METALWORKING FLUIDS (MWF) ALL CATEGORIES 5524

DEFINITION: Metalworking fluids CAS: None RTECS: None

METHOD: 5524, Issue 2 **EVALUATION: FULL** **Issue 2: 29 December 2014**
Issue 1: 15 March 2003

OSHA : No PEL
NIOSH: 0.4 mg/m^3 as thoracic fraction (0.5 mg/m^3 as 'total' aerosol)
Other OELs: [1,2]*

PROPERTIES: Not defined. Fluids may contain varying amounts of mineral oil, emulsifiers, water, alkanolamines, polyethoxyethanols, biocides, surfactants, pressure additives and boron compounds.

SYNONYMS: Metalworking fluids (MWF), metal removal fluids, machining fluids, mineral oils, straight fluids, soluble fluids, synthetic fluids and semi-synthetic fluids

SAMPLING

SAMPLER: Thoracic particles: FILTER + CYCLONE (tared 37-mm, 2-µm polytetrafluoroethylene (PTFE) filter + thoracic cyclone)
Total particulate: tared 37-mm, 2-µm PTFE filter

FLOW RATE: Thoracic – 1.6 L/min,
Total – 2 L/min

VOL-MIN: 768 L at 0.4 mg/m^3 or 0.5 mg/m^3
MAX: Not determined

SHIPMENT: Ship overnight in a refrigerated container

SAMPLE STABILITY: Refrigerate upon receipt; analyze within 2 weeks of collection

BLANKS: At least 5 field blanks per set

BULK SAMPLE: One for each fluid at each site for solubility testing

ACCURACY

RANGE STUDIED: 0.05 to 0.9 mg/sample

BIAS: Not determined

OVERALL PRECISION ($\hat{S}_{rT}$): Total weight- 0.06
Extracted weight - 0.07

ACCURACY (Estimated): Total weight - 0.12
Extracted weight - 0.14

MEASUREMENT

TECHNIQUE: Gravimetric

ANALYTE: Airborne metalworking fluid aerosol

EXTRACTION: Ternary solvent: dichloromethane: methanol:toluene (1:1:1)
Binary solvent: methanol: water (1:1)

BALANCE: 0.001 mg sensitivity; use same balance before and after sample collection

CALIBRATION: National Institute of Standards and Technology Class S-1.1 weights or ASTM Class 1 weights

RANGE: 0.05 to 2 mg per sample

ESTIMATED LOD: Total weight - 0.03 mg per sample [3]
Extracted weight - 0.03 mg per sample weight [3]

PRECISION ($\overline{S}_r$): Total weight - 0.04 (≥ 0.2 mg/sample) [4]
Extracted weight - 0.05 (≥ 0.2 mg/sample) [4]

APPLICABILITY: The method is applicable to all metalworking fluids-straight, soluble, synthetic and semi-synthetic as long as they are soluble in the extraction solvent regimen [4,5]. Only one MWF (Glacier, Solutia Inc.) has thus far been found to be insoluble in the ternary extraction solvent; however, that MWF is soluble in the binary blend and tests have shown that the binary solvent in combination with the ternary solvent is effective in extracting this fluid [6]. **Thoracic samplers** meeting the International Standard ISO 7708 thoracic convention within the performance specifications of the European Standard EN13205, parts 1 through 6 [2] may be considered for this method if they have been validated for the collection of MWF. Depending on the type of thoracic sampler used, the recommended flow rate may differ from that specified above. Sampling at flow rates exceeding those recommended here may result in increased evaporative loss of sample. Welding fume may significantly interfere with proper operation of certain impactor-style samplers.

INTERFERENCES: None identified. However, any material that is collected on the filter and is soluble in the extraction solvents may interfere (positively) with the analysis.

OTHER METHODS: This method is similar to NMAM Method 0500 for Particulates Not Otherwise Regulated [7] and replaces NMAM Method 5026 as a general technique for analysis of MWF. NMAM Method 5026, which employs infrared analysis, may be used solely for the analysis of (straight) MWF that produce mineral oil mists; that method is not recommended for use with water-based fluids [8]. ASTM D7049 is another method that may be used to analyze metalworking fluids [9].

REAGENTS:

1. Dichloromethane, distilled-in-glass (DIG) (See Note)‡
2. Methanol, distilled-in-glass (See Note)‡
3. Toluene, distilled-in-glass (See Note)‡
4. Water, filtered, double deionized (18 MΩ·cm resistivity)
5. Calcium sulfate, desiccant
6. Ternary solvent blend‡: Mix equal volumes of dichloromethane, methanol and toluene in a clean dust-free container. Use a bottle with a screw cap (e.g., a clean, empty solvent bottle): Mix the solvents by gentle swirling, not by violent shaking.
7. Binary solvent blend‡: Mix equal volumes of methanol and water in a clean dust-free container. Use a bottle with a screw cap (e.g., a clean, empty solvent bottle): Mix the solvents by gentle swirling, not by violent shaking.

NOTE: Lower grade solvents have not been evaluated for this method. If it is desired to use ACS or liquid chromatographic grade solvents, in the interest of economy, the user must demonstrate that these solvents perform equally to the DIG grade (blanks ≤ those obtained with the DIG grade).

‡ See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: 37-mm PTFE, 2-µm pore size membrane filter (see Appendix 1 for PTFE filter cleanup procedure) and PTFE supporting pad in 37-mm cassette filter holder. Use a 2-piece (closed face) cassette for sampling 'total' aerosol. For sampling the thoracic fraction, use a 3-piece cassette with thoracic cyclone that samples at 1.6 L/min at the thoracic cutpoint. See Evaluation of Method. Also, see page 5524-1 for discussion of alternative thoracic sampling.
2. Personal sampling pump, 1.6 to 2 L/min, with flexible connecting tubing
3. Cassette shrink bands, cellulose, 37-mm size
4. Microbalance, capable of weighing to 0.001mg
5. Static neutralizer: e.g., ^{210}Po; replace nine months after the production date
6. Forceps (preferably nylon or chrome-plated steel)
7. Extraction funnel, See Figure 1 for specifications p. 5524-10
8. Desiccator
9. Wash Bottle, PTFE
10. Vials, 20-mL and 10-mL, glass, with leak-proof PTFE-lined caps
11. Syringe, gas-tight with large bore needle, e.g., 16-gauge needle
12. Graduated cylinder, glass, 20 mL
13. Paper towels
14. Metal screen for drying filters following extraction, approximately 550 cm^2 or other convenient size. Grid size approximately 12 to 18 mm. Pre-wash screen with ternary blend solvent and allow to dry.

SPECIAL PRECAUTIONS: Dichloromethane is an inhalation hazard and is a suspect carcinogen. Handle all solvents in a fume hood. The solvents are flammable and have associated adverse health effects. Avoid breathing vapors. Avoid skin contact. Use extreme caution when blending the solvents together. The heat of mixing can cause pressure to develop as the solvents are blended, e.g., blowing a stopper from a glass-stoppered container. Use clean containers sealed with PTFE-lined screwcaps.

CALIBRATION AND QUALITY CONTROL:

1. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
2. Process at least three tared media blanks through the measurement process for 'total' aerosol and the extractable materials.

PREPARATION OF FILTERS BEFORE SAMPLING:

3. Number the backup pads with indelible ink and place them, numbered side down, in the filter cassette bottom sections.
4. Pre-weigh the filters by the weighing procedure given in step 5. Record the mean tare weight of sample filters, W_1 and field blanks, B_1 (mg).
5. Weighing procedure:
   a. Equilibrate the filters in an environmentally controlled weighing area or chamber for 1 hour (minimum.)
   b. Zero the balance before each weighing. Using forceps, pass each filter over a static neutralizer. Repeat this step if the filter does not release easily from the forceps or attracts the balance pan. (Static electricity can cause erroneous weight readings.)
   c. Weigh each filter until a constant weight is obtained (i.e., two successive weighings within 10 µg.)
   d. Record the mean of the last two weights to the nearest microgram.
6. Assemble the filter in the 2- or 3-piece filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette and allow to dry. Alternatively, use heavy duty elastic tape instead of the shrink band. Mark with the same number as the backup pad.

SAMPLING:

Bulks: For solubility testing, obtain liquid samples of pure uncut bulk metal-working fluids (MWF) that are expected to be sampled in worker breathing zone. Place these samples in small (e.g., 10 mL) leak-proof glass container(s) that are sealed with a leak-proof PTFE-lined screwcap. Then place them inside of a resealable plastic bag and ship these samples to the laboratory along with the sample filter cassettes.

Air: For collection of a thoracic sample, insert the cyclone into the inlet of a 3-piece cassette. For collection of a "total" sample, do not use the cyclone.

7. Calibrate each personal sampling pump with a representative sampler in line.
8. For thoracic measurements, sample at 1.6 L/min for 8 hours. For 'total' aerosol measurements, sample at 2 L/min for 8 hours. Do not exceed a total filter loading of approximately 2 mg.
9. Submit at least 5 blank filter samples as field blanks and 3 filters for media blanks for each set of samples collected per day. Handle the field blanks in the same way as the field samples; i.e., open each in a non-contaminated environment, then close the sampler and ship it to the lab along with the remaining samples. Media blanks are not opened.
10. Refrigerate all samples that are to be stored overnight (or longer) prior to shipment to the laboratory. Ship all samples in refrigerated containers to the laboratory via overnight express delivery service.
11. Refrigerate the samples immediately upon receipt at the lab until ready for analysis.
12. Analyze the samples within two weeks of receipt at the laboratory.

SAMPLE PREPARATION AND MEASUREMENT:

13. Solubility test of bulk MWF:
    a. Shake the container of bulk MWF to ensure that a homogeneous sample is obtained.
    b. Place 10 mL of the ternary solvent blend in a 20-mL glass vial.
    c. Using a large-bore gas-tight syringe, inject 50 µL of the bulk MWF into the ternary solvent blend. Cap the vial and shake as necessary to dissolve the MWF. The fluid is soluble if the resulting solution is clear and free of precipitates and phase separation.
    d. If the MWF is soluble in the ternary blend, the samples can be extracted with the ternary blend.
14. Wipe dust from the external surface of each filter cassette (containing either samples or blanks) with a moist paper towel to minimize contamination. Discard the paper towel.
15. Remove the top and bottom plugs from the filter cassette. Equilibrate the filters (in the cassettes) for no more than 2 hours in a desiccator that uses calcium sulfate.
16. Remove from the desiccator. Equilibrate for at least 1 hour in the balance room or chamber.
17. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of sample.
    NOTE: If the filter adheres to the underside of the cassette top, very gently lift it away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.
18. Weigh and record (steps 5b through 5d) the post-sampling weight of each filter, W_2 (mg) and blank, B_2 (mg). Record anything remarkable about the filter (e.g., overload, leakage, wet, or torn). Perform the extraction as soon as possible. Store in a clean dust free environment until ready to perform the extraction, etc.

EXTRACTION:

19. Perform all extractions in an exhaust hood. General guidelines (see NOTE below):
    NOTE: Samples weighing less than 0.4 to 0.5 mg (for a 1 m^3 sample) may be extracted as desired. The reason that the cutoffs of 0.4 and 0.5 mg (per 1000 L sample) have been specified is to assure compliance with the occupational exposure limit (OEL). If the gross sample weight indicates that the OEL has not been exceeded, there may be no reason to extract the sample. Otherwise, the usefulness of any extraction data obtained at levels less than 0.4 to 0.5 mg per sample is guided by the limit of quantitation (LOQ) of the extraction procedure. Extraction data obtained at levels between the limit of detection (LOD) and the LOQ of the extraction procedure should be used with appropriate caution due to the imprecision associated with such data.
20. Do not presume that a fluid that is soluble only in the binary-blend should be extracted using only the binary blend. The possibility of mixed exposures always dictates that the extraction procedure with both the binary and ternary solvent blends should be followed. If the weights of samples exceed the amount expected to be collected at the REL, e.g., 0.4 mg (thoracic fraction) or 0.5 mg ('total' aerosol) for a 1 m^3 air sample, then extract the samples and blanks as follows:
    a. Place each filter (membrane side up) in the filter funnel assembly connected to the vacuum source.
    b. Pour one 10-mL aliquot of the *ternary solvent* down the inside wall of the funnel over the filter. Allow the solvent to contact the filter for no more than 5 to 10 minutes. Remove the solvent under slight vacuum.
    c. Pour one 10-mL aliquot of the *binary solvent* down the inside of the funnel over the filter. Allow the solvent to contact the filter for no more than 5 to 10 minutes. Remove the solvent under slight vacuum.
    d. Pour a second 10-mL aliquot of the *ternary solvent* down the inside of the funnel over the filter. Allow at least 30 seconds of contact time. Remove the solvent under slight vacuum. Wash the inner wall of the filter funnel with 1 to 2 mL of the ternary blend contained in a PTFE wash bottle. Remove the solvent under slight vacuum.

e. Turn off the vacuum to the filter funnel.
f. Carefully remove the filter from the filter funnel, place it on the clean metal screen, and allow to dry on the metal screen for at least 2 hours in a fume hood. Do not remove the filter from the funnel while vacuum is applied or the filter may delaminate.

NOTE: One metalworking fluid, Glacier (Solutia Chemical, St Louis), was insoluble in the ternary blend but was soluble in the binary blend. Tests have shown that this fluid is extracted efficiently from the filters using steps 20a through 20e [5].

21. Weigh each filter, including field blanks, following steps 5a through 5d. Record the post-extraction weight, W_3 (mg), of the extracted sample filters and B_3 (mg), for the extracted blank filters. Record anything remarkable about the extracted filter (e.g., torn, wet, delamination, etc.).

CALCULATIONS:

22. Calculate the concentration of 'total' aerosol or thoracic fraction, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1) * 10^3 L/m^3}{V}, (mg/m^3)$$

where: W_1 = mean tare weight of filter before sampling (mg) (step 5)
W_2 = mean post-sampling weight of sample-containing filter (mg) (step 18)
B_1 = mean tare weight of all blank filters (mg) (step 5)
B_2 = mean post-sampling weight of all blank filters (mg) (step 18)

23. Calculate the concentration of extracted MWF aerosol C_{MWF} (mg/m^3), in the air volume sampled, V (L):

$$C_{MWF} = \frac{(W_2 - W_3) - (B_2 - B_3) * 10^3 L/m^3}{V}, (mg/m^3)$$

where: W_2 = mean post-sampling weight (pre-extraction weight) of sample-containing filter (mg) (step 18)
W_3 = mean post-extraction weight of sample-containing filter (mg) (step 21)
B_2 = mean post-sampling weight of all blank filters (mg) (step 18)
B_3 = mean post-extraction weight of all blank filters (mg) (step 21)

24. Report the concentration C as 'total' aerosol or thoracic fraction weight; report the concentration C_{MWF} as the weight of the MWF aerosol.

EVALUATION OF METHOD:

The 'total' weight procedure permits an estimate of the 'total' collected particulate aerosol, including nuisance dust, airborne metal particulate and metal working fluid. If the extraction procedure is used, the technique permits an estimate of the 'total' collected metalworking fluid to which the worker is exposed. The development of the ternary solvent used in this method is described in reference 3. This method was initially tested with representative samples of straight, soluble, semi-synthetic, and synthetic metalworking fluids (MWFs). Samples were spiked onto tared polytetrafluoroethylene (PTFE) membrane filters, stored overnight, and analyzed the following day. The samples were weighed, then the MWF was extracted from the filter with a 1:1:1 blend of dichloromethane:methanol:toluene. The fractions extracted (FE or mass recovered/mass spiked) exceeded 94% for all fluids extracted from the filters over the range from 200 µg to 815 µg for the straight fluid, from 223 µg to 878 µg for the soluble

fluid, from 51 µg to 189 µg for the semi-synthetic fluid, and from 102 µg to 420 µg for the synthetic fluid. For those weights of all four fluids spiked at levels ≥ 200 µg, the relative standard deviation was estimated to be 4% for the total weight procedure and 5% for the extraction procedure. If the sampling imprecision of 5% is included, these estimates become 6% and 7% respectively for the total weight and extraction procedures. Limits of quantitation, estimated from blanks carried through the entire analytical procedure, were 30 µg for the weighing technique and 60 µg for the extraction technique. No estimate of the bias was available [4]. The filters are desiccated to remove excess water from water-based MWF samples.

In a more rigorous test of this method for a 79-plant survey [2], the average limits of quantitation were estimated to be 0.1 mg for both the total and extracted weight procedures. However, there was high variability in these estimates for the sites sampled. The upper 95% confidence limit for the LOQs for both the total weight and extracted weight measurements was 0.3 mg. In order to assess the effectiveness of the extraction step, a secondary extraction of the most heavily-loaded filters obtained in this survey was conducted; on average, less than 5% of the sample weight was removed during the second extraction, indicating that the majority of extractable material had been removed during the first extraction. Samples were refrigerated upon receipt at the laboratory [2,10].

During the 79-plant survey, all thoracic sampling was conducted with a BGI Mdl 2.69 Thoracic sampler. This sampler has a thoracic cut point of 10 µm at 1.6 L/min. The stability of quality assurance (QA) samples, spiked separately with a straight, a soluble, a semi-synthetic, and a synthetic fluid, indicated that the QA samples all lost weight according to simple linear decay equations. This loss in weight was likely due to evaporation of the spiking solvent and water (for soluble, semi-synthetic and synthetic MW fluids.) 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 17 to 26 days, the total weight of samples recovered for all QA samples were greater than or equal to 80% of those expected from the decay equations. For these QA samples, the fractions extracted of all four fluid types were greater than or equal to 90%.

The binary solvent extraction step has been added to assure complete extraction of MWF components that may be incompletely removed by the ternary blend. In addition, the binary solvent extends the procedure to samples that contain ternary blend-soluble fluids co-mingled with ternary blend-insoluble fluids, e.g., Glacier (Solutia Inc.) Tests of the extraction of five MWF (including Glacier) showed that extraction efficiencies using the ternary blend in combination with the binary blend were comparable to those reported in reference 1 using the ternary blend alone (FE greater than 90 %; CV less than 0.10). The binary solvent extractant liquor obtained from the Glacier samples generally contained potassium and phosphorous at levels approximately expected for the mass spiked onto the filters. The binary solvent extracts of the four other test fluids were analyzed for sodium, potassium or boron marker elements. Sodium was present in the extract of the soluble fluid at greater than background levels. The boron marker was not detected in the extract from the semi-synthetic fluid. The potassium marker was not detected in the extract from the synthetic fluid [5].

This method was further evaluated in a six-laboratory round robin study using synthetically generated atmospheres of an aerosol of a soluble MWF at the 0.5 mg/sample level. The data were evaluated according to ASTM standard E691-99. Pooled estimates of the total coefficients of variation were 0.13 for both the total and extracted weight samples. Overall there was no significant bias in the results. LOQs were comparable to those reported above [11].

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* NOTE: Because exposure limits and guidelines may change over time, NIOSH recommends referring to the following sources for updated limits and guidelines. [1,2]

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. See evaluation of procedure which follows these instructions.

EQUIPMENT, SUPPLIES, REAGENTS AND STANDARDS

1. 250 mL glass beaker(s)
2. 500 mL of ternary solvent 1:1:1 ratio of dichloromethane:methanol:toluene in a stoppered container
3. A fume hood
4. Watch glasses to fit the beakers
5. Glass stir rod
6. One box (or as many as required) of 2 micron PTFE filters to be cleaned; recommend cleaning no more than 1 package of 50 filters per 100 mL of solvent
7. Stainless steel forceps to manipulate filters
8. Large, lint-free paper towels
9. Clean, stainless steel metal trays or screen approximately 45 cm x 60 cm (18 inch x 24 inch)
10. Nitrile gloves
11. Clean, wide mouth glass container e.g., ointment jar with Teflon cap or French square bottle

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 watchglass. 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 5. Repeat steps 4 and 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 that has been covered with a large, lint-free paper towel. Alternatively, place them on a clean stainless steel screen. Place them onto the tray or screen, sampling side up. Allow the filters to dry overnight.
   Warning: Keep the hood sash approximately at or below the sash height level as marked on the hood. 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 2-µm 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

This cleanup procedure 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** 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 reported as mean (+/-standard error): 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 following differences were computed: **post-analysis** weights of the filters minus their **treated** or **untreated** weights. 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). For each of the 3 batches, the differences, (**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 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 and was greater than the LOQ of 110 µg determined from the differences in weights between the **treated** and **analyzed** filters. The extraction procedure produced a more consistent blank and therefore a lower average standard deviation from which lower LOD s and LOQs were determined.

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

Figure 1. Schematic diagram of funnel. May be ordered from Case Custom Environmental Equipment, Erlanger, Kentucky (859-250-8558); www.casecustomenvironmentalequipment.com) or equivalent source. Dimensions are given in inches.