WOOD SOLID ANALYSIS IN INDUSTRIAL DUST BY DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY

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I Abstract

Wood is a complex and heterogeneous mixture, and dust produced in wood processing includes wood solids and residual particulate. The standard for wood dust analysis has been to determine total particulates gravimetrically not including any specific analysis of wood content in the dust. Wood dust is an occupational carcinogen and the American Conference of Governmental Industrial Hygienists (ACGIH) has classified oak and beech dusts as A1 (confirmed human) carcinogens.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used to determine wood solids in 521 size-fractionated dust samples collected from 10 wood processing plants. After removal of outliers, the mean respirable, thoracic, and inhalable wood solid percentage (WS%) were 30.5 %, 86.0 % and 63.5 % in the cabinet plant (highest) and 2.2 %, 6.1 % and 5.9% in the sawmill-planing-plywood plants (lowest).

Kruskal-Wallis one way ANOVA on ranks was applied to this size-fractionated WS % by determinants of plant type, job activity, and wood type and there were statistically significant differences within each determinant. Cabinet plants showed the highest content of wood solid in all three size fraction and the differences were statistically significant in comparison to all other plant types. Otherwise, sawmill-planing-plywood plant showed the lowest content of wood solid presumably because of the emission of the resin binders when the making of plywood and processing of primarily green wood. Likewise, working with plywood resulted in statistically

lower WS% than all other wood types. By job activity, sanding showed statistically higher WS% than all other activities except for blow down/compressed air.

A prediction model for inhalable WS% was constructed from the data using determinants of plant type, green and dry wood, hard and soft wood, formaldehyde, PSV (painting, staining, and varnishing) and the reciprocal of inhalable dust weight. The coefficients for the determinants of green wood, green/dry wood, and formaldehyde, were not statistically significant. The predicted value of each inhalable wood solid % is 44.2 % in furniture plants, 63.5 % in cabinet plants, 46.8 % in secondary millworks plant, and 5.93 % in sawmill-planing-plywood plant and there were no significant difference evaluated by Pearson correlation coefficient and Spearman's rho. Two plants (furniture C and sawmill-planing-plywood A) were randomly selected for validation by constructing the same prediction model obtained from the data of the remaining 8 plants. The predicted values of inhalable wood solid percentage are 43.1 % in furniture C, 5.87 % in sawmill-planing-plywood, and there is no significant difference between observed and predicted data.

Finally, the DRIFTS technique was adapted to the specific determination of oak and pine in mixed dust samples by applying the simultaneous equation method to multiple selected wavelength pairs. The four wave number pairs showing the lowest total percentage difference between actual and measured values for 1500 and 2500 ug of oak and pine mixed wood are 21.1% (1250.7, 1265.1 cm^{-1}), 18.9 % (1250.7, 1282.5 cm^{-1}), 21.9 % (1250.7, 1289.2 cm^{-1}), and 23.5 % (1250.7, 1296.0 cm^{-1}). For further evaluation, fifteen archived samples were analyzed for oak and pine content. The mean %difference ± standard deviation (range) between actual and measured values are 33.6 ± 17.7 % (7.50, 55.0 %) in only-oak samples, 23.3 ± 13.1 % (4.55, 38.2 %) in only-pine samples, and 26.5 ± 17.9 % (3.45, 47.7 %) in oak and pine mixed samples. Most actual amount is larger than estimate value because the actual amount is total dust weight at ambient humidity and the estimate value represents only dry wood solids.

This study of wood solid analysis by DRIFTS shows important differences in sources of size-fractionated dust in wood processing industry based on wood solid content, and provides a new analytical standard method for determining the amounts of specific woods in a binary dust mixture in the industrial setting.

II Background and Significance

Wood dust has been classified as a human carcinogen by the International Agency for Research on Cancer (IARC); therefore, its health effects have been variously evaluated.[1] Adverse health effects associated with wood dust exposures include mainly dermatitis, allergic respiratory effects, mucosal and non-allergic respiratory effects, and cancer. Wood is a complex and heterogeneous mixture composed of cellulose, polyoses (hemicelluloses), lignin, and other various extractives. However, current standard analysis of wood dust is to determine 'total airborne particulates' by gravimetric method without including the characteristic of wood dust.[2]

Our research group developed a new analytical diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) technique for determining size-fractionated wood dust in 37-mm glass fiber filter samples collected with the Respicon^{TM} sampler by using two absorbance maxima at 1251 cm^{-1} (softwood) and 1291 cm^{-1} (hardwood or both).[3] Therefore, it is important to apply wood solid analysis based on this new analytical technique to the size-fractionated personal dust samples collected from the wood processing industry.

Since oak dusts are classified as one of the A1 carcinogens by the American Conference of Governmental Industrial Hygienists (ACGIH), it is important to determine the specific amounts of oak dusts among mixture of carcinogenic hardwoods and non-carcinogenic softwoods. Therefore, the DRIFTS technique was applied to particular determination of oak dusts in mixed extra-thoracic wood dust samples collected by Respicon^{TM} sampler.

Ⅲ Literature Review

3.1 Composition of Wood Dust

The Food and Agriculture Organization (FAO) of the United Nations estimated that forests cover about 37.7 million km^2, 30 percent of the global land area. Each American uses, on average, the amount of a 100 foot, 18 inch tree each year in wood and wood products, and therefore, wood is one of indispensable sources with our living life.[4]

Wood dust is created when timber is worked in chipping, sawing, turning, drilling, sanding and so on. For industrial purposes, wood is classified into two types; hardwoods (derived from deciduous trees) and softwoods (derived from coniferous trees). Hardwoods are mostly more dense than softwoods, and the density and hardness of the two groups, however, vary substantially within each family. Wood can also be divided by dry wood (<15~20 % moisture content) and moist (green) wood by the moisture contents.

Cellulose, polyoses (hemicelluloses) and lignin are the fundamental chemical constituents of wood to have a macromolecular structure. Cellulose is the uniform structural element of all woods and nevertheless, the chemical composition of lignin and polyoses is different in softwood and hardwood. Cellulose is the major component (40~50 %) in both softwood and hardwood. Polyoses differ in their sugar composition and the polyoses content of hardwood is higher than that of softwood.

Lignin is in larger amount in softwood than in hardwood and the monomers of lignin are phenylpopane units.

Otherwise, non-polar extractives in wood consist of mainly terpenes, fatty acids, resin acids, waxes, alcohols, sterols, steryl esters and glycerides, and polar extractives of wood comprise mostly tannins, flavonoids, quinones, and lignans.[1] Resin acids, terpenes and aldehydes have been studied in conjunction with wood dust exposure in many softwood processing facilities such as softwood lumber mills, finish sawmills, industrial production of wood pellets and briquettes, and particleboard and medium-density fiberboard products.[5-10] Gallic acid in oak wood dust was adapted as an indicator and a linear correlation with oak dust and gallic acid concentration was shown ($r = 0.95$).[11] Studies to investigate formaldehyde have also been done in facilities manufacturing particle boards, plywood, and MDF made with formaldehyde–based resins.[12-14]

3.2 Wood Processing and Occupational Exposure

Debarking, sawing, sanding, milling, lathing, drilling, veneer cutting, chipping and mechanical defibrating are the essential woodworking processes.[15] The high-risk exposure of wood dust occurs often in sawmills, dimension mills, furniture industries, cabinet makers, and carpenters.[16] Woodworking operations shatter lignified wood cells and break out whole cells and chips. As the wood increases in hardness, so the cells are tightly bound. Consequently, hardwoods can produce more shattering and dust. Likewise, the cells in dry wood are less malleable and easier to be shattered. More likely to shatter cells are woodworking operations performed perpendicular to the natural grain of the wood than those performed parallel to the grain. Also, the level of wood dust can be affected by the various characteristics of the workplace such as age, density, and types of woodworking machinery and the regulatory environment.[1]

3.3 Particle Size Distribution of Wood Dust

The particles of wood dust have irregular shapes and rough surfaces and therefore, the morphological patterns are difficult to be distinguished from each different process. The major part of the wood dust mass was reported as the particles over 10 μm in aerodynamic diameter. Inspirable Particulate Mass (IPM) method was recommended by Hinds et al.(1988) for wood dust sampling because the majority of wood dust was contributed by particles larger than 10 μm.[17] An optical microscopy was used for counting particles of wood dust and 61~65 % of the particles measured 1~5 μ m from this study. Darcy reported the distribution of particle sizes from sanding pine and oak was very similar.[1] Otherwise, from another study, the average mass median aerodynamic diameter of dust showed a little difference between hardwood (18.7 μm; GSD 2.0) and softwood/reconstituted (19.6 μm; GSD 2.1).[18]

3.4 Health Effects

3.4.1 Allergic and Non-Allergic Respiratory Effects

The chemicals related to allergic reactions are mostly found in the inner parts of the tree. Asthma is the most commonly reported allergic respiratory effect due to wood dust.

The exposure to woods such as Western Red Cedar, Cedar of Lebanon, Oak, Mahogany, and Redwood was often reported to cause hypersensitivity and to lead asthma. Exposure to wood dust can cause even chronic obstructive lung disease.[15, 16] From a cross-sectional study of 54 furniture factories (equivalent inhalable dust, 1.19 ± 0.86 mg/m^3) a dose-response relationship was seen between dust exposure and asthma symptoms, and woodworkers had increased frequency of coughing as well as a negative interaction between dust exposure and smoking.[19] Douwes et al.(2001) studied exposure of pine sawmilling workers was associated with an increased prevalence of asthma, cough, eye and nose irritations.[20] An increased risk of developing work-related respiratory symptoms from plywood mill workers in New Zealand appeared because of formaldehyde exposure.[21]

From the respiratory health study of the wood processing industry in our research group, there were no statistically significant adverse effects to any wood solids exposure fraction or any exposures to extrathoracic or tracheobronchial residual particulate in any wood processing facilities, only except to the respirable residual particulate fractions in the milling facility and in the sawmill-planing-plywood facility.[22]

3.4.2 Dermal Irritation and Sensitization

Dermal irritation can be resulted from exposure to the wood itself, dust, bark, sap or lichens growing on the bark. Sensitization dermatitis is commonly caused by fine dust from certain wood species. Once sensitized body sets up an allergic reaction, it reacts seriously when exposed even to a small amount of wood dust. The nickel found in tools, hydroxyquinone and potassium dichromate in wood preservatives, rosin, adhesives, solvents, wet cement, oils, finishes, detergents, mercapto compounds in rubber gloves, and rock wool may cause dermal irritation to wood workers, too.[4, 15]

3.4.3 Biohazards

Exposure to microorganism growing on wood can cause potential health effects as well. Endotoxins and allergenic fungi are the important biohazards observed in wood processing. Exposure to these biohazards can cause adverse effects such as organic dust toxic syndrome (ODTS), bronchitis, asthma, extrinsic allergic alveolitis (EAA), and mucous membrane irritation. Chest tightness, cough, shortness of breath, fever, and wheezing have been found in workers due to airborne endotoxins. Sawmill and chip mill workers, especially, showed high prevalence of regular cough, phlegm, and chronic bronchitis by the lung function test. (1→3)-β-D-glucan, a wall component of a fungal cell is a potential biological agent detected in organic dust, an inflammatory agent, and an agent for the development of allergic alveolitis.[15, 23, 24]

Oppliger et al.(2004) investigated exposure of wood workers to airborne bacteria, fungi, endotoxins and organic dusts at 12 sawmills at debarking, sawing, sorting, planing, and sawing cockpit sites. There were fungi in high concentrations (up to 35,000 CFU/m^3) in all sawmills, and there were more total bacteria, Gram-negative, fungi, endotoxin, and dust at the sorting work sites than at the sawing station.[25] Alwis et al.(1999) studied personal exposure to fungi, bacteria, endotoxin, and (1→3)-β-D-glucan at different woodwork sites at logging, sawmills, wood chipping and joineries. Some of inhalable personal exposures at sawmills and a joinery showed the threshold limit value (TLV) for endotoxin (20 ng/m^3 for an 8 hr shift) exceeded. Significantly positive correlations were between mean personal inhalable endotoxin with Gram-negative bacteria ($p < 0.0001$), and mean inhalable (1→3)-β-D-glucan with total fungi ($p = 0.0003$).[26] In a New Zealand sawmill study, endotoxin exposures in sawmill workers were sufficient to the development of respiratory symptoms, and however, dust measurements were inadequately surrogate for endotoxin and β(1→3)-glucan exposure in sawmill workers.[27]

3.4.4 Carcinogenicity

Wood dust is a human carcinogen founded on sufficient evidence of carcinogenicity from human studies by IARC.[1] The National Institute for Occupational Safety and Health (NIOSH) also regards both hardwood and softwood dust to be potentially carcinogenic to humans. Strong associations with cancer of the nasal cavities and paranasal sinuses were shown in studies of people who had occupations related to wood dust. From nasal cancer study in Sweden, standardized incidence ratios (SIRs) for nasal adenocarcinoma were significantly increased in woodworkers and the SIRs were elevated significantly in the woodworkers exposure to softwood combined with hardwood with a longer occupational history.[16, 28, 29, 31]

A significant dose-related increase in the incidence of skin tumors and mammary tumors in NMRI mice resulted from dermal exposure to a methanol extract of beech wood dust.[28] The use of polar organic solvent extracts of some hardwood dusts has brought about weak positive results for reverse mutations in Salmonella typhimurium, and Δ^3-carene and quercetin from wood were found to be mutagenic in Salmonella. Milham and Hesser reported 1,549 white males showed an association between Hodgkin's disease and wood dust exposure.[16, 28]

3.5 Regulations and Guidelines

The American Conference of Government Industrial Hygienists (ACGIH) TLV as time-weighted average (TWA) is 1 mg/m^3 (inhalable fraction) for all wood species except western red cedar and 0.5 mg/m^3 (inhalable fraction) for western red cedar. Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) as TWAs is 15 mg/m^3 for total dust and 5 mg/m^3 for respirable wood dust fraction. Specially, oak and beech are classified as A1 (confirmed human carcinogen), and birch, mahogany, teak, and walnut are classified as A2 (suspected human carcinogen) by ACGIH.[28, 30, 31]

3.6 Wood Dust Sample Collection and Measurement

Wood dust has been traditionally sampled by the total dust sampling method using a 37 mm diameter PVC filter and it has also been analyzed using gravimetric technique with concentration reported, in mass per unit volume. The dust concentration is calculated from the change in weight of the filter divided by the volume of air sampled, with a detection limit for personal sampling of wood dust of about 0.1 mg/m^3. It is, however, difficult to interpret the biological consequences of such sampled wood dust because there is no information of the particle size distribution. Therefore, health-based particle sampling was required for how particles penetrate and deposit in the human respiratory system.[2, 32]

Health-related sampling is composed of one or more of three progressively-finer size fractions which are shown in Figure 1: inhalable(inspirable), thoracic, and respirable accepted by the International Organization for Standardization (ISO), the American Conference of Governmental Industrial Hygienist (ACGIH), and the European Committee of Standardization (CEN).

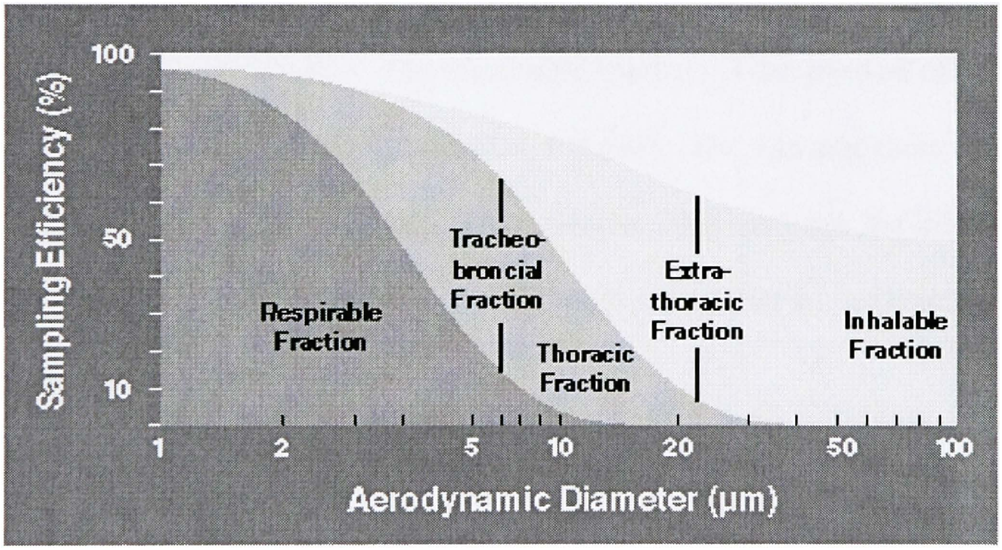


Figure 1 Health-Based Particle-Size-Selective Curves

The inhalable fraction curve shows for particles to enter the respiratory system by way of the nose or mouth. D_{50}, particle diameter equivalent to 50 % sampling efficiency is 100 µm. The inhalable fraction especially includes large particulates to deposit and cause adverse effects on the upper airways. The inhaled fraction of total suspended particles means the total area below the curve. The following equation (1) represents a convention of the inhalability of aerosols.

$$(1)\quad I(d) = 0.5\ (1 + e^{-0.06d})\quad for\quad 0 \leq d \pm 100\ \mu m$$

I(d) is sampling efficiency of inhaled particles as a function of aerodynamic particle diameter (d) in micrometers.

The thoracic fraction is the part of the inhalable particles to pass the larynx and penetrate into the conducting airways of trachea and bifurcations, and the bronchial region of the lung ($D_{50} = 10\ \mu m$). The respirable fraction is the portion of inhalable particles to enter the non-ciliated alveoli ($D_{50} = 4\ \mu m$). The extrathoracic fraction of inhaled particles is gained by subtraction the thoracic fraction from the inhalable. The tracheobronchial fraction of inhaled particles is calculated by subtracting the respirable fraction from the thoracic.[33]

3.7 Aerosol Samplers

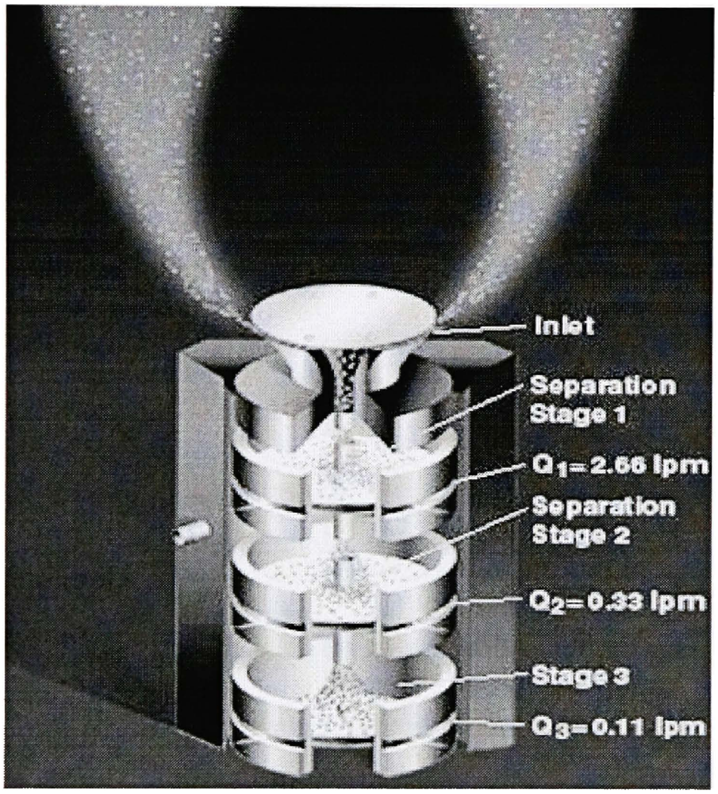


Figure 2 Respicon^{TM} Sampler

3.7.1 Common Aerosol Sampler

Respicon^{TM} sampler (Model 8522, TSI Inc., St. Paul, MN.), shown in Figure 2, is a size-selective gravimetric sampler. It has a circular inlet around the inlet-head perimeter and therefore aerosol can be aspirated into the inlet from all wind direction. The Respicon^{TM} is the only sampler to separate aerosol into the three defined fractions. Aerodynamic particle cut size 50% diameter of collected particles is 4 μm at stage 1, 10 μm at stage 2, and 100 μm at stage 3. Particles are aspirated into the inlet of the Respicon^{TM} sampler at a flow rate of 3.11 L/min and collected on 37-mm diameter filters.

The Institute of Occupational Medicine (IOM) sampler (Cat. No. 225-70, SKC Inc., Eighty Four, PA.) is a conductive plastic sampling head that houses a reusable 25 mm filter cassette with specified filter for the collection of inhalable airborne particles. The particles are collected at the flow rate of 2.0 L/min. Both the cassette and the filter are analyzed gravimetrically as a single unit and therefore, there are no losses of all particles.[34, 35, 36]

Closed-face 37 mm polystyrene/acrylonitrile cassette (CFC) sampler (Millipore Inc., Bedford, MA.) is used for collecting total dust. CFC sampler has an inlet orifice of 4 mm diameter. Aerosol is aspirated into this cassette at a flow rate of 2.0 L/min. The particles collected on a 37 mm diameter filter are analyzed but those to deposit on the inner surfaces are lost.

Prototype Button Sampler (SKC Inc., Eighty Four, PA.) has a hemispherical metal screen inlet. The screen has 381 μm diameter openings and prevents large non inhalable particles (>100 μm aerodynamic equivalent diameter (AED)) from entering the inlet. This curved multi-orifice reduces electrostatic effects and sensitivity to wind direction and velocity. The flow rate is 4.0 L/min and the particles are collected on a 25 mm diameter filter.[34, 37]

3.7.2 Aerosol Sampler Performance

Koch et al.(2002) studied the comparison of the RespiCon^{TM} with IOM inhalable sampler, considered as a reference instrument for the inhalable fraction, at six different workplaces in a nickel refinery. In this study, the tendency of the RespiCon^{TM} to undersample the inhalable dust was corrected by overall empirical correction factor of 1.8 to the concentration value of the extrathoracic fraction as measured by the RespiCon^{TM}. Therefore, the concentration data from statistical analysis reveals systematically lower aerosol exposure values for the RespiCon^{TM} to the IOM sampler.[38]

Li et al.(2000) evaluated using monodisperse solid particles with aerodynamic diameters between 5 and 68 μm, as area samplers, six inhalable aerosol samplers: a Respicon, an IOM, a seven-hole, a conical inhalable sampler (CIS), a prototype button sampler and closed-face 37 mm cassette. The Respicon sampler provided a reasonable match of the inhalable convention. The other five area samplers were highly dependent on wind direction, wind speed, and particle size. Especially, if wind speed is over 0.5 m/sec, those samplers are not suitable for area samplers.[34]

The tare-weight of the IOM plastic filter cassette and the CIS plastic filter holder were not stable because of hygroscopic problems and on the other hand the tare-weight of the IOM stainless steel filter cassette was stable. Therefore, these plastic inhalable aerosol sampler cassettes should be used with field blanks for gravimetric determination of workplace aerosol exposure.[35, 39]

Harper et al.(2002) evaluated the inhalable samplers of the Button, IOM, and 37 mm closed-face cassette (CFC) from 51 good sample pairs in the manufacturing of cabinets, furniture, and shutters. Sampler ratios ranged from 1.19~19 (median 3.35) for IOM/CFC pairs, from 0.49~163 (median 3.15) for IOM/Button pairs, and from 0.36~27 (median 1.2) for CFC/Button pairs.[32] Harper et al.(2004) compared wood dust aerosol size distributions collected by the same three samplers as the previous study. The airborne ultra-large particles (> 100 μm AED) were found in 65 % of the IOM samples, 42 % of the CFC samples and 32 % of the Button samples. After removing the ultra-large particles, the IOM and CFC samplers collected similar quantities of particles up to 30~40 μm AED, and, however, after 40 μm AED the CFC collection efficiency was reduced impressively compared to the IOM. The Button sampler collected significantly less than the IOM between 10.1 and 50 μm AED, and besides less than the CFC between 10.1 and 40 μm AED particle sizes.[40]

Two cascade impactors were evaluated to determine the difference of their particle sampling by Li et al (2001). Marple Personal Cascade Impactor (Marple) has the standard shrouded inlet with the low flow rate (2 L/min) and some area samplers have a simple vertical tube with the flow rate of 15~30 L/min. The sample for D_a greater than 10 μm using a simple vertical inlet was more representative than using the shielded inlet. Tests using the Marple impactor inlet without a visor showed aspiration efficiencies depending on inlet orientation and wind speed.[41]

Rando et al.(2005) evaluated the Respicon™ sampler for size-selective sampling against SKC aluminum cyclone (repirable dust), GK 2.69 cyclone (thoracic dust), and

IOM sampler (inhalable dust) from ten wood processing plants. The result of this study indicated the Respicon^{TM} sampler is an appropriate size-selective sampler for industrial wood processing dust after suitable adjustments to the inhalable and thoracic dust fractions.[42]

3.8 Chemical Analysis of Wood Constituents

Organic matter (extractives), inorganic matter (ash) and the main cell wall components, polysaccharide, and lignin are commonly classified in chemical analysis of wood dust. There is no modern standard method for the extraction of wood. Traditional methods for examining compounds in wood are either steam distillation or extraction with organic solvents in a soxhlet extractor. Isolating and determining polysaccharides are such as hydrolysis with concentrated acids and subsequent dilution steps to achieve secondary hydrolysis.[1]

A high-performance liquid chromatography (HPLC) method was used for the detection of gallic acid (a polyphenol) extracted from oak dust. The linear correlation coefficient between total oak dust and gallic acid concentrations was 0.95.[11] Phenol-formaldehyde resin glue components used in plywood manufacturing were evaluated for respiratory and dermal exposure. Preliminary estimation and allocations of formaldehyde were monitored by detector tube measurements, and all air samples of formaldehyde were analyzed by HPLC.[12] Teschke et al quantified resin acids, abietic and pimaric acids sampled and extracted in a lumber mill, using GC/Mass spectrometry (MS).[5]

A gas chromatograph (GC) and a mass selective detector (MSD) identified and quantified volatile organic compounds (VOCs) emissions from particleboard and medium density fiberboard (MDF). In this study, identified terpenes from particleboard and MDF were α- and β-pinene, camphene, 3-carene, p-cymene, limonene, and borneol. Another predominant compound of more than 50 % of the VOC emissions from particleboard and MDF was aldehydes such as hexanal, pentanal, heptanal, octanal, and nonanal. Other investigators have used GC with flame ionization detection (FID) or GC with MSD for measuring the exposure to monoterpenes collected from diffusion samplers.[5, 6, 7, 9, 14]

Chung et al. studied the quantity, particle size distribution and morphology of dust created during the machining of MDF. Dust collected on Nuclepore filters and on selected stages of the MOUDI, 10-stage impactor with rotating stages to minimize the effect of overloading were examined under the Scanning electron microscope (SEM) for particle morphology. The API (Amherst Process Instrument) Aerosizer measured the particle size distributions of the samples, and formaldehyde in the air and in the dust was analyzed by HPLC.[43]

3.9 Spectroscopic Analysis for Wood Assessment

Ultra Violet resonance Raman (UVRR) spectroscopy was used for defining compounds of p-hydroxyphenyl, guaiacyl, and syringyl lignin structures at three exciting wavelengths of 229, 244 and 257 nm. These three structures were also detected from the wood samples of pine, birch, and compression wood from pine at the characteristic bands.[44]

The potential for near infrared (NIR) spectroscopy was introduced for the rapid assessment of solid wood properties as well as for examining potential applications for wood composites such as fibers, strands, or particles by online monitoring during the wood manufacturing process. The NIR regions are from 780 to 2500 nm in spectra which are characterized by the assignment of the absorption bands to overtones and combinations of fundamental vibrations associated with C-H, O-H, and N-H bonds. Yeh et al. used transmittance NIR spectroscopy for rapid prediction of solid wood lignin contents. This NIR transmittance technique required very little sampler preparation without grinding, and screening.[45, 46]

Fourier Transform Infrared (FTIR) spectrometer can identify unknown as well as known contaminants and can quantify chemicals in mixtures. FTIR spectroscopy can be used to have an insight into the molecular structure and composition of wood from the characteristic molecular vibrations. NIOSH 3800 and EPA method 320 described measurement of organic and inorganic gases by extractive FTIR spectroscopy. Appropriate multivariable least squares analysis can be used for more accurate compound concentrations for overlapping compounds with the FTIR spectroscopy.[47,48,49]

Welling et al. reported an experimental study of terpene emission rates during fresh pine and spruce sawing and processing, and fluctuations in terpene concentrations were measured in one of sawmills by using FTIR spectrometer equipped with mid-band mercury -cadmium-telluride (MCT) detector in this study. From Kazayawoko et al study, the infrared absorption band near 1730 cm^{-1} showed that maleated polypropylene chemically reacted with bleached Kraft cellulose by esterification, and this study indicated both bleached Kraft cellulose and thermomechanical pulps reacted with maleic anhydride.[8, 50]

Also, FTIR spectroscopy was available to explain the effect of ethyl acetoacetate on the pine wood, the structure of the cured resin, and the character of interactions between the wood and resin. Attenuated Total Reflectance (ATR)-FTIR spectroscopy could be used for monitoring the penetration of resins into wood by showing the differences in the chemical composition at different depths from the surface.[19, 51]

Rando et al.(2005) developed a new technique of on-filter determination of size-fractionated wood dust collected from the wood processing industry by diffuse reflectance Fourier-transform infrared (DRIFT) spectroscopy. Two maximum absorbances at 1251 and 1291 cm^{-1} related to the cellulose content of the wood, were proper to quantification of wood dust. An equivalent response of six species except maple at 1291 cm^{-1} was shown and the response at 1251 cm^{-1} was more sensitive for the softwoods. No interference with this analysis appeared from potential particulate contaminants in the industrial wood processing industry such as environmental tobacco smoke, rubber particulate, and acrylic spray finishes.[3]

IV Research Hypothesis

Wood solid analysis by DRIFTS can be a substitute method for a traditional gravimetric analysis of wood dust specifically from wood processing industry, and be adapted to determine carcinogenic woods in wood mixtures.

Research Aims

1. Determine wood solid by DRIFTS technique in 521 size-fractionated personal dust sample sets collected from the wood processing industry during a six-year longitudinal epidemiologic study.

2. Analyze by relevant statistical methods that the wood solid percentage of the size-fractionated personal dust sample sets is correlated with potential determinants such as plant type, wood type, and job activity.

3. Develop, evaluate and validate prediction models for inhalable wood solid percentage by the regression analysis with potential determinants using (1) the entire dataset and (2) a randomly selected subset.

4. Determine the amounts of pine and oak, the latter a confirmed human carcinogenic wood by ACGIH, in mixed wood dust samples using the simultaneous equation method applied to multiple wavelengths in the collected IR spectra.

V Methods and Materials

5.1 Wood Solid Analysis by DRIFTS in Personal Dust Samples Collected from the Wood Processing Industry

5.1.1 Sample Selection and Preparation

521 size-fractionated personal dust sample sets on 37mm glass fiber filters (Omega Specialty, Chelmsford, MA) were selected among 3,488 sets of Respicon samples and archived after collection in the wood processing facility during a six-year longitudinal epidemiologic study about respiratory health of wood workers.[22]

All Respicon samples were analyzed by gravimetric analysis. All of the filters were weighted pre and post 2-3 times on a Satorius microbalance and the average weight calculated in micrograms. Prior to weighting, filters were conditioned in a humidity chamber (55% Relative humidity via a saturated sodium dichromate solution) for at 24 hours. In addition, filters were electrostatically discharged for at least 20 seconds with a Static master (NRD) prior to weighing. After final weight had been analyzed, each filter was stored in polystyrene Petri slides (Millipore). All field sample information was archived by format in Appendix A.

Collected samples on 37mm glass fiber filters (Omega Specialty, Chelmsford, MA) by Respicon^{TM} sampler had apparently heterogeneous surface distribution and high concentrations of dust localized around the filter's center. Therefore, the Respicon sample filter was placed over each back-up glass fiber filter and put in the solventresistant filtration apparatus, and 30ml ethyl acetate was poured onto the filter. The dust cakes were distributed into ethyl acetate by gentle stirring and uniformly redeposited on the top filter. “Holed” filters collected at Respicon^{TM} stage 1 and stage 2 were plugged with glass fiber disc placed on the back-up filter, and the filter sets kept tightly compressed by a piston of 7.5 mm diameter to prevent loss of particles through the hole during re-filtration.

All of these chosen and prepared samples were analyzed via DRIFTS and used for developing and evaluating prediction model about inhalable dust wood solid percentage.

5.1.2 Sample and Reference Analysis by DRIFTS

Galaxy 5000 series (Mattson Instruments Inc., Madison, WI) FTIR spectrometer was provided with an external sampling compartment and a liquid nitrogen-cooled MCT detector (Figure 3). Mattson’s WinFIRST^{TM} software was used for the instrument control. Sampling apparatus was a Minidiff diffuse reflectance unit equipped with Selector x-y translational stage with manual vernier controls (Specac Ltd., Kent, UK) The following was the instrumental conditions: Happ-Genzel apodization, 2x zero fill, 20 kHz forward and backward scanning velocity, 256 co-added scans, 8 cm^{-1} resolution, 400-4000 cm^{-1} scanning range, and 20 signal gain.

The diffuse reflectance stage was modified so that the filter samples may be placed in position reproducibly and scanned using pre-set marks on the stage verniers. The stage was also modified to fit a standard 37mm polystyrene filter cassette bottom as the actual filter sample holder. A mounting tube was attached to the stage via dovetailing with the bottom filter cassette inlet and the other end of the mounting tube was connected via latex tubing to a diaphragm vacuum pump for continuously holding the sample flat during infrared scanning.

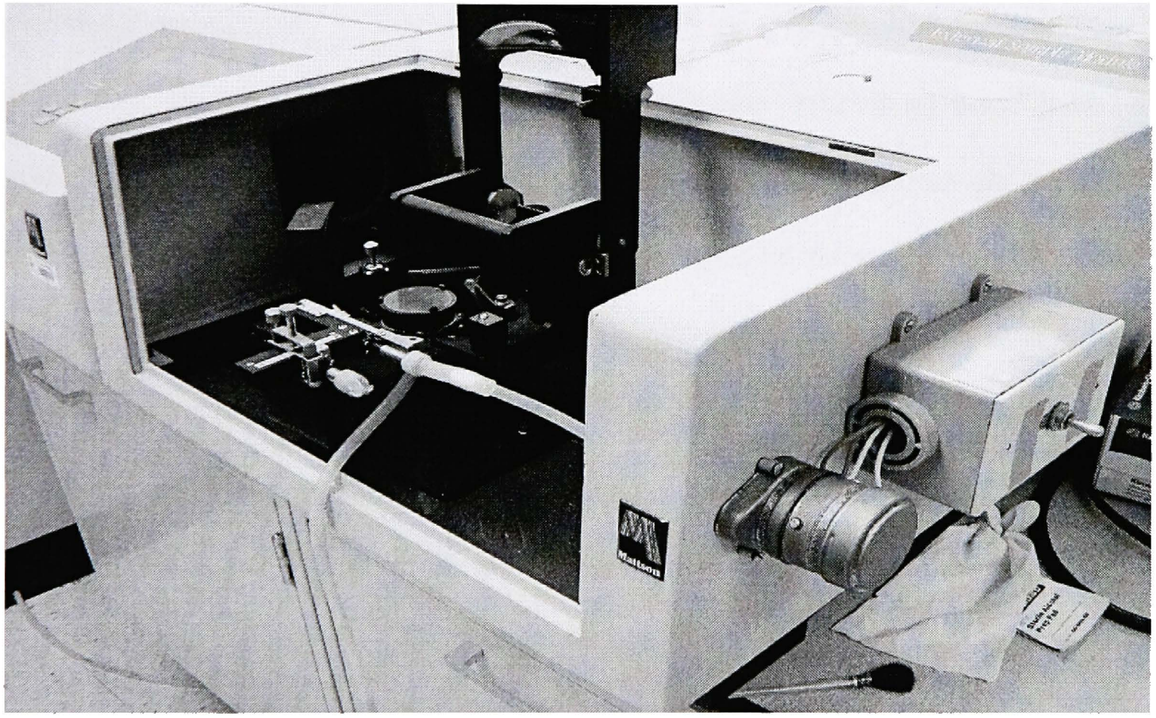


Figure 3 Mattson Galaxy 5000 FTIR Spectrometer

The IR beam scanned across the filter face with x-y translation of a motor (Synchron 600, Hansen Motor Co., Princeton, IN) at the speed of 4 rev/min. The filter was scanned simultaneously while the stage was horizontally moved by the motor, resulting in an average analysis. The first scan finished and the filter was rotated 90°, and then the next FTIR scan of the filter was collected in the same way. Energy throughput from diffuse reflectance of the samples was measured in the beginning and the end of scanning, and net absorbance of the samples was normalized by dividing by the average of energy throughput. The net absorbance was measured at both $1251\mathrm{cm}^{-1}$ and $1291\mathrm{cm}^{-1}$.

Radiata pine dust was used for the reference standards. Size-fractionated radiata pine dusts were collected by Respicon™ sampler from a disc/belt sander (Delta Machine Co., Jackson, TN) in the benchtop polyethylene laboratory hood (Lab Safety Supply Co., Janesville, WI) (Figure 4 &5). After collecting, dust standards were dried in vacuum dessicator. Using the same procedure as for sample preparation, 0.25 mg pine standards of 5 replicate for stage 1 and 1mg pine standards of 5 replicates for each of stage 2 and stage 3 were prepared. Standard stock solution was prepared by suspending in ethyl acetate. Softwood and hardwood samples were compared to these standards and converted to amounts of wood solid by normalized net absorbance at $1251\mathrm{cm}^{-1}$ and $1291\mathrm{cm}^{-1}$, respectively.

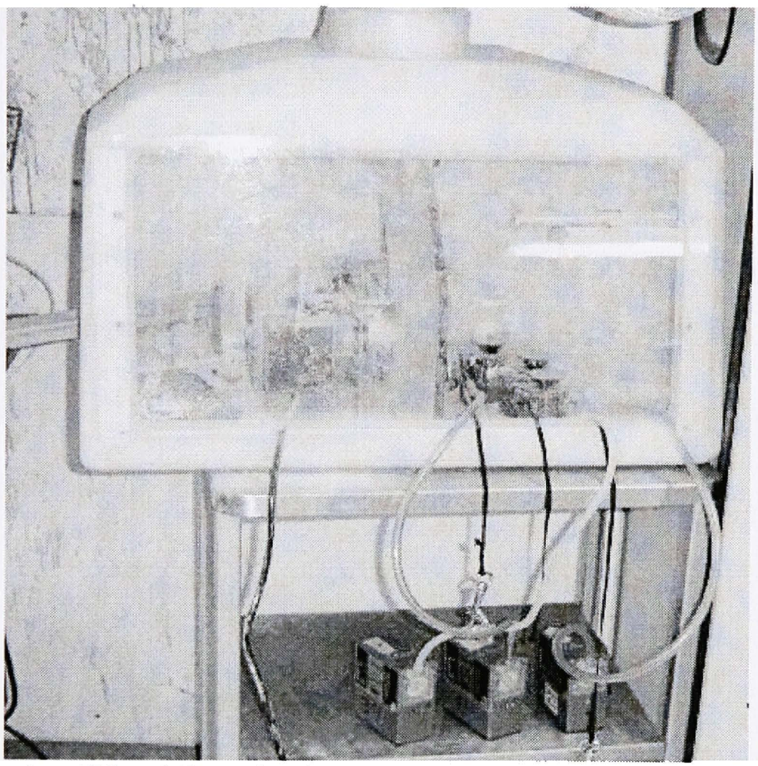


Figure 4 Collecting Wood Dust in the Bench Top Polyethylene Laboratory Hood

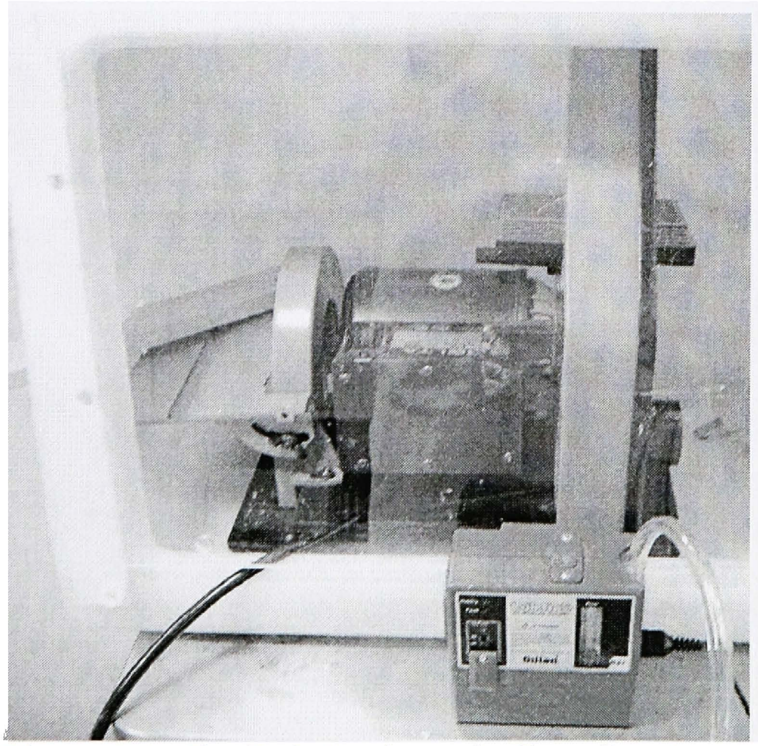


Figure 5 A Disc/Belt Sander and a Sampling Pump

5.1.3 Wood Solid Calculation

From the following formulas, the mass of respirable, thoracic, and inhalable dust collected by Respicon^{TM} sampler could be calculated. Inhalable corrected fraction used the following equations recommended from the Respicon^{TM} manual: the concentration of the extra-thoracic fraction was multiplied by 1.5 for correcting losses of very coarse particles.[52] The amount of wood solid was calculated as a percentage of total dust gravimetrically determined for each size-fraction.

$$(2)\ C_{resp} = \frac{m_1 \times 1000}{Q_1 \times t_s}$$

$$(3)\ C_{thor} = \frac{(m_1 + m_2) \times 1000}{(Q_1 + Q_2) \times t_s}$$

$$(4)\ C_{inh(uc)} = \frac{(m_1 + m_2 + m_3) \times 1000}{(Q_1 + Q_2 + Q_3) \times t_s}$$

$$(5)\ C_{exth} = (C_{inh(uc)} - C_{thor}) \times 1.5$$

$$(6)\ C_{inh(c)} = C_{thor} + C_{exth} = C_{inh(uc)} \times 1.5 - C_{thor} \times 0.5$$

$$= \frac{(m_1 + m_2 + m_3) \times 1000 \times 1.5}{(Q_1 + Q_2 + Q_3) \times t_s} - \frac{(m_1 + m_2) \times 1000 \times 0.5}{(Q_1 + Q_2) \times t_s}$$

C_{resp} : Respirable fraction (mg/m^3)
C_{thor} : Thoracic fraction (mg/m^3)
C_{exth} : Extra-thoracic fraction (mg/m^3)
$C_{inh(c)}$: Inhalable fraction (corrected) (mg/m^3)
$C_{inh(uc)}$: Inhalable fraction (uncorrected) (mg/m^3)
Q_1 : Flow rate through filter #1 (Stage 1) (2.66 Lpm)
Q_2 : Flow rate through filter #2 (Stage 2) (0.33 Lpm)
Q_3 : Flow rate through filter #3 (Stage 3) (0.11 Lpm)
m_1 : Mass deposited on filter #1 (Stage 1) (mg)
m_2 : Mass deposited on filter #2 (Stage 2) (mg)
m_3 : Mass deposited on filter #3 (Stage 3) (mg)
t_s : Sample duration (min)

5.1.4 Statistical Data Analysis of Size-Fractionated Wood Solid Percentage

'Boxplot' by 'Minitab 16.1.0' was applied to removing the outliers of each size-fractionated wood solid percentage data by each facility. First, the outliers of respirable WS% were removed by box plot. As Equation (2) showed, thoracic wood includes respirable wood and therefore the thoracic data of the set of the outliers of respirable WS% were removed and then box plot was applied to thoracic WS%. In the same way, inhalable wood includes respirable and thoracic wood and the inhalable data of the set of the outliers of each respirable and thoracic WS% were removed and then the removal of outliers of inhalable WS% itself was applied by box plot. And then Kolmogorov-Smirnov test was used to access each size-fractionated WS%'s normality.

Kruskal-Wallis One way ANOVA (analysis of variance) on ranks, nonparametric alternative to the one-way ANOVA, determined statistical differences of size-fractionated WS%. And then Mann Whitney tests were applied to determine the significance of differences between pairings within each group such as plant type, job activity and wood type. Plant type was grouped by furniture, cabinet, secondary millworks, and sawmill-planing-plywood; Job activity by sawing, sanding, milling, PSV (painting, staining, and varnishing), debarking/log yard, blow down/compressed air, and others; and wood type by hardwood, softwood, engineered wood, plywood, and mixed wood.

5.2 Developing and Evaluating Prediction Model of the Content of Wood Solid in Inhalable Dust

A prediction model was developed using the data of wood solid percentage of inhalable size obtained from wood solid analysis by DRIFTS in personal dust samples collected from 10 wood processing plants. Linear regression analysis was used to determine prediction model with obtaining coefficients. The determinants of this prediction model are plant type (furniture, cabinet, secondary millwork and sawmill-planing-plywood), wood type (green wood, dry wood, and green/dry wood), hardwood and softwood (hardwood, softwood, and both), formaldehyde, and PSV (painting, staining and varnishing). Correlation for evaluating predicted data vs observed data of inhalable wood solid percentage was performed with by Pearson correlation and Spearman's rho (nonparametric correlation test)

Next, for evaluation and validation of the prediction model approach, another prediction model was generated from 8 of the 10 plants by linear regression model and then the data from remaining two plants (furniture C and sawmill-planing-plywood A) were input into the prediction model from 8 plants and then observed and predicted values were compared by using Pearson correlation and Spearman's rho.

5.3 Multicomponent or Mixed Woods Analysis by DRIFTS

5.3.1 Sample and Standard Preparation

Kiln-dried, dimensional boards of Radiata pine and red oak obtained from local retail lumber store were used for standards and mixed samples. A disc/belt sander with a 5 inch diameter medium grit sanding paper (Norton Abrasives, Niagara Falls, NY) was placed inside a small benchtop fume hood. Wood dust generated from the sander inside the benchtop laboratory hood were collected by Respicon^{TM} samplers on 37 mm diameter, 2 μm pore size teflon filters at the flow rate of 3.1 L/min. After sampling, the collected dust cakes on the stage 3 (extra-thoracic) were carefully scraped from the filter surface, transferred to sample vials, and dried in vacuum dessicator.

Each stock solutions of Radiata pine and oak stock solution were prepared by suspending in ethyl acetate for making standards and mixed samples. Standards of 250, 500, 1000, 1500, 2000, 2500 and 3000 μg from each red oak and Radiata pine were prepared on glass fiber filters. Mixed samples of red oak and Radiata pine were prepared in the following combinations: 500 and 1000 μg, 750 and 750 μg, 1000 and 500 μg, 1000 and 1500 μg, 1250 and 1250 μg, 1500 and 1000 μg, 1000 and 3000 μg, 2000 and 2000 μg, 3000 and 1000 μg. Three replicates were prepared for each combination for DRIFTS analysis. Figure 6 shows from left to right the oak standard of 2000 ug, Radiata pine standard of 2000 ug, and mixture of oak 2000 ug and Radiata 2000ug on Glass fiber filters in polystyrene Petri slides.

Figure 6 Oak 2000ug, Pine 2000ug, and Mixture of Pine 2000ug & Oak 2000ug

5.3.2 Sample and Standard Analysis by DRIFTS

Nicolet 380 FTIR spectrometer (Thermo Electron Corporation, Waltham, MA) was adapted with a liquid nitrogen-cooled MCT detector (Figure 7). The Nicolet FTIR spectrometer is performed with the OMNIC software version 7.3. The instrumental conditions were 256 number of scans, 8 cm^{-1} resolution, 400-4000 cm^{-1} scanning range, Happ-Genzel apodization, 2 levels zero filling, Mertz phase correction, and signal gain 2.0. The base plate on the in-house modified diffuse reflectance apparatus was replaced with the unit to mate with the sample compartment of the Nicolet instrument. Sample or standard filter and a back-up filter in a 37mm polystyrene filter cassette (SKC Inc., Eighty Four, Pennsylvania) were put on a Specac diffuse reflectance stage and a diaphragm vacuum pump was lined into the filter cassette bottom for completely flat condition of each filter as described previously in 5.1.2 (Figure 8).

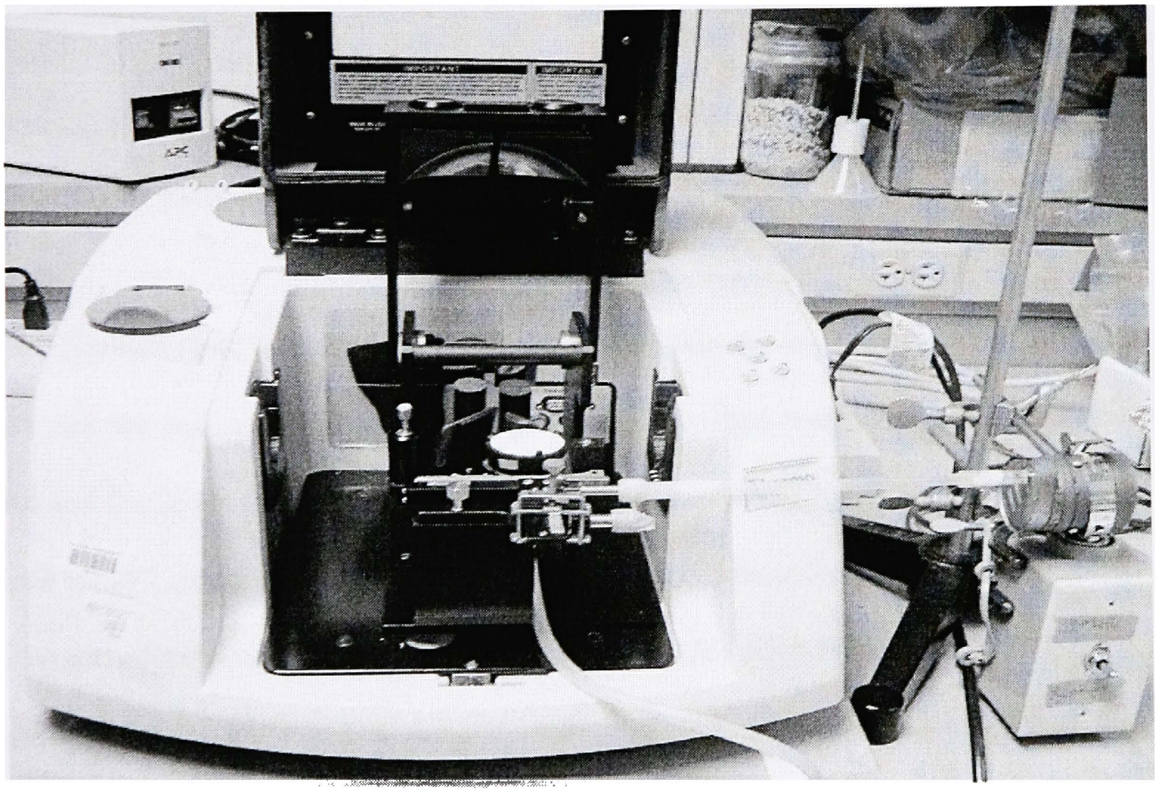


Figure 7 Nicolet 380 FTIR Spectrometer

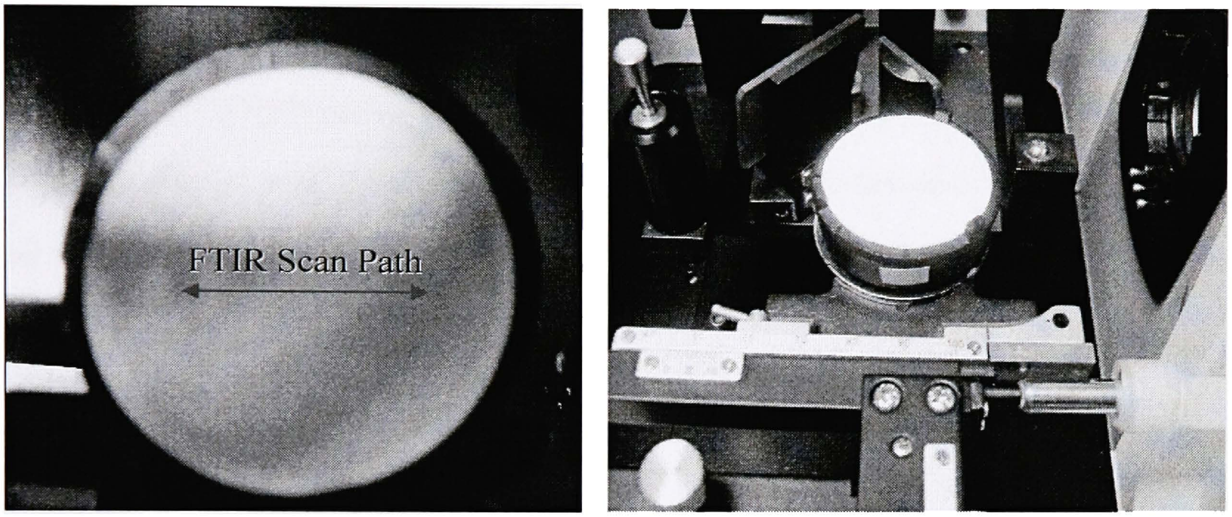


Figure 8 Modified Stage and Filter Holder for DRIFTS Analysis

The required time for collection of the infrared spectra was approximately 3min 15sec and the reversible motor at the speed of 4 rev/min was moved forward and then backward for 3min 22sec. The first scan was finished and the filter holder was rotated to 90°, and then next FTIR scan of the filter was collected in the same way. This scanning procedure was repeated three times for each filter.

Energy throughput from diffuse reflectance of each sample or standard was measured in every scanning at the location of each 3 mm in the 26 mm scanned diameter of each filter. Each average energy throughput was used for normalizing the net absorbance (Kubelka–Munk unit) from the spectrum of each scan. The range of energy throughput in the background was 4.5~5.0V and 3~4.5V (Peak to peak) in the most standards and samples.

After scanning each oak or pine standard of 250, 500, 1000, 1500, 2000, 2500, and 3000 μg, all observable peaks were found and then each oak and pine standard calibration curves were set at each wave number of the chosen peaks. From the oak and pine calibration curves, slopes and R^2 were organized for selecting optimal wave numbers.

5.3.3 Multicomponent DRIFTS Analysis of Mixed Samples via Beer's Law and Simultaneous Equation Method to Multiple Wave Numbers

Multicomponent analysis based on Beer's law was used under the assumption that the absorbance at a specific wave number equals the sum of the absorbances of all chemical species at that wave number. For a two-component mixture:

$$(7)\quad A_t = A_a + A_b = \varepsilon_a \cdot l \cdot c_a + \varepsilon_b \cdot l \cdot c_b$$

A_t : *Total absorbance at a given wave number*

A_a : *Absorbance of component a*

A_b : *Absorbance of component b*

$\varepsilon_{a\ or\ b}$: *Absorptivity of component a or b*

l : *Pathlength*

$c_{a\ or\ b}$: *Concentration of component a or b*

The product of the absorptivity and the pathlength ($\varepsilon \cdot l$) was equal to the slope of the calibration line from each standard (red oak or Radiata pine) curve at a given wave number. This study was adapted to two components (oak and Radiata pine) and at least two equations were needed for solving two unknown concentrations.[53] The wave numbers were determined at which each standard curves of two analyzed components in red oak or Radiata pine showed a good linear regression line.

$$(8)\quad A_{t,\alpha} = \varepsilon_{pine,\alpha} \cdot l \cdot c_{pine} + \varepsilon_{oak,\alpha} \cdot l \cdot c_{oak} = a_{pine,\alpha} \cdot c_{pine} + a_{oak,\alpha} \cdot c_{oak}$$

$$(9)\quad A_{t,\beta} = \varepsilon_{pine,\beta} \cdot l \cdot c_{pine} + \varepsilon_{oak,\beta} \cdot l \cdot c_{oak} = a_{pine,\beta} \cdot c_{pine} + a_{oak,\beta} \cdot c_{oak}$$

$A_{t,\,\alpha\ or\ \beta}$: *Total absorbance at a wave number α or β cm^{-1}*
$\varepsilon_{pine,\,\alpha\ or\ \beta}$: *Absorptivity of pine at α or β cm^{-1}*
$\varepsilon_{oak,\,\alpha\ or\ \beta}$: *Absorptivity of oak α or β cm^{-1}*
c_{pine} : *Amount of pine*
c_{oak} : *Amount of oak*
$a_{pine,\,\alpha\ or\ \beta}$: *Slope of Pine Standard Curve at α or β cm^{-1}*
$a_{oak,\,\alpha\ or\ \beta}$: *Slope of Pine Standard Curve at α or β cm^{-1}*

Various combinations of two wave numbers were used and then six wave numbers (1250.7, 1257.4, 1265.1, 1282.5, 1289.2, and 1296.0 cm^{-1}) were selected via R^2 and slopes. The percents of difference between the actual amount and approximate values were used for evaluating and deciding the optimal multiple wave numbers. Expected value was calculated by the multi-component equations of Beer's law. For example, 'a_{pine}' is the slope of pine standard curve and 'a_{oak}' is the slope of oak standard curve at each wave number. 'c_{pine}' is the real amount of pine included in each mixed sample and 'c_{oak}' is the real amount of oak included in each mixed sample. 'Expected value' was calculated by the multi-component equations of Beer's law. For example, expected value, 0.244461(=$a_1x_1+a_2x_2$) at 1250.7cm^{-1} of Pine500Oak1000 was calculated by 0.206832 x 0.49984 + 0.141004 x 1.00056. Most expected values were approximately similar to observed values of each mixed samples at each of the six selected wave numbers.

5.3.4 Application of Multicomponent DRIFTS Analysis to Archived Wood Processing Samples

Based on the results of this carcinogenic wood study, three types of samples (only oak, only pine, and a mixture of oak and pine) were evaluated from archived samples from a six-year longitudinal epidemiologic study. The archives contained the gravimetric information of wood dust, wood types, and confounding factors.

Fifteen samples (5 oak, 5 pine, 5 oak and pine) collected on 37 mm glass fiber filter at stage 3 (extra-thoracic fraction) of Respicon^{TM} sampler were selected from the archived samples in the furniture plant. Preparing and analyzing sample and standard followed the same procedure described in 5.1. DRIFTS analysis by Nicolet 380 FTIR spectrometer was the same as that of described in 5.3.2. The selected wave numbers from the previous results of the standards and samples described in 5.3.3 were adapted to the archived furniture samples. Using the multicomponent DRIFT analysis procedure with simultaneous equations, the amounts of pine and oak in the selected archived samples were determined.

VI Wood Solid Analysis by DRIFTS in Personal Dust Sample Collected from the Wood Processing Industry

6.1 Descriptive Statistics

From the six-year longitudinal epidemiologic study, 3,488 sets of Respicon samples were collected over the course of the study. 521 sets of samples were selected and analyzed by DRIFTS from valid sets of Respicon samples which didn't include MCE and Teflon filters, blanks and area samples from ten wood processing facilities (Table 1). There are four furniture manufacturing, two cabinets, two secondary millworks, and two sawmill-planing-plywood facilities organized by plant type.

Table 1 Wood Processing Facilities under Study

State	Plant Type	Number of Sample Set
VA	Furniture Manufacturing (Furniture A)	49
NC	Furniture Manufacturing (Furniture B)	48
VA	Furniture Manufacturing (Furniture C)	45
NC	Furniture Manufacturing (Furniture D)	86
MN	Cabinet Manufacturing (Cabinet A)	47
IN	Cabinet Manufacturing (Cabinet B)	39
OR	Wood Mill - Molding, Door, Window Frames, etc) (Secondary Millworks A)	64
PA	Wood Mill - Cabinet Parts (Secondary Millworks B)	56
OK	Sawmill/ Plane mill/ Plywood (Sawmill-Planing-Plywood A)	44
FL	Plywood Assembly (Sawmill-Planing-Plywood B)	43
Total		521

Table 2 Wood Solid Percentage in Size-Fractionated Dust by Plant

		Wood Solid % of Dust		
Plant Type		Respirable	Thoracic	Inhalable
Furniture A	Average	11.8	77.1	49.8
	S.D.	13.6	37.1	22.2
	Number	49	48	46
	Median	5.5	68.8	45.6
Furniture B	Avg.	11.7	58.2	34.4
	S.D.	17.6	36.2	21.3
	Number	48	47	46
	Median	4.7	51.4	29.2
Furniture C	Avg.	19.5	71.5	53.2
	S.D.	17.1	35.4	23.5
	Number	45	44	44
	Median	18.5	78.7	55.1
Furniture D	Avg.	16.2	70.1	45.0
	S.D.	12.5	37.7	26.2
	Number	86	82	82
	Median	13.9	68.6	39.6
Cabinet A	Avg.	35.2	95.3	72.5
	S.D.	21.9	33.7	20.0
	Number	47	47	46
	Median	29.8	89.9	75.3
Cabinet B	Avg.	29.3	81.2	57.1
	S.D.	28.4	43.2	33.9
	Number	39	39	38
	Median	22.6	86.3	49.7
Secondary Millworks A	Avg.	27.5	50.8	38.7
	S.D.	106.1	33.4	22.6
	Number	64	63	55
	Median	5.6	46.1	35.7
Secondary Millworks B	Avg.	16.8	80.0	58.9
	S.D.	15.8	35.5	24.1
	Number	56	56	56
	Median	12.3	73.8	59.6
Sawmill-Planing-Plywood A	Avg.	2.3	7.6	8.2
	S.D.	2.4	8.8	4.7
	Number	44	41	41
	Median	1.3	3.9	7.6
Sawmill-Planing-Plywood B	Avg.	5.5	13.2	7.7
	S.D.	8.8	19.1	7.5
	Number	43	43	43
	Median	2.3	6.2	5.0
Total	Avg.	17.7	61.8	43.3
	S.D.	41.0	42.3	29.1
	Number	521	510	497
	Median	8.5	58.3	40.1

The Table 2 shows WS% (wood solid percentage) in collected dust by each facility analyzed. However, some huge or outlying wood solids data were included in this table with some samples showing several hundred percent wood solids. Most outlying techniques are based on normal distribution data and they are also applied differently from the range of each sample number. All of the data of each size fractionated wood solid percentage collected from wood processing facility didn't show normal distribution by any facility and plant type.

Figure 9 to Figure 18 shows box plot graphs for treating outliers from wood solid percentage data. Each box plot test was only once applied to each size fractionated WS% by each facility. '*' symbol means the outlier of each size fractionated WS% and 'upper and lower whisker' shows the maximum and the minimum data point within 1.5 box heights from each of the top and the bottom of the box. In 'interquartile range box', top line is 75%, middle line is 50%, and bottom line is 25% of the data.

Figure 9 Boxplot of Size-Fractionated WS % for Furniture A

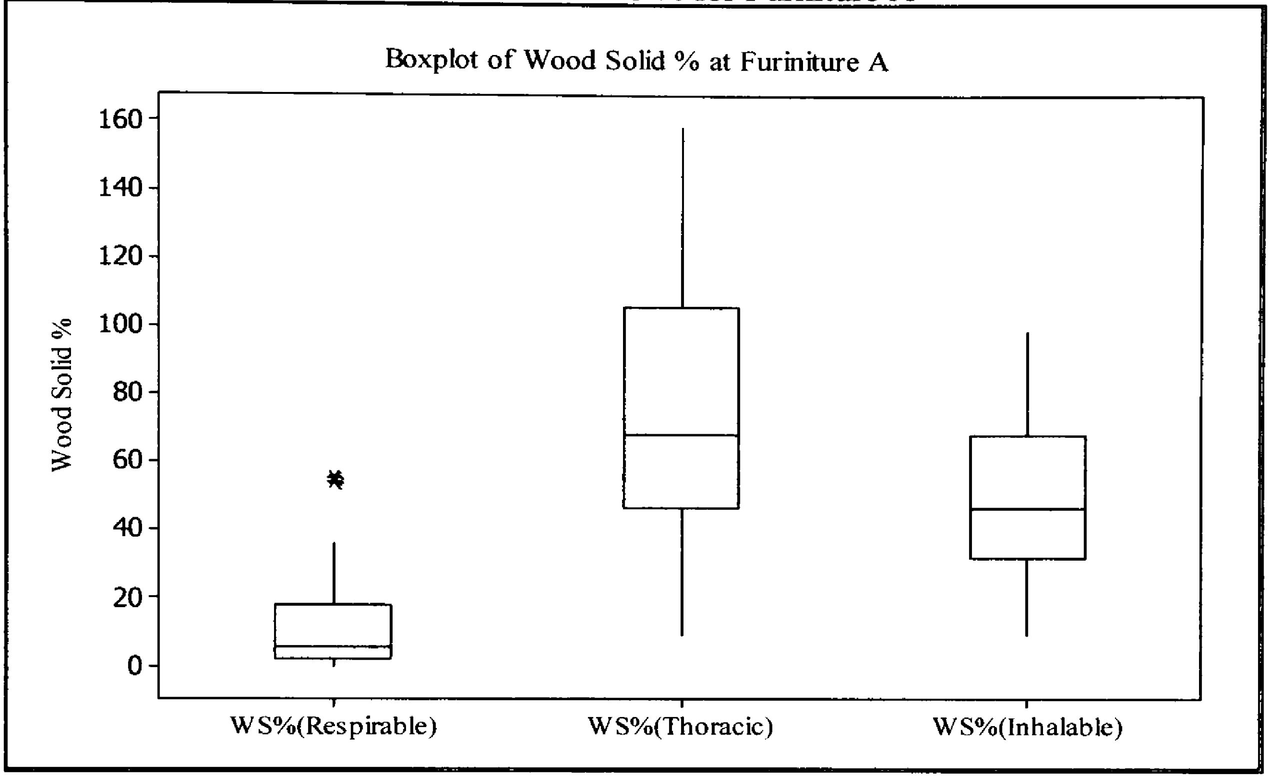


Figure 10 Boxplot of Size-Fractionated WS % for Furniture B

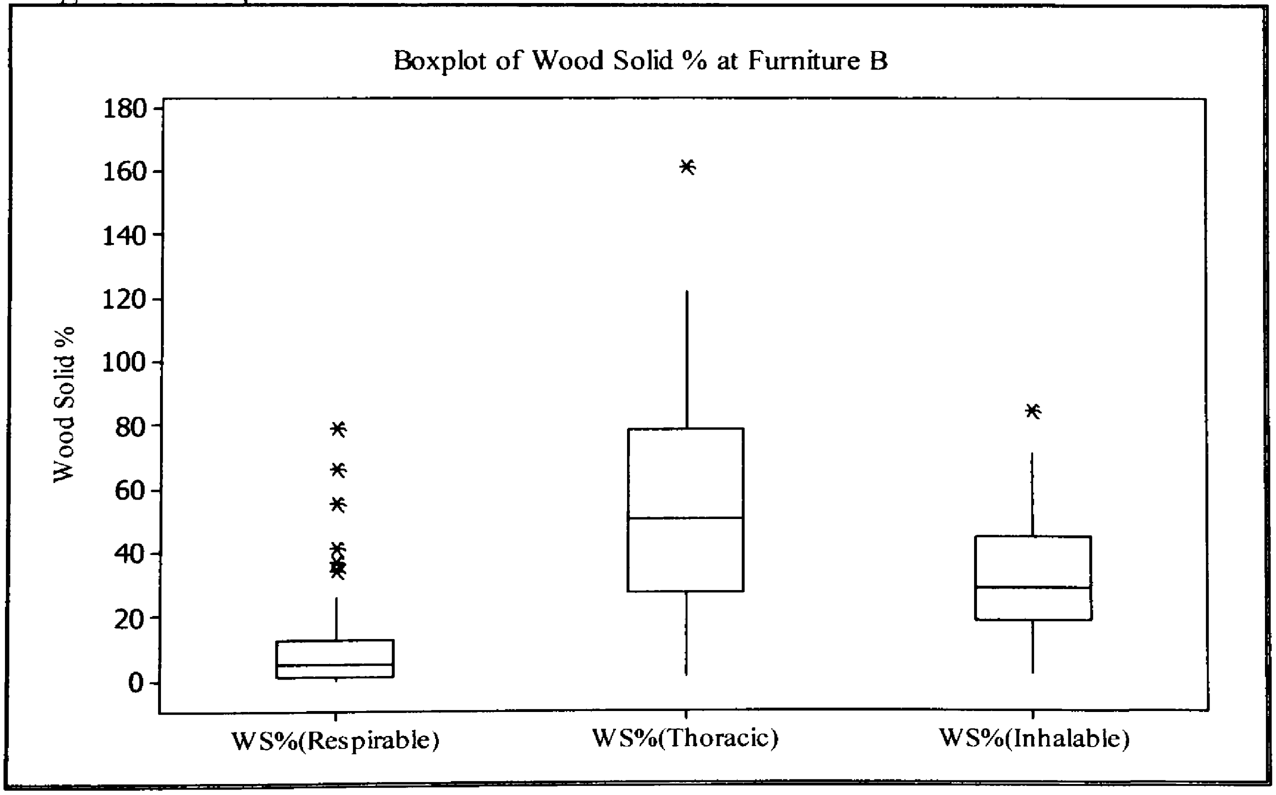


Figure 11 Boxplot of Size-Fractionated WS % for Furniture C

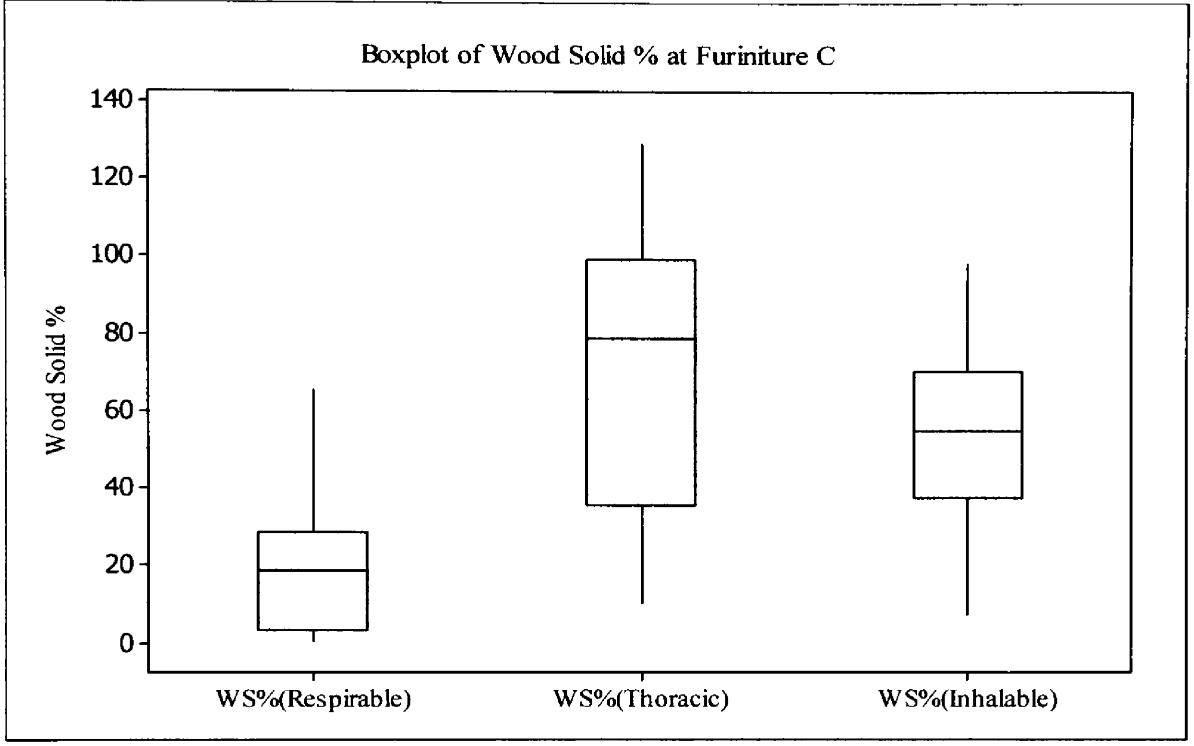


Figure 12 Boxplot of Size-Fractionated WS % for Furniture D

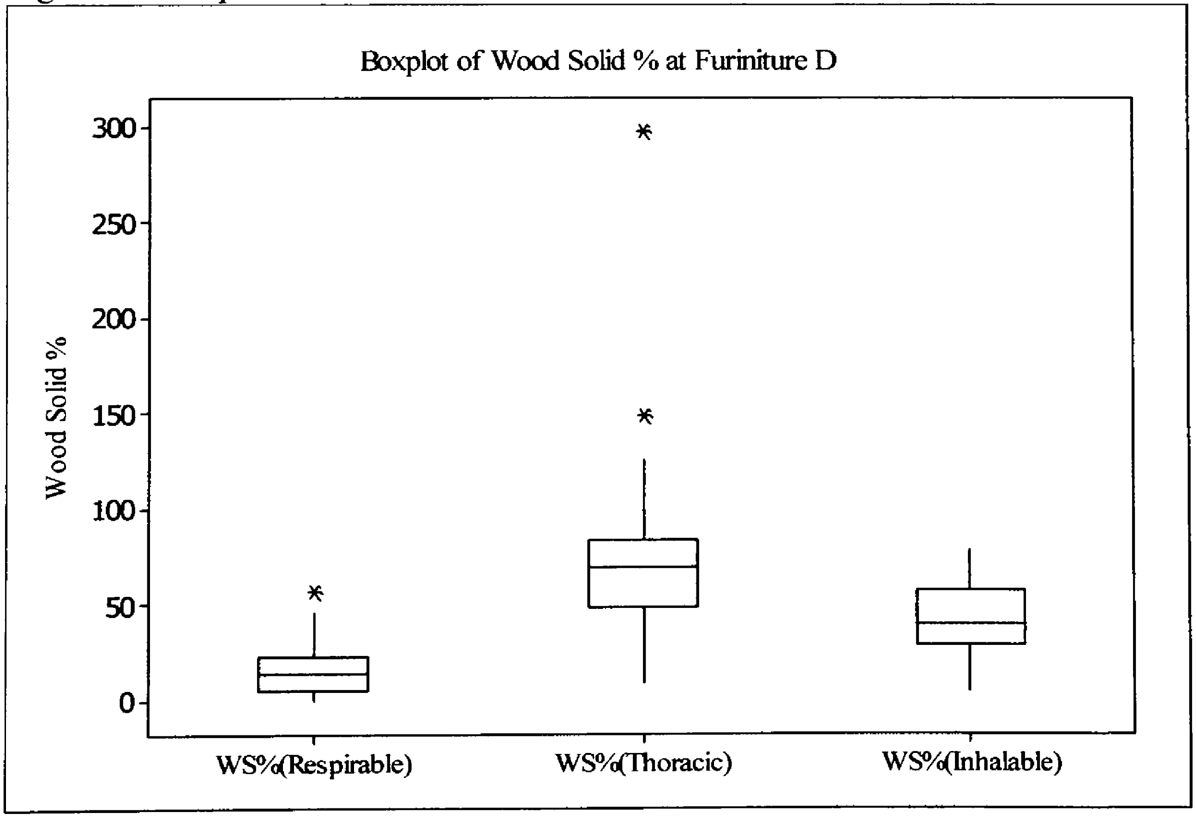


Figure 13 Boxplot of Size-Fractionated WS % for Cabinet A

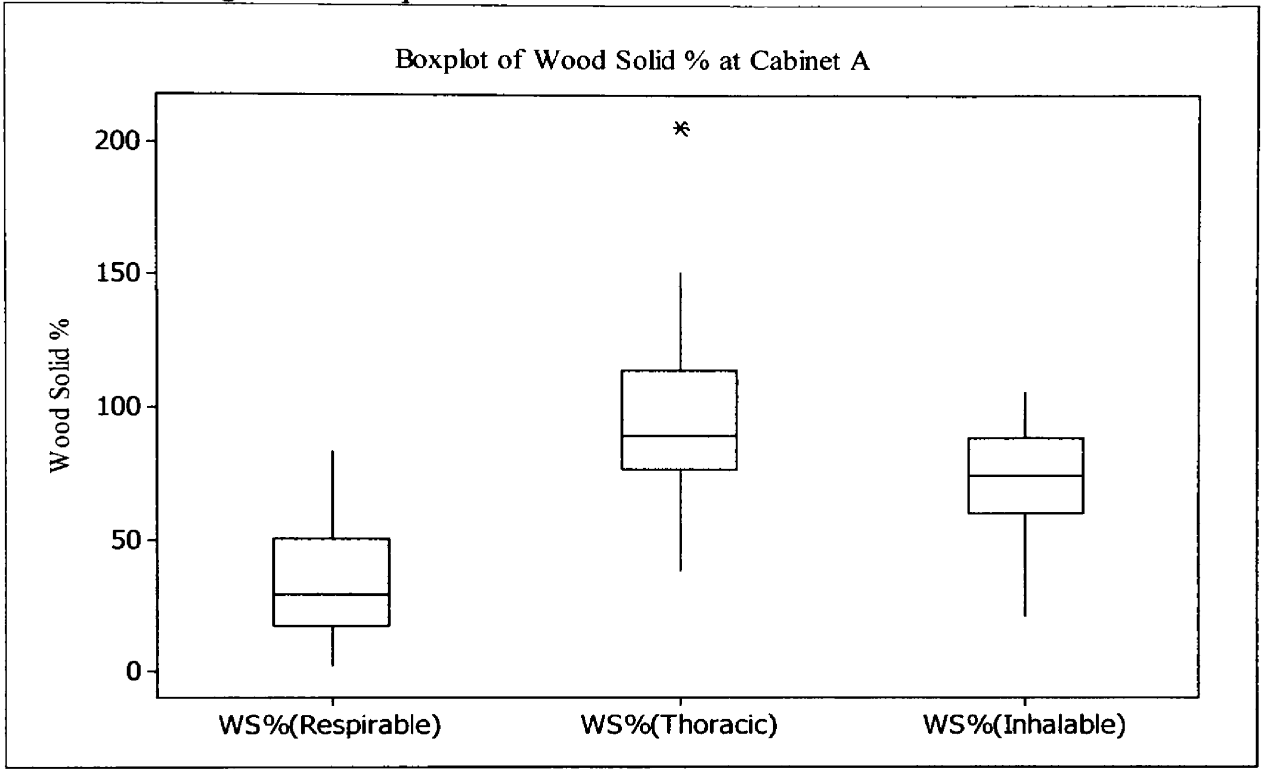


Figure 14 Boxplot of Size-Fractionated WS % for Cabinet B

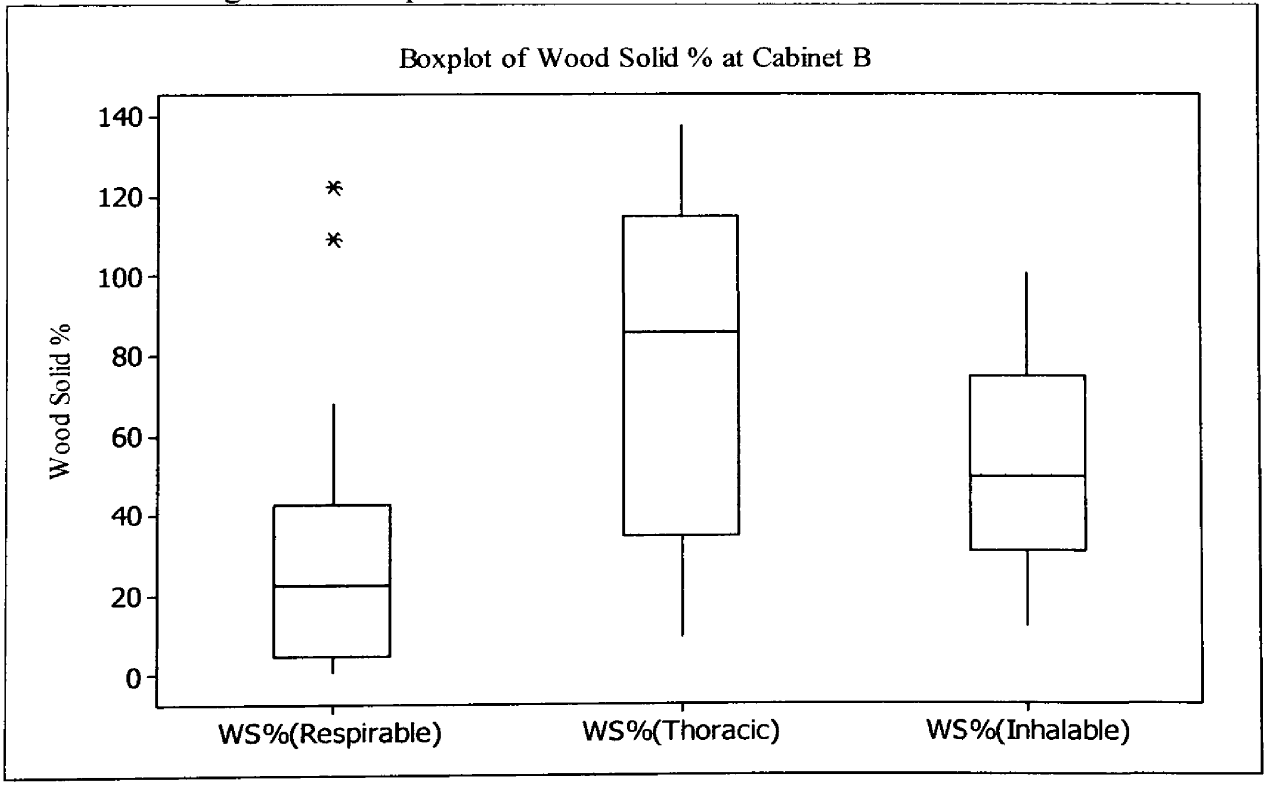


Figure 15 Boxplot of Size-Fractionated WS % for Secondary Millworks A

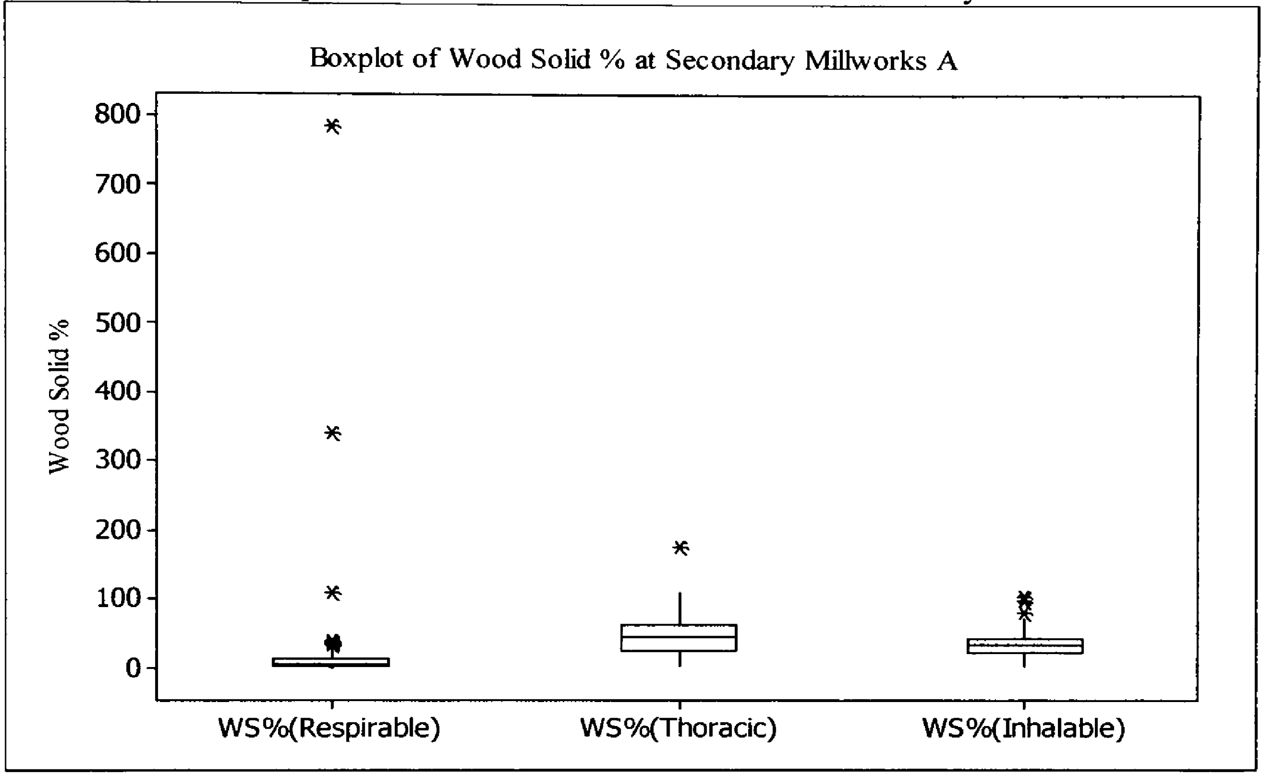


Figure 16 Boxplot of Size-Fractionated WS % for Secondary Millworks B

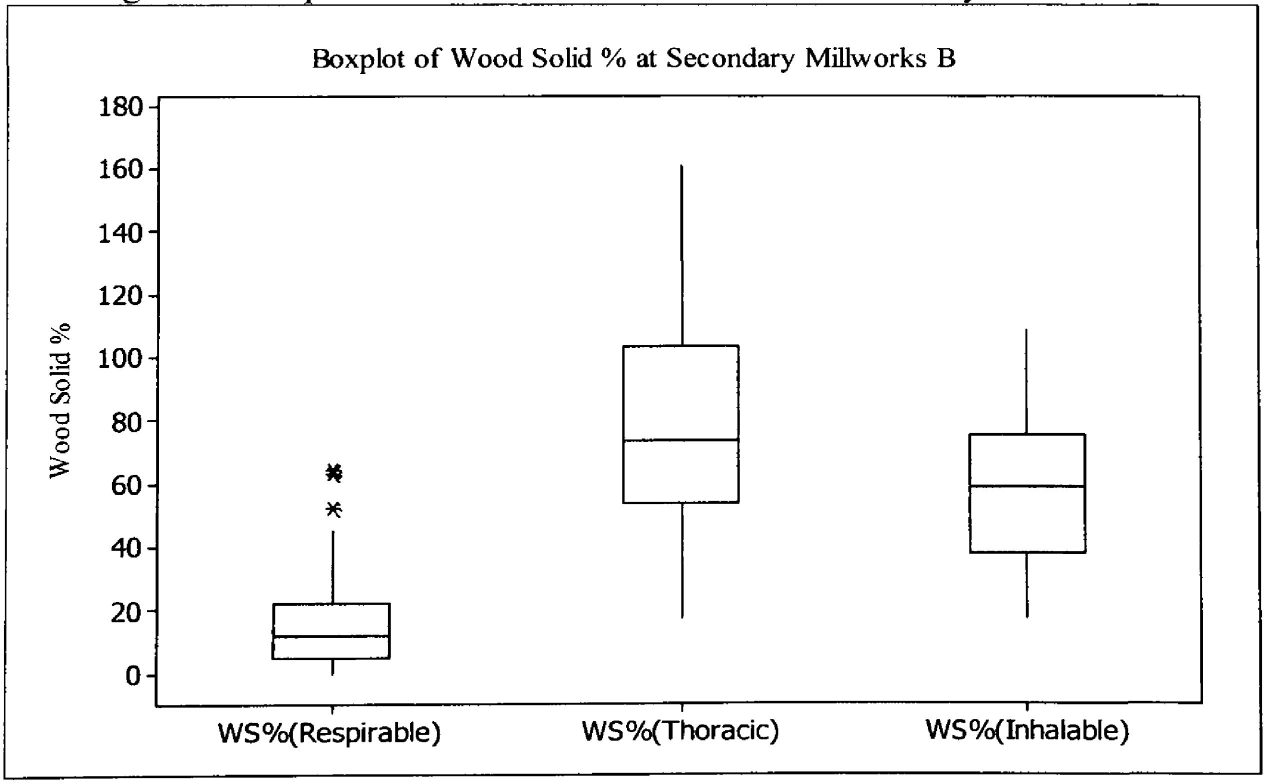


Figure 17 Boxplot of Size-Fractionated WS % for Sawmill-Planing-Plywood A

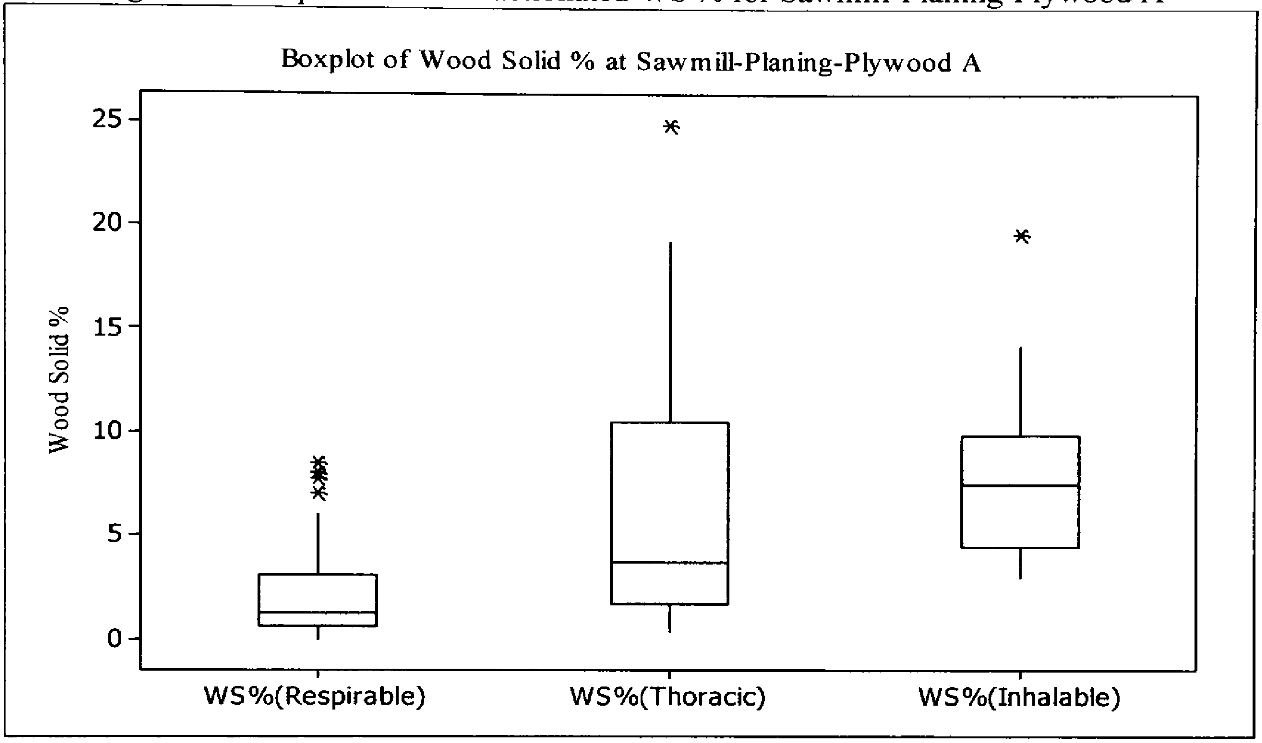
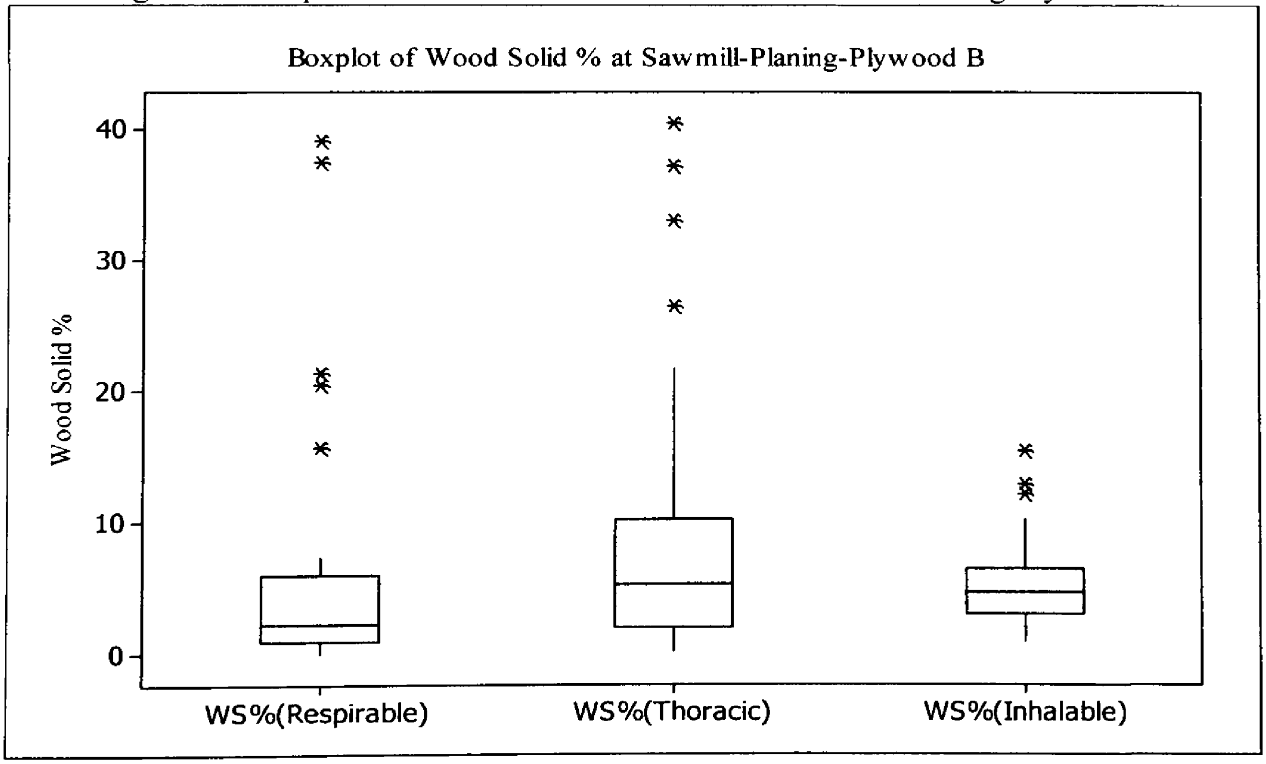


Figure 18 Boxplot of Size-Fractionated WS % for Sawmill-Planing-Plywood B



6.2 Determinants/Correlates of Wood Solid Percentage

Table 3 shows size fractionated WS % by each plant after removal outliers. There are the numbers of outliers removed shown in parentheses as well as each size fractionated WS% by each facility.

Size fractionated wood solid percentage data after box plot outlying are shown for each plant facility in Table 4 and Figure 19 by each plant type. Averages of each respirable, thoracic, and inhalable WS % in collected dust in the furniture plants were 13.4 %, 67.4 % and 44.2 %. Likewise, each average of size fractionated wood solid percentages were 30.5 %, 86.0 % and 63.5 % in the cabinet plant, 10.3 %, 61.7 % and 46.8 % in the secondary millworks plants, and 2.2 %, 6.1 % and 5.9 % in the sawmill-planing-plywood plants. Cabinet plants showed the highest content of wood solid in all three size fraction. Otherwise, sawmill-planing-plywood plant appeared to show the lowest content of wood solid presumably because of the emissions of the resin binders when the making of plywood and processing of primarily green wood.

Figure 20 shows average size-fractionated WS% by wood type. Among wood types, 26.5 %, 89.5 % and 63.6 % in mixed wood were the highest content of WS %, and 2.2 %, 6.4 % and 5.2 % in plywood were the lowest content of WS %. Figure 21 shows average size-fractionated WS % by job activity. Among job activities, 21.5 %, 83.3 % and 59.0 % in sanding were the highest content of WS %, and 1.5 %, 2.1 % and 6.0 % in debarking/log yard were the lowest content of WS %.

Table 3 WS % in Size-Fractionated Dust by Plant After Removal of Outliers

Facility ID	Plant Type		Wood Solid % of Dust		
			Respirable	Thoracic	Inhalable
9001	Furniture A	Average	9.9	77.2	50.0
		S.D.	10.4	37.4	22.4
		Number (# of Outliers)	47(2)	47(1)	45(1)
		Median	5.3	68.5	46.5
9004	Furniture B	Average	5.9	53.7	31.1
		S.D.	6.4	33.4	18.9
		Number (# of Outliers)	42(6)	40(7)	38(8)
		Median	3.4	48.4	28.3
9009	Furniture C	Average	19.5	71.5	53.2
		S.D.	17.1	35.4	23.5
		Number (# of Outliers)	45(0)	44(0)	44(0)
		Median	18.5	78.7	55.1
9011	Furniture D	Average	15.8	66.3	42.3
		S.D.	11.8	26.7	17.6
		Number (# of Outliers)	85(1)	79(3)	79(3)
		Median	13.3	67.8	39.1
9006	Cabinet A	Average	35.2	92.9	72.3
		S.D.	21.9	29.7	20.2
		Number (# of Outliers)	47(0)	46(1)	45(1)
		Median	29.8	89.9	74.3
9007	Cabinet B	Average	24.6	77.3	52.6
		S.D.	20.2	40.6	26.3
		Number (# of Outliers)	37(2)	37(2)	36(2)
		Median	21.2	85.9	49.1
9002	Secondary Millworks A	Average	6.5	46.2	34.0
		S.D.	6.2	27.5	16.1
		Number (# of Outliers)	57(7)	55(8)	47(8)
		Median	4.9	44.7	34.6
9005	Secondary Millworks B	Average	14.3	77.8	58.1
		S.D.	12.2	35.0	24.2
		Number (# of Outliers)	53(3)	53(3)	53(3)
		Median	11.9	73.5	58.6
9000	Sawmill-Planing-Plywood A	Average	1.7	6.2	7.2
		S.D.	1.6	5.3	3.1
		Number (# of Outliers)	40(4)	37(4)	36(5)
		Median	1.0	3.7	7.4

Table 3 (cont.) WS % in Size-Fractionated Dust by Plant After Removal of Outliers

Facility ID	Plant Type		Wood Solid % of Dust		
			Respirable	Thoracic	Inhalable
9010	Sawmill-Planing-Plywood B	Average	2.7	5.9	4.4
		S.D.	2.3	5.3	2.5
		Number (# of Outliers)	38(5)	34(9)	31(12)
		Median	2.1	4.9	4.6
	Total	Average	13.8	60.2	42.6
		S.D.	15.8	39.7	27.0
		Number (# of Outliers)	491(30)	472(38)	454(43)
		Median	7.6	58.1	40.7

Table 4 WS % by Plant Type After Removal of Outliers

Plant Type		Wood Solid % of Dust		
		Respirable	Thoracic	Inhalable
Furniture	Average	13.4	67.4	44.2
	SD	12.9	33.2	21.5
	Numbers	219	210	206
	Median	9.1	67.9	42.9
Cabinet	Average	30.5	86.0	63.5
	SD	21.7	35.6	25.0
	Numbers	84	83	81
	Median	26.8	86.3	66.4
Secondary Millworks	Average	10.3	61.7	46.8
	SD	10.3	35.1	24.0
	Numbers	110	108	100
	Median	6.9	56.5	41.9
Sawmill-Planing-Plywood	Average	2.2	6.1	5.9
	SD	2.0	5.3	3.1
	Numbers	78	71	67
	Median	1.5	3.9	5.2
Total	Average	13.8	60.2	42.6
	SD	15.8	39.7	27.0
	Numbers	491	472	454
	Median	7.6	58.1	40.7

Figure 19 Average of Size-Fractionated WS % by Plant Type

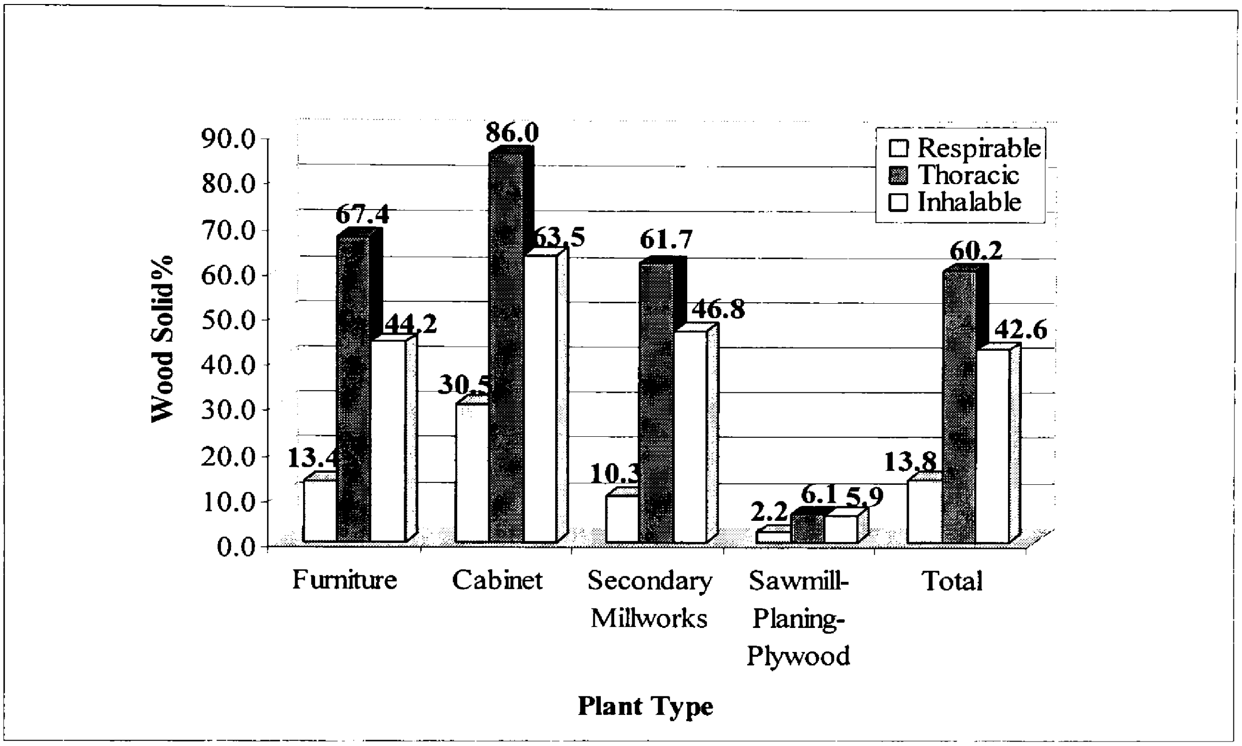


Figure 20 Average of Size-Fractionated WS % by Wood Type

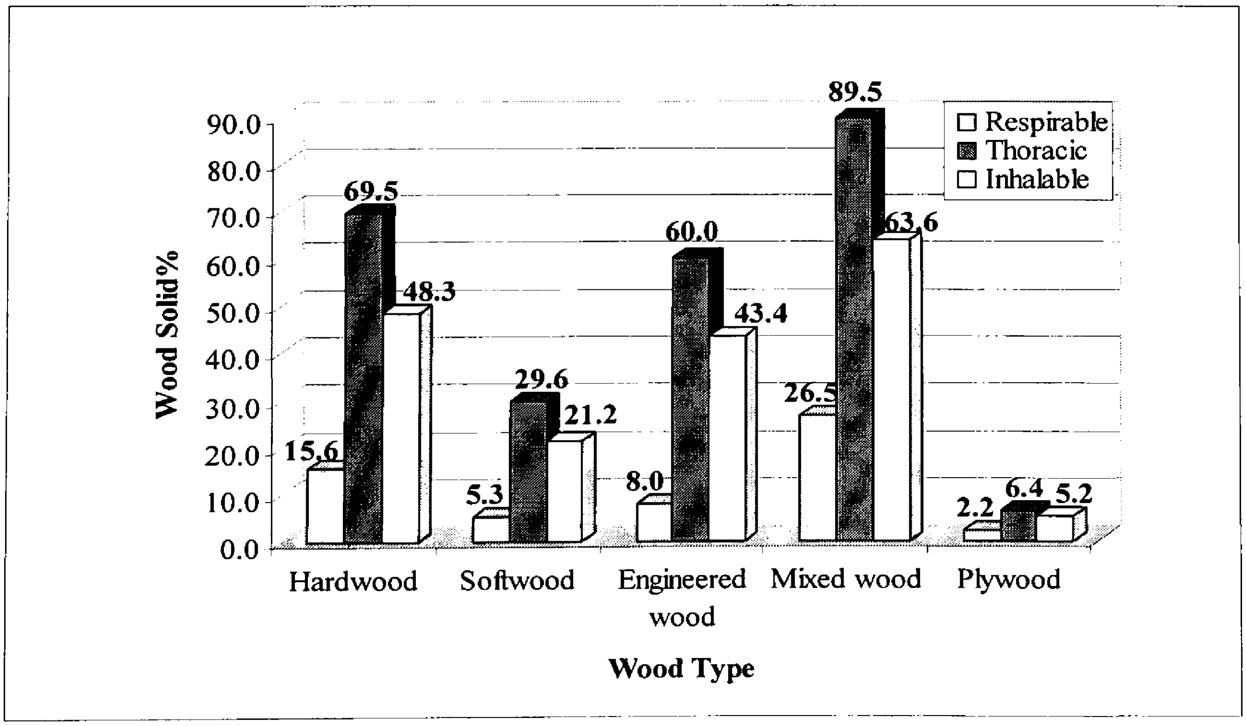


Figure 21 Average of Size-Fractionated WS % by Job Activity

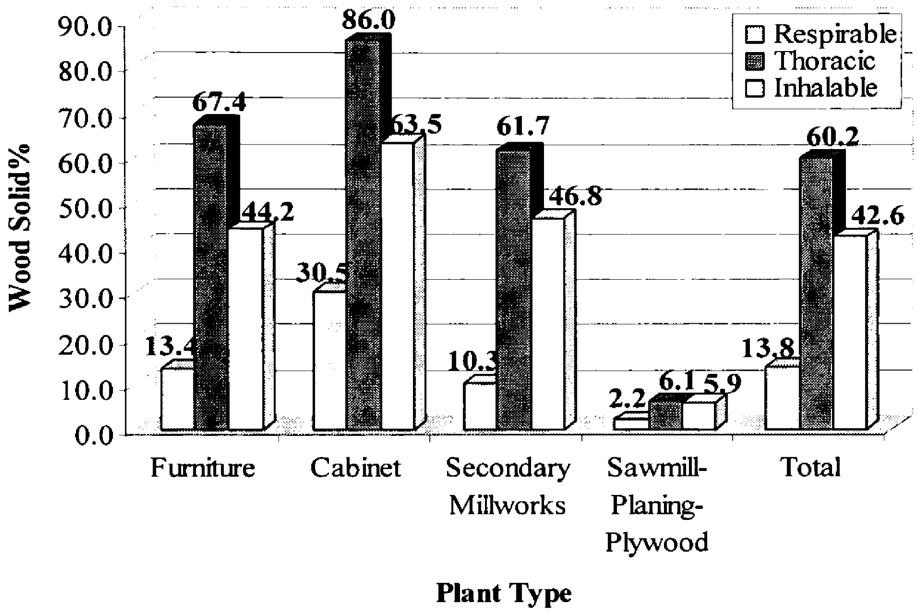


Table 5 One Sample Kolmogorov-Smirnov Test for Normality about Size-Fractionated WS %

	Respirable wood solid%	Thoracic wood solid%	Inhalable wood solid%
N	491	472	454
Kolmogorov-Smirnov Dist.	0.191	0.065	0.061
	$p < 0.001$		

Normality of size-fractioned wood solid percentage was checked by Kolmogorov-Smirnov test in Table 5. In all size-fractionated WS %, this test was failed ($p<0.001$) and it means the data shows non-normal distribution.

Kruskal-Wallis one way ANOVA on ranks was applied to these size fractionated WS % by determinants of plant type, job activity, and wood type. In Table 6, there is a statistically significant difference ($p<0.001$) between plant types for all size-fractionated WS %. Table 7 through Table 9 show multiple comparison analysis by Mann-Whitney test about plant types of size fractionated WS %. All of each respirable, thoracic, and inhalable WS % in the furniture vs secondary millwork were not significantly different ($p>0.05$). All other pairwise comparisons for plant type and WS % were statistically different.

Table 6 Kruskal-Wallis ANOVA on Size-Fractionated WS % by Plant Type

	Plant Type	N	Mean	Mean Rank	Chi-Square	df	Asymp. Sig.
Respirable WS%	Furniture	219	13.4	257.07	143.380	3	.000
	Sawmill-Planing-Plywood	78	2.2	104.31			
	Secondary Millworks	110	10.3	230.62			
	Cabinet	84	30.5	368.85			
	Total	491	13.8				
Thoracic WS%	Furniture	210	67.4	264.15	185.491	3	.000
	Sawmill-Planing-Plywood	71	6.1	43.54			
	Secondary Millworks	108	61.7	241.92			
	Cabinet	83	86.0	324.55			
	Total	472	60.2				
Inhalable WS%	Furniture	206	44.2	239.77	185.690	3	.000
	Sawmill-Planing-Plywood	67	5.9	40.37			
	Secondary Millworks	100	46.8	248.31			
	Cabinet	81	63.5	325.38			
	Total	454	42.6				

Table 7 Multiple Comparison by Mann-Whitney Test about Plant Type of Respirable WS %

	Plant Type	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Z	Asymp.Sig. (2-tailed)
Furniture vs Sawmill-Planing-Plywood	Furniture	219	174.25	38161.00	3011.000	-8.491	.000
	Sawmill-Planing-Plywood	78	78.10	6092.00			
	Total	297					
Furniture vs Secondary Millworks	Furniture	219	171.76	37616.50	10563.500	-1.820	.069
	Secondary Millworks	110	151.53	16668.50			
	Total	329					
Furniture vs Cabinet	Furniture	219	131.05	28701.00	4611.000	-6.719	.000
	Cabinet	84	206.61	17355.00			
	Total	303					
Sawmill-Planing-Plywood vs Secondary Millworks	Sawmill-Planing-Plywood	78	61.26	4778.50	1697.500	-7.053	.000
	Secondary Millworks	110	118.07	12987.50			
	Total	188					
Sawmill-Planing-Plywood vs Cabinet	Sawmill-Planing-Plywood	78	43.95	3428.00	347.000	-9.818	.000
	Cabinet	84	116.37	9775.00			
	Total	162					
Secondary Millworks vs Cabinet	Secondary Millworks	110	72.02	7922.00	1817.000	-7.234	.000
	Cabinet	84	130.87	10993.00			
	Total	194					

Table 8 Multiple Comparison by Mann-Whitney Test about Plant Type of Thoracic WS %

	Plant Type	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Z	Asymp. Sig. (2-tailed)
Furniture vs Sawmill-Planing-Plywood	Furniture	210	175.13	36778.00	287.000	-12.109	.000
	Sawmill-Planing-Plywood	71	40.04	2843.00			
	Total	281					
Furniture vs Secondary Millworks	Furniture	210	165.83	34824.00	10011.000	-1.712	.087
	Secondary Millworks	108	147.19	15897.00			
	Total	318					
Furniture vs Cabinet	Furniture	210	134.19	28180.00	6025.000	-4.116	.000
	Cabinet	83	179.41	14891.00			
	Total	293					
Sawmill-Planing-Plywood vs Secondary Millworks	Sawmill-Planing-Plywood	71	38.89	2761.00	205.000	-10.700	.000
	Secondary Millworks	108	123.60	13349.00			
	Total	179					
Sawmill-Planing-Plywood vs Cabinet	Sawmill-Planing-Plywood	71	36.61	2599.00	43.000	-10.524	.000
	Cabinet	83	112.48	9336.00			
	Total	154					
Secondary Millworks vs Cabinet	Secondary Millworks	108	80.12	8653.00	2767.000	-4.528	.000
	Cabinet	83	116.66	9683.00			
	Total	191					

Table 9 Multiple Comparison by Mann-Whitney Test about Plant Type of Inhalable WS %

	Plant Type	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Z	Asymp. Sig. (2-tailed)
Furniture vs Sawmill-Planing-Plywood	Furniture	206	168.76	34765.00	358.000	-11.655	.000
	Sawmill-Planing-Plywood	67	39.34	2636.00			
	Total	273					
Furniture vs Secondary Millworks	Furniture	206	151.93	31298.00	9977.000	-.445	.656
	Secondary Millworks	100	156.73	15673.00			
	Total	306					
Furniture vs Cabinet	Furniture	206	126.08	25972.00	4651.000	-5.834	.000
	Cabinet	81	189.58	15356.00			
	Total	287					
Sawmill-Planing-Plywood vs Secondary Millworks	Sawmill-Planing-Plywood	67	34.99	2344.00	66.000	-10.723	.000
	Secondary Millworks	100	116.84	11684.00			
	Total	167					
Sawmill-Planing-Plywood vs Cabinet	Sawmill-Planing-Plywood	67	34.04	2281.00	3.000	-10.442	.000
	Cabinet	81	107.96	8745.00			
	Total	148					
Secondary Millworks vs Cabinet	Secondary Millworks	100	75.74	7574.00	2524.000	-4.354	.000
	Cabinet	81	109.84	8897.00			
	Total	181					

Table 10 Kruskal-Wallis ANOVA on Size-Fractionated WS % by Wood Type

	Wood Type	N	Mean	Mean Rank	Chi-Square	df	Asymp. Sig.
Respirable WS%	Hardwood	282	15.6	273.51	102.021	4	.000
	Softwood	126	5.3	157.13			
	Engineered Wood	6	8.0	225.17			
	Mixed Wood	62	26.5	338.44			
	Plywood	15	2.2	101.60			
	Total	491					
Thoracic WS%	Hardwood	273	69.5	270.62	149.408	4	.000
	Softwood	118	29.6	129.69			
	Engineered Wood	6	60.0	237.17			
	Mixed Wood	61	89.5	334.84			
	Plywood	14	6.4	42.71			
	Total	472					
Inhalable WS%	Hardwood	266	48.3	257.43	146.694	4	.000
	Softwood	108	21.2	121.06			
	Engineered Wood	6	43.4	237.67			
	Mixed Wood	61	63.6	325.34			
	Plywood	13	5.2	35.62			
	Total	454					

Kruskal-Wallis one way analysis of variance on ranks was applied to these size fractionated WS% by wood type in Table 10 and there is a statistically significant difference ($p=<0.001$) between wood types from all of each size fractionated WS %. Table 11 through Table 13 show multiple comparison analysis by Mann-Whitney Test about wood types of size fractionated WS%. All of each respirable, thoracic,and inhalable wood solids % in the hardwood vs. engineered wood is not significantly different ($p<0.05$). However, the very small sample number (6) of engineered wood should be considered.

Table 11 Multiple Comparison by Mann-Whitney Test about Wood Type of Respirable WS %

	Wood Type	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Z	Asymp.Sig(2-tailed)/ Exact Sig.[2*(1-tailed Sig.)]
Hardwood vs Softwood	Hardwood	282	235.09	66294.00	9141.000	-7.838	.000
	Softwood	126	136.05	17142.00			
	Total	408					
Hardwood vs Engineered Wood	Hardwood	282	145.23	40956.00	639.000	-1.025	.305
	Engineered Wood	6	110.00	660.00			
	Total	288					
Hardwood vs Mixed Wood	Hardwood	282	163.48	46102.00	6199.000	-3.587	.000
	Mixed Wood	62	213.52	13238.00			
	Total	344					
Hardwood vs Plywood	Hardwood	282	154.21	43487.00	646.000	-4.533	.000
	Plywood	15	51.07	766.00			
	Total	297					
Softwood vs Engineered Wood	Softwood	126	65.31	8229.00	228.000	-1.639	.101
	Engineered Wood	6	91.50	549.00			
	Total	132					
Softwood vs Mixed Wood	Softwood	126	73.16	9218.00	1217.000	-7.666	.000
	Mixed Wood	62	137.87	8548.00			
	Total	188					
Softwood vs Plywood	Softwood	126	73.11	9212.00	679.000	-1.779	.075
	Plywood	15	53.27	799.00			
	Total	141					
Engineered Wood vs Mixed Wood	Engineered Wood	6	17.50	105.00	84.000	-2.205	0.027
	Mixed Wood	62	36.15	2241.00			0.025
	Total	68					
Engineered Wood vs Plywood	Engineered Wood	6	16.67	100.00	11.000	-2.650	.008
	Plywood	15	8.73	131.00			.006
	Total	21					
Mixed Wood vs Plywood	Mixed Wood	62	45.40	2815.00	68.000	-5.106	.000
	Plywood	15	12.53	188.00			
	Total	77					

Table 12 Multiple Comparison by Mann-Whitney Test about Wood Type of Thoracic WS %

	Wood Type	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Z	Asymp.Sig(2-tailed)/ Exact Sig.[2*(1-tailed Sig.)]
Hardwood vs Softwood	Hardwood	273	232.40	63444.00	6171.000	-9.686	.000
	Softwood	118	111.80	13192.00			
	Total	391					
Hardwood vs Engineered Wood	Hardwood	273	140.52	38361.00	678.000	-.721	.471
	Engineered Wood	6	116.50	699.00			
	Total	279					
Hardwood vs Mixed Wood	Hardwood	273	158.05	43147.00	5746.000	-3.785	.000
	Mixed Wood	61	209.80	12798.00			
	Total	334					
Hardwood vs Plywood	Hardwood	273	150.66	41130.00	93.000	-6.003	.000
	Plywood	14	14.14	198.00			
	Total	287					
Softwood vs Engineered Wood	Softwood	118	60.81	7176.00	155.000	-2.317	.020
	Engineered Wood	6	95.67	574.00			
	Total	124					
Softwood vs Mixed Wood	Softwood	118	65.46	7724.00	703.000	-8.813	.000
	Mixed Wood	61	137.48	8386.00			
	Total	179					
Softwood vs Plywood	Softwood	118	70.12	8274.00	399.000	-3.156	.002
	Plywood	14	36.00	504.00			
	Total	132					
Engineered Wood vs Mixed Wood	Engineered Wood	6	18.00	108.00	87.000	-2.108	0.035
	Mixed Wood	61	35.57	2170.00			0.034
	Total	67					
Engineered Wood vs Plywood	Engineered Wood	6	17.50	105.00	.000	-3.464	.001
	Plywood	14	7.50	105.00			.000
	Total	20					
Mixed Wood vs Plywood	Mixed Wood	61	44.98	2744.00	1.000	-5.792	.000
	Plywood	14	7.57	106.00			
	Total	75					

Table 13 Multiple Comparison by Mann-Whitney Test about Wood Type of Inhalable WS %

	Wood Type	N	Mean Rank	Sum of Ranks	Mann-Whitney U	Z	Asymp.Sig(2-tailed) Exact Sig.[2*(1-tailed Sig.)]
Hardwood vs Softwood	Hardwood	266	221.38	58886.00	5353.000	-9.510	.000
	Softwood	108	104.06	11239.00			
	Total	374					
Hardwood vs Engineered Wood	Hardwood	266	136.85	36401.00	706.000	-.483	.629
	Engineered Wood	6	121.17	727.00			
	Total	272					
Hardwood vs Mixed Wood	Hardwood	266	153.44	40815.00	5304.000	-4.218	.000
	Mixed Wood	61	210.05	12813.00			
	Total	327					
Hardwood vs Plywood	Hardwood	266	146.27	38907.00	62.000	-5.869	.000
	Plywood	13	11.77	153.00			
	Total	279					
Softwood vs Engineered Wood	Softwood	108	55.63	6008.00	122.000	-2.563	.010
	Engineered Wood	6	91.17	547.00			
	Total	114					
Softwood vs Mixed Wood	Softwood	108	60.22	6504.00	618.000	-8.759	.000
	Mixed Wood	61	128.87	7861.00			
	Total	169					
Softwood vs Plywood	Softwood	108	64.64	6981.00	309.000	-3.289	.001
	Plywood	13	30.77	400.00			
	Total	121					
Engineered Wood vs Mixed Wood	Engineered Wood	6	19.33	116.00	95.000	-1.932	0.053
	Mixed Wood	61	35.44	2162.00			0.053
	Total	67					
Engineered Wood vs Plywood	Engineered Wood	6	16.50	99.00	.000	-3.421	.001
	Plywood	13	7.00	91.00			.000
	Total	19					
Mixed Wood vs Plywood	Mixed Wood	61	43.98	2683.00	1.000	-5.618	.000
	Plywood	13	7.08	92.00			
	Total	74					

Table 14 Kruskal-Wallis ANOVA on Size-Fractionated WS % by Job Activity

	Job Activity	N	Mean	Mean Rank	Chi-Square	df	Asymp. Sig.
Respirable WS%	Sawing	93	11.3	226.32	50.674	6	.000
	Sanding	135	21.5	313.57			
	Milling	84	10.5	224.44			
	PSV	13	7.6	198.85			
	Others	149	10.8	212.97			
	Debarking/Log Yard	4	1.5	87.38			
	Blow Down/Compressed Air	13	18.1	299.00			
	Total	491					
Thoracic WS%	Sawing	89	52.4	211.08	83.095	6	.000
	Sanding	133	83.3	316.96			
	Milling	81	57.0	226.37			
	PSV	12	55.0	221.08			
	Others	140	45.3	184.14			
	Debarking/Log Yard	4	2.1	20.00			
	Blow Down/Compressed Air	13	78.6	295.23			
	Total	472					
Inhalable WS%	Sawing	86	34.8	191.41	79.803	6	.000
	Sanding	132	59.0	306.17			
	Milling	79	38.6	211.20			
	PSV	10	32.0	178.10			
	Others	132	34.6	186.56			
	Debarking/Log Yard	4	6.0	40.75			
	Blow Down/Compressed Air	11	54.4	286.82			
	Total	454					

Kruskal-Wallis one way analysis of variance on ranks was applied to the size fractionated WS % by job activity in Table 14 and there is a statistically significant difference ($p<0.001$) between job activities from all of each size fractionated WS %. Table 15 through Table 17 show multiple comparison analysis by Mann-Whitney Test about job activity of size fractionated WS %. There are no significant differences in many pairings of job activity: sawing vs. milling, sawing vs. PSV, sawing vs. others, sanding vs. blow down/compressed air, milling vs. PSV, PSV vs. others in all of size fractionated wood solid. Most of sanding is statistically significant with all other job activities except with blow down/compressed air. Based on the result, PSV vs. furniture and PSV vs. cabinet are confounded.

From the results of these analyses, wood solid contents were different from sources of size-fractionated dust in wood processing industry by plant type, wood type, and job activity.

Table 15 Multiple Comparison by Mann-Whitney Test about Job Activity of Repirable WS %

	Job Activity	N	Mean Rank	Sum of Ranks	Mann-WhitneyU	Z	Asymp.Sig(2-tailed)/ ExactSig.[2*(1-tailedSig.)]
Sawing vs Sanding	Sawing	93	90.22	8390.00	4019.000	-4.614	.000
	Sanding	135	131.23	17716.00			
	Total	228					
Sawing vs Milling	Sawing	93	89.18	8294.00	3889.000	-.050	.960
	Milling	84	88.80	7459.00			
	Total	177					
Sawing vs PSV	Sawing	93	54.27	5047.00	533.000	-.689	.491
	PSV	13	48.00	624.00			
	Total	106					
Sawing vs Others	Sawing	93	125.98	11716.50	6511.500	-.787	.431
	Others	149	118.70	17686.50			
	Total	242					
Sawing vs Debarking/Log Yard	Sawing	93	50.23	4671.00	72.000	-2.068	.039
	Debarking/Log Yard	4	20.50	82.00			.036
	Total	97					
Sawing vs BlowDown/Compressed Air	Sawing	93	51.44	4784.00	413.000	-1.844	.065
	BlowDown/CompressedAir	13	68.23	887.00			
	Total	106					
Sanding vs Milling	Sanding	135	125.61	16957.00	3563.000	-4.621	.000
	Milling	84	84.92	7133.00			
	Total	219					
Sanding vs PSV	Sanding	135	77.75	10496.00	439.000	-2.970	.003
	PSV	13	40.77	530.00			
	Total	148					
Sanding vs Others	Sanding	135	172.26	23255.00	6040.000	-5.813	.000
	Others	149	115.54	17215.00			
	Total	284					
Sanding vs Debarking/Log Yard	Sanding	135	71.64	9672.00	48.000	-2.797	.005
	Debarking/Log Yard	4	14.50	58.00			
	Total	139					
Sanding vs Blow Down/Compressed Air	Sanding	135	75.08	10136.00	799.000	-.532	.595
	BlowDown/CompressedAir	13	68.46	890.00			
	Total	148					
Milling vs PSV	Milling	84	49.68	4173.00	489.000	-.604	.546
	PSV	13	44.62	580.00			
	Total	97					

Milling vs Others	Milling	84	120.96	10161.00	5925.000	-.674	.500
	Others	149	114.77	17100.00			
	Total	233					
Milling vs Debarking/Log Yard	Milling	84	45.75	3843.00	63.000	-2.103	.035
	Debarking/Log Yard	4	18.25	73.00			.033
	Total	88					
Milling vsBlow Down/Compressed Air	Milling	84	46.83	3934.00	364.000	-1.927	.054
	BlowDown/CompressedAir	13	63.00	819.00			
	Total	97					
PSV vs Others	PSV	13	79.38	1032.00	941.000	-.170	.865
	Others	149	81.68	12171.00			
	Total	162					
PSV vs Debarking/Log Yard	PSV	13	10.38	135.00	8.000	-2.038	.042
	Debarking/Log Yard	4	4.50	18.00			.045
	Total	17					
PSV vs Blow Down/Compressed Air	PSV	13	10.69	139.00	48.000	-1.872	.061
	BlowDown/CompressedAir	13	16.31	212.00			.064
	Total	26					
Others vs Debarking/Log Yard	Others	149	78.02	11625.50	145.500	-1.744	.081
	Debarking/Log Yard	4	38.88	155.50			
	Total	153					
Others vs BlowDown/Compressed Airl	Others	149	79.26	11809.00	634.000	-2.062	.039
	BlowDown/CompressedAir	13	107.23	1394.00			
	Total	162					
Debarking/Log Yard vs Blow Down/Compressed Air	Debarking/Log Yard	4	3.25	13.00	3.000	-2.604	.009
	BlowDown/CompressedAir	13	10.77	140.00			.006
	Total	17					

Table 16 Multiple Comparison by Mann-Whitney Test about Job Activity of Thoracic WS %

	Job Activity	N	Mean Rank	Sum of Ranks	Mann-WhitneyU	Z	Asymp.Sig(2-tailed)/ ExactSig.[2*(1-tailedSig.)]
Sawing vs Sanding	Sawing	89	79.96	7116.00	3111.000	-5.986	.000
	Sanding	133	132.61	17637.00			
	Total	222					
Sawing vs Milling	Sawing	89	82.28	7323.00	3318.000	-.894	.371
	Milling	81	89.04	7212.00			
	Total	170					
Sawing vs PSV	Sawing	89	50.54	4498.00	493.000	-.430	.667
	PSV	12	54.42	653.00			
	Total	101					
Sawing vs Others	Sawing	89	125.16	11139.00	5326.000	-1.850	.064
	Others	140	108.54	15196.00			
	Total	229					
Sawing vs Debarking/Log Yard	Sawing	89	48.91	4353.00	8.000	-3.219	.001
	Debarking/Log Yard	4	4.50	18.00			.000
	Total	93					
Sawing vs BlowDown/Compressed Air	Sawing	89	49.24	4382.00	377.000	-2.022	.043
	BlowDown/CompressedAir	13	67.00	871.00			
	Total	102					
Sanding vs Milling	Sanding	133	125.89	16743.00	2941.000	-5.566	.000
	Milling	81	77.31	6262.00			
	Total	214					

Sanding vs PSV	Sanding PSV Total	133 12 145	76.02 39.50	10111.00 474.00	396.000	-2.885	.004
Sanding vs Others	Sanding Others Total	133 140 273	172.87 102.92	22992.00 14409.00	4539.000	-7.317	.000
Sanding vs Debarking/Log Yard	Sanding Debarking/Log Yard Total	133 4 137	70.96 3.75	9438.00 15.00	5.000	-3.337	.001
Sanding vs Blow Down/Compressed Air	Sanding BlowDown/CompressedAir Total	133 13 146	73.61 72.38	9790.00 941.00	850.000	-.100	.921
Milling vs PSV	Milling PSV Total	81 12 93	46.98 47.17	3805.00 566.00	484.000	-.023	.982
Milling vs Others	Milling Others Total	81 140 221	127.46 101.48	10324.00 14207.00	4337.000	-2.910	.004
Milling vs Debarking/Log Yard	Milling Debarking/Log Yard Total	81 4 85	44.99 2.75	3644.00 11.00	1.000	-3.341	.001 .000
Milling vsBlow Down/Compressed Air	Milling BlowDown/CompressedAir Total	81 13 94	45.60 59.31	3694.00 771.00	373.000	-1.681	.093
PSV vs Others	PSV Others Total	12 140 152	91.08 75.25	1093.00 10535.00	665.000	-1.196	.232
PSV vs Debarking/Log Yard	PSV Debarking/Log Yard Total	12 4 16	10.50 2.50	126.00 10.00	.000	-2.910	.004 .001
PSV vs Blow Down/Compressed Air	PSV BlowDown/CompressedAir Total	12 13 25	10.92 14.92	131.00 194.00	53.000	-1.360	.174 .186
Others vs Debarking/Log Yard	Others Debarking/Log Yard Total	140 4 144	74.10 16.50	10374.00 66.00	56.000	-2.723	.006
Others vs BlowDown/Compressed Airl	Others BlowDown/CompressedAir Total	140 13 153	74.34 105.62	10408.00 1373.00	538.000	-2.434	.015
Debarking/Log Yard vs Blow Down/Compressed Air	Debarking/Log Yard BlowDown/CompressedAir Total	4 13 17	2.50 11.00	10.00 143.00	.000	-2.944	.003 .001

Table 17 Multiple Comparison by Mann-Whitney Test about Job Activity of Inhalable WS %

	Job Activity	N	Mean Rank	Sum of Ranks	Mann-WhitneyU	Z	Asymp.Sig(2-tailed)/ ExactSig.[2*(1-tailedSig.)]
Sawing vs Sanding	Sawing Sanding Total	86 132 218	74.56 132.27	6412.00 17459.00	2671.000	-6.602	.000
Sawing vs Milling	Sawing Milling Total	86 79 165	78.66 87.72	6765.00 6930.00	3024.000	-1.217	.224

Sawing vs PSV	Sawing	86	48.56	4176.00	425.000	-.060	.952
	PSV	10	48.00	480.00			
	Total	96					
Sawing vs Others	Sawing	86	113.31	9745.00	5348.000	-.721	.471
	Others	132	107.02	14126.00			
	Total	218					
Sawing vs Debarking/Log Yard	Sawing	86	47.15	4055.00	30.000	-2.780	.005
	Debarking/Log Yard	4	10.00	40.00			.002
	Total	90					
Sawing vs BlowDown/Compressed Air	Sawing	86	46.66	4013.00	272.000	-2.287	.022
	BlowDown/CompressedAir	11	67.27	740.00			
	Total	97					
Sanding vs Milling	Sanding	132	125.01	16501.00	2705.000	-5.846	.000
	Milling	79	74.24	5865.00			
	Total	211					
Sanding vs PSV	Sanding	132	74.90	9887.00	211.000	-3.580	.000
	PSV	10	26.60	266.00			
	Total	142					
Sanding vs Others	Sanding	132	163.71	21610.00	4592.000	-6.642	.000
	Others	132	101.29	13370.00			
	Total	264					
Sanding vs Debarking/Log Yard	Sanding	132	70.44	9298.00	8.000	-3.297	.001
	Debarking/Log Yard	4	4.50	18.00			
	Total	136					
Sanding vs Blow Down/Compressed Air	Sanding	132	72.34	9549.00	681.000	-.341	.733
	BlowDown/CompressedAir	11	67.91	747.00			
	Total	143					
Milling vs PSV	Milling	79	45.73	3613.00	337.000	-.754	.451
	PSV	10	39.20	392.00			
	Total	89					
Milling vs Others	Milling	79	116.22	9181.00	4407.000	-1.880	.060
	Others	132	99.89	13185.00			
	Total	211					
Milling vs Debarking/Log Yard	Milling	79	43.91	3469.00	7.000	-3.211	.001
	Debarking/Log Yard	4	4.25	17.00			.000
	Total	83					
Milling vsBlow Down/Compressed Air	Milling	79	43.38	3427.00	267.000	-2.063	.039
	BlowDown/CompressedAir	11	60.73	668.00			
	Total	90					
PSV vs Others	PSV	10	74.80	748.00	627.000	-.263	.792
	Others	132	71.25	9405.00			
	Total	142					
PSV vs Debarking/Log Yard	PSV	10	9.40	94.00	1.000	-2.687	.007
	Debarking/Log Yard	4	2.75	11.00			.004
	Total	14					
PSV vs Blow Down/Compressed Air	PSV	10	7.60	76.00	21.000	-2.394	.017
	BlowDown/CompressedAir	11	14.09	155.00			.016
	Total	21					
Others vs Debarking/Log Yard	Others	132	69.71	9202.00	104.000	-2.061	.039
	Debarking/Log Yard	4	28.50	114.00			
	Total	136					
Others vs BlowDown/Compressed Airl	Others	132	69.91	9228.00	450.000	-2.091	.037
	BlowDown/CompressedAir	11	97.09	1068.00			
	Total	143					
Debarking/Log Yard vs Blow Down/Compressed Air	Debarking/Log Yard	4	3.25	13.00	3.000	-2.481	.013
	BlowDown/CompressedAir	11	9.73	107.00			.010
	Total	15					

6.3 Prediction Model for Inhalable Wood Solid Percentage

6.3.1 Prediction Modeling of 454 Samples of Inhalable Wood Solid Percentage from 10 Plants

Dependent variable was inhalable wood solid percentage and determinants of prediction model A from all of the 10 plants were plant type (furniture, cabinet, secondary millworks, and sawmill-planing-plywood), green vs. dry wood (green wood, dry wood, and green/dry wood), hard vs. soft wood (hardwood, softwood, and hard/softwood), formaldehyde (formaldehyde and no formaldehyde) and PSV (PSV and no PSV). For this prediction regression model A, the reference values were: 'furniture' (plant type), 'dry wood' (green vs. dry wood), 'mixed wood' (hard vs. soft wood), 'no formaldehyde' and 'no PSV'.

All coefficients of the determinants are in Table 18. Coefficient of cabinet was 19.8 % higher, secondary millworks 12.3 % higher, sawmill-planing-plywood 17.2 % lower, hardwood 14.2 % lower, softwood 22.3 % lower, and PSV 12.6 % lower than those of the references. The coefficients of the determinants of green wood, green/dry wood, and formaldehyde were not statistically significant. There is confounding between sawmill-planing-plywood vs green, green/dry wood, and formaldehyde because these materials were only present in the sawmill-planing-plywood factories.

Table 18 Coefficients of Determinants of Prediction Model A for Inhalable WS % from 10 Plants (n=454, R=.669 and R^2=.447)

Model	**Unstandardized Coefficients(B)**	**Std. Error**	**Sig.**
(Constant)	45.6	1.47	.000
Plant Type			
Cabinet	19.8	2.80	.000
Secondary millworks	12.3	3.03	.000
Sawmill-planing-plywood	-17.2	6.38	.007
Green vs. Dry wood			
Green wood	-1.89	5.60	.736
Green/Dry wood mixed	-.848	11.3	.940
Hard vs. Softwood			
Hardwood	-14.2	4.39	.001
Softwood	-22.3	3.79	.000
Formaldehyde			
Yes_Formaldehyde	1.09	5.83	.852
PSV			
Yes_PSV	-12.6	5.10	.014

Figure 22 shows the scatter graph about observed vs predicted inhalable wood solid percentage obtained from 10 plant prediction model A.

Table 19 shows the mean and standard deviation of observed and predicted inhalable wood solid percentage, and both Pearson and Spearman's correlation coefficients from prediction model A. The results were presented for the total number 454 and within the following groups: furniture, cabinet, secondary millworks, and sawmill-planing-plywood. The predicted value of each inhalable wood solid % is 44.2 % in furniture plants, 63.5 % in cabinet plants, 46.8 % in secondary millworks plant, and 5.93 % in sawmill-planing-plywood plant.

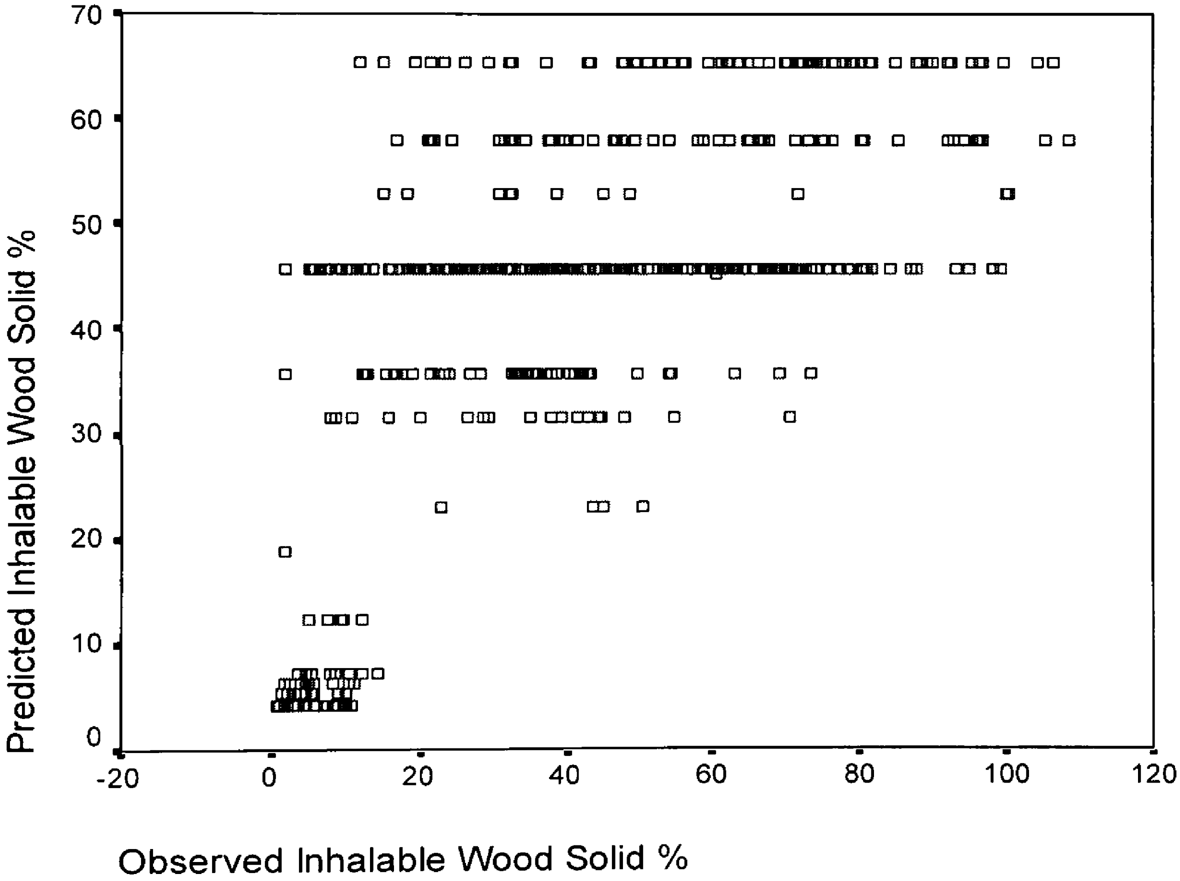


Figure 22 Observed vs Predicted Inhalable WS % on 10 Plants from Prediction Model A

Table 19 Correlation of Predicted and Observed Inhalable WS % from Prediction Model A

	Observed Inhalable WS% Mean±SD	Predicted Inhalable WS% Mean±SD	Pearson Correlation Coefficient	Spearman's rho Correlation Coefficient
Furniture (N=206)	44.2 ± 21.5	44.2 ± 4.39	.196	.171
FurnitureA (N=45)	50.0 ± 22.4	45.6 ± 0.00	*	*
FurnitureB (N=38)	31.1 ± 18.9	38.2 ± 7.78	.017	-.074
FurnitureC (N=44)	53.2 ± 23.5	45.6 ± 0.00	*	*
FurnitureD (N=79)	42.3 ± 17.6	45.6 ± 0.00	*	*
Cabinet (N=81)	63.5 ± 25.0	63.5 ± 4.51	.277	.260
CabinetA (N=45)	72.3 ± 20.2	65.4 ± 0.00	*	*
CabinetB (N=36)	52.6 ± 26.3	61.2 ± 6.03	.152	.176
Secondary millworks (N=100)	46.8 ± 24.0	46.8 ± 11.9	.478	.455
Secondary millworksA (N=47)	34.0 ± 16.1	34.5 ± 3.56	-.128	-.202
Secondary millworksB (N=53)	58.1 ± 24.2	57.6 ± 1.73	-.014	-.009
Sawmill-Planing-Plywood (N=67)	5.93 ± 3.13	5.93 ± 2.28	.294	.260
Sawmill-Planing-Plywood A(N=36)	7.22 ± 3.10	6.35 ± 2.97	.240	.288
Sawmill-Planing-Plywood B(N=31)	4.44 ± 2.47	5.45 ± 0.83	.323	.337
Total (N=454)	42.6 ± 27.0	42.6 ± 18.1	.669	.637

* Cannot be computed because one of the variables is constant

A second predictive model (prediction model B) was constructed in which the reciprocal of inhalable dust weight (mg^{-1}) was added as an additional determinant. Because denominator of wood solid percentage is inhalable dust weight and therefore, this was considered as a determinant.

All coefficients of the determinants of prediction model B are in Table 20. Coefficient of cabinet was 19.1 % higher, secondary millworks 13.5 % higher, sawmill-planing-plywood 9.47 % lower, hardwood 13.6 % lower, softwood 21.1 % lower, PSV 12.7 % lower , and the reciprocal of inhalable dust 6.16 % lower than those of the references. The coefficients of the determinants of sawmill-planing-plywood, green wood, green/dry wood, and formaldehyde were not statistically significant.

Figure 23 are the scatter graph about observed vs predicted inhalable wood solid percentage obtained from 10 plant prediction model B.

Table 21 shows the mean and standard deviation of observed and predicted inhalable wood solid percentage, and both Pearson and Spearman's correlation coefficients from prediction model B. The results were presented for the total number 454 and within the following groups: furniture, cabinet, secondary millworks, and sawmill-planing-plywood.

Table 20 Coefficients of the Determinants of Prediction Model B for Inhalable WS % from 10 Plants (n=454, R=.692 and R^2=.479)

Model	Unstandardized Coefficients(B)	Std. Error	Sig.
(Constant)	49.8	1.64	.000
Plant Type			
Cabinet	19.1	2.72	.000
Secondary millworks	13.5	2.95	.000
Sawmill-planing-plywood	-9.47	6.37	.138
Green vs. Dry wood			
Green wood	-.274	5.45	.960
Green/Dry wood mixed	-7.04	11.1	.526
Hard vs. Softwood			
Hardwood	-13.6	4.27	.002
Softwood	-21.1	3.69	.000
Formaldehyde			
Yes_Formaldehyde	-6.01	5.83	.303
PSV			
Yes_PSV	-12.7	4.96	.011
Reciprocal Inhalalble Dust wt (mg^{-1})	-6.16	1.18	.000

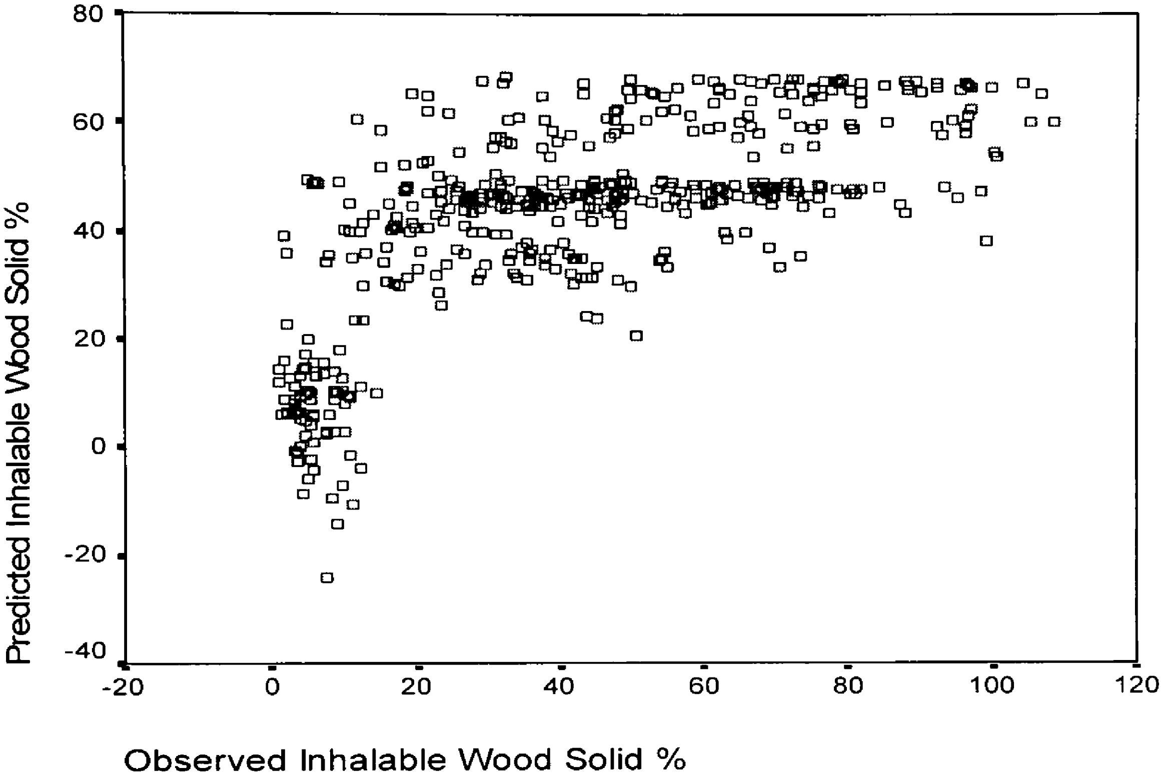


Figure 23 Observed vs Predicted Inhalable WS % on 10 Plants from Prediction Model B

Table 21 Correlation of Predicted and Observed Inhalable WS % from Prediction Model B

	Observed Inhalable WS% Mean±SD	Predicted Inhalable WS% Mean±SD	Pearson Correlation Coefficient	Spearman's rho Correlation Coefficient
Furniture (N=206)	44.2 ± 21.5	44.2 ± 5.87	.361	.337
FurnitureA (N=45)	50.0 ± 22.4	45.6 ± 3.86	.082	.101
FurnitureB (N=38)	31.1 ± 18.9	38.7 ± 8.29	.147	-.027
FurnitureC (N=44)	53.2 ± 23.5	45.5 ± 4.75	.527	.307
FurnitureD (N=79)	42.3 ± 17.6	45.4 ± 4.36	.374	.351
Cabinet (N=81)	63.5 ± 25.0	63.5 ± 5.80	.462	.385
CabinetA (N=45)	72.3 ± 20.2	66.4 ± 1.53	.107	.061
CabinetB (N=36)	52.6 ± 26.3	57.0 ± 7.11	.412	.461
Secondary millworks (N=100)	46.8 ± 24.0	46.8 ± 12.8	.533	.492
Secondary millworksA (N=47)	34.0 ± 16.1	34.2 ± 4.97	-.012	-.041
Secondary millworksB (N=53)	58.1 ± 24.2	57.9 ± 4.42	.349	.275
Sawmill-Planing-Plywood(N=67)	5.93 ± 3.13	5.93 ± 8.27	-.227	-.193
Sawmill-Planing-Plywood A(N=36)	7.22 ± 3.10	3.36 ± 9.53	.051	.085
Sawmill-Planing-Plywood B(N=31)	4.44 ± 2.47	8.92 ± 5.25	-.474	-.403
Total (N=454)	42.6 ± 27.0	42.6 ± 18.7	0.692	0.676

6.3.2 Evaluation and Validation of Prediction Modeling of Inhalable Wood Solid Percentage from 8 Plants

Two plants (furniture C and sawmill-planing-plywood A) were randomly selected for validating the prediction model C and D obtained from the remaining 8 plants. Dependent variable was inhalable wood solid percentage and determinants of prediction model C from 8 plants were plant type (furniture, cabinet, secondary millworks, and sawmill-planing-plywood), green vs. dry wood (green wood, dry wood, and green/dry wood), hard vs. soft wood (hardwood, softwood, and hard/softwood), formaldehyde (formaldehyde and no formaldehyde) and PSV (PSV and no PSV) as shown in Table 22. With this prediction regression model C, the reference values were: 'furniture' (plant type), 'dry wood' (green vs. dry wood), 'mixed wood' (hard vs. soft wood), 'no formaldehyde' and 'no PSV'.

Coefficient of cabinet was 22.3 % higher, secondary millworks 15.2 % higher, hardwood 10.3 % lower, softwood 23.3 % lower, and PSV 12.6 % lower than those of the references from Table 22. The coefficients of the determinants of green wood, green/dry wood, and formaldehyde were not statistically significant.

Table 22 Coefficients of the Determinants of Prediction Model C for Inhalable WS % from 8 Plants (n=374, R=.626 and R^2=.392)

Model	Unstandardized Coefficients(B)	Std. Error	Sig.
(Constant)	43.1	1.73	.000
Plant Type			
Cabinet	22.3	2.97	.000
Secondary millworks	15.2	3.32	.000
Sawmill-planing-plywood	-15.3	7.83	.052
Green vs. Dry wood			
Green wood	-1.69	8.74	.847
Green/Dry wood mixed	-.723	12.1	.953
Hard vs. Softwood			
Hardwood	-10.3	5.04	.041
Softwood	-23.3	4.15	.000
Formaldehyde			
Yes_Formaldehyde	1.81	8.74	.836
PSV			
Yes_PSV	-12.6	5.19	.016

The scatter graphs in Figure 24 and Figure 25 were about observed vs predicted inhalable wood solid percentage of 2 plants applied from the coefficients obtained prediction models C and D. The prediction models C and D were underestimated for the high values of WS % (above 35 %) and overestimated for low values of WS % (below 20 %)

In Table 24 the reciprocal of inhalable dust weight (mg^{-1}) was added to other determinants to create prediction model D. Coefficient of cabinet was 21.2 % higher, secondary millworks 16.4 % higher, hardwood 10.9 % lower, softwood 20.6 % lower, PSV 12.7 % lower, and the reciprocal of inhalable dust 8.79 % lower than those of the references. The coefficients of the determinants of green wood, green/dry wood, and formaldehyde were not statistically significant.

Correlations of predicted and observed inhalable wood solid percentage by prediction models C and D are shown in Table 23 and in Table 25. The predicted values of inhalable wood solid percentage are 43.1 % in furniture C, 5.87 % in sawmill-planing-plywood and 26.3 % in total of these two plants by prediction model C, and 43.1 % in furniture C, -6.63 % in sawmill-planing-plywood and 20.7 % in total of these two plants by prediction model D.

As the results of the predicted values including negative predictive values for sawmill-planing-plywood, this prediction model D was not good fit for evaluating this inhalable WS%. Therefore, from the evaluating and validating prediction model of inhalable wood solid percentage from 8 wood processing plants, model C is recommended.

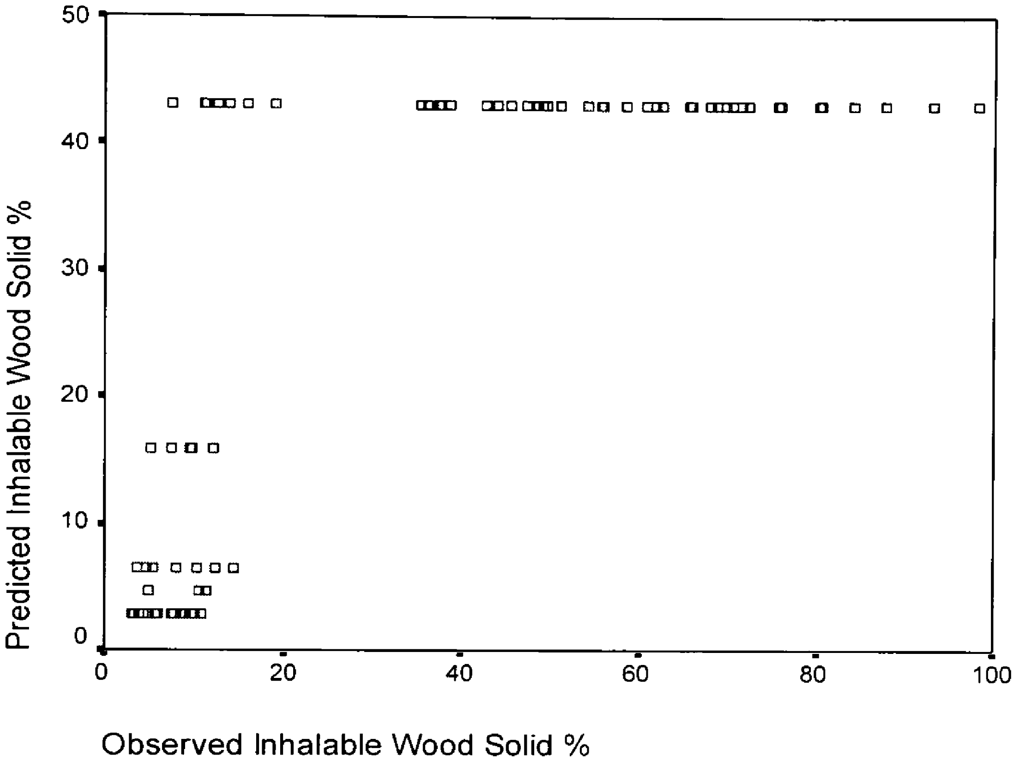


Figure 24 Observed vs Predicted Inhalable WS% on 2Plants from Prediction Model C

Table 23 Correlation of Observed and Predicted Inhalable WS %
from Prediction Model C

	Observed Inhalable WS% Mean±SD	Predicted Inhalable WS% Mean±SD	Pearson Correlation Coefficient	Spearman's rho Correlation Coefficient
Furniture C (n = 44)	53.2 ± 23.5	43.1 ± .00	*	*
Sawmill-Planing-Plywood A (n = 36)	7.22 ± 3.10	5.87 ± 4.72	.209	.288
Total (n = 80)	32.5 ± 28.9	26.3 ± 18.9	.788	.823

* Cannot be computed because one of the variables is constant

Table 24 Coefficients of Determinants of Prediction Model D for Inhalable WS % from 8 Plants (n= 374, R=.662 and R^2 =.438)

Model	**Unstandardized Coefficients(B)**	**Std. Error**	**Sig.**
(Constant)	49.3	2.01	.000
Plant Type			
Cabinet	21.2	2.87	.000
Secondary millworks	16.4	3.20	.000
Sawmill-planing-plywood	-11.9	7.57	.115
Green vs. Dry wood			
Green wood	-3.16	8.41	.707
Green/Dry wood mixed	-1.47	11.7	.900
Hard vs. Softwood			
Hardwood	-10.9	4.86	.025
Softwood	-20.6	4.02	.000
Formaldehyde			
Yes_Formaldehyde	-.476	8.42	.955
PSV			
Yes_PSV	-12.7	4.99	.012
Reciprocal Inhalable Dust wt (mg^{-1})	-8.79	1.61	.000

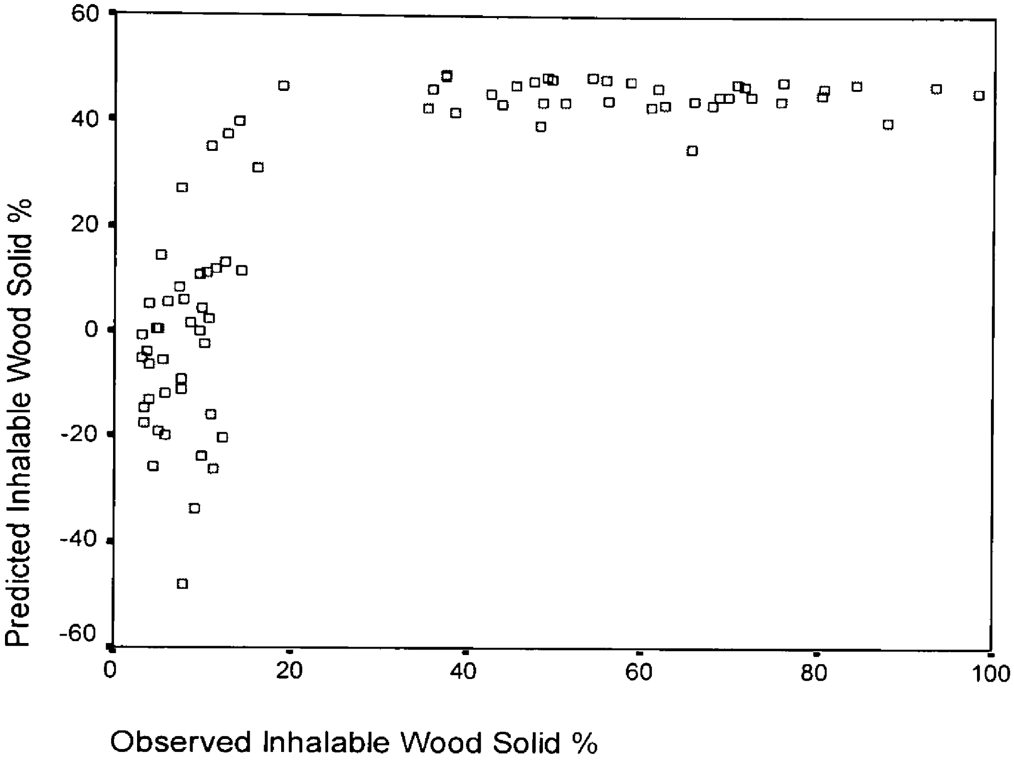


Figure 25 Observed vs Predicted Inhalable WS % on 2 Plants from Prediction Model D

Table 25 Correlation of Observed and Predicted Inhalable WS % from Prediction Model D

	Observed Inhalable WS% Mean±SD	Predicted Inhalable WS% Mean±SD	Pearson Correlation Coefficient	Spearman's rho Correlation Coefficient
Furniture C (N=44)	53.2 ± 23.5	43.1 ± 6.78	.527	.307
Sawmill-Planing-Plywood A(N=36)	7.22 ± 3.10	-6.63 ± 14.5	.108	.145
Total (N=80)	32.5 ± 28.9	20.7 ± 27.2	.792	.795

VII Multicomponent or Mixed Wood Analysis by DRIFTS

7.1 Oak and Pine Standard DRIFTS Analysis

Each 250, 500, 1000, 1500, 2000, 2500, and 3000 μg standard of oak and of pine was analyzed three times by DRIFT spectrometry to include one set of scanning at 0° and one at 90°. Therefore, six spectra of each amount standard were obtained. Energy throughput (Peak to peak) at every 3mm scanned location about each scanning was measured, as well.

Table 26 shows the average of the ten energy throughputs of oak standards and Table 27 shows the results for the pine standards. The energy throughput is severely compromised when the infrared beam was scanned directly on top of localized areas of thick dust cake on the filter surfaces as shown in Tables 26 and 27. So these energy throughputs were used for obtaining normal net absorbances.

Table 26 Average Energy Throughput of Each Oak Standard per Scanning

Standard	1_0°	1_90°	2_0°	2_90°	3_0°	3_90°
Oak250	4.143*	4.086	4.037	4.013	4.342	4.402
Oak500	4.166	4.299	4.305	4.085	4.213	4.122
Oak1000	3.971	3.824	3.855	4.039	3.730	3.601
Oak1500	3.774	3.727	3.816	3.809	3.732	3.762
Oak2000	3.377	3.400	3.498	3.552	3.333	3.355
Oak2500	3.261	3.275	3.345	3.278	3.287	3.304
Oak3000	3.247	3.243	3.111	3.193	3.056	3.012

* Unit : Volt

Table 27 Average Energy Throughput of Each Pine Standards per Scanning

Standard	1_0°	1_90°	2_0°	2_90°	3_0°	3_90°
Pine250	4.353*	4.160	4.186	4.097	4.294	4.420
Pine500	4.122	3.996	4.195	4.186	3.953	4.262
Pine1000	3.913	3.872	4.032	3.943	3.852	3.856
Pine1500	3.790	3.595	3.667	3.754	3.831	3.759
Pine2000	3.547	3.497	3.567	3.402	3.562	3.624
Pine2500	3.456	3.354	3.407	3.432	3.265	3.329
Pine3000	3.116	3.153	3.314	3.262	3.272	3.310

* Unit : Volt

Figure 26 is one set of red oak standard DRIFTS spectra from 250 to 3000 μg (second column of Table 26) and Figure 27 is one set of Radiata pine standard DRIFTS spectra from 250 to 3000 μg (second column of Table 27). Maximum peak of oak standards in Figure 26 was 1.357 K-M (Kubelka-Munk) at around 1289 cm^{-1} and one of pine standards in Figure 27 was 1.626 K-M at 1251 cm^{-1}.

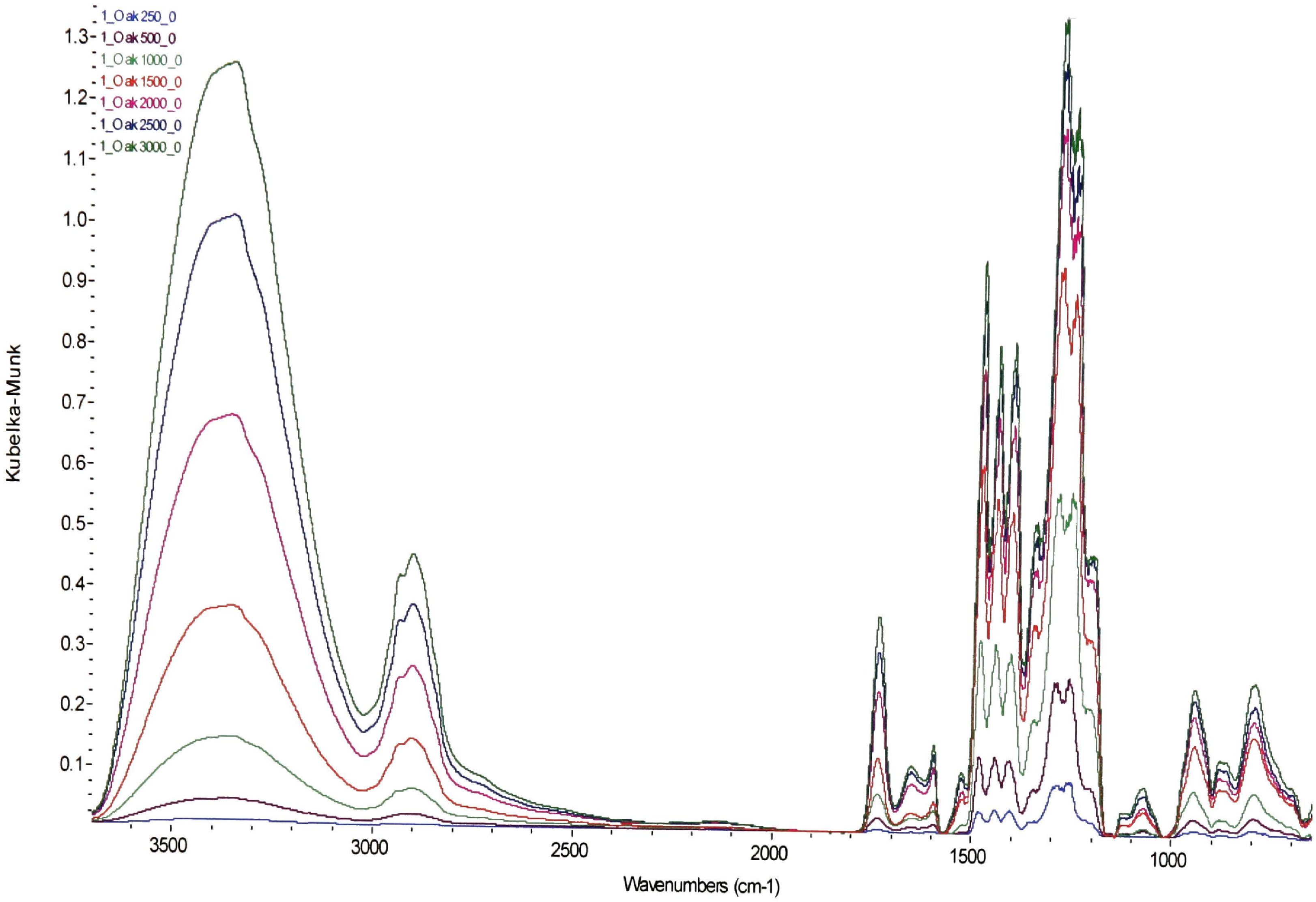


Figure 26 Red Oak Standard DRIFTS Spectra (Kubelka-Munk Unit)

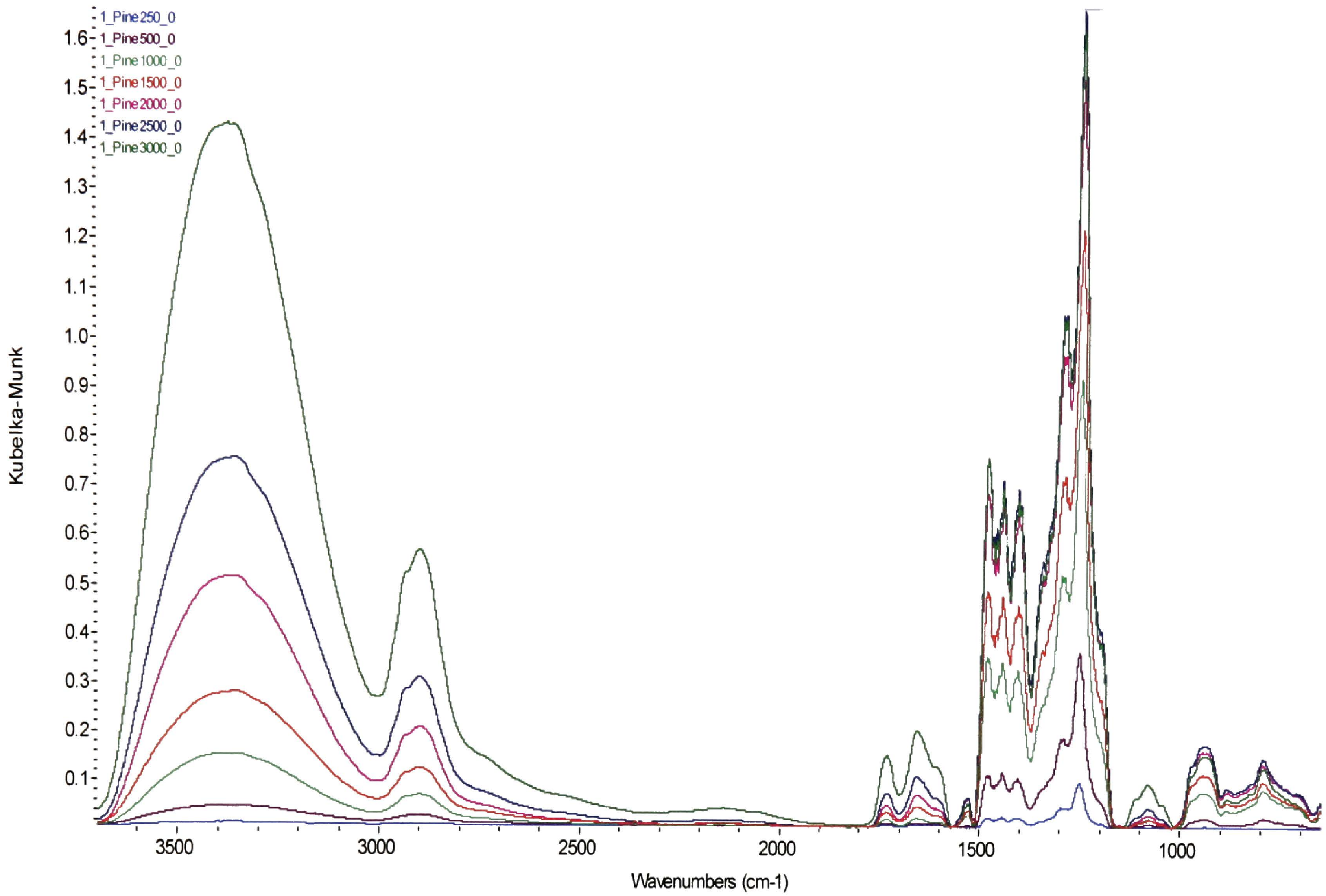


Figure 27 Radiata Pine Standard DRIFTS Spectra (Kubelka-Munk Unit)

Table 28 Selected Wave Numbers from Oak and Pine Standards

Wave Number (cm^{-1})			
664.4	934.4	1282.5	1475.3
671.1	943.1	1289.2	1482.1
695.2	947.9	1291.2	1513.0
703.0	971.0	1296.0	1521.6
710.7	1042.4	1326.9	1527.4
718.4	1070.4	1335.5	1594.9
726.1	1078.1	1343.2	1607.5
734.8	1108.0	1350.0	1650.8
741.5	1115.7	1374.1	1656.6
749.2	1124.4	1398.2	1731.8
789.7	1197.6	1405.0	1734.7
794.6	1205.4	1410.7	2140.7
802.3	1212.1	1429.1	2146.5
840.9	1250.7	1443.5	2900.6
849.5	1257.4	1450.3	2904.4
865.9	1265.1	1459.0	2936.2
881.4	1273.8	1466.7	

Table 28 shows the selected wave numbers at which there are peaks from oak and pine standards such as Figure 26 & 27 except 1291.2cm^{-1}. Exactly huge peaks were at around 1289cm^{-1} and however, 1291.2cm^{-1} was added as one of selected wave numbers based on the previous result from our group work.[3] Most peaks from either oak or pine standard spectra were selected over 650 cm^{-1} (recommended limit) except the region of 2345 cm^{-1} (atmospheric carbon dioxide) and 3330~3450 cm^{-1} (entrained water region in samples).

All wave number position of each peak was not always located at the same in the same oak or pine standards; however, the differences were no more than tenths of each wave numbers. Nonetheless, for analysis, the positions of each wave number were fixed as shown in Table 28. For applying the method of simultaneous equations for multi-component analysis, it is important to use the intensity of absorbance at the exact same wave number position in all samples and standards.

7.2 Oak and Pine Standard Calibration Curve

Signal saturation was observed at 3000μg of each oak standard and pine standard from DRIFTS spectra. Therefore, the working range of all standard calibration graphs was set between 250 to 2500 μg of oak or pine.

Figure 28 shows one of oak standard calibration curves and Figure 29 shows one of pine standard calibration curves. The other graphs about oak or pine standard calibration curves are in Appendix B. Y-axis means normal net absorbance which is net absorbance divided by average energy throughput. Both linear regression and forced zero-intercept linear regression lines are shown.

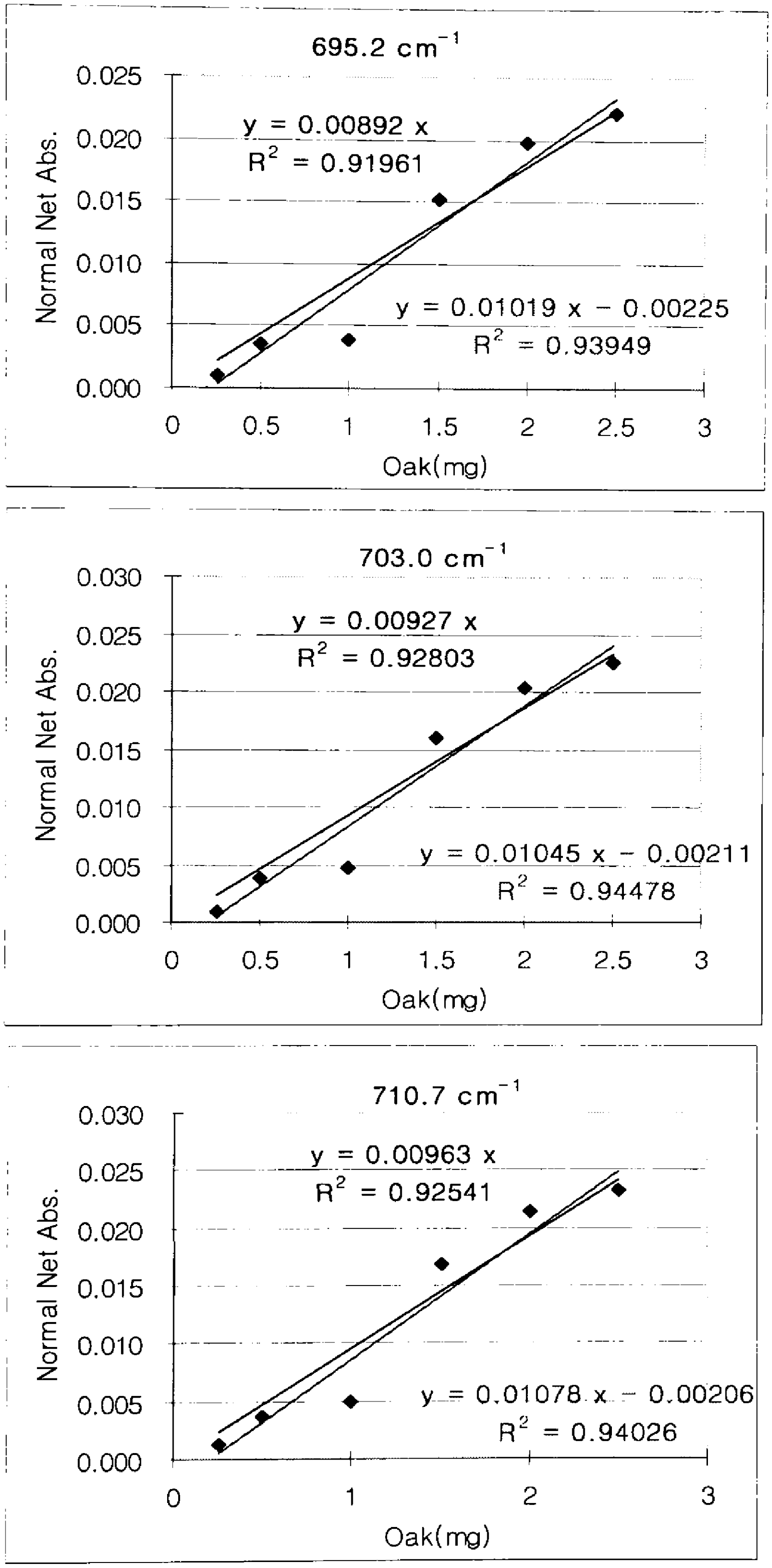


Figure 28 Oak Standard Calibration Curves at 695.2, 703.0 & 710.7 cm^{-1}

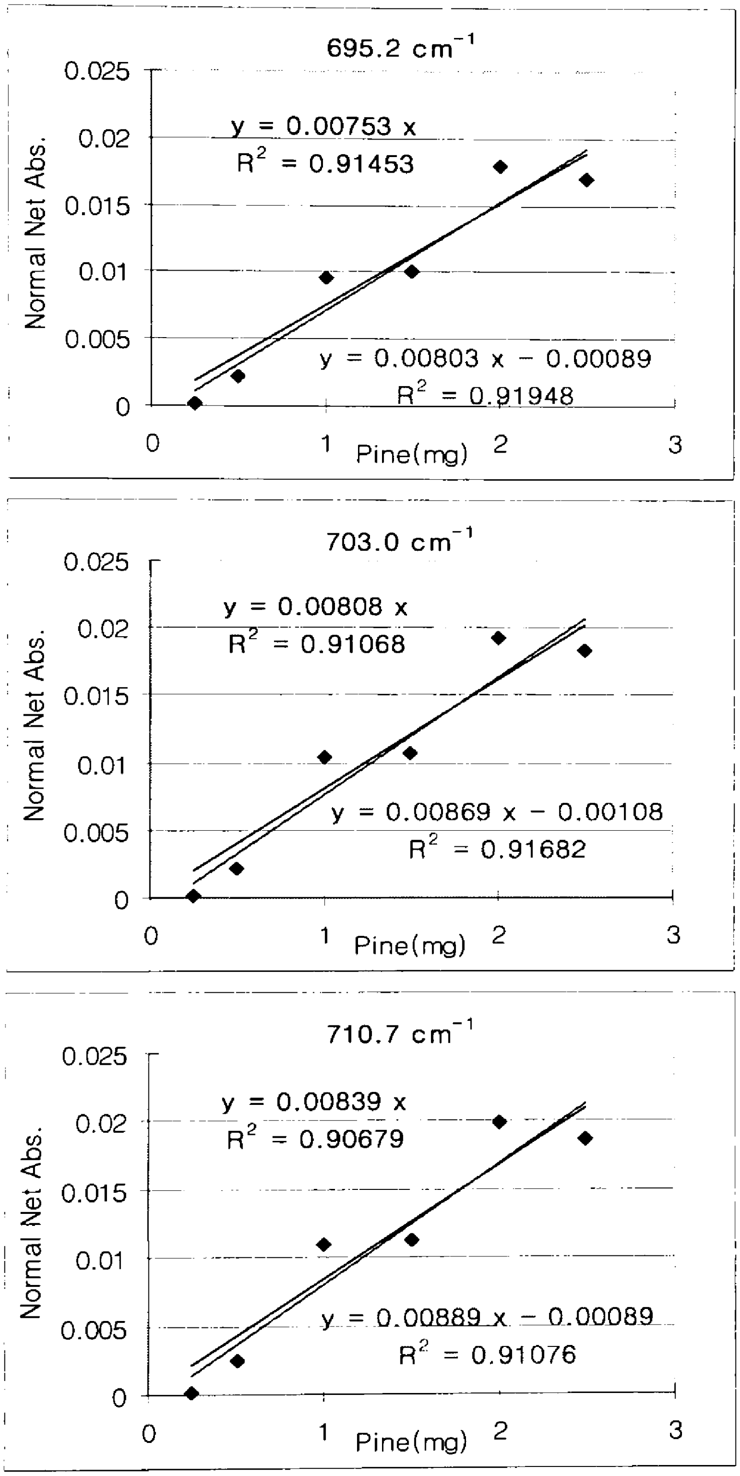


Figure 29 Pine Standard Calibration Curves at 695.2, 703.0 & 710.7 cm^{-1}

Table 29 Slopes and R^2 from Forced Zero-Intercept Linear Regression of Oak and Pine Standards Curves

Wave Number (cm^{-1})	**Oak**		**Pine**	
	Slope	R^2	Slope	R^2
664.4	0.00384	0.81029	0.00388	0.84874
671.1	0.00382	0.84336	0.00354	0.86174
695.2	0.00892	0.91961	0.00753	0.91453
703.0	0.00927	0.92803	0.00808	0.91068
710.7	0.00963	0.92541	0.00839	0.90679
718.4	0.01014	0.93460	0.00847	0.90033
726.1	0.01084	0.92915	0.00891	0.90518
734.8	0.01191	0.93742	0.00950	0.90598
741.5	0.01301	0.93806	0.00968	0.92586
749.2	0.01400	0.93740	0.01033	0.92243
789.7	0.02584	0.95940	0.01607	0.95636
794.6	0.02658	0.95974	0.01634	0.95608
802.3	0.02581	0.95728	0.01468	0.94807
840.9	0.01012	0.91755	0.00897	0.93491
849.5	0.01065	0.92006	0.00856	0.94173
865.9	0.01317	0.92972	0.00810	0.94198
881.4	0.01377	0.93333	0.00904	0.94993
934.4	0.02460	0.95512	0.01945	0.95909
943.1	0.02723	0.95971	0.01942	0.95974
947.9	0.02709	0.96043	0.01915	0.95879
971.0	0.01422	0.96310	0.01521	0.94518
1042.4	0.00330	0.95608	0.00233	0.77976
1070.4	0.00735	0.96945	0.00473	0.85127
1078.1	0.00691	0.96567	0.00510	0.84554
1108.0	0.00321	0.96092	0.00297	0.79757
1115.7	0.00334	0.96227	0.00249	0.76332
1124.4	0.00332	0.96413	0.00124	0.57640
1197.6	0.05576	0.98326	0.04754	0.96424
1205.4	0.05771	0.98325	0.04946	0.96837
1212.1	0.05784	0.98374	0.05663	0.96812
1250.7	0.14100	0.98918	0.20682	0.98506
1257.4	0.14371	0.98559	0.18638	0.98537
1265.1	0.13814	0.98575	0.14568	0.98315
1273.8	0.14085	0.98942	0.11949	0.98199
1282.5	0.14909	0.98878	0.11897	0.97979
1289.2	0.16019	0.98816	0.12722	0.98249
1291.2	0.15879	0.98786	0.12618	0.98200
1296.0	0.15902	0.98827	0.12675	0.98147
1326.9	0.06528	0.97911	0.07512	0.97378
1335.5	0.05782	0.97879	0.06713	0.97446
1343.2	0.06109	0.97641	0.06557	0.97204
1350.0	0.05995	0.97602	0.06167	0.97239

Table 29 (cont.) Slopes and R^2 from Forced Zero-Intercept Linear Regression of Oak and Pine Standards Curves

Wave Number (cm^{-1})	**Oak**		**Pine**	
	Slope	R^2	Slope	R^2
1374.1	0.03350	0.96821	0.03611	0.96504
1398.2	0.08614	0.97855	0.07915	0.97238
1405.0	0.09408	0.98061	0.08317	0.97227
1410.7	0.08934	0.97914	0.07800	0.97426
1429.1	0.06672	0.98179	0.06363	0.97131
1443.5	0.09553	0.98323	0.08569	0.97345
1450.3	0.08225	0.98160	0.07704	0.97229
1459.0	0.06183	0.97976	0.07240	0.97637
1466.7	0.05877	0.97711	0.07080	0.97370
1475.3	0.09394	0.97735	0.08631	0.97516
1482.1	0.10664	0.97548	0.08889	0.97405
1513.0	0.00892	0.90415	0.00171	0.78024
1521.6	0.01014	0.89433	0.00460	0.87869
1527.4	0.01008	0.88847	0.00662	0.88777
1594.9	0.01374	0.92802	0.00617	0.80101
1607.5	0.00945	0.92335	0.00713	0.80916
1650.8	0.01046	0.90475	0.01153	0.82314
1656.6	0.00999	0.89850	0.01179	0.81816
1731.8	0.02964	0.91034	0.00805	0.82993
1734.7	0.03030	0.91259	0.00793	0.83370
2140.7	0.00155	0.87213	0.00172	0.67156
2146.5	0.00155	0.87221	0.00172	0.67019
2900.6	0.03582	0.88163	0.03302	0.83486
2904.4	0.03597	0.88141	0.03293	0.83453
2936.2	0.03342	0.88347	0.03034	0.83366

All of the slopes and R^2 from oak and pine standard curves were organized in Table 29 as taken from Figure 26, Figure 27 and Figures in Appendix B. Forced zero-intercept regressions of each oak and pine standard curve were performed because applying multicomponent analysis based on Beer's law by simultaneous equations method requires that the intercept be equal to zero. The three largest slopes of oak standard calibration curve were 0.16019 at 1289.2cm^{-1}, 0.15902 at 1296.0cm^{-1}, and 0.15879 at 1291.2cm^{-1}, and for pine standards, 0.20682 at 1250.7cm^{-1}, 0.18638 at 1257.4cm^{-1}, and 0.14568 at 1265.1cm^{-1}. For R^2, the three best slopes for oak standard calibration curve are 0.98942 at 1273.8 cm^{-1}, 0.98918 at 1250.7 cm^{-1}, 0.98878 at 1282.5 cm^{-1} and for pine standards, 0.98537 at 1257.4 cm^{-1}, 0.98506 at 1250.7 cm^{-1}, and 0.98315 at 1265.1 cm^{-1}.

7.3 Oak and Pine Mixed Sample Analysis

Mixed samples of red oak and Radiata pine were prepared with 3 replicates each of 500 and 1000 μg, 750 and 750 μg, 1000 and 500 μg, 1000 and 1500 μg, 1250 and 1250 μg, 1500 and 1000 μg, 1000 and 3000 μg, 2000 and 2000 μg, 3000 and 1000 μg.

Table 30 Average Energy Throughput of Oak and Pine Mixed Samples

Mixed Sample	1_0°	1_90°	2_0°	2_90°	3_0°	3_90°
1_Pine500Oak1000	3.734	3.786	3.861	3.785	3.841	3.729
2_Pine500Oak1000	3.878	3.729	3.676	3.729	3.736	3.762
3_Pine500Oak1000	3.868	3.782	3.873	3.807	3.743	3.739
1_Pine750Oak750	3.782	3.648	3.814	3.766	3.743	3.691
2_Pine750Oak750	3.703	3.534	3.821	3.606	3.803	3.733
3_Pine750Oak750	3.822	3.764	3.542	3.585	3.723	3.801
1_Pine1000Oak500	3.665	3.680	3.689	3.600	3.775	3.621
2_Pine1000Oak500	3.675	3.691	3.674	3.747	3.737	3.700
3_Pine1000Oak500	3.632	3.592	3.716	3.701	3.625	3.672
1_Pine1000Oak1500	3.331	3.381	3.357	3.258	3.409	3.365
2_Pine1000Oak1500	3.228	3.173	3.294	3.206	3.356	3.414
3_Pine1000Oak1500	3.350	3.308	3.336	3.391	3.468	3.394
1_Pine1250Oak1250	3.413	3.488	3.332	3.340	3.379	3.214
2_Pine1250Oak1250	3.133	3.214	3.305	3.348	3.256	3.176
3_Pine1250Oak1250	3.368	3.235	3.398	3.155	3.394	3.282
1_Pine1500Oak1000	3.387	3.397	3.354	3.378	3.326	3.418
2_Pine1500Oak1000	3.310	3.311	3.414	3.401	3.176	3.127
3_Pine1500Oak1000	3.370	3.341	3.321	3.171	3.270	3.123

Table 30 (cont.) Average Energy Throughput of Oak and Pine Mixed Samples

Mixed Sample	1_0°	1_90°	2_0°	2_90°	3_0°	3_90°
1_Pine1000Oak3000	3.030	3.088	3.112	3.141	3.142	3.115
2_Pine1000Oak3000	3.015	2.964	3.063	3.053	3.032	3.097
3_Pine1000Oak3000	2.939	2.913	3.113	3.003	2.959	2.968
1_Pine2000Oak2000	3.015	2.991	3.069	3.030	3.099	3.101
2_Pine2000Oak2000	3.004	3.017	2.919	2.941	3.065	2.936
3_Pine2000Oak2000	3.092	3.035	3.020	3.103	2.935	2.945
1_Pine3000Oak1000	3.040	3.056	3.061	3.017	3.053	3.083
2_Pine3000Oak1000	3.147	3.147	3.140	3.169	3.084	3.046
3_Pine3000Oak1000	3.082	3.031	2.982	2.986	3.060	3.041

Table 30 shows the average of energy throughput of each mixed sample of oak and pine. Procedures for sample preparation and measurement were the same as those of oak or pine standard analysis. DRIFTS spectra of mixed samples of oak and pine are shown in Figures 30 and 31. Figure 30 is the part of the spectra of total amount of 1500 μg : Pine 500 μg + Oak 1000 μg, Pine 750 μg + Oak 750 μg, and Pine 1000μg + Oak 500 μg. Figure 31 is the part of the spectra of total amount of 2500 μg : Pine 1000 μg + Oak 1500 μg, Pine 1250 μg + Oak 1250 μg, and Pine 1500 μg + Oak 1000 μg.

As mentioned, saturation was observed from each oak and pine standard of the amount of 3000 μg and therefore, mixed samples of total amount of 4000 μg such as pine 1000 + oak 3000 μg, pine 2000 + oak 2000 μg, and pine 3000 + oak 1000 μg were not analyzed further.

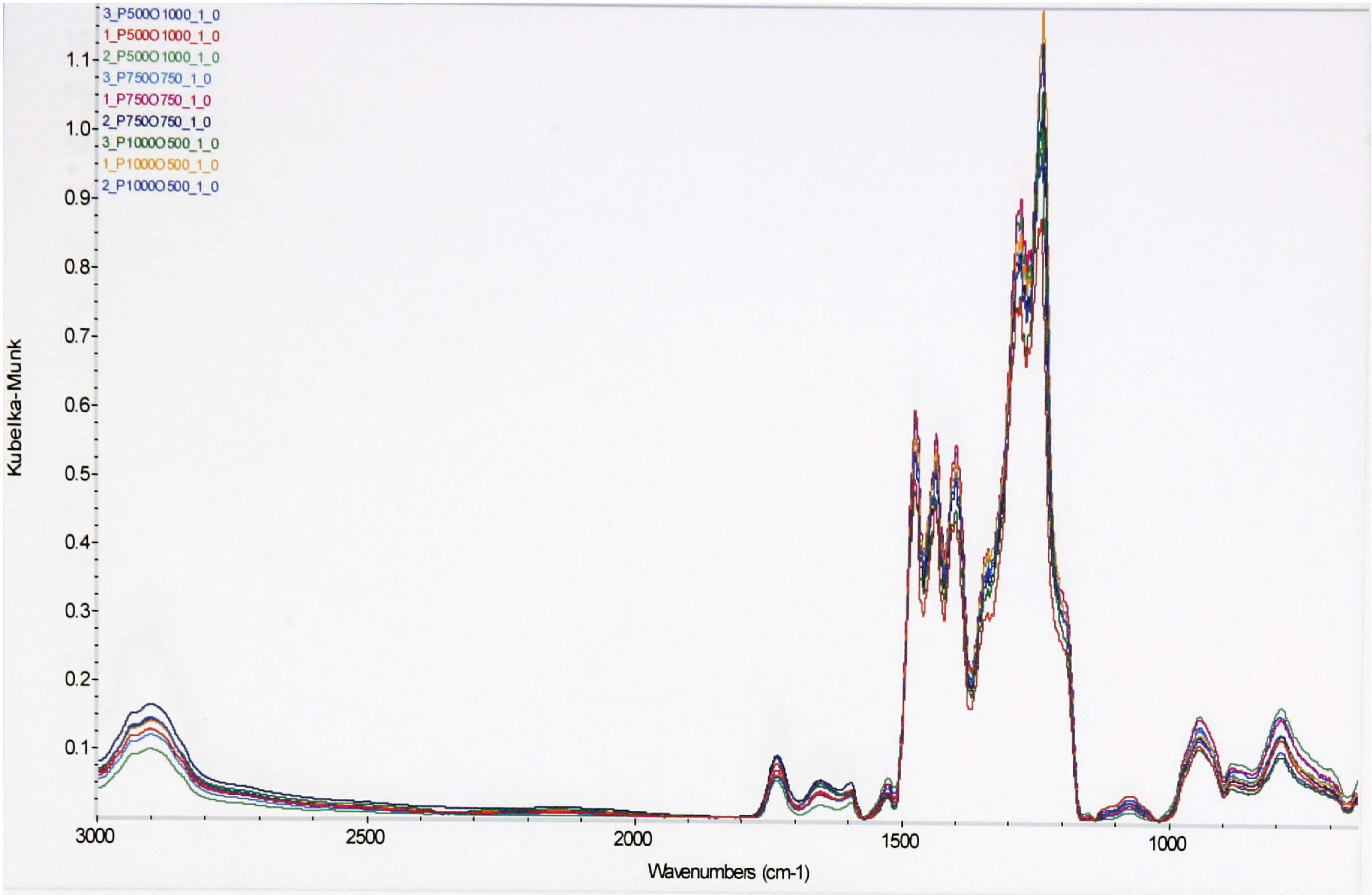


Figure 30 DRIFTS Spectra of Total Amount of Mixed Sample 1500 µg : Pine500µgOak1000µg, Pine750µgOak750µg, and Pine1000µgOak500µg (Kubelka-Munk)

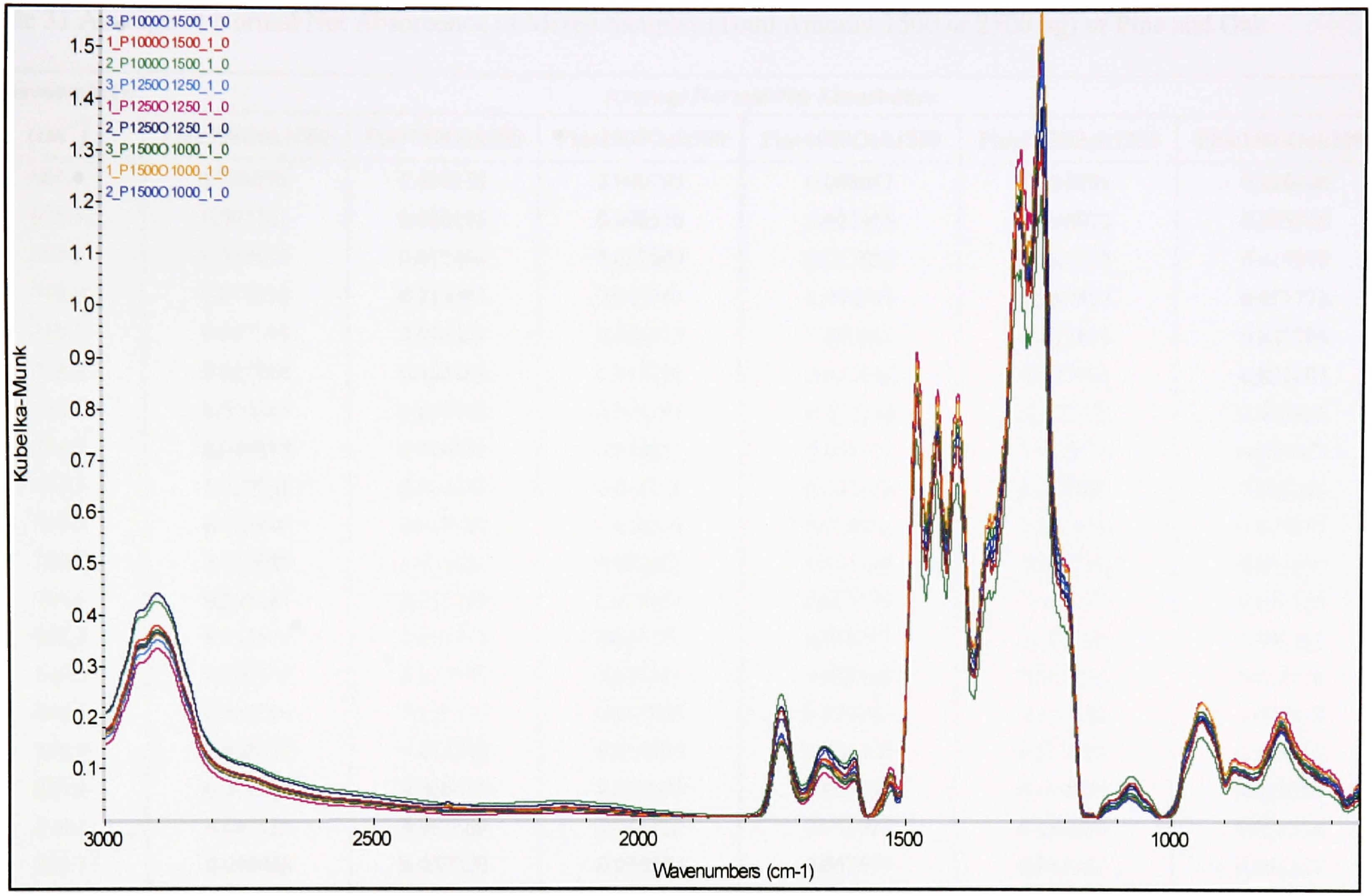


Figure 31 DRIFTS Spectra of Total Amount of Mixed Sample 2500μg : Pine1000μgOak1500μg, Pine1250μgOak1250μg, and Pine1500μgOak1000μg (Kubelka-Munk)

Table 31 Average of Normal Net Absorbance of Mixed Samples (Total Amount 1500 or 2500 μg) of Pine and Oak

Wavenumbers (cm^{-1})	**Average Normal Net Absorbance**					
	Pine500Oak1000	**Pine750Oak750**	**Pine1000Oak500**	**Pine1000Oak1500**	**Pine1250Oak1250**	**Pine1500Oak1000**
664.4	0.008056*	0.006152	0.006795	0.008057	0.010291	0.010746
671.1	0.007761	0.006135	0.006518	0.007455	0.010072	0.009916
695.2	0.015674	0.012454	0.012809	0.017885	0.020333	0.019890
703.0	0.016712	0.013393	0.013311	0.019341	0.022587	0.021773
710.7	0.017319	0.014221	0.013917	0.020263	0.022836	0.022797
718.4	0.017604	0.014466	0.014241	0.021443	0.023969	0.023203
726.1	0.019045	0.015358	0.015295	0.023340	0.025625	0.025012
734.8	0.020814	0.016881	0.016055	0.025391	0.028034	0.027422
741.5	0.022138	0.017653	0.016978	0.027128	0.029380	0.028241
749.2	0.023445	0.018949	0.018068	0.028893	0.030939	0.029877
789.7	0.039007	0.031874	0.029062	0.051531	0.053781	0.051601
794.6	0.039245	0.032347	0.029655	0.052726	0.054692	0.052726
802.3	0.037330	0.030371	0.027537	0.050743	0.051394	0.049402
840.9	0.016911	0.014342	0.014101	0.023066	0.025435	0.024972
849.5	0.016796	0.014112	0.013924	0.023235	0.025128	0.024978
865.9	0.018520	0.015318	0.014560	0.025768	0.027721	0.026714
881.4	0.019308	0.016395	0.015995	0.027706	0.029883	0.029359
934.4	0.033525	0.031400	0.031483	0.053990	0.058204	0.058534
943.1	0.036063	0.033326	0.032874	0.057474	0.061337	0.061227
947.9	0.035670	0.033197	0.032682	0.056723	0.060727	0.060548
971.0	0.021788	0.021708	0.023323	0.033853	0.038750	0.040674
1042.4	0.003276	0.003613	0.002684	0.009492	0.006894	0.006086
1070.4	0.007342	0.007693	0.006209	0.019474	0.015222	0.013627

Table 31 (cont.) Average of Normal Net Absorbance of Mixed Samples (Total Amount 1500 or 2500 μg) of Pine and Oak

Wavenumbers (cm^{-1})	**Average of Normal Net Absorbance**					
	Pine500Oak1000	**Pine750Oak750**	**Pine1000Oak500**	**Pine1000Oak1500**	**Pine1250Oak1250**	**Pine1500Oak1000**
1078.1	0.007270	0.007705	0.006235	0.019581	0.015696	0.014401
1108.0	0.003687	0.004038	0.003102	0.010357	0.007936	0.007287
1115.7	0.003447	0.003673	0.002719	0.009915	0.007276	0.006686
1124.4	0.002910	0.002704	0.001705	0.007868	0.005283	0.004475
1197.6	0.077548	0.078097	0.080482	0.127662	0.137881	0.137330
1205.4	0.081217	0.081923	0.084880	0.130314	0.141763	0.141281
1212.1	0.086054	0.088837	0.094342	0.137873	0.151811	0.152663
1250.7	0.254153	0.280514	0.310382	0.397220	0.441495	0.457953
1257.4	0.249195	0.267781	0.292104	0.384794	0.416884	0.435002
1265.1	0.222304	0.229512	0.239608	0.340144	0.362770	0.362868
1273.8	0.205148	0.204850	0.207808	0.316898	0.332447	0.326125
1282.5	0.209973	0.208779	0.210593	0.328740	0.344570	0.337519
1289.2	0.225683	0.222679	0.224493	0.358390	0.372940	0.361519
1291.2	0.223298	0.220764	0.222154	0.355610	0.369346	0.357950
1296.0	0.222911	0.220177	0.220466	0.354217	0.367058	0.358112
1326.9	0.104168	0.108148	0.116266	0.169666	0.182929	0.187434
1335.5	0.092451	0.096311	0.103974	0.150610	0.165428	0.168374
1343.2	0.093768	0.095979	0.102179	0.152899	0.165697	0.168393
1350.0	0.090742	0.092464	0.097770	0.148556	0.160002	0.162383
1374.1	0.052029	0.053051	0.057227	0.085170	0.093931	0.096400
1398.2	0.124621	0.122997	0.128878	0.207332	0.218472	0.219283

Table 31 (cont.) Average of Normal Net Absorbance of Mixed Samples (Total Amount 1500 or 2500 μg) of Pine and Oak

Wavenumbers (cm^{-1})	**Average of Normal Net Absorbance**					
	Pine500Oak1000	**Pine750Oak750**	**Pine1000Oak500**	**Pine1000Oak1500**	**Pine1250Oak1250**	**Pine1500Oak1000**
1405.0	0.133910	0.133119	0.136679	0.221354	0.234204	0.232286
1410.7	0.128269	0.126906	0.130351	0.209303	0.221646	0.219091
1429.1	0.099593	0.099819	0.103846	0.159725	0.169553	0.171026
1443.5	0.139296	0.137352	0.140995	0.223996	0.235464	0.233597
1450.3	0.122259	0.120529	0.126017	0.196511	0.205907	0.207529
1459.0	0.101434	0.101808	0.111071	0.162613	0.177350	0.181008
1466.7	0.096692	0.099290	0.106981	0.158536	0.169895	0.176023
1475.3	0.136625	0.133567	0.139400	0.228222	0.234133	0.237490
1482.1	0.148987	0.144550	0.145809	0.248783	0.255600	0.254030
1513.0	0.009303	0.005950	0.005676	0.013433	0.013153	0.011346
1521.6	0.012186	0.008506	0.009247	0.020303	0.020558	0.018888
1527.4	0.012737	0.009941	0.010772	0.022365	0.023955	0.022622
1594.9	0.010818	0.012321	0.009606	0.032624	0.027544	0.026800
1607.5	0.008174	0.010708	0.009080	0.027041	0.024017	0.024749
1650.8	0.008990	0.014078	0.012652	0.034167	0.033549	0.035490
1656.6	0.009047	0.013509	0.012722	0.034421	0.033182	0.035555
1731.8	0.021191	0.021814	0.015324	0.060935	0.050960	0.046720
1734.7	0.021681	0.022068	0.015318	0.061414	0.051267	0.046727
2140.7	0.001686	0.002655	0.002048	0.006225	0.004839	0.005538
2146.5	0.001684	0.002653	0.002048	0.006222	0.004834	0.005536
2900.6	0.034189	0.038933	0.036360	0.114644	0.110265	0.112238
2904.4	0.034243	0.038956	0.036320	0.114783	0.110288	0.112185
2936.2	0.031686	0.036114	0.033578	0.106005	0.101538	0.103237

Table 31 is the average of normal net absorbance of mixed samples of pine and oak. All net absorbance (K-M) at each wave number in Table 28 was read from six spectra such as shown in Figure 28. Each net absorbance (K-M) was divided by each energy throughput (Table 30) and the six normalized net absorbances were averaged. And then the average of normal net absorbances from three replicate samples which contained the same amount of oak and pine were averaged. Therefore, for example, 0.008056 marked at 664.4 cm^{-1} of pine500oak1000 was obtained by the average of normal net absorbances divided by each energy throughput at Table 30.

7.4 Selecting Wave Numbers for Applying to Simultaneous Equation Method

Six wave numbers (1250.7, 1257.4, 1265.1, 1282.5, 1289.2, and 1296.0 cm^{-1}) were selected in the middle of wave numbers based on higher R^2 and slopes in Table 29.

For applying to multi-component analysis by simultaneous equations method, those wave numbers were evaluated by the expected value normalized net absorbance (Table 32 & 33). These expected values were compared to observed values from Table 31. 'a_1' is the slope of pine standard curve and 'a_2' is the slope of oak standard curve at each wave number. 'x_1' is the real amount of pine included in each mixed sample and 'x_2' is the real amount of oak included in each mixed sample. 'Expected value' was calculated by the multi-component equations of Beer's law. For example, expected value, 0.244461(=$a_1x_1+a_2x_2$) at 1250.7cm^{-1} of Pine500Oak1000 was calculated by 0.206832 x 0.49984 + 0.141004 x 1.00056. Most expected values were approximately similar to observed values of each mixed samples at each of the six selected wave numbers.

Also, there are summed up three percentages of absolute values of difference between expected and observed values for each wave number and each total amount of 1.5mg and 2.5mg of mixed pine and oak at Table 32 and Table 33. In total amount 1.5mg of pine and oak, the expected value is close to the observed at 1296.0cm^{-1}. In total amount 2.5mg, there is a range of 8~10 % of sum of differences between the expected and the observed across the six wave numbers.

Table 32 Expected and Observed Value of Normal Net Absorbance of Mixed Samples (Total 1.5 mg)

WN	pine	oak	**Pine500Oak1000**		**Pine750Oak750**		**Pine1000Oak500**		**Total of % Difference for each Wave Number**
(cm^{-1})	a_1	a_2	Expected ($a_1x_1+a_2x_2$)	Observed	Expected ($a_1x_1+a_2x_2$)	Observed	Expected ($a_1x_1+a_2x_2$)	Observed	$\sum_{n=3}\frac{\lvert Expected_i - Observed_i \rvert}{Expected_i}\times 100\%$
1250.7	0.206822	0.141004	0.244461*	0.254153	0.260879	0.280514	0.277297	0.310382	23.42
1257.4	0.186375	0.143713	0.236952	0.249195	0.247582	0.267781	0.258213	0.292104	26.45
1265.1	0.145683	0.138139	0.211035	0.222304	0.212890	0.229512	0.214745	0.239608	24.73
1282.5	0.118970	0.149093	0.208643	0.209973	0.201081	0.208779	0.193520	0.210593	13.29
1289.2	0.127221	0.160189	0.223869	0.225683	0.215595	0.222679	0.207320	0.224493	12.38
1296.0	0.126755	0.159018	0.222464	0.222911	0.214366	0.220177	0.206268	0.220466	9.79
Actual Pine Amount (mg)			0.49984		0.74976		0.99968		
Actual Oak Amount (mg)			1.00056		0.75042		0.50028		

Table 33 Expected and Observed Value of Normal Net Absorbance of Mixed Samples (Total 2.5 mg)

WN	pine	oak	**Pine1000Oak1500**		**Pine1250Oak1250**		**Pine1500Oak1000**		**Total of % Difference for each Wave Number**
(cm^{-1})	a_1	a_2	Expected ($a_1x_1+a_2x_2$)	Observed	Expected ($a_1x_1+a_2x_2$)	Observed	Expected ($a_1x_1+a_2x_2$)	Observed	$\sum_{n=3}\frac{\lvert Expected_i - Observed_i \rvert}{Expected_i}\times 100\%$
1250.7	0.206822	0.141004	0.418380	0.397220	0.434798	0.441495	0.451217	0.457953	8.09
1257.4	0.186375	0.143713	0.402007	0.384794	0.412637	0.416884	0.423268	0.435002	8.08
1265.1	0.145683	0.138139	0.352961	0.340144	0.354817	0.362770	0.356672	0.362868	7.61
1282.5	0.118970	0.149093	0.342697	0.328740	0.335135	0.344570	0.327574	0.337519	9.92
1289.2	0.127221	0.160189	0.367599	0.358390	0.359325	0.372940	0.351050	0.361519	9.28
1296.0	0.126755	0.159018	0.365375	0.354217	0.357277	0.367058	0.349179	0.358112	8.35
Actual Pine Amount (mg)			0.99968		1.2496		1.49952		
Actual Oak Amount (mg)			1.50084		1.2507		1.00056		

7.5 Multicomponent Analysis by Simultaneous Equations

For solving multi-component analysis, 'Solver' in 'Microsoft Excel 2002' was used and multicomponent analysis of fifteen combinations from six selected wave numbers was performed.

$$(10)\ A_t = A_{Pine} + A_{Oak} = a_{Pine} \cdot X_{Pine} + a_{Oak} \cdot X_{Oak}$$

A_t : Measured Total Absorbance at a given Wave Number
A_{Pine} : Absorbance of Pine
A_{Oak} : Absorbance of Oak
a_{Pine} : Slope of Pine Standard Curve
a_{Oak} : Slope of Oak Standard Curve
X_{Pine} : Amount of Pine
X_{Oak} : Amount of Oak

The coefficients and constants used for multicomponent analysis by simultaneous equations are shown in Table 34, where 'i' is a given wave number. From these, estimated amounts of pine and oak in mixed samples were calculated. For example, one combination of '1pine500oak1000'is solved by simultaneous equation method of two equations $0.206822 \cdot X_{Pine} + 0.141004 \cdot X_{Oak} = 0.243454$ at $1250.7 cm^{-1}$ and $0.186375 \cdot X_{Pine} + 0.143713 \cdot X_{Oak} = 0.241077$ at $1257.4\ cm^{-1}$, resulting in estimates of 0.2889mg pine (actual 0.49984mg) and 1.3028mg oak (actual 1.00056mg) as shown in Table 35.

Table 34 Coefficients and Constants Used for Multicomponent Analysis by Simultaneous Equations

WN(i)	Pine	Oak	1Pine500Oak1000	2Pine500Oak1000	3Pine500Oak1000	1Pine750Oak750	2Pine750Oak750	3Pine750Oak750
(cm^{-1})	$a_{Pine,i}$	$a_{Oak,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$
1250.7	0.206822	0.141004	0.243454	0.266974	0.252032	0.292140	0.273252	0.276148
1257.4	0.186375	0.143713	0.241077	0.258324	0.248183	0.281994	0.261887	0.259462
1265.1	0.145683	0.138139	0.212632	0.232256	0.222025	0.240045	0.221917	0.226574
1282.5	0.118970	0.149093	0.199306	0.218708	0.211904	0.218839	0.203519	0.203980
1289.2	0.127221	0.160189	0.215379	0.234172	0.227498	0.235492	0.215573	0.216973
1296.0	0.126755	0.159018	0.211872	0.230803	0.226057	0.231015	0.213068	0.216448

WN(i)	Pine	Oak	1Pine1000Oak500	2Pine1000Oak500	3Pine1000Oak500	1Pine1000Oak1500	2Pine1000Oak1500	3Pine1000Oak1500
(cm^{-1})	$a_{Pine,i}$	$a_{Oak,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$
1250.7	0.206822	0.141004	0.318786	0.312364	0.299994	0.393503	0.393411	0.404745
1257.4	0.186375	0.143713	0.300280	0.293218	0.282813	0.385632	0.378342	0.390409
1265.1	0.145683	0.138139	0.243808	0.242466	0.232550	0.336923	0.335420	0.348089
1282.5	0.118970	0.149093	0.217551	0.210857	0.203372	0.325090	0.323499	0.337633
1289.2	0.127221	0.160189	0.230867	0.224613	0.217999	0.358717	0.347277	0.369176
1296.0	0.126755	0.159018	0.227970	0.219797	0.213632	0.351009	0.345107	0.366534

WN(i)	Pine	Oak	1Pine1250Oak1250	2Pine1250Oak1250	3Pine1250Oak1250	1Pine1500Oak1000	2Pine1500Oak1000	3Pine1500Oak1000
(cm^{-1})	$a_{Pine,i}$	$a_{Oak,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$
1250.7	0.206822	0.141004	0.451398	0.433491	0.439597	0.460790	0.462105	0.450965
1257.4	0.186375	0.143713	0.422559	0.414587	0.413507	0.439792	0.431908	0.433306
1265.1	0.145683	0.138139	0.376331	0.361706	0.350273	0.370235	0.357061	0.361309
1282.5	0.118970	0.149093	0.355673	0.345942	0.332096	0.341326	0.337596	0.333635
1289.2	0.127221	0.160189	0.379308	0.379600	0.359913	0.369466	0.357414	0.357677
1296.0	0.126755	0.159018	0.373317	0.373437	0.354420	0.362613	0.357262	0.354459

Table 35 Estimated Pine and Oak Amounts in Mixed Samples (Pine500µgOak1000µg and Pine750µgOak750µg) by Multicomponent Analysis of Simultaneous Equations

WN	WN	1Pine500Oak1000		2Pine500Oak1000		3Pine500Oak1000		1Pine750Oak750		2Pine750Oak750		3Pine750Oak750	
(cm^{-1})	(cm^{-1})	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)
1250.7	1257.4	0.2889	1.3028	0.5643	1.0657	0.3559	1.2653	0.6453	1.1254	0.6804	0.9400	0.9006	0.6375
1250.7	1265.1	0.4544*	1.0600	0.5145	1.1387	0.4371	1.1463	0.8107	0.8827	0.8041	0.7584	0.7721	0.8259
1250.7	1282.5	0.5828	0.8717	0.6376	0.9581	0.5474	0.9845	0.9031	0.7471	0.8565	0.6816	0.8826	0.6639
1250.7	1289.2	0.5680	0.8934	0.6416	0.9523	0.5460	0.9866	0.8947	0.7595	0.8804	0.6465	0.8980	0.6413
1250.7	1296.0	0.5886	0.8632	0.6600	0.9254	0.5463	0.9861	0.9245	0.7159	0.8930	0.6281	0.8919	0.6502
1257.4	1265.1	0.5706	0.9374	0.4796	1.1756	0.4940	1.0863	0.9267	0.7604	0.8909	0.6669	0.6821	0.9209
1257.4	1282.5	0.6829	0.7919	0.6626	0.9382	0.6126	0.9324	0.9910	0.6770	0.9165	0.6337	0.8765	0.6687
1257.4	1289.2	0.6624	0.8185	0.6678	0.9315	0.6102	0.9355	0.9790	0.6926	0.9481	0.5928	0.8971	0.6420
1257.4	1296.0	0.6906	0.7819	0.6925	0.8994	0.6110	0.9345	1.0194	0.6402	0.9653	0.5705	0.8890	0.6525
1265.1	1282.5	0.7889	0.7073	0.8354	0.8003	0.7246	0.8431	1.0516	0.6287	0.9407	0.6144	1.0600	0.5223
1265.1	1289.2	0.7478	0.7506	0.8428	0.7925	0.7184	0.8497	1.0276	0.6539	1.0012	0.5506	1.0971	0.4832
1265.1	1296.0	0.8035	0.6919	0.8928	0.7398	0.7211	0.8468	1.1066	0.5707	1.0352	0.5147	1.0836	0.4974
1282.5	1289.2	-2.0613	2.9816	1.3488	0.3906	0.2928	1.1876	-0.6098	1.9544	5.1366	-2.7337	3.6335	-1.5313
1282.5	1296.0	5.2198	-2.8284	18.3348	-13.1634	-0.3461	1.6975	17.7973	-12.7336	29.7626	-22.3841	8.2632	-5.2255
1289.2	1296.0	-4.1714	4.6574	-3.5790	4.3043	0.4760	1.0421	-5.9501	6.1956	-2.0057	2.9386	2.2904	-0.4645
Actual Amount(mg)		0.49984	1.00056	0.49984	1.00056	0.49984	1.00056	0.74976	0.75042	0.74976	0.75042	0.74976	0.75042

Table 36 Estimated Pine and Oak Amounts in Mixed Samples (Pine1000μgOak500μg and Pine1000μgOak1500μg) by Multicomponent Analysis of Simultaneous Equations

WN (cm^{-1})	WN (cm^{-1})	1Pine1000Oak500		2Pine1000Oak500		3Pine1000Oak500		1Pine1000Oak1500		2Pine1000Oak1500		3Pine1000Oak1500	
		Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)
1250.7	1257.4	1.0086	0.7815	1.0297	0.7049	0.9396	0.7494	0.6320	1.8638	0.9266	1.4310	0.9055	1.5423
1250.7	1265.1	1.2031	0.4961	1.1162	0.5781	1.0775	0.5471	0.8533	1.5391	0.8781	1.5020	0.8507	1.6227
1250.7	1282.5	1.1986	0.5027	1.1977	0.4586	1.1416	0.4531	0.9125	1.4523	0.9274	1.4297	0.9059	1.5417
1250.7	1289.2	1.2186	0.4734	1.2089	0.4420	1.1399	0.4556	0.8198	1.5883	0.9250	1.4333	0.8413	1.6365
1250.7	1296.0	1.2353	0.4490	1.2440	0.3906	1.1709	0.4101	0.8711	1.5130	0.9256	1.4325	0.8444	1.6319
1257.4	1265.1	1.3395	0.3522	1.1768	0.5142	1.1742	0.4451	1.0086	1.3753	0.8441	1.5379	0.8121	1.6634
1257.4	1282.5	1.2633	0.4511	1.2548	0.4130	1.2104	0.3983	1.0080	1.3761	0.9277	1.4295	0.9060	1.5416
1257.4	1289.2	1.2896	0.4170	1.2695	0.3939	1.2076	0.4018	0.8833	1.5378	0.9245	1.4337	0.8196	1.6537
1257.4	1296.0	1.3123	0.3875	1.3169	0.3325	1.2496	0.3474	0.9525	1.4481	0.9252	1.4327	0.8236	1.6485
1265.1	1282.5	1.1914	0.5085	1.3285	0.3542	1.2444	0.3711	1.0074	1.3766	1.0066	1.3666	0.9946	1.4710
1265.1	1289.2	1.2431	0.4539	1.3557	0.3255	1.2386	0.3772	0.7668	1.6304	0.9992	1.3744	0.8264	1.6483
1265.1	1296.0	1.2867	0.4080	1.4485	0.2276	1.3204	0.2909	0.8997	1.4902	1.0015	1.3719	0.8344	1.6399
1282.5	1289.2	4.7784	-2.3537	3.2169	-1.1527	0.8434	0.6911	-15.6738	14.6874	0.4926	1.7767	-10.6577	10.7689
1282.5	1296.0	30.2406	-22.6714	37.9249	-28.8480	24.3952	-18.1022	-31.8534	27.5979	-0.5601	2.6167	-47.8317	40.4320
1289.2	1296.0	-2.6131	3.5166	-6.8547	6.8461	-5.9895	6.1177	-10.9803	10.9598	0.7957	1.5360	0.1208	2.2087
Actual amount(mg)		0.99968	0.50028	0.99968	0.50028	0.99968	0.50028	0.99968	1.50084	0.99968	1.50084	0.99968	1.50084

Table 37 Estimated Pine and Oak Amounts in Mixed Samples (Pine1250μgOak1250μg and Pine1500μgOak1000μg) by Multicomponent Analysis of Simultaneous Equations

WN	WN	1Pine1250Oak1250		2Pine1250Oak1250		3Pine1250Oak1250		1Pine1500Oak1000		2Pine1500Oak1000		3Pine1500Oak1000	
(cm^{-1})	(cm^{-1})	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)	Pine(mg)	Oak(mg)
1250.7	1257.4	1.5361	0.9482	1.1152	1.4386	1.4142	1.0433	1.2224	1.4750	1.6001	0.9302	1.0779	1.6172
1250.7	1265.1	1.1573	1.5037	1.1061	1.4519	1.4120	1.0466	1.4260	1.1763	1.6800	0.8130	1.4137	1.1246
1250.7	1282.5	1.2197	1.4123	1.1273	1.4207	1.3310	1.1654	1.4631	1.1218	1.5145	1.0559	1.4361	1.0918
1250.7	1289.2	1.2392	1.3838	1.0476	1.5377	1.2947	1.2185	1.4295	1.1711	1.5553	0.9960	1.4353	1.0929
1250.7	1296.0	1.2748	1.3315	1.0840	1.4844	1.3272	1.1708	1.4747	1.1048	1.5389	1.0200	1.4472	1.0754
1257.4	1265.1	0.8917	1.7839	1.0997	1.4587	1.4104	1.0482	1.5688	1.0256	1.7361	0.7539	1.6493	0.8762
1257.4	1282.5	1.1119	1.4984	1.1315	1.4174	1.3026	1.1880	1.5451	1.0564	1.4853	1.0791	1.5581	0.9945
1257.4	1289.2	1.1388	1.4635	1.0248	1.5558	1.2543	1.2506	1.4995	1.1155	1.5401	1.0081	1.5562	0.9969
1257.4	1296.0	1.1859	1.4023	1.0734	1.4928	1.2977	1.1944	1.5606	1.0364	1.5181	1.0366	1.5728	0.9753
1265.1	1282.5	1.3197	1.3326	1.1615	1.3935	1.2009	1.2692	1.5227	1.0743	1.2486	1.2680	1.4719	1.0632
1265.1	1289.2	1.3686	1.2809	0.9551	1.6112	1.1091	1.3659	1.4351	1.1667	1.3578	1.1528	1.4696	1.0657
1265.1	1296.0	1.4627	1.1818	1.0486	1.5125	1.1916	1.2790	1.5527	1.0427	1.3130	1.2001	1.5009	1.0327
1282.5	1289.2	4.7108	-1.3734	-13.1451	12.8095	-5.1526	6.3390	-4.5485	5.9188	8.8156	-4.7701	1.3070	1.1948
1282.5	1296.0	44.8933	-33.4371	-33.2471	28.8499	-1.6185	3.5189	10.6745	-6.2284	20.8820	-14.3985	10.3102	-5.9893
1289.2	1296.0	-6.9487	7.8865	-7.3151	8.1793	-6.1780	7.1533	-8.9667	9.4277	5.3118	-1.9874	-1.3049	3.2692
Actual amount(mg)		1.2496	1.2507	1.2496	1.2507	1.2496	1.2507	1.49952	1.00056	1.49952	1.00056	1.49952	1.00056

Tables 35 through 37 are estimated pine and oak amounts in mixed samples by multicomponent analysis of simultaneous equations. The values of either pine or oak were negative in the combinations of wave numbers at (1282.5cm^{-1}, 1289.2cm^{-1}) (1282.5cm^{-1}, 1296.0cm^{-1}) and (1289.2cm^{-1}, 1296.0cm^{-1}) and therefore those combinations are excluded after this for applying multicomponent analysis.

For selecting the optimal wave number pairings for multi-component analysis, the percent differences between the actual and estimated values were calculated and are shown from Table 38 to Table 41. For example, 9.1% at 1250.7 and at 1265.1 cm^{-1} in mixed sample of 1pine500oak1000 in Table 34 was equal to | 0.49984(actual pine amount) – 0.4544 (estimated value)| divided by 0.49984 and then 100(%) was multiplied. Total (%) is equal to pine (%) plus oak (%).

Table 41 shows 1500 ug means sum of total amount of pine and oak: 500 and 1000 ug , 750 and 750 ug, or 1000 and 500 ug, respectively. 2500 ug is the sum of total amount of pine and oak: 1000 and 1500 ug , 1250 and 1250 ug , or 1500 and 1000 ug, respectively. The four lowest averages of total (%) difference of all of 1500 ug and 2500 ug samples were 21.1% at 1250.7 and 1265.1 cm^{-1}, 18.9% at 1250.7 and 1282.5 cm^{-1}, 21.9% at 1250.7 and 1289.2 cm^{-1}, 23.5% at 1250.7 and 1296.0 cm^{-1}. Therefore, these four sets of wave number pairings were selected for use in further analyses.

Table 38 Evaluating the Difference Between Actual Pine or Oak Amount and Estimated Pine or Oak Value in Mixed Sample of 500ug Pine and 1000ug Oak or 750 ug Pine and 750 ug Oak

WN (cm^{-1})	WN (cm^{-1})	1Pine500Oak1000			2Pine500Oak1000			3Pine500Oak1000			**Pine500Oak1000**
		Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	**Avg of Total(%)**
1250.7	1257.4	42.2	30.2	72.4	12.9	6.5	19.4	28.8	26.5	55.3	**49.0**
1250.7	1265.1	9.1*	5.9*	15.0*	2.9	13.8	16.7	12.6	14.6	27.1	**19.6**
1250.7	1282.5	16.6	12.9	29.5	27.6	4.2	31.8	9.5	1.6	11.1	**24.1**
1250.7	1289.2	13.6	10.7	24.4	28.4	4.8	33.2	9.2	1.4	10.6	**22.7**
1250.7	1296.0	17.8	13.7	31.5	32.0	7.5	39.6	9.3	1.4	10.7	**27.3**
1257.4	1265.1	14.2	6.3	20.5	4.1	17.5	21.5	1.2	8.6	9.7	**17.2**
1257.4	1282.5	36.6	20.9	57.5	32.6	6.2	38.8	22.6	6.8	29.4	**41.9**
1257.4	1289.2	32.5	18.2	50.7	33.6	6.9	40.5	22.1	6.5	28.6	**39.9**
1257.4	1296.0	38.2	21.9	60.0	38.5	10.1	48.6	22.2	6.6	28.8	**45.8**
1265.1	1282.5	57.8	29.3	87.1	67.1	20.0	87.1	45.0	15.7	60.7	**78.3**
1265.1	1289.2	49.6	25.0	74.6	68.6	20.8	89.4	43.7	15.1	58.8	**74.3**
1265.1	1296.0	60.7	30.8	91.6	78.6	26.1	104.7	44.3	15.4	59.6	**85.3**

WN (cm^{-1})	WN (cm^{-1})	1Pine750Oak750			2Pine750Oak750			3Pine750Oak750			**Pine750Oak750**
		Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	**Avg of Total(%)**
1250.7	1257.4	13.9	50.0	63.9	9.3	25.3	34.5	20.1	15.0	35.2	**44.5**
1250.7	1265.1	8.1	17.6	25.8	7.3	1.1	8.3	3.0	10.1	13.0	**15.7**
1250.7	1282.5	20.5	0.4	20.9	14.2	9.2	23.4	17.7	11.5	29.3	**24.5**
1250.7	1289.2	19.3	1.2	20.5	17.4	13.8	31.3	19.8	14.5	34.3	**28.7**
1250.7	1296.0	23.3	4.6	27.9	19.1	16.3	35.4	19.0	13.4	32.3	**31.9**
1257.4	1265.1	23.6	1.3	24.9	18.8	11.1	30.0	9.0	22.7	31.7	**28.9**
1257.4	1282.5	32.2	9.8	42.0	22.2	15.6	37.8	16.9	10.9	27.8	**35.8**
1257.4	1289.2	30.6	7.7	38.3	26.5	21.0	47.5	19.7	14.4	34.1	**39.9**
1257.4	1296.0	36.0	14.7	50.7	28.7	24.0	52.7	18.6	13.0	31.6	**45.0**
1265.1	1282.5	40.3	16.2	56.5	25.5	18.1	43.6	41.4	30.4	71.8	**57.3**
1265.1	1289.2	37.1	12.9	49.9	33.5	26.6	60.2	46.3	35.6	81.9	**64.0**
1265.1	1296.0	47.6	24.0	71.5	38.1	31.4	69.5	44.5	33.7	78.2	**73.1**

Table 39 Evaluating the Difference Between Actual Pine or Oak Amount and Estimated Pine or Oak Value in Mixed Sample of 1000 ug Pine and 500 ug Oak or 1000 ug Pine and 1500 ug Oak

WN	WN	1Pine1000Oak500			2Pine1000Oak500			3Pine1000Oak500			**Pine1000Oak500**
(cm^{-1})	(cm^{-1})	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	**Avg of Total(%)**
1250.7	1257.4	0.9	56.2	57.1	3.0	40.9	43.9	6.0	49.8	55.8	**52.3**
1250.7	1265.1	20.3	0.8	21.2	11.7	15.6	27.2	7.8	9.4	17.1	**21.8**
1250.7	1282.5	19.9	0.5	20.4	19.8	8.3	28.1	14.2	9.4	23.6	**24.0**
1250.7	1289.2	21.9	5.4	27.3	20.9	11.6	32.6	14.0	8.9	23.0	**27.6**
1250.7	1296.0	23.6	10.3	33.8	24.4	21.9	46.4	17.1	18.0	35.2	**38.4**
1257.4	1265.1	34.0	29.6	63.6	17.7	2.8	20.5	17.5	11.0	28.5	**37.5**
1257.4	1282.5	26.4	9.8	36.2	25.5	17.5	43.0	21.1	20.4	41.5	**40.2**
1257.4	1289.2	29.0	16.6	45.6	27.0	21.3	48.3	20.8	19.7	40.5	**44.8**
1257.4	1296.0	31.3	22.5	53.8	31.7	33.5	65.3	25.0	30.6	55.6	**58.2**
1265.1	1282.5	19.2	1.6	20.8	32.9	29.2	62.1	24.5	25.8	50.3	**44.4**
1265.1	1289.2	24.4	9.3	33.6	35.6	34.9	70.6	23.9	24.6	48.5	**50.9**
1265.1	1296.0	28.7	18.5	47.2	44.9	54.5	99.4	32.1	41.8	73.9	**73.5**

WN	WN	1Pine1000Oak1500			2Pine1000Oak1500			3Pine1000Oak1500			**Pine1000Oak1500**
(cm^{-1})	(cm^{-1})	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	**Avg of Total(%)**
1250.7	1257.4	36.8	24.2	61.0	7.3	4.7	12.0	9.4	2.8	12.2	**28.4**
1250.7	1265.1	14.6	2.5	17.2	12.2	0.1	12.2	14.9	8.1	23.0	**17.5**
1250.7	1282.5	8.7	3.2	12.0	7.2	4.7	12.0	9.4	2.7	12.1	**12.0**
1250.7	1289.2	18.0	5.8	23.8	7.5	4.5	12.0	15.8	9.0	24.9	**20.2**
1250.7	1296.0	12.9	0.8	13.7	7.4	4.6	12.0	15.5	8.7	24.3	**16.6**
1257.4	1265.1	0.9	8.4	9.3	15.6	2.5	18.0	18.8	10.8	29.6	**19.0**
1257.4	1282.5	0.8	8.3	9.1	7.2	4.8	12.0	9.4	2.7	12.1	**11.1**
1257.4	1289.2	11.6	2.5	14.1	7.5	4.5	12.0	18.0	10.2	28.2	**18.1**
1257.4	1296.0	4.7	3.5	8.2	7.4	4.5	12.0	17.6	9.8	27.4	**15.9**
1265.1	1282.5	0.8	8.3	9.1	0.7	8.9	9.6	0.5	2.0	2.5	**7.1**
1265.1	1289.2	23.3	8.6	31.9	0.0	8.4	8.5	17.3	9.8	27.2	**22.5**
1265.1	1296.0	10.0	0.7	10.7	0.2	8.6	8.8	16.5	9.3	25.8	**15.1**

Table 40 Evaluating the Difference Between Actual Pine or Oak Amount and Approximate Pine or Oak Value in Mixed Sample of 1250 ug Pine and 1250 ug Oak or 1500 ug Pine and 1500 ug Oak

WN	WN	1Pine1250Oak1250			2Pine1250Oak1250			3Pine1250Oak1250			**Pine1250Oak1250**
(cm^{-1})	(cm^{-1})	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	**Avg of Total(%)**
1250.7	1257.4	22.9	24.2	47.1	10.8	15.0	25.8	13.2	16.6	29.8	**34.2**
1250.7	1265.1	7.4	20.2	27.6	11.5	16.1	27.6	13.0	16.3	29.3	**28.2**
1250.7	1282.5	2.4	12.9	15.3	9.8	13.6	23.4	6.5	6.8	13.3	**17.3**
1250.7	1289.2	0.8	10.6	11.5	16.2	22.9	39.1	3.6	2.6	6.2	**18.9**
1250.7	1296.0	2.0	6.5	8.5	13.3	18.7	31.9	6.2	6.4	12.6	**17.7**
1257.4	1265.1	28.6	42.6	71.3	12.0	16.6	28.6	12.9	16.2	29.1	**43.0**
1257.4	1282.5	11.0	19.8	30.8	9.4	13.3	22.8	4.2	5.0	9.3	**21.0**
1257.4	1289.2	8.9	17.0	25.9	18.0	24.4	42.4	0.4	0.0	0.4	**22.9**
1257.4	1296.0	5.1	12.1	17.2	14.1	19.4	33.5	3.8	4.5	8.3	**19.7**
1265.1	1282.5	5.6	6.5	12.2	7.1	11.4	18.5	3.9	1.5	5.4	**12.0**
1265.1	1289.2	9.5	2.4	11.9	23.6	28.8	52.4	11.2	9.2	20.5	**28.3**
1265.1	1296.0	17.0	5.5	22.6	16.1	20.9	37.0	4.6	2.3	6.9	**22.2**

WN	WN	1Pine1500Oak1000			2Pine1500Oak1000			3Pine1500Oak1000			**Pine1500Oak1000**
(cm^{-1})	(cm^{-1})	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	Pine(%)	Oak(%)	Total(%)	**Avg of Total(%)**
1250.7	1257.4	18.5	47.4	65.9	6.7	7.0	13.7	28.1	61.6	89.7	**56.5**
1250.7	1265.1	4.9	17.6	22.5	12.0	18.7	30.8	5.7	12.4	18.1	**23.8**
1250.7	1282.5	2.4	12.1	14.5	1.0	5.5	6.5	4.2	9.1	13.4	**11.5**
1250.7	1289.2	4.7	17.0	21.7	3.7	0.5	4.2	4.3	9.2	13.5	**13.1**
1250.7	1296.0	1.7	10.4	12.1	2.6	1.9	4.6	3.5	7.5	11.0	**9.2**
1257.4	1265.1	4.6	2.5	7.1	15.8	24.7	40.4	10.0	12.4	22.4	**23.3**
1257.4	1282.5	3.0	5.6	8.6	0.9	7.9	8.8	3.9	0.6	4.5	**7.3**
1257.4	1289.2	0.0	11.5	11.5	2.7	0.7	3.5	3.8	0.4	4.1	**6.4**
1257.4	1296.0	4.1	3.6	7.7	1.2	3.6	4.8	4.9	2.5	7.4	**6.6**
1265.1	1282.5	1.5	7.4	8.9	16.7	26.7	43.5	1.8	6.3	8.1	**20.2**
1265.1	1289.2	4.3	16.6	20.9	9.5	15.2	24.7	2.0	6.5	8.5	**18.0**
1265.1	1296.0	3.5	4.2	7.8	12.4	19.9	32.4	0.1	3.2	3.3	**14.5**

Table 41 Evaluating the Difference Between Actual and Estimated Pine or Oak Amounts in Mixed Sample: Final Choice of Wave Number Pairings

WN (cm^{-1})	WN (cm^{-1})	1500 ug Avg of Total(%)	2500 ug Avg of Total(%)	1500&2500ug Avg of Total(%)
1250.7	1257.4	**48.6**	**39.7**	**44.1**
1250.7	1265.1	**19.1**	**23.1**	**21.1**
1250.7	1282.5	**24.2**	**13.6**	**18.9**
1250.7	1289.2	**26.3**	**17.4**	**21.9**
1250.7	1296.0	**32.5**	**14.5**	**23.5**
1257.4	1265.1	**27.9**	**28.4**	**28.2**
1257.4	1282.5	**39.3**	**13.1**	**26.2**
1257.4	1289.2	**41.6**	**15.8**	**28.7**
1257.4	1296.0	**49.7**	**14.1**	**31.9**
1265.1	1282.5	**60.0**	**13.1**	**36.5**
1265.1	1289.2	**63.1**	**22.9**	**43.0**
1265.1	1296.0	**77.3**	**17.2**	**47.3**

7.6 Multicomponent Analysis of Archived Samples by Simultaneous Equations

For further evaluation, fifteen archived samples were analyzed for oak and pine content. These samples were collected from the previous epidemiological study for the wood processing worker health; 5 of the samples contained only oak, 5 contained only pine, and 5 contained oak and pine. All of the samples were collected in the same furniture plant and dust weight (Table 42). The procedure for preparing and analyzing is the same as previously described.

Table 42 Archived Sample Information

Sample ID	Dust Weight(mg)	Wood Type	Plant
15036	0.751	Oak	Furniture D
15033	0.929	Oak	Furniture D
15123	1.04	Oak	Furniture D
15120	1.342	Oak	Furniture D
15243	1.737	Oak	Furniture D
15027	0.581	Pine	Furniture D
9048	0.846	Pine	Furniture D
9165	0.923	Pine	Furniture D
9093	0.992	Pine	Furniture D
9162	1.621	Pine	Furniture D
15255	0.476	Pine & Oak	Furniture D
15267	0.459	Pine & Oak	Furniture D
9123	2.567	Pine & Oak	Furniture D
9156	4.051	Pine & Oak	Furniture D
9153	4.212	Pine & Oak	Furniture D

The coefficients and constants used for multicomponent analysis by simultaneous equations of archived samples are shown in Table 43. From these coefficients and constants, the estimates of pine and oak in archived samples were obtained by multicomponent analysis and are shown in Table 44.

For example in the Table 43, one combination of sample '15036' is solved by simultaneous equation method of two equations $0.206822 \cdot X_{Pine} + 0.141004 \cdot X_{Oak} = 0.099194$ at 1250.7cm^{-1} and $0.145683 \cdot X_{Pine} + 0.138139 \cdot X_{Oak} = 0.090235$ at 1265.1cm^{-1}. The slopes of each wave number are the same as in Table 34. This results in estimates of 0.525mg oak, 0.122mg pine and 0.647mg total (0.751mg dust weight) as shown in Table 44. The dust weight shown in Table 44 represents total dust at ambient humidity, whereas the estimates from the multicomponent analysis by simultaneous equations are for dry wood solids alone.

Table 43 Coefficients and Constants Used for Multicomponent Analysis by Simultaneous Equations about Archived Samples

WN	15036	15033	15123	15120	15243
(cm^{-1})	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$
1250.7	0.099194	0.107676	0.081555	0.203822	0.168820
1265.1	0.090235	0.094747	0.074948	0.193667	0.153516
1282.5	0.069617	0.078381	0.061047	0.171192	0.135369
1289.2	0.066648	0.076488	0.061355	0.170377	0.138326
1296.0	0.062888	0.072038	0.058018	0.162639	0.135139

WN	15027	9048	9165	9093	9162
(cm^{-1})	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$
1250.7	0.068195	0.153907	0.226319	0.156887	0.334411
1265.1	0.059482	0.121833	0.192266	0.121507	0.267037
1282.5	0.044668	0.083702	0.151663	0.089514	0.207351
1289.2	0.043408	0.082493	0.151634	0.088316	0.207580
1296.0	0.040597	0.078021	0.147358	0.080926	0.201790

WN	15255	15267	9123	9156	9153
(cm^{-1})	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$	$A_{t,i}$
1250.7	0.046217	0.049763	0.425510	0.547208	0.611896
1265.1	0.041293	0.044688	0.383932	0.459591	0.518888
1282.5	0.030999	0.034238	0.330783	0.412632	0.463348
1289.2	0.030417	0.033503	0.333551	0.433615	0.485944
1296.0	0.028717	0.031842	0.324690	0.414962	0.470277

Table 44 Estimated Pine and Oak Amounts in Archived Samples by Multicomponent Analysis of Simultaneous Equations

		ID		DustWt	ID		DustWt	ID		DustWt	ID		DustWt	ID		DustWt
		15036		**0.751**	**15033**		**0.929**	**15123**		**1.04**	**15120**		**1.342**	**15243**		**1.737**
WN	WN	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total
(cm^{-1})	(cm^{-1})	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)
1250.7	1265.1	0.122	0.525	0.647	0.189	0.487	0.676	0.0869	0.451	0.538	0.106	1.291	1.396	0.209	0.891	1.100
1250.7	1282.5	0.354	0.185	0.538	0.356	0.242	0.598	0.253	0.208	0.461	0.445	0.794	1.238	0.433	0.563	0.995
1250.7	1289.2	0.427	0.0767	0.504	0.426	0.140	0.565	0.291	0.152	0.443	0.568	0.613	1.181	0.496	0.469	0.966
1250.7	1296.0	0.460	0.0289	0.489	0.464	0.0833	0.547	0.319	0.111	0.430	0.631	0.520	1.151	0.519	0.436	0.955
	Avg	0.341	0.204	0.544	0.358	0.238	0.596	0.237	0.230	0.468	0.437	0.804	1.241	0.414	0.590	1.004

		ID		DustWt	ID		DustWt	ID		DustWt	ID		DustWt	ID		DustWt
		15027		**0.581**	**9048**		**0.846**	**9165**		**0.923**	**9093**		**0.992**	**9162**		**1.621**
WN	WN	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total
(cm^{-1})	(cm^{-1})	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)
1250.7	1265.1	0.129	0.295	0.424	0.508	0.346	0.854	0.517	0.846	1.364	0.565	0.283	0.849	1.064	0.811	1.875
1250.7	1282.5	0.275	0.0800	0.355	0.793	-0.0710	0.704	0.879	0.316	1.195	0.766	-0.0108	0.752	1.467	0.221	1.687
1250.7	1289.2	0.316	0.0199	0.336	0.857	-0.166	0.648	0.979	0.169	1.148	0.835	-0.112	0.694	1.600	0.0255	1.625
1250.7	1296.0	0.341	-0.0165	0.320	0.897	-0.225	0.616	1.013	0.119	1.132	0.902	-0.210	0.638	1.645	-0.0435	1.592
	Avg	0.265	0.0946	0.356	0.764	-0.0289	0.705	0.847	0.363	1.210	0.767	-0.0122	0.733	1.444	0.253	1.695

		ID		DustWt	ID		DustWt	ID		DustWt	ID		DustWt	ID		DustWt
		15255		**0.476**	**15267**		**0.459**	**9123**		**2.567**	**9156**		**4.051**	**9153**		**4.212**
WN	WN	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total	Pine	Oak	Total
(cm^{-1})	(cm^{-1})	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)
1250.7	1265.1	0.0700	0.225	0.295	0.0714	0.248	0.320	0.578	2.169	2.748	1.344	1.910	3.254	1.415	2.264	3.679
1250.7	1282.5	0.179	0.0649	0.244	0.184	0.0826	0.267	1.195	1.265	2.460	1.664	1.440	3.104	1.842	1.638	3.480
1250.7	1289.2	0.205	0.0271	0.232	0.214	0.0394	0.253	1.391	0.978	2.369	1.745	1.321	3.066	1.942	1.491	3.433
1250.7	1296.0	0.220	0.0054	0.225	0.228	0.0185	0.247	1.457	0.880	2.338	1.898	1.096	2.995	2.064	1.312	3.376
	Avg	0.169	0.0806	0.249	0.174	0.0972	0.272	1.155	1.323	2.478	1.663	1.442	3.105	1.816	1.676	3.492

Prepared samples containing only oak or only pine were also evaluated. Each sample of 250, 500, 1000, 1500, 2000, and 2500 μg of oak or pine was prepared and analyzed as the same described previously.

The coefficients and constants used for multicomponent analysis by simultaneous equations of only oak or only pine samples are shown in Table 45. From these coefficients and constants, the estimates of oak and pine in samples obtained by multicomponent analysis are shown in Table 46.

For example in the Table 45, one combination of sample 'pine2000' is solved by simultaneous equation method of two equations $0.206822 \cdot X_{Pine} + 0.141004 \cdot X_{Oak} = 0.429103$ at $1250.7 cm^{-1}$ and $0.145683 \cdot X_{Pine} + 0.138139 \cdot X_{Oak} = 0.309904$ at $1265.1 cm^{-1}$. The slopes of each wave number are the same as in Table 33. This results in estimates of 1.940mg pine (1.999mg actual pine), and 0.197mg oak (0mg actual oak) as shown in Table 46.

From this dry wood estimates analysis, unknown mixture of carcinogenic and non-carcinogenic (oak and pine) wood could be apportioned quantitatively. Therefore, dry wood analysis by DRIFTS with simultaneous equations at multiple wave number pairings is better than quantitative determination of total dust weight in the carcinogenic wood mixture.

Table 45 Coefficients and Constants Used for Multicomponent Analysis by Simultaneous Equations for Oak or Pine Standards

WN	pine250	pine500	pine1000	pine1500	pine2000	pine2500
(cm-1)	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$
1250.7	0.024213	0.085398	0.229989	0.323686	0.429103	0.493337
1265.1	0.014502	0.055745	0.156970	0.222163	0.309904	0.348035
1282.5	0.009387	0.040372	0.122023	0.178406	0.257260	0.286422
1289.2	0.009717	0.043358	0.130073	0.190339	0.271628	0.309496
1296.0	0.009692	0.042860	0.130038	0.187675	0.272135	0.308226
Actual Amount(mg)	0.250	0.500	1.000	1.500	1.999	2.499

WN	oak250	oak500	oak1000	oak1500	oak2000	oak2500
(cm-1)	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$	$A_{p\&o,i}$
1250.7	0.018133	0.064916	0.142851	0.223547	0.295083	0.337350
1265.1	0.018114	0.064825	0.137869	0.224995	0.289217	0.327351
1282.5	0.017555	0.063438	0.137660	0.231063	0.315465	0.363686
1289.2	0.017453	0.066638	0.146741	0.246529	0.339266	0.392442
1296.0	0.017960	0.066134	0.144686	0.244538	0.336727	0.390067
Actual Amount(mg)	0.250	0.500	1.001	1.501	2.001	2.501

Table 46 Estimated Pine and Oak Amounts in Only Oak or Only Pine Standards by Multicomponent Analysis of Simultaneous Equations

		pine250		pine500		pine1000		pine1500		pine2000		pine2500	
WN (cm^{-1})	WN (cm^{-1})	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)
1250.7	1265.1	0.162	-0.0658	0.490	-0.114	1.200	-0.120	1.668	-0.150	1.940	0.197	2.376	0.0138
1250.7	1282.5	0.163	-0.0668	0.501	-0.129	1.215	-0.151	1.643	-0.115	1.970	0.153	2.359	0.0389
1250.7	1289.2	0.165	-0.0705	0.498	-0.125	1.218	-0.155	1.646	-0.119	2.004	0.105	2.329	0.0821
1250.7	1296.0	0.165	-0.0709	0.502	-0.131	1.215	-0.150	1.666	-0.147	1.989	0.126	2.330	0.0809
Actual Amount(mg)		0.250	0	0.500	0	1.000	0	1.500	0	1.999	0	2.499	0

		oak250		oak500		oak1000		oak1500		oak2000		oak2500	
WN (cm^{-1})	WN (cm^{-1})	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)	Pine (mg)	Oak (mg)
1250.7	1265.1	-0.0061	0.138	-0.0216	0.492	0.0365	0.956	-0.105	1.740	-0.0023	2.096	0.0552	2.312
1250.7	1282.5	0.0162	0.105	0.0522	0.384	0.134	0.816	0.0532	1.507	-0.0346	2.144	-0.0700	2.495
1250.7	1289.2	0.0292	0.0858	0.0660	0.364	0.144	0.802	0.0690	1.484	-0.0374	2.148	-0.0853	2.518
1250.7	1296.0	0.0234	0.0943	0.0664	0.363	0.154	0.787	0.0711	1.481	-0.0370	2.147	-0.0903	2.525
Actual Amount(mg)		0	0.250	0	0.500	0	1.001	0	1.501	0	2.001	0	2.501

VIII **Discussion**

Wood Solid Analysis by DRIFTS in Personal Dust Sample Collected from the Wood Processing Industry Study

Wood solid analysis by DRIFTS technique was applied to 521 size-fractionated Respicon sample sets collected from wood processing industry during a six year epidemiologic study. The results were analyzed by Kruskal-Wallis one way ANOVA on ranks with plant type, job activity, and wood type as treatment variables and by Mann-Whitney test for multiple comparisons within treatment.

Currently wood dust analysis is conducted by traditional gravimetric method. However, wood dust in samples collected from wood processing industry includes wood solids and residual particulate matter: some materials from wood, contaminants from its storage and processing, and background particulate contaminants in industrial facilities including engine exhaust, soil and road dust, oil mist, and etc. Therefore, it is important to specifically determine wood solid by DRIFTS technique in size-fractionated airborne particulate samples from wood processing industry.

Removal of Outliers/ Descriptive Statistics

From the Figure 9 through Figure 18, box plot of 'Minitab 16.1.0' was applied to removing the outliers from size-fractionated wood solid percentage (WS %). Several huge WS % data were included in each plant after DRIFT technique. Box plot was selected because of data size and non-normal data distribution of WS %.

For the ten plants, the average of respirable WS % was 13.8 %, thoracic WS % 60.2 %, and inhalable WS % 42.6 % after removing outliers. The lower content of wood solids in respirable dust was shown comparing to thoracic and inhalable dust because of fine particles from non-wood sources such as engine exhaust and environmental tobacco smoke. Also, most of cases WS % of thoracic was larger than WS % of respirable and inhalable by plant or plant type except sawmill-planing-plywood.

Each average of respirable, thoracic, and inhalable WS % in the furniture plant was 13.4 %, 67.4 %, and 44.2 %, in the cabinet plant 30.5 %, 86.0 %, and 63.5 %, and in the secondary millworks plant 10.3 %, 61.7 %, and 46.8 %, and in the sawmill-planing-plywood 2.2 %, 6.1 %, and 5.9 %. Cabinet plants showed the highest content of wood solid in all three size fraction. In sawmill-planing-plywood plant type, WS % was clearly less in the dust than for the other plant types because of the emission of resin binders and exterior dust contamination in the making of plywood while also processing of primarily green wood.

Each average of respirable, thoracic, and inhalable WS % by wood type was 26.5 %, 89.5 % and 63.6 % (highest WS %) in mixed wood, and 2.2 %, 6.4 % and 5.2 % (lowest WS %) in plywood. Each average of size-fractionated WS % by job activity was 21.5 %, 83.3 % and 59.0 % (highest WS %) in sanding, and 1.5 %, 2.1 % and 6.0 % (lowest WS %) in debarking/log yard.

Kruskal-Wallis ANOVA (on Ranks) Size-Fractionated WS % and Multiple Comparison by Plant Type, Wood Type, and Job Activity

Kruskal-Wallis (K-W) one way ANOVA on ranks (nonparametric ANOVA) was used for ANOVA and for multiple comparisons within groups, Mann-Whitney test (nonparametric two independent sample test) was performed.

Plant Type

There is a statistically significant difference ($p<0.001$) between plant types by K-W one way ANOVA on ranks. However, all of size fractionated WS% in the furniture vs secondary millwork were not significantly different ($p>0.05$) whereas all other pairwise WS % comparisons for plant type were statistically different.

Wood Type

There is a statistically significant difference ($p<0.001$) between wood types from all of size fractionated WS %. All of size fractionated WS % in the hardwood vs engineered wood is not significantly different ($p>0.05$). However, this engineered wood has very small sample number (6).

Job Activity

There is a statistically significant difference ($p<0.001$) between job activity from all of size fractionated WS %. There are no significant differences in many pairings of job activity: sawing vs milling, sawing vs PSV, sawing vs others, sanding vs blow down/compressed air, milling vs PSV, and PSV vs others in all of size fractionated WS %. Most of sanding is significantly different with other job activities except with blow down/compressed air.

From the results of these analyses, wood solid contents were different from sources of size-fractionated dust in wood processing industry by plant type, wood type, and job activity.

Prediction Modeling of Inhalable Wood Solid Percentage

The objective is to develop a model for prediction of inhalable WS % from various easily measured determinants. Linear regression analysis was used to determine prediction model by obtaining coefficients for various determinants. Correlation for evaluating predicted data vs observed data of inhalable WS % was performed with Pearson correlation and Spearman's rho (nonparametric correlation test)

1. Prediction Model A of Inhalable WS % from 10 Plants

The equation of coefficients of model A is as follows:

$$\textit{Inhalable WS \%} = 45.6 + 19.8 * \textit{Cabinet} + 12.3 * \textit{Secondary millwork} - 17.2 * \textit{Sawmill-planing-plywood} - 1.89 * \textit{Green wood} - 0.848 * \textit{Green/dry wood mixed} - 14.2 * \textit{Hardwood} - 22.3 * \textit{Softwood} + 1.09 * \textit{Formaldehyde} - 12.6 * \textit{PSV} \tag{11}$$

The coefficients for determinants of green wood, green/dry wood, and formaldehyde, were not statistically significant. There is confounding between sawmill-planing-plywood vs green wood, green/dry wood, and formaldehyde because these materials are only present in the sawmill-planing-plywood factories. The observed and predicted value of each inhalable wood solid % are followed: 50.0 % and 45.6 % in furniture A, 31.1 % and 38.2 % in furniture B, 53.2 % and 45.6 % in furniture C, and 42.3 % and 45.6% in furniture D; 72.3 % and 65.4 % in cabinet A, and 52.6 % and 61.2 % in cabinet B; 34.0 % and 34.5 % in secondary millwork A, and 58.1 % and 57.6 % in secondary millwork B; 7.22 % and 6.35 % sawmill-planing-plywood A, and 4.44 % and 5.45 % sawmill-planing-plywood B. Most correlations between observed and predicted inhalable WS% are statistically significant ($p<0.01$).

2. Prediction Model B of Inhalable WS % from 10 Plants

From the prediction model A, the reciprocal of inhalable dust weight was added as an additional determinant. Because denominator of wood solid percentage is inhalable dust weight and therefore, this was considered as a determinant.

The equation of coefficients of model B is as follows:

*(12) Inhalable WS % = 49.8 + 19.1 * Cabinet + 13.5 * Secondary millwork - 9.47 * Sawmill-planing-plywood - 0.274 * Green wood - 7.04 * Green/dry wood mixed - 13.6 * Hardwood - 21.1 * Softwood - 6.01 * Formaldehyde - 12.7 * PSV - 6.16 * Reciprocal inhalable dust weight*

Coefficients of determinants of green wood, green/dry wood, formaldehyde, and sawmill-planing-plywood there were not statistically significant.

The observed and predicted value of each inhalable WS% are followed: 50.0 % and 45.6 % in furniture A, 31.1 % and 38.7 % in furniture B, 53.2 % and 45.5 % in furniture C, and 42.3 % and 45.4 % in furniture D; 72.3 % and 66.4 % in cabinet A, and 52.6 % and 57.0 % in cabinet B; 34.0 % and 34.2 % in secondary millwork A, and 58.1 % and 57.9 % in secondary millwork B; 7.22 % and 3.36 % sawmill-planing-plywood A, and 4.44 % and 8.92 % sawmill-planing-plywood B. All correlation between observed and predicted inhalable WS% are significant ($p<0.01$).

3. Evaluation and Validation of Prediction Model C of Inhalable WS % from 8 Plants

Two plants (furniture C and sawmill-planing-plywood A) were randomly selected for validating the prediction modeling obtained from the remaining 8 plants (Model C).

The equation of coefficients of model C is as follows:

*(13) Inhalable WS % = 43.1 + 22.3 * Cabinet + 15.2 * Secondary millwork - 15.3 * Sawmill-planing-plywood - 1.69 * Green wood - 0.723 * Green/dry wood mixed - 10.3 * Hardwood - 23.3 * Softwood + 1.81 * Formaldehyde - 12.6 * PSV*

The coefficients of the determinants of green wood, green/dry wood, and formaldehyde were not statistically significant. The observed and the predicted inhalable WS% in furniture are 53.1 % and 43.1 %, in sawmill-planing-plywood 7.22 % and 5.87 %, and in overall 32.5 % and 26.3 %. The predicted values are all within 20 % of the observed which supports the validity of the modeling approach.

4. Evaluation and Validation of Prediction Model D of Inhalable WS % from 8 Plants

From the prediction model C, the reciprocal of inhalable dust weight was again added as one of determinants.

The equation of coefficients of model D is as follows:

*(14) Inhalable WS % = 49.3 + 21.2 * Cabinet + 16.4 * Secondary millwork - 11.9 * Sawmill-planing-plywood - 3.16 * Green wood - 1.47 * Green/dry wood mixed - 10.9 * Hardwood - 20.6 * Softwood - 0.476 * Formaldehyde - 12.7 * PSV - 8.79 * Reciprocal inhalable dust weight*

The coefficients for determinants of green wood, green/dry wood, and formaldehyde were not statistically significant. The observed and the predicted inhalable WS % in furniture are 53.1 % and 43.1 %, in sawmill-planing-plywood 7.22 % and -6.63 %, and in overall 32.5 % and 20.7 %. As the results of the predicted values including negative predictive values for sawmill-planing-plywood, this prediction model D is not good fit for evaluating this inhalable WS %. Therefore, from the evaluating and validating prediction model of inhalable wood solid percentage from 8 wood processing plants, model C is recommended.

Multicomponent or Mixed Wood Analysis by DRIFTS

This study is a mixed wood (oak and pine) analysis by using basically DRIFTS technique for (1) selecting optimal multiple wave numbers based on the lowest differences between actual and estimated values of wood solids, and then (2) determining the amounts of oak and pine in mixed samples using the multicomponent simultaneous equation technique.

Exposure assessment to wood dust is difficult because the etiologic agents of disease are not identified well and the chemical composition is complex. Wood dust was classified as a carcinogen by the International Agency for Research on Cancer (IARC) and American Conference of Governmental Industrial Hygienist (ACGIH) has classified oak and beech dusts as A1 (confirmed human) carcinogens and recommended a threshold limit value of 1mg/m^3 (inhalable fraction) for all other species dusts. Also, the exposure to wood dust has been linked to various respiratory health effects such as hypersensitivity and asthma. Therefore it is important to know each specific amount of the mixed woods: oak, carcinogenic wood and pine, non carcinogenic wood.

Decision of Pairings of Wave Numbers

From the study of the mixture of oak and pine, the optimum combinations of wave numbers were selected: (1250.7 cm^{-1}, 1265.1 cm^{-1}), (1250.7 cm^{-1}, 1282.5 cm^{-1}), (1250.7 cm^{-1}, 1289.2 cm^{-1}), and (1250.7 cm^{-1}, 1296.0 cm^{-1}). The optimal selection of wave number pairings was evaluated by average of total (%) differences between known and estimated amounts of pine and oak in mixed standards: 21.1 % at (1250.7 cm^{-1}, 1265.1 cm^{-1}), 18.9 % at (1250.7 cm^{-1}, 1282.5 cm^{-1}), 21.9 % at (1250.7 cm^{-1}, 1289.2 cm^{-1}), and 23.5 % at (1250.7 cm^{-1}, 1296.0 cm^{-1}).

This work utilized only two total amounts of wood solids, 1500 μg and 2500 μg, with varying composition of oak and pine.

Multicomponent Analysis of Archived Samples by Simultaneous Equations

Multicomponent analysis was performed on fifteen samples: five only oak, five only pine, and five oak and pine from furniture D plant from a six-year longitudinal epidemiologic study. As a result of analyzing, the mean %difference ± standard deviation (range) between actual and estimate values, are 33.6 ± 17.7 % (7.50, 55.0 %) in only-oak samples, 23.3 ± 13.1 % (4.55, 38.2 %) in only-pine samples, and 26.5 ± 17.9 % (3.45, 47.7 %) in mixed oak and pine samples. Most of cases, actual amount is larger than estimate value because actual amount is the total dust weight at ambient humidity and the estimate value represents only dry wood solids obtained from multicomponent analysis by simultaneous equations.

In all of only oak archive samples, small amounts of pine were estimated in Table 44. There are a few possibilities; these samples might be contaminated or mixed due to mishandling, the information in the archives concerning wood types is wrong or missing, or Radiata pine standards prepared in the lab are not representative of pine archive samples of furniture D.

In only oak or only pine standards in Table 46 or only pine archive samples in Table 44, the amount of the alternate component (pine or oak) was estimated as a small negative number by the simultaneous equation method. These numbers were calculated from solver function in Microsoft Excel; if the option to disallow negative values were used in Solver, the result of estimated original data of oak or pine would be changed.

The significant bias observed in samples that contain only one component remains a problem with this method of multicomponent analysis. A contributing factor may be the non-zero intercepts that are observed in some of the wave number standard curves. The method of simultaneous equations requires that there be no constants in the equations so that forced-zero intercept regression analyses had to be done to develop the standard curves. The source of these non-zero intercepts should be investigated further with aim of eliminating them or developing an alternative simultaneous equation algorithm that would allow the input of constants into the component equations.

Further Study

In this work, the mulicomponent simultaneous equation technique was applied to dust samples containing a mixture of the carcinogenic wood, oak and the non-carcinogenic pine. In a similar fashion, the technique could be applied to the analysis of mixtures of pine and other carcinogenic woods, especially beech.

Data obtained in the six-year epidemiologic study of the wood industry showed that in some plants in the furniture and cabinet making segments, more than two species of wood were being used at various plants including maple and birch in addition to oak and pine. The multicomponent simultaneous equation technique is applicable to mixtures containing more than two components.

For example, for three species wood dust, this technique can be applied:

$$(15)\ A_t = A_a + A_b + A_c = \varepsilon_a \cdot l \cdot c_a + \varepsilon_b \cdot l \cdot c_b + \varepsilon_c \cdot l \cdot c_c$$

A_t : Total absorbance at a given wave number

$A_{a,\,b,\,c}$: Absorbance of each component a, b, or c

$\varepsilon_{a,,b,\,c}$: Absorptivity of component a, b, or c

l : Pathlength

$c_{a,b,\,c}$: Concentration of component a, b, or c

This method needs at least three equations to solve for three unknowns along with measuring the absorbance of the sample at three different wave numbers.

IX Conclusions and Recommendations

This wood solid analysis by DRIFTS was applied to size-fractionated samples collected from wood processing industry and the result of analysis showed the different characteristic of wood dust analysis by plant type, job activity, wood type, and so on comparing with the traditional gravimetric method. Gravimetric analysis is a non-specific technique and integrates all particle mass including the non-wood derived particles of the dust.

A mixture of carcinogenic and non-carcinogenic woods (oak and pine) was quantitatively analyzed after finding the optimal pairings of wave numbers for use in multicomponent analysis. This method is helpful for unknown information for wood samples and most importantly, the information of carcinogenic wood can be obtained by this analysis. Further application of this technique to the carcinogenic woods (beech, birch, mahogany, teak, and walnut) is recommended.

This study of wood solid analysis by DRIFTS shows important differences in sources of size-fractionated dust in wood processing industry based on wood solid content, and provides a new analytical standard method for determining the amounts of specific woods in a binary wood dust mixture in the industrial setting.

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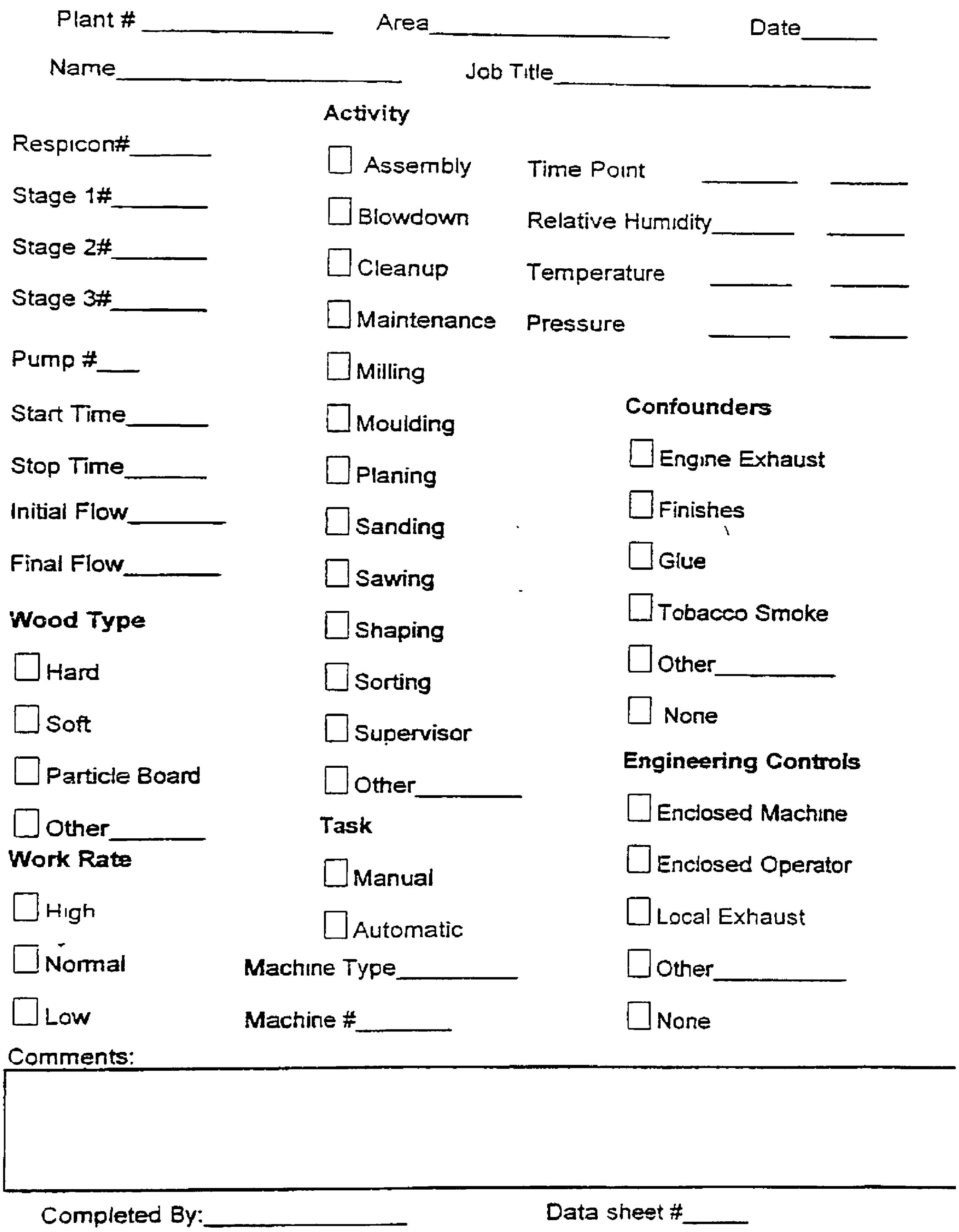
Appendix A

Field Sample Format



Plant # ____________ Area ________________ Date _____

Name ___________________ Job Title _____________________

Respicon# _____

Stage 1# _____

Stage 2# _____

Stage 3# _____

Pump # ___

Start Time _____

Stop Time _____

Initial Flow ______

Final Flow ______

Wood Type

- ☐ Hard
- ☐ Soft
- ☐ Particle Board
- ☐ Other ______

Work Rate

- ☐ High
- ☐ Normal
- ☐ Low

Activity

- ☐ Assembly
- ☐ Blowdown
- ☐ Cleanup
- ☐ Maintenance
- ☐ Milling
- ☐ Moulding
- ☐ Planing
- ☐ Sanding
- ☐ Sawing
- ☐ Shaping
- ☐ Sorting
- ☐ Supervisor
- ☐ Other ______

Task

- ☐ Manual
- ☐ Automatic

Machine Type ________

Machine # ______

Time Point _____ _____

Relative Humidity _____ _____

Temperature _____ _____

Pressure _____ _____

Confounders

- ☐ Engine Exhaust
- ☐ Finishes
- ☐ Glue
- ☐ Tobacco Smoke
- ☐ Other ________
- ☐ None

Engineering Controls

- ☐ Enclosed Machine
- ☐ Enclosed Operator
- ☐ Local Exhaust
- ☐ Other _________
- ☐ None

Comments:

Completed By: ______________ Data sheet # _____

Figure A.1 Field Sample Format

Appendix B

Oak or Pine Standard Calibration Curves

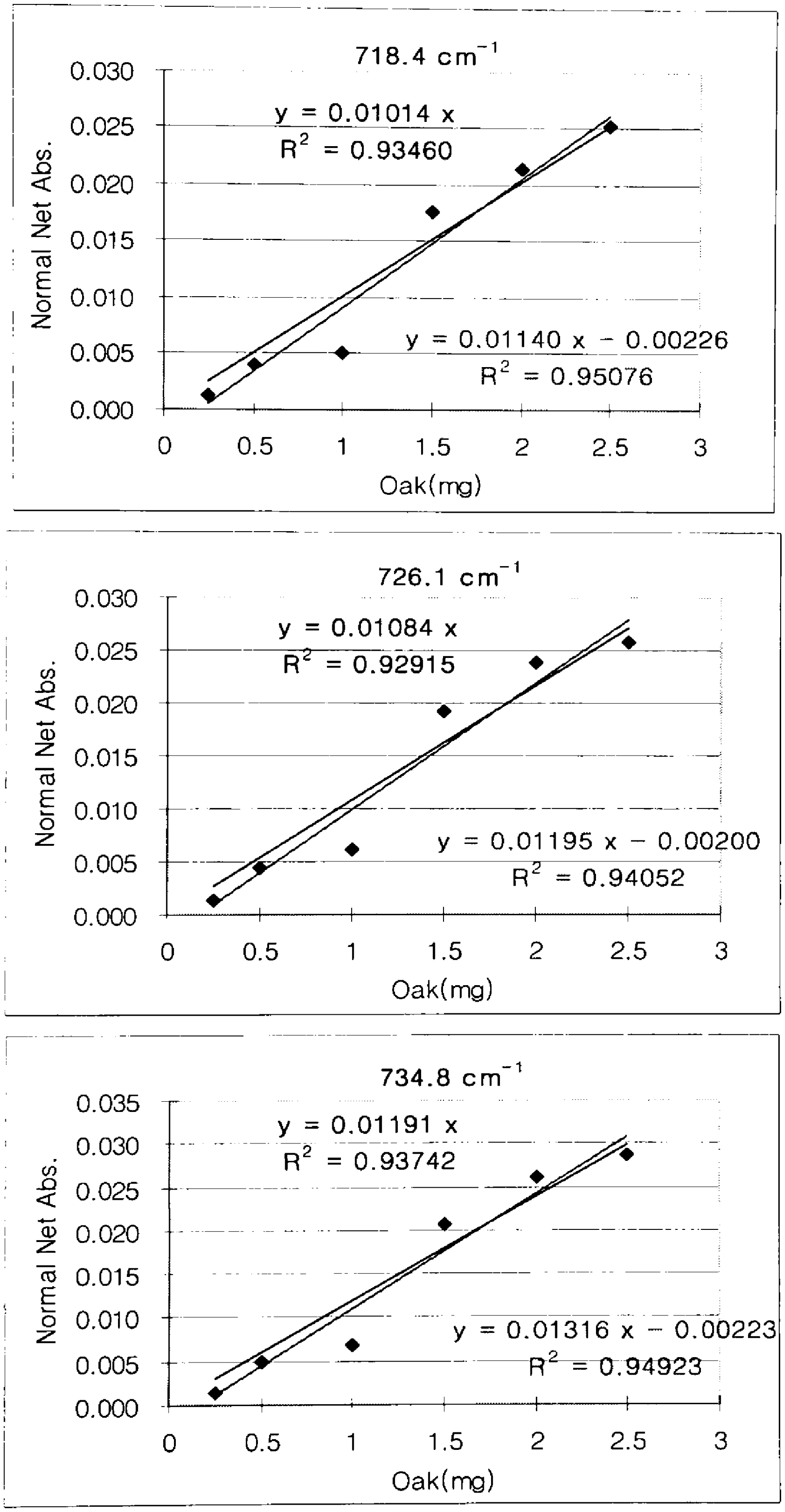


Figure B.1 Oak Standard Calibration Curves at 718.4, 726.1 & 734.8 cm^{-1}

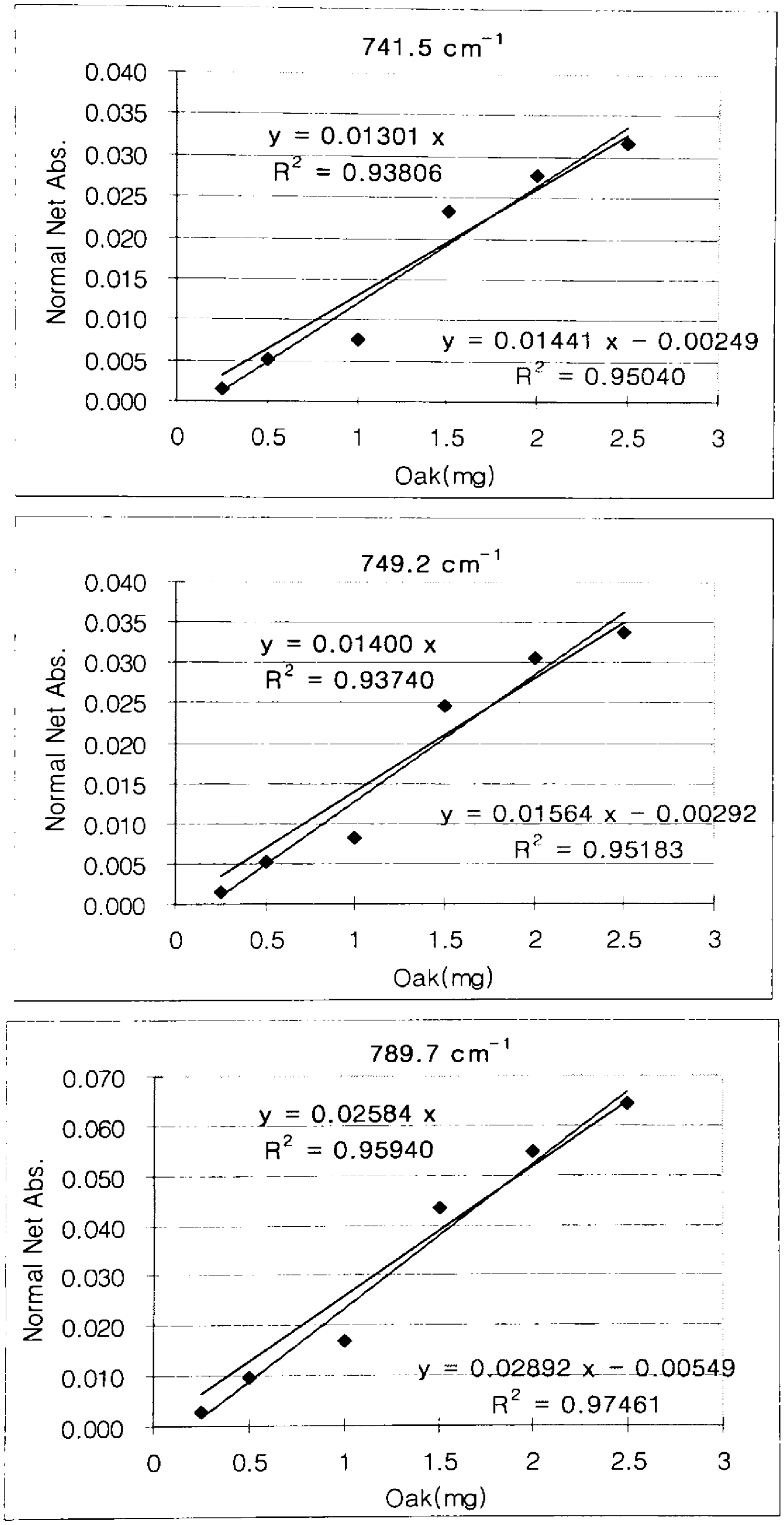


Figure B.2 Oak Standard Calibration Curves at 741.5, 749.2 & 789.7 cm^{-1}

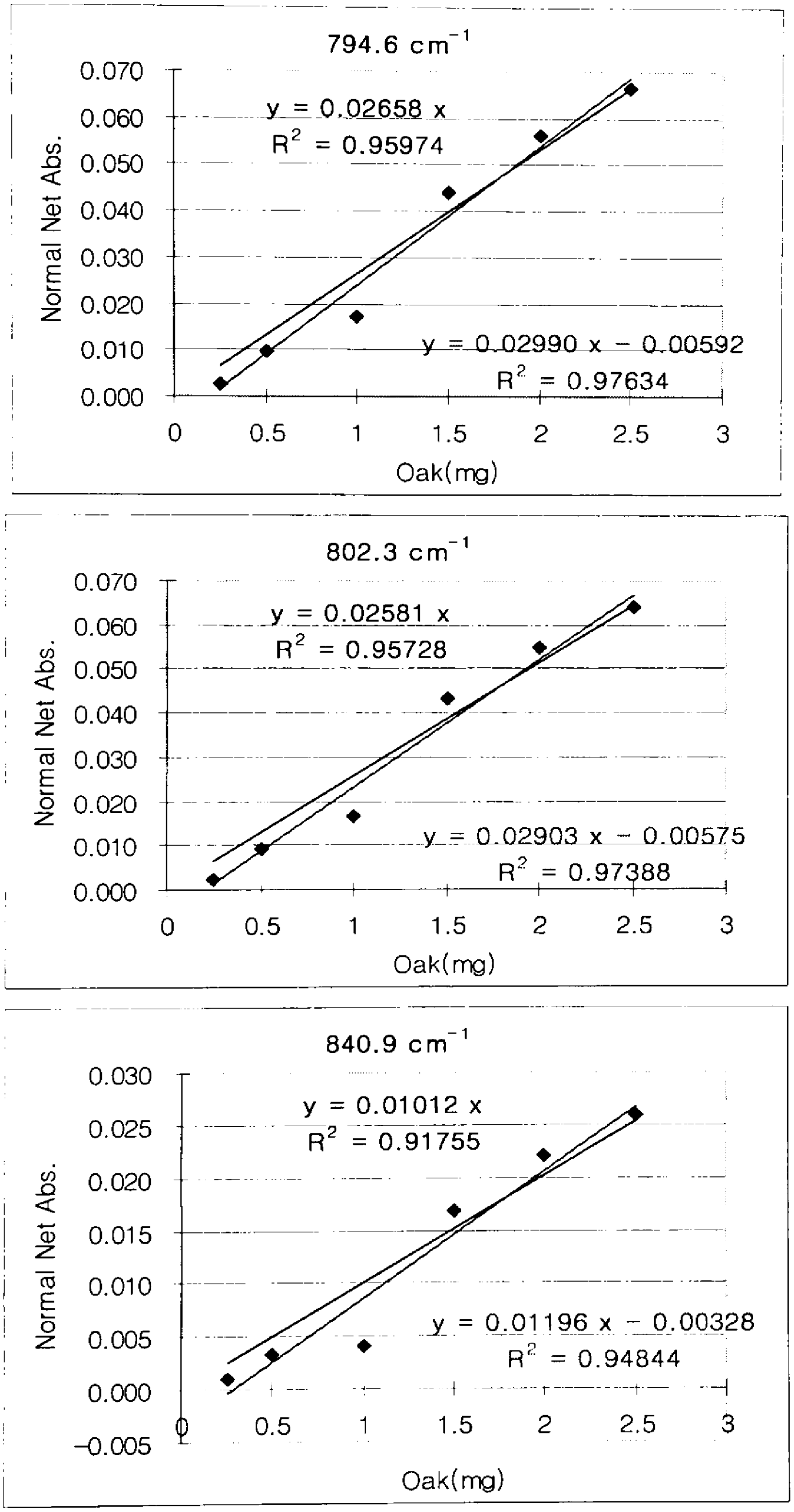


Figure B.3 Oak Standard Calibration Curves at 794.6, 802.3 & 840.9 cm^{-1}

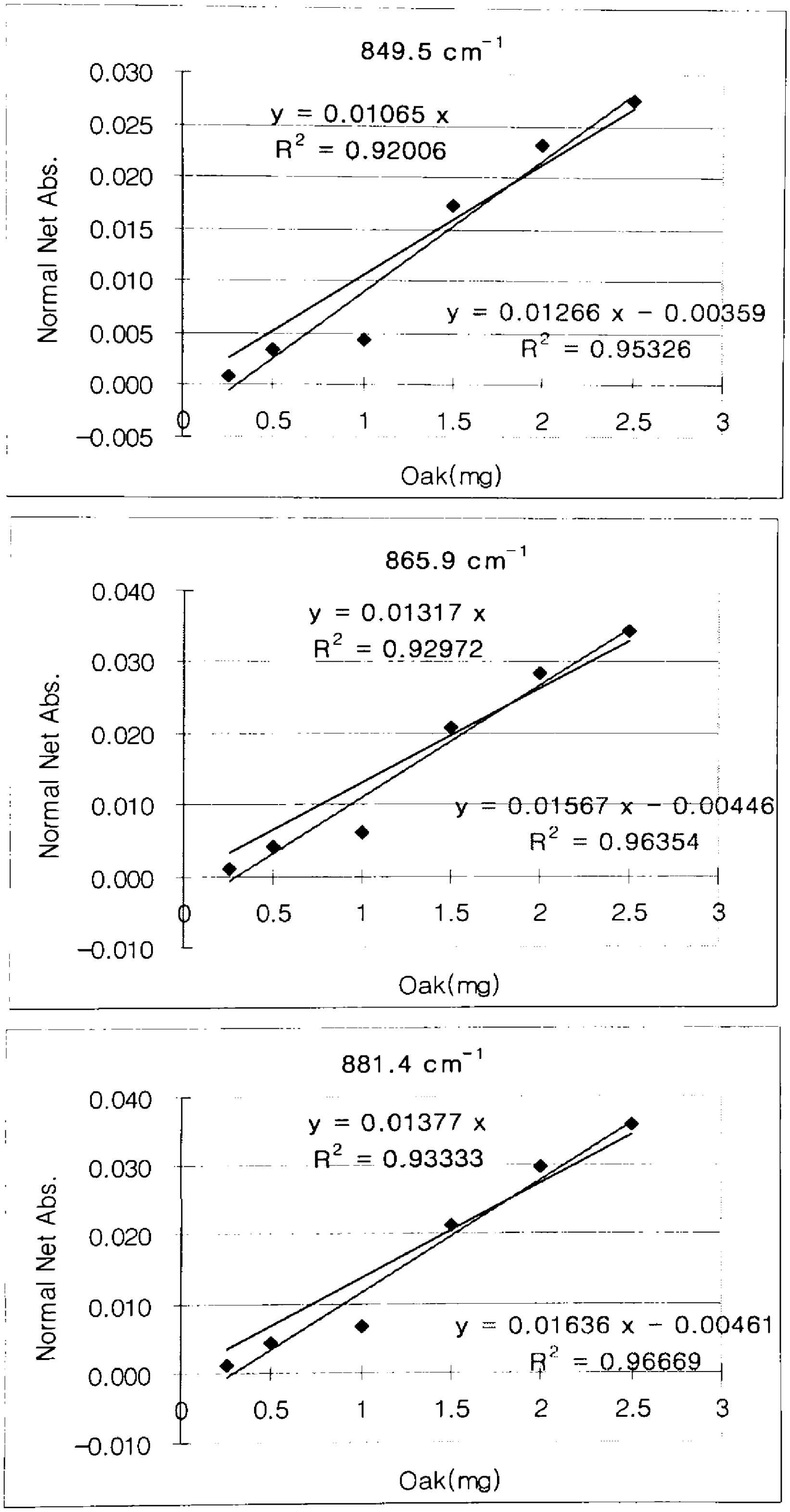


Figure B.4 Oak Standard Calibration Curves at 849.5, 865.9 & 881.4 cm^{-1}

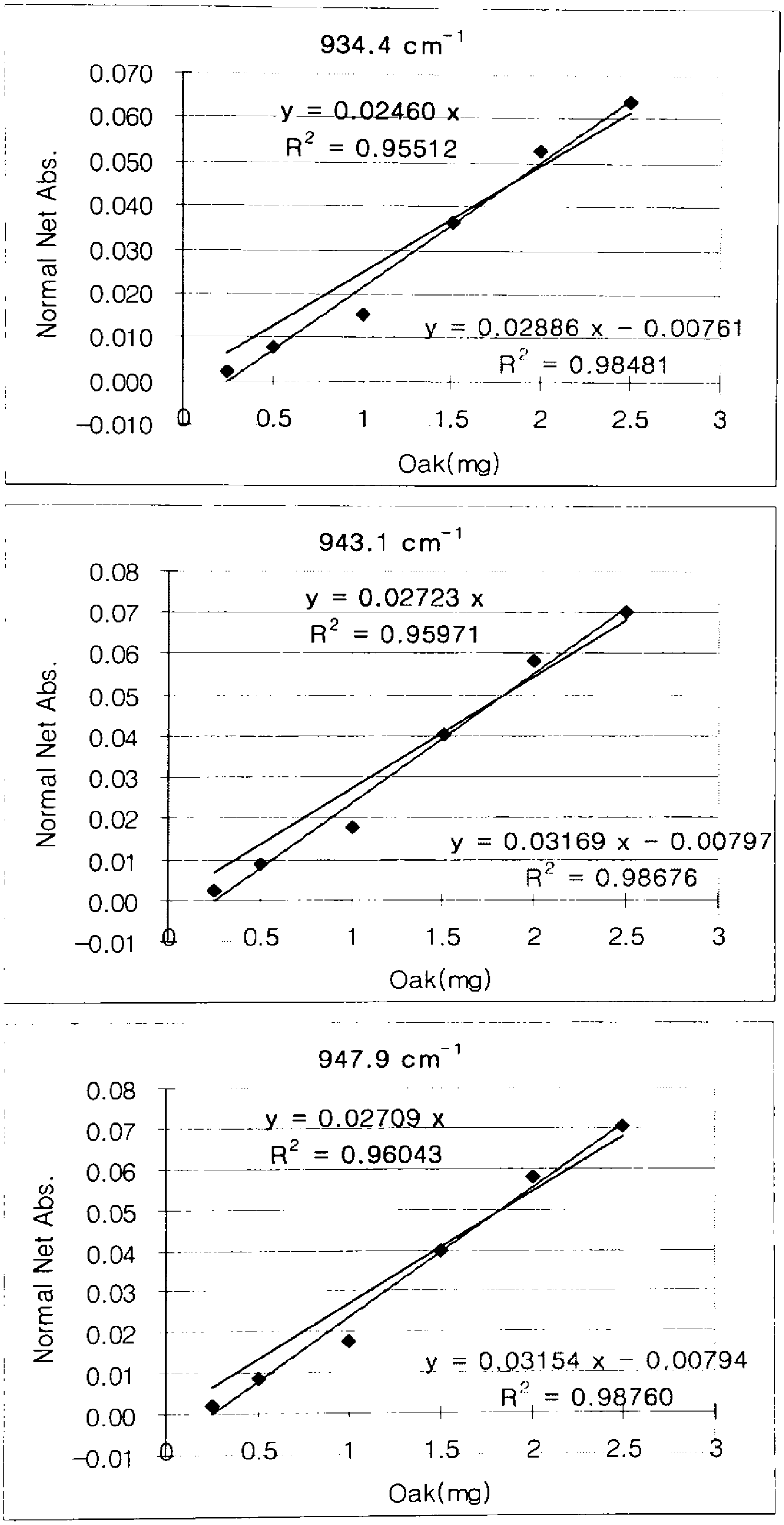


Figure B.5 Oak Standard Calibration Curves at 934.4, 943.1 & 947.9 cm^{-1}

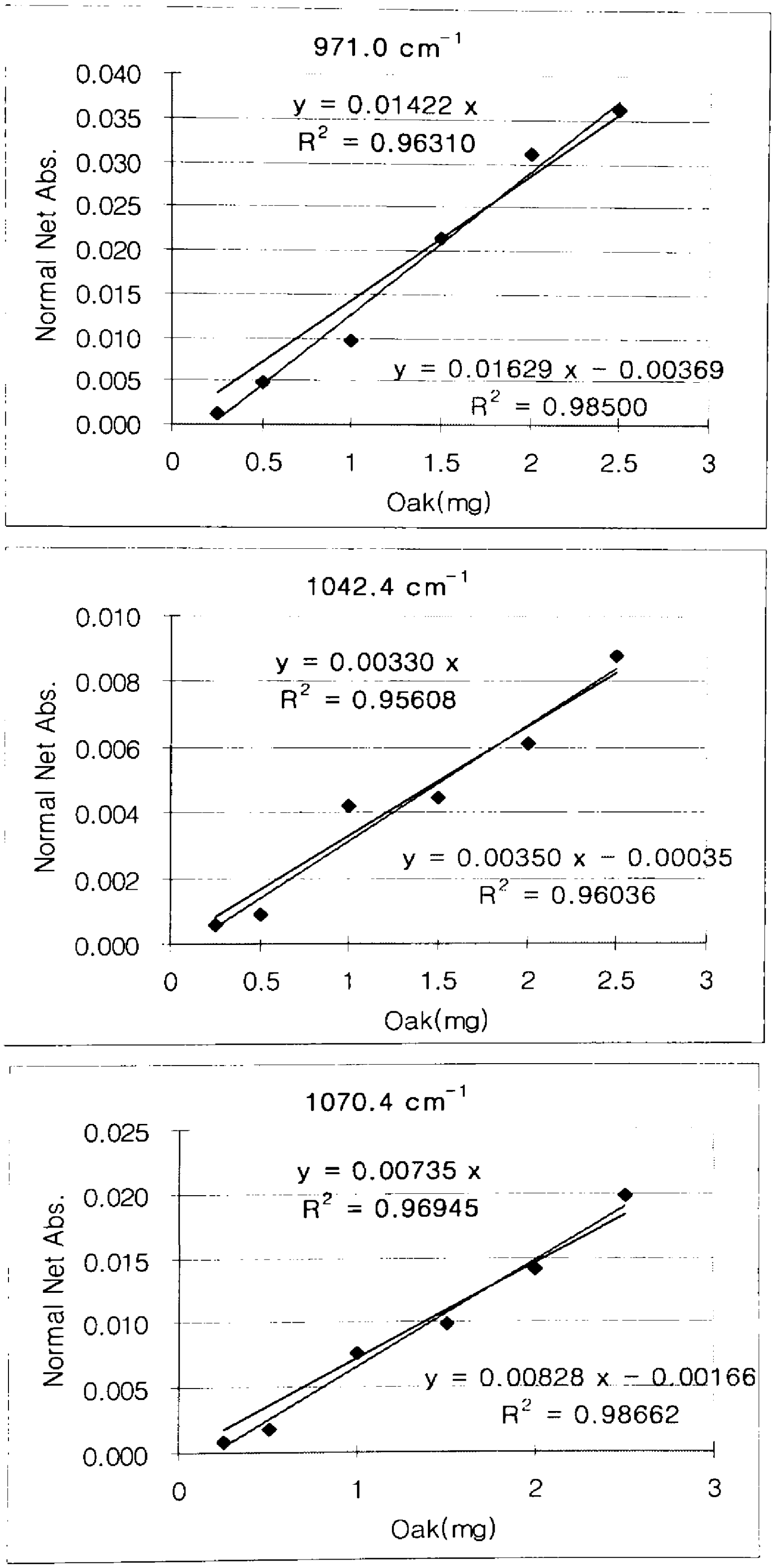


Figure B.6 Oak Standard Calibration Curves at 971.0, 1042.4 & 1070.4 cm^{-1}

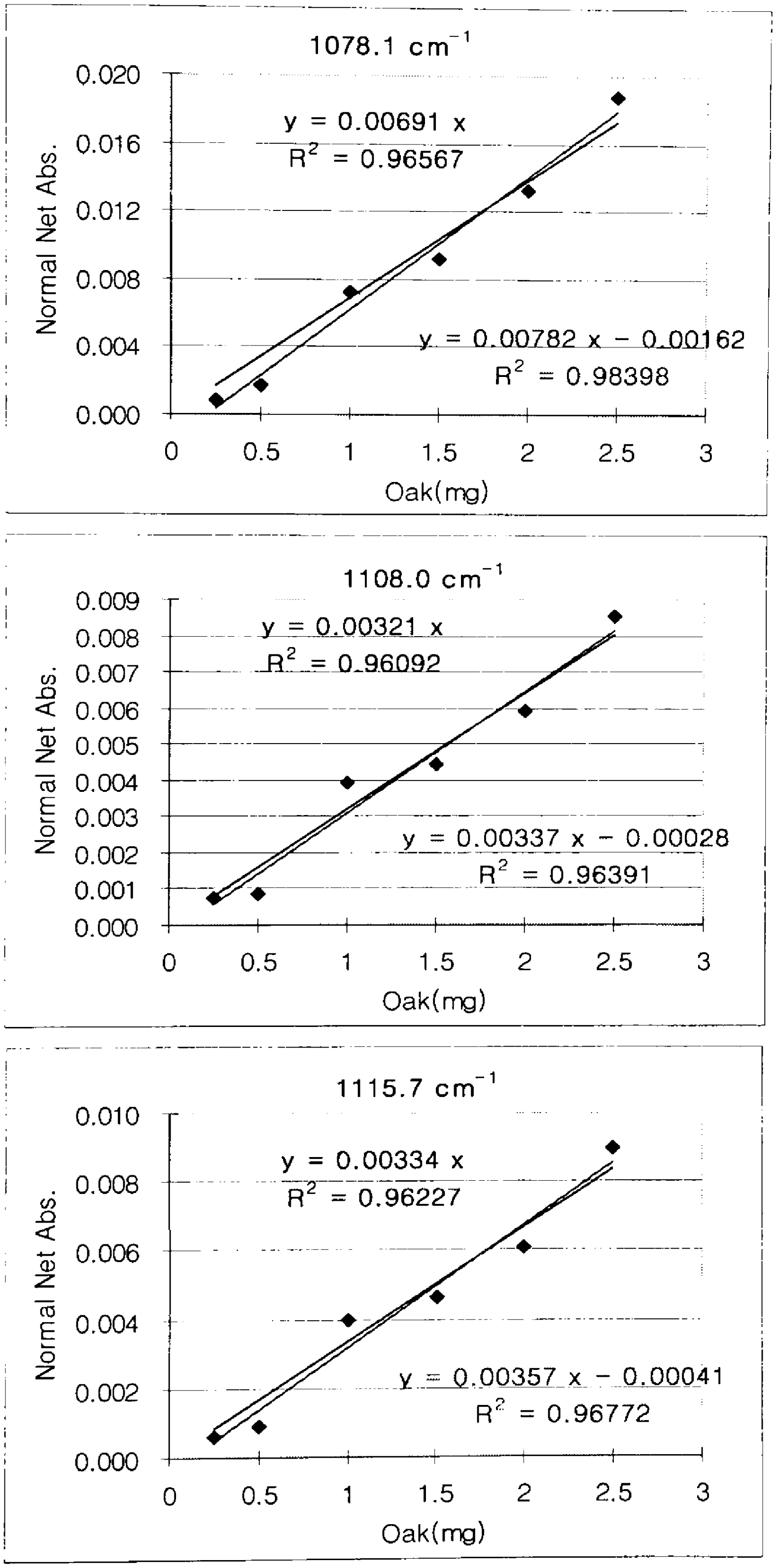


Figure B.7 Oak Standard Calibration Curves at 1078.1, 1108.0 & 1115.7 cm^{-1}

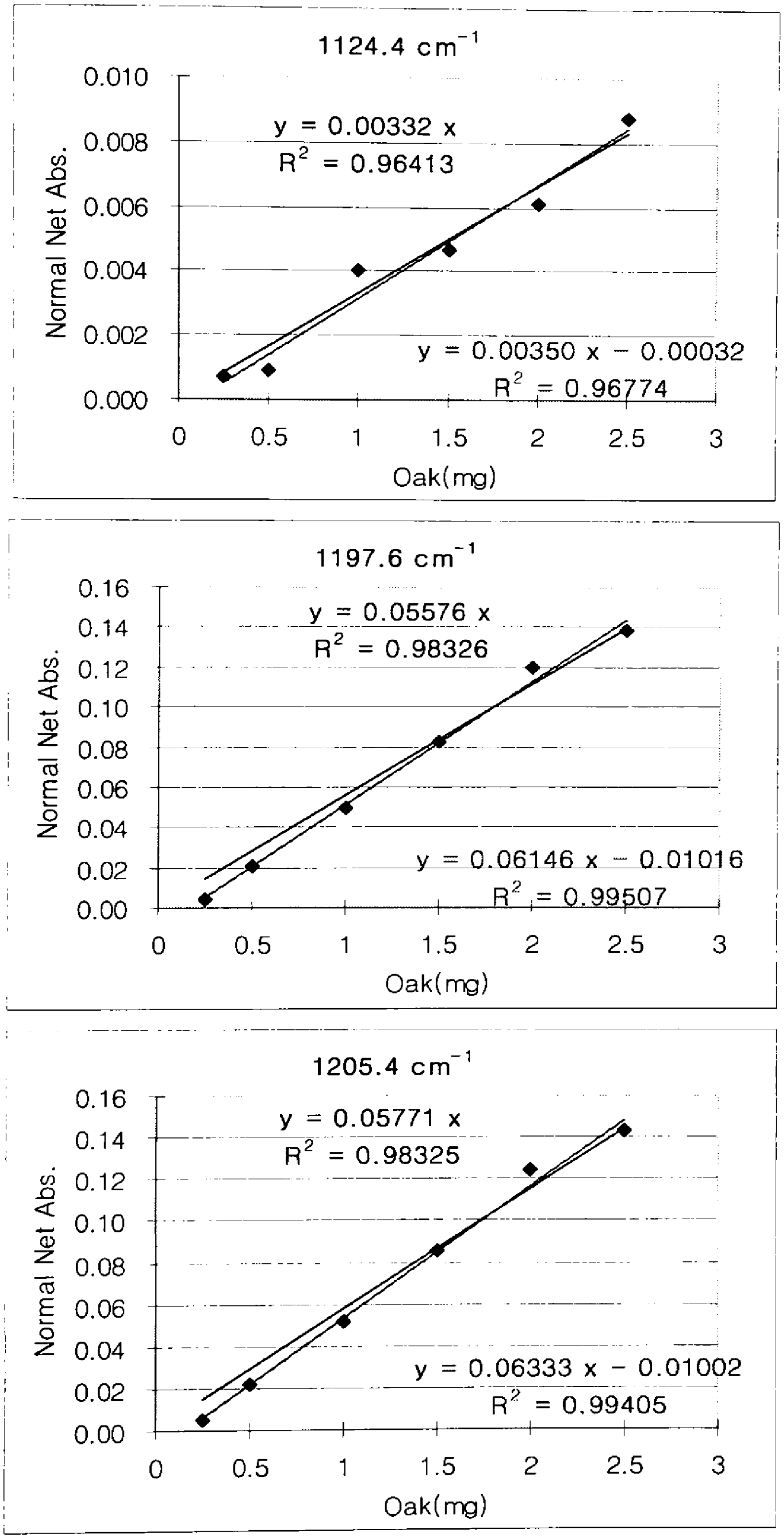


Figure B.8 Oak Standard Calibration Curves at 1124.4, 1197.6 & 1205.4 cm^{-1}

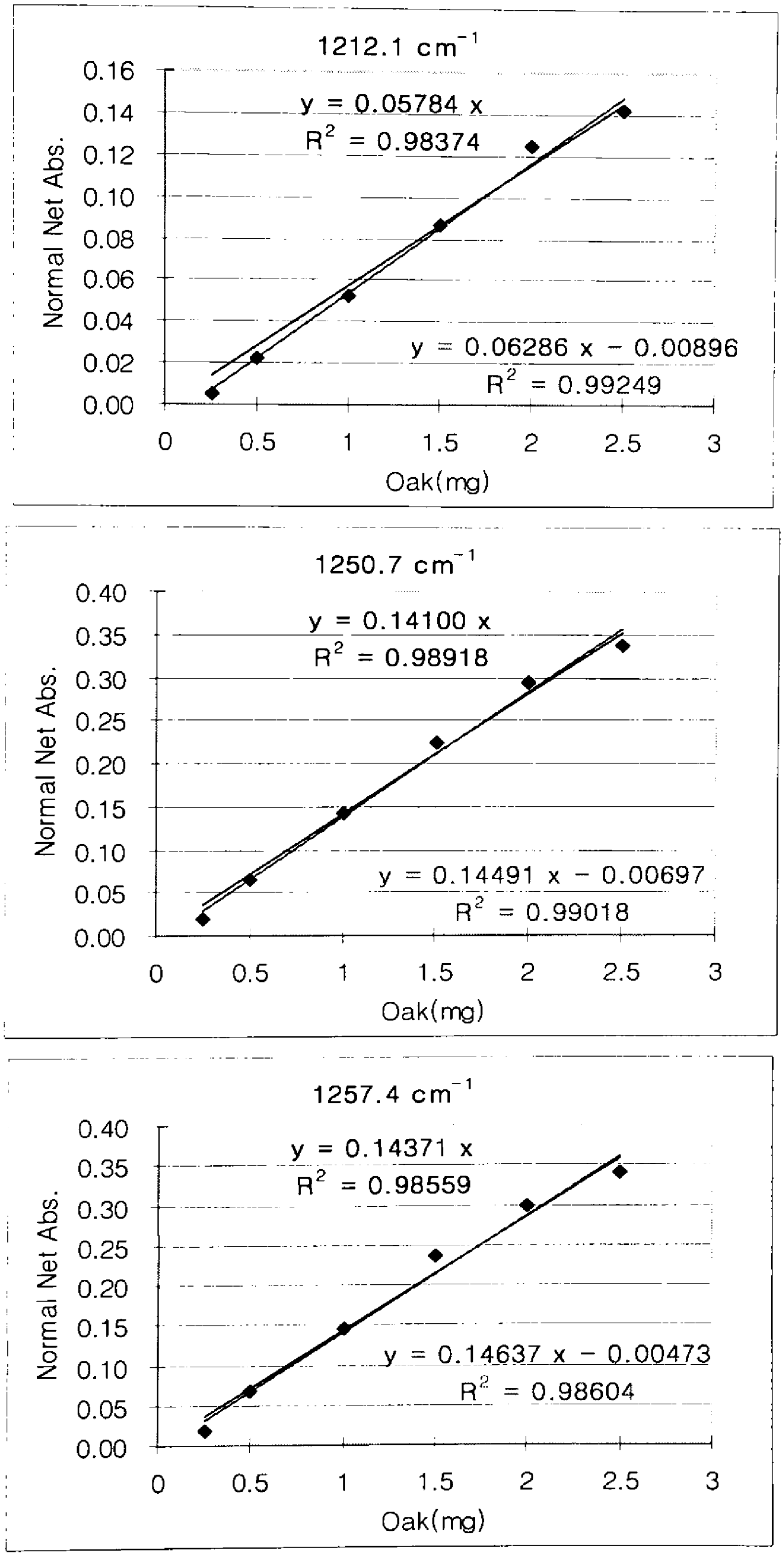


Figure B.9 Oak Standard Calibration Curves at 1212.1, 1250.7 & 1257.4 cm^{-1}

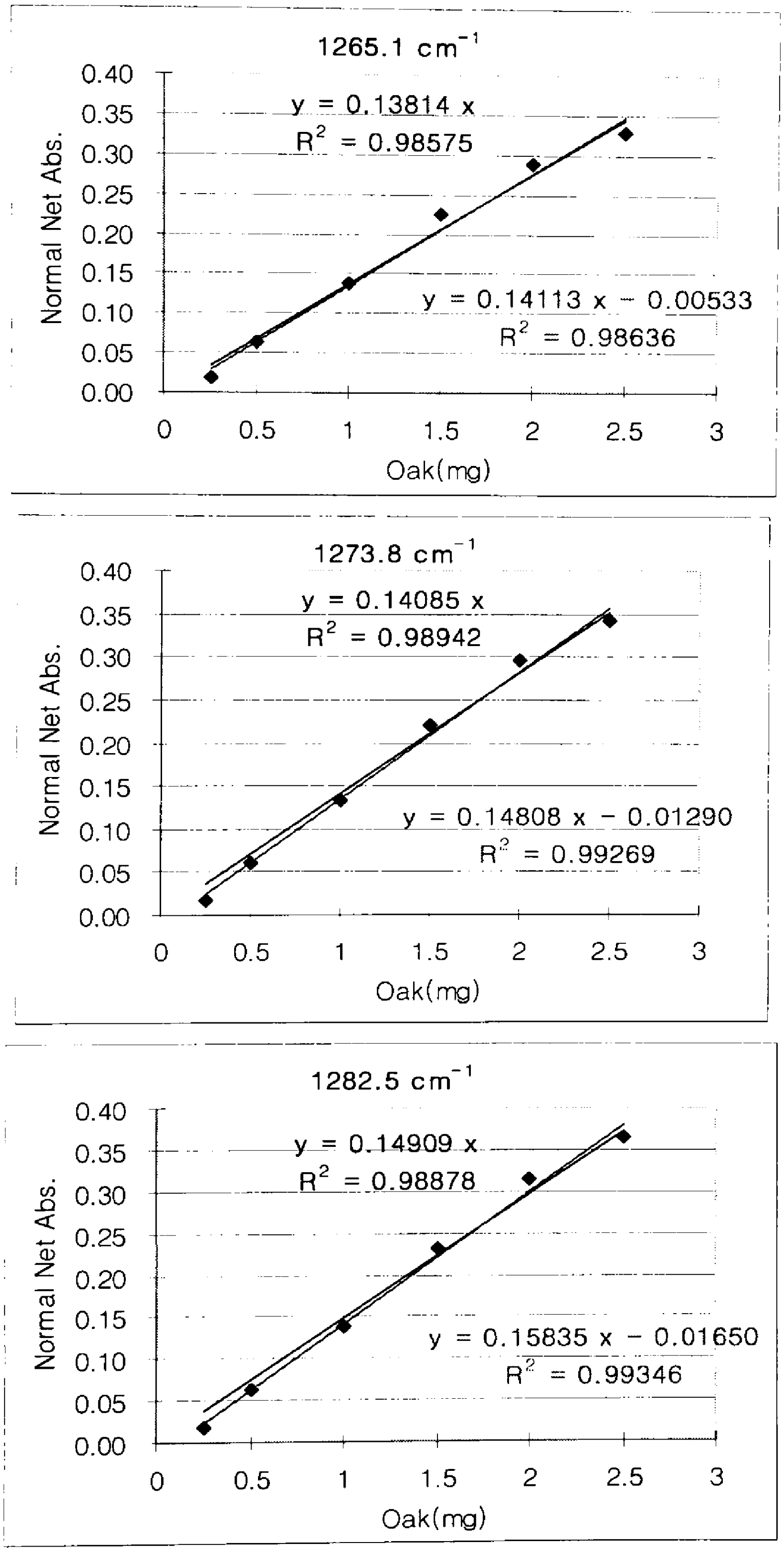


Figure B.10 Oak Standard Calibration Curves at 1265.1, 1273.8 & 1282.5 cm^{-1}

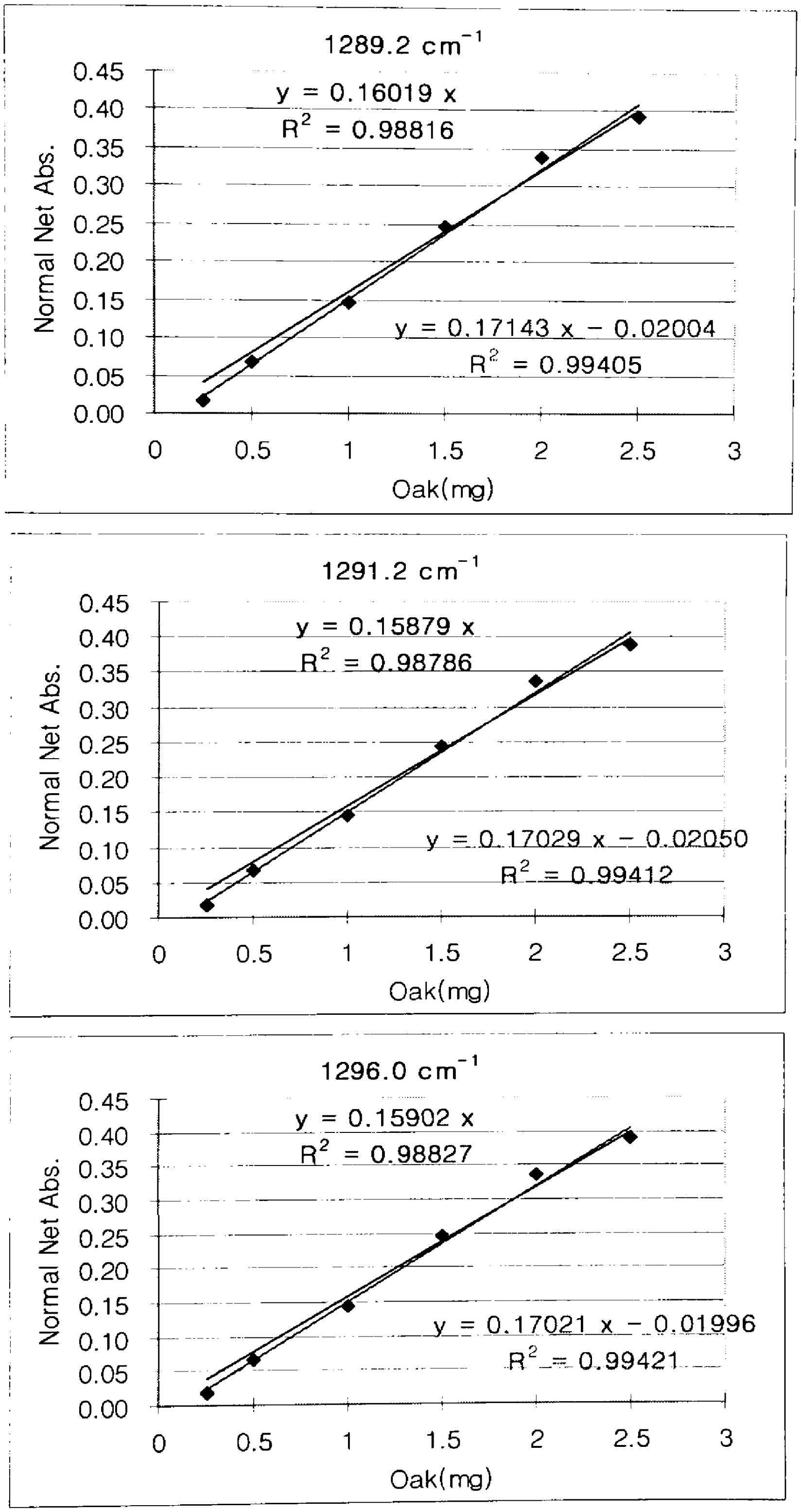


Figure B.11 Oak Standard Calibration Curves at 1289.2, 1291.2 & 1296.0 cm^{-1}

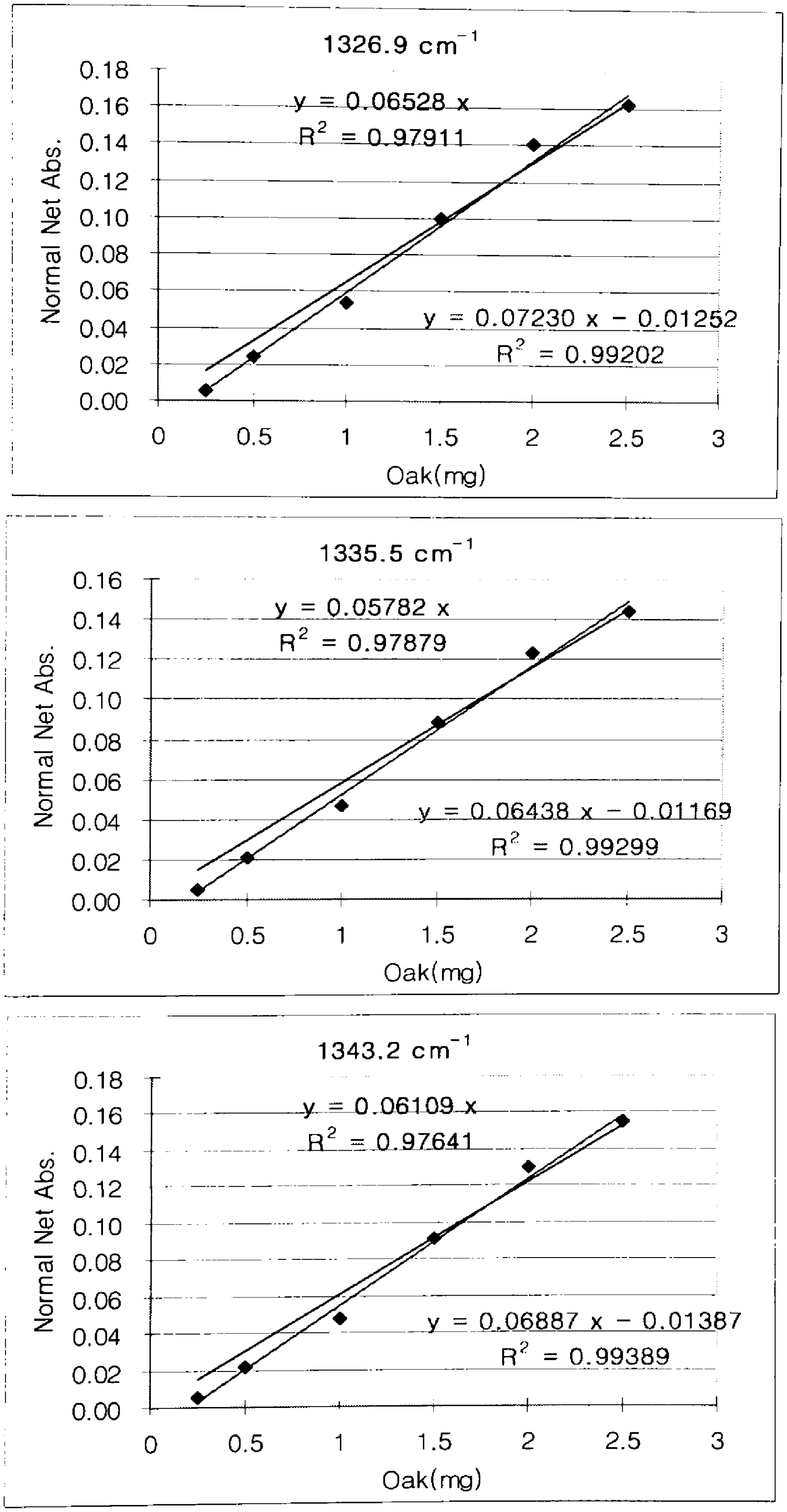


Figure B.12 Oak Standard Calibration Curves at 1326.9, 1335.5 & 1343.2 cm^{-1}

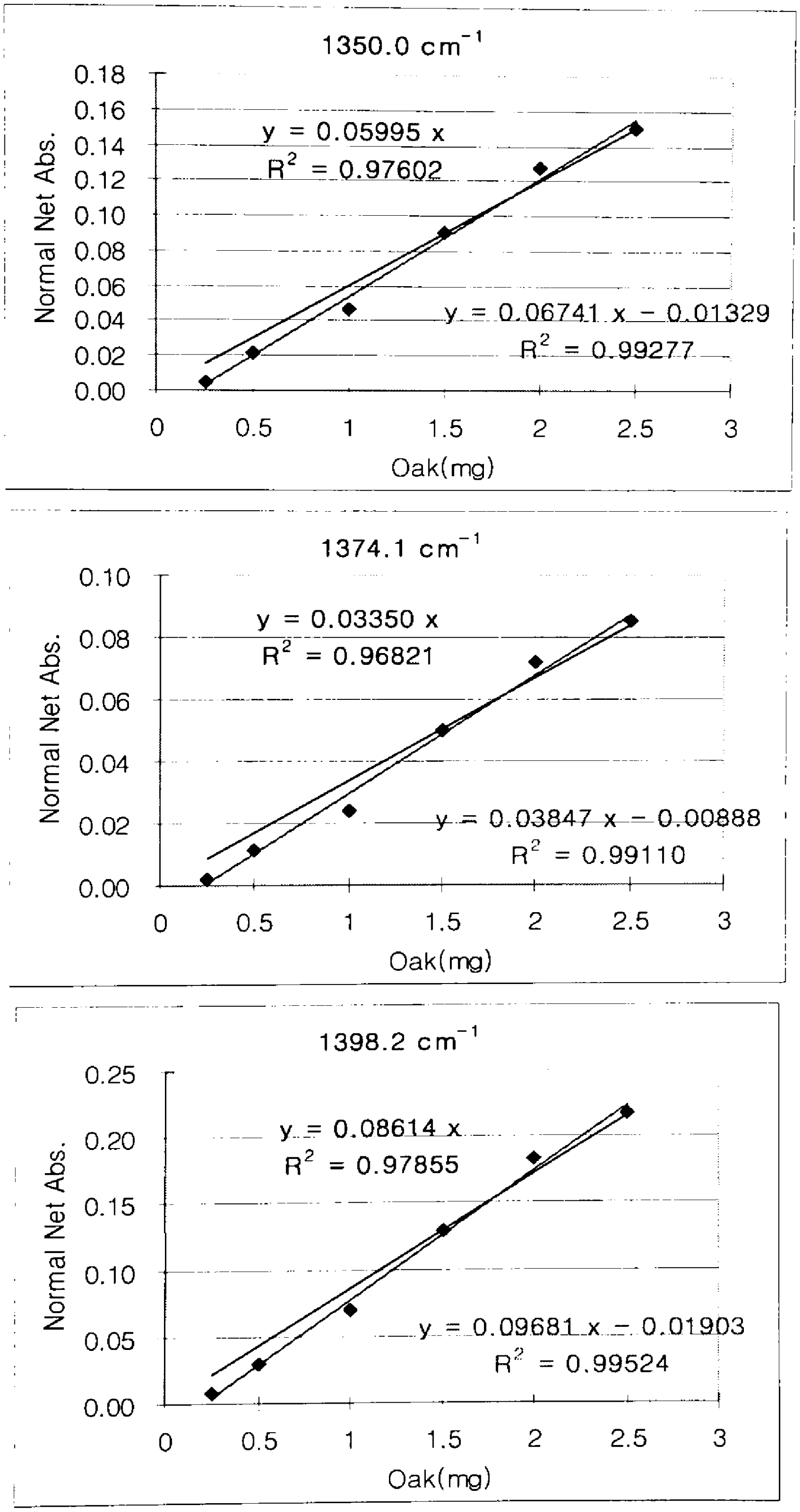


Figure B.13 Oak Standard Calibration Curves at 1350.0, 1374.1 & 1398.2 cm^{-1}

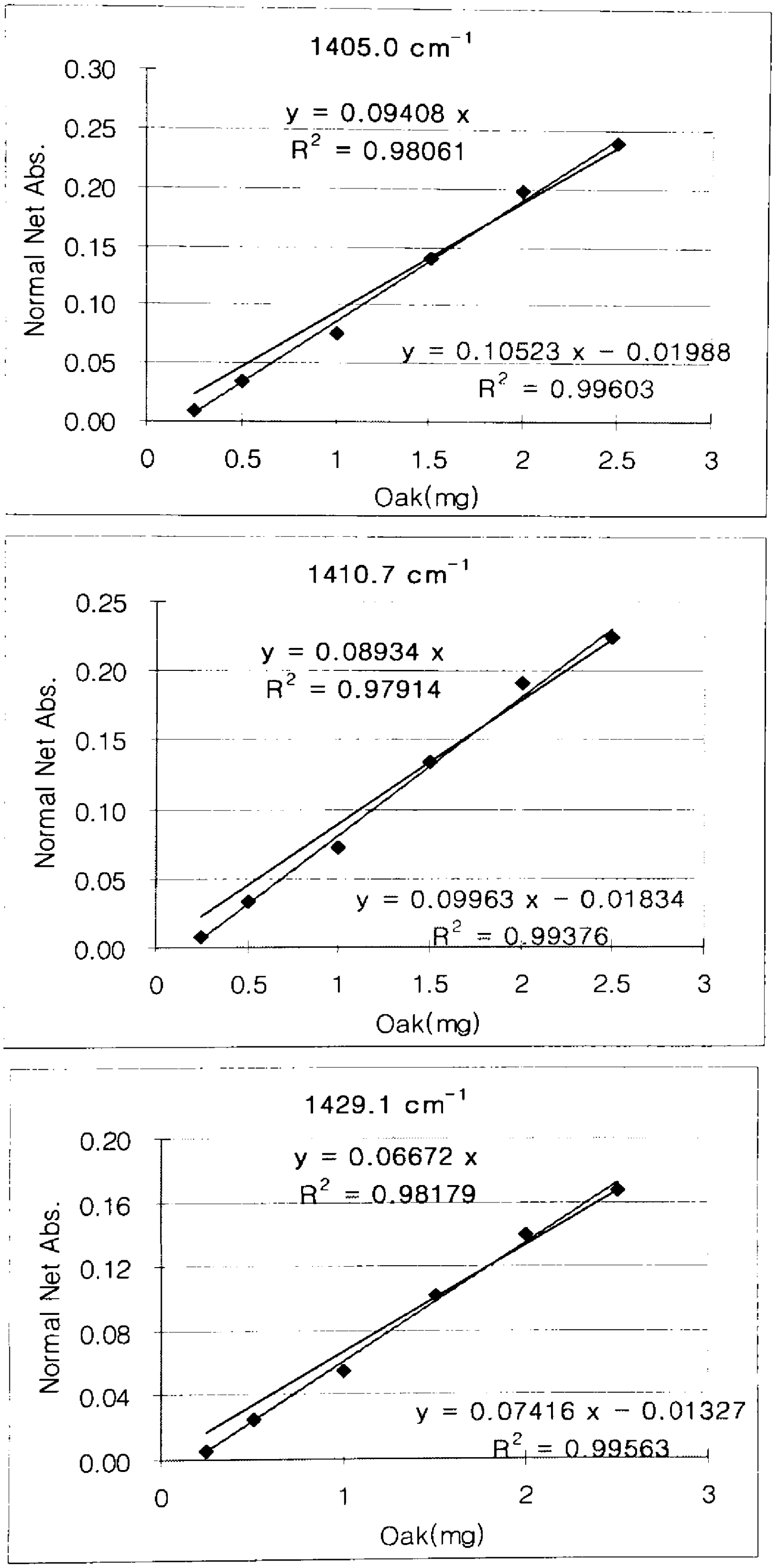


Figure B.14 Oak Standard Calibration Curves at 1405.0, 1410.7 & 1429.1 cm^{-1}

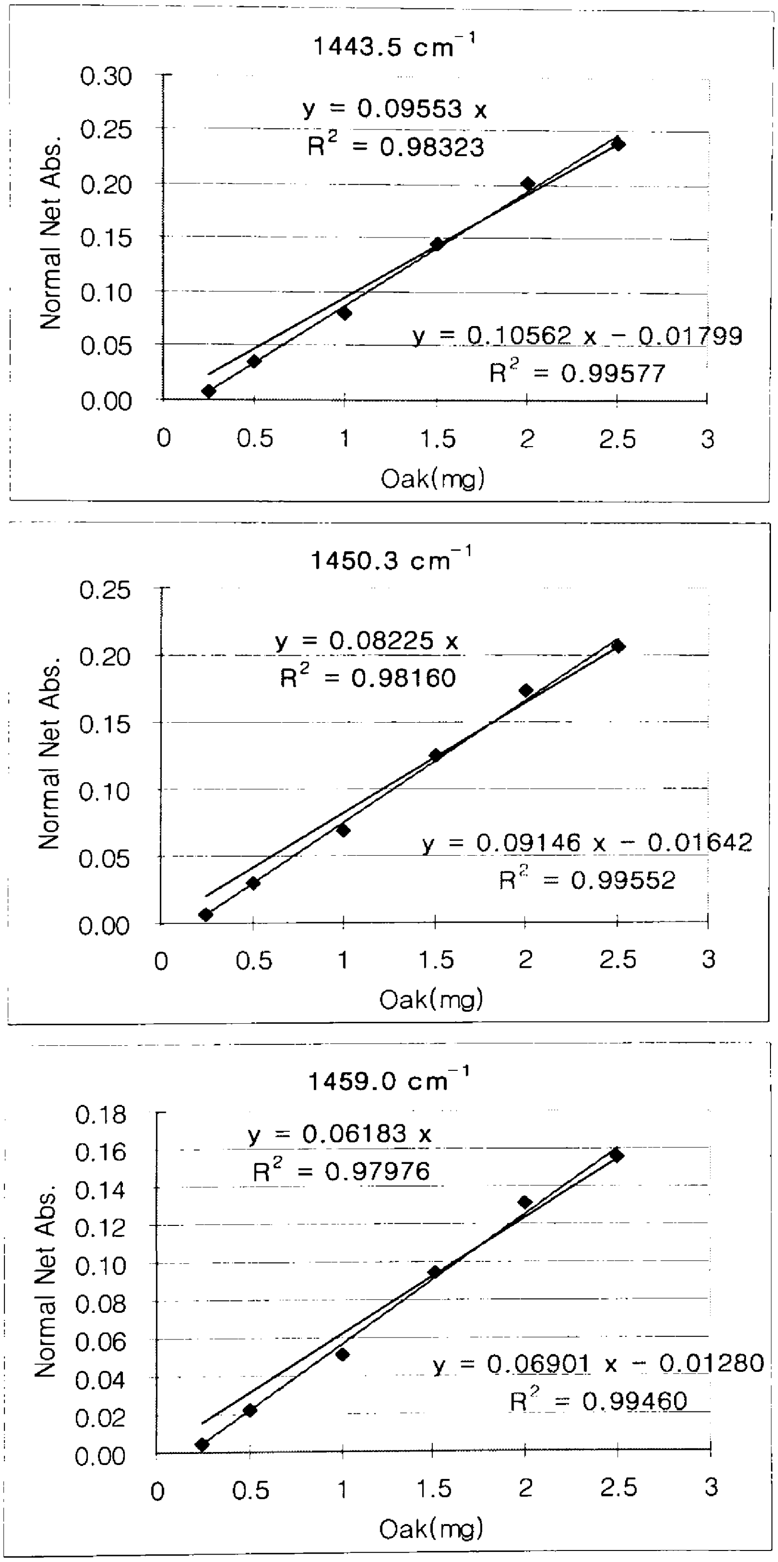


Figure B.15 Oak Standard Calibration Curves at 1443.5, 1450.3 & 1459.0 cm^{-1}

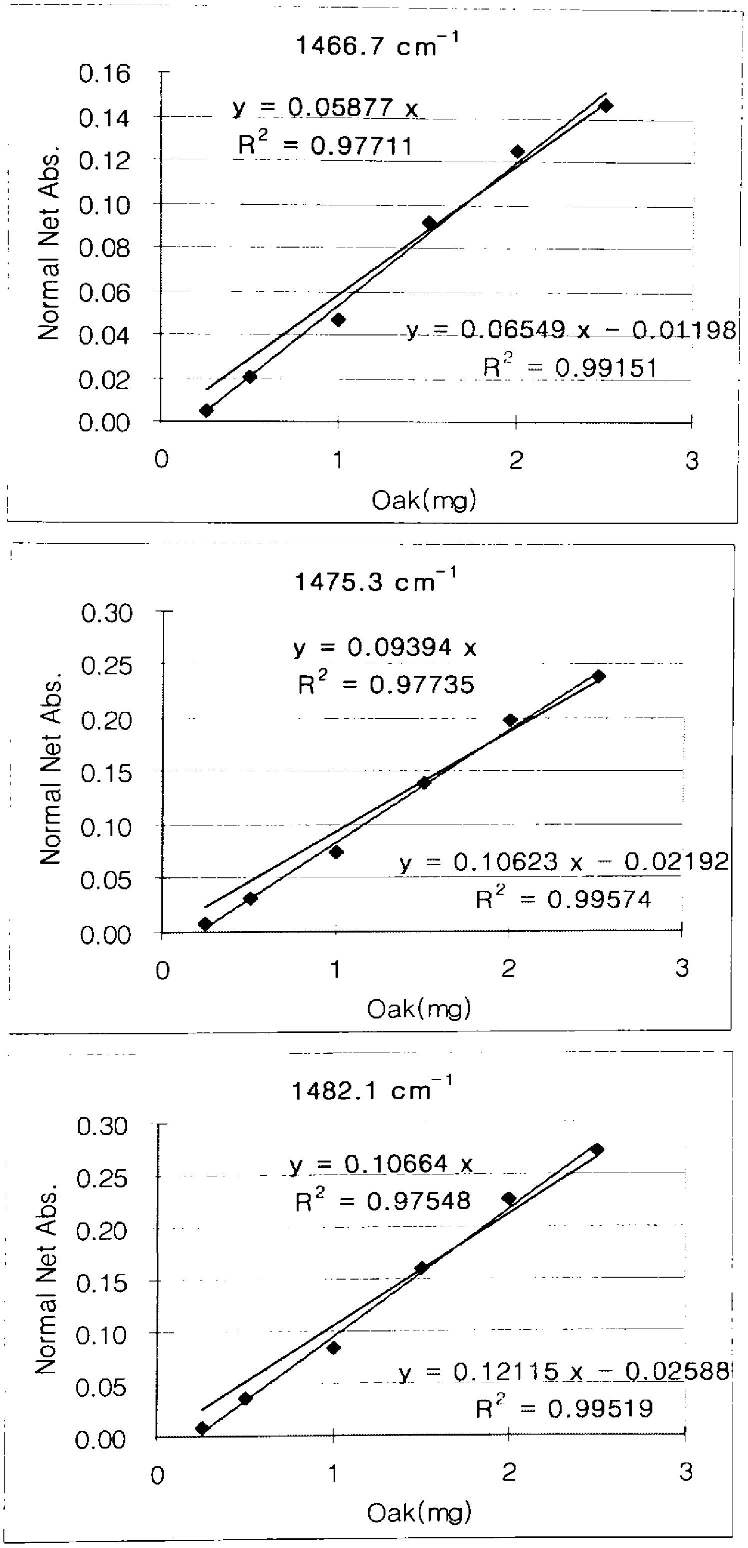


Figure B.16 Oak Standard Calibration Curves at 1466.7, 1475.3 & 1482.1 cm^{-1}

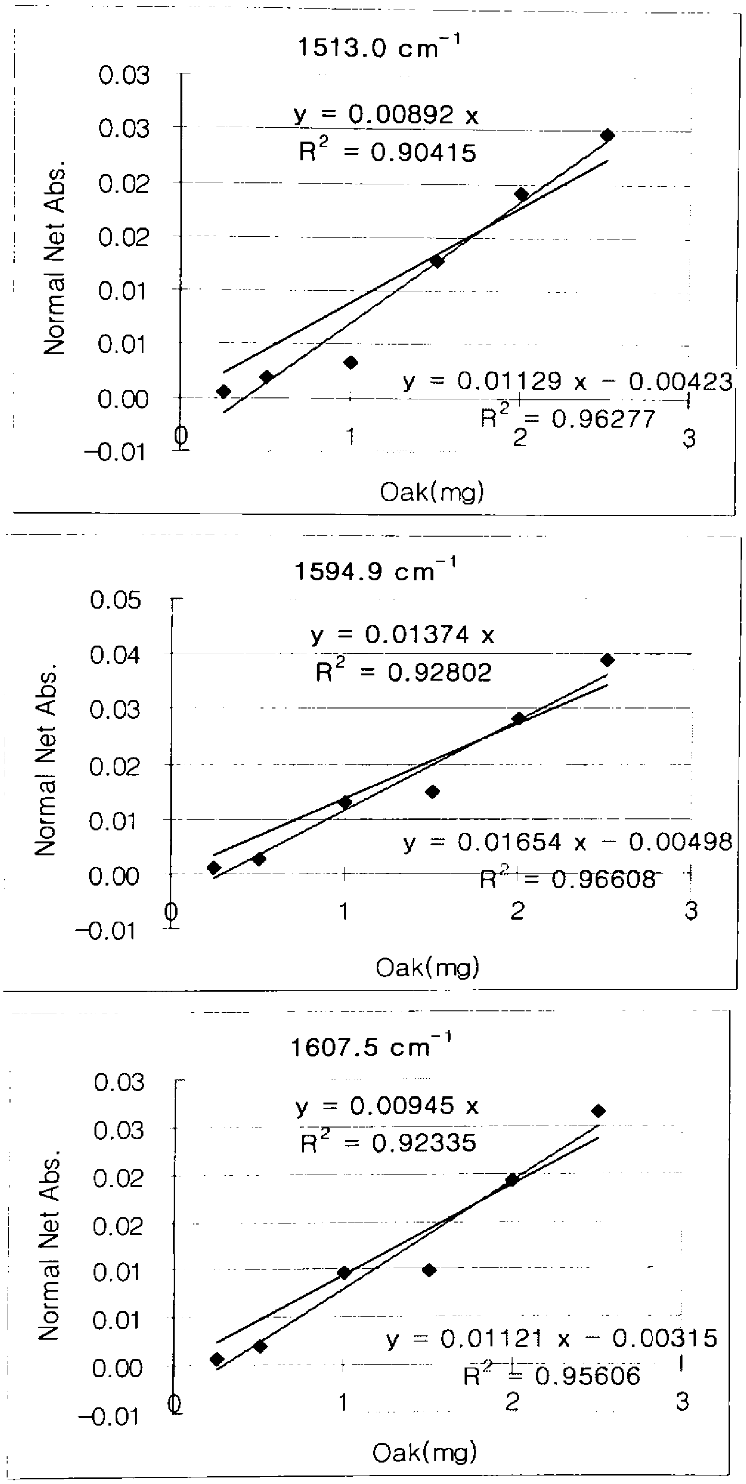


Figure B.17 Oak Standard Calibration Curves at 1513.0, 1594.9 & 1607.5 cm^{-1}

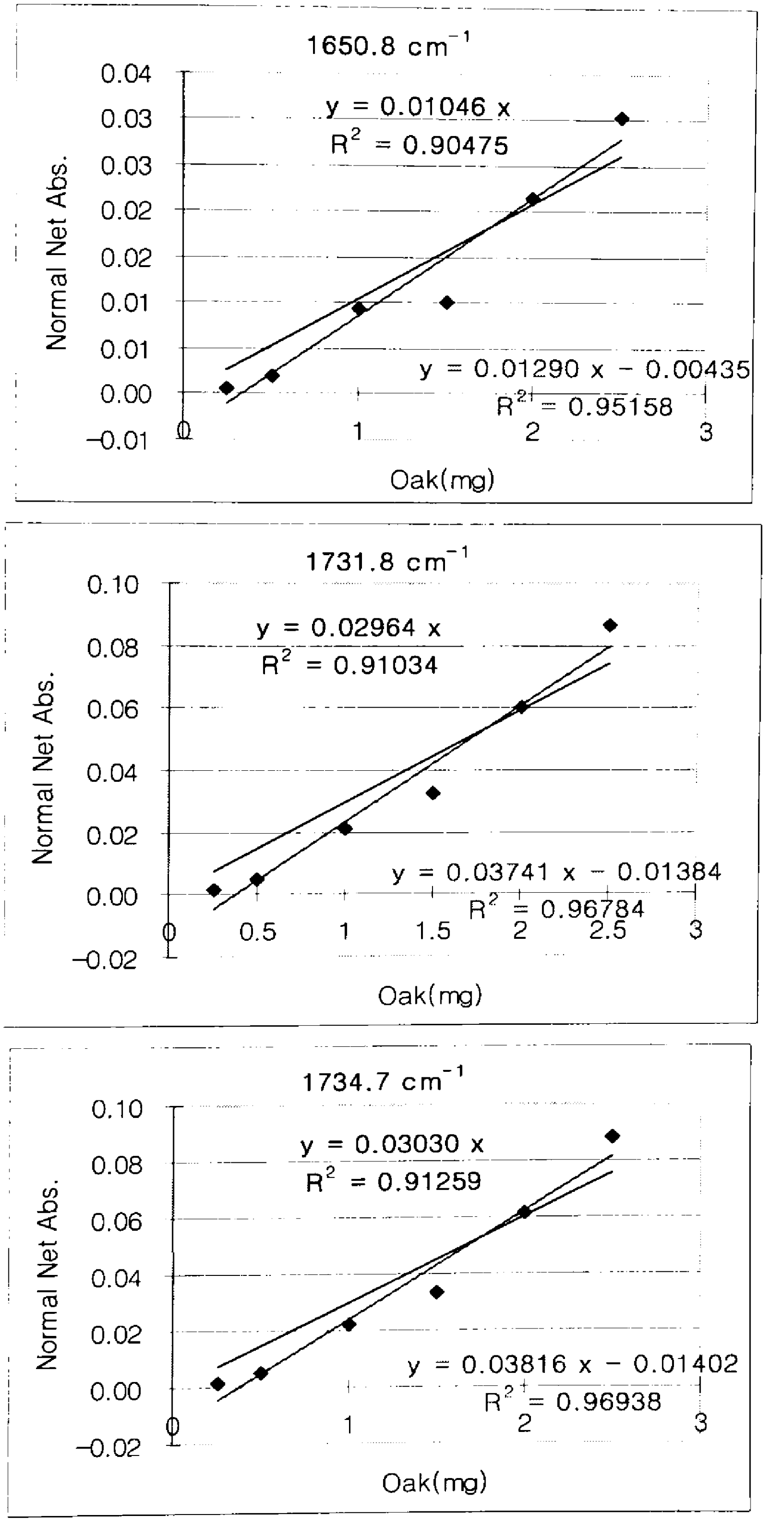


Figure B.18 Oak Standard Calibration Curves at 1650.8, 1731.8 & 1734.7 cm^{-1}

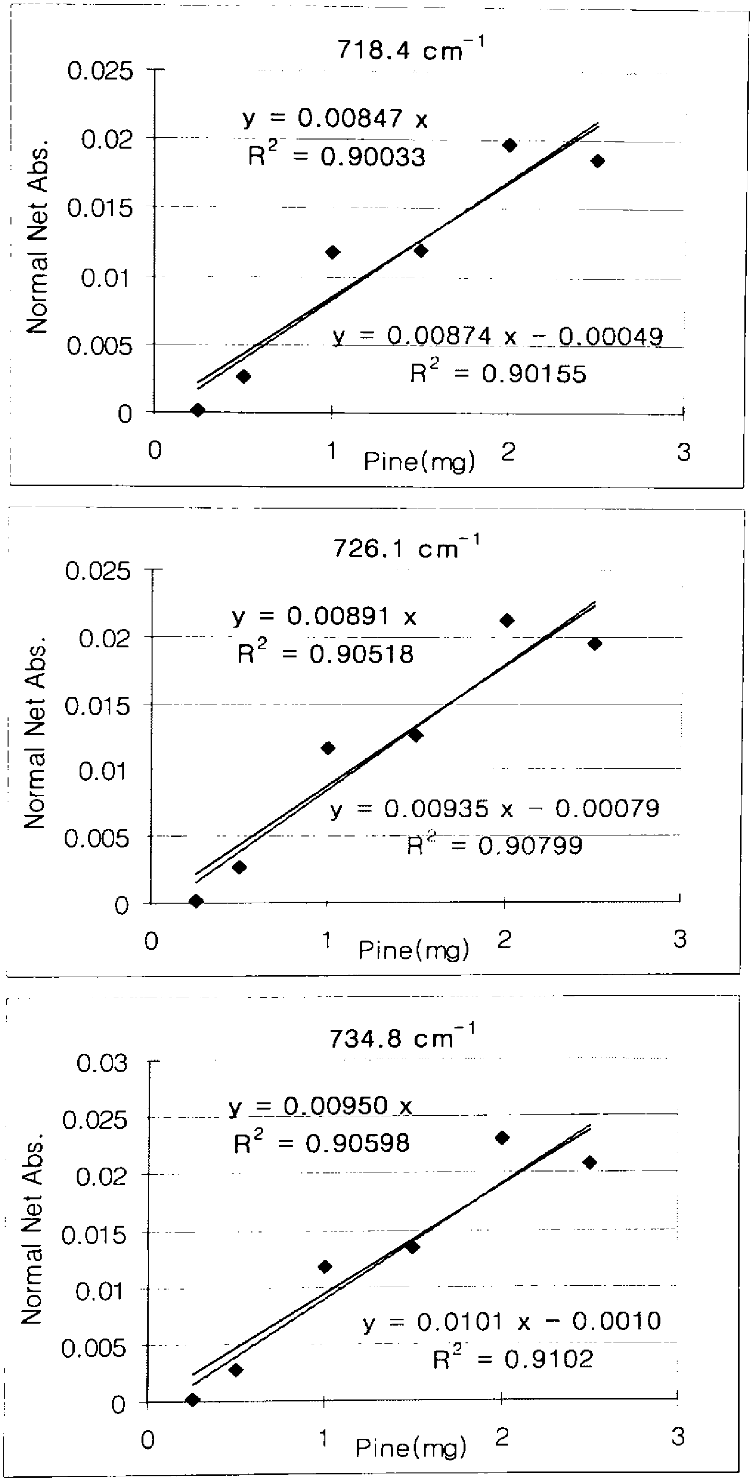


Figure B.19 Pine Standard Calibration Curves at 718.4, 726.1 & 734.8 cm^{-1}

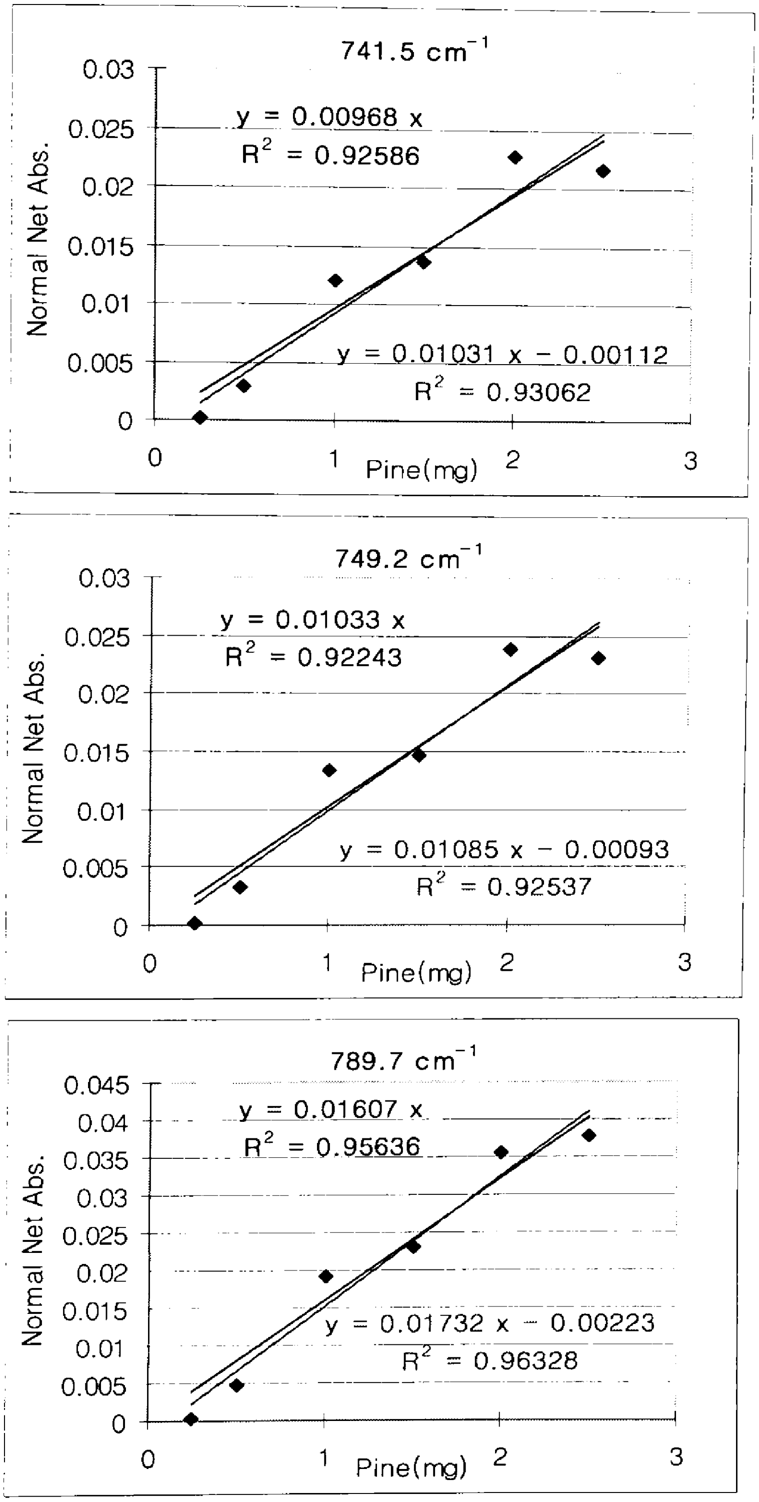


Figure B.20 Pine Standard Calibration Curves at 741.5, 749.2 & 789.7 cm^{-1}

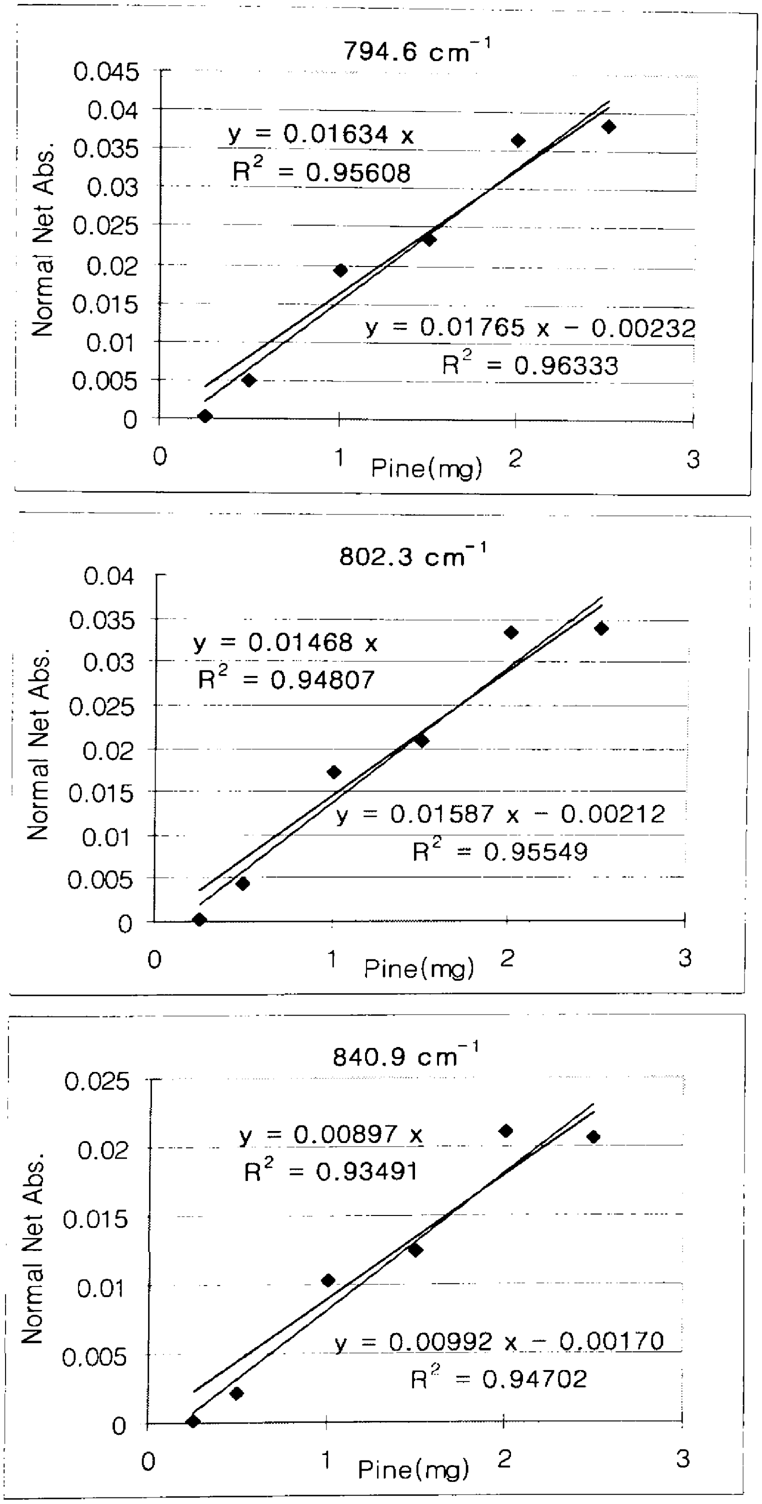


Figure B.21 Pine Standard Calibration Curves at 794.6, 802.3 & 840.9 cm^{-1}

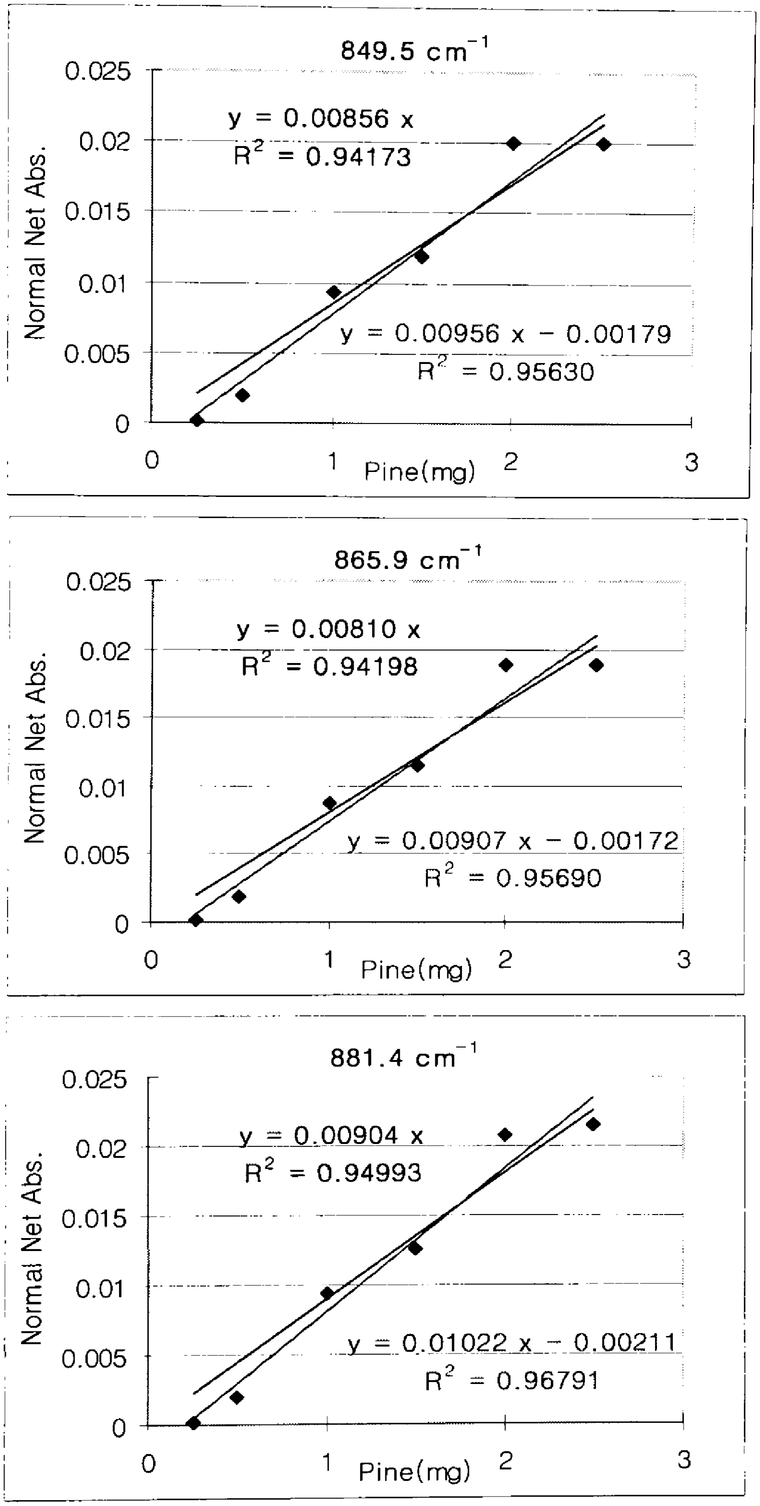


Figure B.22 Pine Standard Calibration Curves at 849.5, 865.9 & 881.4 cm^{-1}

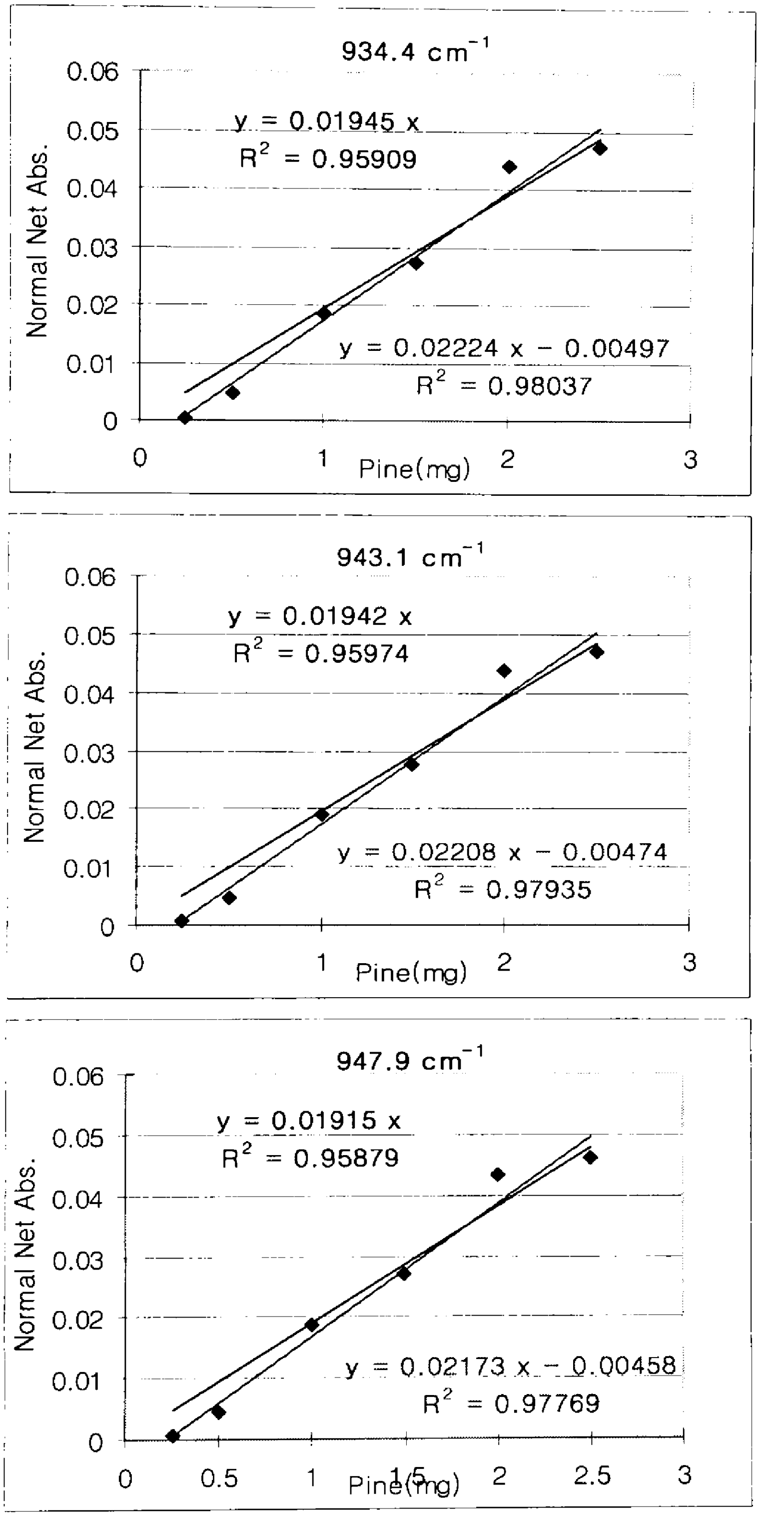


Figure B.23 Pine Standard Calibration Curves at 934.4, 943.1 & 947.9 cm^{-1}

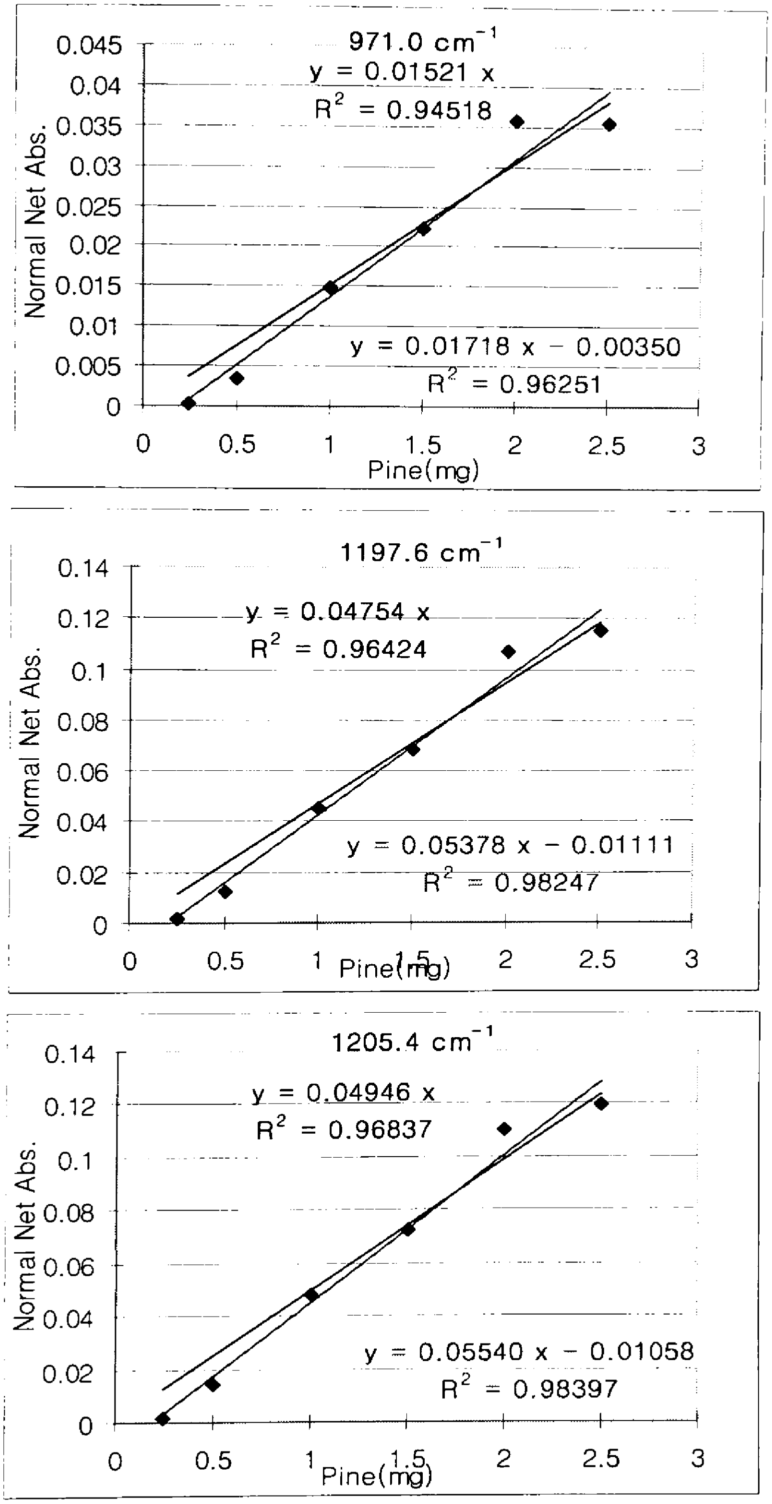


Figure B.24 Pine Standard Calibration Curves at 971.0, 1197.6 & 1205.4 cm^{-1}

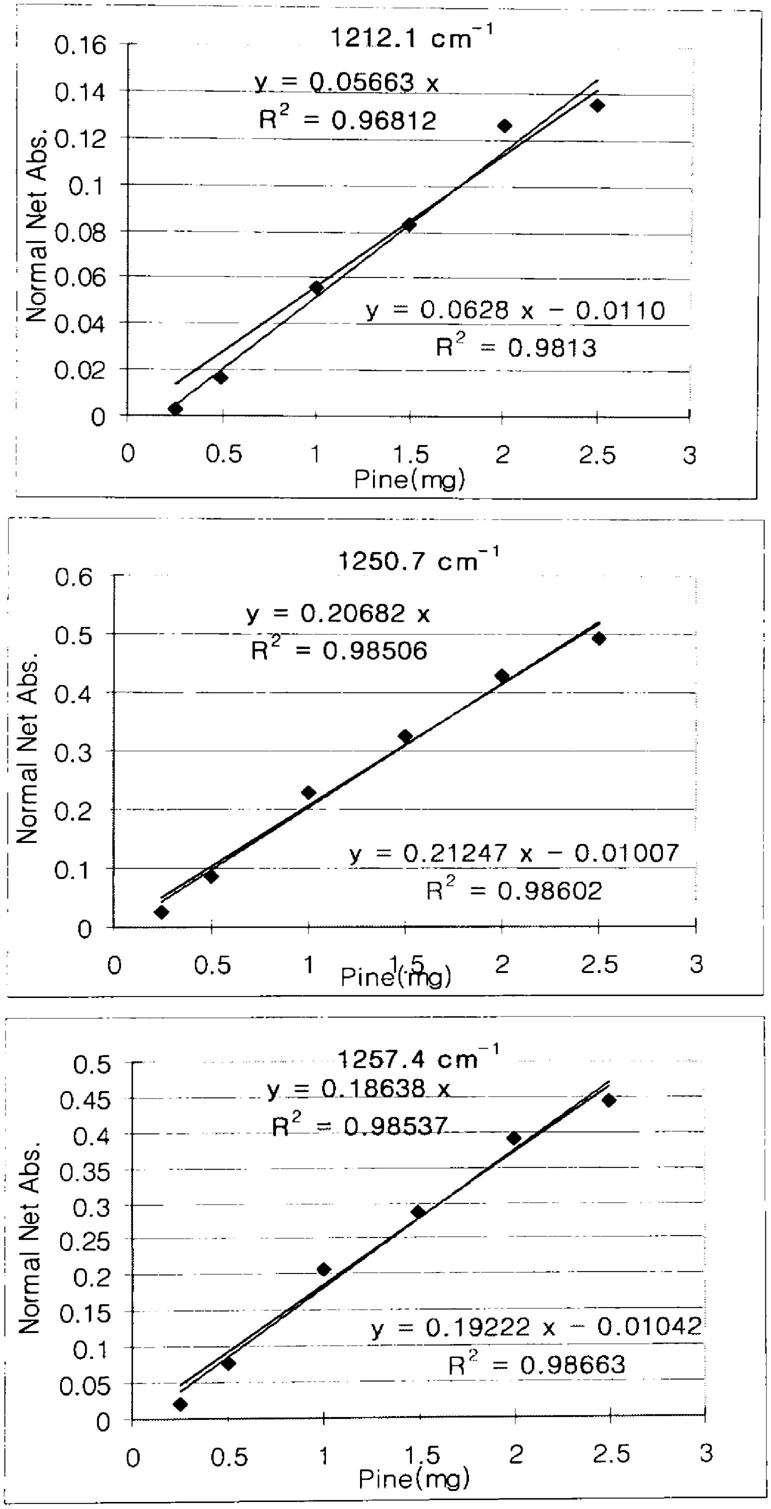


Figure B.25 Pine Standard Calibration Curves at 1212.1, 1250.7 & 1257.4 cm^{-1}

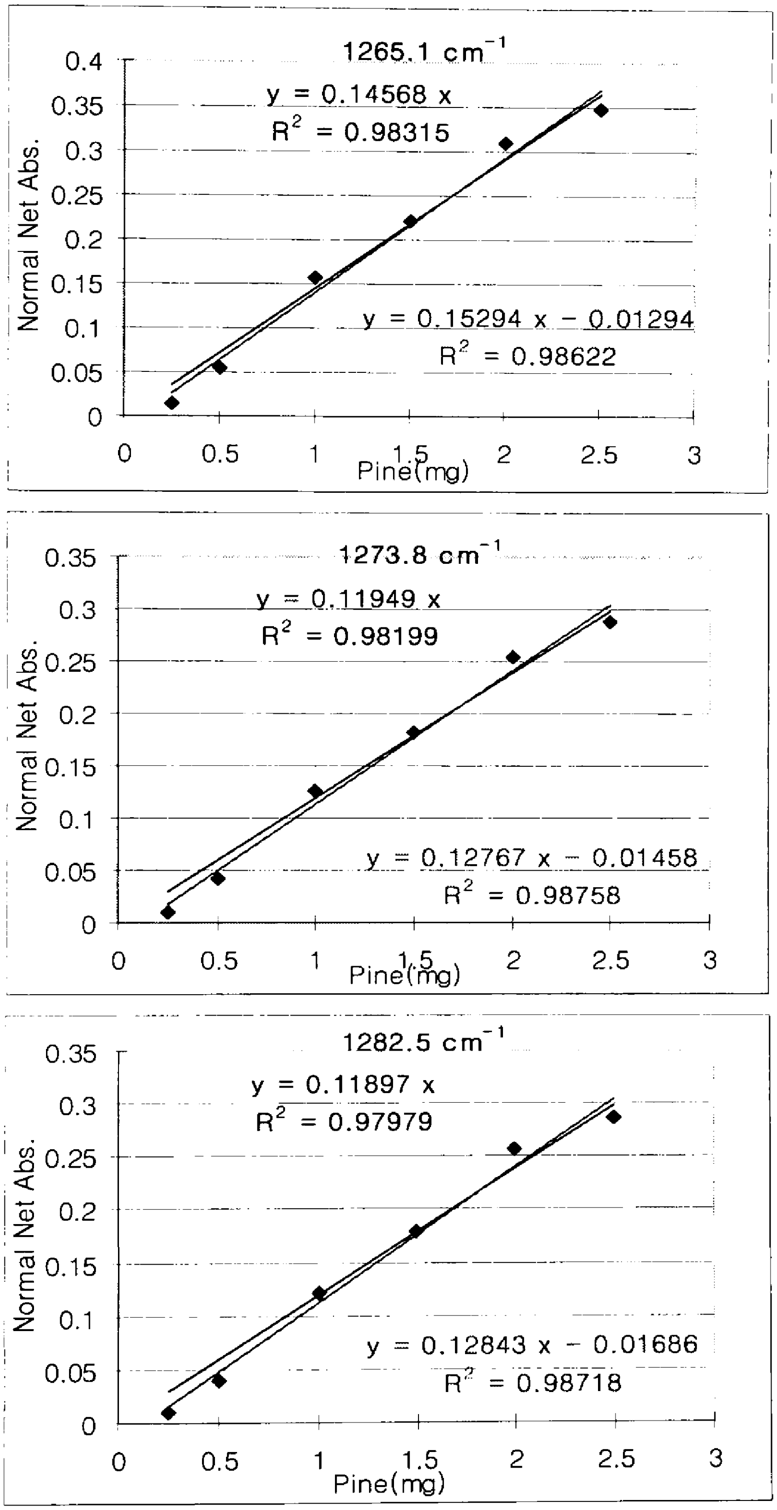


Figure B.26 Pine Standard Calibration Curves at 1265.1, 1273.8 & 1282.5 cm^{-1}

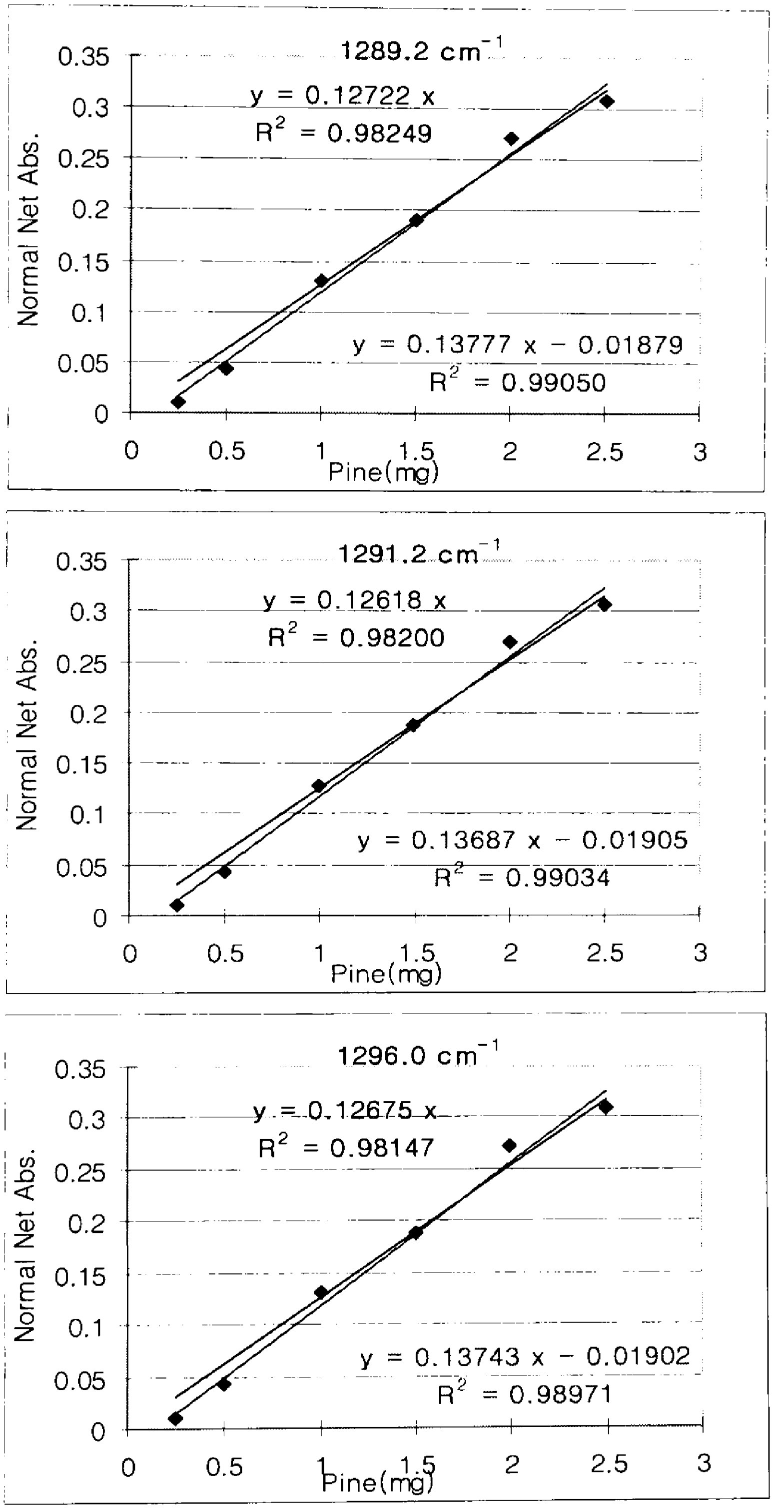


Figure B.27 Pine Standard Calibration Curves at 1289.2, 1291.2 & 1296.0 cm^{-1}

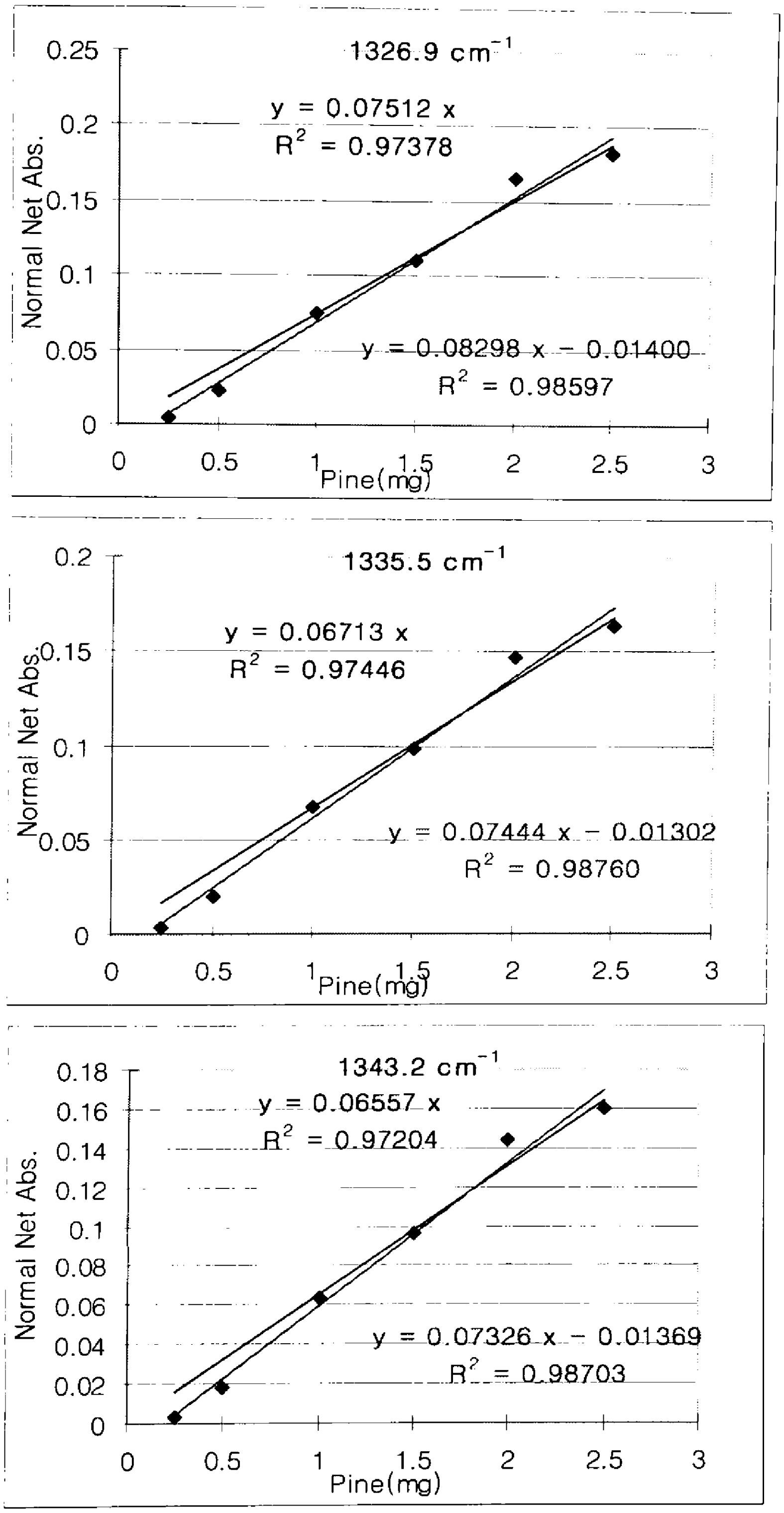


Figure B.28 Pine Standard Calibration Curves at 1326.9, 1335.5 & 1343.2 cm^{-1}

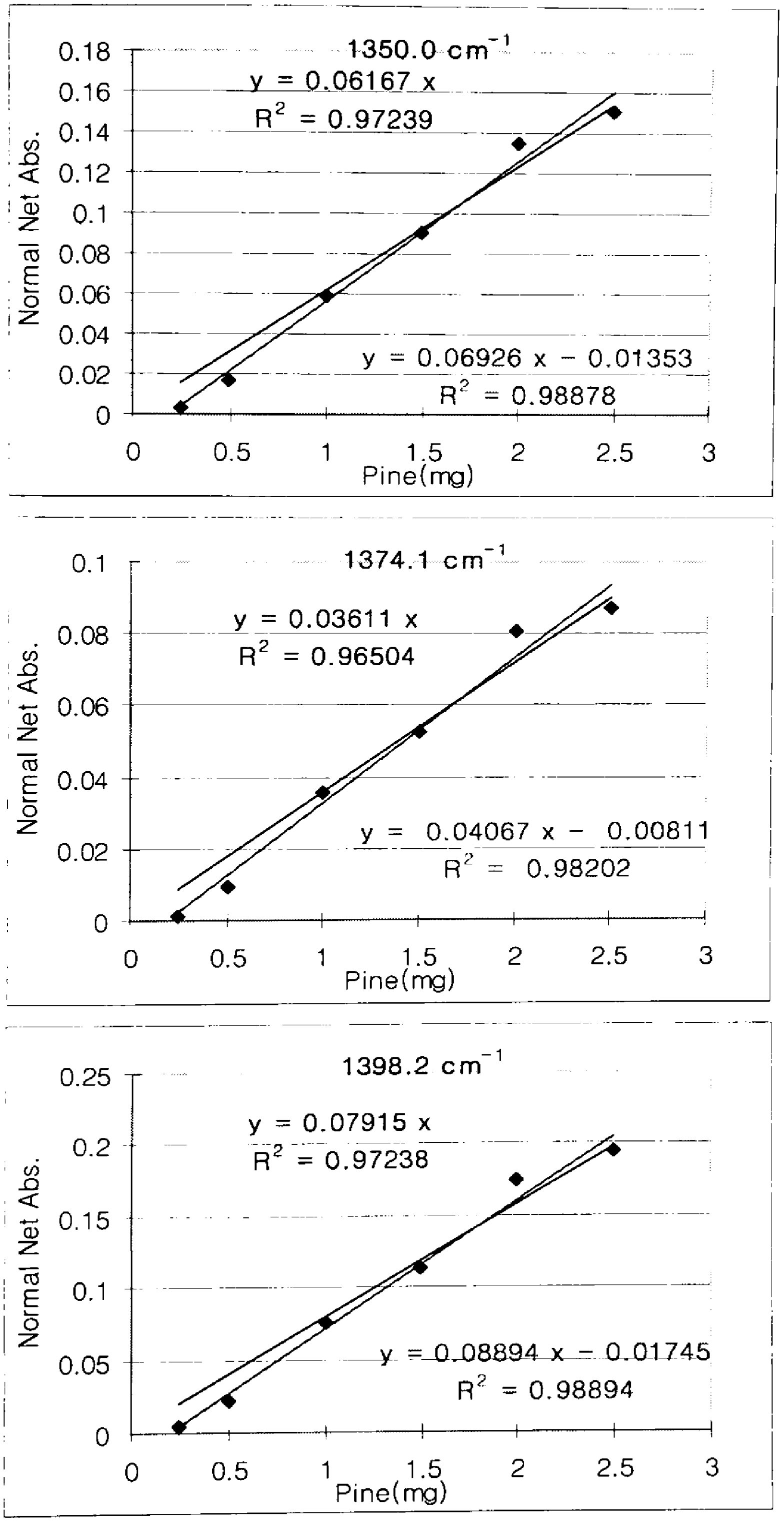


Figure B.29 Pine Standard Calibration Curves at 1350.0, 1374.1 & 1398.2 cm^{-1}

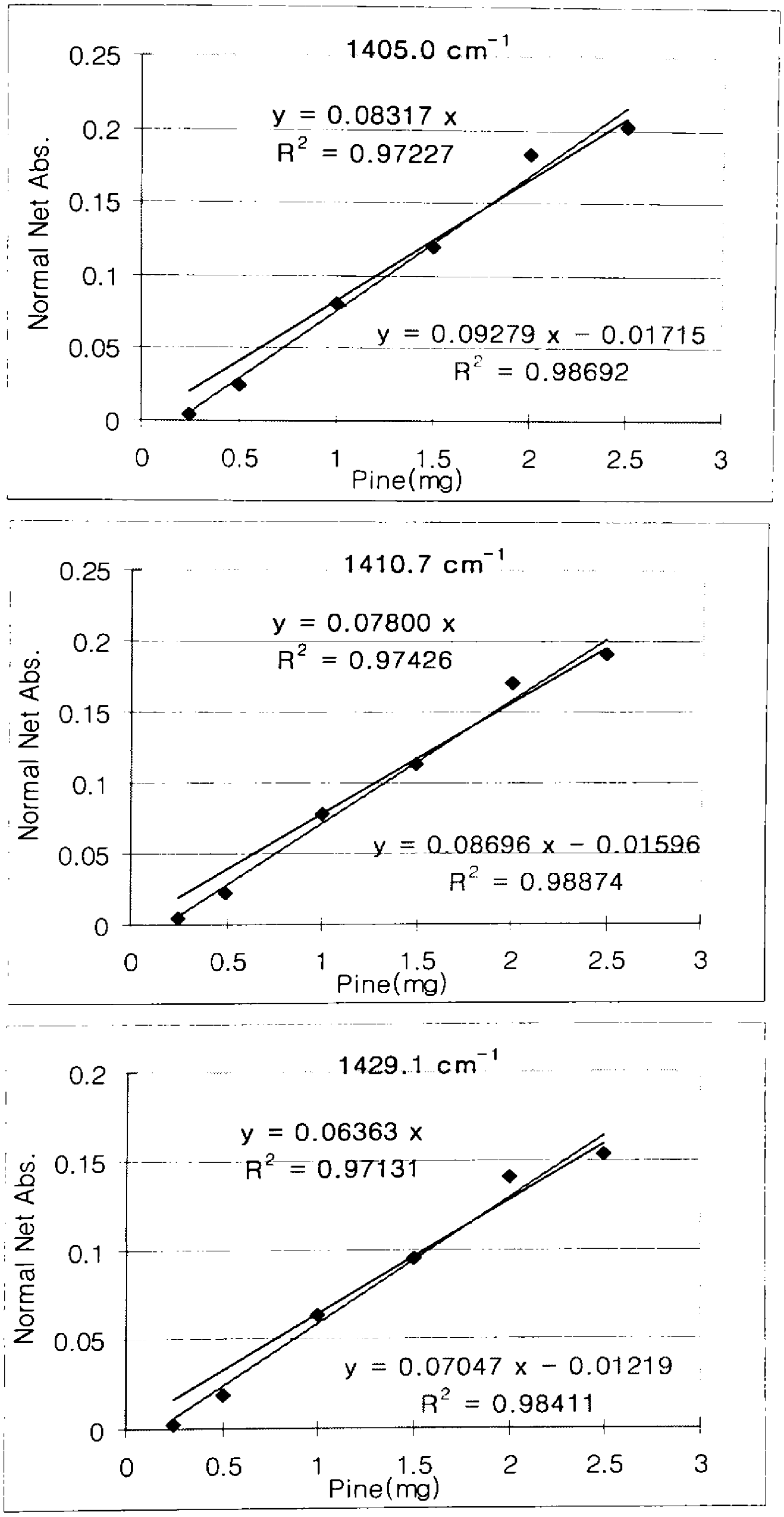


Figure B.30 Pine Standard Calibration Curves at 1405.0, 1410.7 & 1429.1 cm^{-1}

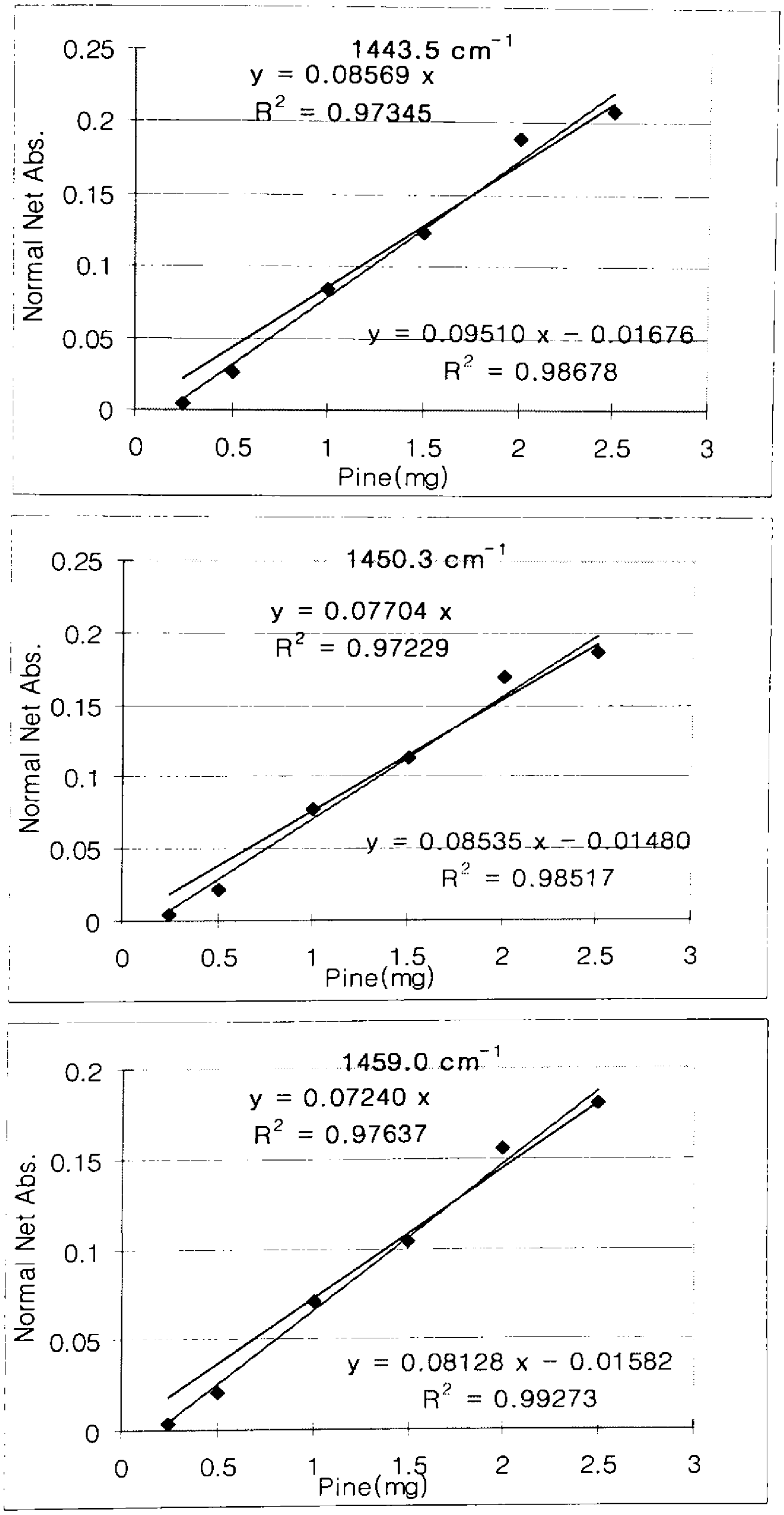


Figure B.31 Pine Standard Calibration Curves at 1443.5, 1450.3 & 1459.0 cm^{-1}

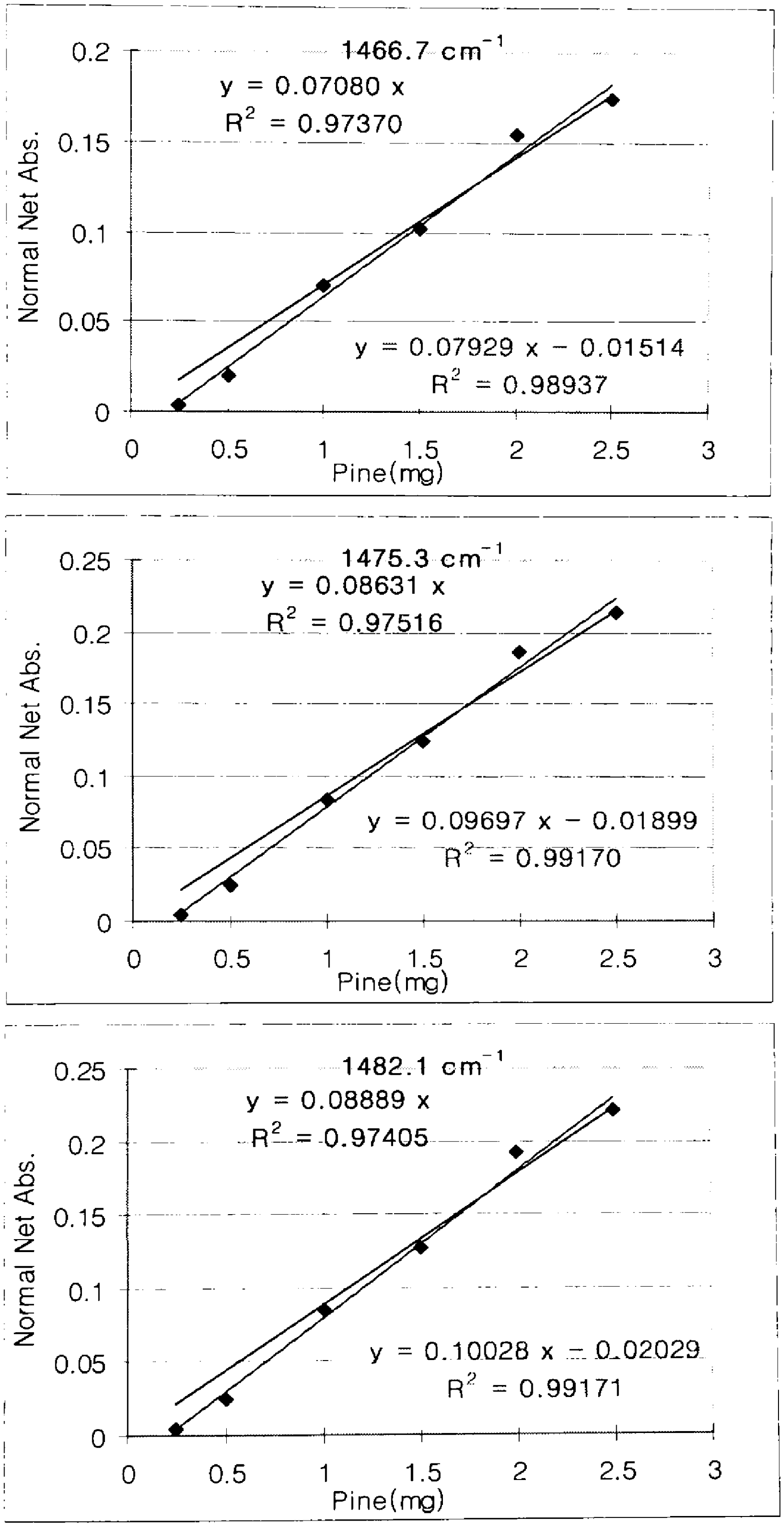


Figure B.32 Pine Standard Calibration Curves at 1466.7, 1475.3 & 1482.1 cm^{-1}