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Development and Evaluation of a Method to Estimate Potential Formaldehyde Dose from Inhalable Dust/Fibers

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A method for the estimation of formaldehyde dose from inhalable dust/fibers using a commercially available inhalable sampler was developed. Filters containing sampled dust/fibers were placed in 10 ml of distilled water and incubated at 37°C for 4 hours to liberate the formaldehyde from the dust/fibers. After incubation, the filter extracts were passed with a 0.45 μm filter to remove particles left in the extracts. Two analytical procedures were used for the analysis of the filter extracts. Either a 4-ml aliquot was analyzed using the chromotropic acid procedure, as outlined in NIOSH Method 3500, or a 1-ml aliquot was treated with 2,4-dinitrophenylhydrazine and a catalytic amount of perchloric acid and analyzed by high-performance liquid chromatography for the resulting 2,4-dinitrophenylhydrazone. The limits of detection for the chromotropic acid procedure and the 2,4-dinitrophenylhydrazine procedure were 0.44 and 0.08 μg per filter sample, respectively. Relative standard deviations of replicate determinations of formaldehyde content by the chromotropic acid procedure were 3.4 percent for textile samples (ca. 180 μg) and 8.2–6.6 percent for wood dust samples (7–11 μg).

Two comparisons of the inhalable samplers with closed-face cassette samplers were conducted at a garment manufacturing plant and a waterbed accessory production plant. The inhalable samplers on average collected more dust/fibers than the closed-face cassette samplers in both studies. In the garment manufacturing plant study, the formaldehyde levels in the dust/fibers were greater for the inhalable samplers than the closed-face cassettes. In the waterbed accessory plant, the formaldehyde levels were comparable for both sampler types. Although the hydrolysis procedure used in this method to liberate formaldehyde from the dust/fibers may not be fully representative of the hydrolysis occurring in the nasal and oropharyngeal passages, the formaldehyde in dust/fibers may be considered an approximation of the localized dose at the point of particle retention in the breathing passages. These results should be reported separately from vapor phase levels of formaldehyde until sufficient data has been collected to allow appropriate epidemiological interpretation of formaldehyde-containing particulate exposures.

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Introduction

There have been many occupational and environmental studies of the health effects from exposure to formaldehyde.(1–4) In two recent mortality studies dealing with occupational formaldehyde exposure, a difference in results has brought into question the source of formaldehyde exposure in each study. In a study by Stayner *et al.*,(1) in which "statistically significant elevations in proportionate mortality were observed for cancers of the buccal cavity (parotid gland), biliary passages and liver (gallbladder), and other lymphatic and hematopoietic sites (multiple myeloma)," formaldehyde exposure was measured to be low level and assumed to be vapor-phase due to offgassing of formaldehyde from cloth used in garment manufacture. In a Blair *et al.* study,(2) in which "cancer overall was not related to formaldehyde exposure," the source of formaldehyde also was assumed to be primarily vapor-phase but due to a number of divergent sources. However, in several of the plants included in this study, the investigators did note the presence of formaldehyde-containing dust.(5) In a reanalysis of this data, Blair *et al.* stated that "the pattern for nasopharyngeal cancer suggests that simultaneous exposure to formaldehyde and particles may be a risk factor for this tumor."(6)

Since the data from both the Stayner study and the reanalysis of the Blair *et al.* study suggest an excess of cancers of the upper respiratory passages, it has been hypothesized that the exposed populations may be receiving additional formaldehyde exposure from the accumulation of inhaled formaldehyde-containing particulate matter.(6) The plants in the Stayner study and the plants in the Blair study where excess nasopharyngeal cancers were found were noted to be dusty. Therefore, the particulate material to which employees were exposed may have contained either adsorbed formaldehyde or chemically bound formaldehyde, the latter of which could be hydrolytically released in the upper respiratory tract after inhalation.(7)

Results of other studies have reported that inhalation of both wood dust and formaldehyde decreased the mucociliary clearance mechanism.(8,9) Since formaldehyde and formaldehyde-containing particles may not be removed as efficiently from the nasal passages by the normal means of mucociliary clearance, the presence of high, localized doses of formaldehyde may contribute to the development of nasal cancers. This premise can only be confirmed by correlation of the occurrence of oropharyngeal cancer to exposure to formaldehyde-containing dust.

To help determine if a relationship between exposure to formaldehyde-containing dust/fibers and the incidence of nasopharyngeal and buccal cavity cancer existed, a method to estimate the amount of formaldehyde released from inhaled dust/fibers was needed. Considerations for sampler design centered on either a closed-face cassette sampler or an inhalable sampler. Previous studies(10) with both open-face and closed-face cassette samplers indicated that the collection efficiency for particles greater than 15 μm in diameter was less than the criterion established by the American Conference of Governmental Industrial Hygienists (ACGIH) for inspirable particulate mass.(11) Previous work in the sampling of workplaces where wood dust was present had shown that samplers designed to meet the ACGIH inhalability criterion consistently collected larger amounts of particulate material when compared with closed-face cassette samplers.(12,13) Based on this previous work, a sampler design which would collect particles that were inhalable (inspirable) was selected. Secondly, to determine the amount of formaldehyde that would be released from the dust/fibers by hydrolysis or desorption after inhalation, the sample preparation should mimic the temperature and humidity conditions that would exist in the nasal and oral breathing passages. Finally, since the levels of formaldehyde to be determined on the dust/fibers samples might be low, a sensitive method would be required. Based on a previous review of the literature,(14) analytical methods that used 2,4-dinitrophenylhydrazine and chromotropic acid for the determination of formaldehyde provided good sensitivity and reliability. This article describes the incorporation of all these considerations into the development of a method for the estimation of formaldehyde dose from inhalable airborne dust/fibers and its application to actual field samples.

Experimental

Equipment and Materials

Ultraviolet/visible spectral measurements of chromotropic acid/formaldehyde adduct were made with a Hewlett–Packard Model 8452-A Diode Array Spectrophotometer using 1-cm path length cells.

Liquid chromatographic determination of the 2,4-dinitrophenylhydrazone of formaldehyde were performed on a system composed of two Waters Model M-6000A pumps (Milford, Massachusetts), a Waters Radial Compression Module Model RCM-100, a Waters Radial Pak C_{18} reversed phase column, a Waters Automated Gradient Controller, a Waters Model 440 ultraviolet detector (365 nm), and a Waters WISP 710B autosampler.

Twenty-milliliter vials (Supelco, Inc., Bellefonte, Pennsylvania) were used for cloth sample analyses. Reagents were obtained from the following sources: 37 percent formalin solution, Pararosaniline, perchloric acid, sodium sulfite from Fisher Scientific, Fairlawn, New Jersey; chromotropic acid, 2,4-dinitrophenylhydrazine (30% water) from Aldrich Chemical Co., Milwaukee Wisconsin; concentrated sulfuric acid, 0.02 N sulfuric acid from Anachemica Chemical, Inc., Champlain, New York; and acetonitrile from American Burdick & Jackson, Muskegon, Michigan.

The following untreated cotton fabrics were obtained from Test Fabrics, Inc., Middlesex, New Jersey: mercerized, combed-cotton broadcloth and polyester/cotton (65%/35%) broadcloth. These cloth samples were analyzed for formaldehyde content and contained less than 2 ppm (w/w) as determined by the chromotropic acid analysis procedure listed below. Samples of blue and gray, postcure-process polyester/cotton cloth (Graniteville Co., Graniteville, South Carolina) were obtained from Rockcastle Manufacturing, Mt. Vernon, Kentucky. This fabric, as supplied by the manufacturer, had been treated with dimethyloldihydroxyethyleneurea (DMDHEU) but was not cured to impart the final crease-resistant finish. Collar fusion material was obtained from Morgan Shirt Factory, Morgantown, West Virginia.

Inhalable samplers (HR-701 I.O.M. Personal Inspirable Dust Sampler) were purchased from Air Quality Research, Berkeley, California. Plastic, closed-face filter cassettes (37-mm) were purchased from Curtin Matheson Scientific Co., Florence, Kentucky. Thirty-seven-millimeter polyvinyl chloride (PVC) filters (5.0-μm pore size), 25-mm AA cellulose ester filters (0.8-μm pore size), 25-mm HA cellulose ester filters (0.45-μm pore size), and 25-mm and 37-mm cellulose back-up pads were purchased from Millipore, Bedford, Massachusetts. Twenty-five-millimeter PVC filters (5.0-μm size) were purchased from SKC, Eightyfour, Pennsylvania. Twenty-five-millimeter nitrocellulose filters (0.2-μm pore size) and 25-mm porous plastic back-up pads were purchased from Nuclepore, Pleasanton, California.

Recovery Efficiency Study

To determine the recovery efficiency of adsorbed formaldehyde from cloth not treated with permanent press resins and the effectiveness of the analytical procedure, 1-g samples of mercerized, combed-cotton broadcloth and polyester/cotton (65%/35%) broadcloth contained in 20-ml screwcap vials were spiked with aliquots of a 1 μg/μL solution of formalin in water at the 10.6, 107, and 1186 μg/sample levels. Vials containing no cloth also were spiked with formaldehyde solutions to act as control samples. Samples were analyzed by the chromotropic acid procedure described below.

Hydrolysis Study

To study the effects of the hydrolysis conditions on permanent press-treated cloth samples, duplicate 1-g samples of both blue and gray postcure-process polyester/cotton cloth were placed in 125-ml, ground-glass-stoppered bottles along with 50 ml of distilled water. The bottles were placed in a 37°C water bath and 5-ml aliquots were removed from each bottle at 1-, 2-, 4-, and 8-hour intervals. The aliquots were analyzed by the chromotropic acid method described below.

Factorial Study

The effects of the parameters of time, temperature, and desorption volume on the amount of formaldehyde recovered from the postcure-process polyester/cotton cloth were determined using a two-level factorial experiment. Pieces of the postcure-process cloth were cut and weighed to an average of 0.0977 ± 0.0009 g. The desorption volumes of distilled water used were 4 and 10 ml; the times for incubation were 2 and 6 hours; the temperatures were 34° and 40°C. The midpoint conditions of 7 ml of distilled water, 4-hour incubation time, and 37°C were replicated four times to check for interaction between variables. The eight runs of the experiment were performed in duplicate. The samples were analyzed by the chromotropic acid procedure described below.

Sampling

Sample cassettes were assembled according to manufacturers' instructions. Closed-face cassette samplers and inhalable samplers were operated at a flow rate of 2 L/min.

In situations where back-up impingers were used with the filter samplers, the impingers were prepared according to NIOSH Method 3500 for formaldhyde.(15) The only deviation from this method was to adjust the sampling rate up to 2 L/min for consistency with the filter sampling recommendations.

Analysis

Bulk Samples: Samples of bulk cloth were placed in 20-ml vials, to which were added 4 or 10 ml of deionized water. Several vials of water only were included as reagent blank samples. The vials were then placed in a water bath controlled at 37°C for 4 hours. Samples were analyzed by either of the two analysis methods listed below.

Impinger Samples: Back-up impinger samples were analyzed by NIOSH Method 3500.(15)

Filter Samples: Sample filters from the inhalable samplers and the closed-face cassette samplers were carefully transferred to 20-ml vials with forceps. With the inhalable samplers, the interior of each inhalable cassette was rinsed with 10 ml of deionized water which was then added to the filter-containing vial. Ten milliliters of deionized water was added to each vial containing the closed-face cassette filters. Several vials containing only water were included as reagent blanks.

The sample vials were placed in a water bath (Equatherm Model 392-134 Waterbath, Curtin Matheson Scientific, Inc., Cincinnati, Ohio) controlled at 37°C for 4 hours. The vials were removed from the water bath after incubation and the solutions were filtered using a 0.45-μm filter (Acro LC13 filters, No. 4453, Gelman Sciences, Ann Arbor, Michigan) to remove any particulate material. Samples were analyzed by either of the methods listed below.

For formaldehyde determination by the chromotropic acid method, a 4-ml aliquot of each solution was analyzed by the procedure described in NIOSH Method 3500.(15) The amount of chromotropic acid added to the sample could react with a maximum of 42 μg of formaldehyde per sample aliquot. (Whenever the amount of formaldehyde approached 30 μg per aliquot, the sample was diluted and reanalyzed.) The absorbance at 580 nm was then compared to results obtained from analysis of calibration standards containing known amounts of formaldehyde via the calibration software of the computer-controlled spectrophotometer. A reference wavelength of 800 nm was used to compensate for base-line drift during analysis. The computer software compiled the absorbances of the samples at 580 nm and performed either a linear or second order least squares regression analysis on the calibration standards. The resulting equation was used to determine the amount of formaldehyde present in each sample.

Calibration standards were prepared by dilution of a standard solution of formalin in distilled water (1 mg/ml) and analyzed in the same manner as the samples. The calibration range usually covered 1 to 25 μg of formaldehyde/4-ml aliquot. A limit of detection(16) of 0.44 μg formaldehyde/filter sampler was determined in laboratory evaluation of this method.

For the analysis of samples by the 2,4-dinitrophenylhydrazine method (2,4-DNP),(17) 1 ml of the aqueous solution obtained after incubation and filtration of the samples was mixed with 3 ml of acetonitrile containing 2,4-DNP (1.3 mg/ml). This amount of 2,4-DNP could react with 590 μg of formaldehyde/ml. (When formaldehyde levels approached 400 μg/ml, samples were diluted before addition of the 2,4-DNP solution.)

Calibration standards were prepared by addition of known amounts of formaldehyde to 1-ml aliquots of water. These standard solutions were then mixed with 3 ml of acetonitrile containing 2,4-DNP (1.3 mg/ml).

One drop of 1 N perchloric acid was added to each of the sample and calibration solutions (1 ml aliquot in 3 ml of 1.3 mg/mL 2,4-DNP) to catalyze the reaction to form the corresponding hydrazone. The hydrazone was determined by high-performance liquid chromatography using a C_{18} reversed phase column and an ultraviolet detector (365 nm). The mobile phase was 32.5 percent methanol, 32.5 percent water, and 35 percent acetonitrile. A limit of detection(16) of 0.08 μg formaldehyde/filter sample was determined during the laboratory evaluation of this method.

All data are reported in the text as the mean with the associated 95 percent confidence interval.(18)

Results and Discussion

Laboratory Studies

Early in this research, the issue of true level of formaldehyde in the dust/fibers samples being analyzed needed to be addressed. No material was available that had a known amount of formaldehyde on dust/fibers. To solve this problem, several yards of blue, postcure-process, permanent-press finish, polyester/cotton (65%/35%) fabric used at one of the planned sites for the field evaluation of the method under development were obtained. While this material could not be considered a standard reference material, analysis of several portions of this cloth indicated that the formaldehyde concentration in this material was approximately 1600–1700 μg/g (ca. 1600–1700 ppm) when analyzed using both methods described above. The consistency of formaldehyde content of the cloth indicated that it should provide a good approximation of the lint and fibers which would be collected during a field study. This material was used for evaluation of method performance for much of the method development work.

Another alternative for the preparation of standards for formaldehyde on cloth was to fortify samples of cloth with known amounts of formaldehyde. One potential problem with this approach was incomplete recovery of the formaldehyde from the cloth. To determine if there was irreversible adsorption of formaldehyde to untreated, cotton-based fabrics, several types of test fabrics were fortified with known amounts of formaldehyde solution (1 μg/μL). Average recoveries of formaldehyde from both mercerized, combed-cotton broadcloth samples and the control samples were 85.8 ± 5.2 percent and 85.5 ± 4.3 percent, respectively (6 samples per level; 3 levels), and were equivalent at all three concentration levels. The less than stoichiometric recovery for these samples, including the reference samples, is probably due to loss of formaldehyde into the headspace of the sample vial.

With the polyester/cotton broadcloth, the recovery was dependent on loading. At 10.6 μg/sample, recovery was 0.6 ± 0.7 percent. Recovery increased to 45 ± 3.4 percent and 77.8 ± 3.8 percent at 107 and 1186 μg/sample, respectively. In comparison with the results of the mercerized cloth, these results indicated that irreversible adsorption of formaldehyde into the polyester/cotton broadcloth had occurred, at least in the lower two levels. These results indicated that the fortification of cloth was of limited use for the preparation of standards.

In an attempt to simulate temperature conditions for hydrolysis which might exist in the nasal passages, distilled water at 37°C was selected for hydrolysis of formaldehyde from the permanent press resin-treated cloth. It was assumed that other compounds present in the nasal passages would either not affect the hydrolysis process substantially or would interact in the process in ways which would be difficult to simulate in the laboratory. These conditions were used to help determine the amount of time required for hydrolytic release of formaldehyde bound to permanent press resin-treated cloth. With the exception of one point, the results of the hydrolysis study of permanent press resin-treated cloth were duplicated, as shown in Figure 1. The formaldehyde released by hydrolysis rose quickly during the first hour and then leveled off. Although these results indicate that 2 hours would be the best desorption time for blue and gray cloth samples, collar fusion material,

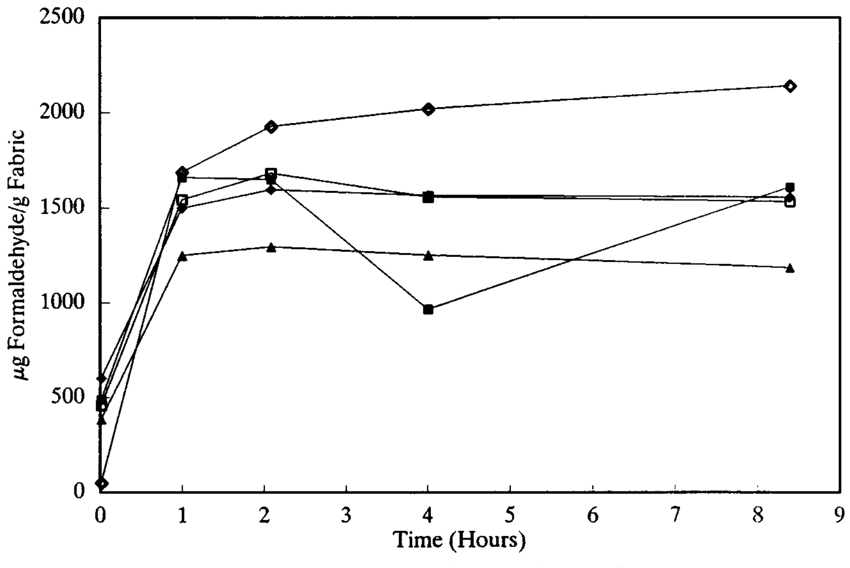

FIGURE 1. Yield of formaldehyde from 1-g samples of postcure, permanent press fabric over time. Results from replicate samples of blue and gray cloth and a single sample of collar fusion material are presented in the graph.

a formaldehyde resin-treated fabric, was found to continue releasing formaldehyde beyond 8 hours under the same hydrolytic conditions.

To further define the optimal hydrolysis time for release of bound formaldehyde, information obtained from biological systems on the clearance of particles from the respiratory tract was considered. In literature studies, 75–80 percent of particles of ca. 10 μm diameter were cleared from the upper respiratory tract after 4.5 hours(19,20) Other work indicated that the location of the particle deposition may dramatically affect clearance times.(21) Particles deposited in the ciliated epithelium were cleared in several hours, while those deposited in the pharnyx and larnyx were swallowed almost immediately. However, other studies with animals indicated that formaldehyde exposure repressed mucociliary function,(22,23) which would result in a reduced clearance rate for particles deposited in the ciliated epithelium. Based on these findings of other researchers and the kinetic work described above, a hydrolysis time of 4 hours was selected.

To evaluate the parameters of time, temperature, and desorption volume on the recovery of formaldehyde, a two-level factorial experiment was performed. Of the three variables studied, only desorption volume had a statistically significant effect on formaldehyde release. Use of the larger desorption volumes (7 and 10 ml) caused larger amounts of formaldehyde to be recovered. This finding may be due to the increased capacity of the larger volume of water to contain formaldehyde and the reduced headspace volume in the desorption vials.

The loss of adsorbed formaldehyde from the dust/fibers during sampling was a concern, since the capacity of dust/fibers for formaldehyde adsorption had not been studied extensively.(24) To study the ability of the cloth to adsorb and retain gaseous formaldehyde, seven circles (0.1 g each) of the blue postcure-process cloth were placed in a desiccator (approximately 31 cm in diameter by 21 cm deep) containing about 50 g paraformaldehyde. The cloth was left for 2 days, then removed and analyzed for formaldehyde content. Seven additional circles of blue postcure-process cloth which were not exposed to formaldehyde were stored in a sealed plastic bag for the same amount of time and analyzed as control samples. The control samples contained 183.8 ± 6.5 μg of formaldehyde, as determined by the chromotropic acid method. The same samples, when analyzed using the 2,4-DNP method, contained 174.8 ± 3.6 μg of formaldehyde. The samples exposed to formaldehyde vapor contained 2137 ± 250 μg (chromotropic acid method) and 2082 ± 240 μg (2,4-DNP method) of formaldehyde. These results demonstrated the agreement of the two analysis methods and indicated that the cloth could adsorb a large amount of formaldehyde vapor. The larger amount of variability observed with the vapor-spiked cloth circles was probably due to offgassing of the adsorbed formaldehyde during handling of the samples prior to analysis.

To study the possible loss of this adsorbed formaldehyde during sampling and handling, six circles of formaldehyde-saturated, postcure-process cloth were placed in 25-mm filter cassette holders. Three of the holders contained cellulose back-up pads and three contained plastic back-up pads. The cassettes were attached to impingers in series containing 1 percent sodium bisulfite solution. Ambient air was sampled through all six cassettes at approximately 1 L/min for 1 hour. Replicate samples of the ambient air were taken to verify background levels of formaldehyde in the air (10 μg/m^3). The cloth circles, back-up pads, back-up impingers, and cassette rinses were analyzed for formaldehyde content. The total amount of formaldehyde found for each sample was 1734 ± 228 μg of formaldehyde, which was similar to the amount of formaldehyde found in postcure-process cloth exposed to formaldehyde alone (2137 ± 250 μg). The most interesting finding of this experiment was the distribution of formaldehyde in the cloth, back-up pad, and impingers. Since the samples could not be analyzed on the day of preparation, the adsorbed formaldehyde tended to equilibrate between the various parts of the sampler during overnight storage. With cellulose back-up pads, 31 ± 12 percent of the formaldehyde was found on the cloth, 52 ± 22 percent of the formaldehyde was found on the back-up pad, and 15 ± 7 percent of the formaldehyde was found in the impingers. With the plastic back-up pads, 60 ± 36 percent of the formaldehyde was found on the cloth, 37 ± 4 percent of the formaldehyde was found in the impinger, and less than 0.5 percent of the formaldehyde was found on the back-up pad. Apparently, the cellulose ester back-up pads have a large capacity for retention of formaldehyde vapor. Also, 6 ± 5 percent of the formaldehyde was found in the cassette rinse of the cellulose pad-containing cassettes, while less than 0.1 percent of the formaldehyde was found in the rinse from the plastic pad-containing cassettes. The higher levels of formaldehyde in the rinses from the cellulose pad-containing cassettes may be explained by the presence of several fibers of cellulose remaining in the cassettes after removal of the cloth and back-up pads. The rinsing of the cassettes may have removed these fibers and given rise to the level of formaldehyde found. These results indicated that if a filter/back-up pad sampler is to be used for formaldehyde in dust/fibers sampling, the back-up pad should also be analyzed to determine formaldehyde content. They also indicate that a plastic back-up pad would be preferable to a cellulose ester back-up pad. The overall implication of this experiment is that there is a possibility of loss of adsorbed formaldehyde from samples, although the majority of the adsorbed formaldehyde remained adsorbed on the cloth in this experiment. This implication extends to other inhalable particles that could adsorb formaldehyde. The method can only measure formaldehyde in particles/fibers where the formaldehyde is either chemically bound to the particle/fiber or is so strongly adsorbed that it cannot be stripped from the particle/fiber by the air flowing through the sampler. Formaldehyde vapor lost from particles/fibers would be considered to be part of the vapor phase measurement (e.g., impinger or sorbent tube sample).

To evaluate the method's performance on a different matrix, a bulk sample of floor refinishing dust was obtained. The resin system used in this refinishing operation was urea-formaldehyde-based and similar to the resin system used for the treatment of the postcure-process polyester/cotton cloth. The bulk dust was ground in a freezer mill to a powder consistency (ca. 10–50 μm as determined by optical microscopy). Analysis of 1- to 5-mg portions of this dust (37°C, 4-hour incubation, chromotropic acid analysis) gave variable results (20%–50% relative standard deviation [RSD]). The variability was found to be due to the presence of the particles in the solution analyzed with the chromotropic acid method. The heat (95°C) and strong acid conditions (concentrated sulfuric acid) of the chromotropic acid method analysis most probably contributed to additional hydrolysis of the resin and subsequent release of formaldehyde from the particles present. This additional release of formaldehyde would positively bias the results. When the dust-containing solutions were filtered through a 0.45-μm pore size filter, analysis results were lower and more precise. Analysis of six filtered and six unfiltered 2-mg samples of the dust weighed into vials gave results of 11.0 ± 0.8 μg/mg (6.6% RSD) and 74.7 ± 16.4 μg/mg (20.9% RSD), respectively. This finding indicated the necessity of a filtration step in the analysis procedure to improve precision and remove potential positive bias in the method.

To study the storage stability of the urea-formaldehyde-based floor refinishing dust, 2-mg portions of dust were weighed and analyzed for formaldehyde content over a 21-day period. Dust samples were stored at both ambient and reduced temperature and analyzed by the chromotropic acid method. No difference in formaldehyde results due to storage conditions or length of storage was noted. The average result of 32 samples was 6.9 ± 0.2 μg/mg (RSD = 8.2%). It should be noted that this set of samples was prepared from the same bulk sample as the filtered samples described above (11.0 ± 0.8 μg/mg). This finding indicates that there is the possibility of formaldehyde loss from the dust during storage, since the two sets of analyses were performed a month apart. Although no loss of formaldehyde was noted over the 21-day storage period, the precautions taken for the storage of these samples (screw-cap vials) were different than the way the bulk dust was stored (ground-glass-stoppered Erlenmeyer flask).

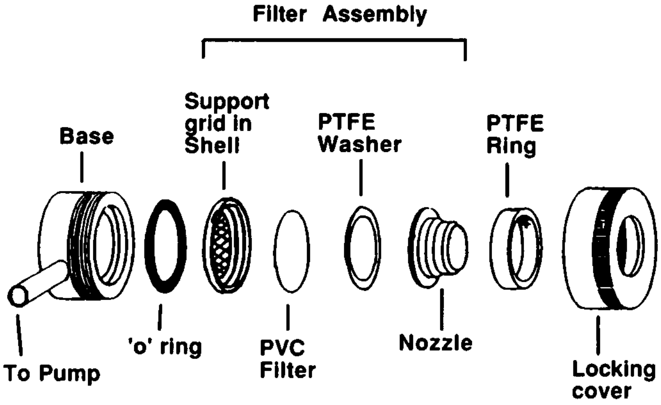

FIGURE 2. Diagram of inhalable cassette sampler.

At the time when sampler design was a consideration in this research, a sampler developed by researchers at the Institute of Occupational Medicine (IOM) in Edinbor-

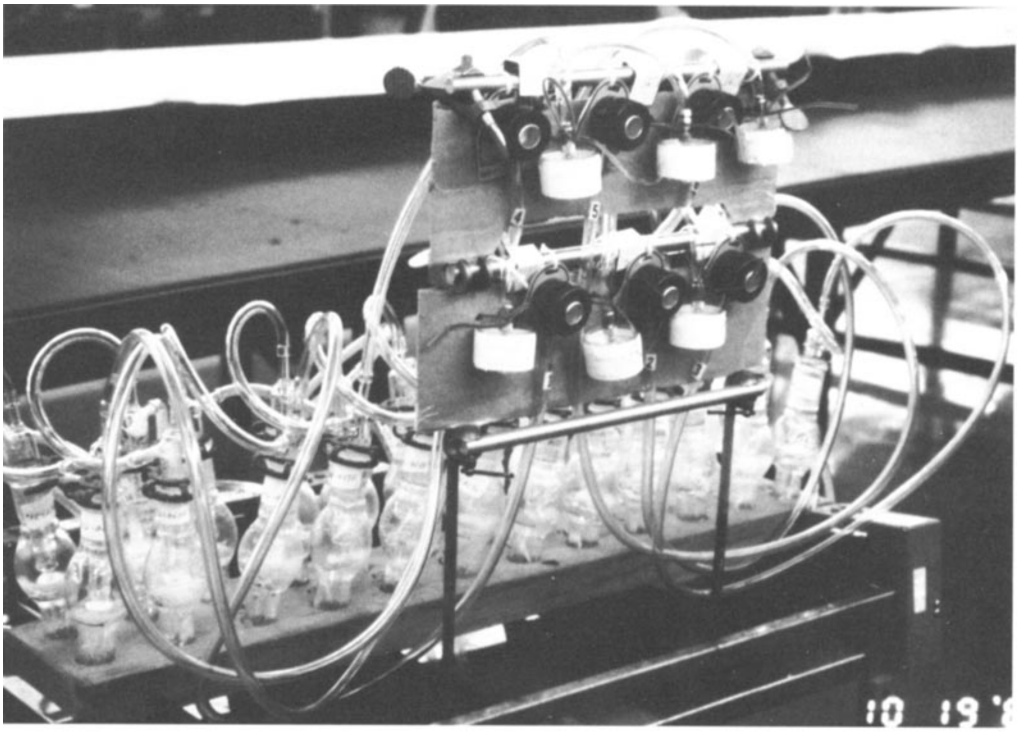

FIGURE 3. Photograph of sampling stand containing inhalable samplers, closed-face cassette samplers, and impingers.

ough, Scotland, became commercially available (Figure 2).(25) One of the key elements of this sampler was that its performance characteristics followed the inhalability criterion proposed by Vincent and Armbruster(26) and adopted by ACGIH.(11) This personal sampler had a cylindrical body, 37-mm in diameter and 27-mm long, with a 15-mm diameter inlet that faced forward. A 25-mm filter was contained in a light metal cassette having a 15-mm diameter inlet tube that protruded 1.5 mm beyond the body of the sampler. Since inhalability was of concern in the measurement of formaldehyde content of airborne dust, the use of this type of sampler should provide a more accurate representation of the potential inhalable dose. One published study(12) on the comparison of this sampler with open- and closed-face, 37-mm filter cassette samplers found that the inhalable sampler collected higher amounts of dust than either of the other two samplers. This finding was attributed to the hypothesis that the inhalable sampler had a higher sampling efficiency for particles larger than 15 μm than the cassette filters.

To evaluate filters for use in the inhalable sampler, four filter types (nitrocellulose, AA cellulose ester, HA cellulose ester, and PVC membrane) were analyzed by the chromotropic acid method to determine the formaldehyde blank of each filter type. The PVC filters had the lowest blank value (0.11 μg per filter) and were the most durable when folded for transfer into desorption vials. This filter type also has been used in nuisance dust methods(27,28) and was the logical choice for use in this research.

Field Studies

A field evaluation of the method was arranged at a garment production plant. This plant produces uniform shirts and trousers for a variety of commercial customers from the same type of material used in the sampling and analytical method development work and was the source of the postcure-process cloth used in the method development. Total dust/fibers sampling during a preliminary visit to the plant indicated that the cutting and layout area and the turn-and-ticket operation had higher levels of dust/fibers than the rest of the plant.(29) In the cutting and layout area, fabric was laid out on long tables in multiple layers and the patterns for the garments to be made were cut using electric shears. The cutting operation was responsible for the dust/fibers generation in this area. The turn-and-ticket operation was a station that used a vacuum device to turn the trouser legs right side out for further processing in the plant. As the legs of the trousers were pulled into the machine by vacuum, fibers and dust from the cloth were dispersed into the air.

Two sampling stands were constructed to hold in close proximity six inhalable samplers and six closed-face cassette samplers each (Figure 3). The samplers were attached to each stand in two rows of six samplers, with each row containing three inhalable and three closed-face cassette samplers. The samplers were arranged so that samplers of the same type were not adjacent, either horizontally or vertically. Two impingers containing 1 percent aqueous sodium bisulfite solution were downstream of each sampler to collect vapor phase formaldehyde. Cardboard backing was used on the stand to block drafts from blowing past the samplers in the same way as a person wearing the sampler would. The closed-face cassettes were attached to the stand so that the cassette opening was directed down toward the floor. The inhalable samplers were maintained in a vertical position with the inlet facing out, as they would be worn on a worker's lapel. At the turn-and-ticket operation, the sampling stand was placed on top of the vacuum device. In the cutting and layout area, the sampling stand was placed on a mobile cart and intermittently moved to stay in close proximity to the cutters as they worked. Samples were collected at 2 L/min for approximately 8.5 hours.

Both the inhalable and closed-faced samplers held preweighed filters so that gravimetric dust/fibers measurements could be made for each sampler. Results from gravimetric analyses of most samples indicated that only small amounts of dust/fibers were collected, as shown in Table I.

TABLE I. Results of Field Study for Formaldehyde in Dust/Fibers Conducted at Garment Production Facility

	Filters[A]		Backup Impingers[A]
Sample Location	Dust[B] (mg/m^3)	Formaldehyde, Bound[C] ($\mu g/m^3$)	Formaldehyde, Vapor[D] ($\mu g/m^3$)
Inhalable			
Cut and Spread	<0.1	0.4	36
	0.3	0.6	23
	0.5	1.4	20
	<0.1	0.6	25
	0.4	0.4	30
	<0.1	0.5	19
	0.4 ± 0.3[E,F]	0.7 ± 0.4[E]	26 ± 7[E]
Turn and Ticket	0.2	1.5	4
	0.5	1.8	2
	0.2	1.0	1
	0.4	1.6	1
	0.4	1.9	1
	0.8	1.4	2
	0.4 ± 0.2[E]	1.5 ± 0.3[E]	2 ± 1[E]
Closed-Face Cassettes			
Cut and Spread	<0.1	<0.1	50
	<0.1	<0.1	39
	<0.1	0.2	19
	<0.1	<0.1	23
	0.1	<0.1	40
	<0.1	<0.1	46
	0.1[F]	0.2[F]	36 ± 13[F]
Turn and Ticket	0.1	0.3	48
	<0.1	0.5	26
	0.1	0.3	25
	0.1	0.4	26
	0.1	0.4	20
	0.1	0.3	24
	0.1 ± 0[E,F]	0.4 ± 0.1[E]	28 ± 10[E]

[A] A volume of 1040 L was sampled for all samples.
[B] Limit of detection for gravimetric measurements was 0.1 mg.
[C] Expressed as $\mu g/m^3$ of formaldehyde adsorbed or bound on particles.
[D] Expressed as $\mu g/m^3$ of formaldehyde in the vapor phase.
[E] Average concentration with 95% confidence interval.
[F] Values less than the limit of detection were not included in averages.

Based on these results, no significant conclusions could be drawn about the comparability of the two sampler types. However, there were visible depositions of fibers on all filters, which indicated a potential for exposure to formaldehyde-containing particles.

Impinger samplers for formaldehyde were placed downstream of both the inhalable samplers and closed-faced cassette samplers to measure vapor-phase concentration. The impinger results were similar except for the inhalable samplers at the turn-and-ticket operation. Since both sampler types were sampling a similar atmosphere, the impinger results from both types of samplers should be the same. The impinger results for the inhalable samplers were much lower than the results for the other samplers. The reason for these lower results was not apparent.

The filters from both samplers were analyzed for total formaldehyde content using the chromotropic acid method. Results from these analyses are shown in Table I. Since the back-up pads in the closed-faced cassettes were cellulose, they were also analyzed for adsorbed formaldehyde content separately. The formaldehyde levels found on the back-up pads were not significantly greater than the amount of formaldehyde found on the field blank backup pads (ca. 1 µg). The chromotropic acid analysis results of the filters from the turn-and-ticket operation samples showed that the inhalable samplers collected more formaldehyde than the closed-face cassette samplers. The results were similar for the cutting area samples, with inhalable sampler results demonstrating higher formaldehyde content than closed-face cassette sampler results. The variability in results within a given sampler type may be attributable to the low levels of dust/fibers collected on each type of sampler. Due to the low levels of formaldehyde found on the samples, reanalyses of the samples were attempted with the 2,4-DNP method. Unfortunately, the formaldehyde-containing solutions from the incubated samplers were not stable (ca. 4 weeks storage at 0°C) and results were approximately one-fifth of the chromotropic acid analysis results.

A second field study of the method was scheduled at a waterbed accessory production plant. The primary products of this plant are constructed of particle board containing either urea-formaldehyde or phenol-formaldehyde resins. A preliminary visit to the plant indicated the potential for dust exposure from the various sawing operations in the plant. Sampling was conducted at a location where two miter saws were used simultaneously to cut waterbed rails to length. The two sampling stands used in the previous field study were placed side by side across an aisle from the two saws. Only two inhalable and two closed-face cassette samplers had back-up impinger sets on each sampling stand. After 4 hours sampling time, there was a notable buildup of dust on both the closed-face cassette and inhalable samplers. To prevent filter overloading, sampling was stopped after 4.5 hours. Results from the sample analyses are shown in Table II.

The results from the impingers backing up the inhalable and closed-face cassette samplers indicated that the vapor-phase concentration of formaldehyde was higher than the concentration in the field study conducted at the garment production plant. Also, there were no significant differences in the impinger results between the sampler types as observed in the previous field study.

Dust levels in this plant were sufficiently high to allow comparison of gravimetric results of the two sampler types. The levels of dust measured by the inhalable samplers were statistically greater than the levels measured by the closed-face cassette samplers. Again, these findings were consistent with the results of Vinzents.(12)

Except for three samples (one closed-face cassette and two inhalable samplers), the composition of the dust was fairly uniform with an average formaldehyde concentration of 3–5 µg/mg dust. These results agreed with duplicate analyses of the two bulk samples of saw dust from the cutoff saws collected on the same day (3.6 and 4.6 µg/mg).

Formaldehyde levels found with the inhalable samplers on sampling stand B were statistically higher than the levels found with the closed-face cassettes on stand B (Table II).

TABLE II. Results of Field Study for Formaldehyde in Dust Conducted at Waterbed Accessory Production Facility

	Filters[A]		Backup Impingers[A]
Sample Location	Dust[B] (mg/m^3)	Formaldehyde, Bound[C] (µg/m^3)	Formaldehyde, Vapor[D] (µg/m^3)
Inhalable			
Sample stand A	3.1	17	—[E]
	3.5	1	142
	2.8	16	—[E]
	3.3	12	136
	3.1	2	—[E]
	2.9	14	—[E]
	3.1 ± 0.3[F]	10 ± 7[F]	139 ± 9[F]
Sample stand B	2.6	13	—[E]
	2.2	12	137
	3.1	12	—[E]
	2.1	11	—[E]
	2.1	11	—[E]
	1.4	8	111
	2.3 ± 0.5[F]	11 ± 2[F]	124 ± 165[F]
Closed-Face Cassettes			
Sample stand A	2.3	11	145
	1.7	9	—[E]
	0.4	8	—[E]
	1.6	10	158
	1.6	8	—[E]
	1.1	9	—[E]
	1.5 ± 0.6[F]	9 ± 1[F]	152 ± 83[F]
Sample stand B	1.3	7	—[E]
	1.7	4	—[E]
	1.6	5	137
	1.8	9	147
	1.6	8	—[E]
	1.8	5	—[E]
	1.6 ± 0.2[F]	6 ± 2[F]	142 ± 64[F]

[A] A volume of 540 L was sampled for all samples.

[B] Limit of detection for gravimetric measurements was 0.1 mg.

[C] Expressed as µg/m^3 of formaldehyde adsorbed or bound on particles.

[D] Expressed as µg/m^3 of formaldehyde in the vapor phase.

[E] No impinger backup.

[F] Average concentration with 95% confidence interval.

The formaldehyde levels found in dust samples taken on sampling stand A were not statistically different between sampler types. The A and B terminology is used to differentiate between the two sampling stands. When the results from both the sampling stands were combined, no significant difference in the level of formaldehyde determined on the dust collected by either type of sampler was found.

A possible explanation of why a larger difference in formaldehyde levels was not observed in the second field study was that the smaller particles ($< 15\ \mu m$) may have contributed the majority of the bound formaldehyde released by the hydrolysis step. If the hydrolysis step was primarily a surface reaction on the particle, then the smaller particles would provide the greatest surface area per unit weight and subsequently contribute a greater amount of formaldehyde to the sample result. In this instance, the larger particles, which would be collected more efficiently by the inhalable samplers, may not contribute significantly to the amount of formaldehyde determined. If this were the case, and if the inhalable and closed-face samplers collected the smaller particles with similar efficiency, then similar results could be expected. A second possible explanation for the differences in sampler results was that the particle size distributions between the two sampling stands was different. In this instance, additional information on the size distribution of the dust would have helped explain the results.

In the course of these two field studies, several difficulties were encountered with the method that were related to the design of the inhalable sampler. The clip that was used to close the cassette after sampling was difficult to handle and may have contributed to dust/fibers loss during attachment and removal prior to analysis. After the sample cassette had been disassembled prior to analysis, the transfer of the dust/fibers from the inside of the cassette was not straight forward, since rinsing the inside of the cassette was required. We are currently investigating other means of recovery of the dust/fibers from the sampler prior to analysis. Sample vials (straight-sided, 32-mm inside diameter vials, Nalgene #2118-0001) have been obtained that can hold the entire aluminum cassette of the sampler. This would allow more complete transfer of dust, since a cassette could be thoroughly immersed to rinse all dust/fibers into water without loss of dust/fibers or rinsing water while transferring to a narrow-mouthed vial. However, no comparative work has been done with these vials, other than to determine that these vials do not contribute to the formaldehyde blank.

Conclusions

A method for the estimation of the potential formaldehyde dose in inhaled dust/fibers has been presented. The method incorporated an inhalable sampler for the collection of the dust/fibers. Filters containing sampled dust/fibers were removed from the inhalable sampler filter cassette, placed in 10 ml of distilled water, and incubated at 37°C for 4 hours to liberate the formaldehyde from the dust/fibers. The use of a hydrolysis step in the analysis scheme attempted to mimic the temperature and residence time of particles in the nasal and oropharyngeal passages, where the dust/fibers would be deposited after inhalation. After incubation, the filter extracts were filtered with a 0.45-μm filter to remove any particles left in the extracts. For sample analysis, either a 4-ml aliquot was analyzed using the chromotropic acid procedure, as outlined in NIOSH Method 3500,(15) or a 1-ml aliquot was treated with 2,4-DNP and a catalytic amount of perchloric acid and analyzed by high-performance liquid chromatography for the resulting 2,4-dinitrophenylhydrazone. The limits of detection for the chromotropic acid procedure and the 2,4-DNP procedure were 0.44 μg and 0.08 μg per filter sample, respectively. The relative standard deviation of replicate determinations was 3.4 percent for textile samples containing about 180 μg of formaldehyde and 8.2–6.6 percent for wood dust samples containing 7–11 μg of formaldehyde.

Caution should be exercised in the way in which the data collected with this method are interpreted. The levels of formaldehyde found in the dust/fibers samples taken during the field studies were significantly lower than the formaldehyde air concentrations in both field studies when the results were expressed in $\mu g/m^3$. Although the hydrolysis procedure used in this method to liberate formaldehyde from the dust/fibers may not be fully representative of the hydrolysis occurring in the nasal and oropharyngeal passages, the formaldehyde in dust/fibers levels may be considered an approximation of the localized inhaled dose at the point of particle retention in the breathing passages. This value should not be compared to the vapor phase exposure that would encompass the entire respiratory tract. When performing studies to evaluate formaldehyde levels both in the vapor phase and in dust/fibers, it is recommended that separate measurements be taken for each determination. These results should be reported separately until sufficient data has been collected to allow appropriate epidemiological interpretation of formaldehyde-containing particulate exposures.

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