

**BACKUP DATA REPORT
NIOSH Method No. 5524**

Title: Metalworking fluids

Analyte: Metalworking fluids

Author/developer: Robert Glaser

Date: Oct 30, 2013

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NMAM Method No 5524
Analyte: Metalworking fluids (MWF)
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Substance: metalworking fluids (MWF)

Exposure Limits: Exposure to certain MWFs has been related to occupational asthma, hypersensitivity pneumonitis (HP), and possibly to cancer. NIOSH recommends that exposure to metal working fluids (MWF) be maintained at < 0.4 mg/m³, measured as thoracic particulate or < 0.5 mg/ m³ measured as total particulate.

Metal working fluids (MWF) are primarily formulated to remove metal debris from the work surfaces of metal parts that are being turned, ground, milled or drilled; they also provide lubrication and cooling to the work piece and to the work tool. These fluids are also used to cool and lubricate in cold metal-forming operations such as stamping, punching, hobbing or drawing [1].

There may be as many as 600 compounds in MWF, including mineral oils, emulsifiers, water, alkanolamines, polyethoxyethanols, biocides, surfactants, chlorinated paraffins and boron compounds. Despite the complexity of their formulations, they are generally classified into four categories according to the amount of mineral oil that they contain. Straight fluids contain essentially 100 % mineral oils and/or other organic additives but no water. Soluble fluids contain large amounts of mineral oil (up to 80%) and emulsifying agents to form emulsions when mixed with water. Semi-synthetic fluids contain surfactants to dissolve relatively small amounts of mineral oil (5-30%) and are soluble in water. Synthetic fluids contain no mineral oil and are soluble in water [2].

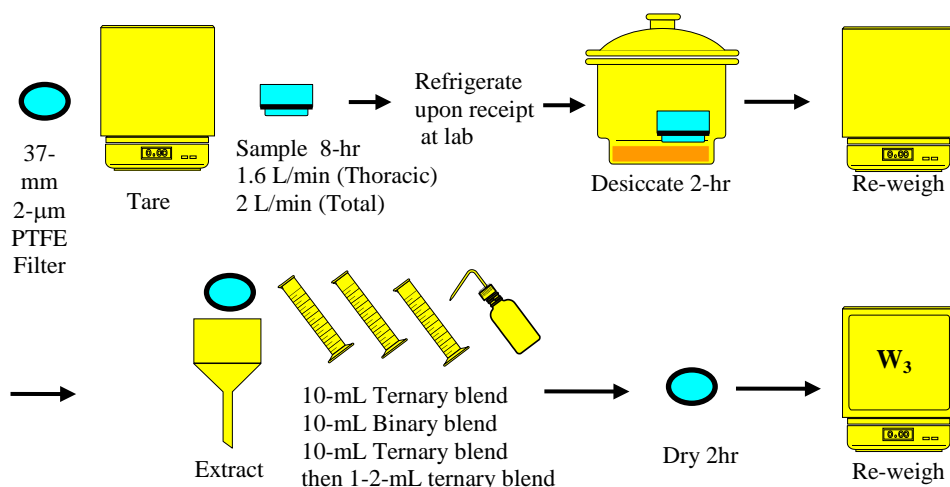
Chemicals Used for Evaluation: Samples of metalworking fluids for the spiking tests were obtained from Cincinnati Milacron Chemical Corporation (Cincinnati Ohio, USA) and Solutia Inc., (St Louis, Missouri). The dichloromethane, methanol and toluene used in this study were distilled-in-glass (DIG) grade and obtained from various sources by contractors performing the performance tests. Distilled/deionized water from in-house sources was also used.

Synopsis

In areas of the USA where there are metalworking facilities in rural areas, agricultural debris may be a significant source of interference, especially during planting and harvest times. There may also be background dust levels due to in-plant construction. Furthermore, urban ambient particulate levels as high as 0.1 mg/m^3 have been reported by the EPA in US cities [3]. Furthermore, there may be significant levels of metal particulate generated during many metalworking processes, in particular, during welding operations.

For these reasons, NIOSH adapted ASTM method PS-42-97 [4] for metalworking fluids to support the standard. Using this procedure, MWF is extracted and separated from co-mingled background particulate using a ternary blend of equal parts of dichloromethane, methanol and toluene [5,6]. A later extraction using 1:1 methanol:water was added for a single fluid (Solutia) that was found to be insoluble in the ternary blend [7]. In this way, exposure to MWF *only* is determined. NIOSH has designated this as NMAM Method 5524. The analytical procedure is described graphically in Figure 1 below.

Figure 1. Measurement of MWF using NMAM Method 5524. (1st line) The filter is tared (W_1). Sampling is conducted as indicated; samples are refrigerated during storage, then desiccated prior to weighing (W_2). (2nd line) The filter is extracted using the ternary (1:1:1 dichloromethane:methanol:toluene) and binary (1:1 methanol:water) blends, dried and reweighed (W_3). Total weight, $W_T = W_2 - W_1$; MWF is measured as Extractable Weight, $W_E = W_2 - W_3$; and the fraction extracted, $FE = W_E/W_T$.



Analytical Aspects

Extraction

Using the method described above, the filters are extracted in a specially designed filter funnel. The funnel uses no frit, but a photo etched stainless steel screen to support the filter. The funnel has been designed with a precisely-machined narrow circular lip at the base of an upper heavy stainless steel weight to engage the 37-mm sampling filters. When inserted into the funnel base, it mimics the way the inlet sampling cassette component engages the perimeter of a filter contained in the outlet sampling cassette component. In this way, the same narrow perimeter around the filter (that is unexposed to sample flow) is engaged and only the sampling surface of the filter is available for extraction. That screen does not plug and even if damaged, is replaceable. A graphic of this funnel is shown in Figure 2.

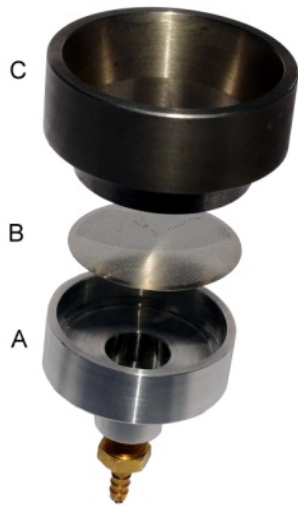


Figure 2. Filter funnel consists of (A) a 37-mm ID X 28 mm long aluminum body with hose barb to connect to a vacuum extraction flask. This body retains (B) a 37-mm photo-etched stainless steel screen support for the PTFE filter to be extracted. A 25-mm long X 50-mm OD (upper section) X 37-mm OD (lower section) heavy stainless steel funnel spout (C) holds the PTFE filter (not shown) in place against the 37-mm photo-etched screen. Completely assembled, the device is ~ 73 mm long.

Filter Pretreatment

Recent problems with high background contamination on the filters have necessitated use of a pretreatment technique for the filters. This was developed under contract to NIOSH and is given as Appendix 1 in the revised method. It is also given in this report as Appendix [1]. The cleanup procedure has been used in several recent sequences (sequences 11525-CA, -CC, and -CG) for analysis of MWF. LODs and LOQs of 30 µg/sample and 90 µg/sample respectively have been reported [8].

Gravimetry

All gravimetric analyses were carried out using a Mettler Mdl MT 5 six-place balance. Filters were conditioned for 2 hours in a controlled humidity/temperature chamber. While it is assumed this standard procedure of a 2-hr desiccation would stabilize weights and remove water, the efficacy of the step was not measured. They are then weighed by first passing them through a ^{210}Po source to neutralize static charges. MWF content is determined by further extracting, drying and then re-weighing the filters.

Specificity

This technique is specific to MWF as a group only. The criteria document specifies that only exposures to the total mass of MWF are to be considered. Tests (see below) have shown that the extraction regimen can remove all four classes of MWF. This permits the MWF to be separated from miscellaneous solid particulates such as machining swarf, welding fumes, agricultural debris, and construction dust, etc.

Solvent Development

This method involves determination of the total/extractable weights of MWF samples; extractions are performed using a 1:1:1 blend of toluene:dichloromethane:methanol and a 1:1 blend of methanol:water. The development of the ternary solvent for nine (9) test fluids of MWF is described in reference [5]; the initial evaluation of the ternary blend with spiked MWF samples is described in reference [6]. The use of this solvent was validated during a survey of 79 US plants for exposures to MWF [8,9]. The fluids encountered in this survey are listed in Appendix 2 of this report. Of 122 fluids encountered, only one (Solutia) was found to be insoluble in the ternary blend. Solutia was found to be soluble in the binary solvent blend of methanol:water. The binary blend was therefore added to the extraction regimen. The more comprehensive evaluation of this extraction regimen is discussed below under 'Spiking Experiments.'

Samples of all MWF samples encountered were tested for solubility in the ternary solvent blend by injecting 50-uL aliquots of the pure MWF into the ternary blend [9]. All fluids encountered in that survey are listed in Appendix 2 of this report; all were soluble except for Solutia.

Method Evaluation

The method has been subjected to significant rigorous evaluation [5, 6, 8, 9,10]. Validation has included 'spiking experiments' with the ternary blend only to extract 4 test fluids of MWF [6] and with the combination binary/ternary blends to determine accuracy, precision, robustness, stability, and limits of detection and quantitation for 5 test fluids of MWF (including Solutia) [10]. The results of the analyses of these 5 test fluids using the combination ternary and binary blend are presented below. The method was further validated according to ASTM standard E 691-99 specifications in a 'six-laboratory round robin evaluation [11].' These samples were obtained from synthetic atmospheres of an aerosolized test MWF in air. These results are discussed below as well.

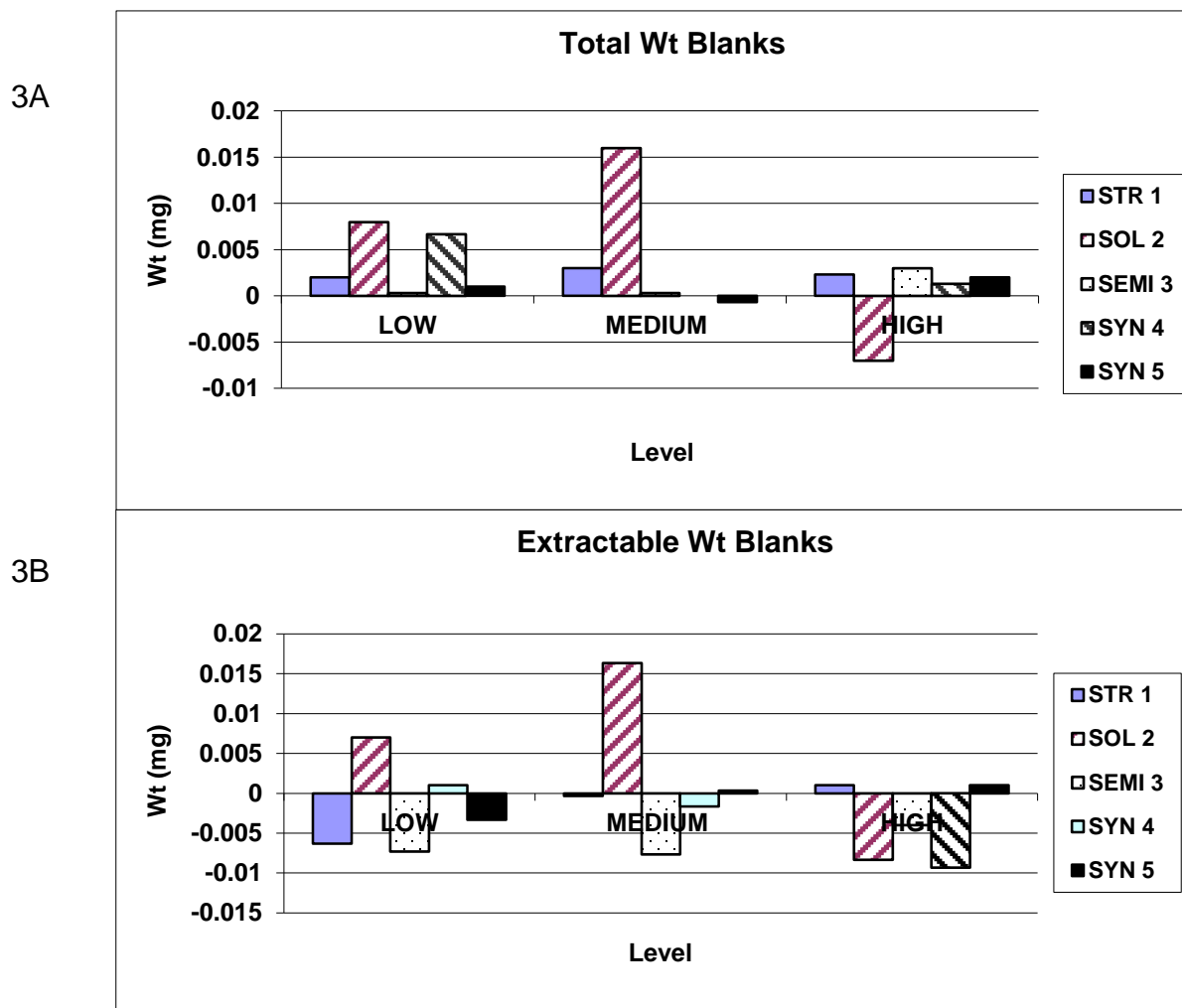
Spiking Experiments

The accuracy and precision of the analysis of MWF were initially estimated by spiking separate sets of PTFE filters with aerosolized aliquots of the four types of conventional MWF (STR 1, SOL 2, SEMI 3, and SYN 4) contained in the ternary blend. An additional filter set was spiked with a synthetic fluid (SYN5), dissolved in methanol:water. MWF extraction efficiencies were studied over four different concentration levels and results are described in detail below.

LOD/LOQ

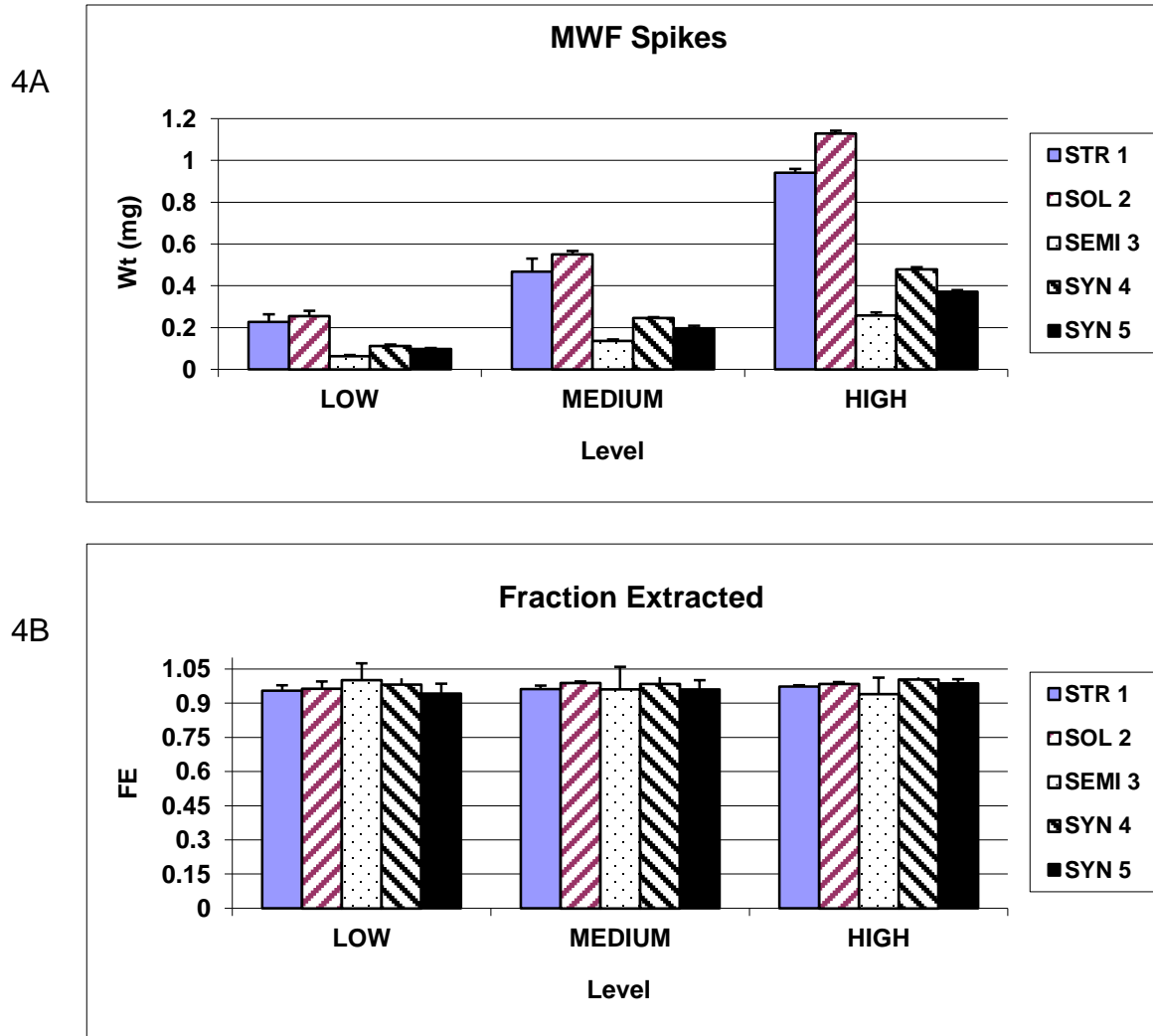
Spiking experiments were carried out by metering known volumes of MWF in the ternary or binary solvent blends onto filters. Therefore, blank PTFE filters were spiked with identical volumes of the neat ternary blend or binary blends to exactly replicate production of the samples. Samples were spiked with the ternary delivery solvent at 3 levels; volumes ranged from 5-20 μ L of the solvent. These spikes were allowed to evaporate from each set of blank filters. The LODs and LOQs for total and extractable weights were then obtained by carrying these filters through NMAM Method 5524. The weights of these blanks are shown in Figs 3A and 3B below.

Figure 3A and 3B.



Limits of quantitation were determined to be 73 μg and 80 μg respectively for the total-weight and extracted-weight procedures. Since the volumes of solvent spiked varied by fluid, the blanks were assigned separately to each fluid. The masses of each sample spiked onto the filters are shown in Fig 4A. Samples were spiked at the following levels: straight: 230 - 940 μg , soluble: 260-1130 μg , semisynthetic: 64 – 260 μg , synthetic I: 110 – 480 μg and synthetic II: 90 - 372 μg . Following spiking, the samples were dried by storage for 24 hours. The fraction extracted at each level is shown in Fig 4B. On average, fractions extracted (weight recovered/weight spiked) for all fluids for all levels tested exceeded 94%.

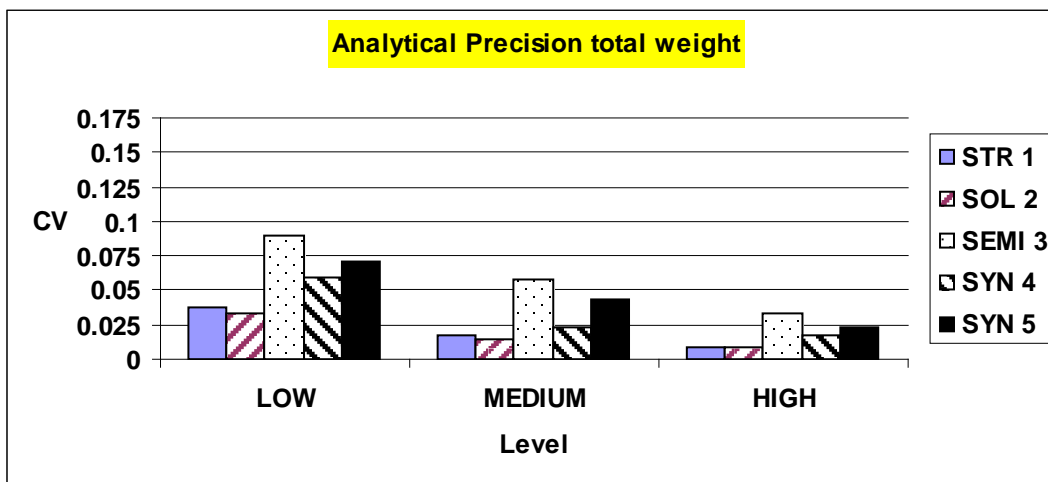
Figure 4A and 4B.



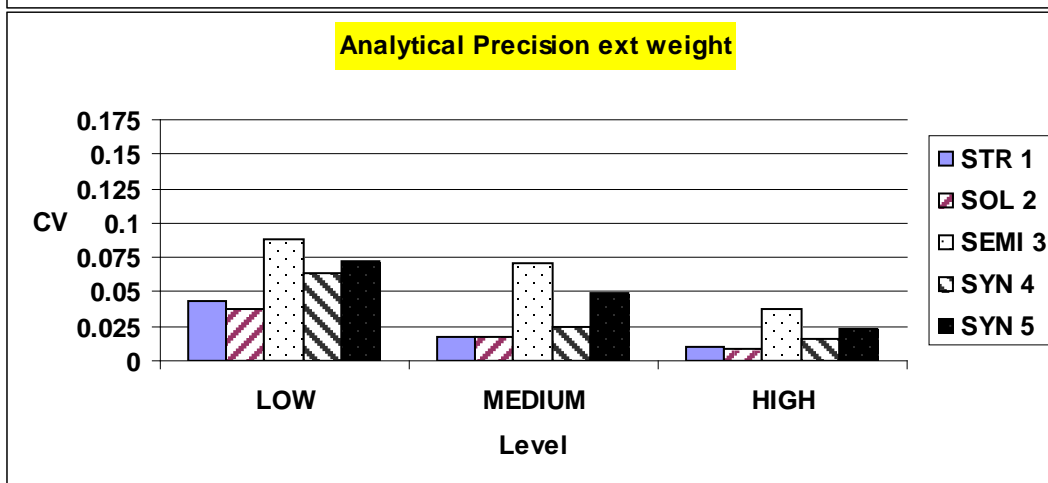
The precision of the analysis of the total weight samples are shown in Figure 5A; the precision of the analysis of the extracted weight samples are shown in Figure 5B. Note that the spiking error has been removed from these estimates using techniques described in NOTE 1 in reference 6. Pooled estimates of the coefficients of variation of analysis over all samples tested were 0.043 for the total weight samples and 0.046 for the extracted weight samples.

Figure 5A (top) Analytical precision of the method for total weight
 5B (bottom) Analytical precision for extracted weight.

5A



5B

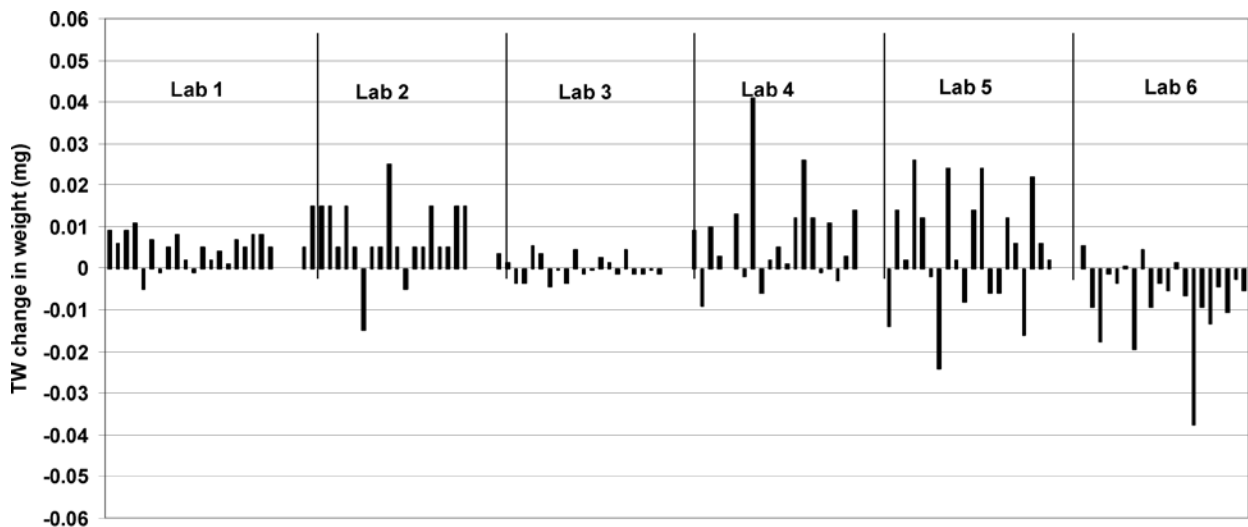


Six-lab performance testing of NMAM Method 5524 using dynamically-generated samples

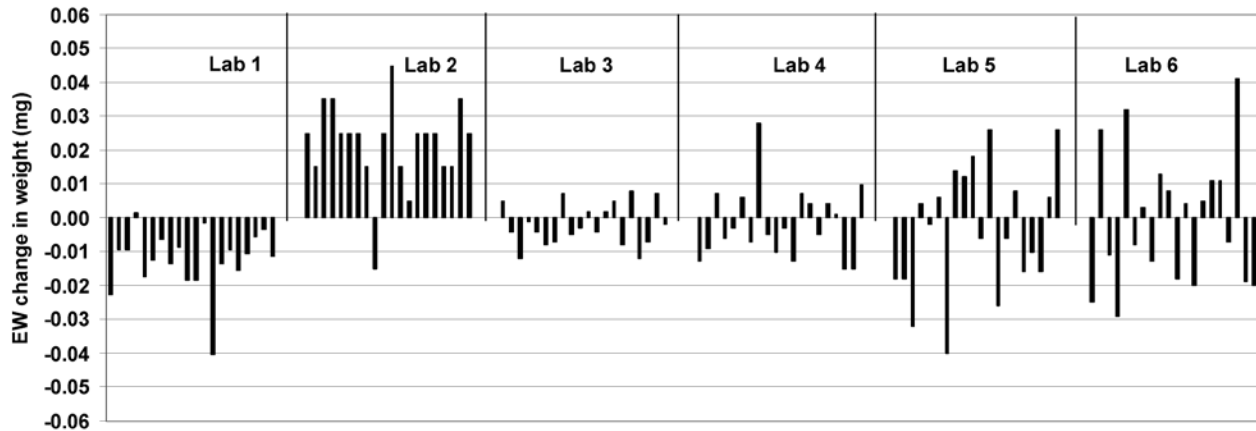
A performance test of NMAM Method 5524/ASTM Method D-7049-04 for analysis of metalworking fluids (MWF) was conducted [11]. These methods involve determination of the total and extractable weights of MWF samples; extractions are performed using a ternary blend of toluene:dichloromethane:methanol and a binary blend of methanol:water. Six laboratories participated in this study. Statistical evaluation of the data obtained was conducted according to the ASTM E691-99 inter-laboratory method comparison standard [12].

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). The results of these analyses are shown in Figs 6A and 6B below for each lab. 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 analysis.

Figure 6. Six-lab preliminary blank study:
(A top) Total weight (TW) blanks
(B bottom) Extractable weight (EW) blanks.



(A)



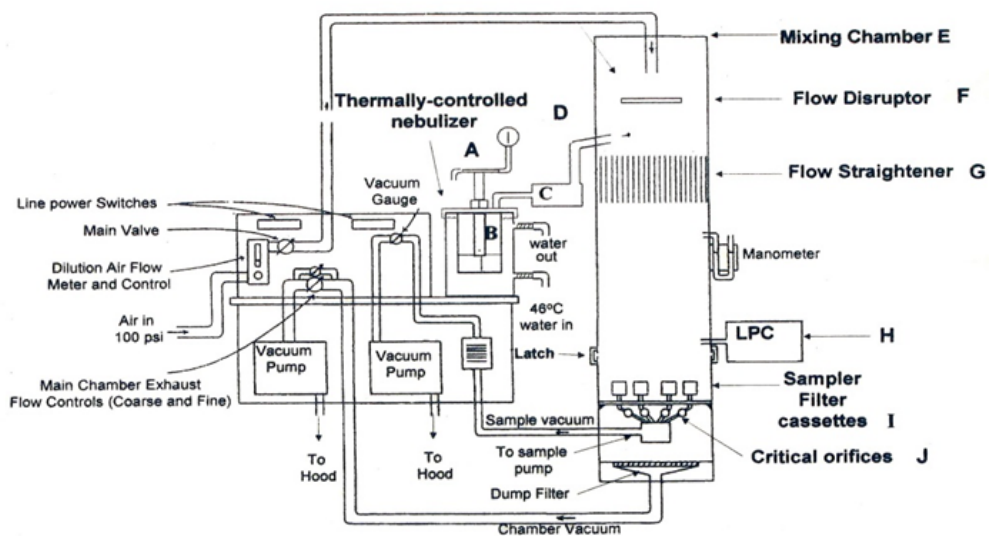
(B)

Dynamically-Generated Samples

Generator Construction

A generation system that had been built for the production of solid aerosols [13] was modified to produce liquid MWF aerosols. A diagram of this system is shown in Figure 7. High pressure air —21 psi (144.8 kPa) (A) was passed through a Collison nebulizer (model C-27, BGI Inc., Waltham, MA) (B) to produce a stream of aerosol. In order to mitigate problems with adiabatic cooling and formation of significant levels of precipitates of higher molecular weight MWF components 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 foot (0.3 m) diameter x 8 foot (2.44 m) long cylindrical mixing chamber (E), where it was diluted with air, supplied at around 400 cubic foot per hour (11.3 m³/hr). Flow was disrupted by a metal plate at (F) in the mixing chamber. A 1 foot (0.3 m) diameter x 4 inch (10.2 cm) thick section of metal aviation honeycomb was provided at point (G) to provide laminar air flow. Diluted samples of the airstream were obtained at point (H) using a laser particle counter (MDL 217A, Met One Inc., Grants Pass, OR) capable of monitoring the number of particles ≥ 500 nm generated. This permitted the same number of particles and therefore the same mass (~0.5 mg) to be deposited from run to run. Samples were collected at 2 Liter per 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 which in turn was connected to a series of tandem sampling pumps (Gast, Benton Harbor, MI).

Figure 7. Liquid Aerosol Generator

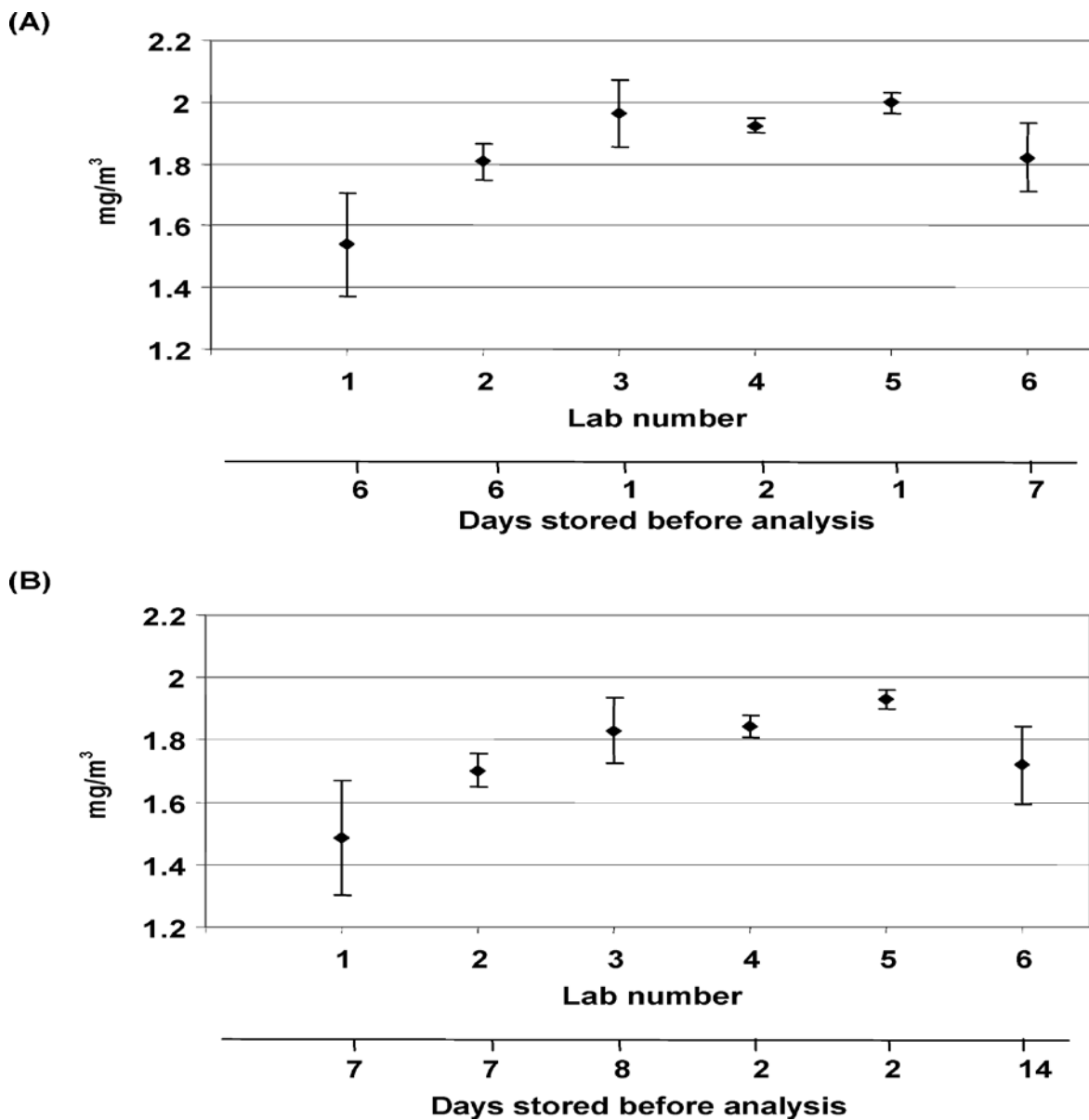


Dynamically-generated samples of a semi-synthetic MWF aerosol were then collected on tared polytetrafluoroethylene (PTFE) filters, distributed to the six participating labs and analyzed according to NMAM Method 5524 by all participants. Sample masses deposited (~0.4–0.5 mg) corresponded to amounts expected in an 8-hr shift at the NIOSH REL of 0.4 mg/m³ (thoracic) and 0.5 mg/m³ (total particulate). All sampling was conducted at approximately 2L/min. The generator output was monitored with a calibrated laser particle counter. The reported concentrations are shown in Figs 8A and 8B above. In this study, one laboratory (Lab 1) reported concentrations that were 19% lower and less precise (CV = 0.20) than the average results reported by the five other labs.

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 [12]. The calculated h statistic indicated that the nonconsistent laboratory (Lab 1) was significantly biased relative to the other five labs; in addition, the

computed k statistic indicated that this laboratory's results were significantly less precise than the other five labs. This study generally indicated that samples analyzed within 7 days of collection were quantitatively and precisely recovered.

Figure 8. (A) Concentrations ($\text{mg}/\text{m}^3 \pm 95\% \text{ CI}$) for the total weight analyses from the six-lab performance study. Each point for each lab represents the mean of 12 samples. (B) Concentrations ($\text{mg}/\text{m}^3 \pm 95\% \text{ confidence intervals}$) for the extracted weight analyses from the six-lab performance study.

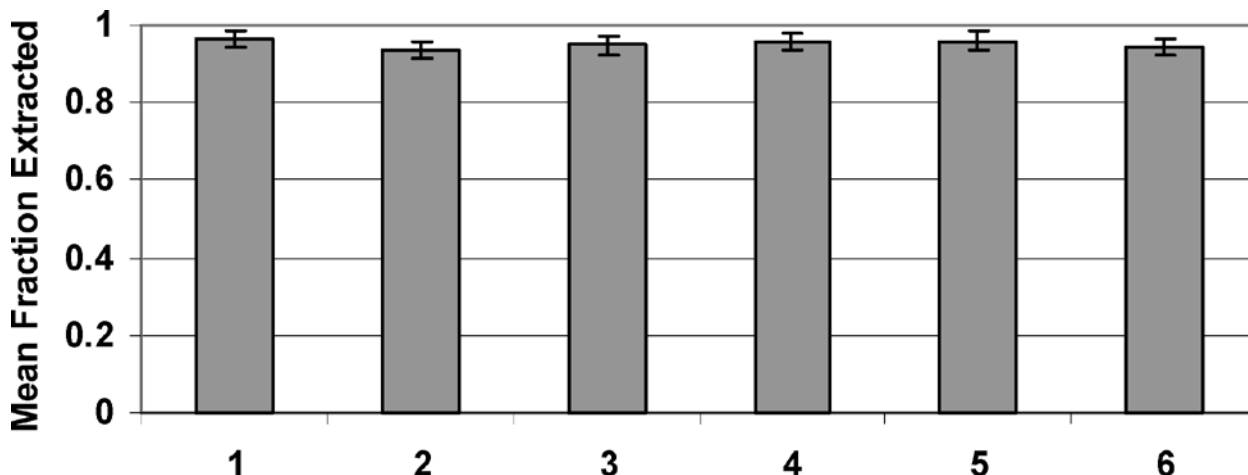


Fractions Extracted of Dynamically-generated samples

The fractions extracted (FE, or extracted weight/total particulate weight) $\pm 95\%$ confidence limits for each lab are plotted in Figure 9. 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 all six labs, the average fraction extracted was $\geq 94\%$ (CV = 0.025). The extraction data is much more precise (coefficient of variation [CV] = 0.025) than the reported concentration data shown in Figure 8.

The fractions extracted data were tested using an analysis of variance technique, and there were no statistical differences in the fractions extracted among the six labs. The precision estimates for the remaining five labs (excluding Lab 1) were not different statistically ($\alpha = 0.005$) for either the total or extractable weights. 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.

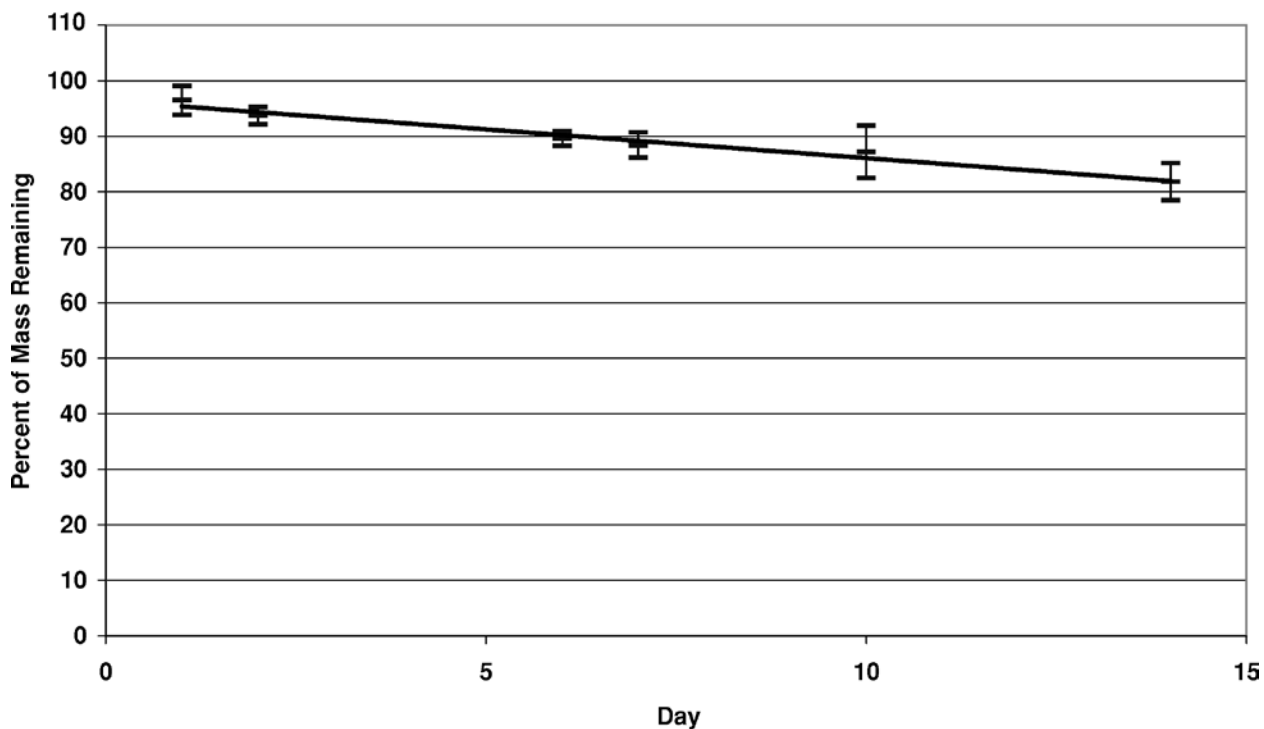
Figure 9. Fractions Extracted of Test MWF reported by six participating laboratories in round robin test.



Further Stability testing

From the above data obtained with the dynamically-generated samples, it is important to note that the regimen involved unrefrigerated overnight shipment and refrigerated storage for periods up to 7 days prior to analysis. Despite this, the samples still retained 84–90% of the initial mass loading after storage for 7 days. Similar experiments have been conducted in our laboratories under even less stringent storage conditions. Figure 10 shows a decay curve for nine filters loaded with ~0.4 mg of dynamically-generated MWF aerosol. The samples were stored in an open face position (supported in lower cassette halves with no upper halves in place) in a temperature- (~26°C) and humidity-controlled (35–45% RH) environmental chamber. This figure shows that the average weight decreased by <20% after 2 weeks storage; that is, the sample recovery still met minimum NIOSH requirements for storage under these suboptimal conditions. However, this is but one of several MWF formulations; there are hundreds if not thousands of formulations of MWF. It is prudent to refrigerate MWF samples during shipment in order to mitigate loss of semi-volatile components or possibly bacterial decomposition of samples stored for extended periods during shipment.

Figure 10. Percent remaining of ~0.4-mg aerosol samples of the test semi-synthetic MWF stored in an open-face cassette at ambient conditions for periods ranging from 1–14 days. Data follows equation: Percent remaining = $-1.167 \times \text{day} + 97.7$.



Conclusions

These studies provide confidence in the ruggedness of the NMAM Method 5524 sampling and analytical procedure and also support for consideration by ASTM as a fully validated standard. Aerosolized samples of a test soluble MWF sampled at concentrations corresponding to either of the NIOSH thoracic and total particulate RELs could generally be shipped unrefrigerated, stored refrigerated up to 7 days, and then analyzed quantitatively and precisely for MWF using the NIOSH/ASTM procedures. However, there are many other formulations of MWF than those evaluated here. It is therefore prudent to ship and store MWF samples under refrigeration to mitigate possible sample loss in such fluids.

REFERENCES

1. National Institute for Occupational Safety and Health (NIOSH): *Criteria for a Recommended Standard: Occupational Exposure to Metalworking Fluids*. DHHS (NIOSH) Pub. No. 98-102. Cincinnati, Ohio: NIOSH, 1998.
2. Darcy, J: *Exposure to Metalworking Fluids*, Metalworking Fluids Symposium Dearborn, MI, 2008.
3. National Air Quality and Emissions Trends Report 198. U.S. Environmental Protection Agency, Office of Air Quality, Planning and Standards Technical Support Division. Research Triangle Park, N.C. EPA-450-91-0, 1993.
4. ASTM International: *Provisional Standard Test Method for Metal Removal Fluid Aerosol in Workplace Atmospheres* (ASTM PS42-97). West Conshohocken, Pa.: ASTM, 1997.
5. Glaser, R.A.: Data supporting a provisional American Society for Testing and Materials (ASTM) method for metalworking fluids, Part 1: A solvent blend with wide-ranging ability to dissolve metalworking fluids. *J. Test. Eval.* 27:171–174 (1999).
6. Glaser, R.A., S. Shulman, and P Klinger: Data supporting a provisional American Society for Testing and Materials (ASTM) method for metalworking fluids, Part 2: Preliminary report of evaluation of a ternary solvent blend in a provisional ASTM method for metalworking fluids (P-42-97). *J. Test. Eval.* 27:131–136 (1999).
7. Bureau Veritas North America Novi, MI, Sequences 11525-CA, -CC, and -CG, 2013.
8. Piacitelli, G.M., W.K. Sieber, D.M. O'Brien, R.T. Hughes, R.A. Glaser, and J.D. Catalano: Metalworking fluid exposures in small machine shops: An overview. *Am. Ind. Hyg. Assoc. J.* 62:356–370 (2001).
9. Glaser, R.A., S. Shulman, R. Kurimo, and G. Piacitelli: 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. *J. Test. Eval.* 30:439–451 (2002).
10. Glaser, R.A., R. Kurimo, C. Neumeister and S. Shulman: Data supporting ASTM method D 7049-04 for metalworking fluids. *J. Test. Eval.* 33:323–330 (2005).
11. Glaser, R.A., R. Kurimo, & S. Shulman: Performance Testing of NIOSH Method 5524/ASTM Method D-7049-04, for Determination of Metalworking Fluids. *J. Occup. Environ Hyg.* 4(8):583-595 (2007).
12. ASTM International: *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method* (ASTM E 691-99). West Conshohocken, Pa.: ASTM, 2006.
13. Carsey, T.: LISA: A new aerosol generation system for sampler evaluation. *Am. Ind. Hyg. Assoc. J.* 48:710–717 (1987).

Appendix 1: Procedure to remove PTFE filter contaminants that are soluble in and extracted with the ternary blend.

Use this procedure to prevent high blanks from being obtained following extraction of PTFE filters. The filters are rinsed with ternary solvent (1:1:1 dichloromethane:methanol:toluene) described in NMAM Method 5524. The filters are air-dried and protected from airborne contamination prior to weighing and assembly into cassettes for field sampling.

A. EQUIPMENT, SUPPLIES, REAGENTS AND STANDARDS

1. 250 mL glass beaker(s)
2. 500 mL of ternary solvent 1:1:1 ratio of methanol, toluene and dichloromethane in a stoppered container
3. A fume hood
4. Watch glasses to fit the beakers
5. Glass stir rod
6. One box of 2 micron PTFE filters to be cleaned (or as many as required); recommend cleaning no more than 1 package of 50 filters per 100 mL of solvent
7. Stainless steel forceps to manipulate the filters
8. Large lint-free towellettes
9. Clean stainless steel metal trays or screen approximately 18" x 24"
10. Nitrile gloves
11. Clean wide mouth glass container, e.g., ointment jar with Teflon® cap or French square bottle

B. PROCEDURE

Perform all of the following tasks inside a fume hood!

1. Wear nitrile gloves throughout this procedure to protect yourself from the solvent and to protect the filters from skin oil during handling.
2. Pour approximately 100 mL of ternary solvent into a 250 mL glass beaker.
3. Remove the PTFE filters from the package and remove the plastic spacers from between the filters. Place the filters individually (sample side up) into the beaker filled with ternary solvent. Be careful that the filters stay separated from each other and do not clump together.
4. Carefully stir the filters with the glass stir rod; do not allow the filters to turn over. Cover the beaker with the watch glass. Allow the filters to extract in the solvent in the beaker for 10 minutes.
5. Decant the ternary solvent out of the beaker and into a waste bottle. Use the stirring rod to compress and retain the filters in the beaker as the solvent is slowly decanted off.
6. Refill the beaker with 100 mL of fresh ternary solvent after decanting following step 2.5. Repeat steps 2.4 and 2.5 two times for a total of three solvent washes.
7. After the three rinses are complete, drain off as much solvent as possible. Remove the filters from the beaker using forceps and place them onto a clean stainless steel metal tray or screen that has been covered with a large lint-free paper towel. Place them onto

the tray sampling side up. Allow the filters to dry overnight. It is recommended that the filters contact the stainless steel screen directly. Make sure that lint-free paper towels are used.

Warning: Keep the hood sash approximately *half* way open. If the sash is pushed lower, the higher air flow may blow the filters off the drying tray or screen. Place a sign on the sash indicating that it is to be left at this height overnight and **not to be moved**.

8. Place the dried filters in a clean French square glass bottle or a wide-mouthed Teflon® capped ointment jar. Label the container "PTFE Filters rinsed with MWF solution," giving the date, initials, and number of filters. Do not store filters in plastic containers. Filters are now ready to be used for sampling. Since the filters are not separated by spacers, use care to remove them from the storage container for use.

Cleanup Procedure Evaluation

The cleanup procedure described in Appendix 1 has been incorporated into NMAM Method 5524 in order to deal with reported spurious weight gains and losses before and after analysis of the PTFE filters used with this method. It is believed that trace levels of dust or extractable material are entrained in these filters during the manufacturing process. This cleanup procedure has been evaluated using 60 filters from three different batches of PTFE filters (20 filters/batch) [1]. Prior to cleaning, the filters were weighed (**untreated filters**), then washed with the ternary blend according to the procedure in Appendix 1, dried, and then reweighed (**treated filters**).

Results: The differences in each of the 3 batches were compared by subtracting the **treated** filter weights from their **untreated filter** weights. For all 60 samples, the overall mean difference in weights (+/-the standard error of the mean) was 0.2 µg (+/-1.4 µg). For each of the 3 batches, the differences in weight were: 5 µg (+/-2.5 µg), 2 µg (+/-2.0 µg), and -3 µg (+/-2.7 µg) for batches 1, 2 and 3, respectively. The weight differences were not statistically significant from zero overall or by batch using a paired t-test ($p = 0.05$) and allowing for multiple comparisons.

To determine if the washing procedure affected the filter's performance for analysis of metalworking fluids, each of the filters was analyzed according to the procedure of NMAM Method 5524, which includes extraction with the binary and ternary solvent blends. The differences in the **post-analysis** weights of the filters and their **treated** or **untreated** weights were computed. The average difference in the weights of the 60 untreated filters and their **post-analysis** weights (reported as mean +/- standard error of the mean) was: 34 µg (+/-1.9 µg). For each of the 3 batches, the differences in the **untreated** and **post-analysis** weights were: 30 µg (+/-3.9 µg), 38 µg (+/-2.0 µg) and 34 µg (+/-3.3 µg) for batches 1, 2 and 3, respectively. These differences are statistically significantly different from zero, both overall and individually by batch, using a paired t-test ($p=0.05$) and allowing for multiple comparisons.

The average differences in the weights of the 60 treated filters and their post-analysis weights were: 34 µg (+/-1.4 µg). Again the differences in weight are reported as mean +/-standard error

of the mean. For each of the 3 batches, the differences in the **post-analysis minus treated** weights were: 35 µg (+/-3.4 µg), 36 µg (+/-2.0 µg) and 31 µg (+/-1.8 µg) for batches 1, 2 and 3, respectively. These differences are statistically significantly different from zero, both overall and individually by batch, using a paired t-test ($p=0.05$) and allowing for multiple comparisons.

In summary, the weight differences were statistically different from zero by batch and overall using a paired t-test for both the **post-analysis minus treated** weights and for the **post-analysis untreated** weights ($p = 0.05$). However, the untreated/treated-weight differences were not statistically different using the same tests.

These experiments indicate that cleaning the filters lowered the overall LOQ of the analytical method. The LOQ determined from the differences in weights between the **untreated** and **analyzed** filters was 140 µg. This was substantially higher than the LOQ of 110 µg determined from the differences in weights between the **treated** and **analyzed** filters.

1. NIOSH [2014]. CEMB Analytical Services Report: Sequence 11600-CA. Novi, Michigan: Bureau Veritas North America, unpublished.

APPENDIX 2: List of metalworking fluids that have been found to be soluble in the ternary blend. The individual fluids have been identified by type and manufacturer.

Manufacturer			
All Power	KOOLMIST 77	Semi-synthetic	Yes
Americhem Corp	AM Cutting 2506 Oil	Straight	Yes
	Angler OIL Cut 121-M straight oil	Straight	Yes
	ACT 734 Synthetic Coolant	Synthetic	Yes
	ACI 4926 Carbide Grinding Fluid	Synthetic	Yes
	ACITemplex 4966	Semi-synthetic	Yes
	ACI 4931 Mach and Tap Fluid	Straight	Yes
	Blasocut 2000 Universal	Soluble	Yes
	Clearedge 6519	Semi-synthetic	Yes
	Drawfree 811 (Previously Iloform)	Soluble	Yes
	Safety Cool 407	Soluble	Yes
	Syntilo 9951	Synthetic	Yes
Chemtrol Inc.	CT-345-J	Semi-synthetic	Yes
Citgo Petroleum	Citgo Cutting Oil 205	Soluble	Yes
	Citcool 22	Synthetic	Yes
CLC Lubricants	CLC Cut PX2 NS	Straight	Yes
	CLC ChemCut MX-CG	Straight	Yes
	ChemFinish 605	Straight	Yes

Manufacturer	Tradename	Type	Soluble
Cutting & Grinding Fluids Inc.	CG 650 D	Soluble	Yes
	CG 5352 R	Straight	Yes
	CG 5352 RR	Straight	Yes
	KoolKut 692	Soluble	Yes
DA Stuart Co	Dascool LN 231-78	Semi-synthetic	Yes
	Dascool 2223	Semi-synthetic	Yes
	Superkool 25 straight	Straight	Yes
	Surgrind 86	Synthetic	Yes
Die-Casting ID Corp	ID DUA Chem 202	Semi-synthetic	Yes
Diversy Corp	LUBRICOOLANT AC	Soluble	Yes
	LUBRICOOLANT 4D	Soluble	Yes
DoALL Co.	DoAll 80	Straight	Yes
	KoolAll 940	Semi-synthetic	Yes
	KoolAll 948	Semi-synthetic	Yes
ELF Lubricants North America Inc.	Elfdraw S 13	Synthetic	Yes
Enterprise Oil Co	Duracut 130	Straight	Yes
ETNA Products	Master Draw B 942/I	Soluble	Yes
Fuchs Lubricants	FuchsVelvesol 96	Soluble	Yes
	Lus-Co-Cut 570ST	Straight	Yes
	Lus-Co-Cut 514 CMP Straight oil	Straight	Yes
	Lus-Co-Cut 400 Straight oil	Straight	Yes
	Renodraw 419NC	Soluble	Yes
	Renocut 471 Straight oil	Straight	Yes
	Shamrock LF	Soluble	Yes
	Ultracool 430	Synthetic	Yes
Hangsterfer's Lab Co	Hangsterfer's Hard Cut # 531	Straight	Yes
Houghton Intl	Cut Max 570	Straight	Yes
	Cut MaxTPO-46	Straight	Yes
	Hocut 787 H	Soluble	Yes
Intercon Enterprises	JokischW2-OP	Semi-synthetic	Yes
ITW Fluid Prod Group	Accu-Lube LB-2000	Straight	Yes
	Accu-Lube LB 3000	Straight	Yes
	Rustlick PB-10 Soluble	Soluble	Yes
	Rustlick WS 5050	Soluble	Yes
Lillyblad	DB BROMUS B water soluble	Soluble	Yes
	DB Water Soluble oil D	Soluble	Yes
Lyondell Petrochemical	Transkut HD 200	Straight	Yes

Manufacturer	Tradename	Type	Soluble
Master Chemical	Trim E 190	Soluble	Yes
	Trim CE/CE	Soluble	Yes
	Trim O M287	Straight	Yes
	TRIMSOL	Soluble	Yes
	Trim Microsol 265	Soluble	Yes
	TRIMSOL Silicone Free	Soluble	Yes
Metalworking Lubricants	METKUT 20546-TX-40	Straight	Yes
Milacron	Cimstarr 60-LF	Semi-synthetic	Yes
	Cimstar 3700	Semi-synthetic	Yes
	Cimtech 100	Synthetic	Yes
	CimstarQualStar	Semi-synthetic	Yes
	Cimtap II		Yes
	Cimperial 1010	Soluble	Yes
	Cimperial 1011	Soluble	Yes
	Cimstar 55	Semi-synthetic	Yes
	Cimstar 540	Semi-synthetic	Yes
	Cimtech 400	Synthetic	Yes
	C10TX	Soluble	Yes
Mobil Oil Corp	Mobil Mobilmet Omicron	Straight	Yes
	Mobil Mobilmet Nu oil	Straight	Yes
	MobilVascul 18F	Straight	Yes
	MobilmetAlpha Straight Oil	Straight	Yes
	Mobilmet Omega	Straight	Yes
	Vacmul 281	Straight	Yes
	Mobil Hydraulic AW 68 Straight Oil	Straight	Yes
	Mobilmet Upsilon	Straight	Yes
	Vacmul 3A Honing Oil/EDM	Straight	Yes
Monroe Fluid Tech Co	Prime Cut Soluble Oil	Soluble	Yes
Motor Oil Inc.	Thredkut 99 cutting oil	Straight	Yes
	Kleercut CF	Straight	Yes
National Oil Products	National Oil Products 3115 cutting oil	Straight	Yes
	National Oil Products Supreme Soluble HD	Soluble	Yes
OakiteProducts Inc	OakiteControlant 650 NS	Synthetic	Yes
Ocean State Oil	Hycut 4 Straight Oil	Straight	Yes
	Neil Cut 570 Cutting Straight Oil	Straight	Yes
Perkins Products	Perkut 296-H	Straight	Yes
	Perkool 5005- EP	Semi-synthetic	Yes

Relton Corp	ReltonA-9 Aluminum Cutting Fluid	Soluble	Yes
Rex Oil & Chemical Co	Titan Cutting Straight Oil	Straight	Yes
	Magic Cutting Oil	Straight	Yes
Richards Apex Prod. formerly GWhitefieldRichards Co	Near-a-Lard # 62	Straight	Yes

Manufacturer	Tradename	Type	Soluble
Rock Valley Oil & Chemical Co	Rockpin Straight Oil	Straight	Yes
Solar Chem Co	Solar Cut	Synthetic	Yes
Solutia	Glacier	Synthetic	No
Spartan Chem Co	COOLSPAR	Synthetic	Yes
StecoCorp	TAP Magic Aluminum	Semi-synthetic	Yes
	Tapmagic Extra Cutting Fluid	Straight	Yes
Stirling Industries Division	Tufcut 316	Straight	Yes
	RaecutA-1	Straight	Yes
	16228 HONING OIL	Straight	Yes
Sunnen Products	Sunnen Honnig Oil MB 30-55	Straight	Yes
Tapmatic Corp	LPSTapmaticPlus 2	Synthetic	Yes
Texaco	Texaco Sulfur Oil (Sultex)	Straight	Yes
	Texaco Sultex F	Straight	Yes
	Texaco 2731 Almag Special	Straight	Yes
	Texaco 01659 rando HD 68 brass st oil	Straight	Yes
Trico Mfg	TriCool	Synthetic	Yes
Union Butterfield	Union Butterfield Tapping & Cutting Oil	Straight	Yes
Unocal Refining	Unocal KooperKut 11HD	Straight	Yes
US Oil Co Inc.	Blanking Oil 250	Straight	Yes
	Alkut 810	Straight	Yes
	US Drawlube 1517	Straight	Yes
	Vanishing Oil 300	Straight	Yes
	Gem Soluble CP	Soluble	Yes
	US Cut 6040	Straight	Yes
	Spindle Oil ISO 10 Al St Oil	Straight	Yes
	321-SS Cutting Straight Oil	Straight	Yes
ValeniteInc	ValCoolTurntech	Semi-synthetic	Yes
	ValcoolVNT 800	Soluble	Yes
Varoum Chemical	Gauge Sterling Brass Cutting Oil	Straight	Yes
	Metacut MS Steel Cutting Oil	Straight	Yes
	GM 465	Straight	Yes
Viking Chemical Co	Cut Rite 305 CFX	Straight	Yes

Vulcan Oil & Chem	Ultrasol Soluble Oil	Soluble	Yes
	J-Cut 931 Cutting Oil	Straight	Yes
	Poseidon R&O HD	Straight	Yes
WS Dodge Oil Co	Pale Oil (all Viscosity grades)	Straight	Yes

Manufacturer	Tradename	Type	Soluble
	Combo base 82 Additive	Straight	Yes
	Deosol 202	Soluble	Yes
	Pale Straight Oil 55	Straight	Yes
	Superkut Cutting Oil 72/200	Straight	Yes
ZEP Products	ZEP Lubeze 14	Straight	Yes