

Predicting
Carcinogenic
Formaldehyde
Emissions
using a Real-
Time Sensing
System with
Automated
Data Fusion

Dezember 2014



Installation of a NIR-
Spectroscope in a
particleboard plant
in South Carolina

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Abstract

This paper deals with near infrared spectroscopy and the installation of a NIR-spectroscope at the Flakeboard particleboard plant in South Carolina. The aim of the project was to measure the formaldehyde, which is released during the production of particleboards, using a real time sensing system with automated data fusion. The data is unfortunately not yet processed.

1. Introduction

The bio-based products industry is an important contributor to the U.S. economy accounting for approximately six percent of the total U.S. manufacturing gross domestic product (GDP), placing it on par with the automotive and plastics industries (American Forest and Paper Association 2010).

The industry generates more than \$200 billion a year in sales and employs approximately 900,000 people earning \$50 billion in annual payroll. The industry is among the top 10 manufacturing employers in 42 states (American Forest and Paper Association 2010).

The bio-composites sector of this industry is facing a new challenge from legislation that limits the amount of formaldehyde (CH₂O) emissions from engineered panels from 0.09 to 0.11 ppm. Urea-formaldehyde (UF) resin technologies (critical binder that emits CH₂O) do not provide cost effective solutions for bio-composite manufacturers. To meet legislated CH₂O emissions standards, press cycle times must be reduced resulting in lower production throughput and higher per unit costs which are both not competitive and sustainable for the industry. Alternative resin technologies to alleviate CH₂O emissions (melamine, phenol-formaldehyde or polymeric diphenylmethane diisocyanate resins) are expensive and are not cost effective solutions for the industry.

The research hypothesis is to accurately predict in a real-time setting CH₂O carcinogenic emissions from manufactured product using on-line sensing technology.

1.1. Formaldehyde as a Toxic Air Contaminant

In 1992 formaldehyde was identified as a toxic air contaminant. It can influence the DNA or even damage it. The inhalation of formaldehyde

causes cancer in the region of the throat behind the nose. Since 1992 more evidence in humans for nasopharyngeal cancers was listed in California. Moreover studies of IARC (International agency for research on cancer) demonstrate nasal cavity cancers in rats from inhalation (Proposed Airborne Toxic Control Measure to Reduce Formaldehyde Emissions from Composite Wood Products 2007). So the fact that formaldehyde is harmful to humans, animals and environment is absolutely certain.

The exposure and thus the inhalation of formaldehyde is not only noxious for workers but also for customers since wood-based engineered products such as particleboards release formaldehyde for a longer period of time not only during pressing or the production. Workplace exposures associated with significant decrement in lung function, wheezing, shortness of breath, respiratory and eye, nose and throat irritations. Furthermore, some studies reveal that there is a higher risk of asthma in young children when exposed to higher formaldehyde levels in homes or even schools (Proposed Airborne Toxic Control Measure to Reduce Formaldehyde Emissions from Composite Wood Products 2007).

1.2. Emissions from composite wood products

There is a formaldehyde Emission from particleboard of about 450 tons per year. And this is not only during the manufacturing process but also in fabrication facilities, from home constructions and during transportation. In the US there is a particleboard production of 5.4 billion square feet according to statistics from 2002 (Proposed Airborne Toxic Control Measure to Reduce Formaldehyde Emissions from Composite Wood Products 2007). In the following graph typical formaldehyde levels are shown.

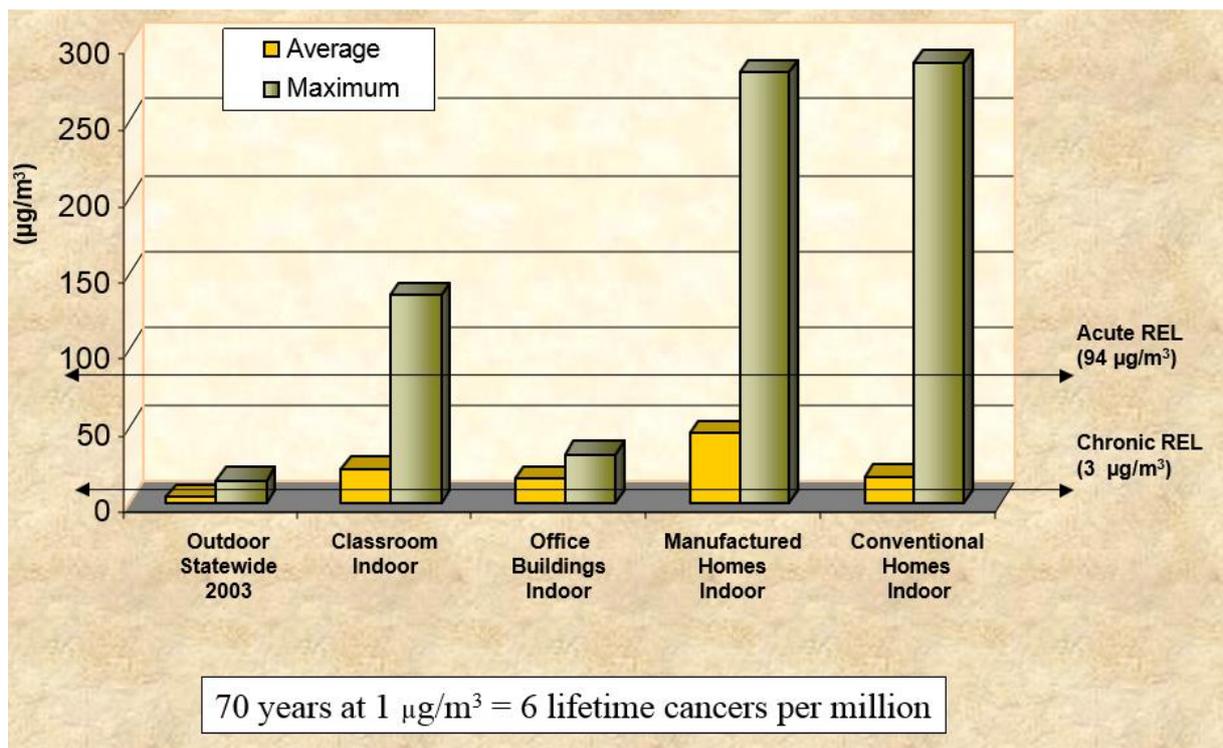


Figure 1: Typical formaldehyde levels, Source: Proposed Airborne Toxic Control Measure 26.4.2007

1.3. Off-line measuring of formaldehyde emissions

Since the late 70’s indoor air quality and formaldehyde emissions have been an issue with still increasing importance. In the 1980 Germany first set world’s product emission guidelines. There are at least eight different off-line formaldehyde test methods for wood products in Europe and North America. Following the most important test methods are described (Measuring and controlling volatile organic compound and particulate emissions from wood processing operations and wood-based products ©1995).

1.3.1. Large test chamber (WKI)

The walls of the chamber are typically made out of glass, stainless steel or aluminium metal plates. Parts of the chamber form a channel which circulates the air in the chamber. The particleboard sits in the chamber for a certain period of time. Then the concentration of formaldehyde is

determined by bubbling air through a water solution and analysing that solution with Chroma tropic acid wet chemistry. There are mainly two different types of test chambers: Parallel air flow chamber and test chambers with circular air ventilation. The test conditions are as following: Temperature: 23°C; relative humidity: 45%; loading rate: 1.0m²h/m³; air exchange rate: 1.0/h; air velocity at the surface of the test pieces: 0.1 to 0.3m/s (Measuring and controlling volatile organic compound and particulate emissions from wood processing operations and wood-based products ©1995).

1.3.2. Extraction method: perforator

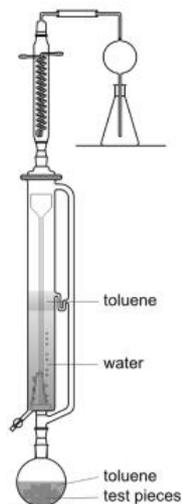


Figure 2: Perforator apparatus, Source: <https://www.scienceopen.com>

For the perforator method, which is standardized as European norm EN 120, small pieces of the particleboard or MDF are needed. It is the most common test method for particleboards and MDF in Europe. This method is a procedure for the extraction with toluene in a perforator apparatus. Through the acetylaceton method the extracted formaldehyde, which is sampled in water, can be determined analytical (Measuring and controlling volatile organic compound and particulate emissions from wood processing operations and wood-based products ©1995). In figure 2, the construction of the method is shown.

1.3.3. Emission method: Flask method

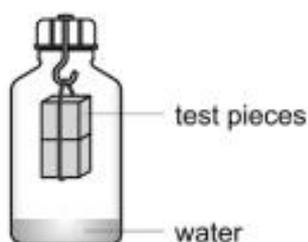


Figure 3: Flask method, Source: <https://www.scienceopen.com>

The flask method is a very simple technique. A container, mostly used bottles, with a volume of 500ml is needed. The test sample's weight should be at 20 to 25g. This piece of particleboard or MDF is stored in a closed container over water. The test takes between 13 and 24 hours. The temperature in the container should be at 40°C while the water absorbs the emitted formaldehyde (Measuring and controlling volatile organic compound and particulate emissions from wood processing operations and wood-based products ©1995). The graph above shows the flask method in simplified terms.

1.4. NIR- Spectroscopy

In wood based panel companies is a steady increasing demand for high and consistent quality products. This is among other things challenging for the company Flakeboard. Flakeboard is producing approximately 20 different particle board types on the same production line within several hours. Due to regulations concerning the formaldehyde emissions, and to meet requirements and avoid production failures, a diligent monitoring of the production process is necessary. Therefore on-line methods, which work non-destructively, such as NIR-spectroscopy, should be integrated (Thoemen 2010).

Infrared spectrometry records absorption of radiation in the range of 400 to 4000cm^{-1} due to changes in vibrational modes of chemical bonds. The infrared absorptions requirement is that the excited vibration should imply variations in the dipole moment of the bond. Functional groups such as hydroxyls, carbonyls, carboxyls and amides can be identified (Stenius ©2000).

NIR- Spectroscopy shows overtones and combinations of fundamental vibrations. On the one hand it is simple and rapid to distinguish general characteristics of the sample, on the other hand it is rather difficult to interpret the spectra, plus the information needs to be related to other chemical data (Stenius ©2000).

Through a NIR camera, hyperspectral images from the moving surface can be scanned. To analyse NIR data modern multivariate techniques such as principal components analysis (PCA) and similar techniques can be used (Thoemen 2010). Moreover most IR spectrometer software includes libraries of spectra to identify the different substances (Stenius ©2000).

1.4.1. Principle of NIR- Spectroscopy

Near Infrared spectroscopy covers wavelengths from 760- 2500nm. It has less energy than visible spectral range but does induce molecular vibrations. NIR spectroscopy excites vibrations of covalent molecular bonds (Polytec GmbH Waldbronn 2014) There are three effects that occur when using electromagnetic radiation with a sample:

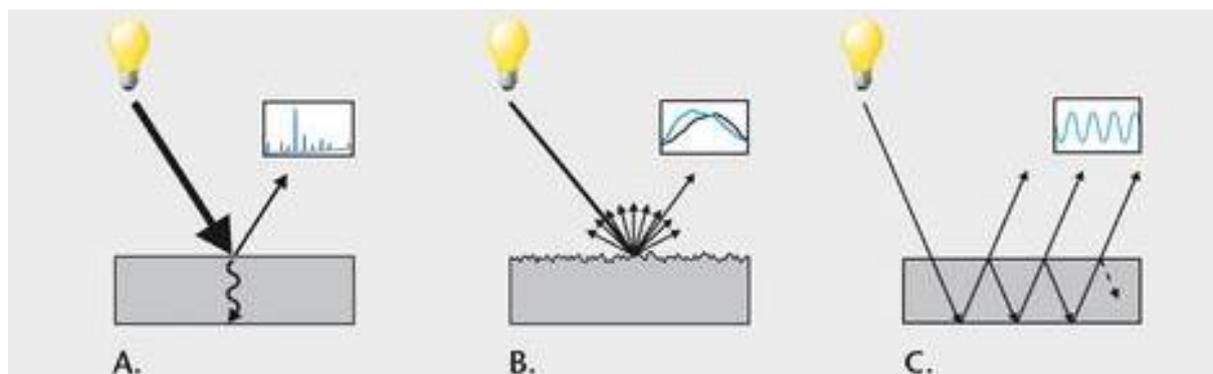


Figure 4: Theory of NIR- Spectroscopy

The absorbance or reflection, which is shown in figure 4, is used for the qualitative and quantitative identification of composition. In graphic 4 the surface effect is shown. It determines physical characteristics of the sample. The interface effect implies that the thickness, especially of thin layers, can be measured (Polytec GmbH Waldbronn 2014).

1.4.2. Fields of application

Since NIR spectroscopy induces vibrations of covalent molecular bonds it is an appropriate technique to determine the water content. Thus it is often used for organic and pharmaceutical products, such as corn, milk and feedstuff. Also proteins (N-H bonds) and fat contents (C-H bonds) can be examined. Furthermore through NIR spectroscopy various molecular structures and groups can be observed in polymers. Therefore it is used for quality assurance and process control in e.g. the chemical, pharmaceutical and food industry. Moreover it is possible to determine brightness parameter and colour values (Polytec GmbH Waldbronn 2014). Moreover in the forest products industry NIR spectroscopy is used for predicting the mechanical properties of wood composites (Timothy G. Rials et al. 2001).

1.5. Regulations

Formaldehyde is produced and used on a large scale worldwide. The production of wood binding adhesives and resins is one of the major uses. ARB, the Air Resources Board, says that the major source of exposure is from inhalation of formaldehyde which is emitting from composite wood products containing urea-formaldehyde resins. Since California is one of the biggest purchasers in the US also other States have to adapt to the regulations. In graph 5 you can see the worldwide formaldehyde Standards for composites.

Comparison of Worldwide Formaldehyde Standards for Composites (using equivalent U.S. large chamber test values)						
Standard	European E1	Japanese F***	Japanese F****	CPA EPP	CARB Phase I (2009)	CARB Phase II (2011)
Maximum Emission Level (ppm)	0.14	0.09*	0.05*	0.20	0.18 (PB) 0.21 (MDF)	0.09 (PB) 0.11 (MDF)

*Standard applies only to structural building materials and built-in cabinets

Figure 5: Comparison of worldwide formaldehyde standards for composites, Source: http://www.flakeboard.com/docs/CPA/CPA_FactSheet.pdf

1.5.1. TAC- Toxic air contaminant

In 1992 in California formaldehyde was designated as a toxic air contaminant (TAC). TACs are air contaminants that are considered hazardous to human health or which may cause or contribute to an increase in deaths or in serious illness. Present there are more than 250 compounds which are categorized as TACs and formaldehyde is one of them. TACs are considered to have no safe level of exposure (California Department of Public Health (CDPH) 2013).

1.5.2. ATCM- Airborne toxic control measurement

This regulation was implemented in 2009 and consists of two phases. The first phase’s aim was to reduce the formaldehyde emission from particleboards to 0.18 ppm, the second phase’s goal, which was implemented 2010 to 2012, was to set the emission down to 0.09 ppm (California Environmental Protection Agency).

2. Flakeboard

The company Flakeboard was founded in 1960 by two German families and has four decades now been defining the industry of composite wood panels. Flakeboard is a world-scale producer of a variety of particleboard, medium density fibreboard and FIBREX ® thin high density MDF. In 1972 Flakeboard introduced a continuous thin board line in North America. In 2005 a 45,000 square foot melamine lamination plant was built, which includes a fully automated high throughput 5´x20´ melamine press. The single line press in Sault Ste. Marie is producing the mayor volume of MDF in North America (Flakeboard Company 2012).

Flakeboard operates a continuous and two single opening melamine presses, single or dual sided paper lamination, 9-stage direct print line, pegboard press and a state-of-the-art paint line for finishing operations. All in all, Flakeboard owns a total of nine value-added finishing lines (Flakeboard Company 2012).

In 2006 Flakeboard procured three MDF and three particleboard plants from the company Weyerhaeuser. Those purchased plants are located in Malvern, Arkansas; Albany, Oregon; Eugene, Oregon; Simsboro, Louisiana and Bennettsville, South Carolina. In the case of the latter, it comprises the particleboard plant where the NIR-spectroscope was installed. This investment enhanced the company with 1.1 billion square feet of capacity. Flakeboard continues to invest in new product developments, cutting-edge technology and sets new standards in the manufacture of composite wood panels (Flakeboard Company 2012).

2.1.1. Product portfolio

Fibrex, particleboard and MDF are the major products Flakeboard is concentrating on. Of each product there are many varieties in composition, particle size, thickness and mechanical properties. For particleboard for example there are the following products in Flakeboards product portfolio: Terra Particleboard, Duraflake Particleboard, UltraPine Particleboard, Dura FR Fire-rated Particleboard, Vesta particleboard and several more (Flakeboard Company 2012).

2.1.2. Finishes

As already mention previously, Flakeboard occupies several plants including lines for finishing operations. Here the finishes Flakeboard is performing: Direct print, decorative paper overlays, paint and thermally fused melamine (Flakeboard Company 2012).

2.2. Location of Spectroscope

The NIR spectroscope was installed after the cross cut saw which is located right behind the hot press. This location has been chosen due to the fact, that right after the press, the particleboard releases the most formaldehyde. In figure 6 the location where the spectroscope was installed is shown. A disadvantage of this location could be that the pollution of the lens through dust and unreacted formaldehyde is higher than later on the conveyor belt.



Figure 6: Location of installation of the NIR-spectroscope

2.3. Time measurement

During the installation of the spectroscope time measurements of the processes of the particleboard production have been made. This was especially necessary to check if the sensor head is measuring at the right moment and if it is mounted in an accurate way. The times, mentioned following, are the ones for the thickest board Flakeboard is producing.

From Start cutting to NIR: ~25sec

From finish cutting to NIR: ~14sec

NIR: ~3,48sec

Time to next board: ~0,27sec

3. Methodology and Material

3.1. Particleboard

Particleboards are produced by reducing round wood into small particles, applying adhesive to the particles and consolidating a loose matt. In a hot press the adhesive cures and the material is pressed into a panel product. Typically a particleboard consists of three layers. The core usually contains coarser material than the surfaces. Smoother faces allow an easier application of finishes such as overlays, paintings or veneers. The core material can be exchanged by e.g. kenaf or jute to gain specific properties such as sound absorbing boards. Particleboard is used for furniture, flooring systems, in manufactured houses, for stair treads and as underlayment. Depending on the application, indoor or exterior, either UF, PF or MF resins are used (Wood handbook 1999).

Worldwide 35% of the wood-based composite board production is defined by particle-based composites. Particleboard kept its major market share worldwide for decades, but lost influence in North America as well as in Central Europe. Nevertheless in South-East Asia, Latin America and Eastern Europe rising production capacities can be seen. Europe is still the premier producer of particleboards. Due to the cheap raw materials, which may also derive from recycled materials, the demand is maintained constant. There is also the possibility to combine particleboards with other materials such as paperboards, cement, and non-wood lignocellulose materials. In Europe the main use for particleboards is for the furniture industry because of its low weight and price compared to other panels. In the flooring and building industry there is a remote loss, for the simple reason that there are different products such as MDF and OSB. In 2009 in the USA a new regulation for free formaldehyde emission for particleboards was implemented (Aguilera und Davim).

There is an overcapacity for wood-based panels of about 15-20%, especially particleboard and MDF which has a big influence on sales prices and consequently on manufacturers. The goals nowadays are the reduction of board weight, reduction of emissions and the use of recycled materials. However, these goals and regulations might endanger several production lines so that they even have to close their activities. The guidelines for low formaldehyde emission will increase competition between the manufacturers and the moment of application could create supplementary pressure to the current world financial crises (Thoemen 2010).

3.2. Wood adhesives

Because adhesives are used in many different applications with wood, a wide variety of types are used (Vick 1999). The manufacturing of wood based products, such as oriented strand board, fibreboard and particleboard is the largest wood market. Depending on the distribution of wood and adhesives, the compressive strength, modulus of rupture, structure, durability, susceptibility and many more properties will be determined. The adhesive is applied to the wooden particles, formed into mats and finally pressed under heat into boards. Due to the fact, that there is a hot press used, an adhesive that doesn't react immediately at room temperature (pre-mature cure) but is heat-activated during the pressing is required. This applies especially for thinner boards. Most adhesives used in wood bonding have formaldehyde as a co-monomer, generating concerns about formaldehyde emissions. The trend of using engineered wood products has increased the consumption of adhesives (Roger M. Rowell 2005).

3.2.1. Formaldehyde adhesives

Formaldehyde, H_2CO , is a colourless gas with a pungent, characteristic odour. Its melting point is at 181°K and its boiling point is at 252°K (McQuarrie und Rock ©1991). It is an important precursor to many other materials and chemical compounds. Commercial solutions of formaldehyde in water, called formol, were formerly used as disinfectants and for preservation of biological specimens. Frequently it is used in nail hardeners and nail varnish. The most common wood adhesives are based on reactions of formaldehyde with phenol, resorcinol, urea, melamine or mixtures thereof. In view of its widespread use, toxicity and volatility is a significant consideration for human health. 2011 the US National Toxicology Program NTP described formaldehyde as known to be a human carcinogen. The reactions can involve three steps:

- Formaldehyde reaction with a nucleophilic centre of the comonomer to form a hydroxymethyl derivative
- Condensation of two of these hydroxymethyl groups to form a bismethylene ether group, with loss of a water molecule
- Elimination of formaldehyde from the bismethylene ether to form a methylene bridge (McQuarrie und Rock ©1991)

3.2.2. Phenol Formaldehyde Adhesives

Phenol formaldehyde adhesives are the oldest of synthetic polymers, having been developed at the beginning of the 20th century (Detlefsen 2002). PF is widely used due to its outstanding durability. It has a good adhesion to wood, a high strength of the polymer and an excellent stability of the adhesive itself. In general phenol formaldehyde adhesives can meet the bonding needs for most wood applications if cost and heat curing times are not an issue (Roger M. Rowell 2005).

3.2.3. Urea Formaldehyde and Mixed Urea Formaldehyde Adhesives

Urea formaldehyde adhesives positive aspects are: very low cost, non-flammable, very rapid cure rate and a light colour. However the bonds are not water-resistant and the most crucial downside is that formaldehyde continues to evolve from the adhesive. UF is particularly used for interior grade plywood and particleboard. Usually an additional charge of urea is added to reduce formaldehyde emissions from the resin. The UF resins contain a latent acid catalyst that produces an acid catalyst during the heat cure. To meet formaldehyde emission regulations during production and for indoor applications a lower formaldehyde and or urea ratio in products has been set. However, this does not sacrifice in ultimate strength and robustness properties of the products. Especially the poor water-resistance of urea formaldehyde adhesives has led to the development of melamine-urea-formaldehyde adhesives (Roger M. Rowell 2005).

3.2.4. Melamine Formaldehyde Adhesives

Melamine formaldehyde adhesives are most commonly used for exterior plywood, particleboards, finger joints and for impregnating paper sheets which is used in plastic laminates. The high cost of melamine has led to the use of melamine- urea-formaldehyde adhesives and is as much water resistant as MF resins. According to Roger M. Rowell there are two types of condensation reactions that can occur:

- Bismethylene ether formation by the reaction of two hydroxymethyl groups, $RCH_2OH + R'CH_2OH \rightarrow RCH_2OCH_2R' + H_2O$
- Methylene bridge formation by reaction of the hydroxymethyl group with an amine group, $RNH_2 + R'CH_2OH \rightarrow RHNCH_2R' + H_2O$

The reaction conditions of time, temperature, formaldehyde- melamine ration, pH and catalyst will influence the composition and structure of the resin. To give good polymerization to the final product the MF adhesive needs to be activated by e.g. lowering the pH and raising the temperature (Roger M. Rowell 2005).

3.3. NIR Spectroscopy

For the spectrometer as well as for the sensor head, systems by Polytec have been chosen. A steel case protects the equipment from contamination.

NIR spectroscopy becomes more and more common due to its numerous possible applications. A white light source illuminates the sample. This light is wholly or partially absorbed by the sample. By recording the reflection or transmission spectra the ranges of absorption become visible. These so called absorption bands allow the detection of the ingredients of the sample, whereby the concentration of ingredients can be determined by the degree of absorption (Polytec).

3.4. Polytec Spectrometer System



Figure 7: Spectrometer System, Source: www.polytec.com

Through the entrance slit the light is fed via an SMA fibre connector into the polychromator. The achromatic lens system focuses the light. The now paralleled light is deflected at the transmission grating and is split into its spectral components. The detector unit now displays the spectral components. At the end of the polychromator a cooling element with fan is installed to prevent the system of overheating.

Before using the spectra, it is necessary to standardize the sample spectra against a reference spectrum. Polytec recommends a diffuse, physical white reference standard.

3.5. Conveyor Belt Sensor Head



Figure 8: Conveyor Belt Sensor Head, Source: www.polytec.com

The conveyor belt sensor head from Polytec has an integrated special halogen lamp. The reflected light of the material being measured is captured by the optical system of the sensor head. It is especially designed for measuring solid samples on conveyor belts and can be operated at measurement distances of 10 to 50cm. By choosing the mounting location it is important to avoid vibrations and extreme changing external light pollution. Polytec also recommends cleaning the lens only with light detergent solutions or alcohol-based disinfectants (Polytec).

4. Results

The NIR-spectroscope has been installed at the Flakeboard particleboard plant and first data has already been taken. However, the spectroscope's lens gets dirty due to the non-reacted formaldehyde in the glue. The lens gets cleaned from time to time; as a consequence another problem occurs: It is uncertain when exactly the window of the lens gets cleaned. On the one hand it is necessary to know the exact time of cleaning and on the other hand more data has to be collected to be able to show sound results.

Another factor that might influence the significance of the data, especially at the Flakeboard particleboard plant, is the fact that they produce a lot of different products with varying particle sizes and board thicknesses.

5. Discussion

There are problems through contamination of the sensor head. It has to be cleaned almost every day to ensure accurate data. Also the exact time of cleaning the sensor should be known. Therefore a statement can be made.

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