



A Comparison of Two Laboratories for the Measurement of Wood Dust Using Button Sampler and Diffuse Reflection Infrared Fourier-Transform Spectroscopy (DRIFTS)

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ABSTRACT

The current measurement method for occupational exposure to wood dust is by gravimetric analysis and is thus non-specific. In this work, diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) for the analysis of only the wood component of dust was further evaluated by analysis of the same samples between two laboratories. Field samples were collected from six wood product factories using 25-mm glass fiber filters with the Button aerosol sampler. Gravimetric mass was determined in one laboratory by weighing the filters before and after aerosol collection. Diffuse reflection mid-infrared spectra were obtained from the wood dust on the filter which is placed on a motorized stage inside the spectrometer. The metric used for the DRIFTS analysis was the intensity of the carbonyl band in cellulose and hemicellulose at $\sim 1735\text{ cm}^{-1}$. Calibration curves were constructed separately in both laboratories using the same sets of prepared filters from the inhalable sampling fraction of red oak, southern yellow pine, and western red cedar in the range of 0.125–4 mg of wood dust. Using the same procedure in both laboratories to build the calibration curve and analyze the field samples, 62.3% of the samples measured within 25% of the average result with a mean difference between the laboratories of 18.5%. Some observations are included as to how the calibration and analysis can be improved. In particular, determining the wood type on each sample to allow matching to the most appropriate calibration increases the apparent proportion of wood dust in the sample and this likely provides more realistic DRIFTS results.

KEYWORDS: button sampler; diffuse reflection; DRIFTS; wood infrared spectrum; wood dust

INTRODUCTION

The worldwide practice to assess exposures to wood dust is to collect the aerosol in a workers breathing zone with a sampling device and to determine the mass collected on a filter in a known volume of air assuming all the collected dust is wood (NIOSH, 1994; OSHA, 2003). A gravimetric procedure makes sense in terms of simplicity where recommended or regulated standards for acceptable exposure are relatively high. However, as exposure limits are lowered and become more difficult to meet, there is more interest in assessing the actual wood content of the collected dust. Occupational exposure to airborne wood is implicated in the development of several symptoms and diseases, including nasal carcinoma. In 1995, wood dust was classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC). However, under US regulations 29 CFR 1910.1000 Table Z-3, wood dust is still considered as a Particle Not Otherwise Regulated (PNOR), sometimes also referred to as a 'nuisance' dust, with a Permissible Exposure Limit of 15 mg m^{-3} . The American Conference of Governmental Industrial Hygienists (ACGIH®) has recommended different limits over the years that might be applied to provide a threshold of safety against the onset of non-cancer endpoints, such as decrements in pulmonary function, with separate designations for potentially cancer-causing or allergenic species. Their current Threshold Limit Value (TLV®) for most wood species is 1 mg m^{-3} , set in 2005. A comprehensive study (Kauppinen *et al.*, 2006) of woodworking facilities in member and accession countries of the European Union suggests that two-thirds of woodworkers are currently exposed above 1 mg m^{-3} and the situation is unlikely to be different in the USA or elsewhere. Environmental non-wood dust could contribute considerably towards a sample exceeding 1 mg m^{-3} , so that a method of distinguishing the wood content is important. While dust contribution from other sources might be limited in the woodworking industries, it may be especially important in construction. In consideration of possible changes in the classification of wood dust from a nuisance dust to one that may become specifically regulated, infrared spectroscopy has been employed in three previous studies in which direct on-filter measurement and analysis were used for determination of occupational wood dust (Rando *et al.*, 2005; Chirila

et al., 2011; Kwon *et al.*, 2013). Fourier Transform Infrared (FT-IR) spectroscopy in the near-IR or mid-IR ranges has been long promoted as a non-destructive and rapid means of analysis of the molecular structure of cellulose, hemicellulose, and lignin in wood dust, paper, or solid wood (Obst, 1982; Grandmaison *et al.*, 1987; Mitchell, 1988; Zavarin *et al.*, 1990; Orton *et al.*, 2004). The research groups at Tulane University and National Institute for Occupational Safety and Health (NIOSH) have worked to harmonize an analytical method to estimate the mass of wood particles collected on a filter from the infrared spectrum of wood dust. More precisely, diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) or diffuse reflection (DR) was used in conjunction with a motorized stage to accommodate a filter for direct analysis of the wood dust. DRIFTS analysis for wood has become widely used since the late 1980s with the introduction of off-axis units (Mitchell, 1988), such as the one used here for which specular reflectance is minimized (Fig. 1) (Chirila *et al.*, 2011). In DRIFTS analysis, a beam of infrared light is focused on the surface of a sample and the diffuse reflected light is collected by a system of mirrors and analyzed by an infrared detector. The result is a plot of infrared light intensity versus wavenumber, which is a function of the combined effects of absorption and reflection of the sample surface.

The infrared spectrum of wood is composed of a strong absorption $\sim 3400 \text{ cm}^{-1}$ from O–H stretching vibration, a prominent C–H stretching absorption at $\sim 2900 \text{ cm}^{-1}$, and strong features in the 'fingerprint' region consisting of overlapping bands due to vibrations in the cellulose and lignin polymers below 1800 cm^{-1} , as described by Owen and Thomas (1989). In prior studies (Rando *et al.*, 2005; Chirila *et al.*, 2011) other absorption bands corresponding to cellulose and lignin, respectively, were used, but in this study, the choice of the carbonyl band ($\sim 1735 \text{ cm}^{-1}$) for quantitative analysis is based on the fact that this band is far enough from the cutoff frequency of the glass fiber filter ($\sim 1500 \text{ cm}^{-1}$), and it can provide specific spectral information that can potentially be used to distinguish between softwood and hardwood (Kwon *et al.*, 2013). In a study by Barker and Owen (1999), it was shown that the carbonyl band for 12 types of softwood gave a mean value of 1737.5 cm^{-1} with a standard deviation of 2.7 cm^{-1} , while 32 types of hardwoods

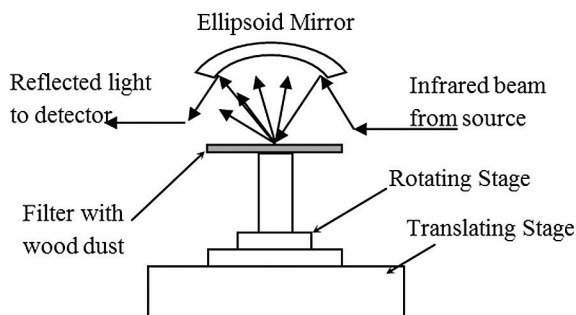


Figure 1 Picture of the motorized stage in the diffuse reflection unit inside the FT-IR spectrometer and a schematic of the diffuse reflection process (from [Chirila et al., 2011](#)).

have a mean value of 1745.2 cm^{-1} with a standard deviation of 3.9 cm^{-1} . This value tends to depend on the type of carbonyl group giving rise to the absorption. Moreover, due to higher cellulose and hemicellulose content in hardwood compared to softwood, the carbonyl band has a stronger intensity in hardwood compared to softwood ([Owen and Thomas, 1989](#); [Moore and Owen, 2001](#)). Carbonyl groups occur abundantly within the polymer components of wood, but they tend to predominate in the branched-chain hemicellulose polymer. Infrared spectra of isolated lignin and holocellulose (cellulose + hemicellulose) confirm this conclusion in that the carbonyl absorption is much stronger and more prominent in the latter ([Owen and Thomas, 1989](#)).

The field samples were obtained with Button aerosol sampler (SKC Inc., Eighty Four, PA). The choice of this personal inhalable sampler is based on several factors, including side-by-side studies of inhalable samplers ([Harper and Muller, 2002](#); [Harper et al., 2004](#); [Görner et al., 2010](#); [Kauffer et al., 2010](#); [Lee et al., 2011](#)) that show the Button sampler collects similar (although slightly lower) mass of wood dust when compared with other samplers. The Button aerosol sampler operates at 4 l min^{-1} to meet the inhalable convention of the International Organization for Standardization ([ISO 7708, 1995](#)) and consists of a spherical shell inlet with numerous regularly spaced holes, $381\text{ }\mu\text{m}$ in diameter, covering a porosity of 21% of the total surface ([Kalatoor et al., 1995](#)). The uniform distribution of the holes on the curved inlet results in an even distribution of particles on the filter surface and the sampler's inlet screen should minimize the collection of particles larger than $100\text{ }\mu\text{m}$ (i.e. those

not covered by the ISO inhalable convention), thus preventing the overestimation of inhalable wood dust. The features that make the Button sampler attractive in this analysis are the higher sampling flow rate resulting in larger collected dust mass for a given sampling duration, the even deposition of dust particles across the filter, minimal wall loss ([Li et al., 2000](#)), and the reduced number of large projectile particles (which are probably not inhaled by workers) compared to other inhalable samplers ([Harper and Muller, 2002](#)). Other samplers may not be suitable because they collect exceedingly large particles, require re-deposition of the sample for analysis, or may use an unsuitable filter.

In this study, we analyzed the reproducibility of the DRIFTS method implemented by the research group at Tulane University by using a similar experimental setup and analysis of the same standard and field samples at the Tulane and NIOSH laboratory. Further adjustments to the calibration parameters along with a detailed sample-by-sample analysis can likely provide an improved method with more realistic results.

METHODS

The standard samples for calibration were prepared at Tulane University (New Orleans, LA) from wood dust of red oak, southern yellow pine, and western red cedar generated from lumber pieces and airborne dust collected using a Respicon sampler, as described previously ([Kwon et al., 2013](#)). The wood dust from the different stages of the Respicon was combined and a weighed amount was homogenized in ethyl acetate suspension and aliquots of different volumes were deposited on 25 mm glass fiber filters using a filtration apparatus with

21 mm inner diameter to form the calibration filters. There were 13 filters with each type of wood for calibration measurements with mass ranging from 0.125 to 4 mg. All field samples and calibration standards were stored in static-dissipative Filter Keepers (Omega Specialty Instruments Division of SKC, Inc.). The field samples after weighing were hand carried by air to Tulane for analysis there, and the field samples and calibration filters were subsequently hand carried by air to the NIOSH laboratory in Morgantown, WV. Great care was taken in the transportation and handling of filters to prevent sample loss. The results of the Tulane analyses have been published separately (Kwon *et al.*, 2013).

The field samples were obtained from six wood product industry factories (sites A–F) where various types of wood, such as: red oak, pine, western red cedar, maple, cherry, etc. were used to produce plywood, hardwood flooring, engineered hardwood flooring (which is different from standard hardwood flooring), door skins, shutters, and kitchen cabinetry (Lee *et al.*, 2012). A total of 181 field samples and 31 blanks were provided for DRIFTS analysis. As noted, the field samples were collected using Button samplers. Pre-weighed type AE glass fiber filters (SKC Inc.) of 25 mm diameter were loaded inside each sampler and inhalable dust was collected at a nominal flow rate of 4 l min⁻¹. After collection, the filters were re-weighed then washed with ethyl acetate in the same way as the calibration filters to remove soluble organic interferences (Rando *et al.*, 2005). The area of wood dust deposition is ~21 mm diameter.

The present method of analysis builds on the studies described previously (Rando *et al.*, 2005; Chirila *et al.*, 2011; Kwon *et al.*, 2013). Briefly, each filter is set onto the motorized stage in the spectrometer and is translated and rotated during the collection of two averaged spectra from orthogonal diameters of the filter. With this procedure we are attempting to take into consideration possible uneven deposition of the dust and to map a large area of the filter given that the focused infrared beam is between 6 and 9 mm in diameter. The analysis consists of measuring the intensity of the diffuse reflection band at ~1735 cm⁻¹, which is then used to estimate wood dust mass, based on calibration curves constructed from standard laboratory samples. The experimental parameters are summarized in Table 1.

In summary, we used a Research Series FT-IR spectrometer (Mattson, Madison WI) equipped with a diffuse reflection unit (Specac Inc., Kent, UK) fitted with a motorized filter stage shown in Fig. 1 (Chirila *et al.*, 2011). Since the purpose of this work was to check the reproducibility of the method, differences between the two methods were minimized where possible, given that there are unavoidable differences between the hardware and software of different instruments. In particular, the same approach to calibration used by the Tulane group was maintained in the NIOSH laboratory. The differences in DRIFTS analysis of the field samples by the two laboratories were evaluated by using equivalence test, as this method is designed to measure equivalence rather than difference and allows

Table 1. Experimental parameters for the two laboratories

Equipment	Parameter	NIOSH laboratory	Tulane group
Spectrometer	FT-IR	Mattson Research	Nicolet 380
	Detector	MCT	MCT
	# Accumulations	256	256
	Spectral units	Kubelka–Munk and log 1/R	Kubelka–Munk and log 1/R
	DRIFTS accessory	Specac, Inc.	Specac, Inc.
Motorized filter stage	Manufacturer	In-house at NIOSH	In-house at Tulane
	Travel distance	17 mm	17 mm
	Time	102 s	129 s
	# Diameters	Two orthogonal	Two orthogonal

some arbitrary margin of error between two labs. Since the data from Tulane and NIOSH are not independent we used Schuirmann's test from SAS (9.3), a well-established statistical method which involves conducting a two one-sided test (TOST) for the mean difference (Schuirmann, 1987). This test maximizes the statistical comparison between labs. Kwon *et al.* (2013) reported results for 181 samples that excluded blanks and samples outside of their calibration range. Some of these samples (22) were recorded as below the limit of detection (LOD) in either laboratory (5 samples by Tulane only, 10 by NIOSH only, and 7 by both laboratories) and so were removed to avoid errors due to different limits of detection (Ogden, 2010). Nine samples were removed as having gravimetric mass greater than 4 mg. Twelve samples (8 from site E) where the difference between the two laboratories was greater than three times the standard deviation of the average difference were considered analytical outliers and removed. The remaining 138 pairs of sample results met the criteria for inclusion in the comparison between the two laboratories.

We also examined alternative calibration parameters as described below, and determined the effect of those on the differences. In addition, we show a methodology for determining the predominant form of dust (hardwood versus softwood), so that the most appropriate calibration for a specific sample can be selected. In this further analysis, 155 sample results from the NIOSH laboratory above the LOD and within calibration range were used.

RESULTS AND DISCUSSION

The following refers to the analysis of the samples in the NIOSH laboratory. The analysis of the samples in the Tulane laboratory has been published previously (Kwon *et al.*, 2013). The standard samples were prepared using red oak, southern yellow pine, and western red cedar. For spectroscopic comparison only, two more wood dusts were analyzed: cherry and maple, and the spectra from each type of woods are represented in Fig. 2 (a) for the hardwoods: maple, cherry, and red oak; and in (b) for the softwoods: western red cedar and southern yellow pine. Two main bands, B1—at $\sim 1735\text{ cm}^{-1}$ and B2—at $\sim 1595\text{ cm}^{-1}$ are of interest for this discussion. The carbonyl band at 1735 cm^{-1} is attributed to C = O stretching vibration in the cellulose and hemicellulose polymers with the

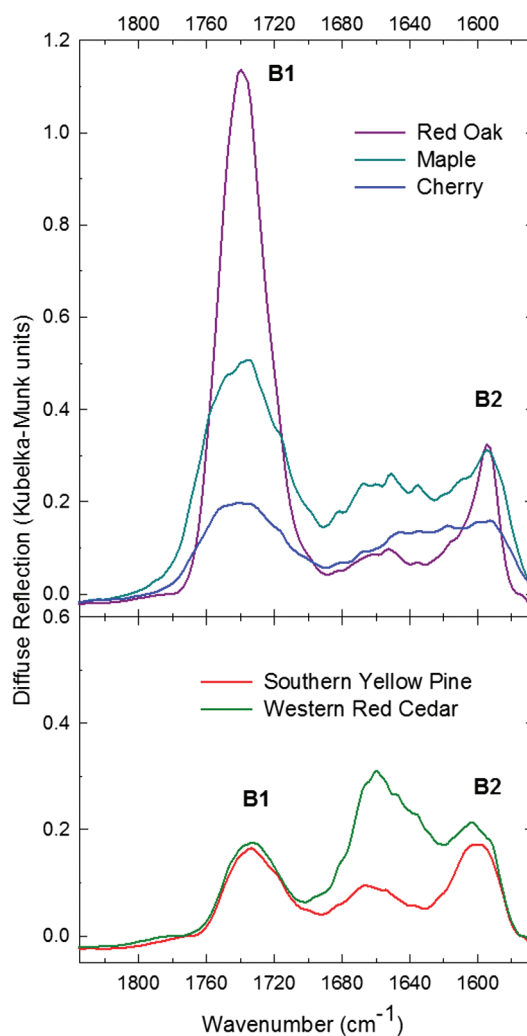


Figure 2 Diffuse reflection infrared spectra from hardwood and softwood standards. The ratio B1/B2 can be used to differentiate between hard and softwood dust. For most hardwoods $B1/B2 > 1$ and for softwoods $B1/B2 \leq 1$.

peak position known to vary from 1733 to 1745 cm^{-1} for softwood and hardwood, respectively (Owen *et al.*, 1989; Barker and Owen, 1999). The band at 1595 cm^{-1} is due to lignin molecules and is also known to vary in peak position and intensity for different types of wood. The peak position and relative intensity of these two bands can be used to differentiate between various types of wood dusts. From the upper part of Fig. 2, we can see that for the hardwoods (red oak and maple) B1 is higher than B2, whereas for the softwoods (western red cedar and southern yellow pine) in the lower part of Fig. 2 the intensity of the two bands is comparable

with B1 being lesser. The exception is the cherry for which the intensity B1/B2 is similar to the softwoods, but for which the peak positions are the ones expected for hardwood. This simple type of spectral analysis can serve as a key tool for labeling the field samples according to the most predominant type of wood (hard or soft) present on the filter and thus allowing application of a more appropriate calibration matched to the sample. However, it cannot accurately determine the proportions of hard and soft wood on a filter containing mixed wood dusts.

The carbonyl band at 1735 cm^{-1} gives the best sensitivity as shown in Fig. 2. Figure 3 shows the calibration curves we obtained measuring the standard filters. Each data point represents the DR mass obtained from the average of the peak intensity of the carbonyl band in two diffuse reflection spectra collected from each sample. The diffuse reflection values are shown in units of Kubelka–Munk or log 1/R (reflectance). These functions are two alternative representations of the diffuse reflection measurement, just as absorption and transmission represent equivalently the transparency property of a material, and just as the peak intensity of an absorption band is proportional

with concentration of the specific molecular group giving rise to that band, the diffuse reflection intensity is proportional to the concentration of the molecular groups. Ideally, this relationship between peak intensity and concentration is linear (Beer's law); however it is not unusual to observe non-linear behaviors due to experimental conditions, particle size, sample type, or preparation (Fuller and Griffiths, 1980; Brimmer and Griffiths, 1986; Olinger and Griffiths, 1988; Sirita *et al.*, 2007). Even though our samples are not infinitely thick, which is an assumption for application of the Kubelka–Munk law, the analysis can still be performed using the mass per area or the filter coverage in place of the concentration as described previously (Sirita *et al.*, 2007; Chirila *et al.*, 2013). As more wood dust is added to the filter, it is the filter coverage that influences the DRIFTS intensity. Since all samples have the same area, coverage is proportional to mass if the thickness of deposit does not vary. The layer thickness does not build as rapidly as the filter coverage (Chirila *et al.*, 2013, Figure 7) until a critical mass is reached and from whereon saturation of the infrared bands intensity can be observed. This is a reason to consider dilution of samples with more than 4 mg of dust (in this study nine samples contained more than 4 mg of dust but were excluded from the comparisons).

There are four sets of data in Fig. 3, one for western red cedar in units of log 1/R, one for southern yellow pine in units of log 1/R and two sets for red oak, one in log 1/R and the other in Kubelka–Munk (K–M) units. The method applied in the Tulane study consists in using log 1/R units for the softwoods and Kubelka–Munk for red oak and for reproducibility reasons we have applied the same method. We recognize the calibration in K–M units is not linear but we have used a linear fit for compatibility with the Tulane calibration. We also added a representation of the red oak data in log 1/R units which gave a better result as can be seen in Fig. 3 and Table 2 where we have listed the fitting parameters side-by-side between the Tulane and NIOSH calibrations.

Yellow pine calibration was used to estimate DR mass from site A, red oak calibration was used to estimate DR mass from sites B, E, and F, western red cedar was used for site D, and for site C, it was reported that the factory used a mixture of 85% hardwoods and 15% softwoods. A calibration function was computed based on this information and the calibration function

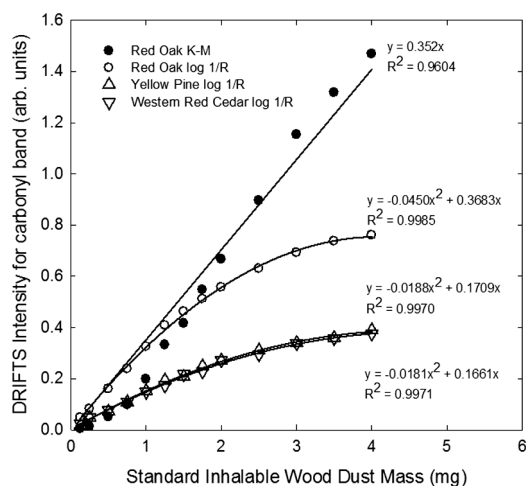


Figure 3 Calibration curves for the standard inhalable wood dusts. DRIFTS intensity data shown as log 1/R and Kubelka–Munk units for red oak, and as log 1/R for yellow pine and western red cedar. The values were recorded at the carbonyl peak. The curves represent the best fit of the data, except for the linear fit of red oak as Kubelka–Munk which was computed for the method equivalency investigation.

for a mixture of red oak and yellow pine was found to be $y = -0.033x^2 + 0.338x$, whereas the Tulane study used $y = -0.042x^2 + 0.344x$ for the same site.

For the determination of the analytical LOD and limit of quantitation (LOQ), a blank filter was measured twelve times and the standard deviation (SD) at 1735 cm^{-1} was computed. The LOD was calculated as $\text{LOD} = 3 \times \text{SD}$ and LOQ was calculated as $\text{LOQ} = 10 \times \text{SD}$. The values obtained for LOD were $\sim 34\text{ }\mu\text{g}$ for red oak, $36\text{ }\mu\text{g}$ for the mixed wood, and $70\text{ }\mu\text{g}$ for yellow pine and western cedar. The values for LOQ were estimated as $110\text{ }\mu\text{g}$ for red oak, $120\text{ }\mu\text{g}$ for mixed wood, $230\text{ }\mu\text{g}$ for southern yellow pine, and $230\text{ }\mu\text{g}$ for western red cedar as determined from using $\log 1/R$ function for the diffuse reflection, with a coefficient of variation (CV) of 3.9% for red oak, 3.4% for yellow pine, and a rather high 11.2% for western red cedar (in units of Kubelka–Munk). These values are different from those previously

reported (Kwon *et al.*, 2013) because of differences in equipment and calibration curves. We chose to report the CV from spectra in units of Kubelka–Munk since in the limit of small concentration, the signal-to-noise ratio (SNR) for this function becomes proportional to the square root of concentration (Fuller and Griffiths, 1980), whereas the SNR for $\log 1/R$ becomes linearly proportional to the concentration.

Field samples were measured under the same experimental conditions as the standard filters: two DRIFTS spectra for each sample collected across two orthogonal diameters of the filter were averaged and the peak intensity of the carbonyl band recorded. Then calibration functions were applied for each site set based on the information received from each sampling site and a DR mass was computed. The results are presented in Table 3 as NIOSH DR mass from each sampling site along with the corresponding DR mass from Tulane lab.

Table 2. Calibration parameters from forced-zero, linear fitting ($y = ax$) for red oak in Kubelka–Munk units and quadratic fitting ($y = ax + bx^2$) for red oak, southern yellow pine and western red cedar in $\log (1/R)$ units. R^2 is the coefficient of determination for the regression analysis (not the square of reflectance)

Standards	NIOSH			Tulane University		
	a	b	R^2	a	b	R^2
Red oak	0.352	—	0.960 (K–M)	0.406	—	0.983 (K–M)
	0.368	–0.045	0.999 ($\log 1/R$)	—	—	—
Southern yellow pine	0.171	–0.019	0.997 ($\log 1/R$)	0.162	–0.021	0.998 ($\log 1/R$)
Western red cedar	0.166	–0.018	0.997 ($\log 1/R$)	0.165	–0.022	0.998 ($\log 1/R$)

Table 3. Average diffuse reflection (DR) mass from Tulane and NIOSH for each sampling site compared to NIOSH gravimetric mass. Samples below the limit of detection or beyond calibration range in either laboratory were not included, nor were samples considered outliers in the comparison (138 samples met criteria)

Sampling site	DR mass by Tulane (mg)	DR mass by NIOSH (mg)	Gravimetric mass (mg)
Site A	0.244	0.199	0.358
Site B	0.488	0.314	1.108
Site C	0.175	0.170	0.406
Site D	1.073	0.900	1.078
Site E	0.761	0.780	1.634
Site F	0.533	0.461	1.624

A comparison of the individual sample results is shown graphically in Fig. 4.

The difference between DR mass and gravimetric mass is in part the result of non-wood material contribution to the gravimetric mass. The difference between DR masses determined in different laboratories is dependent on the sampling site. One way to examine this variation is to introduce a new variable that will measure relative difference (RD) as the normalized mass difference between Tulane (T) and NIOSH (N): $RD = (T - N) * 100 / \text{mean of T\&N}$. The mean value of the RD is 18.5 (NIOSH laboratory underestimating) with 90% confidence interval (13.91, 23.17). If we regard $RD = 25$

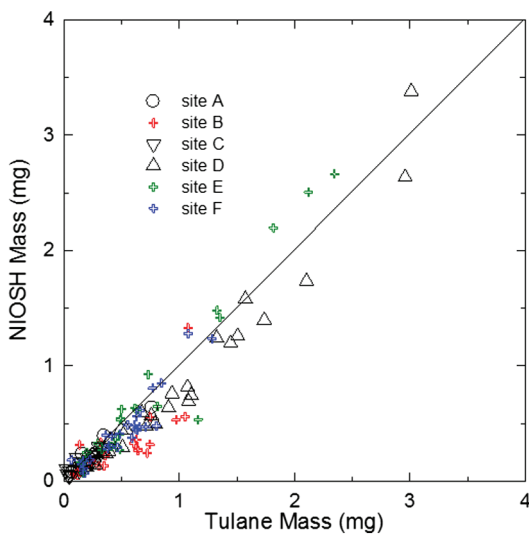


Figure 4 Mass distribution of all the field samples by site. NIOSH mass from this work, Tulane mass from Kwon *et al.* (2013).

as an arbitrary selection to be considered as acceptable we get significant $P = 0.0112$, so that overall the two laboratories would be considered as equivalent (Table 4).

The underestimation of NIOSH measurements compared to those from Tulane may be due to sample losses between the analyses, though we went to great lengths in storage and transportation to minimize this risk. Although 'true' values are not available for these samples, it is possible that they may lie between the results from the two laboratories and with these initial results, we anticipate the method may be sufficiently robust to be used by other laboratories to obtain results within an acceptable range. This can be confirmed by recruiting other laboratories to participate in the analysis, which is possible in the future because the analysis is not destructive.

The results presented above are based on the predominant wood type reported by the industrial hygienist for each site, but we noticed that some of the samples from sites reported as hardwood would present a softwood spectral characteristic or vice versa. When this observation was taken into consideration and sample-by-sample analysis using the calibration that most closely matched the spectral characteristics was performed, we obtained an increase in the computed mass and we refer to this new mass as 'DR mass by NIOSH Recalculated'. Mean results by site are presented in Table 5 and individual samples are plotted in Fig. 5. A total of 103 samples out of the 155 field samples above NIOSH LOD and within calibration range gave a recalculated NIOSH mass higher than 25% of the NIOSH DR mass, which represents ~66% of the samples. This change is entirely due to a better match of the field samples with standard samples

Table 4. Equivalence test output for all field samples and by site

Sampling site	Number of samples	Mean difference %	Equivalent within 25% <i>P</i> value	Equivalent within 30% <i>P</i> value
All	138	18.5	0.0112	<0.0001
Site A	21	21.1	0.2156	0.0414
Site B	21	44.7	0.9788	0.9393
Site C	22	-1.3	0.0009	0.0002
Site D	25	26.2	0.6295	0.1521
Site E	23	6.0	0.0030	0.0005
Site F	26	15.9	0.0834	0.0184

Table 5. Results from applying the sample-by-sample analysis (155 NIOSH samples)

Sampling site	Number of samples	DR mass by NIOSH	DR mass by NIOSH recalculated	Gravimetric mass (mg)
Site A	21	0.199	0.199	0.358
Site B	23	0.293	0.777	1.019
Site C	26	0.171	0.342	0.389
Site D	27	0.992	0.894	1.125
Site E	32	0.608	1.118	1.332
Site F	26	0.461	1.663	1.624

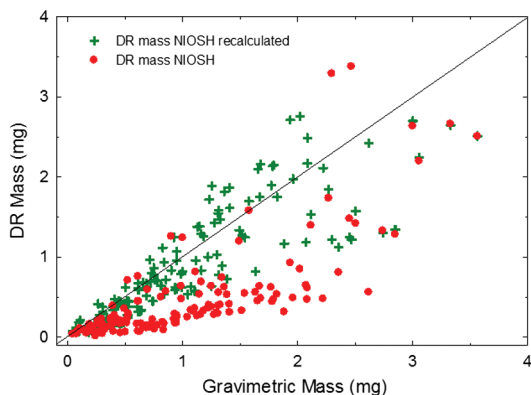


Figure 5 Field samples gravimetric mass (x) plotted against wood dust mass from diffuse reflection (y) as per original calculation (DR mass NIOSH) and recalculated mass (DR mass NIOSH recalculated) considering the reassignment of a sample where appropriate from softwood to hardwood and vice versa, and from use of quadratic calibration in place of linear for hardwood samples.

in terms of spectral characteristics. In these factories, the greatest contributor to the airborne dust mass is wood. There may be other contributions from vehicle exhaust, ambient soil, sprays, etc., that are not otherwise extracted from the samples by ethyl acetate (Rando *et al.*, 2005). However, it is not expected that these contributions would be more than the wood contribution, which would appear to be the case in some situations when the DR mass is compared to the gravimetric mass. Thus the recalculated DR mass is intuitively a more likely representation of the true mass of wood in the sample, and this procedure likely provides a more realistic assessment of exposure.

However, there would be a slightly greater expense in the additional analytical work of examining each spectrum individually to select the calibration parameters.

It is not possible at this point to determine accurately the contribution of this analytical procedure to the uncertainty of overall wood dust measurements, since standard protocols for this determination require a minimum of six participating laboratories (ASTM International, 2011). However, an average RD of 18% compares favorably with an average gravimetric difference of 34% between paired field samples (Lee *et al.*, 2011).

CONCLUSIONS

DRIFTS has been used in one laboratory to estimate the mass of wood dust on a set of air sample filters collected in different woodworking factories and then the method was reproduced as closely as possible to re-analyze the same samples in this study. The results from the two laboratories were compared in terms of experimental setup, calibration parameters, and resulting average DR wood dust mass. Calibration curves were constructed in both laboratories using the same sets of prepared filters from the inhalable sampling fraction of red oak, southern yellow pine, and western red cedar in the range of 0.125–4 mg of wood dust deposited on 25 mm glass fiber filters. The field samples were then analyzed using exactly the same procedure to build the calibration curve. This method resulted in 62.3% of the samples measuring within 25% of the average result with a mean difference between the laboratories of 18.5%. Some observations have been included as to how the calibration and analysis can be improved. In particular, determining the wood type on each sample

to allow matching to the most appropriate calibration increases the apparent proportion of wood dust in the sample and this likely provides more realistic results. This method is one of several directions (Materazzi *et al.*, 2013) being investigated with the aim to elucidate the specific concentration of wood dust in air with more specificity than gravimetric analysis of all dust. Such a method would allow for more precise epidemiological studies and control of exposures. It is limited in that it is more useful for common situations where the wood is of one type, hard or soft, although calibration based on settled dust from the area of concern could be employed for most accurate characterization in mixed wood situations.

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DISCLAIMER

The findings and conclusions in this paper are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

REFERENCES

- ASTM International. (2011) *Standard practice for conducting an Interlaboratory Study to determine the precision of a test method (ASTM E691)*. West Conshohocken, PA: ASTM International.
- Barker B, Owen NL. (1999) Identifying softwoods and hardwoods by infrared spectroscopy. *J Chem Educ*; 76: 1706–9.
- Brimmer PJ, Griffiths PR. (1986) Effect of absorbing matrices on diffuse reflectance infrared spectra. *Anal Chem*; 58: 2179–84.
- Chirila MM, Lee T, Flemmer MM *et al.* (2011) Quantitative mid-infrared diffuse reflection of occupational wood dust exposures. *Appl Spectrosc*; 65: 243–9.
- Fuller MP, Griffiths FR. (1980) Infrared microsampling by diffuse reflectance Fourier transform spectroscopy. *Appl Spectrosc*; 34: 533–9.
- Grandmaison JL, Thibault J, Kaliaguine S *et al.* (1987) Fourier transform infrared spectroscopy and thermogravimetry of partially converted lignocellulosic materials. *Anal Chem*; 59: 2153–7.
- Görner P, Simon X, Wrobel R *et al.* (2010) Laboratory study of selected personal inhalable aerosol samplers. *Ann Occup Hyg*; 54: 165–87.
- Harper M, Muller BS. (2002) An evaluation of total and inhalable samplers for the collection of wood dust in three wood products industries. *J Environ Monit*; 4: 648–56.
- Harper M, Akbar MZ, Andrews ME. (2004) Comparison of wood-dust aerosol size-distribution collected by air samplers. *J Environ Monit*; 6: 18–22.
- IARC. (1995) *IARC monographs on the evaluation of the carcinogenic risks to humans. Wood dust and formaldehyde*. Vol. 62. Lyon, France: International Agency for Research on Cancer.
- ISO 7708. (1995) *Air quality – particle size fraction definitions for health-related sampling*. Geneva, Switzerland: International organization for Standardization.
- Kalatoor S, Grinshpun SA, Willeke K *et al.* (1995) New aerosol sampler with low wind sensitivity and good filter collection uniformity. *Atmos Environ*; 29: 1105–12.
- Kauffer E, Wrobel R, Görner P *et al.* (2010) Site comparison of selected aerosol samplers in the wood industry. *Ann Occup Hyg*; 54: 188–203.
- Kauppinen T, Vincent R, Liukkonen T *et al.* (2006) Occupational exposure to inhalable wood dust in the member states of the European Union. *Ann Occup Hyg*; 50: 549–61.
- Kwon C-W, Chirila MM, Lee T *et al.* (2013) Determination of airborne wood dust in Button samples by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). *Int J Environ Anal Chem*; 93: 1356–66.
- Lee T, Harper M, Slaven JE *et al.* (2011) Field evaluation of five different large-particle samplers for wood dust in Southeastern US wood product industries. *Ann Occup Hyg*; 55: 180–91.
- Li S, Lundgren DA, Rovell-Rixx D. (2000) Evaluation of six inhalable aerosol samplers. *Am Ind Hyg Assoc J*; 61: 506–16.
- Materazzi S, Vecchio S, Di Angelis Curtis S. (2013) Thermal analysis and health and safety. *J Therm Anal Calorim*; 112: 529–33.
- Mitchell AJ. (1988) Infra-red spectroscopy transformed – new applications in wood and pulping chemistry. *Appita*; 41: 375–80.
- Moore AK, Owen NL. (2001) Infrared spectroscopic studies of solid wood. *Appl Spectrosc Rev*; 36: 65–86.
- NIOSH. (1994) *NIOSH Manual of Analytical Methods; Method 0500: Issue 2*. Cincinnati, OH: National Institute for Occupational Safety and Health.
- Obst JR. (1982) Guaiacyl and syringyl lignin composition in hardwood cell components. *Holzforschung*; 36: 143–52.
- Ogden TL. (2010) Handling results below the level of detection. *Ann Occup Hyg*; 54: 255–56.
- Olinger JM, Griffiths PR. (1988) Quantitative effects on an absorbing matrix on near-infrared diffuse reflectance spectra. *Anal Chem*; 60: 2427–35.
- Orton CR, Parkinson DY, Evans PD *et al.* (2004) Fourier Transform Infrared Studies of heterogeneity, photodegradation, and lignin/hemicellulose ratios within hardwoods and softwoods. *Appl Spectrosc*; 58: 1265–71.
- OSHA. (2003) Occupational Safety and Health Administration; Method number PV2121: Gravimetric determination.

- Owen NL, Thomas DW. (1989) Infrared studies of "hard" and "soft" woods. *Appl Spectrosc*; 43: 451–55.
- Rando RJ, Gibson RA, Kwon CW *et al.* (2005) On-filter determination of collected wood dust by diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). *J Environ Monit*; 7: 675–80.
- Schuirmann DJ. (1987) A comparison of the two one-sided tests procedure and the power approach for assessing the equivalence of average bioavailability. *J Pharmacokinet Biopharm*; 15: 657–80.
- Sirita J, Phanichphant S, Meunier FC. (2007) Quantitative analysis of adsorbate concentrations by diffuse reflectance FT-IR. *Anal Chem*; 79: 3912–8.
- Zavarin E, Jones SJ, Cool LG. (1990) Analysis of solid wood surfaces by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. *J Wood Chem Technol*; 10: 495–513.