reported to the nearest microgram. All measured aerosol masses were blank corrected using the appropriate field blanks.

Three-Lab Follow-Up Performance Test

The samples were all collected on a single day and shipped to the participants via overnight delivery service. Tracking information provided by the overnight delivery service indicated that all samples had arrived at the participating laboratories within 17 hr of their shipment from the NIOSH labs. To eliminate any time effect of storage, the participants were instructed to analyze the samples the day that they were received. The sample cassettes were opened, placed in a desiccator for 2 hr, and then the filters were equilibrated in each participant's weighing room for 1 hr prior to determination of their weights.

After the initial weighing, each filter was placed back into the outlet half of the cassette and the inlet half of the cassette reassembled over the outlet half. To further prevent dust from settling on the filters, the inlet and outlet ports were capped. The cassettes were stored in the weighing rooms at ambient temperatures. The samples were reweighed at 3 days and 7 days postgeneration. No extractions were performed. All measured aerosol masses were blank corrected using the appropriate field blanks.

RESULTS AND DISCUSSION

Evaluation of the Generation System

The generation system (Figure 1), originally developed for the generation of solid aerosols,(14) was modified to produce liquid aerosols by nebulizing solutions of MWF. A unique calibration procedure was developed to reproducibly deposit known masses of MWF aerosol on the filters. This technique involved monitoring the generator output with a laser particle counter (LPC) that had been calibrated in several previous runs against masses of the study MWF deposited on filters.

A typical calibration curve comparing the masses deposited on filters with the particle counts of the LPC is shown in Figure 2. The coefficient of determination (R^2) was ≥ 0.97. In preliminary runs, where approximately 80 samples were generated, samples weighing from 0.4 to 0.5 mg (masses of MWF expected at either of the NIOSH RELs for a full-shift sample) could be deposited on filters with ~7–10% precision. Thus, this technique provided an accurate and precise technique for depositing known quantities of MWF aerosol on the filters.

Analyses of Blanks: Determination of the LOQ

The results of the analyses of the initial set of 20 blanks, obtained in the preliminary study from each of the six participating labs, are presented in Figure 3A for the total weight analyses and in Figure 3B for the extracted weight analyses. The limits of quantitation (LOQs or 10 times the standard deviation of the blanks) provide a more realistic lower useful limit for the method than the limits of detection (LOD or 3 times the standard deviation of the blanks). Using techniques described by Kennedy et al.,(15) the standard deviations of each lab were pooled across all of these labs to estimate LOQs of 0.094 mg and 0.136 mg, respectively, for the total and extracted weight procedures.

A similar analysis of the blank data obtained from the *six*-lab performance evaluation study yielded estimates of the LOQ for the total and extracted weight procedures of 0.064 mg and 0.067 mg, respectively. Analysis of the blank data obtained from the *three*-lab performance study produced estimates of the LOQ for the total weight procedure of 0.133 mg.

The variability in LOQs from lab to lab and from study to study computed here deserves comment. These estimated LOQs are comparable to those reported.(4,6,10,13) The best estimates of the LOQ for the method are likely to be obtained

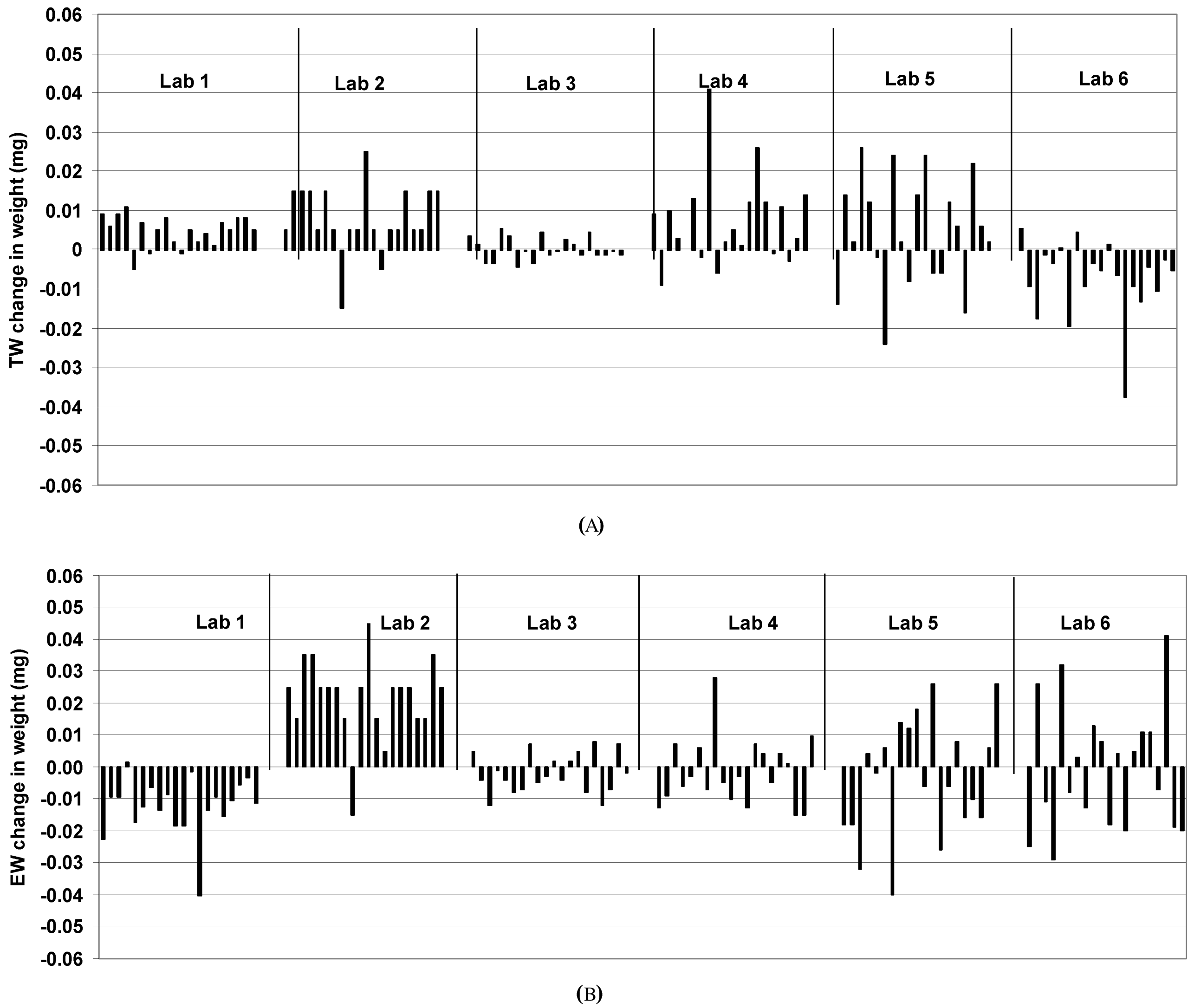

FIGURE 3. (A) Results of analysis of blank samples by six labs for estimation of the LOD and LOQ of the total weight. Blanks are media blank corrected. Twenty samples were analyzed by each lab. (B) Results of analysis of blank samples by six labs for estimation of the LOD and LOQ of the extracted weight. Blanks are media blank corrected. Twenty samples were analyzed by each lab.

from multiple laboratories analyzing multiple blank samples that have been subjected to the rigors of shipment. The above cited references provide estimates of the LOQs that were determined by single labs; not all studies involved transport of samples. The two six-laboratory studies described here may thus provide the best estimates of these parameters, since they were computed using data from multiple laboratories that analyzed a large number of blank samples. Of the two, the 20-sample blank run analyzed by each of six labs in the preliminary run should thus provide the most conservative and more realistic set of estimates.

If weighing imprecision is the only source of analytical variability, these LOQs should permit 8-hr monitoring of concentrations as low as 0.1 mg/m^3 for the total weight measurements and 0.14 mg/m^3 for extracted weight (MWF) measurements. However, it may be necessary to consider sampling imprecision as well as other sources of analytical variability, for example, sample losses during storage, in establishing the lower useful limits of the method.

Analysis of Generated Samples

Six-Lab Comparison

The results of the analyses of the actual generated aerosol samples by the six laboratories are presented in Figure 4A for the total weight samples, and in Figure 4B for the extracted weight samples for each of the six participating labs. The level of precision associated with the total weight analyses (0.02 to 0.20 including Lab 1, or 0.02 to 0.13 excluding Lab 1) corresponds to that expected from our preliminary calibration results of 0.07–0.10 for the total weight analyses.

These data were evaluated according to statistical techniques described by Kennedy et al.;(15) the precision (or

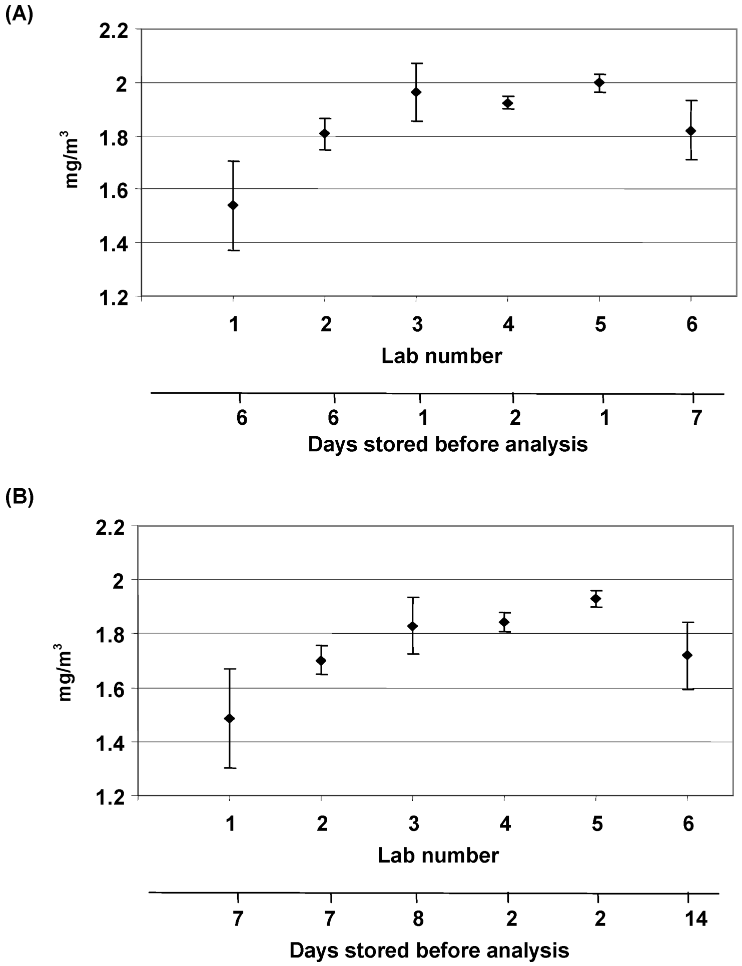

FIGURE 4. (A) Concentrations (mg/m^3 ± 95% CI) for the total weight Analyses from the six-lab performance study. Each point for each lab represents the mean of 12 samples. (B) Concentrations (mg/m^3 ± 95% confidence intervals) for the extracted weight analyses from the six-lab performance study. Each point for each lab represents the mean of 12 samples.

coefficients of variation) were determined to be 0.13 (0.09 excluding Lab 1) and 0.13 (0.09 excluding Lab 1) for the total weight and extracted weight methods, respectively.

Comparison of the ranges reported above for each laboratory, and to the ranges of 0.04 to 0.06 for total weight measurements and 0.04 to 0.05 for extracted weight measurements reported by Glaser et al.(4,6) and Harper(13) must be made carefully. The current estimates include both the intra- and inter-laboratory precision, whereas the previous estimates were for single laboratories only (intra-laboratory); those estimates were also made for spiked samples.

The results reported here also include the effect of storage prior to analysis. All participating laboratories were instructed to complete the initial gravimetric analysis within 7 calendar days of receipt. However, only Labs 1, 2, and 6 stored the samples for more than 2 days. Though Labs 2 and 6 stored their samples for 6 and 7 days respectively, they reported total weight concentrations that were respectively 17% and 18% greater than Lab 1, which stored samples for 6 days.

The mean concentration estimated by our calibration procedure for the four sampling sessions was 1.94 mg/m^3. From Figure 4A, the mean of the concentrations reported by each of the six participating labs was computed to be 1.84 mg/m^3; this implies an overall method bias of −5%. For the six laboratories, the estimated concentrations were 80% (Lab 1), 93% (Lab 2), 101% (Lab 3), 99% (Lab 4), 101% (Lab 5), and 94% (Lab 6) of the true mean generated concentration. To fully evaluate the performance of multiple laboratories, ASTM recommends the computation of the h and k consistency statistics; the h statistic is a measure of bias between labs; the k statistic is an indicator of homogeneity of intralab precision.(16) Computed values of each statistic for each lab are compared with critical values of either statistic to determine whether the results from a laboratory are consistent with those of the other test laboratories at the 99.5% level of confidence. The h and k parameters are plotted in Figure 5A for the total weight measurements, and in Figure 5B for the extracted weight measurements. These values have been pooled over all four sets of analyses by each of the labs. For the h statistic, Figure 5A indicates that no laboratory exceeded the critical (99.5% confidence limit) values of the data; thus, all labs were bias consistent. However, Figures 5A and 5B indicate that the computed k statistics for Lab 1 exceeded the 99.5% confidence limits and was thus precision-nonconsistent with the rest of the test laboratories for both sets of analyses.

The fractions extracted (FE, or extracted weight/total particulate weight) ±95% confidence limits for each lab are plotted in Figure 6. It is apparent that all of the MWF samples were quantitatively extracted by all labs, including Lab 1, which reported particulate masses for a few samples that were 58–72% of those reported by the other labs. For each lab tested, FE was no less than 0.94. The solubilities of at least 120 MWFs in the ternary blend have been tested; all but one were soluble.(7) The insoluble fluid (a synthetic fluid) readily dissolved in a 1:1 binary blend of methanol:water. The extraction efficiencies of MWF using this procedure compare well or exceed the extraction efficiencies of 83–95% reported previously by Glaser(4,6) and Harper.(13) This reflects the utility of the extraction solvent. The extraction data is much more precise (coefficient of variation [CV] = 0.025) than the reported concentration data shown in Figure 4. The fractions extracted data was tested using an analysis of variance technique, and there were no statistical differences in the fractions extracted among the six labs.

Three Lab Follow-Up Comparisons

The results reported by Lab 1 were lower and significantly less precise ($p = 0.05$) than the results reported by the other five labs for both the extracted and total weights. This laboratory appeared to have experienced problems with sample loss. MWF contains certain semivolatile materials (including water, lighter components of the oil fractions, monoethanolamine, and others); such materials may evaporate more readily depending on, for example, temperature, storage time, and humidity of the laboratory. To determine if this was the case,

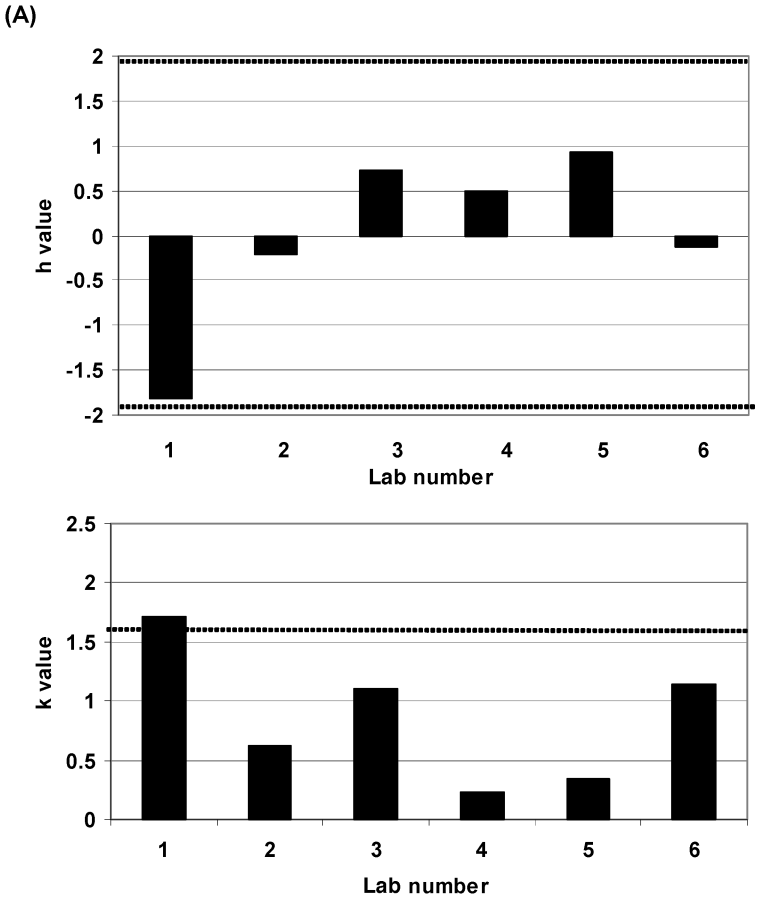

FIGURE 5. Computed h and k parameters for the total weight analyses for the six-lab performance study. The dotted lines in each graph denote the critical values (99.5% CI) for each statistic. Since the computed k statistic for Lab 1 exceeded the 99.5% CI of the data (dashed line), that lab was precision-nonconsistent See ASTM standard E 691–99(16) for details regarding the computation of these statistics. (B) Computed h (top) and k parameters for extracted weight analyses for the six-lab performance atudy. The dotted lines in each graph denote the critical values (99.5% CI) for each statistic. Because the computed k statistic for Lab 1 penetrated the 99.5% CI of the data (dashed line), that lab was precision-nonconsistent. See ASTM standard E 691-99(16) for details regarding the computation of these statistics. (*Continued*)

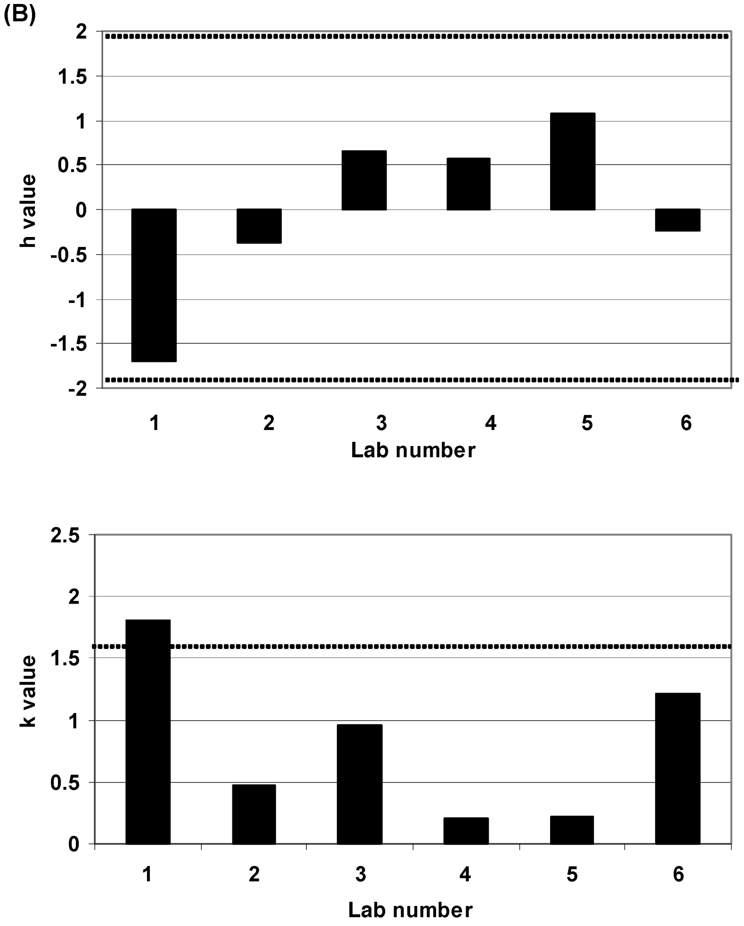

FIGURE 5. (*Continued*).

another performance study was undertaken to compare results obtained by Lab 1 with those obtained by a new laboratory (Lab 7) and Lab 5. In the follow-up test, the samples were stored under nonoptimal conditions (ambient temperatures and in open cassettes) in all three labs to determine whether weight decay occurred more readily at Lab 1 relative to the other labs. The results for all three labs for all 3 days are shown in Figure 7.

The results of the weighing experiments indicated that Lab 5 and the check Lab 7 reported very similar results. Lab 1 reported results that were more precise and accurate than those reported in the six-lab study; losses were ≤17% for any lab over the 7-day storage period. However, for each lab, each day's recovery differs statistically from that of other days. Estimates of the coefficients of variation of analysis of the total weight

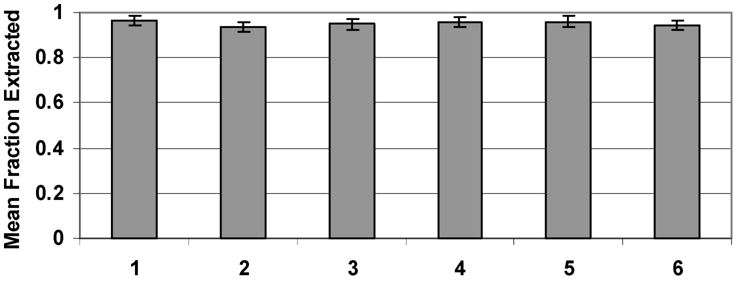

FIGURE 6. Fractions extracted (±95% CI) for each lab from the six-lab performance study.

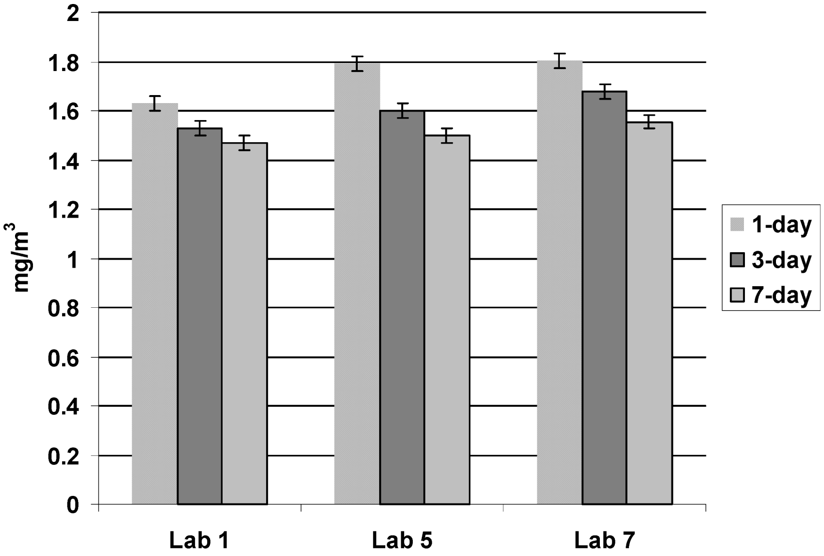

FIGURE 7. Concentrations (mg/m^3 [±95% CI]) for the total weight analyses from the three-lab performance study. Stored at ambient temperatures in cassettes unsealed to atmosphere.

samples (1-day storage only) for the three-lab study over all samples over all labs tested were also computed as above$^{(15)}$ to be 0.07 (or 0.045, excluding Lab 1).

The accuracy and precision of the analyses for the three labs were compared using the ASTM-recommended h and k consistency statistics. Comparing the 1-day data only, the critical value of the k statistic was not exceeded by any of the labs. However, the value of the h (bias) statistic for Lab 1 was at the critical lower limit for the data (computed Lab 1: h statistic = −1.15; critical value = −1.15). This marginally significant negative bias of Lab 1 largely reflects the high degree of agreement between Labs 5 and lab 7. If the lower initial masses reported by this lab had been due, for example, to higher temperatures or lower relative humidities or other factors, it might be expected that these samples would have exhibited a greater rate of sample loss than the two comparison labs. The slope of the decay curve for the Lab 1 results is actually less than that observed by the comparison labs. In addition, the recorded temperatures and relative humidities of all three labs were comparable. Thus, the reasons for the lower masses reported by Lab 1 are unclear.

Although there is no ready explanation for the lower results obtained by Lab 1, the information obtained in this study is still useful and provides significant support for the NIOSH/ASTM methods for the following reasons:

- These are suboptimal conditions of storage. After the initial weighing, the samples were stored at the ambient temperature and relative humidity of the weighing rooms, that is, they were not refrigerated. To mitigate dust contamination, each sampler was lightly reassembled with the filter and backup pad in place. However, the cassette was not recompressed shut and thus was not well sealed. Leakage could have occurred through the seams between the sampler halves.
- Even under these suboptimal storage conditions, the samples still retained 84–90% of the initial mass loading after storage for 7 days. Those experiments have been repeated in our laboratories under even less stringent storage conditions. Figure 8 shows a decay curve for nine filters loaded with ~0.4 mg of MWF aerosol; the samples were stored in an open face position (supported in the lower cassette half with no upper half in place) in a temperature- (~26°C) and humidity-controlled (35–45% RH) environmental chamber. This figure shows that the weight decreased by <20% after 2 weeks' storage; that is, the sample recovery still met minimum NIOSH requirements for storage under these suboptimal conditions.

Sample Stability Issues

The storability of MWF samples is an issue that deserves further comment. In the preparation of straight, soluble, semisynthetic and synthetic fluid quality assurance samples, our previous research$^{(10)}$ indicated significant differences between the amounts spiked onto the filter—based on density and the amounts found after the filters had been dried and then purged for 8 hr. The differences were especially pronounced for semisynthetic and synthetic fluids. These results were attributed to the fact that the spikes, made by dissolving the test MWF in the ternary solvent, contained substantial amounts of water that was also metered onto the filters. That water may be slowly lost as it evaporates from the filter; hence there may be substantial losses of weight in such samples.

Weight loss will also occur as low molecular weight semivolatile components, including the lighter mineral oils, low molecular weight fatty acid components of synthetic

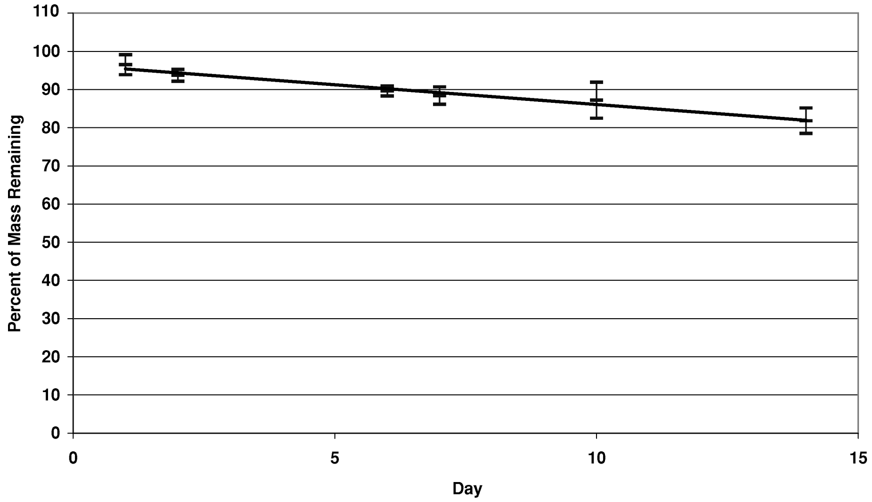

FIGURE 8. Percent remaining of 400-μg aerosol samples of the test semisynthetic MWF stored in an open-face cassette at ambient conditions for periods ranging from 1–14 days. Data follows equation: Percent remaining $= -1.167 \times$ day $+97.7$.

fluids,(17) and ethanolamines among other volatile compounds evaporate during storage. Glaser et al.(10) suggest that recovery of spiked MWF may be affected by the presence of volatile organics in the MWF, the mass of sample collected, and the duration and temperature of storage. Overnight transportation of MWF samples from point of origin to the laboratory, refrigeration of MWF samples immediately on receipt at the laboratory, and analysis of MWF samples as soon as possible after collection were recommended.

Such recommendations were also repeated in the work of Verma et al.,(12) who looked extensively at the storage of spiked samples of all four types of MWF. They concluded that samples should be shipped refrigerated or frozen and then refrigerated during storage and analyzed as soon as possible after collection. In Glaser et al.(10) and Verma et al. the samples were prepared by spiking a bolus of the MWF onto filters. The results presented in this article were obtained by loading filters with an aerosol of a semisynthetic MWF. The samples were not shipped refrigerated or frozen; they were, however, refrigerated during storage prior to analysis.

Although the samples were analyzed over a 7-day period, five of the six labs reported concentrations that were 93–101% of the mean concentration of 1.94 mg/m^3; even the one nonconsistent lab reported average concentrations that were within 20% of this mean concentration. In the 2-week sample storage study conducted in our laboratories, the mean weights following 1-day storage results were not statistically different from the initial sample weights. Because these samples were exposed to the ambient environment in unsealed containers, overnight shipment of samples in sealed but unrefrigerated cassettes is unlikely to result in significant sample losses.

It is reasonable that the weight of an aerosolized sample will stabilize much more readily than a sample produced by spiking a bolus of solvent-containing MWF onto a filter:

- *Spiked* samples can lose weight via two mechanisms. The first involves evaporative loss of the solvent(s) used to deliver the spiking bolus (generally, several microliters of the ternary blend in which small amounts of MWF are dissolved). Due to the high vapor pressures of the spiking solvent components, it is to be expected that this should be a relatively rapid process. As was pointed out in Glaser et al.,(10) a major component of water-soluble fluids is the water itself. A bolus of a water-based sample applied to a filter should penetrate the filter matrix forming an amorphous multilayered spot. Air will dry the surface layer of the bolus before the subsurface material. Water and other volatiles from the innermost layer(s) are likely to be removed at a much slower rate than the water on the surface. Trapped water molecules may only slowly pass through outer semisolid layer(s) and through the hydrophobic PTFE filter matrix itself. That is, the drying bolus acts like a permeation device with water and other volatile materials slowly diffusing during storage and/or dessication. Previous results(10) for spiked samples have indicated that a synthetic fluid lost up to 70% of its weight (presumably as water) and that a semisynthetic fluid lost 60% of its weight (again presumably as water).
- *Aerosolized* samples may also lose small amounts of weight via evaporation. However, there is no solvent involved in application of such samples to the surfaces of filters. In addition, the surface area of an aerosolized MWF is many times greater than that of a spiked sample. Thus, an aerosolized sample will be air dried as it is collected on the filter due to the contact of this very large sample surface area with the ambient airstream being pulled through the sampler. This generally means that samples collected as aerosols will lose much less weight during storage than spiked samples. In addition, the aerosol sample may not penetrate the membrane surface as readily as a spiked bolus;

the relatively large volume of solvent is likely to facilitate the penetration by the spike.

The loss of straight MWF from filters during sampling has been a primary focus of study. Park et al.(18) compared the losses in weight of samples that had been loaded as an aerosol and purged with clean air. They reported losses of ≥30 % for both a light and a heavy fluid after 240 min of purging. They studied losses during both sampling and dessication. Generally, used oil samples lost less weight than their fresh oil counterparts. However, a high viscosity oil actually lost a greater percentage of its weight than a low viscosity oil. During desiccation, spiked filters lost ∼ 2–4 times the weight of filters that sampled aerosolized MWF. McAnneny et al.(19) have demonstrated that up to 35% of an aerosol of an unused straight fluid is lost during sampling itself; however, they did not study the loss of weight of the collected sample during storage.

It has also been shown that samples prepared from older fluids, purged of their volatiles, generally lost less weight than samples prepared from fresh fluids.(20) The makeup of the filter may also affect the concentration of mineral oils reported. Raynor et al.(21) developed a model that successfully predicted significant differences in trapping efficiencies for oil mist among several filter media for straight fluids; fluid viscosity is also important. Volckens et al. generated atmospheres of straight(22) and soluble and synthetic fluids(23) at ∼ the 0.5 mg/m^3 and 5 mg/m^3 levels and measured those concentrations using an electrostatic precipitator (ESP) and several conventional filters. Generally, PTFE filters produced results that were most comparable to the ESP. The ESP was evaluated because it may be generally less prone to losses of semivolatile components than filters. For the synthetic fluid, the measured concentrations by all filters were comparable to those of the ESP at both test levels. For the soluble fluid, PTFE filters measured concentrations that ranged from 84% (low level) to 98% (high level) of those measured by the ESP. For the straight fluid, PTFE filters measured concentrations that ranged from 55% (low level) to 104% (high level) of those measured by the ESP. Volckens et al. attribute these differences to evaporation of semivolatile material from the filter. The straight fluid contained higher levels of semivolatile components (oils) than the soluble fluid, which contained higher levels of semivolatiles than the synthetic test fluid.

Although Volckens et al. did not study storage of these samples, they provide significant evidence that the semivolatiles are stripped from the filters during sampling and may not be a significant issue during storage. However, the authors do point out that evaporation of the MWF aerosol from the filters at the higher test levels may have been reduced by the saturation of the test air with vapor. Simpson et al.(24) reported for spiked samples that mineral oils with viscosities of >18 cSt would be predicted to lose ≤5% of their total mass during sampling; they did not study the stability of stored samples. Presumably such considerations would extend to storage of such samples.

The MWF employed in this study contained a substantial amount (30–35%) of severely hydrotreated moderate-to-heavy naphthenic oils, triethanolamine (unspecified levels) and ∼40% water. To nebulize that fluid, it was necessary to reduce its viscosity by diluting it further with water (to ∼1.6% v/v). Thus, the generated atmosphere contained a substantial amount of water both as MWF-entrained aerosol as well as in the vapor phase. In spite of the large amount of water in the challenge atmosphere, the apparent stability of the samples indicated that they had been purged of a significant proportion of water (and other volatile material) as air passed through the filter(s) during sampling.

In a previous study(10) using spiked samples, it was noted that water is a major component of the fluids. If the loss of water from these samples was the most significant reason for weight loss during storage, such losses may be of little health consequence. In fact, the NIOSH/ASTM analytical techniques include a dessication procedure to eliminate water. If major components such as lighter hydrocarbons, ethanolamines and other semivolatile components are being lost during sampling or storage (including desiccation), then the sampling and analytical technique is understating the exposure to these toxic components.

There may be thousands of formulations of MWF and it would be an extremely difficult task to evaluate the sampling, analysis, and storage of even a small fraction of them according to the ASTM performance testing procedures. In addition, there are many permutations of possibilities for mixed exposures to multiple MWF as well as to solid particulate matter. The results presented here suggest that aerosolized samples of a water-based fluid will lose significantly less weight during storage than might be expected from samples prepared as spikes alone, that is, compared with the results in Verma et al.(12)

Straight fluids collected on filters will also likely be stripped of semivolatile materials to some degree. This may bias the method since the sampling procedure will underestimate that proportion of the aerosol due to semivolatile components. However, the strict precautions relative to refrigerated/frozen transport of samples recommended by Verma et al. may be unnecessary, since those components of the sample may have largely evaporated during sampling.

CONCLUSIONS

A study of the performance of six labs to analyze MWF using NIOSH Method 5524/ASTM Method D-7049-04 was conducted. Best estimates of the LOQs were obtained from a preliminary analysis of 20 blank samples by each lab. The LOQs for the total and extracted weight analysis were 0.094 mg and 0.136 mg respectively. For the six-lab study, the method coefficients of variation were estimated to be 0.13 for total weight analyses and 0.13 for the extracted weight analyses. In this study, one lab reported concentrations that were 19% lower and less precise (CV = 0.20) than the average results reported by the five other labs. On average, the bias of the method was estimated to be –5%.

The data from all six labs were evaluated by computation of the ASTM-recommended h and k consistency statistics, which are measures respectively of the bias and precision of the technique. The calculated h statistic indicated that the nonconsistent lab was *not* significantly biased relative to the other five labs; however, the computed k statistic indicated that this lab's results were significantly less precise than the other five labs.

Whereas this study generally indicated that samples analyzed within 7 days of collection should be quantitatively and precisely recovered, a follow-up study was conducted comparing the one nonconsistent laboratory with two other labs. In the second study, the nonconsistent lab improved its results such that it was within 10% of the results reported by the other two labs.

However, the h statistic indicated that its bias was marginally statistically significantly lower than the other two labs. The computed k statistic indicated that this lab was now precision consistent. The finding of a statistically significant negative bias by this lab may reflect the high degree of agreement between the comparison labs.

Although this one laboratory did experience problems, there was no demonstrable overall bias to the analytical method. The three-lab follow-up study also indicated that recovery was quantitative for samples stored at room temperature in cassettes that were sealed only to prevent deposition of dust—conditions that should be suboptimal for storage. For the three-lab study, the analytical method coefficient of variation was estimated to be 0.07 for the total weight analyses.

In a separate storage study, 97% of the mass of samples of the test MWF aerosol were recovered following storage for 24 hr on filters in open cassettes at ambient conditions; the weight decrease was not statistically significant. It is likely that the high surface area of an aerosol sample relative to a spiked sample will facilitate much greater drying of that sample during collection and mitigate weight losses during shipment as well as storage. For sample transit times $\leq$24 hr, these results do not appear to support freezing or refrigeration of samples during shipment.

However, refrigerated transport may be prudent for extended transit times or when ambient temperatures are very high. In addition, samples should be refrigerated as soon as they are received by the laboratory. The loss of MWF aerosol from filters during *sampling* as well as during *storage* is an area that warrants further research. Techniques to mitigate the losses of such materials, for example, improved sample collection and/or storage techniques, may also require further investigation. This study should foster confidence in the ruggedness of the analytical procedure and provide support for consideration by ASTM as a fully validated standard.

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