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Determination of airborne wood dust in Button samples by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

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Emerging concerns regarding the toxicity of inhaled wood dust support the need for techniques to quantitate wood content of mixed industrial dusts. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis technique was applied to the determination of wood content of 181 inhalable dust samples (geometric mean concentration: 0.895 mg/m^3; geometric standard deviation: 2.73) collected from six wood product industry factories using 25 mm glass fibre filters with the Button aerosol sampler. Prior to direct DRIFTS analysis the filter samples were treated with ethyl acetate and re-deposited uniformly. Standards ranging from 125 μg to 4000 μg were prepared for red oak, southern yellow pine, and red cedar and used for quantitation of samples depending upon the wood materials present at a given factory. The oak standards spectra were quantitated by linear regression of response in Kubelka-Munk units at 1736 cm^{-1}, whereas the pine standards and the cedar standards spectra were quantitated by polynomial regression of response in log 1/R units at 1734 cm^{-1}, with the selected wavenumbers corresponding to stretching vibration of free C=O from cellulose and hemicelluloses. For one factory which used both soft- and hardwoods, a separate polynomial standard curve was created by proportionally combining the oak and pine standards polynomial regression equations based on response (log 1/R) at 1734 cm^{-1}. The analytical limits of detection were approximately 52 μg of oak, 20 μg of pine, 30 μg of cedar, and 16 μg of mixed oak and pine for the factory with mixed woods. Overall, the average of dry wood dust percentage of inhalable dust was approximately 56% and the average dry wood dust weight was 0.572 mg for the Button samples. Across factories, there were statistically significant differences ($p < 0.001$) for the percentage of dry wood dust in inhalable dust with factory averages ranging from 33.5 to 97.6%.

Keywords: DRIFTS; inhalable dust; Button samples; wood

1. Introduction

Currently, the standard analysis for wood dust samples is to gravimetrically determine total airborne particulate mass after filter collection [1]; yet industrial wood processing dust is a complex and heterogeneous mixture of wood, comprising cellulose, hemicelluloses, lignin and other various extractives, along with varying amounts of non-wood

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particulate matter, such as soils, combustion engine exhaust, machine oils, glues, resins, and surface coatings [2,3]. Exposures to dust in wood processing industries have been linked to asthma and some other respiratory symptoms in wood workers [4–12]. Wood dust has been classified as 'carcinogenic to humans' (Group 1) by the International Agency for Research on Cancer (IARC) [2]. With increasing concerns about the toxicity of inhaled wood dust, especially the potential carcinogenicity of certain hardwoods, there is a need for sensitive and specific analytical techniques that can determine wood dust in the presence of other particulate contaminants in workplace atmospheres [2,3,14]. Furthermore, techniques that can differentiate wood and non-wood materials in dust will be needed to support any future epidemiology assessing the contributions of wood and non-wood fractions to the overall risk for cancer and other adverse health effects arising from exposure to wood processing dust.

Our laboratory previously developed a new analytical diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique for determining size-fractionated wood dust collected on 37 mm glass fibre filters and applied the method to analysis of archived personal samples of respirable, tracheobronchial, and extra-thoracic wood processing dust collected with Respicon^{TM} samplers over 5 years from 10 wood processing facilities [3,14,15]. It was shown that respiratory health effects among the workers at the facilities were relatable to exposure to the non-wood fraction of airborne particulate matter but not to wood dust, itself, as determined by the original DRIFTS technique [14].

In this current work, we report the application of a revised DRIFTS analysis technique to the determination of wood content of 181 inhalable dust samples collected previously by National Institute for Occupational Safety and Health (NIOSH) investigators and their collaborators from six wood products industry facilities using 25 mm glass fibre filters with the Button aerosol sampler [16]. For this work, the DRIFTS instrumentation was modified to accommodate the smaller 25 mm diameter filters used with the Button sampler, and based on a revision of our original technique proposed by Chirila *et al*. [17], the wavelengths used for quantitation and the spectral transformations applied to the data were modified, as described below.

2. Experimental

Personal inhalable dust samples were collected from workers in six wood product industry facilities producing variously plywood, engineered hardwood flooring, hardwood flooring, door skins, shutters, and kitchen cabinetry (Table 1) [16]. Button samplers [18,19] (SKC Inc., Eighty Four, PA) were loaded with 25 mm Type AE glass fibre filters (SKC Inc.) and used to collect personal inhalable dust samples at a nominal flow rate of 4 L/min. For each facility the major product, wood type, and the corresponding descriptive statistics of collected inhalable dust are shown in Table 1 (data collected and provided by NIOSH). A total of 181 archived samples and 31 field blanks were provided by NIOSH for DRIFTS analysis. Overall, the geometric mean (GM) of the inhalable dust concentration from the samples was 0.895 mg/m^3 and the geometric standard deviation (GSD) was 2.73.

Kiln-dried, dimensional boards of red oak, southern yellow pine, and western red cedar were obtained from local retailers and used in the preparation of analytical standards. The choice of wood species was based on those reportedly being processed at each of the respective facilities. Red oak standards were used for analysis of samples from factories B, C, E and F; southern yellow pine for factories A and C; and red cedar for factory D. To

Table 1. Wood product, wood type, and descriptive statistics of inhalable dust collected from Button samplers for each factory.

			Inhalable dust (mg/m^3)		
Factory	Product	Wood type	Mean ± SD[a]	GM[b]	GSD[c]
A ($N=29$)	Plywood	Pine	0.659 ± 0.800	0.488	1.94
B ($N=30$)	Engineered hardwood flooring	Red oak, maple, walnut, hickory, and poplar	1.003 ± 1.068	0.678	2.56
C ($N=31$)	Door skin	Pine, oak, and gum	0.979 ± 1.711	0.446	3.26
D ($N=27$)	Shutter	Western red cedar	1.336 ± 0.961	1.046	2.04
E ($N=35$)	Hardwood flooring	Red oak, white oak, and maple	2.458 ± 2.150	1.850	2.09
F ($N=29$)	Kitchen cabinetry	Oak, maple, cherry, and MDF (Medium-Density Fibreboard)	1.924 ± 0.895	1.718	1.64
All samples ($N=181$)			1.421 ± 1.533	0.895	2.73

[a]SD: standard deviation
[b]GM: geometric mean
[c]GSD: geometric standard deviation

produce inhalable wood dusts for preparation of standards, lumber pieces were sanded with a disc/belt sander (Delta Machine Co., Jackson, TN) with a medium grit abrasive that was placed inside a small bench-top polypropylene laboratory hood (Lab Safety Supply Co., Janesville, WI). Respicon samplers [20] loaded with 2 μm pore size Teflon filters (SKC Inc.) in each of the three stages were then used to collect the dust at the flow rate of 3.1 L/min. Inhalable dust standards of each of red oak, southern yellow pine, and red cedar were made by mixing dust cakes of the three Respicon stages (respirable, tracheobronchial, and extra-thoracic), and then placed in a vacuum desiccator for drying prior to use.

Stock solutions of each wood standard were prepared by suspending known amounts of the dried inhalable dust in ethyl acetate. A 25 mm glass fibre filter was placed in the solvent-resistant filtration apparatus constructed from a 25 mm carbon-filled black polypropylene conductive cassette with extension cowl (SKC Inc.). Approximately 17 mL ethyl acetate was poured into the filtration apparatus, the standard stock solution aliquot was added and stirred into the solvent, and then vacuum was applied to the filtration apparatus until the filter and dust cake appeared dry. The same pre-treatment procedure by ethyl acetate, without adding the standard aliquot, was applied to the archived inhalable dust filter samples and field blanks prior to DRIFTS analysis for uniformly depositing the heterogeneous dust cakes as well as washing away interfering natural wood extracts and non-wood particulates [3]. For DRIFTS background correction, a blank glass fibre filter was used after pre-treatment with ethyl acetate.

A Nicolet 380 Fourier Transform Infrared (FTIR) Spectrometer (Thermo Electron Co., Waltham, MA) equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector with OMNIC software version 7.3 (Thermo Electron Co., Madison, WI) was used to analyze the filter samples under the following conditions: 256 number of scans, $4\,cm^{-1}$ resolution, Happ-Genzel apodization, no zero filling, Mertz phase correction, 2.0 signal gain. For DRIFTS analysis, the following were used: a Minidiff diffuse reflectance

unit (Specac Ltd., Kent, UK) equipped with Selector x–y translational stage with manual vernier control attached to a 4 rev/min reversible motor (Hansen Motor Co., Princeton, IN), and a diaphragm vacuum pump that continuously held the filter flat during the infrared scanning. The DRIFTS apparatus modified for filter samples was fitted with a special filter holder constructed from a 25 mm polystyrene filter cassette bottom (SKC Inc.) modified by removing the upper rim and painted matte black to minimize scattered radiation. The reversible motor was moved forward and then backward for 2 min 12 s over the IR beam scan path length of 17 mm centred within the 25 mm glass fibre filter surface; the required scanning time at the mirror velocity of 3.80 cm/s was approximately 2 min 9 s.

Each filter sample in the filter holder was scanned horizontally and then the filter holder was rotated 90° and scanned again. Energy throughput values at the beginning and the ending of each scan were checked for stability and typically were in the range of 4 ~ 4.5 V (peak-to-peak) about the background filter. The average of the two orthogonal DRIFTS scans was used for the analysis. Each spectrum was saved as a wavenumber (cm^{-1}) for the X-axis unit and % transmittance for the Y-axis by the OMNIC software. The spectra of oak standards and samples from hardwood-processing factories were then converted to Kubelka-Munk units (KMU) with the function built into the OMNIC program which used the following transformation:

$$\mathrm{KMU} = (1 - \mathrm{R}) \times |1 - \mathrm{R}|/2\mathrm{R} \quad (1)$$

where R, the relative reflectance, is the ratio of the reflected intensity from the sample to the reflected intensity from the glass fibre filter background. In contrast, the spectra of each of the pine standards and cedar standards and samples from factories processing softwoods were converted to log 1/R (R: relative reflectance) using OMNIC's built-in function which provided a better correlation with pine or cedar dust mass. All spectra of each of Kubelka-Munk unit and log 1/R unit were read at the exact same wavenumbers for quantitative evaluation of each sample spectrum.

Thirteen standards of each red oak, southern yellow pine, and red cedar were analyzed by DRIFTS, ranging from approximately 125 μg to 4000 μg of inhalable dust. The DRIFTS spectra of red oak standards of inhalable size were analyzed at a wave-number of 1736 cm^{-1} (Figure 1), and the DRIFTS spectra of each of southern yellow pine and red cedar standards of inhalable size were analyzed at 1734 cm^{-1} (Figure 2 and Figure 3). For quantitation, all signal intensities at 1734 or 1736 cm^{-1} were corrected for baseline by subtracting the measured response at 1836 cm^{-1} for each of the standards and samples. The absolute intensity at 1836 cm^{-1} was chosen because the baseline in this region is nearly flat and free of absorbance bands and the one-point baseline correction method was used as the baseline intensity on the other side of the cellulose band at around 1570 cm^{-1} is rapidly changing as illustrated in Figure 4.

3. Results and discussion

Figure 4 shows DRIFTS spectra of representative samples and field blanks, one set obtained from a factory processing hardwoods (Factory E) and the other from a factory processing softwoods (Factory A). A region of prominent intensity around 1735 cm^{-1} is

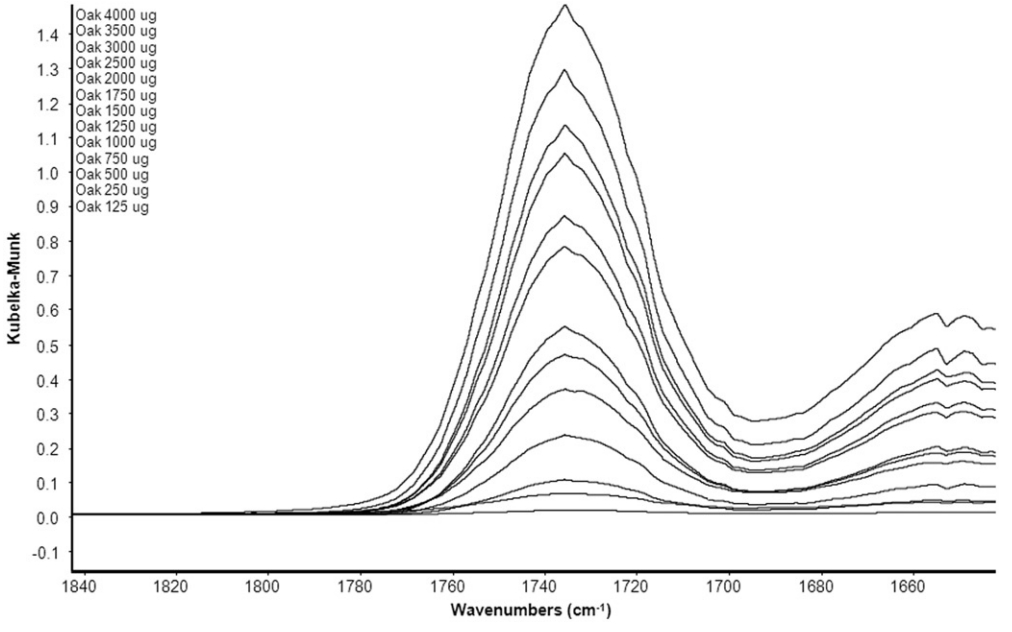

Figure 1. DRIFTS spectra of inhalable oak dust standards.

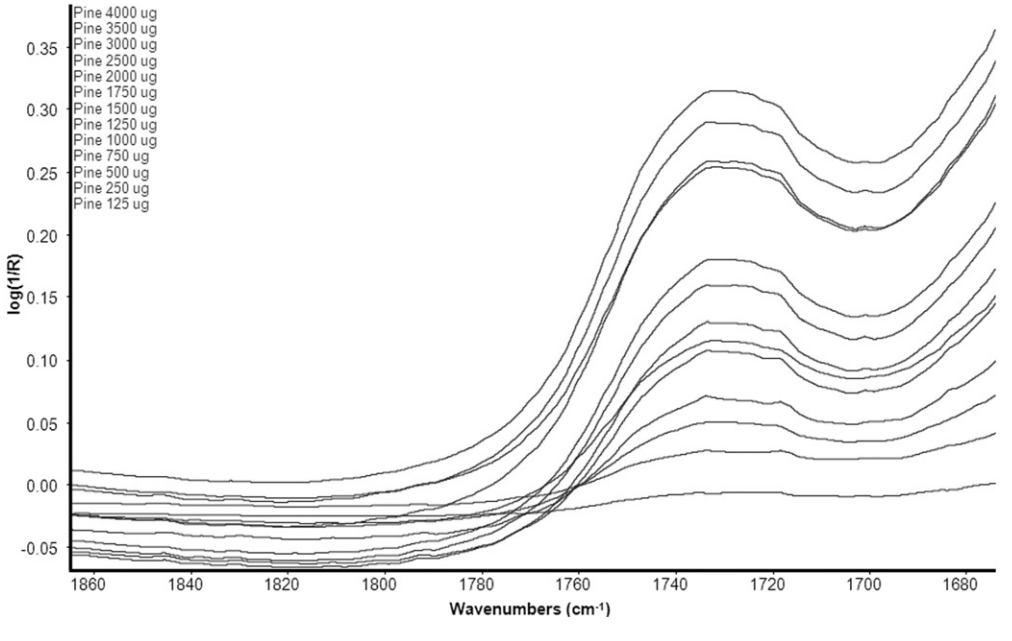

Figure 2. DRIFTS spectra of inhalable pine dust standards.

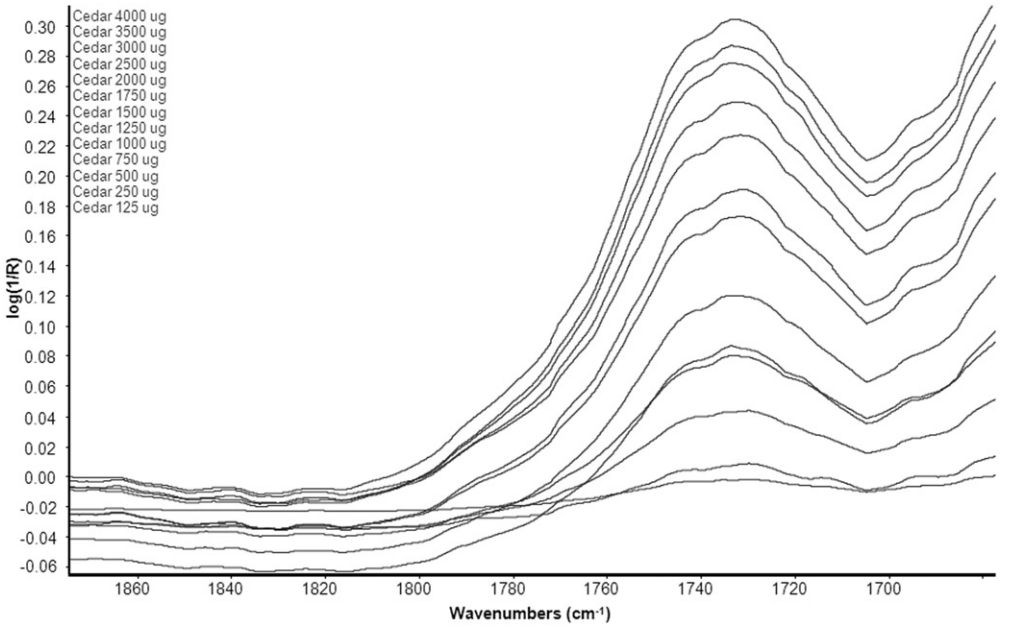

Figure 3. DRIFTS spectra of inhalable cedar dust standards.

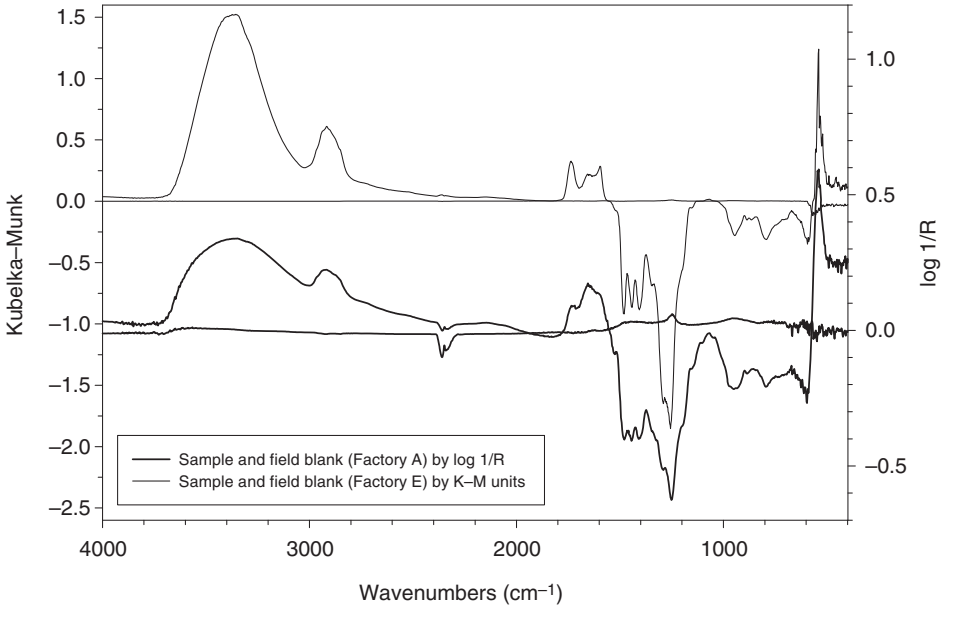

Figure 4. DRIFTS spectra of representative samples and field blanks (factory A processing softwood and factory E processing hardwood).

seen in the samples and was used for quantitation, as described before. The negative response in the region of about 1100 to 1600 cm^{-1} seen in the samples but not in the field blanks is the result of the background reflected intensity of the glass fibre filter being reduced by the dust cake. For wood dust, this region contains absorbance bands around 1510 and 1595 cm^{-1} associated with lignin content that have been used for DRIFTS analysis and quantitation of dust samples transferred to silver filters prior to analysis [17]. Our technique allows direct analysis of samples collected on glass fibre filter without the need to transfer to silver filters but negates the ability to use the lignin bands for quantitation.

Owen *et al.* marked 1737 cm^{-1} as one of three peaks noted from redwood with DRIFTS analysis [21]. Pandey *et al.* compared IR bands including 1740 ± 4 cm^{-1} obtained via transmission, photo acoustic spectroscopy (PAS) and DRIFTS from some wood species of undiluted wood powders [22]. These wave numbers are assigned to stretching vibration of free C=O from cellulose and hemicelluloses in wood dust [23,24] and were chosen based on a recent modification of our original DRIFTS method for on-filter analysis of wood processing dust [17].

Figure 5 shows a slope of 0.4057 and the r^2 value of 0.9835 from forced-zero intercept linear regression of Kubelka-Munk unit of red oak standards response at 1736 cm^{-1}. Figure 6 shows the forced-zero intercept polynomial regression equation is $y = -0.0212x^2 + 0.1617x$ with r^2 value of 0.9976 for log 1/R unit of response for southern yellow pine standards at 1734 cm^{-1}; and for red cedar standards, the forced-zero intercept polynomial regression equation is $y = -0.0219x^2 + 0.1648x$ with r^2 value of 0.9975 for log 1/R unit at 1734 cm^{-1}. The two second-order polynomial regression standard curves for southern yellow pine and red cedar were nearly identical.

Factory C (door skins product) utilized both soft and hardwoods: pine, oak, and gum. It was inappropriate to apply either pine standard or oak standard for specific analysis of each sample from that factory because there was no specific information about wood types present in the individual samples. As an alternative, based on the factory's overall reported

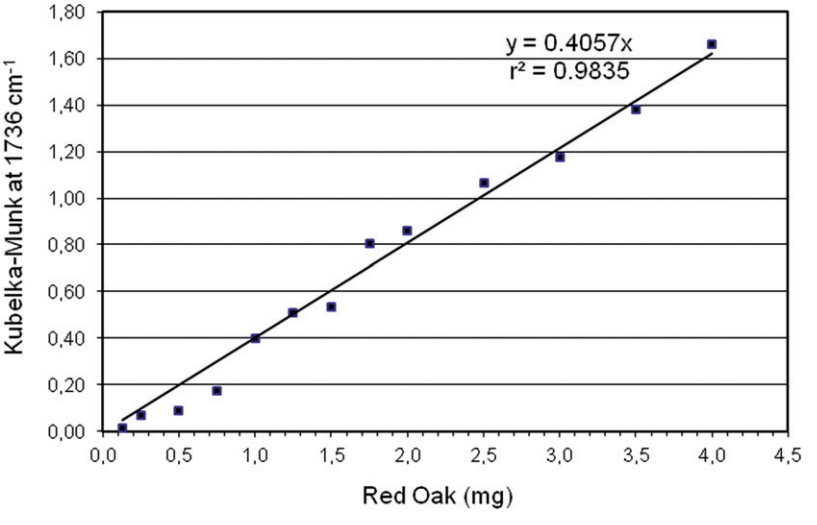

Figure 5. DRIFTS standards for inhalable red oak dusts at 1736 cm^{-1}.

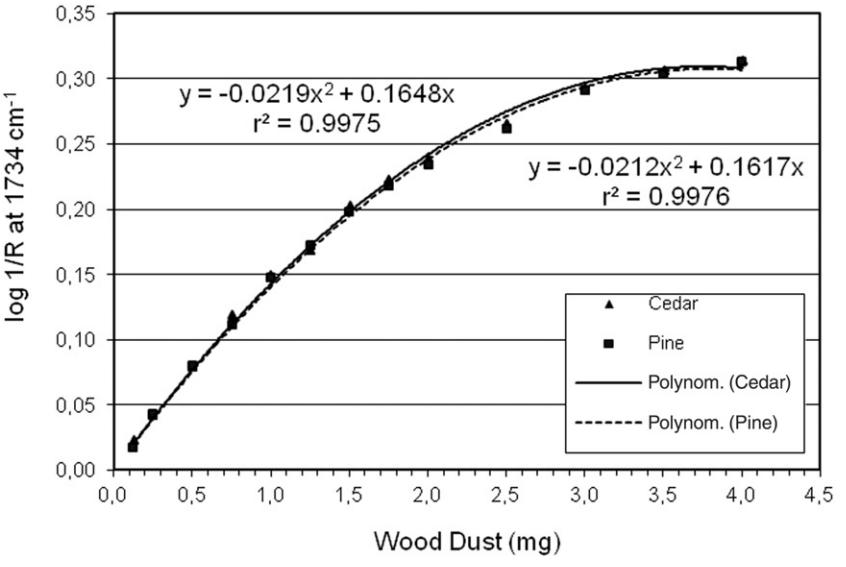

Figure 6. DRIFTS standards for inhalable southern yellow pine and red cedar dusts at 1734 cm^{-1}.

wood stock composition of 15% pine and 85% hardwood, a new polynomial standard curve ($y = -0.0416x^2 + 0.3442x$) was created by proportionally combining the oak and pine standards polynomial regression equations for log 1/R at the same wave number of 1734 cm^{-1}.

The lower range of measurement is equal to the analytical limit of detection (LOD) of the technique. Within the constraints of potential day-to-day instrument variability, the LODs were approximately 52 μg of oak, 20 μg of pine, 30 μg of cedar, and 16 μg of oak and pine for factory D as an average estimate. All 31 field blanks and 7 of 181 samples were below the limit of detection. Polynomial regression equations of each of southern yellow pine and red cedar standards are quadratic functions with the maxima representing upper limits for the range of measurement. Up to 3.80 mg pine and 3.74 mg cedar could be measured by DRIFTS analysis as upper limits; therefore, only one sample, from factory D, out of a total of 181 samples was found to be 'out of range' for DRIFTS analysis.

The results of DRIFTS analysis of the archived Button samples from each of the factories are shown in Table 2. Averages and standard deviations of dry wood dust mass by DRIFTS analysis, and averages and standard deviations of dry wood dust as a percentage of inhalable dust for each factory are shown (Table 2). After analysis by DRIFTS, all 181 samples were further processed to calculate dry wood dust as a percentage of the gravimetric inhalable dust mass based on the archival data provided by NIOSH. For these calculations, the seven sample results that were below detection limit were conservatively set equal to the detection limit. Factory A and factory D that use types of softwood, showed the highest average percentage of dry wood dust; however factory A showed the lowest average dry wood dust mass (0.197 mg) by DRIFTS. The average percentage of dry wood dust was below 50% for each of the factories B, E, and F which use types of hardwood.

Overall, the average of dry wood dust percentage in inhalable dust was $55.9 \pm 24.8\%$ and the average dry wood dust mass by DRIFTS analysis was 0.572 ± 0.353 mg for the 181

Table 2. Summary of dry wood dust in inhalable dust as determined by DRIFTS analysis for 181 Button samples.

Factory	Number of samples	Average gravimetric mass ± SD[a] (mg)	Average DRIFTS mass ± SD (mg)	Average dry wood in inhalable dust ± SD (%)
A	29	0.285 ± 0.237	0.197 ± 0.144	74.0 ± 20.5
B	30	1.159 ± 1.107	0.447 ± 0.404	38.4 ± 18.8
C	31	0.775 ± 1.572	0.278 ± 0.479	43.6 ± 24.2
D	27	1.190 ± 1.033	1.117 ± 0.844	97.6 ± 22.4
E	35	1.743 ± 1.638	0.861 ± 1.002	48.4 ± 20.9
F	29	1.621 ± 1.008	0.524 ± 0.344	33.5 ± 14.4
Total	181	1.129 ± 0.541	0.572 ± 0.353	55.9 ± 24.8[b]

[a]SD: standard deviation
[b]Significant differences across plants (Kruskal-Wallis one way ANOVA on ranks, $p < 0.001$)

Button samples. In comparison, overall average of dry wood percentages of inhalable dust was approximately 41% as determined in a 5 year longitudinal respiratory health effects study in the wood processing industry by our research group [15].

Across factories, there were statistically significant differences ($p < 0.001$) for the dry wood dust percentage in inhalable dust by Kruskal-Wallis one way analysis of variance (ANOVA) on ranks. From pairwise multiple comparison tests (Dunn's method), factories A and D, which use only softwoods, were significantly different from the remaining factories, all of which use only hardwoods or a mixture of hardwood and softwood (factories B, C, E, and F). Furthermore, there were no significant differences between any of the factories in that latter group which used some or only hardwood.

Because the standards used in DRIFTS analysis are vacuum-dried and kept under vacuum, DRIFTS measures the dry wood component of the sample. Kiln-drying reduces the water content of wood to very low levels and very little more is absorbed from the ambient environment under normal relative humidity, so for the situations sampled in this study much of the difference between gravimetric masses and dry wood mass by DRIFTS is most likely attributable to other environmental dusts. However, in a 'wet-wood' situation, such as a primary sawmill or paper-making process, large differences could be expected as a result of the high moisture content in the wood. This may also be an issue for risk-assessment, as wet-wood is associated with much higher endotoxin levels than is kiln-dried wood [25].

4. Conclusions

Inhalable wood processing dust collected on 25 mm glass fibre filters with Button aerosol samplers from six wood processing industry factories was analyzed by DRIFTS technique. The average percentage of wood dust in inhalable dust in the 181 samples was approximately 56% and there were significant differences in the average wood dust content across the six factories. These results illustrate that a significant proportion of airborne inhalable dust found in the wood processing industry, regardless of factory type, can originate from sources other than the wood material being processed. Therefore

assessments of exposure to wood dust and the potential health risks associated with that exposure, require the application of measurement techniques that can selectively determine the wood content of industrial wood processing dusts. The commonly used gravimetric technique for analysis of such industrial wood processing dust samples is non-specific and may result in greatly overestimating the actual exposure to wood dust, *per se*. The DRIFTS analysis described in this work offers a specific and sensitive technique for direct determination of wood content of industrial dust collected on 25 mm glass fibre filters with the Button sampler.

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