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Evaporative Losses from Semi-Volatile Mist Samples

FINAL PERFORMANCE REPORT

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LIST OF ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ASTM	American Society for Testing and Materials
BEHS	bis (2-ethylhexyl)sebacate
d_d	droplet diameter
ESP	electrostatic precipitation sampler
GF	glass fiber
H_i	heat of vaporization
k	thermal conductivity of air
Lpm	liters per minute
$\dot{m}_i$	mass rate of evaporation from a droplet
M_i	molecular weight
MCE	mixed cellulose ester
MWF	metalworking fluid
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
Q	ventilation rate for test chamber
REL	recommended exposure limit
STEL	short term exposure limit
TLV	threshold limit value
TWA	time-weighted average
V	volume of test chamber
ΔT	change in temperature

ABSTRACT

Metalworking fluid mists pose potential respiratory, cancer, and dermatological concerns for machinists and other exposed workers. Thus, measuring mist concentrations accurately for regulatory and health study purposes is important. However, most metalworking fluids are semi-volatile. This leads to the possibility that collected mist droplets can evaporate from sampling filters after they have been captured. If this evaporation occurs, mist concentrations will be underestimated. The purpose of this research was to utilize numerical modeling, laboratory experimentation, and field measurements to determine important factors that might influence the extent of evaporative losses of metalworking fluid mist from sampling filters.

Numerical models were developed (1) to predict the evaporation of droplets from the point of generation until sampling onto a filter, and then (2) to predict the amount of the sampled mist that evaporated from the filters. Predictions developed from these models were compared to laboratory experiments to validate the models. The laboratory experiments were also used to investigate factors that influence evaporative losses. Field measurements were utilized to understand the extent of evaporative losses in real machining environments.

Results of the laboratory experiments indicated that evaporative losses as great as 60% were possible for straight oils. The loss on a percentage basis was greater for more volatile oils and when mist concentrations were low. The degree of mixing within the environment being sampled did not have a significant effect on the amount of evaporative loss from the sampling filters. Straight oils showed greater propensity for evaporative loss than soluble oils and synthetic fluids. Numerical modeling yielded similar predictions as the laboratory experiments. However, the models predicted less evaporation overall than measured in the experiments. Field measurements showed that evaporative losses could be significant in real machining environments. Measurements of mist levels in an automobile engine plant indicated that losses from sampling filters could be as high as 50%.

Industrial hygienists could use samplers other than filters to measure mist concentrations. Electrostatic samplers have been shown to have much less evaporative loss than filters. Real-time light scattering instruments can also measure mist concentrations with reasonable accuracy with proper calibration. For situations in which filters are used for sampling, estimating the true metalworking fluid mist concentration by doubling the measured mist concentration would likely give a result that would be greater than or equal to the true mist concentration. This adjustment might be an appropriate conservative estimate of mist concentration that could protect workers from excessive exposure to potentially harmful metalworking fluid droplets.

SIGNIFICANT FINDINGS

Metalworking fluids have the potential to volatilize from sampling filters, leading to mist concentration measurements that are too low. Laboratory experiments conducted in this research demonstrated that evaporative losses as high as 60% were possible under the right conditions. For oils, evaporative losses increased as the vapor pressure of the compounds in the oil increased. However, water-based fluids generally exhibited less evaporative loss from sampling filters than straight oils because the water evaporated almost completely before the mist ever reached the sampling filter. If the volatile compounds did not collect on the filter, they could not evaporate from it. The laboratory tests with oils also indicated that evaporation was greater, on a percentage basis, as mist concentration decreased. The degree of mixing within an environment did not have a significant impact on the sampling losses due to evaporation.

Numerical models used to predict droplet evaporation in a well-mixed environment and evaporation from filters agreed partially with experimental results. In general, the models indicated correctly how different factors influenced evaporative losses from sampling filters. However, the models predicted less evaporation than was actually measured in experiments. The reasons for this lack of agreement between the models and experimental results are uncertain. Some of the experimental conditions such as the size distribution of the mist as it was generated or the mist generation rate may have been measured inaccurately. In addition, interactions of vapor with surfaces within the environment may play more of a role in droplet/vapor interactions than previously recognized.

Measurements of mist concentrations in the field yielded mixed results. Many facilities had mist levels so low that gravimetric methods of measuring mist concentration were not accurate. Measurements at higher concentrations indicated that evaporation from sampling filters was greater than expected. In an automobile manufacturing facility, losses of almost 50% were found at some locations. Further research is needed to determine the factors influencing the extent of the evaporative losses.

TRANSLATION OF FINDINGS

The findings of this study suggest that evaporative losses are not likely to be an important problem when metalworking fluid mist concentrations are high, approaching the OSHA permissible exposure limit of 5 mg/m^3. However, when mist concentrations are near the NIOSH recommended exposure limit (REL) of 0.5 mg/m^3, evaporative losses may be a substantial problem. Losses are likely to be more important for straight oils than for soluble oils and more important for soluble oils than for synthetic fluids. In some situations when concentrations are near the NIOSH REL, losses can be expected to be nearly 50%.

If industrial hygienists want to be sure that they estimate mist concentrations accurately, they have several options. First, they could use a sampler other than a filter. The electrostatic sampler used in this study has been shown to be much less susceptible to evaporation artifacts than sampling filters. Another option is to use a real-time instrument such as a Dusttrak. However, the Dusttrak needs to be calibrated against a non-volatile oil mist because it underestimates mist concentrations with its factory calibration, which is performed with an SAE test dust. Industrial hygienists could also multiply their mist concentrations determined using a sampling filter by a correction factor of 2 to obtain an estimate of the true mist concentration. A factor of 2 accounts for a 50% loss of sample, about the maximum observed in this study. Thus, multiplying by 2 is a conservative recommendation that would be protective of machinists and other workers who might be exposed to metalworking fluid mist.

Perhaps the most important recommendation from this project is that persons interested in measuring metalworking fluid mist concentrations should be aware of the potential problem of evaporative loss from filter during sampling. With that awareness comes the possibility of sampling intelligently and interpreting data carefully in order to minimize the problem.

SCIENTIFIC REPORT

Background

Machining operations use metalworking fluids (MWFs) to cool, lubricate, clean, and protect metal tools and work pieces. Several classes of MWFs are available: straight oils, refined petroleum-based oils; soluble oils, petroleum-based oils mixed with water to form an emulsion; semi-synthetic fluids, dilute emulsions of oil in water; and synthetic fluids, aqueous solutions containing no oil (Howell et al., 1995). The fluids contain many additives and can be contaminated with tramp oils, microorganisms, metal particles, and dirt. NIOSH (1977) has estimated that more than 1.2 million workers in the United States work with or near MWFs.

When MWFs are applied during machining, small mist droplets are generated. Woskie et al. (1994) measured mass median diameters for MWF mist droplets between 5.5 and 8.0 μm, with geometric standard deviations ranging from 2.4 to 3.3. Because they are so small, MWF mist is capable of traveling through a workroom to deposit on distant surfaces or enter workers' breathing zones. Exposure to the droplets poses several potential health problems for workers, including cancers of the larynx, stomach, pancreas, and rectum (Vena et al., 1985; Silverstein et al., 1988; Tolbert et al., 1992; Eisen et al., 1994; Calvert et al., 1998), chronic cough and phlegm (Järvholm et al., 1982; Oxhøj et al., 1982; Sprince et al., 1997), reduced lung function (Kennedy et al., 1989), occupational asthma (Hendy et al., 1985; Robertson et al., 1988; Rosenman et al., 1995), and hypersensitivity pneumonitis (Bernstein et al., 1995; Rose et al., 1996; Kreiss and Cox-Ganser, 1997; Freeman et al., 1998; Shelton et al., 1999). Workers exposed to MWFs also develop contact dermatitis and other skin ailments (de Boer et al., 1989; Pryce et al., 1989; Alomar, 1994; Sprince et al., 1996).

Currently, the Occupational Safety and Health Administration (OSHA) has no standards specific for MWF mists. For mineral oil mist, OSHA has a permissible exposure limit (PEL) of 5 mg/m^3 for an 8-hour time weighted average (TWA). For other kinds of mist, the appropriate PEL is for particulates not otherwise regulated: 15 mg/m^3 for the total aerosol and 5 mg/m^3 for the respirable fraction for a TWA. NIOSH (1998) has recommended an exposure limit for MWF aerosols of 0.4 mg/m^3 for the thoracic particulate mass over a 10-hour TWA. The American Conference of Governmental Industrial Hygienists (ACGIH) has a threshold limit value (TLV) of 5 mg/m^3 for an 8-hr TWA for mineral oil mist and a short-term exposure limit (STEL) of 10 mg/m^3 (ACGIH, 2003). In its notice of intended changes, ACGIH indicates that it will establish a TLV of 0.2 mg/m^3 for mineral oil.

Several sampling protocols are available for MWF mists. All involve sampling onto filters. NIOSH (1998) recommends sampling the mists using NIOSH Method 0500 for total particulates not otherwise regulated (NIOSH, 1994) with the caveat that an inlet selective for the thoracic size fraction should be used. Method 0500 calls for sampling the mist onto a 37-mm diameter, 5-μm pore size polyvinyl chloride (PVC) membrane filter at a flow of 1-2 Lpm. The filter is weighed before and after sampling. The difference between the weights, corrected by differences in weights for field blank filters, is used to calculate the mist concentration.

For mineral oil mists, an alternative protocol is NIOSH Method 5026 (NIOSH, 1994). In this method, the oil mist is sampled onto a 37-mm diameter, 0.8 or 5-µm pore size PVC or mixed cellulose ester (MCE) filter at a flow of 1-3 Lpm. After sampling, the filter is treated with carbon tetrachloride (CCl_4) to desorb the oil droplets that have been collected by the filter. The absorbance of the solvent extract is then measured in an infrared spectrophotometer. By comparison to absorbances of calibration standards and samples taken from filter blanks, the concentration of the oil mist can be calculated. Method 5026, which requires a more difficult analysis than Methods 0500 and 0600, will only provide information on compounds that are soluble in CCl_4.

The American Society for Testing and Materials (ASTM) has developed provisional method PS42-97 for determining workplace concentrations of MWF aerosols (ASTM, 1997). In this method, MWF mists are sampled onto a pre-weighed, 37-mm polytetrafluoroethylene (PTFE) membrane filter at a flow of 2 Lpm. The filter is removed from its holder, weighed again, and then placed in a mixture of dichloromethane, methanol, and toluene to extract the liquid portion of the aerosol from the filter. After the filter is dried, it is weighed a third time. The difference between the initial and post-sampling weights is used to calculate the total MWF aerosol concentration. The difference between the post-sampling and post-extraction weights is used to calculate the concentration of the liquid phase in the MWF aerosol. All of the samples are compared to blanks.

D'Arcy et al. (1995) reviewed three methods used internally by automobile companies to sample MWF mist. One method calls for sampling onto a pre-weighed, 37-mm glass fiber (GF) filter. After weighing the post-sample filter so that total aerosol can be calculated, the filter is immersed in trichloroethylene to desorb the liquid portion of the aerosol. The dried filter is weighed again to determine the liquid portion of the MWF aerosol. A second method samples onto a pre-weighed 37-mm PTFE filter. After a post-sampling weight is taken, the liquid portion of the sample is desorbed in toluene. The post-extraction weight is used to compute the liquid portion of the aerosol concentration. The third method samples onto a pre-weighed 37-mm PVC filter. After sampling, the filter is desiccated for 8-24 hours and then weighed to determine the total MWF aerosol. D'Arcy et al. showed that the three methods yielded comparable concentrations when tested side-by-side.

The cited methods all use filters to collect the mist. Many compounds in MWFs are volatile or semi-volatile. Water will evaporate readily from airborne droplets. In addition, organic compounds in the petroleum-based oils used in straight oils, soluble oils, or semi-synthetic fluids can evaporate from droplets. Raynor et al. (1996) showed that the amount of evaporation from airborne MWF mist droplets will depend on temperature, MWF composition, mist concentration, size distribution, and the length of time the mist has been airborne.

When filters capture MWF mist droplets, the collected liquid can evaporate further. Similar observations have been made for a variety of compounds during outdoor atmospheric sampling (Van Vaeck et al., 1984; Zhang and McMurry, 1992; Eatough et al., 1995; Cheng and Tsai, 1997). Cooper et al. (1996) and Cooper and Leith (1998) showed that straight and soluble oils residing on filters in MWF mist collection equipment evaporated into passing air. McAneny et al. (1995) measured losses of mass as high as 40% after 4 hours when clean air was passed through PVC and GF filters that had collected mineral oil mist previously. The loss of non-volatile oleic acid was less than 10% after 4 hours. Leith et al. (1996) demonstrated that the mass of mineral oil lost from pre-loaded PVC and MCE filters when clean air was passed through them was substantially higher than for an electrostatic precipitation sampler (ESP) through which clean air was passed. The authors explain this difference by noting that the collection surface in a filter (the fibers) is exposed more to the passing air than the collection surface in an ESP (a wall). Volckens et al. (1999) showed that a comparison of PVC and GF filters to an ESP in the field indicated that the filters yielded concentrations of about 20-25% of the concentration determined with the ESP. In laboratory tests intended to replicate the field conditions, these authors found that differences between the filters and ESP were more pronounced at lower mist concentrations.

Raynor and Leith (1999) explained with theory how collected MWF mist evaporates from filters. The diffusion of vapor away from liquid collected on filter fibers happens very rapidly so that air emerging from filters can be saturated readily with the liquid present on the filter. The authors developed a numerical model to predict evaporation from filters and showed that the model matched laboratory data. Raynor et al. (1999) used theory and experimental data to demonstrate that evaporation from sampling filters is likely to occur whenever the vapor phase of the air passing through a filter is not in equilibrium with the droplets that have been collected.

Specific Aims

The development of non-evaporative devices is an active area of research that may lead to better, albeit more expensive, samplers in the future. Another alternative is to continue measuring mist concentration in the same way since the historical concentration data upon which exposure limits are based were gathered using the potentially flawed methodology. However, if methods can be developed to correct current and historical mist concentration measurements made using filters, data analysis could be improved so that better links can be drawn between MWF mist exposure and health effects. In addition, the importance of evaporative losses for the myriad of conditions found in machining operations should be evaluated. Therefore, this research aimed to:

(1) Develop numerical models that explain the processes of evaporative loss during sampling of MWF mists,
(2) Validate the models using measurements made in the laboratory and field data, and
(3) Evaluate the importance of evaporative losses in the field by making measurements of MWF mist concentration in different situations.

The research rests on the contention that integration of numerical modeling with the field and laboratory measurements is useful for gaining a thorough understanding of the processes that affect evaporation of semi-volatile liquids from filters.

Methods

Aim #1: Develop numerical models

Modeling evaporation of collected droplets from a sampling filter involves two steps. First, the evaporation or growth of airborne droplets must be modeled from the time they are generated until the time they are sampled. Second, the evaporation of sampled droplets from the filter must be modeled based on the output from the droplet evaporation model.

The evaporation of airborne droplets moving through ventilation duct in plug flow was modeled by Raynor et al. (1996). However, this "no mixing" model is not appropriate for sampling workplace air, because workplace air is closer to being well mixed. As a result, mist droplets generated at different times co-exist and must be tracked over time in the model.

The "perfect mixing" droplet evaporation model used in this study was based on the Raynor et al. (1996) no mixing model with several modifications. First, droplet temperature changes contributed by the change of state from liquid to vapor were incorporated into the model. These temperature changes are important for soluble oils and synthetic and semi-synthetic fluids because they contain so much water. The temperature change, ΔT, for each droplet diameter and age was modeled using the equation

$$\Delta T = \sum_{i} \frac{\dot{m}_i H_i}{2\pi d_d k M_i} \tag{1}$$

in which $\dot{m}_i$ is the mass rate of evaporation for compound i, H_i is the heat of vaporization for i, d_d is the droplet diameter, k is the thermal conductivity of air, and M_i is the molecular weight of i.

In addition to modeling the temperature change, the perfect mixing model also allows for dissolved components to be part of the droplet. This capability is important for MWFs that contain water. To model the dissolved materials, dissociation constants and solubility limits are needed for the dissolved substances in addition to properties such as density and molecular weight. The dissolved substances are assumed to be nonvolatile.

The most important modification for moving from a no mixing model to a perfect mixing model is to include the capability of tracking droplets generated at different times. In the no mixing model, Raynor et al. (1996) tracked the changes of diameter for droplets generated at one point in time and considered their joint effect on vapor concentrations in the air. In the perfect mixing model, droplets were generated into a volume V ventilated at a volumetric air flow rate Q. Droplets were tracked in fractional time increments of the time V/Q, typically 0.1, 0.025, or 0.005. All particles generated in each individual time increment were tracked together. The changes in droplet composition and mass were modeled for some upper time limit that was a multiple of V/Q, typically 5. If droplets were tracked beyond 5V/Q, they were lumped together with other droplets that had been tracked beyond the upper limit. Droplet concentrations within each time interval were reduced by the ventilation in accordance with a perfect mixing assumption at each time step.

The filter evaporation model used in this study was virtually identical to the model developed by Raynor and Leith (1999). The only changes were to add the capabilities of modeling temperature changes for liquid evaporating from the filter and to account for dissolved materials.

Aim #2: Validate the models

To validate the perfect mixing droplet evaporation model, tests were conducted in a 1 m^3 chamber built for this study, see Figure 1. Air was drawn into the chamber through filters using a reciprocal blower (Gast, Benton Harbor, MI). The chamber was lined with aluminum foil to minimize adsorption of vapor onto the walls of the chamber. Droplets were generated into the chamber using a Collison nebulizer (BGI Inc., Waltham, MA). Droplet concentrations were tracked by a Dusttrak (TSI Inc., Shoreview, MN). The size distribution of the mist was tracked using an Aerodynamic Particle Sizer 3310 (TSI Inc., Shoreview, MN). The airflow through the chamber was monitored using a calibrated orifice in the tubing running from the chamber to the blower. The rate of aerosol nebulized into the chamber was tracked by weighing the nebulizer before and after tests.

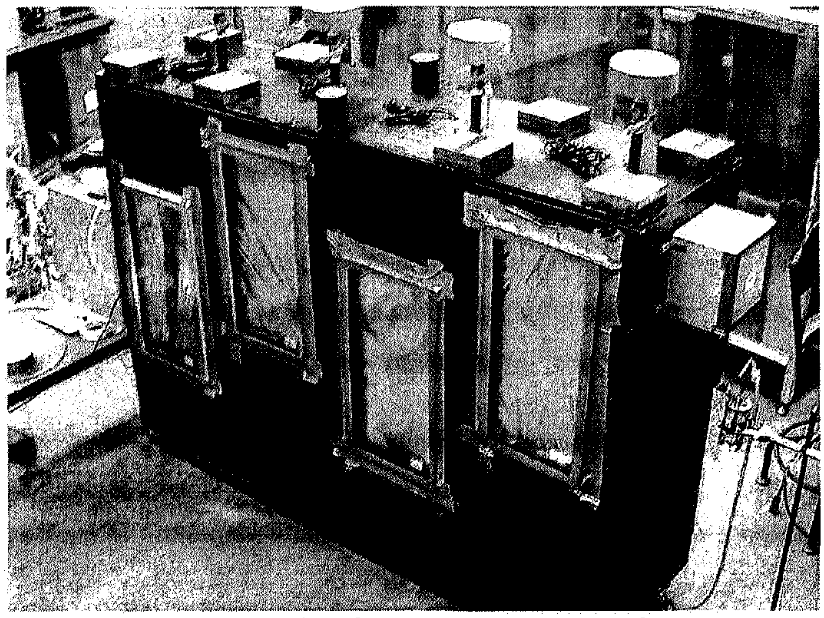

FIGURE 1: Test chamber for experiments to evaluate numerical models.

Four fluids were used for testing: bis (2-ethylhexyl)sebacate (BEHS), a non-volatile oil; hexadecane, a semi-volatile alkane; a low volatility straight oil MWF (Ilocut, Castrol, Downers Grove, IL); and a high volatility straight oil MWF (EDM40, Trim, Perrysburg, OH). Tests were performed with each fluid four times. Each test lasted an hour. Tests were conducted at a "high mist generation rate" with air flows of 7.5 and 15 m^3/hour and at a "low mist generation rate" with air flows of 3.75 and 7.5 m^3/hour. The high and low mist generation rates varied from fluid to fluid because each fluid had different vapor pressures. Mist concentration and size distribution was measured every minute for the hour-long test for comparison to the perfect mixing droplet evaporation model.

To validate the filter evaporation modeling, two MWFs were nebulized into the test chamber, the low and high volatility straight oils discussed previously. Two mist generation rates were used, 10 mg/hr and 40 mg/hr, in combination with two air flow rates, 5 m^3/hr and 20 m^3/hr. The four combinations of mist generation rate and ventilation rates produced mist concentrations of approximately 0.5, 2, and 8 mg/m^3. In addition, two kinds of mixing within the chamber were achieved by the use of baffles and larger entries. To achieve a low level of mixing within the chamber, air entered through a 15 cm x 15 cm opening covered with a pleated HEPA filter. In addition, the mist had to pass around three baffles before being sampled. For a high level of mixing, the baffles were removed and the air entered the chamber through a filtered pipe at much higher velocity. Thus, four factors were tested: fluid volatility, mist generation rate, air ventilation rate, and degree of mixing. Two levels of each variable were tested in a complete factorial for a total of 16 test runs.

In each of the runs, which lasted approximately four hours, the mist was collected by six samplers. Two pre-weighed 37 mm fiberglass filters and a pre-weighed 37 mm PTFE membrane filter were placed in closed face cassettes attached to calibrated sampling pumps (Airchek 52, SKC, Eighty Four, PA). Sampled air passed first through short brass tubes that ran through the side of the chamber. The brass tubes were attached to the filter cassette inlets with Tygon tubing. In addition, two electrostatic samplers (ESPs, Aerosol Associates, Chapel Hill, NC) were connected to brass tubes leading from the chamber. The ESPs, one of which is shown in Figure 2, were utilized because Volckens et al. (1999) found that ESP mist samples yielded much less evaporative loss than filter samples. Pre-weighed aluminum substrates were placed in the ESPs upon which the mist was deposited. In addition, a Dusttrak was used to monitor mist concentration in 10-second intervals.

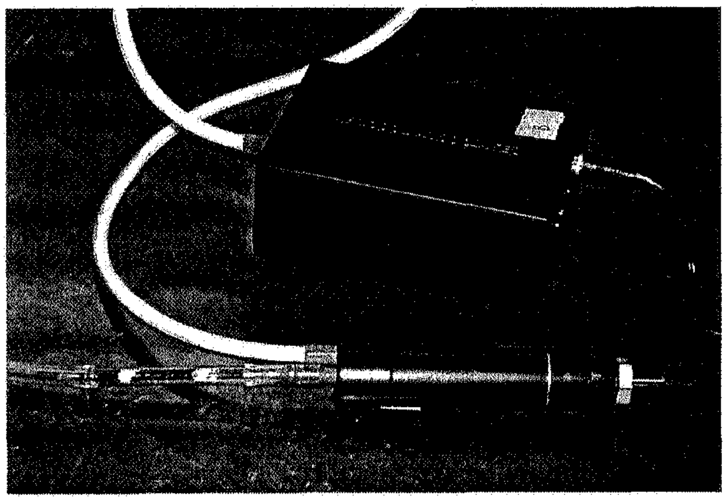
FIGURE 2: Electrostatic sampler (ESP).

The filters and substrates were weighed before and after sampling using a microbalance. The mass gain divided by the sampling flow and time provided a measure for mist concentration by each sampling method in each of the 16 test combinations.

Similar tests were conducted later using other fluids. In this case, BEHS, hexadecane, a soluble oil, and a synthetic fluid were tested at mist generation rates of 10 and 40 mg/hr and ventilation rates of 5 and 20 m^3/hr. The baffles in the chamber were removed so that only the high mixing level was tested. Each combination of fluid, mist generation rate, and ventilation rate was tested once for a total of 16 additional runs. The same six samplers used in the earlier tests were utilized for these experiments as well.

The results of the measurements were compared to modeling predictions. The high mixing level measurements were compared to the perfect mixing droplet evaporation model tied to the filter evaporation model. The low mixing measurements were compared to the no mixing droplet evaporation model tied to the filter evaporation model.

Aim #3: Field Measurements

Finding sites in which to perform field measurements was the most difficult part of fulfilling this aim. We were able to measure mist concentrations within an automotive company engine manufacturing facility for one week in April 2003. We also made extensive mist measurements in a telecommunications parts manufacturer in January and February 2003. However, the remaining companies contacted fell into two categories: (1) their mist concentration levels were so low that they would not produce measurable mist concentrations in an 8-hour sample, or (2) they were not interested in having anyone come in to monitor mist concentrations. We attempted to work with a local precision machining trade organization to find more sites and also tried to work with an occupational physician who has conducted research in machining facilities to find sites. Neither avenue produced many companies willing to participate within the Twin Cities area. Traveling further from the Twin Cities was not feasible due to budget limitations.

At the telecommunications parts manufacturer, mist concentrations were measured using a Dusttrak twice on one day throughout a workroom in which approximately 30 CNC machines were located. The goal of these measurements was to find minimum and maximum mist concentration locations at which paired ESP and 37-mm fiberglass filter samples could be located. On a second day, three samplers were collocated at each location identified previously. The three samplers included a Dusttrak, a 37-mm PTFE filter contained in a polystyrene closed-face cassette, and an ESP containing an aluminum substrate. The filters and substrates were pre-weighed along with field and laboratory blanks. Workplace air was drawn through the samplers for about 7½ hours. The filters and substrates were returned to the laboratory along with the field blanks and then reweighed for determination of the mist concentrations in the workplace.

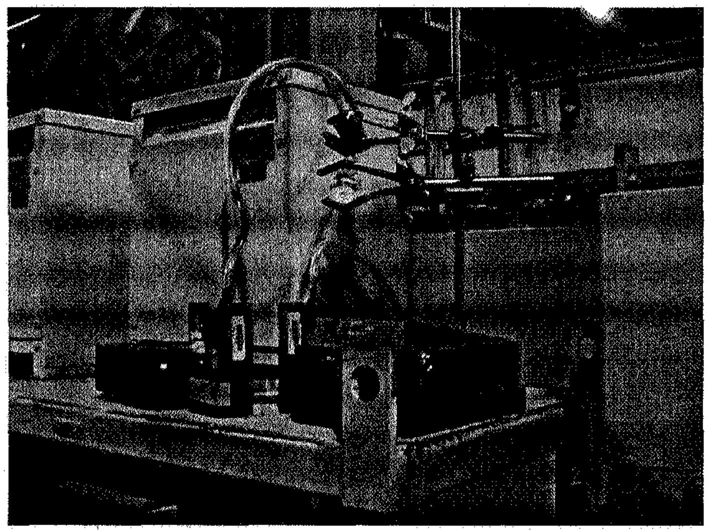

FIGURE 3: Collocated 37-mm PTFE filter cassette, electrostatic, and Dusttrak samplers at the automotive production facility.

At the automotive facility, the company had already performed measurements identifying elevated mist concentrations at several points throughout the plant. Six locations were selected for collocated sampling with the Dusttrak, the 37-mm filters, and the ESPs, see Figure 3. Samples were taken for approximately 8 hours at each location. The pre-weighed filters and substrates, together with field blanks, were returned to the laboratory for final weighing. From the weight difference and the sampling flow rate and time, mist concentrations were calculated.

Results and Discussion

Aims #1 & #2: Develop Numerical Models and Validate the Models

Figure 4 shows the experimental results and model predictions for mist concentrations that developed in a well-mixed test chamber. The results demonstrate that the model generally predicts higher concentrations, or less droplet evaporation, than observed in tests. In particular, the model predicts concentrations several times higher for Trim EDM40 than were observed in experiments.

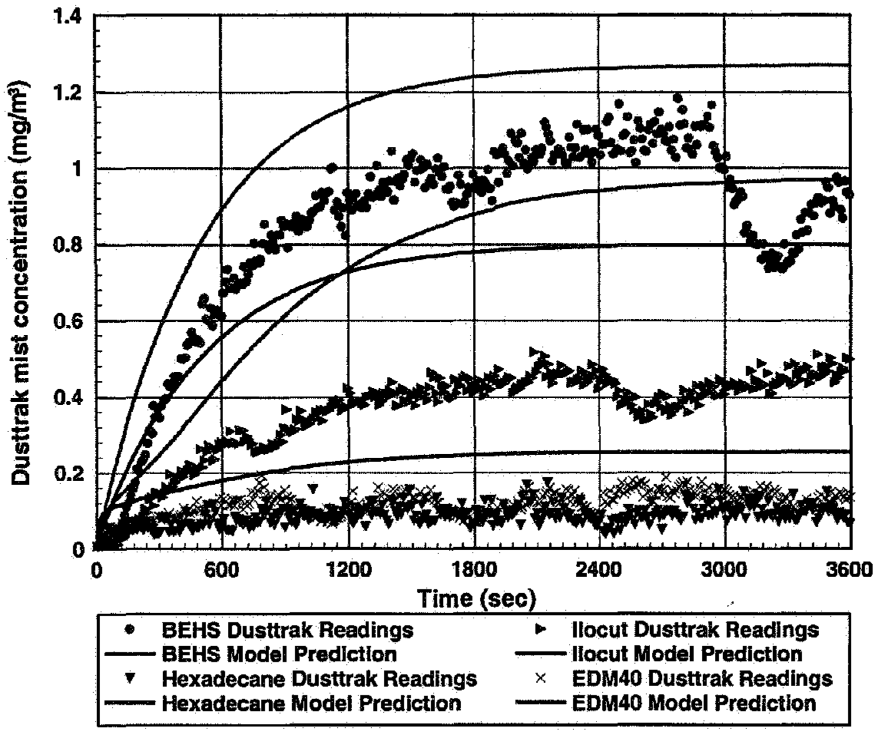

FIGURE 4: Experimental results and droplet evaporation model predictions for mist concentration for tests using four different fluids nebulized into a test chamber. Air flow through the chamber was 7.5 m^3/hr in all cases.

The discrepancies between the experimental results and the modeling predictions may have arisen for several reasons. First, the composition of the fluids may not be modeled accurately. The composition of the multicomponent fluids was assumed to be n-alkanes with vapor pressures predicted by analysis on a gas chromatograph. This analysis may be in error. Second, the compounds in the fluids may interact to increase their activity coefficients higher than the assumed activity coefficient of 1. Third, measurements of the experimental mist generation rate may have been inaccurate. Because the mist generation rates were so low, the rates used in modeling for BEHS and the Castrol Ilocut may have been off by as much as 50%. The mist generation rates used in modeling for hexadecane and the Trim EDM40 may have been off by as much as 10%. Fourth, the model may not properly take into account interactions that occur between the vapor phase and the chamber walls. Condensation was allowed to occur on the walls, but the accuracy of the approach used to model condensation was not tested experimentally. Furthermore, the model does not even consider the possibility of vapor adsorption to the walls. The possibility of adsorption was reduced by placing aluminum foil over the inside walls of the test chamber.

The results of the factorial sampling study in the test chamber are presented in Figure 5. In this figure, the light mineral oil is the high volatility MWF and the heavy mineral oil is the low volatility straight oil. The bars indicate the loss for each combination of fluid volatility, mist generation rate, ventilation rate, and mixing level. The loss was calculated by comparing the two measurements of mist concentration by the fiberglass filters and the measurements of concentration by the ESPs with the assumption that the ESPs experienced no evaporative loss. The statistical analysis of the data indicated that the fluid volatility was the biggest factor affecting evaporative loss. The higher volatility fluid experienced more loss from the sampling filters than the less volatile MWF.

After the fluid volatility, the mist generation rate and the ventilation rate were significant to the extent that they affected mist concentration. Evaporation of sampled mist was much greater on a percentage basis at low concentrations than at high concentrations. However, the influence of mixing level was not significant in this study even though evaporative losses were slightly higher at a well-mixed level than at a poor mixing level.

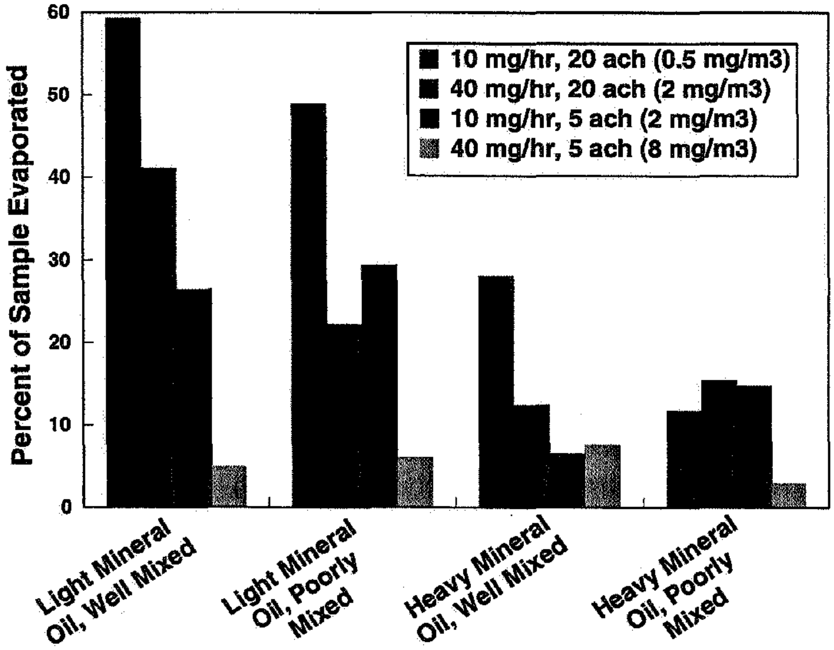

FIGURE 5: Evaporative losses on a percentage basis experienced by fiberglass filters in chamber experiments.

Results of numerical modeling of these experiments are shown in Figure 6. The figure demonstrates that the modeling predicted substantially less evaporation than was observed during the experiments. However, the relative importance of the different factors was generally the same in the modeling predictions. The more volatile fluid exhibited more evaporative loss than the less volatile fluid and lower mist concentrations resulted in more evaporation on a percentage basis than higher mist concentrations.

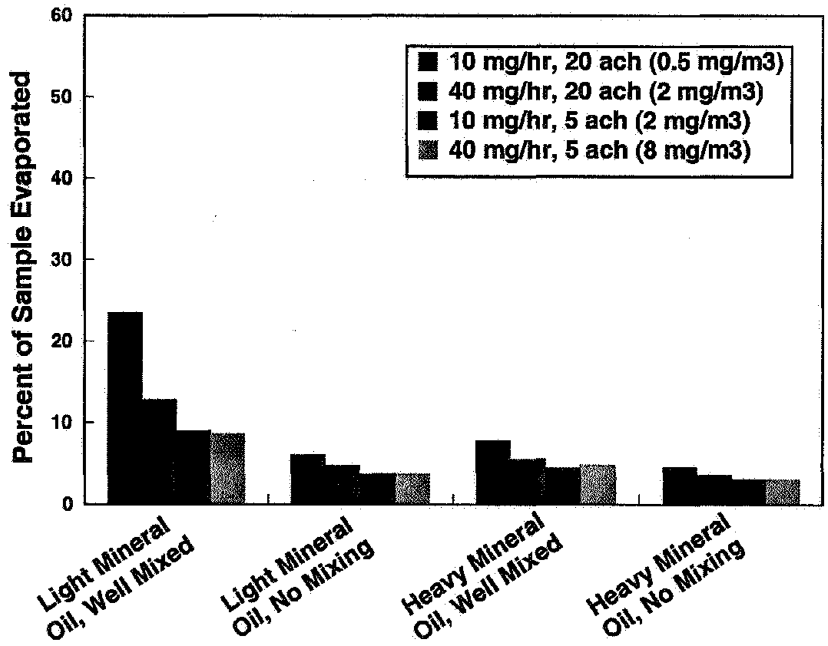

FIGURE 6: Evaporative losses on a percentage basis for fiberglass filters according to numerical models using conditions from the chamber experiments.

The reasons for the differences between the model predictions and the experimental results are uncertain. The models may have some inaccuracies in input data, including activity coefficients, vapor pressures, and initial size distributions. However, sensitivity analyses indicate that these inaccuracies would not lead to the discrepancies observed between Figures 5 and 6. The experiments may have had some error. First, the experiments could not provide the ideal no mixing or perfect mixing utilized in the models. Second, the mist generation rates varied somewhat with time. Modeling suggests that variation in mist levels leads to more evaporation than a constant mist level for the same average concentration. Other assumptions in the model may also contribute to the discrepancies. In particular, the model originally did not assume that vapor could condense or adsorb onto the walls of the test chamber. This was a questionable assumption. Although wall condensation was incorporated into the droplet evaporation models, the accuracy of the approach used has not been assessed.

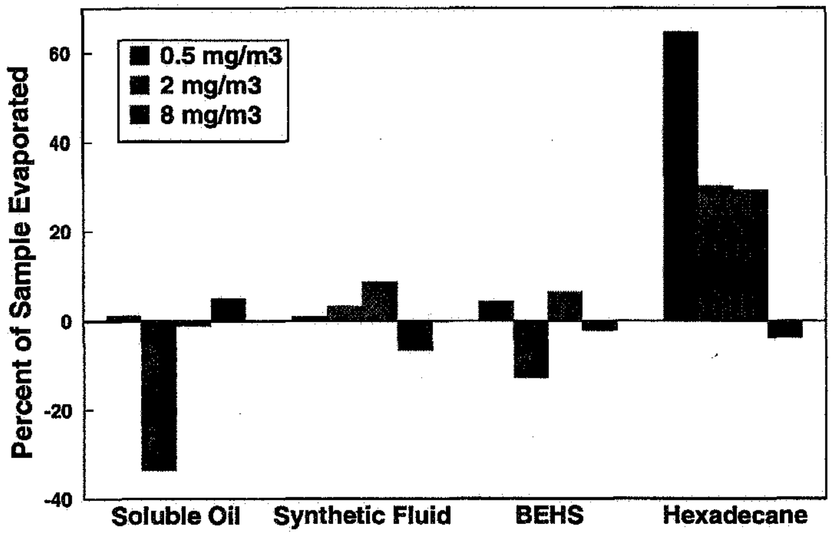

FIGURE 7: Evaporative losses on a percentage basis experienced by fiberglass filters in chamber experiments with fluids other than straight oil MWFs.

Figure 7 shows results for evaporative loss experiments with other fluids. Relatively volatile hexadecane showed significant losses that were higher on a percentage basis as concentration decreased. Non-volatile BEHS exhibited almost no evaporative losses. The soluble oil and synthetic fluid also did not show evaporative loss. The water portion of these fluids evaporated from mist droplets so rapidly that little water was present by the time the droplets were sampled onto filters. Thus, the water portion was not present to evaporate from the sampling filter. The large negative evaporative loss bar for the soluble oil could not be explained from a review of the experimental conditions and test procedures.

Aim #3: Field Measurements

At the telecommunications part manufacturer, the first day's measurements with the Dusttrak provided the map of mist concentration within the facility shown in Figure 8. The figure shows that higher concentrations were found in the relatively poorly ventilated area near the top of the figure. Therefore, one of the sets of samplers was located near the highest concentration measured in that area. The second set of samplers was located across the room in the relatively low mist concentrations near the bottom of the figure.

Unfortunately, the mist concentrations measured during the tests were too low to be determined effectively. The increases in mass on the filters and the ESP substrates were easily within the limit of quantification for the microbalance. In the high mist area, the filter showed a mist concentration of 0.088 mg/m^3 whereas the ESP measured a concentration of 0.055 mg/m^3. At the same location, the Dusttrak with a 2.5 µm inlet showed a concentration of 0.028 mg/m^3. In the low mist area, the filter gave a concentration of 0.022 mg/m^3 and the ESP substrate had no increase in mass. The Dusttrak, with a 2.5 µm inlet, provided a concentration of 0.008 mg/m^3.

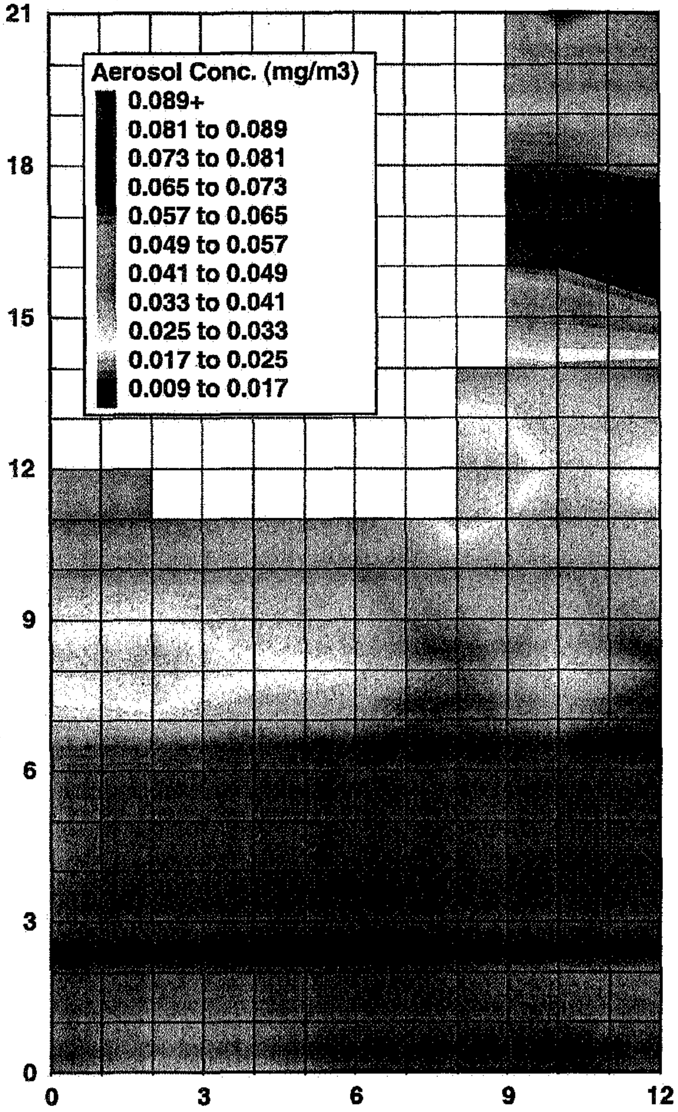

FIGURE 8: Map of mist concentrations measured with the Dusttrak at the telecommunications parts manufacturer. Numbers on the x and y axes represent numbers of 10-ft square pads of concrete floor.

If the numbers generated in this test were reliable, they would suggest that the filters were not experiencing any evaporative loss or that the ESP substrates were experiencing more evaporative loss than the filters. However, a more likely explanation is that the mist concentrations in these tests were too low to be measured dependably. This result is indicative of a problem experienced at other sites visited as well. In most cases, the mist concentrations were too low to yield measurements that were significant statistically.

The measurements in the automobile engine manufacturing plant were more reliable because the mist concentrations were higher. The results of these measurements are shown in Table 1. If the concentrations measured by the ESP are considered to be indicative of no evaporative losses, then the evaporative loss experienced by the PTFE filters ranged from 26.3% to 46.7% for the five sampling comparisons for which both filter and ESP data were valid. The differences in loss percentage among the locations could not be tied to particular factors such as ventilation, machining process, or fluid type.

The results for the Dusttrak, which had a 10 µm inlet in these tests, indicate that it measured less mist than detected by the electrostatic samplers. The Dusttrak concentrations ranged from 48% to 78% of the concentrations measured using the ESP. These results are similar to those of other researchers who have observed that the Dusttrak produces concentrations lower than measured gravimetrically when it is used with its factory calibration.

TABLE 1: Mist concentrations measured at the automobile manufacturing facility using PTFE filters, ESPs, and Dusttraks.

Site	Date	Location	Post #	Concentration using PTFE filter (mg/m^3)	Concentration using ESP (mg/m^3)	Concentration using Dusttrak (mg/m^3)
1	4/23/03	4V Crankshaft	OB-7	0.83	1.49	0.732
2	4/23/03	2V Crankshaft	F-10	0.48	0.66	0.370
3	4/24/03	2V Cylinder Head	E-19	0.50	0.93	0.729
4	4/24/03	Connecting Rod	J-7	0.21	0.37	0.176
5	4/25/03	Cast Iron Block	Q-10	——	0.99	0.566
6	4/25/03	Cast Iron Block	S-15	0.88	1.19	0.912

The results of the measurements in the field could not be predicted well by the models. In most cases, the model would predict a smaller difference between the filters and the ESPs than was actually observed. The reasons for these differences are not certain.

The evaluation of the modeling would have been enhanced by more field measurements. In retrospect, more money should have been budgeted for travel to conduct this part of the research. Many small manufacturers in the Twin Cities area were not interested in having researchers make measurements of mist in their facilities. Larger companies, such as automobile and farm equipment manufacturers, outside the Twin Cities would have been more likely to allow sampling in their plants.

Conclusions

Evaporation of MWF mist collected by sampling filters is a valid concern for industrial hygienists. Under proper conditions, evaporative losses as high as 60% were measured in the experimental portion of this research and losses of almost 50% were observed in the field portion of the research. Losses will be larger when straight oils are sampled than when soluble oils are sampled. In turn, losses are likely to smaller for synthetic fluids than for soluble oils. For straight oils, highly volatile fluids will exhibit larger losses than low volatility fluids. The percentage of a sample lost due to evaporation will increase as mist concentration becomes smaller. The research shows the potential for volatilization to lead to mist concentration measurements that are smaller than the actual concentrations.

The models developed in this research work only partially. They tend to predict less evaporation than is actually observed in experimental measurements. However, the models do predict directionally the importance of different factors such as fluid volatility, mist concentration, and degree of mixing. A significant amount of additional research would be required to refine these models.

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STUDENTS SUPPORTED BY THIS PROJECT

Sumati Dhawan, MS – Ms. Dhawan performed many of the original tests to characterize the test chamber used in this research.

Mira Grice, MS – Ms. Grice used data gathered as a Research Assistant on this project to write her Plan B paper that was required of her to complete her MS degree from the University of Minnesota.

PUBLICATIONS

No papers have been published yet from this research. However, two manuscripts are in preparation and will be submitted from the work. The first, entitled "Multicomponent Droplet Evaporation in a Well-Mixed Environment", will discuss the new droplet evaporation model for perfect mixing. This manuscript will be sent to a journal in the fall of 2004. The second manuscript, entitled "Factors Influencing Evaporative Losses from Semi-Volatile Mist Samples", will review the laboratory experiments conducted in this research and the modeling conducted to match those experimental results. Much of this second manuscript has already been prepared as part of Ms. Mira Grice's MS project. The manuscript will be submitted to a journal by the end of 2004.

Portions of this research have been presented at an American Conference of Governmental Industrial Hygienists symposium on metalworking fluids held in 2002 and on two separate occasions at the American Industrial Hygiene Conference and Exposition.