Quantitative Mid-Infrared Diffuse Reflection of Occupational Wood Dust Exposures

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Occupational exposure to airborne wood dust has been implicated in the development of several symptoms and diseases, including nasal carcinoma. However, the assessment of occupational wood dust exposure is usually performed by gravimetric analysis, which is non-specific. In this study, a mid-infrared (mid-IR) diffuse reflection method was adapted for direct on-filter determination of wood dust mass. The cup from the diffuse reflection unit was replaced with a horizontal translational stage and a filter with wood dust was set thereon. Diffuse reflection (DR) spectra were collected from filters with six different diameters in order to average the signal from the most filter surface. Two absorption bands around 1595 and 1510 cm^{-1}, attributed to lignin, were monitored for quantitative analysis. Calibration curves were constructed for standard extrathoracic red oak and yellow pine (aerodynamic particle diameters between 10 and 100 μm). Calibration of DR intensity versus known wood dust mass on the filter using the Kubelka–Munk function showed a nonlinear dependence for mass of less than 10 mg of wood dust. The experimental data and small-thickness samples indicate that Kubelka–Munk conditions are not obeyed. Alternatively, the pseudo-absorption function log(1/*R*), for which *R* is the relative reflectance, while still giving nonlinear dependence against mass, is closer to a linear dependence and has been preferred by other researchers. Therefore, we consider the use of the log(1/*R*) function for mid-infrared DR analysis of neat, small-thickness wood dust samples. Furthermore, we suggest the use of a silver metal membrane filter for direct on-filter analysis of wood dust rather than the glass fiber filters that have been used previously.

Index Headings: **Infrared spectroscopy; IR spectroscopy; Mid-IR spectroscopy; Diffuse reflection; Kubelka–Munk; Wood dust; Lignin; Occupational exposure.**

INTRODUCTION

It is estimated that in 25 countries in Europe, about 3.6 million workers were exposed to airborne wood dust between 2000 and 2003 and that over 0.5 million workers may be exposed to a dust level (any type of wood dust) exceeding 5 mg/m^3.[1] This exposure is greater than the threshold limit value of 1 mg/m^3, which is the Recommended Exposure Limit (REL) of the National Institute for Occupational Safety and Health and which has also been adopted by the American Conference of Governmental Industrial Hygienists for all inhalable wood dusts except Western Red Cedar (0.5 mg/m^3).[2] The practice worldwide to assess exposures to wood dust is to collect the aerosol in a worker's breathing zone with a sampling device and to determine the mass collected on a filter in a known volume of air.[3] This gravimetric analysis assumes that all collected particles are of interest, because weighing cannot differentiate between wood dust and other particulates.

In consideration of possible changes in the classification of wood dust from a nuisance dust to one that is specifically regulated, improved techniques are needed that are fast, reliable, and can identify and quantify wood dust. Previously, quantitative mid-infrared (mid-IR) diffuse reflection (DR) analysis was employed in conjunction with direct on-filter analysis in a study of silica in respirable airborne dusts deposited on a vinyl/acrylic copolymer filter.[4] Direct on-filter determination of wood dust mass by mid-IR DR spectroscopy was first adapted and applied to the field of industrial hygiene by Rando et al.[5] Those authors made several changes to the original diffuse reflection method. First, they replaced the analysis cup with a stage that accommodates the 37 mm filter for direct analysis; second, they collected background reflection from a blank glass fiber filter (GFF) rather than from potassium bromide; and finally, they collected the diffuse reflection spectrum from across the filter through the use of a motorized stage that translates in the horizontal plane. An absorption band found in the mid-IR spectrum of cellulose was used as the basis for the analysis of total wood dust collected from industrial environments.

This adapted DR method, however, has only been demonstrated in a single laboratory. In order to evaluate the robustness and reproducibility of the procedure, our initial aim was to establish the procedure in our laboratory. Various technical and conceptual challenges were encountered during our study. This resulted in several further modifications to the on-filter mid-IR diffuse reflection method for wood dust. Some of the critical changes include the use of a silver metal membrane filter instead of the glass fiber filter, the selection of lignin bands instead of cellulose for the construction of calibration curves, and the use of the log(1/*R*) function instead of the Kubelka–Munk function for the calibration curves. We also report a small inconsistency observed in the IR spectra related to the use of glass fiber filters and two different commercially available data acquisition software programs.

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With regard to the infrared analysis of wood, Fourier transform infrared (FT-IR) spectroscopy in the near-infrared or mid-IR ranges has long been promoted as a rapid means of analysis of the molecular structure of cellulose and lignin in paper, solid wood, or wood powder.[6–23] Infrared bands reported around 1230, 1270, 1510, and 1595 cm^{-1} are derived from lignin and are absent or contribute very little to the isolated cellulose or hemicellulose spectrum.[6,10,11,16] Other studies of diffuse reflection on wood also assign peaks around 1510 and 1595 cm^{-1} to aromatic ring breathing vibrations in lignin.[12,14] Despite consistency in the qualitative assignments of these bands to lignin, and of theoretical considerations for the use of the Kubelka–Munk (K-M) function in quantitative measurements,[24,25] experiments show departure of this function from linear behavior as a function of sample concentration.[4,17,26–30] This behavior is due to several factors such as non-homogeneous scattering and absorption factors through the sample, specular reflection contributions, variation in the sample particle size, sample preparation, semi-infinite depth of sample, and the absorbent nature of material used as background and matrix for diluting the sample.

The departure from linearity of the Kubelka–Munk function has been observed in several studies and the various authors have proposed several solutions to bring the K-M function to linear dependence. Corrections include changing the absorptivity of the matrix by adding a small fraction of absorbent material to a non-absorbent matrix;[26,27] correcting for baseline offset;[28] converting reflectance R to the $\log(1/R)$ function as pseudo-reflectance; and modifying the Kubelka–Munk function by a factor to account for surface absorptivity.[29,30] A recent study[31] of mid-IR DR spectroscopy on 241 samples of forages compared the calibration of absorption bands using R, $\log(1/R)$, interferograms, single-beam spectra, and the Kubelka–Munk data format. The study concluded that the Kubelka–Munk function and interferograms did not perform as well as the other functions and that accurate calibrations can be developed using $\log(1/R)$, R, or single-beam spectra.

In this article, we present our findings from qualitative and quantitative analysis of extrathoracic wood dust using the diffuse reflection technique on neat wood dust samples deposited on silver metal membrane filters. We have constructed the calibration curves using lignin absorption bands at 1510 and 1595 cm^{-1} and represented the data as Kubelka–Munk and log $(1/R)$ functions.

EXPERIMENTAL

Our samples consist of wood dust deposited on silver membrane filters (SMF). Standard extrathoracic red oak and yellow pine wood dust (aerodynamic particle diameter size range 10 to 100 μm with a geometric mean of 30 μm) obtained from Tulane University were produced by the wood dust generation procedure described by Rando et al.[5] Dried milled yellow pine and red oak were weighed and suspended in a known volume of ethyl acetate (A.C.S. 99.5% reagent, Fisher Scientific, Pittsburgh, PA) to make 1 mg/mL wood dust stock suspension. Ethyl acetate has low polarity, low viscosity, and high dielectric constant, which prevents emulsification and enhances the filtration of suspended wood dust. Further, the infrared properties of the filters used in this study are not altered after being immersed in ethyl acetate. Because of the volatility of ethyl acetate, samples were all prepared at the same time and the weighed mass of wood dust was used as the calibration standard. The wood dust was deposited on silver metal membrane filters (37 mm, SKC Inc., Eighty Four, PA) by filtering the stock solution through a 37 mm filtration apparatus provided by ALS Laboratory Group, Salt Lake City, UT (formerly Datachem). For calibration experiments, 12 samples of each type of wood dust were prepared. The wood dust mass of these samples ranged from approximately 0.5 mg to 8 mg, based on the mass range of field measurements.

A Research Series FT-IR spectrometer (Mattson, Madison, WI) equipped with a mercury cadmium telluride detector was used to obtain the diffuse reflection spectra. The data collection parameters were 4 cm^{-1} resolution, 300 averaged scans, gain of 10, moving mirror velocity of 12.5 kHz, and Happ–Genzel apodization. A Selector (Specac Inc., Orpington, Kent, UK) DR accessory was used in the sample compartment. To measure DR from wood dust deposited on the SMF, the cup from the Selector was replaced with a flat stage that can accommodate a 37 mm filter. The stage could translate and rotate (Fig. 1). A Sigma Koki (Tokyo, Japan) SGSP26-50 motorized stage provided the base for the translation assembly and the x-axis movement. An Oriel (Stratford, CT) manual stage provided the y-axis adjustment and an OptoSigma (Santa Ana, CA) manual stage provided the z-axis adjustment along with the height adjustment from the Selector unit. The travel distance for all the measurements was 31 mm and the travel time was 187 seconds (the time necessary to collect 300 scans). A bracket and extension arm attached to the OptoSigma stage provided access to the sampling chamber. A Sigma Koki SGSP-40YAW motorized rotational stage was mounted on the opposite end of the extension arm. A custom-machined sample holder was attached to the rotational stage to place the sample at the proper location for scanning. The two motorized stages were connected to a Sigma Koki SHOT-602 2-Axis Stage Controller, which in turn was connected to the serial port of a laptop computer. A custom program, written in-house using Microsoft (Redmond, WA) Visual C, allowed the operator to move the sample linearly a fixed distance at a specified speed and to rotate the sample by a predetermined amount. A vacuum tube was connected to the back of the stage to ensure that the filter was secured in place during measurements.

One sample was prepared as wood dust mixed with potassium bromide to compare the diffuse reflection measurements of wood dust on the silver filter with measurements from wood dust mixed with potassium bromide. The stage was replaced with the original diffuse reflection cup from the Selector unit. Potassium bromide was mixed with wood dust at 10% concentration by weight.

RESULTS AND DISCUSSION

Because filter choice is important for correct operation of the air samplers, but also for the diffuse reflection measurements, a short discussion on this subject is of value here. The initial choice of GFF was driven by our main goal of reproducing the method described by Rando et al.,[5] the large use of GFF in many personal samplers for gravimetric determination of occupational exposure, and their inexpensive cost compared to, for example, silver metal membrane filters (SMF). In Fig. 2 we present the background spectra from potassium bromide in the cup, the SMF, and the GFF on the stage. The background spectrum from the silver filter is very similar to the spectrum obtained from KBr, which makes this filter appropriate for diffuse reflection measurements, whereas the GFF has a strong

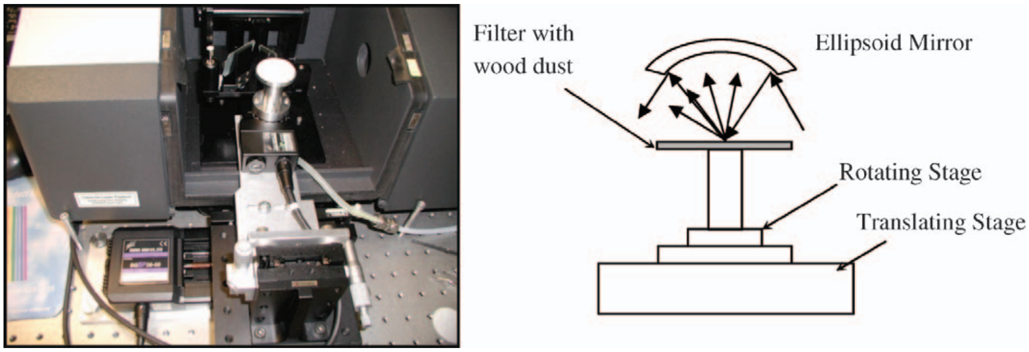

FIG. 1. Photo and schematic diagram of the rotating/translating stage for diffuse reflection unit. The stage was controlled by in-house software.

absorbance from 2000 to 600 cm^{-1} due to borosilicate, making the GFF unsuitable for infrared diffuse reflection measurements.

However, in preliminary studies we attempted to use the GFF and encountered an interesting situation that merits attention. The spectra we obtained from wood dust on a GFF when using Win First software were very similar to the spectra previously published by Rando et al.[5] However, when Omnic software was used, the infrared spectrum from wood dust in the region from 1500 to 1000 cm^{-1} was reversed and all of the reflection bands in this region were pointing downward, whereas the bands in the 3500 to 3000 cm^{-1} region had the usual upward profile. This behavior is due, in part, to the strong absorbance of borosilicate in the GFF below 2000 cm^{-1}, but it is also due to the Omnic software algorithm for the K-M function. The Omnic algorithm uses the following expression for the Kubelka–Munk function:

$$f(R) = (1 - R) \times |1 - R| / 2R \tag{1}$$

whereas Win First software uses the following formula:

$$f(R) = (1 - R)^2 / 2R \tag{2}$$

[private communication, Roy Rando, Tulane University, 2007], where R, the relative reflectance, is the ratio of the reflected intensity from the sample over the reflected intensity from the background. When reflectance from the blank filter is less than the reflectance from the sample, R becomes > 1 and the $f(R)$ function in Omnic becomes negative, whereas for the same situation, Win First computes a positive value for $f(R)$, making it difficult to detect anomalies. A similar spectral distortion was observed by Yeboah et al.[32] for a sample less absorbent than the background.

In order to illustrate how the choice of filter influences the data, Fig. 3 shows the diffuse reflection spectra collected from red oak in three different setups: (a) red oak mixed with KBr in the Selector unit cup, with background from neat KBr, using Omnic, (b) red oak deposited on SMF with background from blank SMF using Omnic, and (c) red oak deposited on GFF with background from blank GFF, using Win First. When Omnic software was used for red oak on the GFF sample, a mirror spectrum was obtained with all the bands shown in Fig. 3c pointing downward. The Win First software used with the glass fiber filter can introduce anomalies that might be hard to identify. From here on, the data shown are from wood dust on SMF using the Omnic software.

Figures 4a and 4b show mid-infrared range spectra from

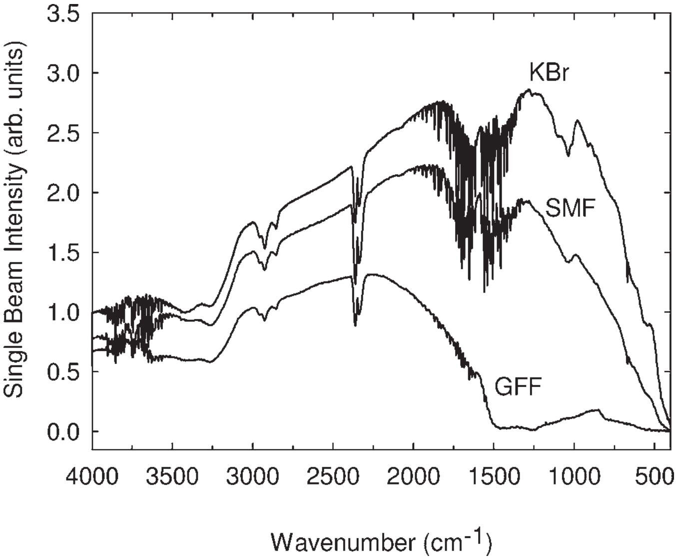

FIG. 2. Single-beam spectra representing the background from potassium bromide (KBr), blank silver metal membrane filter (SMF), and blank glass fiber filter (GFF).

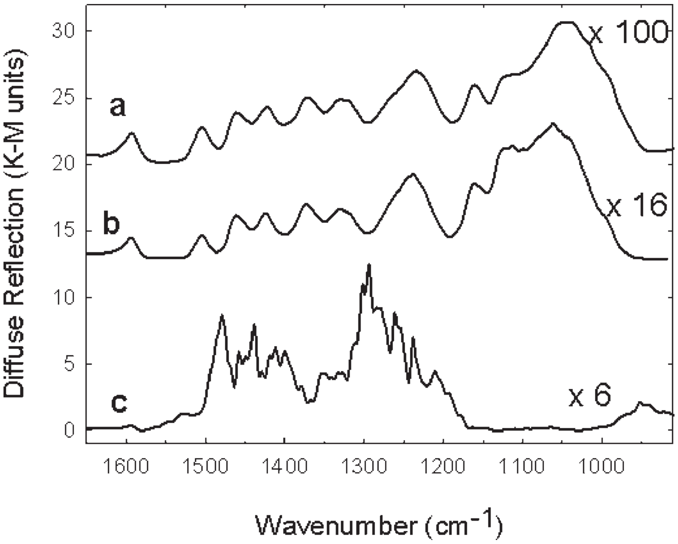

FIG. 3. Diffuse reflection spectra from red oak: (***a***) mixed with KBr; (***b***) on SMF; and (***c***) on GFF. Spectra were normalized and vertically displaced for easy visual comparison.

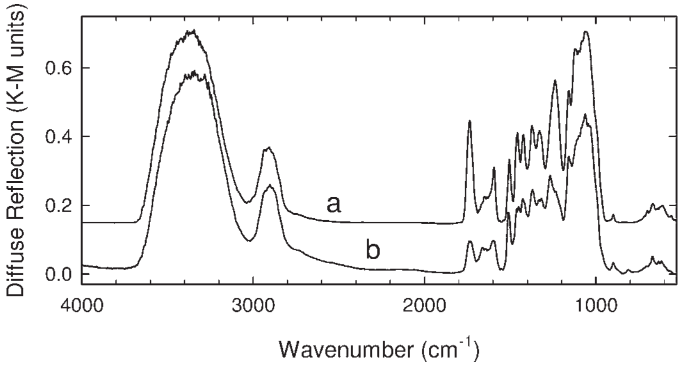

FIG. 4. Diffuse reflection spectra from standard extrathoracic (***a***) red oak and (***b***) yellow pine. Each sample contains approximately 2 mg of wood dust on SMF.

standard extrathoracic red oak and yellow pine, respectively, deposited on SMF. As reported by other authors,$^{6–17}$ we observed several bands: a strong and broad OH stretching band centered around 3380 cm^{-1}, a prominent C–H stretching absorption at about 2900 cm^{-1}, and a strong "fingerprint" region from 1800 to 600 cm^{-1} that contains many overlapping and discrete bands specific to cellulose, hemicellulose, and lignin.

Figure 5 shows a closer look at some of the similarities and differences in the spectrum of red oak and yellow pine in the "fingerprint" region. Labels point out several important bands. The contribution of partially overlapping bands L1 at 1240 cm^{-1} and L2 at 1270 cm^{-1} comes from the two types of lignin, syringil and guaiacyl, respectively.^{7,13,15,17,20} For yellow pine, and softwood in general, the intensity at 1270 cm^{-1} is much greater than the intensity at 1240 cm^{-1} because lignin in softwoods consists largely of guaiacyl lignin.^{7} For red oak, and hardwood in general, the two bands have comparable contributions because lignin in hardwoods consists of both syringyl and guaiacyl lignins.^{7,11,23} The bands labeled L3 and L4 around 1510 and 1595 cm^{-1} are contributions from aromatic ring stretching vibrations in the phenylpropane monomer of the lignin matrix.^{6,9,11} The relative intensity L3 : L4 is about 1 : 1 in red oak and 2 : 1 in yellow pine. Grandmaison et al.^{9} and Owen et al.^{11} observed this trend and used it to differentiate hardwood from softwood. The band around 1740 cm^{-1}, labeled C, is assigned to stretching vibrations of free $C{=}O$ from cellulose and hemicellulose, as it is absent in isolated lignin^{6,7,10,11,15,16} and in Raman spectra of wood.^{19} The broad band from 1200 to 1000 cm^{-1} is due to an overlap of bands from C–O bonds in lignin, cellulose, and hemicellulose. This high degree of overlapping makes this broad band difficult to use for mass calibration.

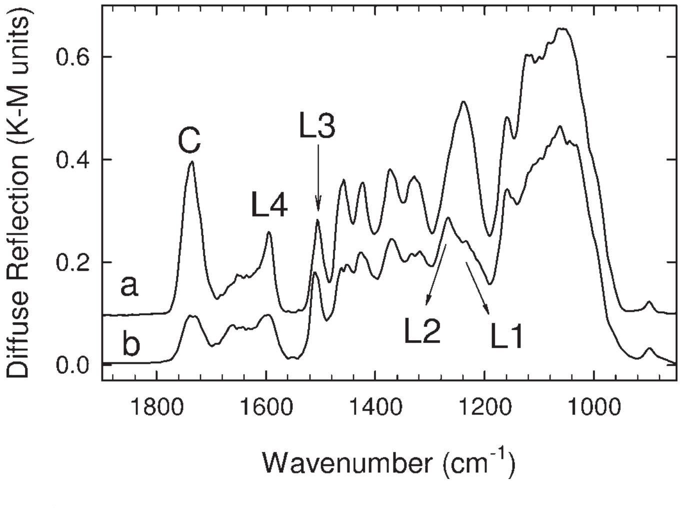

FIG. 5. Diffuse reflection spectra in the finger print region for: (***a***) red oak and (***b***) yellow pine. Bands labeled L1 through L4 are assigned to characteristic bending or stretching of different aromatic groups of lignin. The band labeled C is assigned to the carbonyl stretch in cellulose and hemicellulose.

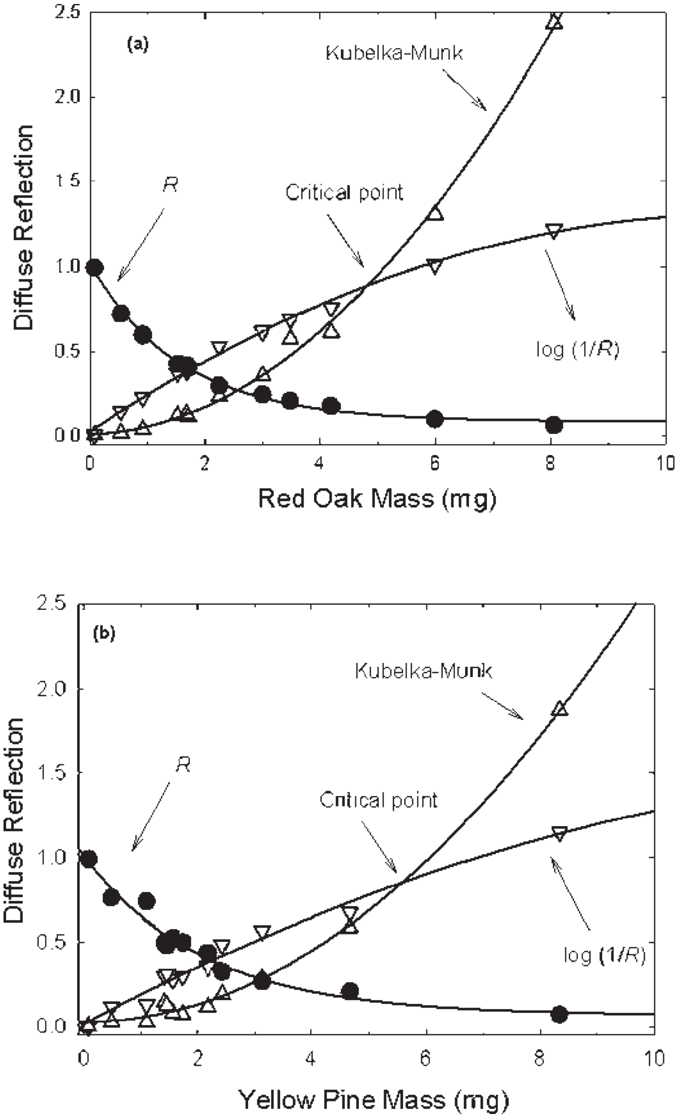

FIG. 6. Calibration curves: (**a**) red oak and (**b**) yellow pine. (∇) Log(1/*R*), (Δ) Kubelka–Munk, and (●) relative reflection. The critical point marks the condition of total coverage of the filter with wood dust.

Among the five bands described, L3 (1510 cm^{-1}) and L4 (1595 cm^{-1}) were the most stable in day-to-day experiments and had no overlapping, facilitating their selection for the calibration curves. One-point baseline correction was applied by subtracting the value at 1850 cm^{-1}, the point at which the baseline was nearly flat and close to zero. Peak areas and peak heights were also evaluated for these two bands and results were similar. Peak heights were selected because the measurement of peak area was lengthier and the proximity of

TABLE I. Fitting parameters for calibration data up to 10 mg of wood dust.

	Function			
	Linear regression, $y = a \times \text{mass}$		Quadratic regression, $y = (a \times \text{mass}) + (b \times \text{mass})$	
Wood dust	log(1/*R*)	K-M	log(1/*R*)	K-M
Red Oak	$R^2 = 0.969$ $a = 0.148$	$R^2 = 0.933$ $a = 0.299$	$R^2 = 0.997$ $a = 0.228$ $b = -0.010$	$R^2 = 0.997$ $a = 0.009$ $b = 0.034$
Yellow Pine	$R^2 = 0.970$ $a = 0.132$	$R^2 = 0.914$ $a = 0.223$	$R^2 = 0.979$ $a = 0.186$ $b = -0.006$	$R^2 = 0.996$ $a = 0.001$ $b = 0.026$

the other bands made it difficult to assign the baseline correction.

The calibration curves for standard extrathoracic red oak and yellow pine are presented in Fig. 6. Each data point represents the sum of peak heights at 1510 and 1595 cm^{-1} extracted from the Kubelka–Munk spectra and from log(1/*R*) spectra. Olinger et al.[22] observed a similar behavior of the Kubelka–Munk and pseudo-reflection functions for carbazole diffuse reflectance in the near-infrared range. Their study concluded that, for an absorbent material, the infrared beam penetrates little more than one particle diameter into the sample, and the absorption should depend primarily on the number density of the analyte particles in the top layer and less on the scattering factor. Each plot in Fig. 6 contains two fitted curves obtained with quadratic functions, one for the K-M data and the other for log(1/*R*) data. These two functions are most commonly used when diffuse reflection data is reported. In the same way that transmission is converted to absorbance, the DR spectrum must be converted to a different form in order to convert relative reflectance *R* to a parameter that varies linearly with concentration. By analogy to transmission spectrometry, most practitioners of near-infrared DR spectrometry convert *R* to log(1/*R*),[24] whereas the Kubelka–Munk function is used for the mid-IR region. One assumption of the Kubelka–Munk theory is an infinitely thick sample, which in our case is not achieved, because the infrared spectrum changes as more wood is added to the filters. We are in fact measuring K-M and log(1/*R*) values as a function of surface concentration of wood dust on the filter and the mass of wood dust on the filters is a direct measure of the thickness of the wood dust layer.

For each set of calibration curves, the equality K-M function = log(1/*R*) gives two solutions. One is $R = 1$ for zero mass (total reflection, no absorption) for both red oak and yellow pine, which corresponds to the situation of the blank filter with no wood dust. The other solution gives $R = 0.13$ for a mass of 4.8 mg of red oak and $R = 0.14$ for a mass of 5.5 mg of yellow pine. We notice that it takes more yellow pine than red oak to obtain this condition, which suggests that red oak absorbs more strongly than yellow pine. If we assume that all particles are 36 μm diameter spheres (30 μm is the aerodynamic diameter, the geometric mean of the extrathoracic particles), we estimate that for full coverage of the filter with a monolayer of red oak particles (density 0.7 g/cm^3) we would need 1.36×10^6 particles, which gives a mass of 16 mg of red oak and 11 mg of yellow pine, respectively. The coordinates of the critical points are a function of the absorptivity and scattering coefficient and should be different for different materials. The form of our calibration curves is similar to those described by Sirita et al.[29] in their study of mid-IR DR of chemical reactions in catalysts. Analogous to their work, the critical points here represent the situation of full coverage of the filter with at least one layer of wood dust particles. As more wood dust particles are added above the critical point mass, we enter the true Kubelka–Munk regime. Below the critical point, the pseudo-absorbance function log(1/*R*) is more appropriate to represent the coverage of the filter surface with wood dust.

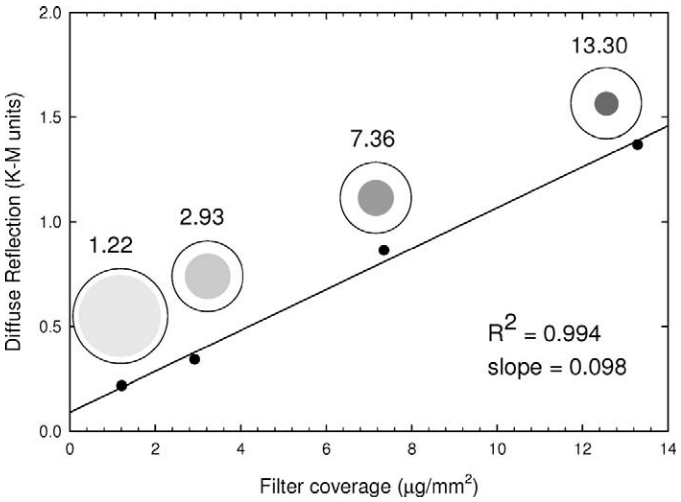

FIG. 7. Diffuse reflection intensity from four samples, each containing 1 mg of wood dust deposited on different sized areas. The numbers represent the mass concentration of filter coverage estimated for each filter.

When the data was fitted to a linear regression, the coefficients of determination were above 0.90 for both types of wood dust and for each set of functions. When quadratic functions were used to fit the same data, the coefficients of determination improved in all cases. A summary of these coefficients and fitting parameters is presented in Table I. Regression analyses were performed using SigmaPlot version 11.0 (SPSS Inc., Chicago, IL). Regression equations were calculated using the least square (LS) method. The final equations were chosen based on four concepts: coefficient of determination (R^2), with higher values preferred; model assumption checks, such as predicted vs. residual, model parsimony, with fewer parameters being preferred; and the ability to adequately describe the outcome equation in a scientifically meaningful way. Saturation in the log(1/*R*) data as the wood dust mass increases is intuitive because with increased wood dust depth, the light penetrates less into the material as it is more absorbed. As more wood dust mass is deposited onto the filter, the thickness of the wood dust layer becomes closer to the true Kubelka–Munk condition of "infinite depth".

In the low-mass range, below 1 mg of wood dust, the method needs improvement. We have prepared four samples of 1 mg of wood dust each deposited on filters with different areas (35 mm, 23 mm, 13 mm, and 9 mm diameter disks), resulting in four different mass concentrations or levels of filter coverage (Fig. 7). From this figure, we can estimate that samples of approximately 78 μg of wood dust can be measured with a filter coverage of 1.22 μg/mm^2 deposited on a 9 mm disk.

For the validation of the calibration data and the method, we used field samples from wood-processing workplaces collected with personal inhalable samplers.[3] The data in Fig. 8 represent the mass of wood dust determined from the calibration curve

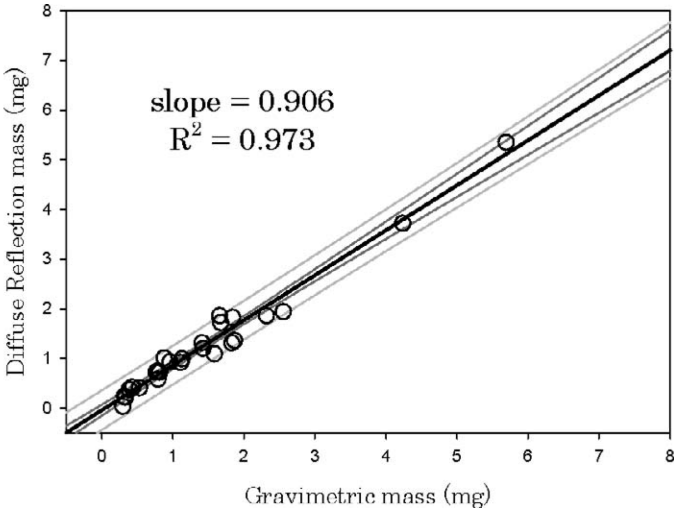

FIG. 8. Validation of the method with field samples.

against the mass of wood dust determined by weighing the samples. The small departure from the ideal slope of unity is negligible and this very good agreement is because this facility used only one type of softwood dust and the particles sizes collected on the filter were similar in size to the calibration particles (i.e., fine particles).

In Fig. 9, we present another set of field samples. The results from this set show underestimation of the mass of wood dust using diffuse reflection spectroscopy. There could be several explanations for this underestimation. We know this facility processed mixed hardwoods, which introduces variation in the infrared spectrum. Also, working activities such as chipping and sawing have the potential to produce large particles rather than fine ones. Large particles will provide a large contribution to the total mass but a proportionally smaller contribution to the filter coverage and to the diffuse reflection spectrum intensity.[33] This is an important setback to the method; however, large particles will not be inhaled by the workers. Thus, only weighing the samples can in fact, overestimate the exposure of workers to inhalable wood dust.[34] To demonstrate the importance of particle size and filter coverage, we show in the bottom panel of Fig. 9 images of two samples with similar mass but different particle sizes and thus different filter coverage. Sample G4024 gives much smaller diffuse reflection mass due to the presence of large particles, which again, contribute little to the filter coverage, and which also absorb more and scatter less energy than do smaller particles.

CONCLUSION

The newly introduced analysis of wood dust deposited on glass fiber filters (GFF)[5] is an easy and low-cost method of analyzing wood dust for industrial hygiene sampling, but the method has problems due to the high absorbance of the filter. Based on this study, we suggest the use of silver metal membrane filters (SMF) instead of GFFs for mid-IR DR analysis of wood collected in working environments, and if possible, SMF should be used for industrial hygiene air sampling so that re-deposition is not required. The use of SMF with little sample preparation gave results similar to typical diffuse reflection measurements of wood traditionally mixed with potassium bromide and set in a cup.

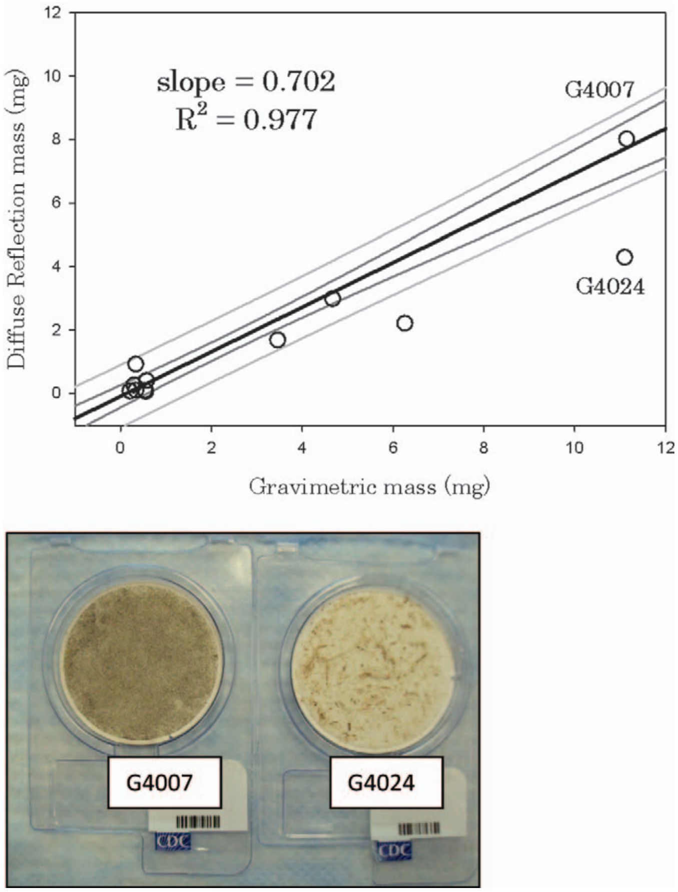

FIG. 9. Validation data using field samples from one sampling site (**top**) and two representative field samples from the set (**bottom**). These two samples have similar gravimetric mass but different levels of filter coverage due to particle size and thus different diffuse reflection masses.

Calibration curves constructed from monitoring the infrared bands at 1510 and 1595 cm^{-1} from benzene ring stretching vibrations in lignin show small departure from the expected linear dependence when using either the Kubelka–Munk function or the log(1/*R*) function. In light of previous studies and with a better resolution on the axis of diffuse reflection, we recommend the use of the log(1/*R*) function for samples that will measure a relative reflection *R* of more than approximately 0.15. For samples measuring *R* less than 0.15, the Kubelka–Munk assumptions become fulfilled and this function can be used to estimate the mass of wood dust.

Measurements of the field samples show that the method becomes very important when particles collected on filters are larger than extrathoracic size. These particles contribute to the total wood dust mass but overestimate the dose to workers as they would not be inhaled. In the low mass range, our data show that analysis of samples with less than 1 mg of wood dust could be difficult and the procedure may need further improvement. Re-depositing the wood dust on a smaller area could easily lower the detection limit down to less than 100 μg of wood dust.

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